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Methods of synthesis of Group 4 – 9 transition metal imido complexes

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Contents

I.	Introduction	671
II.	Intermolecular imidation methods	672
III.	Intramolecular imidation methods	696
IV.	Conclusion	701

Abstract. The synthetic routes to Group 4 – 9 transition metal imido complexes are considered. Both common and less common approaches are analysed. The classification of the methods for the synthesis of imido complexes is based on the way of formation of the imido ligand, the change in the metal oxidation state during imidation and the type of imidation reagent. The bibliography includes 415 references.

I. Introduction

The chemistry of transition metal imido complexes is currently a priority avenue of research in coordination chemistry which arouses an ever increasing interest. The intensive development of this field is caused by a number of reasons, first of all, successful use of imido complexes in organic synthesis and in metal complex catalysis and also as promising materials for various purposes.

It is expedient to distinguish two groups of stoichiometric and catalytic reactions involving imido complexes. The first group includes various nitrogen group transfer reactions (redox reactions and metathesis) with direct participation of the imido ligand of the complex. Examples are amination of alkenes to give *vic*-amino alcohols and *vic*-diamines,[1–3] allylamines[4] and aziridines;[4–6] hydroamination of carbodiimides,[7] alkenes,[8] alkynes and allenes;[9–12] transfer of the imido groups onto tertiary phosphines and isocyanides yielding iminophosphoranes[13–21] and carbodiimides, respectively;[22,23] condensation of organic isocyanates to give carbodiimides;[24] and metathesis of carbodiimides[25,26] and imines.[27–31]

The second group comprises reactions involving transition metal imido complexes in which the imido ligand does not undergo chemical transformation but acts as a 'spectator ligand' stabilising the complex. These reactions are exemplified by alkene dimerisation[32] and polymerisation;[33–43] C–H bond activation;[44–47] and alkene cyclopropanation.[48] Special mention should be made of the metathesis of unsaturated hydrocarbons catalysed by Schrock imidocarbene complexes.[49,50] These reactions include ring-opening metathesis polymerisation (ROMP) of cyclic alkenes;[51–58] ring-closing metathesis (RCM) of dienes[59–69] and diynes;[70] asymmetric ring-opening metathesis/cross metathesis (AROM/CM) of acyclic and cyclic alkenes;[64,69–73] and a tandem of asymmetric ring-opening and ring-closing metathesis reactions (AROM/RCM).[64,69,74–76] R Schrock was awarded the Nobel Prize in 2005 for the invaluable contribution to the development of organic synthesis.

In recent years, the use of imido complexes of some metals as promising starting compounds for the chemical vapour deposition (MOCVD) of nitrides has been reported.[77–82]

The chemistry, spectroscopic characteristics and structures of transition metal imido complexes have been considered comprehensively in reviews.[83–86] The present review is devoted to comparative analysis of the methods of synthesis of Group 4 – 9† transition metal complexes with terminal imido RN groups containing alkyl, aryl and trialkylsilyl organic groups. Due to the limited size of the publication, we leave aside the complexes containing bridging imido ligands; they are mentioned only in the cases where a complex contains both bridging and terminal imido ligands. The review is focused on the imido derivatives of d elements; examples of imido compounds formed by f elements reported in the literature are few in number and represented in the review by only uranium complexes.‡ This review covers publications up to the end of 2004.

Imidation methods are usually classified according to the types of imidating agents.[83–86] The classification used in this review takes into account consecutively the way of formation of the imido ligand, the change in the metal oxidation state during imidation, the type of the imidating agents and the nature of the starting compounds. All the methods of synthesis of imido complexes known to date can be divided into two large groups. The first one includes intermolecular imidation methods in which the imido complex is formed using an external imidating agent. In the case of intermolecular imidation, the formal oxidation state of the metal in the complex can either change or remain unchanged depending on the nature of the agent and the starting metal-containing compound.

The second group comprises intramolecular imidation methods in which the imido group is formed from another nitrogen-containing ligand present in the metal complex. Nitride and amide complexes are used most often as the starting compounds; examples of the transformation of other nitrogen-containing

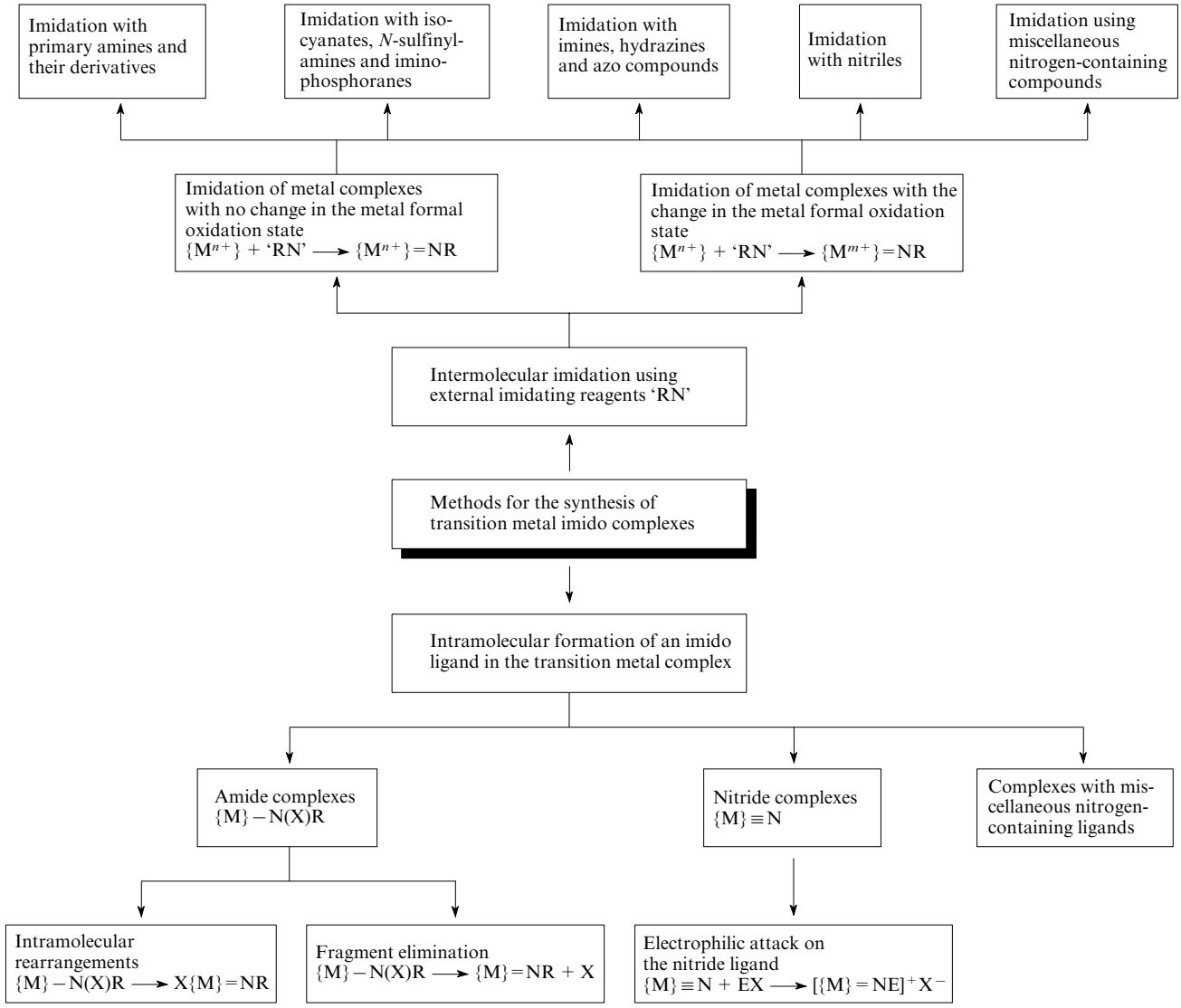
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† Group 10 and 11 transition metals are beyond the scope of the review, as they form complexes with bridging imido ligands.[87,88]

‡ Data on the imido derivatives of p elements can be found in recent reviews.[89,90]

Scheme 1



ligands are scarce. In the intramolecular imidation, the formal oxidation state of the metal usually remains unchanged.

Scheme 1 shows the classification of the methods of synthesis of transition metal imido complexes used in this review.

II. Intermolecular imidation methods

1. Imidation of metal complexes with no change in the metal oxidation state

a. Imidation with primary amines

Primary amines were historically the first compounds proposed as external imidation agents. Nevertheless, methods using these reagents have still not lost their practical value, which is determined first of all by wide choice, ready availability and relatively low cost of aliphatic and aromatic amines. Amines are suitable for imidation of metal-containing compounds of various types, among which metal oxides and halides are used most often.

The imidation of oxides (imido-deoxygenation) with primary amines is accompanied by elimination of water and can be carried out for transition metals of Groups 7 and 8, such as Tc, Re, and Os. For example, the first known imido complex, $Bu^tN{=}OsO_3$, was prepared by treatment of osmium tetraoxide with *tert*-butylamine.[2,91] Subsequently, this approach has been used to prepare other osmium monoimido complexes.[2,3,92]

$$OsO_4 + RNH_2 \longrightarrow \underset{(69\%-81\%)}{RN{=}OsO_3} + H_2O$$

R = Bu^t, CMe_2Et, $CMe_2CH_2Bu^t$, Ad.

Table 1 presents examples of rhenium and technetium imido complexes obtained by imido-deoxygenation with amines. For this type of complexes, this is the main method of synthesis, which is usually more convenient than imido-deoxygenation using isocyanates, *N*-sulfinylamines, iminophosphoranes, hydrazines, formamidines and hydrazides.

In bi- and polynuclear oxo complexes [for example, $Re_2O_3(S_2CNEt_2)_4$][106] containing both bridging and terminal oxo groups, only the latter undergo the oxo–imido exchange.

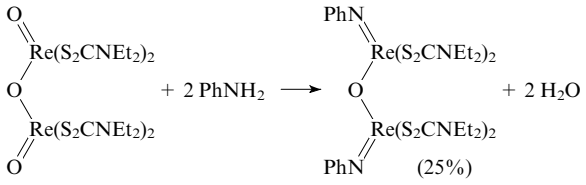


Table 1. Synthesis of rhenium and technetium imido complexes by imido-deoxygenation with primary amines.

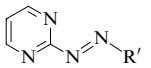
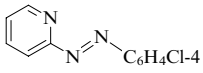
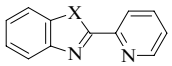
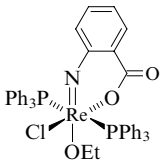
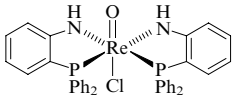
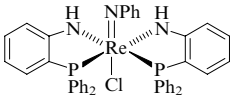
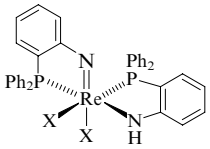
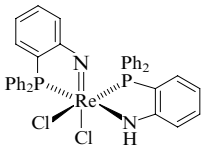
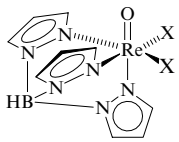
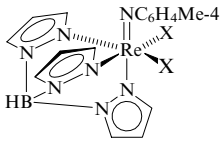
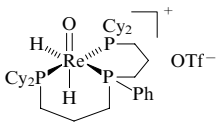
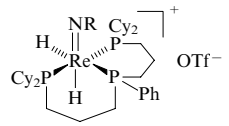
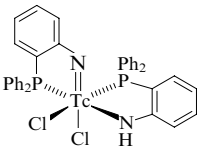
Starting compound	Amine (RNH_2)	Product	Yield (%)	Ref.
$ReOCl_3L_2$		$RN{=}ReCl_3L_2$		
L = $PPhEt_2$	$PhNH_2$	R = Ph	–	93
L = PPh_3	4-$FcC_6H_4NH_2$	R = 4-FcC_6H_4	44	94
	2-$XC_6H_4NH_2$ (X = NH_2, 2-NH_2-3-HOC_6H_3, 2-NH_2-3-MeC_6H_3)	R = 2-XC_6H_4	61 – 77	95
L_2 = 				
R′ = Ph	$PhNH_2$	R = Ph	65	96
R′ = C_6H_4Cl-4	4-$ClC_6H_4NH_2$	R = 4-ClC_6H_4	70	96
L_2 = 	4-$XC_6H_4NH_2$ (X = H, Cl, Me)	R = 4-XC_6H_4	75 – 80	97
L_2 = bipy	$PhNH_2$	R = Ph	65	98
L_2 = 				
X = O	$PhNH_2$	R = Ph	81	99
X = S	$PhNH_2$	R = Ph	79	99
$ReOCl_3(PPh_3)_2$	2-$HO_2CC_6H_4NH_2$ – EtOH (see [a])		59	100
	$PhNH_2$		60	101
$ReOX_2(OEt)(PPh_3)_2$ X = Cl, Br, I	2-$Ph_2PC_6H_4NH_2$		69 – 83	102
$(Bu^n_4N)[ReOCl_4]$	2-$Ph_2PC_6H_4NH_2$		81	102
	4-$MeC_6H_4NH_2$			
X = Cl			50	103
X = I			84	103
	$PhNH_2$, 4-$MeC_6H_4NH_2$, $CyNH_2$		56 – 92	104
(Cy is cyclohexyl, OTf is triflate)		(R = Ph, 4-MeC_6H_4, Cy)		
$(Bu^n_4N)[TcOCl_4]$	4-$MeC_6H_4NH_2$ – PPh_3 (see [a])	4-$MeC_6H_4N{=}TcCl_3(PPh_3)_2$	–	105

Table 1 (continued).

Starting compound	Amine (RNH_2)	Product	Yield (%)	Ref.
$(Bu^n_4N)[TcOCl_4]$	2-$Ph_2PC_6H_4NH_2$		73	102

[a] Additional reagents present in the reaction mixture and in the final products are indicated.

For Group 4–6 metals, imido-deoxygenation with primary amines is inapplicable with rare exceptions, because of high oxophilicity of the metal. In this case, imidation requires additional promoting reagents, for example, a $Me_3SiCl-Et_3N$ mixture, which chemically binds water (see Section II.1.c). Imido-deoxygenation of polymolybdates $(Bu^n_4N)_2[Mo_6O_{19}]$ (**1a**) and $(Bu^n_4N)_4[Mo_8O_{26}]$ (**1b**) with aromatic amines occurs efficiently in the presence of dicyclohexylcarbodiimide (DCC) (Scheme 2).[107–109] The reaction of polymolybdate **1a** with *p*-phenylenediamine in the presence of triethylamine has been reported.[110] Depending on the reactant ratio, this gave imido complexes with different compositions, in particular $(Bu^n_4N)_2[H_2NC_6H_4N{=}\{Mo_6O_{17}\}{=}NC_6H_4NH_2]$, $(Bu^n_4N)_4$. $.[\{Mo_6O_{18}\}{=}NC_6H_4N{=}\{Mo_6O_{18}\}]$, *etc*.

For successful imidation of the oxo complex $MoOCl_2.(S_2CNEt_2)_2$ (**2**) with various amines, adjustment of the reaction conditions for each particular case is required. For example, when sterically unhindered *ortho*-substituted anilines, *o*-$NH_2C_6H_4NH_2$ and *o*-$HSC_6H_4NH_2$ are used, the reaction is carried out in the presence of triethylamine (Scheme 3, paths *a* and *b*).[111, 112] In the case of sterically hindered anilines, the reaction yields the target oxo–imido metathesis products only in the presence of the strong base Bu^nLi (Scheme 3, path *c*).[113] Meanwhile, imido-deoxygenation of complex **2** under the action of various *p*-phenylenediamines, 1,5-bis(dimethylamino)naphthalene and *para*-substituted anilines can proceed without any auxiliary reagents (Scheme 3, paths *d*–*f*).[114]

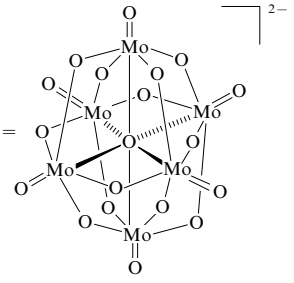
Scheme 2

$(Bu^n_4N)_2[Mo_6O_{19}]$ (**1a**)

$ArNH_2$, DCC → $(Bu^n_4N)_2[\{Mo_6O_{18}\}{=}NAr]$

$H_2N-R-NH_2$, DCC → $(Bu^n_4N)_4[\{Mo_6O_{18}\}{=}N-R-N{=}\{Mo_6O_{18}\}]$

$[Mo_6O_{19}]^{2-}$ =

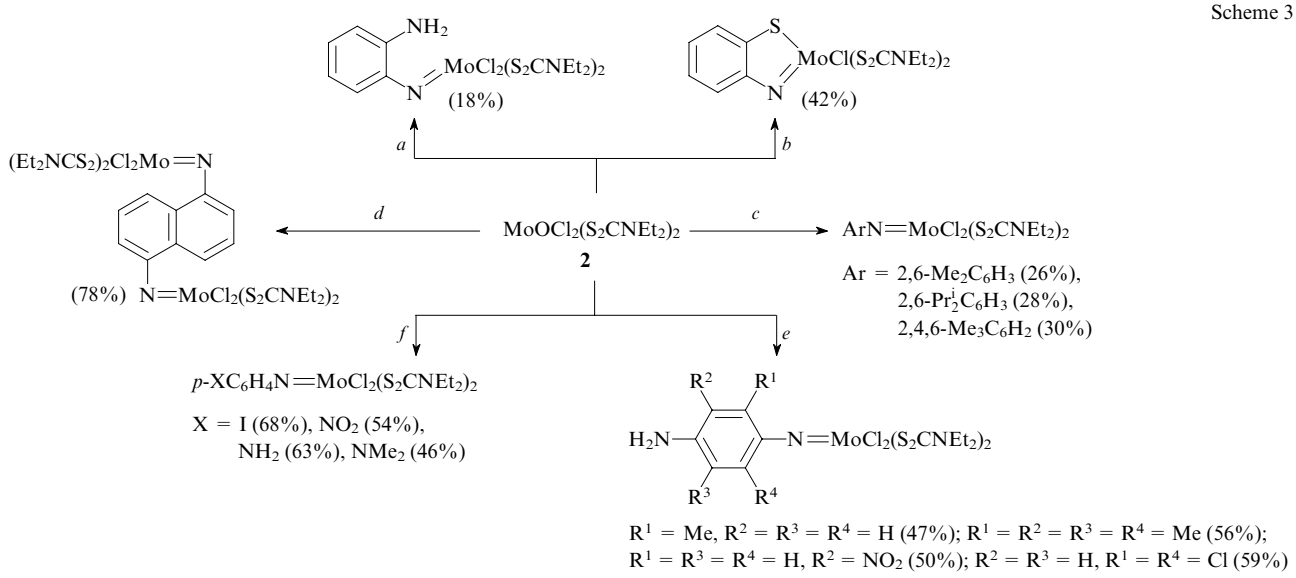


Ar = 2,6-$Me_2C_6H_3$ (95%), 2,6-$Et_2C_6H_3$ (95%), 2,6-$Pr^i_2C_6H_3$ (91%), 4-I-2,6-$Me_2C_6H_2$ (72%), 4-(HC≡C)-2,6-$Me_2C_6H_2$ (91%);
R = 4-$C_6H_4O(CH_2)_nOC_6H_4$-4 (n = 3, 4, 8; 49%–76%).

$(Bu_4N)_4[Mo_8O_{26}]$ (**1b**) + $ArNH_2$ $\xrightarrow{DCC}$ $(Bu_4N)_2[(ArN{=})_2\{Mo_6O_{17}\}]$

Ar = 2,6-$Me_2C_6H_3$ (62%), 2,4,6-$Me_3C_6H_2$ (65%), 4-I-2,6-$Pr^i_2C_6H_2$ (63%).

Scheme 3

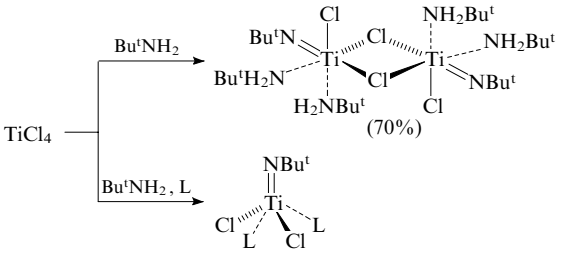


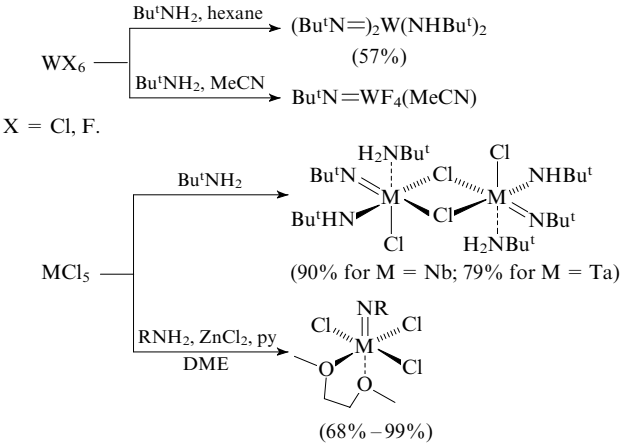
R^1 = Me, $R^2 = R^3 = R^4$ = H (47%); $R^1 = R^2 = R^3 = R^4$ = Me (56%);
$R^1 = R^3 = R^4$ = H, R^2 = NO_2 (50%); $R^2 = R^3$ = H, $R^1 = R^4$ = Cl (59%)

(*a*) *o*-$H_2NC_6H_4NH_2 \cdot 2\,HCl-Et_3N$; (*b*) *o*-$H_2NC_6H_4SH-Et_3N$; (*c*) $ArNH_2-Bu^nLi$; (*d*) 1,5-$(H_2N)_2C_{10}H_6$; (*e*) *p*-$(H_2N)_2C_6R^1R^2R^3R^4$; (*f*) *p*-$XC_6H_4NH_2$.

The complex Tp′W(=NPh)(CO)I [Tp′ is tris(3,5-dimethylpyrazol-1-yl) borate] was prepared by imido-deoxygenation of Tp′W(O)(CO)I with aniline in the absence of other reagents.[115] No such reactions are known for metals of titanium and vanadium groups, which is due to higher oxophilicity of these elements.

The imido-dehalogenation (replacement of halogen atoms by the imido function) of transition metal halides with primary amines is widely used in the synthesis of imido complexes. The reaction of amines with homoleptic halides of Group 4–6 transition metals, for example, with $TiCl_4$,[116–118] $NbCl_5$,[77,119–121] $TaCl_5$,[77,120] WX_6 (X = F, Cl),[122,123] usually afford dimeric imido complexes; however, the reaction carried out in the presence of n-donor compounds [py, 4-$Bu^tC_5H_4N$, MeCN, 1,2-dimethoxyethane (DME), *etc.*] results in mononuclear complexes.

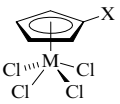
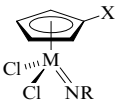
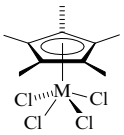
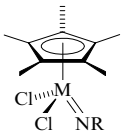
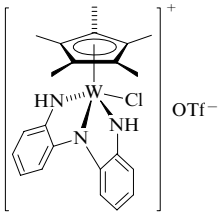
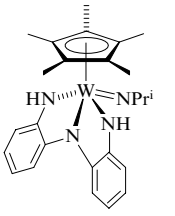
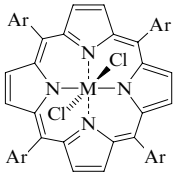
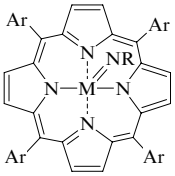
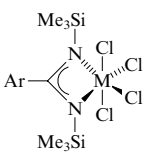
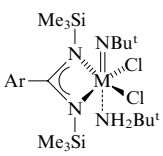
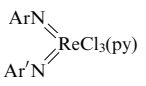
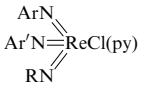




M = Nb, Ta; R = Bu^t, Ph, 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$, anthracen-2-yl, Ad, 2-naphthyl, 4-NCC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$.

Various heteroleptic transition metal chlorides are also successfully used for the preparative synthesis of imido complexes. Examples of imido complexes prepared by imido-dechlorination of heteroleptic metal chlorides with primary amines are summarised in Table 2. It is noteworthy that some of these can be prepared with equal success by imido-dehalogenation with trimethylsilylamines (see Section II.1.c, Table 5).

Table 2. Synthesis of Group 4–8 transition metal imido complexes by imido-dechlorination with primary amines.

Starting compound	M	Ar or X	R in RNH_2	Product	Yield (%)	Ref.
	Mo	H, Me, Pr^i	Bu^t, Pr^i, Pr^n, Ph, 2,6-$Me_2C_6H_3$		36–83	124–126
		CH_2Cl	2,6-$Me_2C_6H_3$		65	127
	W	H	Bu^t		35	124
		Me	Bu^t		70	125
		CH_2Cl	Bu^t		70	127
	Mo		Bu^t, Pr^i, C_6F_5, 2,6-$Pr^i_2C_6H_3$		39–75	128, 129
	W		Bu^t, Pr^i, C_6F_5, 2,6-$Pr^i_2C_6H_3$		45–70	129, 130
	Re		Me		65	131
			Bu^t		56	131
			Pr^i		70	132
	V	4-MeC_6H_4	Bu^t, 4-XC_6H_4 (X = H, Me, Cl, OMe)		54–69	133
	Ru	4-$Bu^tC_6H_4$	4-XC_6H_4 (X = H, Me, Cl, I)		40–75	15
	Nb	2,4,6-$Pr^i_3C_6H_2$	Bu^t		59	134
	Ta	2,4,6-$Pr^i_3C_6H_2$	Bu^t		53	134
		2,6-$Pr^i_2C_6H_3$ (Ar), 2,6-$Me_2C_6H_3$ (Ar′)	4-MeC_6H_4, 4-$NO_2C_6H_4$, 2-$Bu^tC_6H_4$		–	135

A convenient preparative-scale method for the synthesis of arylimido complexes of Group 4–6 transition metals is transimidation with various anilines. The method is based on equilibrium replacement of some imido ligands by other imido ligands.

$$\{M\}{=}NR + R'NH_2 \rightleftharpoons \{M\}{=}NR' + RNH_2.$$

tert-Butylimido complexes are the best starting compounds, because in this case, the shift of the equilibrium toward the substitution product is easily attained by removing volatile *tert*-butylamine from the reaction mixture. This method has opened the way to various arylimido titanium complexes (Table 3).

Transimidation with amines is successfully used to prepare arylimido complexes of other metals. This method was first used to prepare vanadium phenylimido complexes **3**.[143, 144]

$$Bu^tN{=}V(OR)_3 + PhNH_2 \longrightarrow \underset{\mathbf{3}}{PhN{=}V(OR)_3} + Bu^tNH_2$$

R = $SiMe_3$ (53%), Et (22%), Bu^t (69%).

The method appeared to be especially convenient for the synthesis of asymmetric bisimido complexes. For example, treatment of the symmetric bisimido complex $(Bu^tN{=})_2MoCl_2(DME)$ with one equivalent of $C_6F_5NH_2$ or 2,6-$Pr^i_2C_6H_3NH_2$, gave the complexes $(Bu^tN{=})(RN{=})MoCl_2(DME)$ (R = C_6F_5, 2,6-$Pr^i_2C_6H_3$) containing two different imido ligands in high yields (> 90%).[145, 146]

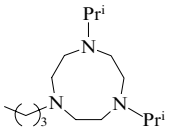
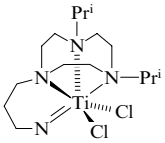
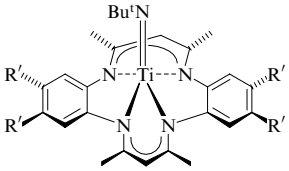
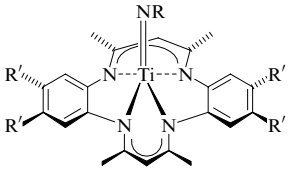
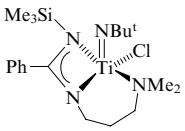
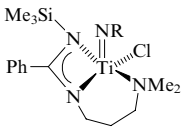
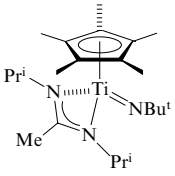
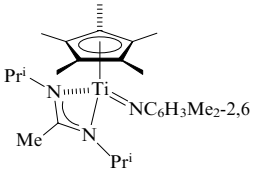
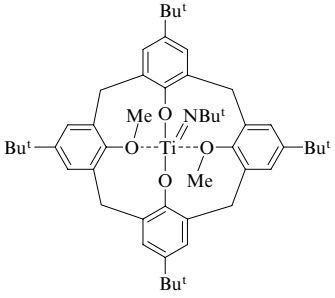
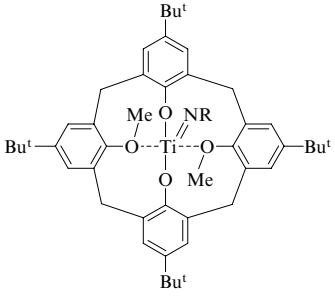
The reaction of $(Bu^tN{=})_2CrCl_2$ with two equivalents of 2,6-diisopropylaniline gives bis(arylimido) complex **4**.[147]

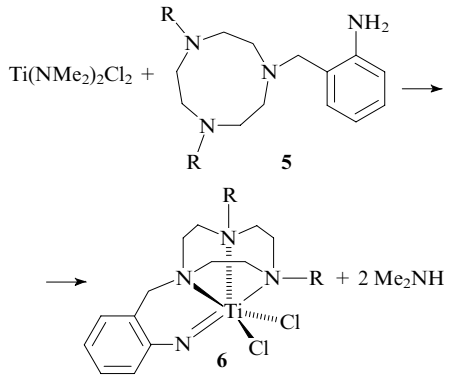
$$(Bu^tN{=})_2CrCl_2 + 2\,ArNH_2 \longrightarrow \underset{\mathbf{4}\ (60\%)}{(ArN{=})_2Cr(Cl)(NHBu^t)} + Bu^tNH_3Cl$$

Ar = 2,6-$Pr^i_2C_6H_3$.

Other metal-containing compounds, for example dimethylamido, carbene and σ-alkyl complexes of transition metals, can also be used in the imidation with amines. The reaction of titanium diamide complex $Ti(NMe_2)_2Cl_2$ with amine **5** afforded imido chelate **6**.[148]

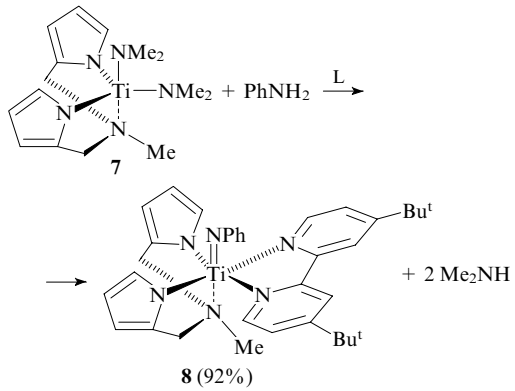
Table 3. Synthesis of titanium imido complexes by transimidation with amines.

Starting compound	R in RNH_2	Product	Yield (%)	Ref.
$Bu^tN{=}TiCl_2(py)_3$	Ph, 4-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$	$RN{=}TiCl_2(py)_3$	36–86	118
	4-$Me_3SiOC_6H_4$		77	136
	4-$NH_2C_6Me_4$		91	137
$Bu^tN{=}TiCl_2(py)_3$			74	138
$Bu^tN{=}TiCl_2(TMEDA)$	2-$Bu^tC_6H_4$	2-$Bu^tC_6H_4N{=}TiCl_2(TMEDA)$	–	116
 (R′ = H, Me)	4-XC_6H_4 (X = H, Me, NO_2, NMe_2)		75–95	139
	2,6-$Me_2C_6H_3$, C_6F_5		90–93	140
	2,6-$Me_2C_6H_3$		> 95	141
	4-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$, 4-FcC_6H_4		84–100	142



R = Me (58%), Pr^i (64%).

A similar exchange of the NMe_2 ligands in titanium polyamide complex **7** yielded imido complex **8** containing simultaneously three types of metal – nitrogen bonds.[149]



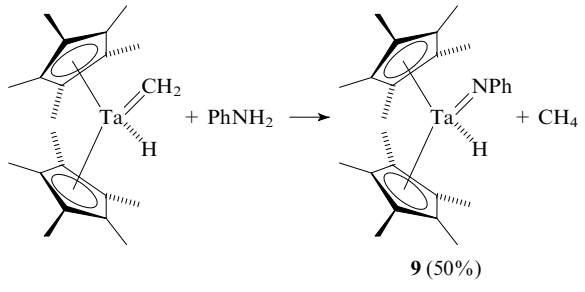
L is 4,4′-bis(*tert*-butyl)-2,2′-bipyridyl.

Imido-deamidation of homoleptic niobium and tantalum dimethylamide complexes $M(NMe_2)_5$ by amines is a convenient method for the synthesis of mixed imidoamide complexes of these metals $(RN{=})M(NMe_2)_3$ [R = Bu^t, 2,6-Pr$^i_2$C$_6$H$_3$; M = Nb (79%), Ta (86%)].[150, 151] By combining imido-deamidation and chloro-deamidation of the homoleptic complex $V(NMe_2)_4$ as a one-pot process, a series of d^1-vanadium complexes have been prepared.[152, 153]

$$V(NMe_2)_4 + ArNH_2 \xrightarrow{Me_3SiCl} ArN{=}VCl_2(NHMe_2)_2 + 2\ Me_2NSiMe_3$$

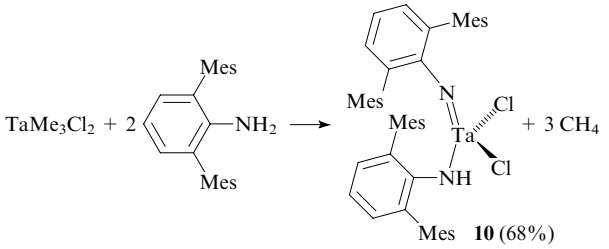
Ar = 2,6-Me$_2$C$_6$H$_3$ (79%), 2,6-Pr$^i_2$C$_6$H$_3$ (88%), 2,6-Cl$_2$C$_6$H$_3$ (96%), Ph (80%), C$_6$F$_5$ (73%).

Examples of a methylene ligand displacement in carbene complexes by primary amines are known. In particular, this approach was used in the synthesis of tantalum imidohydride complex **9**.[154]



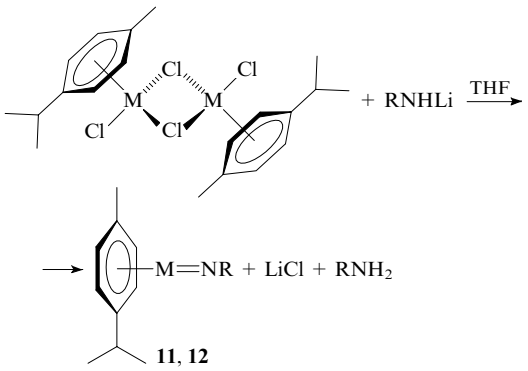
[Complex **9** is produced in higher yield in the redox imidation of $(\eta^5\text{-Cp}^*)_2TaCl$ (see Section II.2.f, Table 12).]

Tantalum imidoamide complex **10** containing sterically hindered aryl groups has been prepared by imido-dealkylation of the trimethyl complex $TaMe_3Cl_2$ on treatment with 2,6-disubstituted aniline.[155]

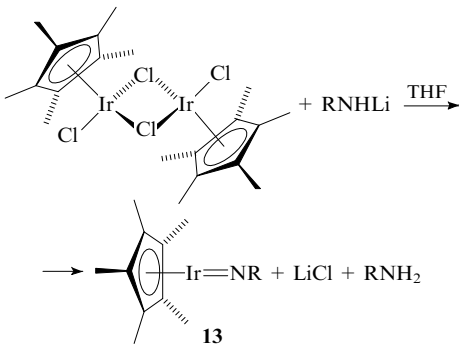


b. Imidation with lithium derivatives of primary amines

Lithium amides are widely used to prepare transition metal imido complexes. Examples of imidation of various homo- and heteroleptic Group 4 and 5 metal halides with lithium amides are given in Table 4. Lithium amides are, however, used much more rarely to prepare derivatives of transition metals of Group 6 – 9. Only a few examples of imidation of complexes containing Os, Ru and Ir in low oxidation states with lithium derivatives of a number of sterically hindered amines have been reported. In particular, imido-dechlorination of osmium[168, 169] and ruthenium[170, 171] arene chlorides or iridium pentamethylcyclopentadienyl chlorides[172, 173] led to unusual mononuclear d^6-complexes **11** – **13**.



11: M = Os; R = Bu^t (60%), 2,6-Pr$^i_2$C$_6$H$_3$ (36%), 2,6-Me$_2$C$_6$H$_3$ (96%);
12: M = Ru; R = 2,4,6-Bu$^t_3$C$_6$H$_2$ (40%).



R = Bu^t (91%), 2,6-Me$_2$C$_6$H$_3$ (33%), Bu^{t}Me$_2$Si (90%), 2,6-Pr$^i_2$C$_6$H$_3$ (77%).

c. Imidation with trimethylsilylamines

The use of trimethylsilyl derivatives of primary amines is among the most common methods for intermolecular imidation. Two versions of this process are known: one uses pre-synthesised mono- or bis(trimethylsilyl)amines, while in the other, trimethylsilyl derivatives of amines are prepared *in situ* by introducing the

Table 4. Synthesis of Group 4 and 5 transition metal imido complexes by imido-dechlorination with alkali metal amides.

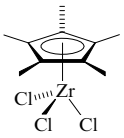
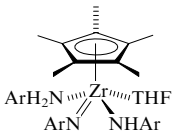
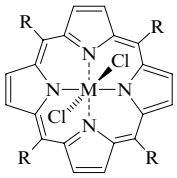
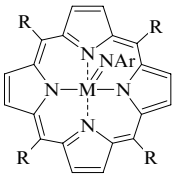
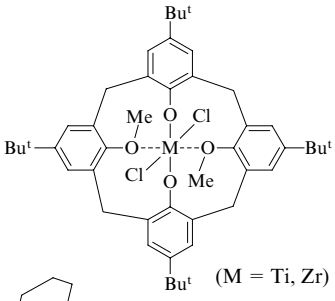
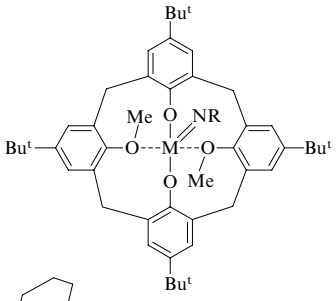
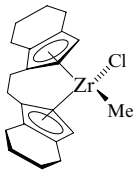
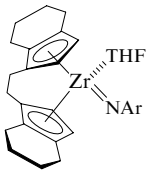
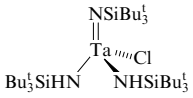
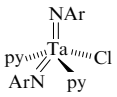
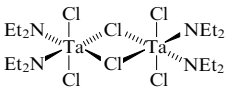
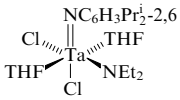
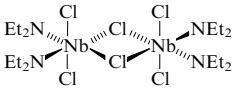
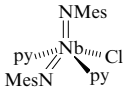
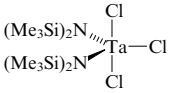
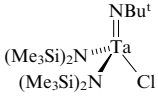
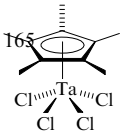
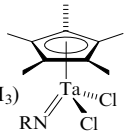
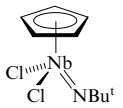
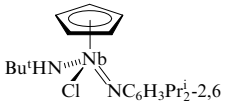
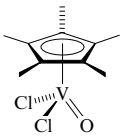
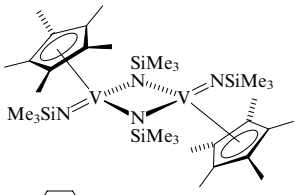
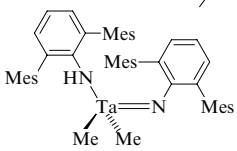
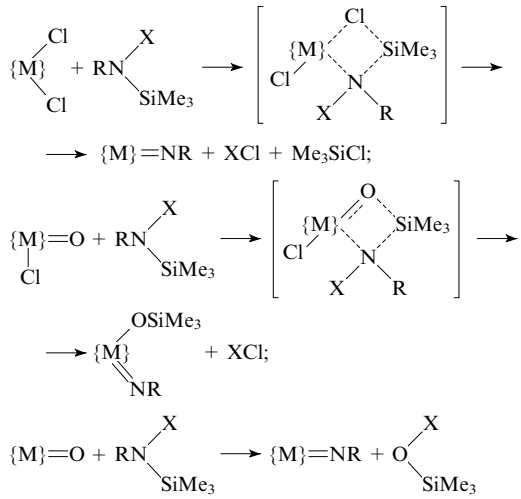
Starting compound	Reagents	Product	Yield (%)	Ref.
$MCl_4(THF)_2$ (M = Zr, Hf)	ArNHLi (Ar = 2,6-$Pr^i_2C_6H_3$)	$ArN{=}M(NHAr)_2(THF)_2$	85 (Zr), 49 (Hf)	156
	ArNHLi, THF (Ar = 2,6-$Pr^i_2C_6H_3$)		44	156
 (M = Zr, Hf, R = Ph; M = Ti, R = 4-MeC_6H_4)	ArNHLi [Ar = 2,6-$Pr^i_2C_6H_3$ (for Zr, Hf); Bu^t, Ph, 4-MeC_6H_4 (for Ti)]		93 (Zr) 60 (Hf) 87–94 (Ti)	157 157 158
 (M = Ti, Zr)	RNHLi (R = Bu^t, 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$) or MesNHK (for Ti); 2,6-$Pr^i_2C_6H_3$NHLi (for Zr)		75–100 (Ti); 61 (Zr)	142 142
	ArNHLi, THF (Ar = 2,6-$Me_2C_6H_3$, 4-MeC_6H_4)		65	159
MCl_5 (M = Nb, Ta)	$Bu^tNHLi + Me_2NLi$	$Bu^tN{=}M(NMe_2)_3$	20 (Nb) 40 (Ta)	150 160
$TaCl_5$	$Bu^t_3SiNHLi$		82	45
$TaCl_3(NEt_2)_2(OEt_2)$	ArNHLi, py (Ar = 2,6-$Pr^i_2C_6H_3$)		60	161
	2,6-$Pr^i_2C_6H_3$NHLi, THF		61	161
	MesNHLi, py		79	162
	Bu^tNHLi		71	163
 165	RNHLi (R = Bu^t, 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$, 2,6-$Mes_2C_6H_3$, 2,6-(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$)		64–85	46, 164,

Table 4 (continued).

Starting compound	Reagents	Product	Yield (%)	Ref.
	$2,6\text{-}Pr^i_2C_6H_3NHLi$		31	166
	$(Me_3Si)_2NLi$		–	167
$TaMe_3Cl_2$	$2,6\text{-}Mes_2C_6H_3NHLi$		71	155

$RNH_2 - Me_3SiCl - B$ ternary system in the reaction (B is a base). Either the initial amine or another amine (most often, triethylamine or pyridine) is used as the base, and homo- and heteroleptic halides of Group 4 – 6 metals and oxo complexes of Group 5 and 6 metals, in particular, sodium or ammonium metallates, are used as the metal-containing compounds. The formation of imido complexes is due to thermodynamically favourable replacement of oxygen or chlorine atoms in the starting compounds by imido groups. In the former variant, Me_3SiCl, $(Me_3Si)_2O$ or HCl (a base is added for binding of HCl) are formed together with target complexes (Scheme 4).

Scheme 4



X = H, $SiMe_3$.

Imido-dechlorination of transition metal chlorides with trimethylsilylamines proceeds smoothly and, most often, gives products in high yields. Examples of imido complexes obtained by this method are presented in Table 5. Note that the use of primary amines (see Section II.1.a) and lithium amides (Section II.1.b) in imido-dechlorination gives most often comparable results.

Another type of starting compounds frequently used for imidation with silylamines are oxohalides of Group 5 and 6 transition metals. The synthesis of imido complexes using these compounds is chronologically one of the earliest, because V, Cr, Mo and W oxohalides are easily available (either commercially or synthetically). Imidation can be accompanied by replacement of either oxygen or chlorine atoms. The first vanadium imido complex $MeN{=}VCl_3$ was prepared by imido-deoxygenation of $VOCl_3$.[187] Later, the same method was used to prepare the phenylimide analogue, $PhN{=}VCl_3$.[188]

$$VOCl_3 + (Me_3Si)_2NR \longrightarrow RN{=}VCl_3 + (Me_3Si)_2O$$

R = Me (80%), Ph.

Conversely, the reaction of $WOCl_4$ with $4\text{-}MeC_6H_4NHSiMe_3$ in the presence of 2,2′-bipyridyl involves replacement of chlorine atoms to give the oxo – imido complex $4\text{-}MeC_6H_4N{=}W(O)Cl_2 \cdot (bipy)$.[185] The introduction of chlorotrimethylsilane directs the reaction along the imido-deoxygenation route. For example, on treatment with trimethylsilylamines, the chlorine atoms in chromium and molybdenum dioxodichlorides are replaced by the imido group, giving rise to silyloxyimido complexes $(RN{=})_2M(OSiMe_3)_2$ [M = Cr: R = Bu^t (54%),[123,150] Ad (26%);[189] M = Mo: R = Bu^t (93%), 1-norbornyl (80%),[123,150] Me_3Si (60%)[190]], whereas treatment with amines or their monosilyl derivatives in combination with chlorotrimethylsilane leads to imido-deoxygenation.[191 – 193]

$$MoO_2Cl_2(THF)_2 \xrightarrow[DME]{ArNHSiMe_3 - Me_3SiCl - B} (ArN{=})_2MoCl_2(DME) + BH^+Cl^- + (Me_3Si)_2O \quad (95\%)$$

Ar = $2,6\text{-}Pr^i_2C_6H_3$, B = $2,6\text{-}Me_2C_5H_3N$.

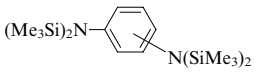
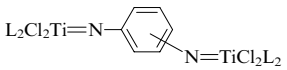
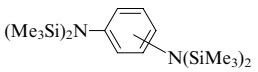
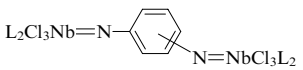
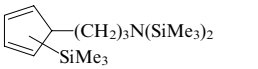
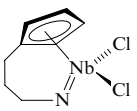
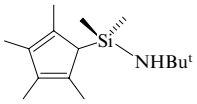
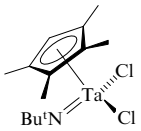
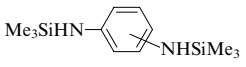
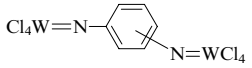
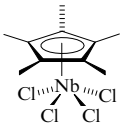
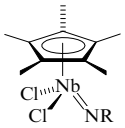
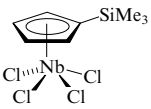
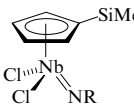
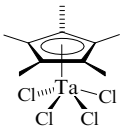
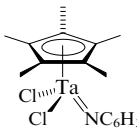
$$WO_2Cl_2 \xrightarrow[DME]{ArNHX - Me_3SiCl - B} (ArN{=})_2WCl_2(DME) + BH^+Cl^- + (Me_3Si)_2O$$

Ar	X	B	Yield (%)
$2,6\text{-}Pr^i_2C_6H_3$	H	$2,6\text{-}Me_2C_5H_3N$	70
	$SiMe_3$	$2,6\text{-}Me_2C_5H_3N$	64
$2,4,6\text{-}Me_3C_6H_2$	H	Et_3N	91

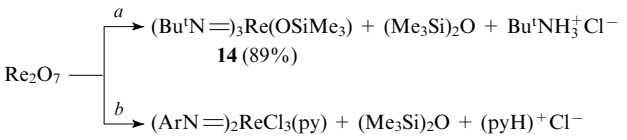
It is noteworthy that diimidomolybdenum dichlorides are prepared more conveniently directly from sodium or ammonium molybdate (see below).

Examples of the synthesis of imido complexes by treatment of transition metal oxides with silylamines are known. The complex $(Bu^tN{=})_2Cr(OSiMe_3)_2$, which is the key compound in the chemistry of d^0-chromium imido complexes, can be obtained by imido-deoxygenation of chromium(VI) oxide with $Bu^tNHSiMe_3$

Table 5. Synthesis of Group 4 – 6 transition metal imido complexes by imido-dehalogenation with trimethylsilylamines.

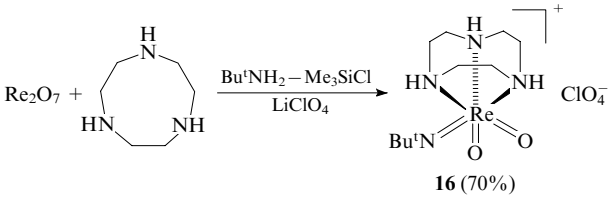
Starting compound	Amine	Auxiliary reagent (L)	Product	Yield (%)	Ref.
$TiCl_4$	 (*meta*- and *para*-isomers)	4-$Bu^tC_5H_4N$, TMEDA		72 – 86	137
	$Bu^tNHSiMe_3$	py	$Bu^tN{=}TiCl_2(py)_3$	50	79
$NbCl_5$	 (*ortho*-, *meta*- and *para*-isomers)	4-$Bu^tC_5H_4N$, MeCN		88 – 90	137
		–		38	174
	$Bu^tNHSiMe_3$	PMe_3	$Bu^tN{=}NbCl_3(PMe_3)_2$	–	119
	$4\text{-}Me_3SiC_6H_4N(SiMe_3)_2$	MeCN	$4\text{-}Me_3SiC_6H_4N{=}NbCl_3(MeCN)_2$	96	175
	$4\text{-}Me_3SiOC_6H_4N(SiMe_3)_2$	MeCN	$4\text{-}Me_3SiOC_6H_4N{=}NbCl_3(MeCN)_2$	87	136
$TaCl_5$	$HN(SiMe_3)_2$	py	$Me_3SiN{=}TaCl_3(py)_2$	71	176
	$2,6\text{-}Pr^i_2C_6H_3NHSiMe_3$	THF	$2,6\text{-}Pr^i_2C_6H_3N{=}TaCl_3(THF)_2$	82	177
		–		45	39
TaX_5 (X = Cl, Br)	$2,6\text{-}Pr^i_2C_6H_3NHSiMe_3$	TMEDA, DME, THF, py	$2,6\text{-}Pr^i_2C_6H_3N{=}TaX_3L_2$	29 – 82	178
$MoCl_5$	$2\text{-}NCC_6H_4N(SiMe_3)_2$	MeCN	$2\text{-}NCC_6H_4N{=}MoCl_3(MeCN)_2$	65	179
WCl_6	$2\text{-}NCC_6H_4N(SiMe_3)_2$	–	$[2\text{-}NCC_6H_4N{=}WCl_4]_2$	91	179
	 (*ortho*- and *para*-isomers)	–		79, 90	180
	$Bu^tNHSiMe_3$	–	 R = Bu^t	78	181
	$MeN(SiMe_3)_2$	–	R = Me	60	181
	$2,6\text{-}Me_2C_6H_3NHSiMe_3$	–	R = $2,6\text{-}Me_2C_6H_3$	81	181
	$2,6\text{-}Me_2C_6H_3NHSiMe_3$	$Me_2C_5H_3N$	R = $2,6\text{-}Me_2C_6H_3$	46.5	182
	$MeN(SiMe_3)_2$	–	 R = Me	60	181
	$2,6\text{-}Pr^i_2C_6H_3NHSiMe_3$	–	R = $2,6\text{-}Pr^i_2C_6H_3$	77	181
	$4\text{-}Me_3SiC_6H_4NHSiMe_3$	–	 R = $SiMe_3$	90	175
	$RNHSiMe_3$ (R = $SiMe_3$, $2,6\text{-}Pr^i_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$)	–	R = $SiMe_3$, $2,6\text{-}Pr^i_2C_6H_3$, $2,6\text{-}Me_2C_6H_3$	89	183
	$2,6\text{-}Pr^i_2C_6H_3NHSiMe_3$	–		72	181
$RN{=}WCl_4(THF)$ (R = $2,6\text{-}Pr^i_2C_6H_3$)	$2,6\text{-}Pr^i_2C_6H_3NHSiMe_3$	THF	$(2,6\text{-}Pr^i_2C_6H_3N{=})_2WCl_2(THF)_2$	87	184
$(PhN{=}WCl_4)_2$	$4\text{-}MeC_6H_4NHSiMe_3$	bipy	$(PhN{=})(4\text{-}MeC_6H_4N{=})WCl_2(bipy)$	–	185
$(PhN{=}W(OEt)_2Cl_2)_2$	$Bu^tNHSiMe_3$	bipy	$(PhN{=})(Bu^tN{=})W(OEt)_2(bipy)$	–	186

(yield < 30%).[150] Silyloxyrhenium trioxide $ReO_3(OSiMe_3)$ reacts with three equivalents of $Bu^tNHSiMe_3$ to give the trisimido complex $(Bu^tN{=})_3Re(OSiMe_3)$ (**14**) in 64% yield.[194] Complex **14** is also formed in the reaction of rhenium(VII) oxide with *tert*-butylamine in the presence of chlorotrimethylsilane.[195] The introduction of aromatic amines, together with Me_3SiCl and pyridine, allows one to synthesise complexes **15** of a different composition.



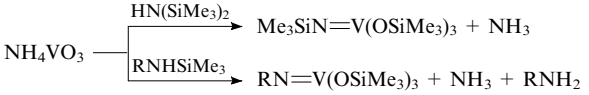
(*a*) $Bu^tNH_2 - Me_3SiCl$; (*b*) $ArNH_2 - Me_3SiCl - py$;
Ar = 2,6-$Me_2C_6H_3$ (83%), 2,6-$Pr^i_2C_6H_3$ (76%).

The successive addition of *tert*-butylamine, chlorotrimethylsilane, 1,4,7-triazacyclononane and lithium perchlorate to rhenium(VII) oxide yielded cationic rhenium oxo – imido d^0-complex **16**.[196]



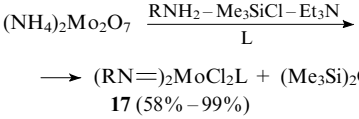
The reaction of osmium tetraoxide with $Bu^tNHSiMe_3$ affords either osmium dioxo diimido $(Bu^tN=)_2OsO_2$[197] or osmium tetraimido $(Bu^tN=)_4Os$ complexes depending on the amount of the amine.[198] It is worth noting that a similar reaction with trimethylsilylanilines proceeds as a redox process (see Section II.2.e).

For the synthesis of V, Mo and Re imido complexes, it is rather convenient to use their metallates, in particular, NH_4VO_3, Na_2MoO_4, $(NH_4)_2Mo_2O_7$ and NH_4ReO_4. The use of these compounds opened up the route to a broad range of imido derivatives. Thus ammonium vanadate reacts with silylamines giving imidotrimethylsilyl oxide complexes.[143, 199]



R = Pr^n, Bu^t (72%).

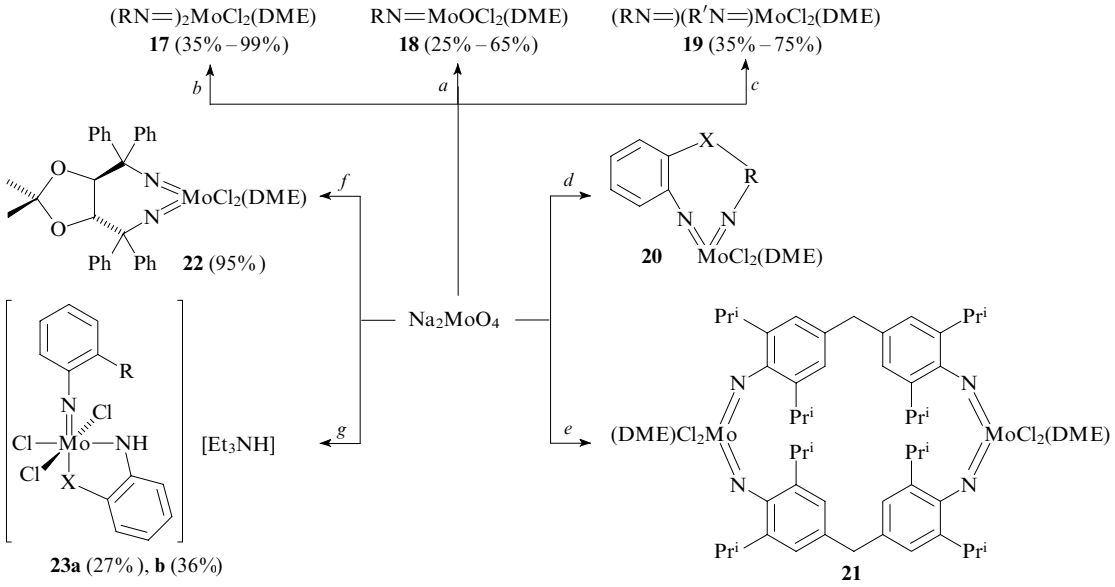
Schrock[200, 201] developed a general method for the synthesis of molybdenum bisimido complexes **17** [L = DME: R = Bu^t, C_6F_5, Ph, 2-$Bu^tC_6H_4$, 2,6-$Pr^i_2C_6H_3$, 2,6-$Me_2C_6H_3$, 4-Br-2,6-$Pr^i_2C_6H_2$, 4-CN-2,6-$Pr^i_2C_6H_2$, 3,5-$Me_2C_6H_3$, 2-$Pr^iC_6H_4$, 2-$CF_3C_6H_4$, Ad, 2-$(CH_2{=}CHCMe_2CH_2CH_2)C_6H_4$ (see Ref. 202); L = py: R = 2-PhC_6H_4] based on the one-pot reaction between ammonium molybdate and two equivalents of a primary amine, which takes place in the presence of chlorotrimethylsilane and triethylamine in a coordinating solvent L (usually in 1,2-dimethoxyethane).



L = DME, py.

Gibson and co-workers,[203] without changing the synthetic strategy as a whole, proposed to use sodium molybdate instead of ammonium molybdate. A number of publications [204 – 213] demonstrate broad synthetic potential of this approach. Starting from Na_2MoO_4, oxo – imido complexes (**18**) [R = Ad,[204] 2,4,6-$Ph_3C_6H_2$,[205] C_6F_5 (Ref. 206)] (Scheme 5, path *a*) and bisimido complexes (**17**) [R = 2,6-$Et_2C_6H_3$,[207] 4-Fc-2,6-$Pr^i_2C_6H_2$, 4-(FcC≡C)-2,6-$Pr^i_2C_6H_2$,[208] 2-$Bu^tC_6H_4$, 2-Me-6-$Pr^iC_6H_3$,[209] 2-NCC_6H_4,[210] 2,5-$Cl_2C_6H_3$, 2,6-$Cl_2C_6H_3$ and 2,4,6-$Cl_3C_6H_2$ (Ref. 206)] were prepared (Scheme 5, path *b*), respectively. The ease of imido-deoxygenation is noticeably affected by the steric factor and by the electronic effects of substituents in the starting anilines. Thus the reaction of Na_2MoO_4 with sterically hindered 2,4,6-triphenylaniline precludes incorporation of more than one imido group into the molybdenum coordination sphere.[205] The reaction with weakly nucleophilic perfluoroaniline results in a bisimido and oxo – imido products mixture with a substantial predominance of the latter. In the series of polychloroanilines, the yield of the target bisimido complexes decreases with a decrease in the nucleophilicity of the initial aniline, and 2,4,6-tribromoaniline does not enter into the reaction.[206] The introduction of two different amines into the reaction allows one to prepare asymmetric diimidomolybdenum dichlorides **19** [R = Bu^t: R′ = C_6F_5,[145] 2,6-$Pr^i_2C_6H_3$;[146, 204] R = Ad, R′ = C_6F_5 [145] (Scheme 5, path *c*). This procedure with Na_2MoO_4 was also used to prepare some molybdenum bisimido chelates **20** [R = *o*-C_6H_4; X = CH_2, $(CH_2)_2$; R = CMe_2, X = CH_2)] (Scheme 5,

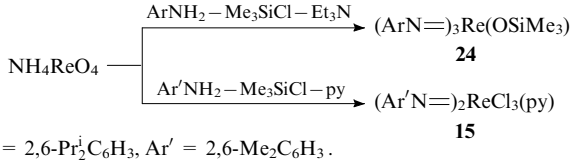
Scheme 5



(*a*) $RNH_2 - Me_3SiCl - Et_3N$; (*b*) RNH_2 (2 equiv.) – $Me_3SiCl - Et_3N$; (*c*) $(RNH_2 + R'NH_2) - Me_3SiCl - Et_3N$;
(*d*) *o*-$H_2NC_6H_4XRNH_2$-*o* – $Me_3SiCl - Et_3N$; (*e*) (4-H_2N-3,5-$Pr^i_2C_6H_2)_2CH_2 - Me_3SiCl - Et_3N$;
(*f*) TADDAMIN – $Me_3SiCl - Et_3N$; (*g*) *o*-$H_2NC_6H_4XH - Me_3SiCl - Et_3N$;
R, R′, X — see text.

path *d*)[211,212] and **21** (Scheme 5, path *e*),[211] and the first molybdenum complex based on chiral (4*S*,5*S*)-4,5-di(aminodiphenyl)-methyl-2,2-dimethyl-1,3-dioxolane (TADDAMIN) (complex **22**, Scheme 5, path *f*).[213] The reactions of sodium molybdate with anthranilic acid and aniline-2-sulfonic acid are more complicated under similar conditions to give monoanionic (**23a**) [R = C(O).OSiMe$_3$, X = C(O)O] and dianionic (**23b**) (R = $SO_3^-[Et_3NH]^+$, X = SO_3) complexes (Scheme 5, path *g*); their structure was confirmed by X-ray diffraction.[210]

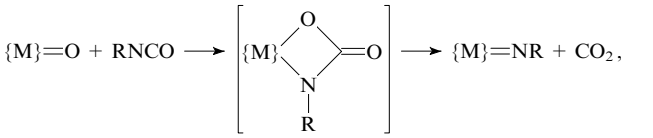
Ammonium perrhenate can be used to prepare rhenium d^0-complexes of various compositions. For example, the reaction of NH_4ReO_4 with 2,6-diisopropylaniline in the presence of chlorotrimethylsilane and triethylamine gives trisimido complex **24**.[214] The use of excess pyridine instead of triethylamine results in bisimido complex **15**.[195]

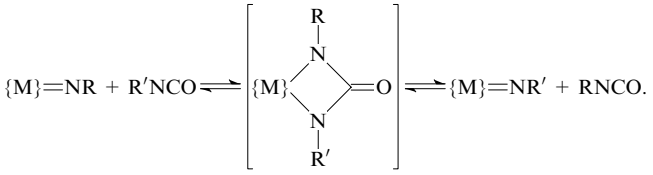


Ar = 2,6-$Pr^i_2C_6H_3$, Ar′ = 2,6-$Me_2C_6H_3$.

d. Imidation with organic isocyanates

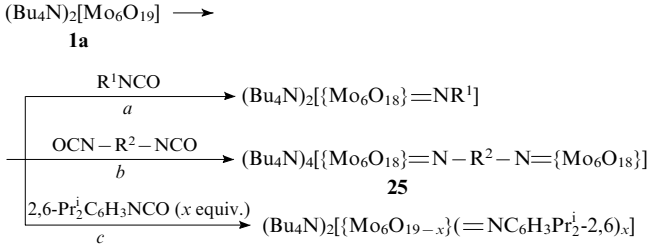
Metathesis imidation of transition metal complexes with alkyl and aryl isocyanates are widely used in synthetic practice. Isocyanates are mainly used for imidation of oxo complexes (for example, Group 5–7 transition metal oxohalides, Table 6); in some cases, imido complexes are used as the starting compounds. In the former case, metathesis imido-deoxygenation with carbon dioxide evolution takes place, while in the latter case, equilibrium transimidation occurs.



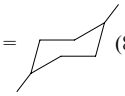
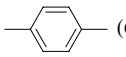
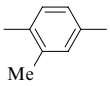


The reactions proceed *via* the formation of four-membered metallacycle intermediates, *viz*. *N*,*O*-carbamates and *N*,*N*′-ureates. *N*,*O*-Carbamates were not detected experimentally, while *N*,*N*′-ureates were in some cases isolated and characterised by spectral methods and X-ray diffraction.[215–218] In both cases, to attain satisfactory yields of the products, long-term refluxing of the reactants in high-boiling solvents (xylene, toluene, octane, *etc*.) is most often required; therefore, this method is inapplicable to thermally unstable complexes. Yet another drawback of the method is toxicity of organic isocyanates.

The imidation of polyoxo complexes by this method allows one to introduce varying numbers of imido groups in the complex. It was shown using polymolybdate **1a** as an example that by varying the amount of isocyanate used, one can incorporate one to five imido groups into the anion.[233,234] The use of diisocyanates in the reaction with polymolybdate **1a** yields complexes **25** containing two polymolybdate moieties bridged by diimido ligands.[235] Compounds of this type can also be prepared by imido-deoxygenation with amines, iminophosphoranes or by cross-coupling, the yields being comparable in all cases.



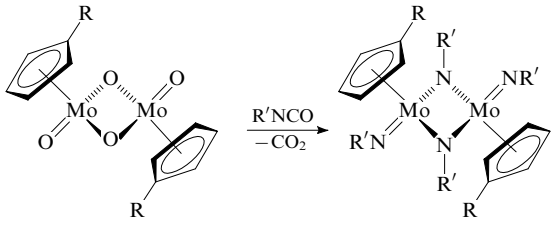
(*a*) R^1 = Bu^n (56%), Cy (73%), Fc (19%);

(*b*) R^2 =  (80%),  (60%),  (60%);

(*c*) *x* = 1–5 (20%–86%).

By the use of three equivalents of 2,6-disubstituted aryl isocyanates in the reaction with silyloxytechnetium and -rhenium trioxides, all oxygen atoms were replaced by imido functions to give trisimido d^0-complexes (RN=)$_3$M(OSiMe$_3$) [M = Tc: R = 2,6-$Me_2C_6H_3$ (61%), 2,6-$Pr^i_2C_6H_3$ (60%);[236] M = Re: R = 2,6-$Me_2C_6H_3$ (82%), 2,6-$Pr^i_2C_6H_3$ (46%), 2,6-$Cl_2C_6H_3$ (79%)[237]].

Examples of successful use of isocyanates for the synthesis of imido derivatives of transition metal σ- and π-complexes are known. In particular, the reactions of binuclear cyclopentadienyl



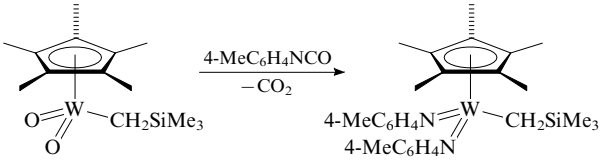
R = H: R′ = Ph (41%); R = Me: R′ = Ph (26%), 4-MeC_6H_4 (10%); R = Pr^i, R′ = Ph (12%).

Table 6. Synthesis of Group 5–7 transition metal imido complexes by imido-deoxygenation with organic isocyanates.

Starting compound	R in RNCO	Product	Yield (%)	Ref.
$VOCl_3$	4-XC_6H_4 (X = H, Me, CF_3, OMe, Cl, Br, F), 2,6-$Pr^i_2C_6H_3$	RN=VCl_3	84 (X = Me) 99	219–222 221
$VOCl_3$	4-$OCNC_6H_4$	Cl_3V=NC_6H_4N=VCl_3	84	223
$WOCl_4$	Me, Et, Pr^i, Bu^n, Bu^t, Cy, Ph, 4-MeC_6H_4, 2-PhC_6H_4, 2-$Bu^tC_6H_7$, 2-$C_{10}H_7$, 2,6-$Pr^i_2C_6H_3$	(RN=WCl_4)$_2$	70–98	25, 193, 209, 224–227
$WOCl_4$	4-$OCNC_6H_4$	Cl_4W=NC_6H_4N=WCl_4	–	228
WO_2Cl_2	2,6-$Pr^i_2C_6H_3$	(RN=)$_2WCl_2$(DME)	64	193
MoO_2Cl_2	Bu^t, 2,6-$Pr^i_2C_6H_3$	(RN=)$_2MoCl_2$	95	229, 230
$ReOCl_3L_2$ (L = PPh_3, PEt_2Ph)	Ph	RN=$ReCl_3L_2$	–	231, 232
$ReOCl_4$	Ph	(RN=$ReCl_4$)$_2$	88	185

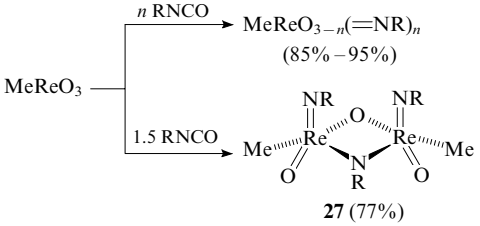
complexes $[(\eta^5\text{-}RC_5H_4)MoO(\mu\text{-}O)]_2$ with aryl isocyanates were reported. This reaction is a rare example of imido-deoxygenation occurring with replacement of both terminal and bridging oxygen atoms in the initial compound.[238 – 240]

The synthesis of tungsten bisimido complex **26** has also been reported.[217]



26 (23%)

Study of the reaction of methyltrioxorhenium $MeReO_3$ with aryl isocyanates has shown that by varying the reactant ratio, one can obtain products with different imido-deoxygenation degrees. Upon the addition of one, two or three equivalents of aryl isocyanate to $MeReO_3$, mono-, bis- or tris-imido complexes, respectively, are formed,[131, 241] while the addition of 1.5 equiv. RNCO results in the binuclear complex **27** containing terminal and bridging imido ligands.



27 (77%)

R = 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$; n = 1 – 3.

It has been noted above that this method is mainly used to imidate thermally stable compounds. The imido-deoxygenation of, for example, the complex $MoO_2(S_2CNEt_2)_2$ with aryl isocyanates is accompanied by thermally induced destruction of the diethyldithiocarbamate group. As a result, the target bisimido complexes $(ArN{=})_2Mo(S_2CNEt_2)_2$ (**28**) are formed in low yields comparable with the yields of side products, *i.e.*, imido disulfide (**29**) and various binuclear (**30**) complexes.[242 – 246]

$$MoO_2(S_2CNEt_2)_2 \xrightarrow{ArNCO} \underset{\mathbf{28}}{(ArN{=})_2Mo(S_2CNEt_2)_2} + \underset{\mathbf{29}}{ArN{=}Mo(S_2)(S_2CNEt_2)_2} + \underset{\mathbf{30}}{[X{=}Mo(\mu\text{-}X')(S_2CNEt_2)]_2}$$

Ar = 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$, 2,6-$Cl_2C_6H_3$; X, X′ = NAr, O, S.

The destruction products become predominant if aryl isocyanates without *ortho*-substituents, for example, phenyl and *p*-tolyl isocyanates, are used.

Transition metal imido complexes can also undergo transimidation with isocyanates; however, this method is seldom used in practice, unlike transimidation with primary amines. This is due to the very low rate of the process and the need to use high-boiling solvents. Nevertheless, this approach is one of the few known methods for the synthesis of bis(arylimido)chromium d^0-complexes **31**.[247]

$$(Bu^tN{=})_2CrCl_2 \xrightarrow[-Bu^tNCO]{ArNCO} \underset{\mathbf{31}}{(ArN{=})_2CrCl_2}$$

Ar = Mes (75%), 2,6-$Me_2C_6H_3$ (80%).

During thermolysis of the binuclear complex $[(\eta^5\text{-}C_5Me_5)Mo(=NPh)(\mu\text{-}NPh)]_2$ with excess 4-MeC_6H_4NCO, successive replacement of two phenylimido groups by *p*-tolylimido groups was observed; transimidation involved only the terminal imido groups, while bridging ligands remained intact even after long-term heating (8 weeks) with an excess of the starting isocyanate.[248]

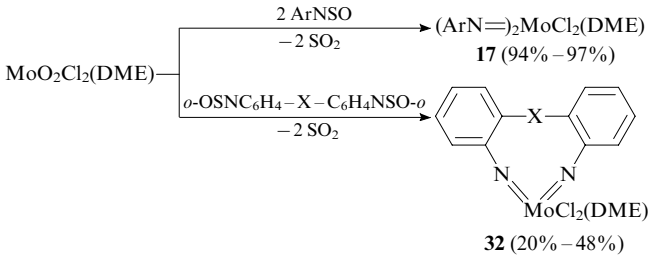
e. Imidation with *N*-sulfinylamines

The scope of using *N*-sulfinylamines for the synthesis of transition metal imido complexes has remained scarcely studied until recently. As regards the type of action, *N*-sulfinylamines are analogous to organic isocyanates, but they have advantages of being more readily available and more reactive toward imido-deoxygenation. It is essential that they are effective with both electron-donating and electron-withdrawing substituents. For example, sulfinyl derivatives of arylamines readily imidate the complex $ReOCl_3(PPh_3)_2$ (see Ref. 249).§

$$ReOCl_3(PPh_3)_2 + ArNSO \longrightarrow ArN{=}ReCl_3(PPh_3)_2 + SO_2$$

Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$.

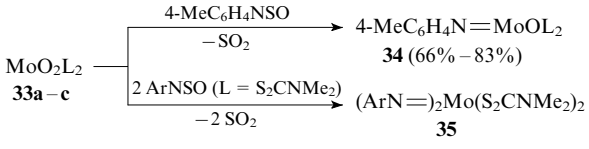
Molybdenum dioxodichloride easily undergoes imido-deoxygenation under the action of a number of halogen-substituted *N*-sulfinylanilines ArNSO to give corresponding bisimido complexes **17**.[206, 250] This approach was successfully used to prepare bisimido chelates **32**,[250, 251] the structure of which was confirmed by spectroscopic means.



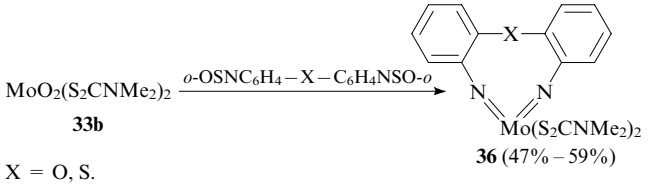
32 (20% – 48%)

Ar = C_6F_5, 2,6-$Cl_2C_6H_3$, 2,4,6-$Cl_3C_6H_2$, 2,4,6-$Br_3C_6H_2$; X = O, S.

Owing to the high reactivity, *N*-sulfinylamines can be efficiently used for imidation of some thermally labile complexes, for example, molybdenum dioxobis(dialkyldithiocarbamates) (**33a**,**b**). On treatment of complexes **33** with one equivalent of *N*-sulfinylanilines, monosubstitution takes place to give products **34**,[252] while the action of two equivalents of *N*-sulfinylanilines or one equivalent of *N*-sulfinyl derivatives of some diamines allows the preparation of full substitution products (compounds **35** or **36**, respectively),[251, 253] whose structure was confirmed by spectroscopic means.



L = S_2CNEt_2 (**33a**), S_2CNMe_2 (**33b**), acac (**33c**); Ar = 4-MeC_6H_4 (64%), 2,4,6-$Cl_3C_6H_2$ (86%), 2,4,6-$Br_3C_6H_2$ (73%).



36 (47% – 59%)

X = O, S.

N-Sulfinylamines are able to transimidate transition metal imido complexes; however, this reaction is of low practical value due to the low rate. Only prolonged heating ($\geqslant$ 40 h) of 2,6-

§ For the imidation of $ReOCl_3(PPh_3)_2$, amines, isocyanates, iminophosphoranes and hydrazines can be used with equal success.

diisopropyl-*N*-sulfinylaniline with chromium d^0-complex $(Bu^tN{=})_2Cr(OSiMe_3)_2$ does give the transimidation product $(2,6\text{-}Pr^i_2C_6H_3N{=})_2Cr(OSiMe_3)_2$ in a good yield (72%).[251]

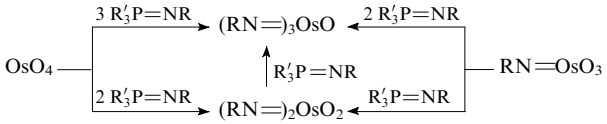
e. Imidation with iminophosphoranes

Iminophosphoranes are seldom used as imidating reagents. To some extent, this is due to their lower synthetic availability as compared with other imidating agents. Iminophosphoranes readily enter into imido-deoxygenation with transition metal oxides. The oxo–imide exchange is facilitated by the formation of phosphine oxides in addition to the imido complexes.

$$\{M\}{=}O + R'_3P{=}NR \longrightarrow \{M\}{=}NR + R'_3P{=}O.$$

Examples of imido derivatives obtained using this synthetic approach are given in Table 7.

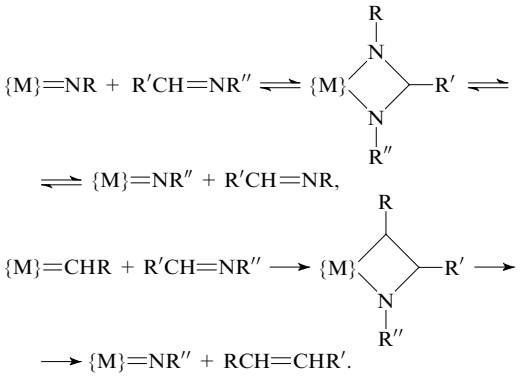
An essential advantage of iminophosphoranes is that they allow imidation of metal oxides that possess pronounced oxidative properties without reduction of the metal. For example, iminophosphoranes $R'_3P{=}NR$ enter into metathesis with osmium tetraoxide or osmium oxoimides to yield bis- and tris-imido complexes $(RN{=})_2OsO_2$, $(RN{=})_3OsO$ with retention of the d^0 configuration of the metal.[2]



R = Bu^t, Ad, CMe_2Et; R′ = Bu^n, Ph.

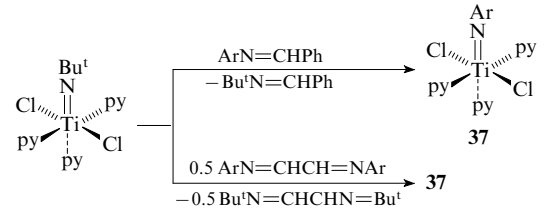
g. Imidation with imines and 1,4-diazabuta-1,3-dienes

Examples of formation of transition metal imido complexes upon the action of the Schiff bases on other imido or carbene complexes of this metal are documented. In the former case, reversible metathesis transimidation takes place, while in the latter case, irreversible alkylidene–imine methathesis occurs giving rise to imido complexes and alkenes.



Both processes are believed to proceed *via* the intermediate formation of four-membered azametallacycles.[29,31] In particular, this mechanism was confirmed by isolation and identification of the 2,4-diazametallacyclobutane intermediate formed upon treatment of zirconocene-imide $Cp_2Zr(=NBu^t)(THF)$ with $PhCH{=}NPh$.[31,262,263]

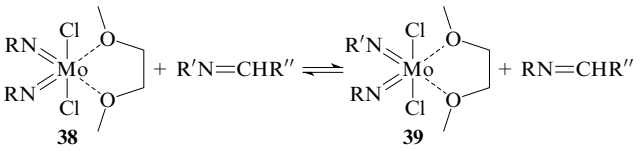
A study of the reaction of stoichiometric amounts of the complex $Bu^tN{=}TiCl_2(py)_3$ and the Schiff bases $ArN{=}CHPh$ (NMR detection and a preparative experiment) has shown that the equilibrium is completely shifted towards the formation of the arylimido complex **37**,[264] the imido–imine methathesis being slower for sterically more hindered 2,6-dimethylphenylimine (the process is over only after 96 h) than for *p*-tolylimine (4 h).



Ar = 4-MeC_6H_4, 2,6-$Me_2C_6H_3$.

A similar imido–imine metathesis takes place during imidation of the complex $Bu^tN{=}TiCl_2(py)_3$ with 1,4-diazabuta-1,3-dienes.[265]

During the imido–imine exchange between molybdenum bisimido complexes **38** and various Schiff bases, the equilibrium (a 1:1 ratio of the initial complex **38** and product **39**) can be attained relatively fast (after ~20 h) only for the imido ligand with alkyl groups (example *a*), whereas for aryl substituents (example *b*) this ratio is attained only in 18 days.[29]

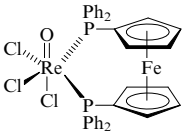
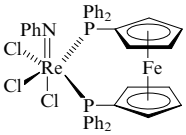


(*a*) R = Bu^t, R′ = Pr, R″ = Ph; (*b*) R = 2,6-$Pr^i_2C_6H_3$, R′ = Ph, R″ = Bu^t.

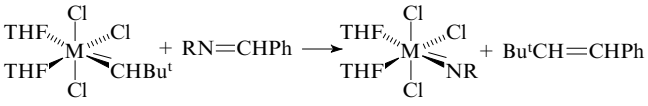
Thus, imido–imine metathesis reactions are seldom useful for the synthesis of transition metal imido complexes, because they are too slow. The best outcome of transimidation is attained when primary amines are employed (see Section II.1.a). Nevertheless, the imido–imine exchange underlies catalytic metathesis of azomethines, for which some molybdenum[27–30] and zirconium[31] imido complexes have been proposed as catalysts.

Niobium and tantalum carbene complexes $Bu^tCH{=}MCl_3(THF)_2$ (M = Nb, Ta) undergo alkylidene–

Table 7. Synthesis of Group 6–8 transition metal imido complexes by imido-deoxygenation with iminophosphoranes.

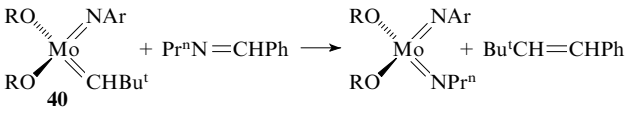
Starting compound	R in $R{=}NP'_3$	Product	Yield (%)	Ref.
$(Bu^n_4N)_2[Mo_6O_{19}]$	4-MeC_6H_4, 4-$(CH_2{=}CH)C_6H_4$	$(Bu^n_4N)_2[RN{=}\{Mo_6O_{18}\}]$	90	254, 255
$MoOCl_2(S_2CNEt_2)_2$	Ph	$PhN{=}MoCl_2(S_2CNEt_2)_2$	60	256
$ReOCl_3(PPh_3)_2$	Ph, 4-MeC_6H_4	$RN{=}ReCl_3(PPh_3)_2$	–	257, 258
$ReOCl_3(PPh_3)_2$	4-$(Ph_3P{=}N)C_6H_4$	$(Ph_3P)_2Cl_3Re{=}N-C_6H_4-N{=}ReCl_3(PPh_3)_2$	–	259
	Ph		–	260
$Ru_2O_2(CH_2SiMe_3)_6$	$SiMe_3$	$Ru_2(=NSiMe_3)_2(CH_2SiMe_3)_6$	38	261

imine metathesis with some azomethines to give the corresponding imidochlorides and a *cis*- and *trans*-alkene mixture.[266, 267]



M = Nb: R = Ph (40%); M = Ta: R = Ph, Me, Bu^t (80%–81%).

A study of the reactions of various molybdenum alkoxide imidocarbene complexes (ArN=)(Bu^{t}CH=)Mo(OR)$_2$ (**40**) with Schiff bases has demonstrated that the rate of alkylidene–imine metathesis depends substantially on the nature of the RO-ligands.[29]

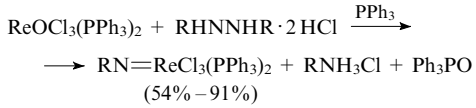


Ar = 2,6-Pr$^i_2$C$_6$H$_3$; R = C(CF$_3$)$_2$Me, C(CF$_3$)Me$_2$.

For example, when complex **40** containing ligands Me(CF$_3$)$_2$CO is treated with Pr^{n}N=CHPh, complete exchange is attained after 20 h, while the exchange depth in complex **40** with less fluorinated Me$_2$(CF$_3$)CO ligands is only 10% over the same period of time. The complex with ligands Bu^{t}O does not enter into this reaction.

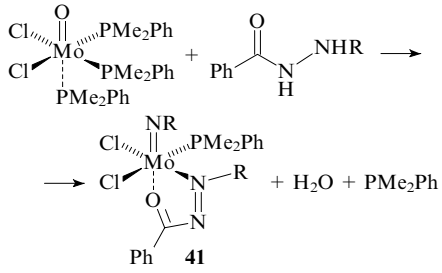
h. Imidation with hydrazine derivatives and azo compounds

Hydrazine derivatives and azo compounds are typical imidating oxidants (see Section II.2.b); however, there are some examples where a redox process involving these compounds does not result in a change in the formal oxidation state of the metal. This may be due to the presence of another reducing agent, and this role may be played, in particular, by hydrazine. For instance, treatment of the rhenium oxo complex ReOCl$_3$(PPh$_3$)$_2$ with a number of dialkylhydrazines in the presence of triphenylphosphine leads to imidodeoxygenation of the starting complex.[268] This is obviously a redox reaction, nevertheless, rhenium retains its d^2-configuration, because triphenylphosphine acts as a reducing agent.



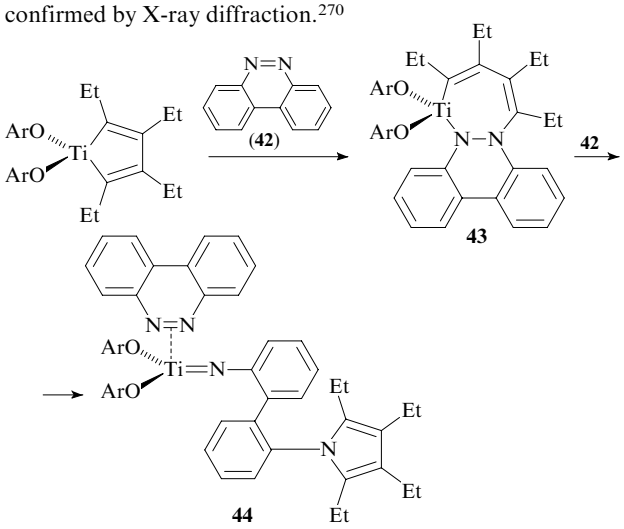
R = Me, Et, Pr^n, Cy.

Substituted benzohydrazides can also function as imidating agents. On treatment with phenylhydrazides, the oxo complex ReOCl$_3$(PPh$_3$)$_2$ is converted into the imido complex RN=ReCl$_3$(PPh$_3$)$_2$.[269] The reaction of MoOCl$_2$(PMe$_2$Ph)$_3$ with *N*-arylbenzohydrazides results in imido complex **41**,[257, 269] the formation of the imido ligand being accompanied by autooxidation of benzohydrazide.



R = 4-XC$_6$H$_4$ (X = H, Cl, Me, MeO), 1-C$_{10}$H$_7$.

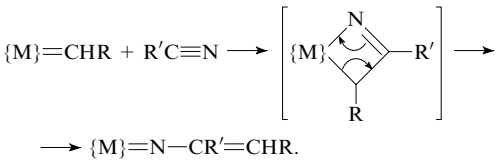
An example of insertion of benzo[*c*]cinnoline **42** into the Ti–C bond in the complex Et$_4$C$_4$Ti(OAr)$_2$ to give complex **43** containing 2,3-diazatitanacyclohepta-4,6-diene fragment is reported (the conclusion about the structure of complex **43** was based on spectroscopic characteristics). Treatment of complex **43** with the second equivalent of benzo[*c*]cinnoline induces an intramolecular bond redistribution in the complex, which is thus converted into imido complex **44**, the structure of which was confirmed by X-ray diffraction.[270]



Ar = 2,6-Ph$_2$C$_6$H$_3$.

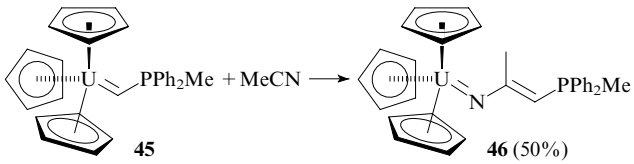
i. Imidation with nitriles

Nitriles have also found application as imidating reagents, but processes involving these compounds differ from those for all reagents described previously. Whereas reactions with isocyanates, *N*-sulfinylamines, imines, iminophosphoranes, *etc*., occur as metathesis, nitriles are formally inserted into the metal–carbon bond as a result of an electrocyclic rearrangement.



Typical examples of synthesis of imido complexes by this method are presented in Table 8.

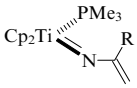
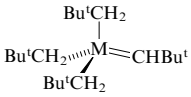
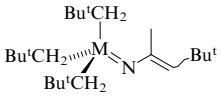
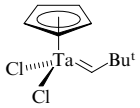
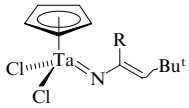
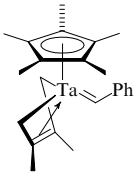
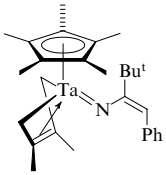
The insertion of acetonitrile into the metal–carbon multiple bond in uranium complex **45** has been described.[275] This reaction yields imido complex **46**.

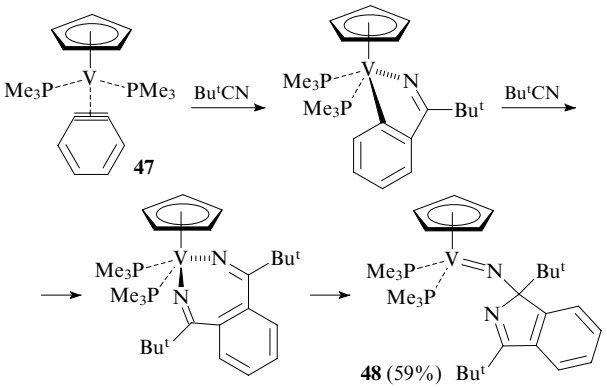


Examples of reactions involving two nitrile molecules are known. The high-spin vanadium d^2-complex **47** reacts with two equivalents of pivalonitrile to give imido complex **48**,¶ in which the imido ligand contains 1,3-di(*tert*-butyl)isoindol-1-yl as the organic group.[276] It is believed that this compounds is formed upon two successive steps of nitrile insertion into the metal–carbon bonds with subsequent rearrangement of the intermediate into a more stable product.

¶ The structure of complex **48** was confirmed by X-ray diffraction data.

Table 8. Synthesis of transition metal imido complexes using nitriles.

Starting compound	R in RCN	Product	Yield (%)	Ref.
	Bu^t, Cy		–	271
 (M = Nb, Ta)	Me	 (*E*,*Z*-isomers)	–	272
	Ph, Me	 (*E*,*Z*-isomers)	60 – 61	273
	Bu^t		48	274



j. Imidation with transition metal imides

In some studies, the possibility has been demonstrated to prepare transition metal imido complexes by the equilibrium metathesis transfer of the imido ligand from one metal complex to another. This intercomplex exchange can occur for oxo, carbene and imido complexes of Group 5 – 8 metals (Scheme 6).

Scheme 6

$$\{M\}{=}O + \{M'\}{=}NR \rightleftharpoons \{M\}{=}NR + \{M'\}{=}O,$$

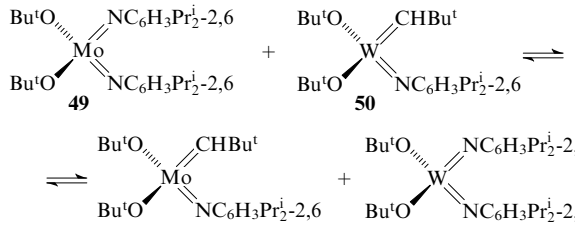
$$\{M\}{=}CHR + \{M'\}{=}NR \rightleftharpoons \{M\}{=}NR + \{M'\}{=}CHR,$$

$$\{M\}{=}NR + \{M'\}{=}NR' \rightleftharpoons \{M\}{=}NR' + \{M'\}{=}NR.$$

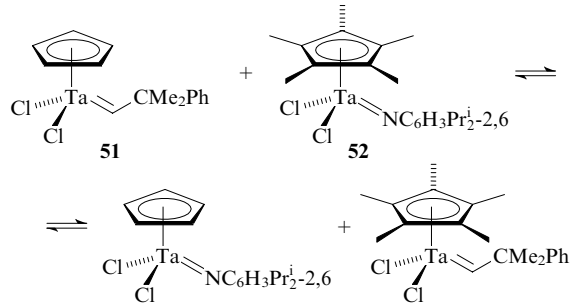
In the reactions shown in Scheme 6, the equilibrium is shifted toward the formation of thermodynamically more favourable products.

Upon the oxo – imido exchange, the imido group is bound preferably to the more electron-deficient metal. Examples of imido complexes prepared by intercomplex oxo – imido exchange are presented in Table 9.

The Schrock carbenes can undergo metathesis with the imido complexes; however, unlike the oxo – imido metathesis, this approach is of low utility for preparative purposes due to the low reaction rate and the difficulty of isolation of the desired product from the equilibrium mixture. Thus NMR monitoring of the reaction of tetrahedral molybdenum bisimido complex (**49**) with tungsten imidocarbene (**50**) complex showed that the equilibrium is attained only after several days at 60 °C.[280]



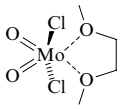
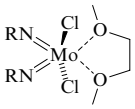
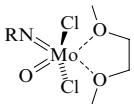
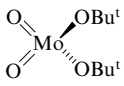
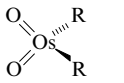
In the reaction of alkylidene – imido metathesis between half-sandwich tantalum complexes **51** and **52**, the equilibrium can be reached over the same time under more drastic conditions (120 °C).

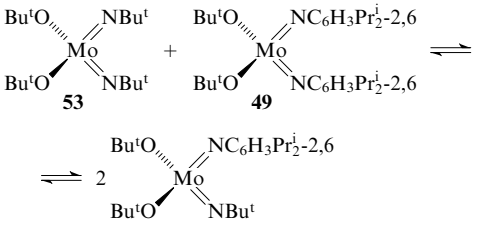


The possibility of equilibrium imido – imido exchange between Group 5 and 6 metal complexes was demonstrated; however, in this case, too, a low reaction rate was noted. Thus symmetric molybdenum bisimido complexes with *tert*-butyl- (**53**) and 2,6-diisopropylphenylimido (**49**) ligands slowly exchange the imido ligands only at elevated temperature ($K_{60\,^\circ C}$ = 25), apparently, for steric reasons.[280]

The rate of intercomplex imide exchange can be considerably affected by Brønsted acids. Thus the addition of $(Et_2O)_2HB[C_6H_3(CF_3)_2\text{-}3,5]_4$ into a mixture of complexes **49** and **53** substantially accelerates the exchange reaction ($K_{25\,^\circ C}$ = 95, $k = 5.0 \times 10^{-6}$ dm^3 mol^{-1} s^{-1}).[283]

Table 9. Synthesis of transition metal imido complexes by intercomplex ligand exchange.

Starting compound	Imidating complex	Product	Yield (%)	Ref.
$VOCl_3$	$RN{=}V(OSiMe_3)_3$	$RN{=}VCl_3$		
	R = Me_3Si		38	277
	R = Bu^t		68	144
				
	R = 2,4,6-$Me_3C_6H_2$		59	278
	R = Bu^t		100	279
	2,6-$Pr^i_2C_6H_3N$, OBu^t, Mo, 2,6-$Pr^i_2C_6H_3N$, OBu^t	2,6-$Pr^i_2C_6H_3N$, OBu^t, Mo, OBu^t, O	–	280
OsO_4	2,6-$Pr^i_2C_6H_3N$, OBu^t, Mo, 2,6-$Pr^i_2C_6H_3N$, OBu^t	2,6-$Pr^i_2C_6H_3N$, O, Os, 2,6-$Pr^i_2C_6H_3N$, O	83	281
 (R = CH_2SiMe_3, CH_2Bu^t, CH_2CMe_2Ph)	2,6-$Pr^i_2C_6H_3N{=}Ta(OBu^t)_3$	2,6-$Pr^i_2C_6H_3N$, R, Os, 2,6-$Pr^i_2C_6H_3N$, R	50 – 70	282

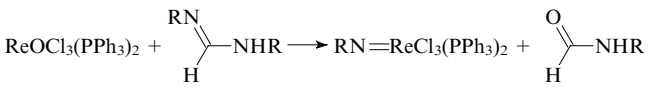


53 **49**

k. Imidation using miscellaneous nitrogen-containing compounds

Examples of the use of some other nitrogen-containing compounds as imidating reagents, in particular, formimidamides, isocyanides and iminoboranes have been documented.

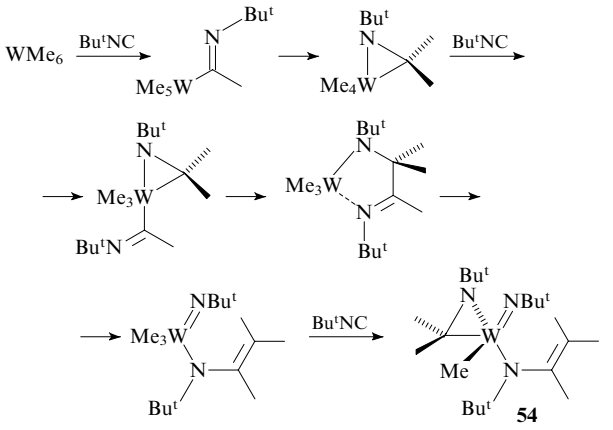
Formimidamides imidate the oxo complex $ReOCl_3(PPh_3)_2$ to give the imido complexes $RN{=}ReCl_3(PPh_3)_2$.[284] It is noteworthy that in this case, the yields of rhenium arylimido complexes are lower than those attained upon imidation with amines and hydrazines.



R = Ph (40%), 4-FC_6H_4, 4-ClC_6H_4 (33%), 4-MeC_6H_4 (36%).

When Group 4 – 6 metal σ-alkyl complexes react with isocyanides, these are inserted into the metal – carbon bond to afford azavinyl intermediates, which undergo intramolecular rearrangement to yield imido products. (These reactions present no interest from the preparative standpoint, because they are not straightforward and their outcome is not always predictable.) The reaction may involve one to three isocyanide molecules. The homoleptic complex WMe_6 reacts with three equivalents of *tert*-butyl isocyanide to yield imido complex **54**, the structure of which was confirmed by X-ray diffraction. Presumably, this product is formed in a complicated sequence of insertion and rearrangement reactions (Scheme 7).[285, 286]

Scheme 7

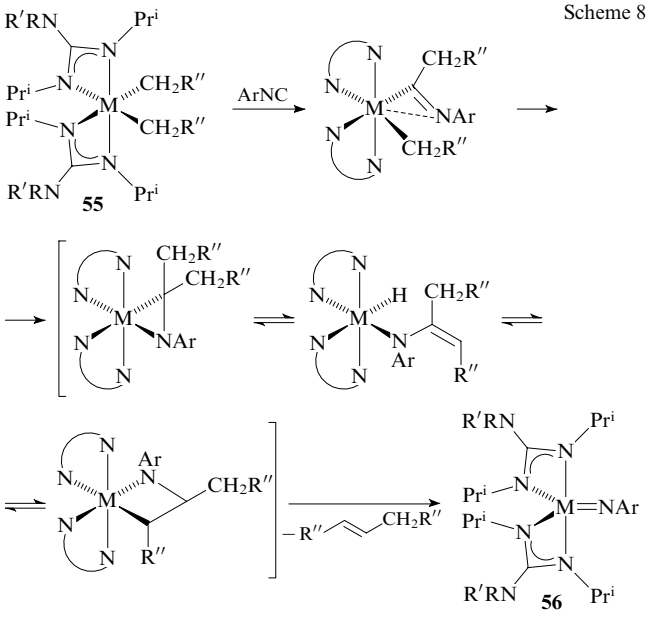


54

An example of formal substitution of an arylimido group for the alkyl groups in guanidinate complexes **55** on treatment with one equivalent of aryl isocyanide has been reported.[287, 288] The formation of imido complexes **56** is attributed to redistribution of bonds in the intermediate resulting from isocyanide insertion into the metal – carbon bond (Scheme 8).

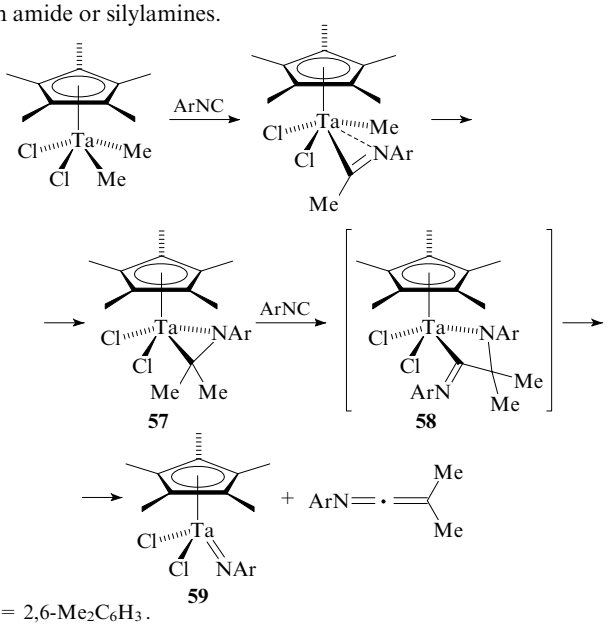
On treatment of the complex (η^5-C_5Me_5)$TaMe_2Cl_2$ with 2,6-$Me_2C_6H_3NC$, isocyanide is also inserted into the metal – carbon bond, which is followed by migration of the other methyl group to the electrophilic acetimidoyl carbon atom to give aza(tantalum)-cyclopropane complex **57**, which was isolated and characterised by spectroscopic means.[289] This complex easily reacts with a second isocyanide molecule to give thermally unstable azatantalacyclobutane intermediate **58**, which eliminates arylketeneimine to give imido complex **59**, which is formally the substitution product of an imido ligand for two methyl groups in the starting complex.

Scheme 8



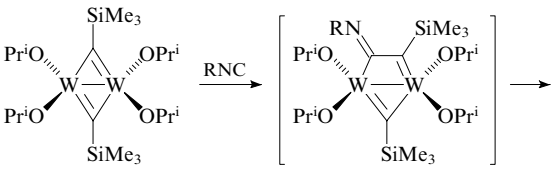
M = Ti, Zr; R = R′ = Me; R = Pr^i, R′ = H; R″ = Me, CH_2Ph; Ar = 2,6-$Me_2C_6H_3$.

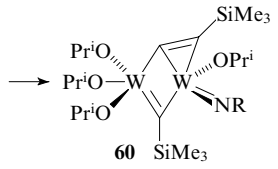
Note that half-sandwich complex **59** and its analogues can easily be prepared by simpler methods, for example, by imido-dehalogenation of the tetrachloride (η^5-C_5Me_5)$TaCl_4$ with lithium amide or silylamines.



Ar = 2,6-$Me_2C_6H_3$.

The binuclear μ-bis(carbyne) complex [(Pr^{i}O)$_2$W(μ-$CSiMe_3$)$_2$]$_2$ also undergoes an intricate sequence of intramolecular transformations when treated with aliphatic or aromatic isocyanides to give imido complex **60**.[290]





R = Bu^t, 2,6-$Me_2C_6H_3$ (> 60%).

There are examples of the use of iminoboranes as imidating agents. For example, tungsten hexachloride undergoes imido-dechlorination under the action of iminoborane Bu^{t}B=NBu^t to yield dimeric complex **61**.[291]

$$2\,WCl_6 + 2\,Bu^tN{=}BBu^t \longrightarrow [Bu^tN{=}WCl_4]_2 + 2\,Bu^tBCl_2$$

61 (80%)

Complex **61** and other imidotungsten tetrachloride complexes can be synthesised by simpler methods, for example, by imido-dechlorination of tungsten hexachloride with silylamines and by imido-deoxygenation of tungsten oxochloride with isocyanates.

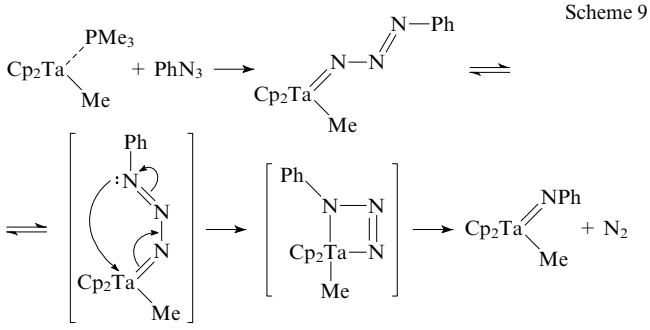
2. Imidation of metal complexes with the change in the formal oxidation state of the metal

a. Imidation with azides

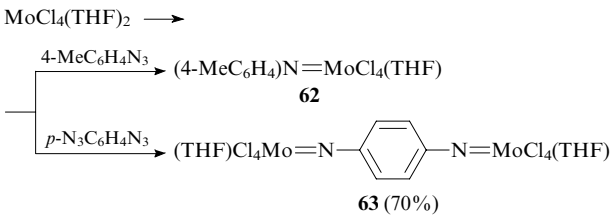
Imidation of metal complexes with organic azides is accompanied by an increase in the formal oxidation state of the metal and has the highest practical value among the methods of this group. The method is successfully used to prepare imido derivatives of various metal complexes with C-, O-, S-, N- and P-ligands. Aryl and trialkylsilyl azides are used most often.

In a study of decamethylvanadocene imidation with phenyl azide Ph$-{}^{15}$N=N=N containing an isotope label, the imido complex was found to contain only a labelled nitrogen atom.[292,293] This led to the assumption that the process occurs *via* a metal complex adduct with the azide involving the internal nitrogen atom. However, in a study of the reaction of V(NRAr)$_2$I [R = $C(CD_3)_2Me$, Ar = 2-F-5-MeC_6H_3] with $MesN_3$, the azide complex MesN=N−N=V(NRAr)$_2$I with a V=N bond involving the terminal nitrogen atom was isolated and characterised by X-ray diffraction. This complex was found to be easily converted into the imido product MesN=V(NRAr)$_2$I on gentle heating.[294] Similar results have been obtained in a study of the reaction of the complex (η^5-Cp)$_2$TaMe(PMe_3) with phenyl azide.[295,296] Kinetic studies of this reaction with isotope labelling suggest a mechanism in which the complex formation with phenyl azide involving the terminal nitrogen atom is the initial step, which is followed by dinitrogen extrusion (Scheme 9).

Scheme 9

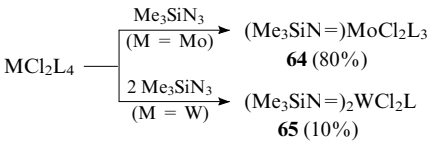


Transition metal chlorides in intermediate oxidation states are the simplest compounds suitable for imidation with aryl azides. Mononuclear (**62**)[297] and binuclear (**63**)[298] molybdenum complexes were prepared by treatment of molybdenum tetrachloride with appropriate azides.



Trimethylsilyl azide is rarely used for imidation of transition metal chlorides. This is due to the fact that the trimethylsilylimido chlorides formed are as a rule labile and readily eliminate chlorotrimethylsilane to give nitrido complexes. Thus it was found that vanadium tetrachloride reacts with Me_3SiN_3 yielding the unstable complex $Me_3SiN{=}VCl_3$,[299] which, as has been specially shown,[277] readily eliminates Me_3SiCl to afford vanadium chloronitride.

By varying the ratio of molybdenum (or tungsten) dichloride and trimethylsilyl azide used in the reaction, one can obtain labile complexes **64** and **65**, respectively.[300]



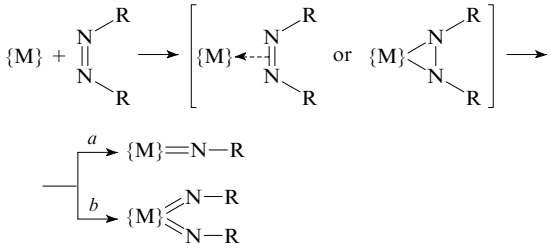
M = Mo, L = PMe_3; M = W, L = PPh_2Me.

Organic azides are effective imidating agents for diverse metal complexes containing mono- and polydentate O-, S-, N- and P-ligands (Table 10). They are successfully used to prepare imido derivatives of metallocenes and Group 4–9 transition metal carbene and σ-alkyl complexes (Table 11).

b. Imidation with azo compounds, hydrazines and their derivatives

Azo compounds are typical reagents imidation with which is accompanied by an increase in the formal oxidation state of the metal. They can be used in reactions with various mononuclear π-complexes and binuclear metal complexes. The mechanism of formation of imido derivatives from mononuclear complexes is not entirely clear; however, the process is considered to proceed *via* an η^2-diazene or diazametallacyclopropane intermediate, in which activation of the N=N bond and a decrease in its order take place and which is further converted into the mono- (path *a*) or bis-imido (path *b*) complex (Scheme 10).[321, 325–327]

Scheme 10



However, examples are known where imidation follows a different mechanism. In a systematic study of the reaction of Cp_2TaMeL with azobenzene, the formation of diazametallacyclopropane product **66**, which is not converted into imido complex **67**, was confirmed by X-ray diffraction. Having studied

Table 10. Synthesis of transition metal imido complexes using organic azides.

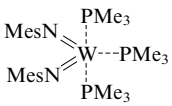
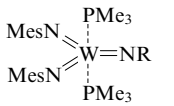
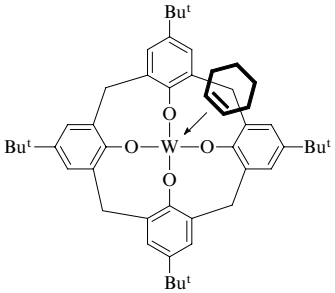
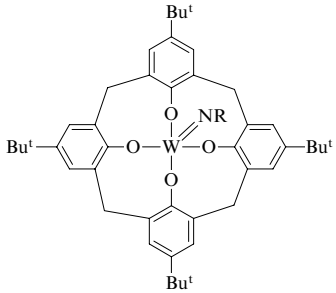
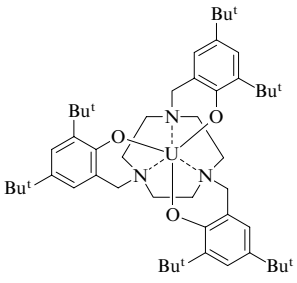
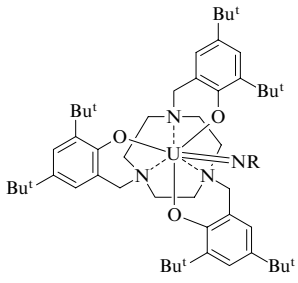
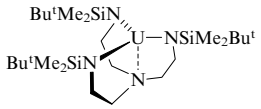
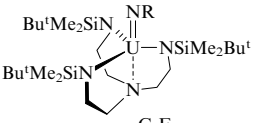
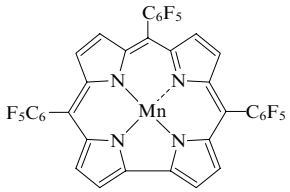
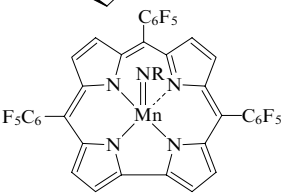
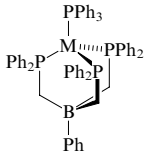
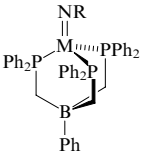
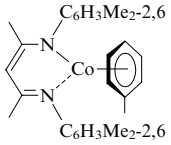
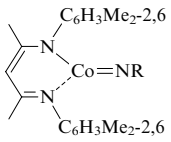
Starting compound	R in RN_3	Product	Yield (%)	Ref.
$Ti(\eta^2\text{-EtC}{\equiv}\text{CEt})(TTP)$ (see [a])	Me_3Si	RN=Ti(TTP)	38	158
Cr(TPP) (see [a])	4-XC_6H_4 (X = Me, Cl, I, MeO)	RN=Cr(TPP)	60–65	19, 301
$Mo(CO)_2(S_2CNEt_2)_2$	Ph	$(RN{=})_2Mo(S_2CNEt_2)_2$	50	302
$W(CO)_2(PPh_3)(S_2CNEt_2)_2$	4-MeC_6H_4	$RN{=}W(CO)(S_2CNEt_2)_2$	–	303
	Me_3Si, Bu^tMe_2Si		–	304
$W(OC_6H_3Me_2\text{-}2,6)_4$	Me_3Si	$RN{=}W(OC_6H_3Me_2\text{-}2,6)_4$	–	305
	Me_3Si Ph_3C		70 13	306 306
	Me_3Si		39	307

Table 10 (continued).

Starting compound	R in RN_3	Product	Yield (%)	Ref.
	Me_3Si		90	308
	Mes, 2,4,6-$Cl_3C_6H_2$		70 – 80	309
	4-MeC_6H_4			
M = Co			97	310
M = Fe			50	311
	Ad		50	312
$[Os(TTP)]_2$ (see [a])	4-$NO_2C_6H_4$	$(RN{=})_2Os(TTP)$	42	313
$[Os(4\text{-Cl-TPP})]_2$ (see [a])	4-$NO_2C_6H_4$	$(RN{=})_2Os(4\text{-Cl-TPP})$	58	314
$[Ru(TPP)]_2$ (see [a])	4-$NO_2C_6H_4$	$(RN{=})_2Ru(TPP)$		314

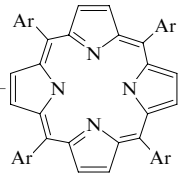
[a] TPP, TTP, 4-Cl-TPP —  [Ar = Ph (TPP), 4-MeC_6H_4 (TTP), 4-ClC_6H_4 (4-Cl-TPP)].

Table 11. Synthesis of imido derivatives of organometallic compounds using organic azides.

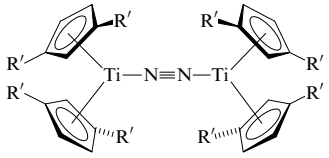
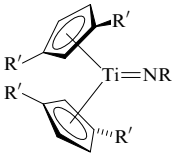
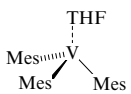
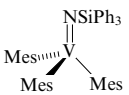
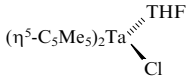
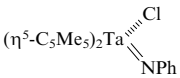
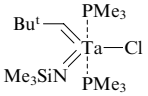
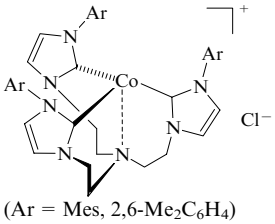
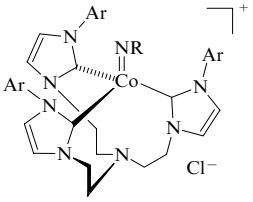
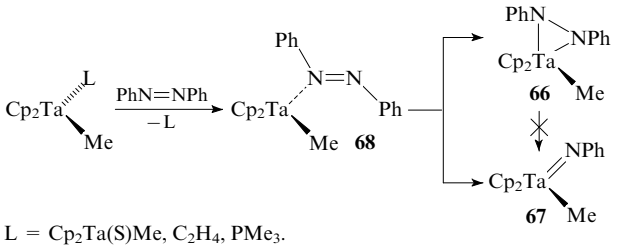
Starting compound	R in RN_3	Product	Yield (%)	Ref.
 ($R' = SiMe_3$)	Me_3Si Mes		53 94	315 315
$(\eta^5\text{-}C_5Me_5)_2V$	Ph, C_6F_5, 2,6-$Me_2C_6H_3$, 2-PhC_6H_4	$(\eta^5\text{-}C_5Me_5)_2V{=}NR$	39 – 70	292, 293, 316
$(\eta^5\text{-}C_5H_5)_2V$	$SiPh_3$	$(\eta^5\text{-}C_5H_5)_2V{=}NSiPh_3$	80	317
	Ph_3Si		–	304
	Ph		76	318
$Bu^tCH{=}TaCl(PMe_3)_4$	Me_3Si		–	267

Table 11 (continued).

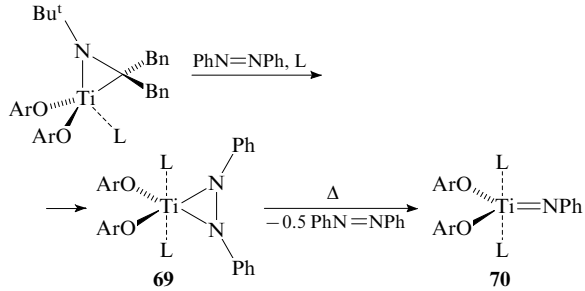
Starting compound	R in RN_3	Product	Yield (%)	Ref.
$(\eta^5\text{-}C_5Me_5)_2U(Cl)(NPh)\ Li^+(TMEDA)$	Ph Me_3Si	$(\eta^5\text{-}C_5Me_5)_2U(NR)(NPh)$	81 – 85 72	319, 320
$(\eta^5\text{-}C_5Me_5)_2U(Cl)_2\ Na^+$	Ph Ad	$(\eta^5\text{-}C_5Me_5)_2U(NR)_2$	84 71	321
$(\eta^5\text{-}MeC_5H_4)_3U(THF)$	Ph, Me_3Si	$(\eta^5\text{-}MeC_5H_4)_3U{=}NR$	50	322
$(\eta^5\text{-}MeC_5H_4)_3U(THF)$	3-$C_6H_4N_3$ 4-$C_6H_4N_3$	$(\eta^5\text{-}MeC_5H_4)_3U{=}N\text{-}C_6H_4\text{-}N{=}U(\eta^5\text{-}MeC_5H_4)_3$	37 48	323 323
 (Ar = Mes, 2,6-$Me_2C_6H_4$)	4-MeC_6H_4, 4-$MeOC_6H_4$		100	324

the process kinetics, the researchers suggested that adduct **68** is the true intermediate on the route to imido product **67**.[328]



L = $Cp_2Ta(S)Me$, C_2H_4, PMe_3.

It was found that mononuclear bisimido complexes are formed along path *b* only starting from d^4-complexes, while monoimido products (path *a*) are obtained by treating d^2-complexes with azo compounds. Thus on treatment with azobenzene, the d^2-complex $(\eta^2\text{-}Bu^tN{=}CBn_2)Ti(OC_6H_3Pr^i_2\text{-}2,6)_2L$ is converted into η^2-azo complex **69**. The latter is thermally unstable and is transformed on heating into imido d^0-complex **70**.[325]



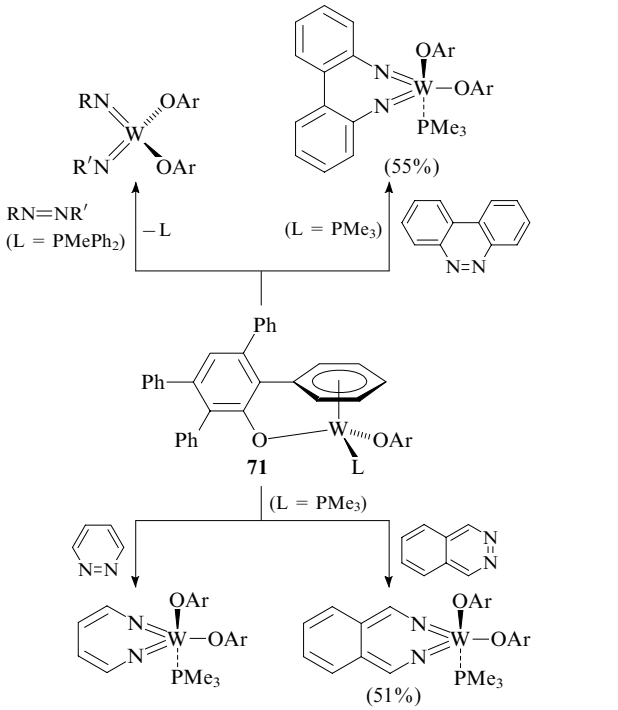
Ar = 2,6-$Pr^i_2C_6H_3$, L is 4-pyrrolidinopyridine.

The d^2-complex (TTP)Ti(η^2-EtC≡CEt) and azobenzene taken in 2 : 1 ratio react in a similar way. The first step is replacement of the diethylacetylene molecule by the azo ligand to give the complex (TTP)Ti(η^2-PhN=NPh), which was isolated and characterised. In the second step, the azo complex reacts with another (TTP)Ti(η^2-EtC≡CEt) molecule, being converted into monoimido d^0-complex (TTP)Ti=NPh.[158, 326]

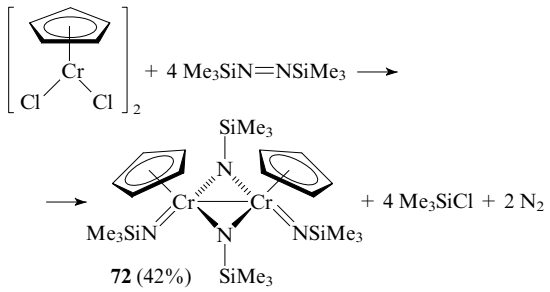
The oxidative addition of symmetric and non-symmetric (including cyclic) azo compounds to tungsten d^4-complex **71** has been studied.[329, 330] The structure of bisimido d^0-complex formed (Scheme 11) was confirmed by X-ray diffraction.

The reaction of dimeric d^3,d^3-complex $[CpCrCl_2]_2$ with four equivalents of $Me_3SiN{=}NSiMe_3$ results in binuclear d^1,d^1-complex **72**, which contains, according to X-ray diffraction data, both terminal and bridging ligands.[331]

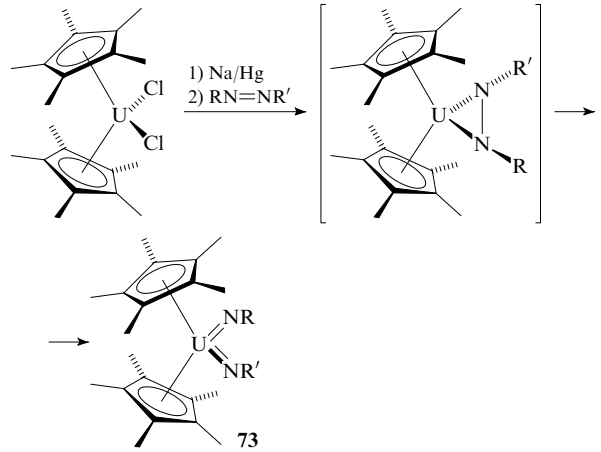
Scheme 11



Ar = 2,3,5,6-Ph_4C_6H; L = PMe_3, $PMePh_2$; R, R′ = Ph, 4-MeC_6H_4, Mes.



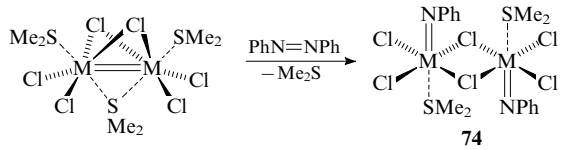
A two-stage method for the synthesis of symmetric and asymmetric bisimido uranium complexes **73** is based on the reaction of azo compounds with the complex $[(\eta^5\text{-}C_5Me_5)_2UCl.(NaCl)]$, which is formed *in situ* upon the reduction of decamethyluranocene dichloride with sodium amalgam.[321]



R = R′ = Ph (92%); R = Ph, R′ = $SiMe_3$ (70%).

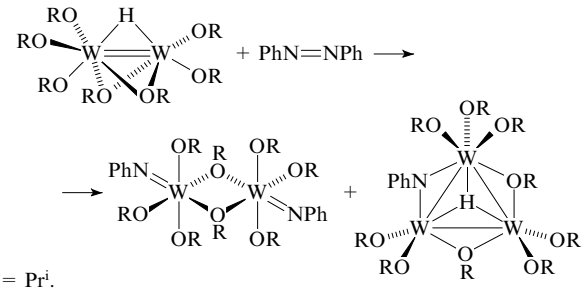
Complexes **73** can also be prepared by imidation of the complex $(\eta^5\text{-}C_5Me_5)_2UCl_2$ with azides or diphenylhydrazine.

Imidation of binuclear complexes containing multiply bonded metal atoms follows a different route as compared with the imidation of mononuclear complexes. The reaction of azobenzene with binuclear complexes $M_2Cl_6(SMe_2)_3$ proceeds as the metathesis of multiple bonds, M=M and N=N, to give imido dimers **74**.[332, 333]



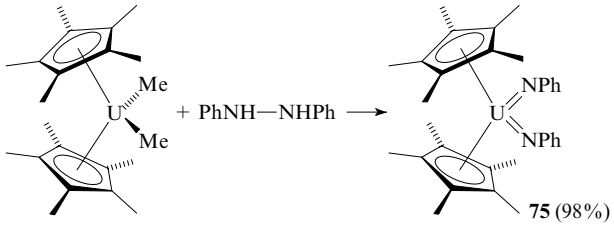
M = Nb (55%), Ta (58%).

The reaction of azobenzene with the binuclear complexes $W_2(\mu\text{-}H)(OPr^i)_7$ and $W_2(OPr^i)_6(py)_2$,[334] which also contain metal–metal multiple bonds, follows a more complex pattern, as indicated by the formation of a mixture of products, including clusters.

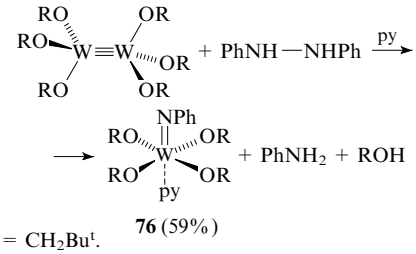


R = Pr^i.

Imidation with hydrazine derivatives is usually a redox process. In those cases where other reducing agents are present or hydrazines undergo autooxidation, the initial electronic configuration of the metal can be retained (see Section II.1.h); however, more often, is oxidation state increases. The oxidative imidation of transition metal complexes with hydrazine derivatives can be exemplified by a one-stage synthesis of diimido complex **75**.[319]



The imidation of the binuclear complex $W_2(OCH_2Bu^t)_6$ on treatment with 1,2-diphenylhydrazine is accompanied by oxidative cleavage of the metal–metal triple bond to give imido complex **76**.[334]



R = CH_2Bu^t.

Conversely, the reaction of ammonium pertechnetate with phenylhydrazide in the presence of phosphines and small amount of a hydrohalic acid is accompanied by the reduction of technetium giving rise to d^2-complexes **77**.[335, 336]

$$NH_4TcO_4 + PhNHNHAc \xrightarrow{HX\ (aq.),\ L} \underset{\mathbf{77}}{PhN{=}TcX_3L_2}$$

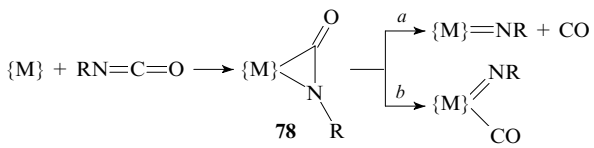
X = Cl, Br; L = PPh_3 (68%–75%), $PMePh_2$ (30%).

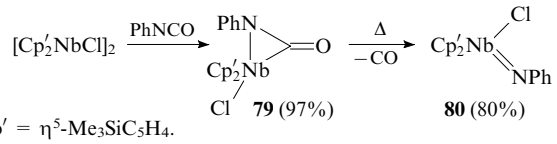
c. Imidation with organyl isocyanates

The imidation with isocyanates is usually a metathesis-type reaction occurring without a change in the formal oxidation state of the metal in the complex (see Section II.1.d). However, there are some examples where complexes of metals in low oxidation states are inserted into the N=C bond of isocyanates to give azametallacyclopropane derivatives **78** (oxidative insertion, Scheme 12), which can subsequently be converted into imido complexes with elimination of carbon monoxide (path *a*) or form imido carbonyl complexes (path *b*).

The d^2-complex $[(\eta^5\text{-}Me_3SiC_5H_4)_2NbCl]_2$ coordinates phenyl isocyanate PhNCO to give stable compound **79** (characterised by X-ray diffraction). Thermolysis of complex **79** occurs with elimination of carbon monoxide to give imido complex **80**.[337–339]

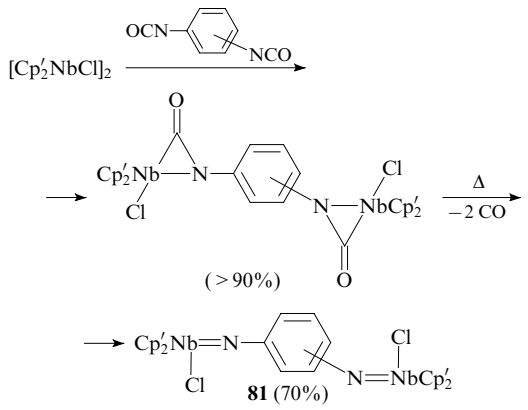
Scheme 12





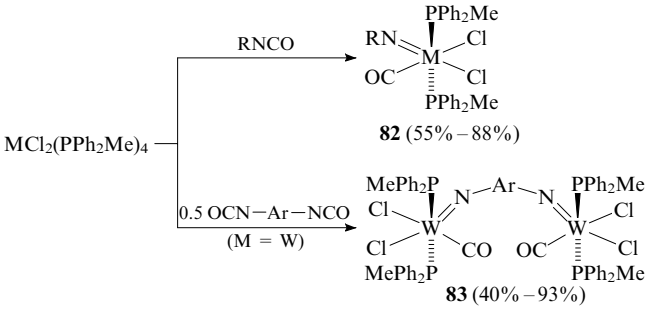
Cp′ = η⁵-$Me_3SiC_5H_4$.

With diisocyanates [1,3- or 1,4-$(OCN)_2C_6H_4$], binuclear imido complexes **81** are formed.



Cp′ = η⁵-$Me_3SiC_5H_4$.

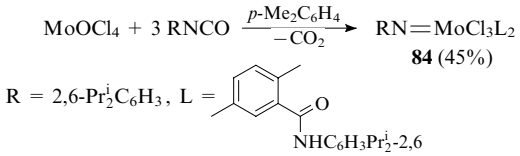
Molybdenum and tungsten d^4-complexes MCl_2L_4 also react with various isocyanates RNCO; however, in this case, the insertion of the complex into the C=N bond is not accompanied by carbon monoxide evolution, but rather results in the formation of d^2-imido carbonyl complexes **82**.[340–342] A series of binuclear tungsten complexes **83** have been obtained in this way using various diisocyanates OCN–Ar–NCO.[343, 344]



M = Mo, W; R = Bu^t, $SiMe_3$, Ph, 4-MeC_6H_4; Ar = 1,4-C_6H_4, 1,4-(2-MeC_6H_3), 1,4-(2,3-$Me_2C_6H_2$), 1,4-(2,5-$Me_2C_6H_2$), 1,4-C_6Me_4, 1,3-(4-MeC_6H_3), 1,3-C_6H_4, 1,5-$C_{10}H_6$, (4-C_6H_4)CH_2(C_6H_4-4), 1,1′-(2,6-$Me_2C_6H_2$-4-)$_2$, 1,1′-(2-$MeOC_6H_3$-4-)$_2$.

A few examples are known where imidation with isocyanates results in reduction of metal compounds having pronounced oxidative properties. For example, osmium tetraoxide is reduced by three equivalents of 2,6-$Pr^i_2C_6H_3NCO$ to give the imido d^2-complex (2,6-$Pr^i_2C_6H_3N$=)$_3$Os in 50% yield.[345] It should be noted that a similar reaction pattern is observed when OsO_4 is treated with trimethylsilylanilines (see Section II.2.e), whereas trimethylsilyl derivatives of aliphatic amines and iminophosphoranes imidate osmium tetraoxide with retention of the oxidation state.

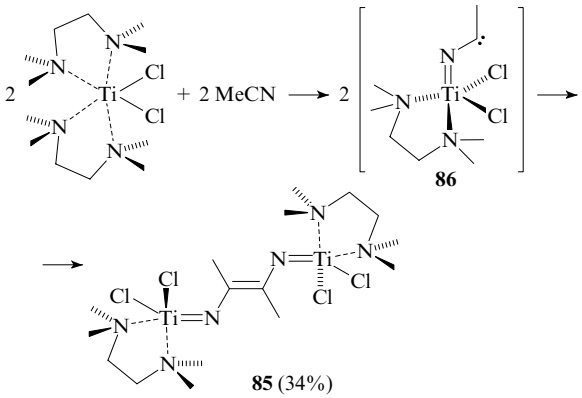
The imido-deoxygenation of molybdenum oxotetrachloride with excess 2,6-$Pr^i_2C_6H_3NCO$ in *p*-xylene is also accompanied by the reduction of molybdenum and results in imido d^1-complex **84**.[346]



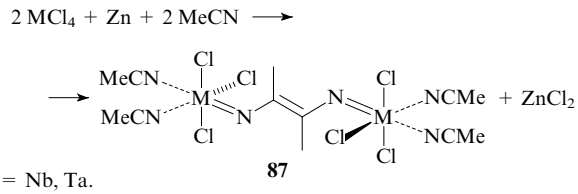
d. Imidation with nitriles

Group 4 and 5 transition metal halides in intermediate oxidation states can undergo redox reactions with nitriles to give binuclear imido complexes, the diimido fragment of which is formed by coupling of coordinated nitrile molecules. The mechanism of this multistep process has not been studied in detail so far.

The reaction of the complex $(TMEDA)_2TiCl_2$ with acetonitrile is a typical example of this type of reactions. It was suggested that the formation of binuclear complex **85** is due to dimerisation of mononuclear carbene intermediates **86**;[347] however, the possibility of stepwise (two-step) coupling to give, first, a single and then a double carbon–carbon bond cannot be ruled out either.

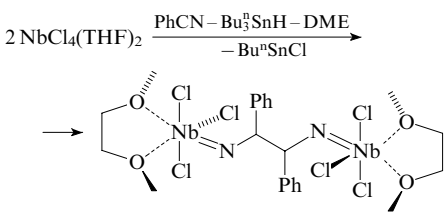


In the reduction of niobium or tantalum tetrachlorides with zinc in acetonitrile, a similar coupling of two nitrile molecules takes place to give binuclear diimido complexes **87**.[348]



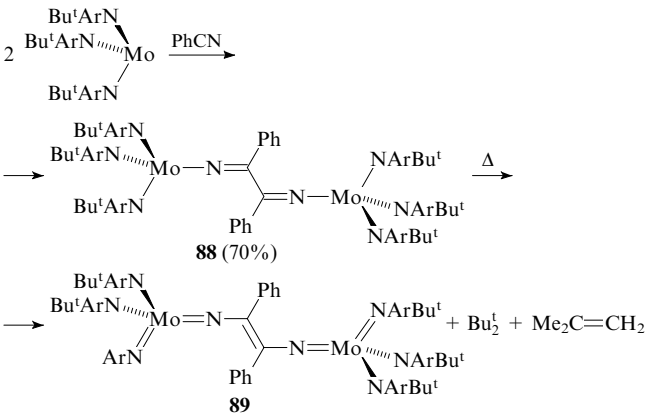
M = Nb, Ta.

Under the action of an equimolar amount of tributyltin hydride in 1,2-dimethoxyethane, niobium tetrachloride induces hydrodimerisation of benzonitrile. Presumably, this reaction involves successively the formation of the hydride Cl_3NbH, insertion of benzonitrile into the Nb–H bond and recombination of the Cl_3Nb=N–C˙(Ph)H radicals thus formed.[349]



The reaction of trisamido complex $Mo(NBu^tAr)_3$ with benzonitrile gives diiminato complex **88**, the nitrile coupling product. Thermolysis of complex **88** is accompanied by homolytic cleavage of the Bu^t–N bond of the amido ligand followed by bond redistribution in the molecule, resulting in binuclear imidoamide

complex **89**.[350] The formation of *tert*-butyl radicals is confirmed by the presence of their recombination and disproportionation products.

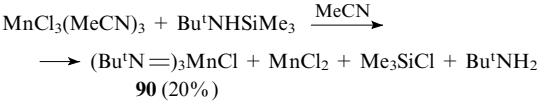


Ar = 3,5-$Me_2C_6H_3$.

e. Imidation with amines, lithium amides and *N*-trimethylsilylamines

The imidation with amines and their lithium and trimethylsilyl derivatives usually proceeds with no change in the formal oxidation state of the metal (see Sections II.1.a–c). However, some reactions are accompanied by an increase in the metal oxidation state. This may be due to the action of some extraneous oxidant, disproportionation processes or other reasons. Examples of oxidative imidation of transition metal complexes involving amines or lithium amides are given in Table 12.

A unique compound **90**, which is the key derivative in the chemistry of manganese imido d^0-complexes, was prepared by the reaction of manganese(III) chloride with $Bu^tNHSiMe_3$ in acetonitrile.



Presumably, complex **90** is formed in a multistep disproportionation of intermediate manganese compounds.[358, 359]

Table 12. Synthesis of transition metal imido complexes by oxidative imidation with amines and their lithium derivatives.

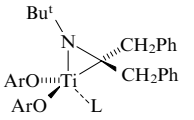
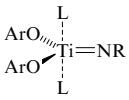
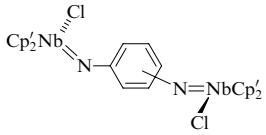
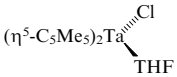
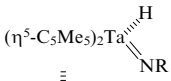
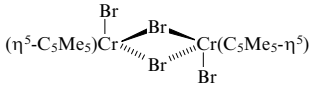
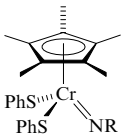
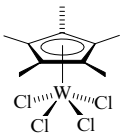
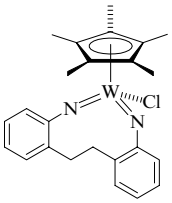
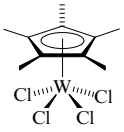
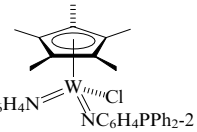
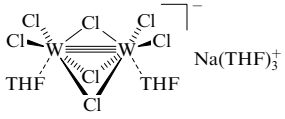
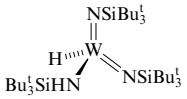
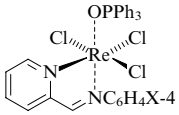
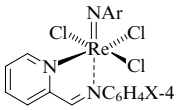
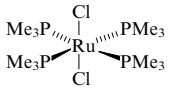
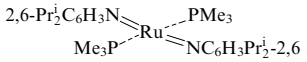
Starting compound	Imidating reagent	Product	Yield (%)	Ref.
 (Ar = 2,6-$Pr^i_2C_6H_3$, L is 4-pyrrolidinopyridine)	RNH_2–L (R = Bu^t, Ph)		–	325
 ($Cp' = \eta^5$-$Me_3SiC_5H_4$)	1,3- or 1,4-$(H_2N)_2C_6H_4$	 (*meta*- and *para*-isomers)	60–75	339
	RNHLi (R = Bu^t, Ph)		83–90	318
	(PhS)NRLi (R = Bu^t, 4-MeC_6H_4, 2,6-$Pr^i_2C_6H_3$, 2-$Bu^tC_6H_4$)		30–59	351, 352
	1,2-$(2\text{-}NH_2C_6H_4)_2C_2H_4$		46	353
	2-$NH_2C_6H_4PPh_2$		30	353
	$Bu^t_3SiNHLi$		50–60	354

Table 12 (continued).

Starting compound	Imidating reagent	Product	Yield (%)	Ref.
 (X = Me, Cl)	$ArNH_2$ (Ar = Ph, 4-ClC_6H_4)		70 – 75	355
$ReCl_4(OPPh_3)_2$	2-$MeNHC_6H_4NH_2$	2-$MeNHC_6H_4N{=}ReCl_4(OPPh_3)$	22	356
	2,6-$Pr^i_2C_6H_3NHLi - O_2$		16	357

For metal compounds with pronounced oxidative properties, the imidation reactions can be accompanied by reduction of the metal. For example, on treatment with excess *N*-trimethylsilylalkylanilines, osmium tetraoxide undergoes reductive imidation to give tris(imido) d^2-complex **91** as the only osmium-containing reaction product.[198]

$$OsO_4 + ArNHSiMe_3 \longrightarrow \underset{\mathbf{91}}{Os(=NAr)_3}$$

Ar = 2,6-$Me_2C_6H_3$ (46%), 2,6-$Pr^i_2C_6H_3$ (62%).

It is of note that imidation of osmium tetraoxide with aliphatic silylamines is not accompanied by its reduction (see Section II.1.c).

Ammonium pertechnetate is also reduced by a mixture of 2,6-diisopropylaniline and chlorotrimethylsilane in the presence of pyridine to give monoimido d^2-complex **92** (see Ref. 85, p. 268).

$$NH_4TcO_4 + ArNH_2 + Me_3SiCl \xrightarrow{py} \underset{\mathbf{92}}{ArN{=}TcCl_3(py)_2}$$

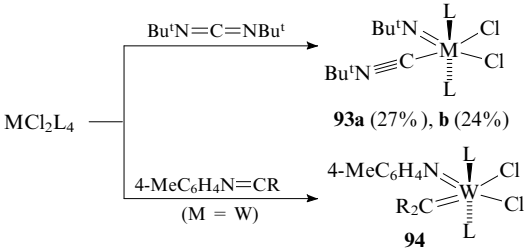
Ar = 2,6-$Pr^i_2C_6H_3$.

It should be noted that no reduction of rhenium takes place in the imidation of ammonium perrhenate under similar conditions (see Section II.1.c).

f. Imidation with miscellaneous nitrogen-containing compounds

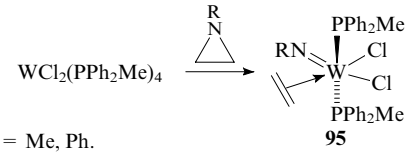
The use of other nitrogen-containing organic compounds as sources of imido groups is a specific case. A few examples of oxidative imidation of complexes of metals in low oxidation states with carbodiimides, aldimines, ketimines, sulfodiimines, aziridines, 2*H*-azirines and nitroso compounds have been reported.

Thus reactions of *N*,*N*′-di(*tert*-butyl)carbodiimide [341, 342, 360] and ketimine 4-$MeC_6H_4N{=}CR_2$ (see Ref. 361) with molybdenum and tungsten dichlorides MCl_2L_4 occur as oxidative addition to give imidoisocyanide (**93a**,**b**) and imidocarbene (**94**) complexes.



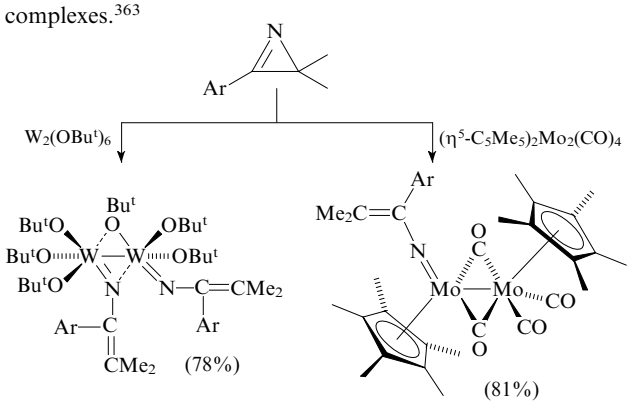
M = Mo (**a**), W (**b**); L = PPh_2Me; R_2 = Me_2, $(CH_2)_4$ (45%).

The reaction of tungsten dichloride with *N*-substituted aziridines is accompanied by ring opening and results in imidoethylene complexes **95**.[362]



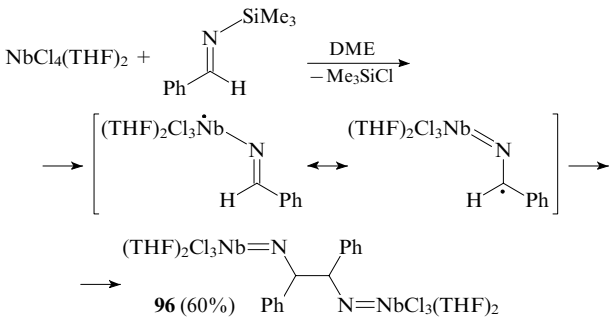
R = Me, Ph.

2*H*-Azirines can also be cleaved by treatment with some binuclear complexes of Group 6 metals to give various imido complexes.[363]



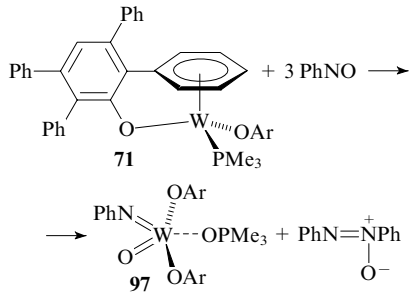
Ar = Ph, 4-$Bu^tC_6H_4$.

The reaction of niobium tetrachloride with an equimolar amount of *N*-benzylidene-*N*-trimethylsilylamine results in the formation of binuclear d^0,d^0-complex **96** with a diimido bridging ligand.[349]



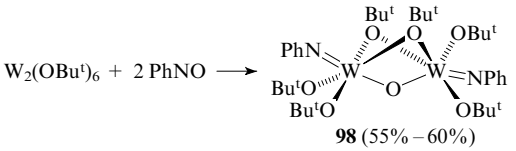
The formation of complex **96** is believed to be due to dimerisation of mononuclear radical intermediates.

The formation of imido complexes in the reactions with nitrosoarenes and sulfodiimines follows a complex route and is formally an oxidative addition of the metal to the nitrogen – heteroatom bond. For example, d^4-complex **71** is oxidised with nitrosobenzene to give oxoimido d^0-complex **97** and azoxybenzene.[330]

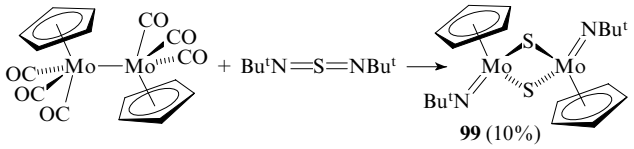


Ar = 2,3,5,6-Ph_4C_6H.

The reaction of two equivalents of nitrosobenzene with the d^3,d^3-complex $W_2(OBu^t)_6$, containing multiply bonded metal atoms, affords dimeric d^0,d^0-complex **98** with bridging *tert*-butoxide ligands and an oxygen atom.[364] Thus, the outcome of the process is asymmetric oxidative addition of nitrosobenzene to metal sites accompanied by cleavage of the metal–metal bond.



Long-term refluxing of the binuclear complex $[(\eta^5\text{-Cp})Mo(CO)_3]_2$ with sulfodi(*tert*-butyl)imine in benzene induces oxidative imido-decarbonylation to give disulfido complex **99** in low yield.[365]



III. Intramolecular imidation methods

The other strategy of the synthesis of transition metal imido complexes is based on intramolecular formation of the imido group in the metal complex from nitrogen-containing ligands of a different type. Intramolecular imidation procedures are not so numerous as intermolecular imidation methods and are less often used in synthetic practice. The N-ligand precursors used to construct the imido group are nitrido, amido and some other ligands.

1. Transition metal nitrides

Complexes of transition metals of Group 6–8 with terminal nitrido ligands are convenient substrates for the synthesis of neutral and cationic imido complexes. The imido complexes are formed upon an electrophilic attack by alkylating reagents on the nitrogen atom of the nitride group of anionic or neutral transition metal complexes (Scheme 13). Trialkyloxonium tetrafluoroborate, methyl iodide, alkyl and trimethylsilyl triflates, tritylhexafluorophosphate, and so on are used as alkylating reagents.

Scheme 13

$$N\equiv\{M\} + EX \longrightarrow [E-N=\{M\}]^+X^-,$$

$$[N\equiv\{M\}]^- + EX \longrightarrow E-N=\{M\}+X^-.$$

A kinetic study of the reaction of the nitrido complex $(NBu^n_4)[N\equiv Os(CH_2SiMe_3)_4]$ with methyl iodide has shown that the reaction is first order with respect to each reactant, which is indicative of the S_N2 mechanism.[366] It is worth noting that only electron-enriched nitrido complexes, for example, osmium and ruthenium nitride s- and p-complexes and molybdenum, tungsten, rhenium and osmium complexes with S-, O- and N-ligands possess nucleophilicity sufficient for this electrophilic attack. Table 13 presents examples of the use of Group 6–8 transition metal nitrido complexes for the synthesis of the corresponding imido complexes.

Table 13. Synthesis of Group 6–8 transition metal imido complexes by alkylation of nitrides.

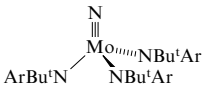
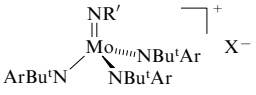
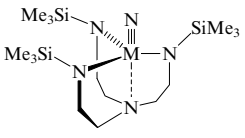
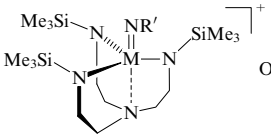
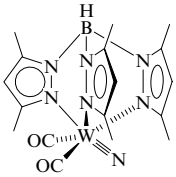
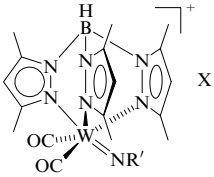
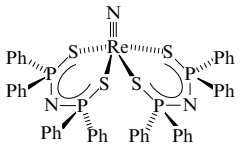
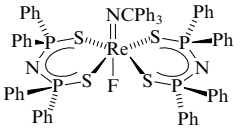
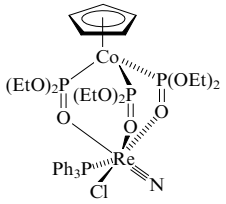
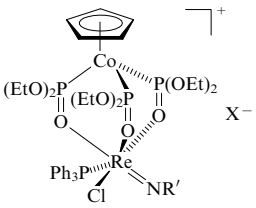
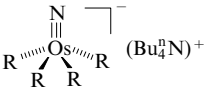
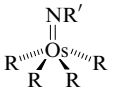
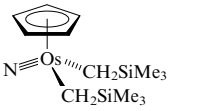
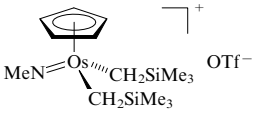
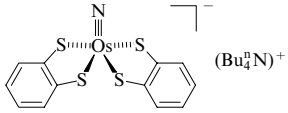
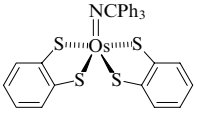
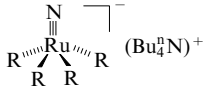
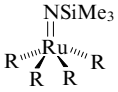
Starting compound	Alkylating agent	Product		Yield (%)	Ref.
$N\equiv Mo(S_2CNR_2)_3$ ($R = Me, Et$; $R_2 = (CH_2)_4$)	$[Me_3O]BF_4$, MeI $2,4\text{-}(NO_2)_2C_6H_3Cl$, Ph_3CBF_4	$[R'N=Mo(S_2CNR_2)_3]^+X^-$ ($R' = Me$, $2,4\text{-}(NO_2)_2C_6H_3$, Ph_3C)		–	367, 368
 ($Ar = 3,5\text{-}Me_2C_6H_3$)	MeI Me_3SiOTf	 X^-	$R' = Me$ $R' = Me_3Si$	92 89	369 369
 (M = Mo, W)	MeOTf, Me_3SiOTf	 OTf^-	($R' = Me$, Me_3Si)	79–93	370
	MeOTf Ph_3CPF_6	 X^-	$R' = Me$ $R' = CPh_3$	70 –	371 372
$N\equiv Re(S_2CNEt_2)_2(PMe_2Ph)$	Ph_3CPF_6	$[Ph_3CN=Re(S_2CNEt_2)_2(PMe_2Ph)]^+PF_6^-$		85	373

Table 13 (continued).

Starting compound	Imidating reagent	Product		Yield (%)	Ref.
	Ph_3CBF_4			53	374
	Ph_3CBF_4 MeOTf BnBr		$R' = CPh_3$ $R' = Me$ $R' = Bn$	60 58 41	375 375 375
 (R = Me, CH_2SiMe_3, CH_2Ph)	$R'OTf$ (R' = Me, Et, Me_3Si), $[Me_3O]BF_4$, $[Et_3O]BF_4$, MeI	 (R' = Me, Et, Me_3Si)		–	366, 376, 377
	MeOTf			90	378
	Ph_3CPF_6			55	379
 (R = CH_2SiMe_3)	Me_3SiOTf			92	380

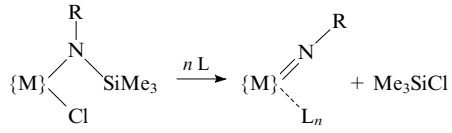
2. Transition metal amides

Intramolecular imidation methods based on the transformation of amido ligands have been reported. In this case, imido ligands are formed upon either 1,2-elimination of fragments of the initial amide groups or intramolecular interligand transfer of a hydrogen atom or trialkylsilyl groups.

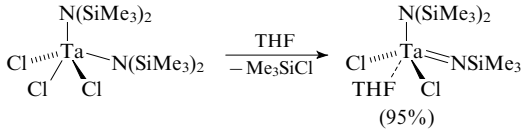
a. Synthesis of imido complexes with elimination of an amido group fragment

An imido ligand may be formed from an amide ligand upon elimination of molecules such as trialkylsilyl halides, primary and secondary amines, alkanes, hydrogen halides, *etc*. Depending on the structure of the starting amido complex and the nature of the leaving molecule, these reactions may be induced thermally or chemically. In some cases, a combination of these variants is used.

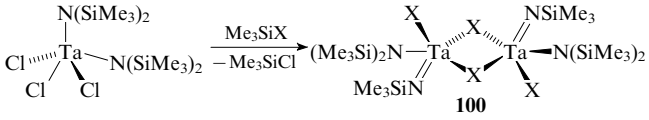
Trimethylsilylamidometal chloride easily eliminate chlorotrimethylsilane in the presence of various n-donor compounds L. The formation of a stronger Si – Cl bond and steric crowding in the metal coordination environment arising upon the formation of adducts with n-donors are apparently the driving forces of the process.



On treatment of the complex $TiCl_3[N(SiMe_3)_2]$ with pyridine, a Me_3SiCl molecule is eliminated to give the imido complex $Me_3SiN{=}TiCl_2(py)_2$.[381] The same is observed for the tantalum diamido complex $TaCl_3[N(SiMe_3)_2]_2$ on treatment with tetrahydrofuran.[382]

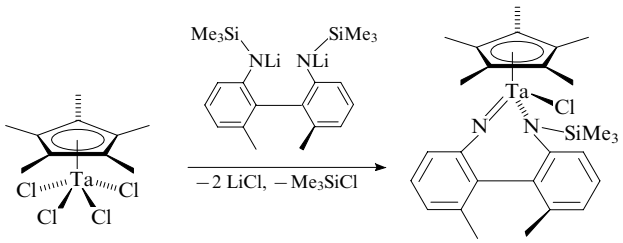


Elimination of chlorotrimethylsilane can take place spontaneously in the synthesis of bis(trimethylsilyl)amido complexes or in parallel with other transformations. For instance, on treatment of $TaCl_3[N(SiMe_3)_2]_2$ with trimethylsilyl halides, elimination of trimethylsilyl chloride, resulting in dimeric imido complexes **100**, takes place in parallel with ligand exchange.[163, 382]



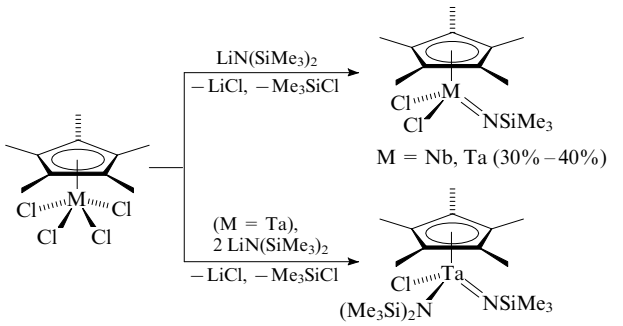
X = Br (25%), I (75%).

Upon the reaction of equimolar amounts of the complex $(\eta^5\text{-}C_5Me_5)TaCl_4$ and dilithium derivative of 2,2′-bis(trimethylsilylamino)biphenyl, amido – imido complex **101** was isolated; the complex is obviously formed upon spontaneous elimination of chlorotrimethylsilane from the reaction intermediate.[383]



101 (68%)

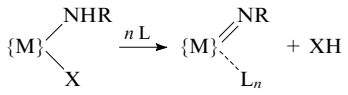
The reaction of the complexes $(\eta^5\text{-}C_5Me_5)MCl_4$ (M = Ta, Nb) with one [384] or two [167] equivalents of lithium hexamethyldisylazide proceeds in a similar way



M = Nb, Ta (30%–40%)

It is noteworthy that spontaneous elimination of chlorotrimethylsilane is apparently the key step in the formation of the imido complexes in the reaction of transition metal polyhalides with bis(trimethylsilyl)amines (see Section II.1.c).

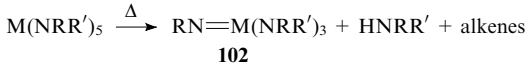
Polyamido (more rarely, alkylamido) complexes eliminate amines (alkanes) on treatment with n-donor compounds or on heating, resulting in the formation of imido products.



X = NHR, Alk.

Examples of the use of this synthetic approach are listed in Table 14.

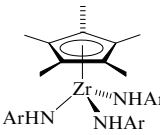
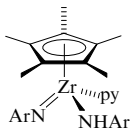
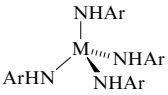
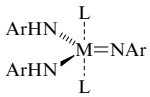
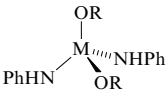
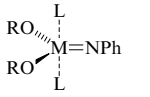
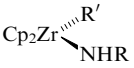
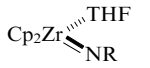
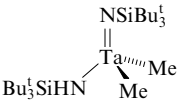
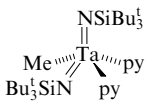
In some cases, thermolysis of polyamido complexes leading to imido products occurs in a more complicated way. Thus thermolysis of homoleptic sterically hindered complex $Nb(NMeBu^n)_5$ involves elimination of butylmethylamine and but-1-ene, which affords mixed amido–imido complex **102** in low yield.[391] Thermolysis of the complexes $Ta(NR_2)_5$ proceeds in a similar way.[392, 393]



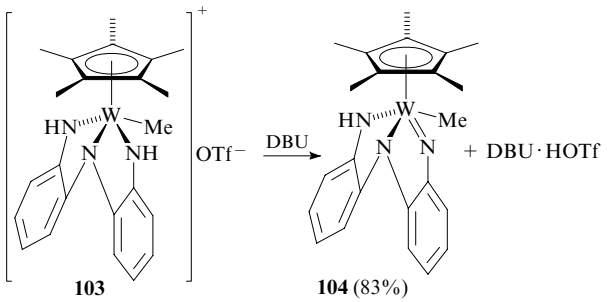
102

M = Nb: R = Bu^n, R′ = Me;
Me = Ta: R = R′ = Et (35%–47%), Pr^n, Bu^n; R = Bu^n, R′ = Me.

Table 14. Synthesis of transition metal imido complexes from amides by elimination of amines and alkanes.

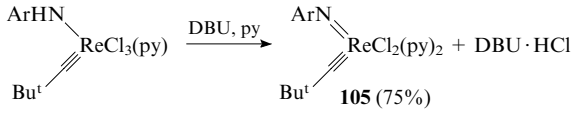
Starting compound	Reaction conditions	Product	Yield (%)	Ref.
$(Bu^t_3SiNH)_3TiCl$	THF, Δ	$Bu^t_3SiN{=}Ti(NHSiBu^t_3)Cl(THF)$	83	385
 (Ar = 2,6-$Pr^i_2C_6H_3$)	py, Δ		76	386
 (M = Zr, Hf; Ar = 2,6-$Pr^i_2C_6H_3$)	4-pyrrolidinopyridine (L)		40–70	387, 388
 (M = Ti: R = 2,6-$Pr^i_2C_6H_3$, 2,6-$Ph_2C_6H_3$; M = Zr: R = 2,6-$Bu^t_2C_6H_3$)	4-pyrrolidinopyridine (L)		40 (Zr)	325, 387, 388
 (R = Bu^t, R′ = Me; R = 2,6-$Me_2C_6H_3$, $SiMe_2Bu^t$, R′ = CH_2Bu^t)	THF, Δ		69–72	389
	py, Δ		68	45
$(\eta^5\text{-}C_5Me_5)_2U(NHR)_2$ (R = Bu^t, Et, 2,6-$Me_2C_6H_3$)	THF, Δ	$(\eta^5\text{-}C_5Me_5)_2U(THF)(NR)$	–	390

Neutral and cationic monoalkyl- and monoarylamido complexes can be deprotonated under the action of nitrogenous bases to give the corresponding imido products. The cationic complex **103** is deprotonated with diazabicyclo[5.4.0]undecene (DBU) to give neutral imido complex **104**.[132]



103 **104** (83%)

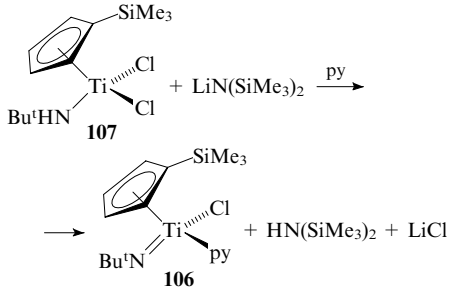
The amidocarbyne complex $Bu^tC{\equiv}Re(NHC_6H_3Pr^i_2\text{-}2,6).Cl_3(py)$ is also deprotonated with DBU in the presence of pyridine to give imidocarbyne complex **105**.[394]



105 (75%)

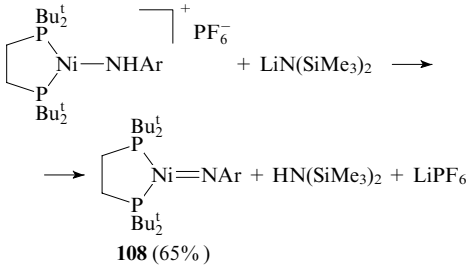
Ar = 2,6-$Pr^i_2C_6H_3$.

Half-sandwich titanium imido complex **106** was prepared by deprotonation of *tert*-butylamido complex **107** with lithium hexamethyldisilazide.[395]



107 **106**

The only, to our knowledge, nickel complex **108** with a terminal imido group was synthesised in a similar way.[396]



108 (65%)

Ar = 2,6-$Pr^i_2C_6H_3$.

Examples of transformations of monoamido complexes into imido complexes upon abstraction of a hydride ion are known. Thus amido carbonyl complexes **109** are converted into cationic imido products **110a–d** under the action of trityl cation.[372, 397]

$$Tp'W(CO)_2NHR + Ph_3C^+PF_6^- \longrightarrow [Tp'W(CO)_2(=NR)]^+PF_6^- + Ph_3CH$$

109a–d **110a–d** (78%–86%)

R = Bu^n (**a**), Bu^t (**b**), Ph (**c**), CH_2Ph (**d**).

The complexes $Tp'W(CO)_2(NHR)$ (**109b,c**) and the related complex $Tp'W(CO)(PhC{\equiv}CMe)(NHPh)$ (**111**) are oxidised to the corresponding imido derivatives **112** and **113** under the action of molecular iodine.[398]

$$Tp'W(CO)_2(NHR) \xrightarrow[-HI]{I_2} [Tp'W(CO)_2(=NR)]^+I^-$$

109b,c **112**

R = Bu^t (**b**), Ph (**c**).

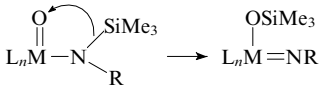
$$[Tp'W(CO)(MeC{\equiv}CPh)(NHPh)] \xrightarrow[-NaI,\ -Et_3NHI]{I_2,\ Et_3N,\ NaBAr_4} [Tp'W(CO)(MeC{\equiv}CPh)(=NPh)]^+BAr_4^-$$

111 **113** (79%)

Ar = $C_6H_3(CF_3)_2$-3,5.

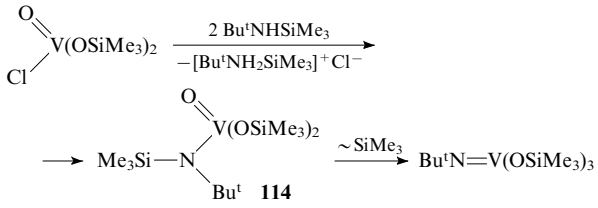
b. Synthesis of imido complexes through intramolecular migration of an amido group fragment

In some cases, imido complexes of Group 5–7 transition metals are formed upon intramolecular rearrangement of amido, mainly oxotrimethylsilylamido, complexes. In the synthesis of these complexes, spontaneous 1,3-migration of the trimethylsilyl group from the nitrogen atom of the amido ligand to the oxo group often takes place.



Thus, the reaction of $VOCl_3$ with three equivalents of $NaN(SiMe_3)_2$ results in the imido complex $Me_3SiN{=}V(OSiMe_3).[N(SiMe_3)_2]_2$.[399] Presumably, the reaction involves intermediate formation of the unstable oxotriamido complex $O{=}V[N(SiMe_3)_2]_3$, which is spontaneously rearranged to the final product.

The reaction of the oxo complex $O{=}V(OSiMe_3)_2Cl$ with two equivalents of *tert*-butyl(trimethylsilyl)amine yielded the complex $Bu^tN{=}V(OSiMe_3)_3$. This product may have formed upon 1,3-migration of the trimethylsilyl group in the intermediate oxo-amido complex **114**.[150]

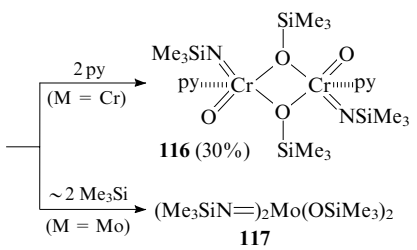


114

The reaction of chromyl chloride with hexamethyldisilazane has been shown to furnish dioxoamido d^0-complex **115a**. Treatment of the latter with excess pyridine results in its reduction accompanied by 1,3-migration of the trimethylsilyl group to give dimeric imido d^1-complex **116**, the structure of which was con-

$$MO_2Cl_2 \xrightarrow[-2\,(Me_3Si)_2NH_2^+Cl^-]{4\,(Me_3Si)_2NH} MO_2[N(SiMe_3)_2]_2 \longrightarrow$$

115a,b



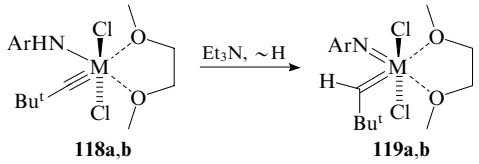
116 (30%) **117**

M = Cr (**a**), Mo (**b**).

firmed by X-ray diffraction.[190] The reaction of molybdenum dioxodichloride with hexamethyldisilazane yields diimido complex **117**. By analogy with the previous case, this outcome was attributed to the intramolecular rearrangement of dioxodiamido complex **115b**.

The formation of the rhenium imido complex $(Me_3SiN{=})_2Re(OSiMe_3)_2[N(SiMe_3)_2]$ in the reaction of ReO_3X (X = Cl, $OSiMe_3$) with three equivalents of $LiN(SiMe_3)_2$ apparently also includes 1,3-migration of the $SiMe_3$ group.[400]

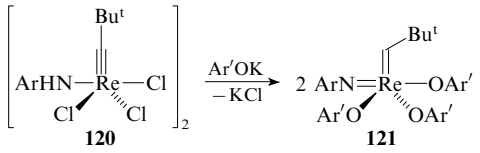
Yet another type of intramolecular rearrangement resulting in imido complexes is observed for monoarylamidocarbyne complexes. In particular, it was shown that triethylamine induces interligand migration of the proton in amidocarbyne complexes of molybdenum (**118a**)[191] and tungsten (**118b**),[193,401] resulting in imidocarbene complexes **119a**,**b**.



118a,**b** **119a**,**b**

M = Mo (**a**), W (**b**); Ar = 2,6-$Pr^i_2C_6H_3$.

Rhenium amidocarbyne complexes behave in a similar way. On treatment of dimer **120** with six equivalents of potassium polyhalogenophenoxides, proton migration from the amido group to the carbyne group to give imidocarbene complexes **121** takes place in addition to the replacement of chlorine atoms.[402]



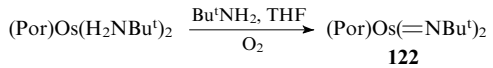
120 **121**

Ar = 2,6-$Pr^i_2C_6H_3$; Ar′ = 2,6-$Cl_2C_6H_3$ (67%), C_6F_5 (78%), C_6Cl_5 (48%).

3. Transition metal complexes with other types of nitrogen-containing ligands

Metal complexes with other types of nitrogen-containing ligands can also be used to synthesise imido complexes. In particular, examples of transformation of metal-coordinated primary amines, nitriles, nitrosoarene, nitrosyl and some other ligands into imido ligands have been reported.

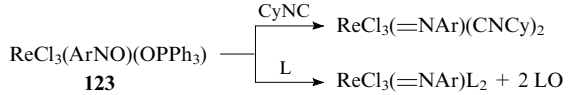
Thus osmium porphyrin complexes containing coordinated *tert*-butylamine are oxidised under aerobic conditions to give imido derivatives **122**.[403]



122

Por = TTP (68%), TPP (70%), 4-Cl-TPP (75%), 3,4,5-$(MeO)_3$-TPP (72%) (Ar = 3,4,5-$(MeO)_3C_6H_2$, see notation in Table 10).

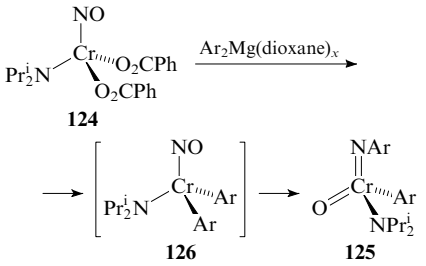
Rhenium nitrosoarene complex **123** is converted into imido complexes under the action of oxophilic tertiary phosphines or isocyanides.[404]



123

L = Ph_3P, $PhEt_2P$.

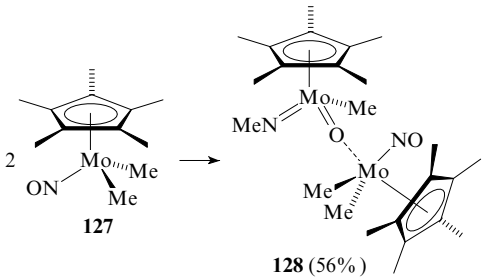
Examples of spontaneous rearrangements of dialkyl(aryl)-nitroso complexes of Group 6 metals involving nitrogen–oxygen bond cleavage and resulting in imido complexes have been described. The reaction of nitrosyl complex **124** with diarylmagnesium leads to imido complex **125**[405] with one σ-aryl ligand, which was characterised by X-ray diffraction. This product is believed to result from the rearrangement of unstable intermediate bis(σ-aryl) complex **126**.



124 **126** **125**

Ar = 2-MeC_6H_4.

A similar transformation occurs on storage of dimethylnitrosyl complex **127** in solution. According to X-ray diffraction data, the rearrangement of complex **127** gives dimer **128** comprising fragments of the intramolecular rearrangement product and the starting complex moieties.[406]

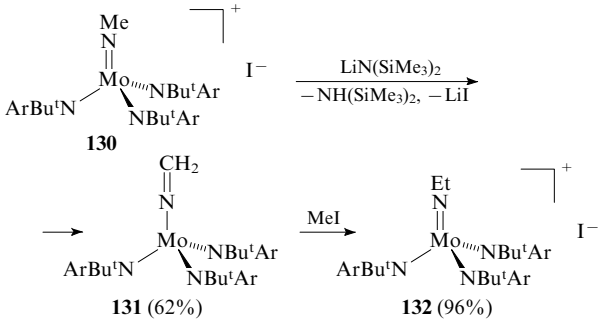


127 **128** (56%)

Replacement of the counter-ion in the cationic complex *trans*-$[CrCl(MeCN)(dmpe)_2]^+(BPh_4)^-$ (dmpe is $Me_2PCH_2CH_2PMe_2$) on treatment with barium triflate in methanol involves a redox process resulting in the ethylimido d^2-complex *trans*-$[EtN{=}CrCl(dmpe)_2]^+(OTf)^-$ in parallel with the protonation of the coordinated acetonitrile molecule.[407] The formation of the ethylimido d^2-complex was confirmed by both spectroscopy and X-ray diffraction.

Examples of modification of an imido ligand directly within the complex are documented. It was demonstrated that imido complex **129** can be used in the palladium-catalysed Sonogashira cross-coupling, which opens the way to various metal complexes containing conjugated systems of multiple bonds[408–410] (Scheme 14).

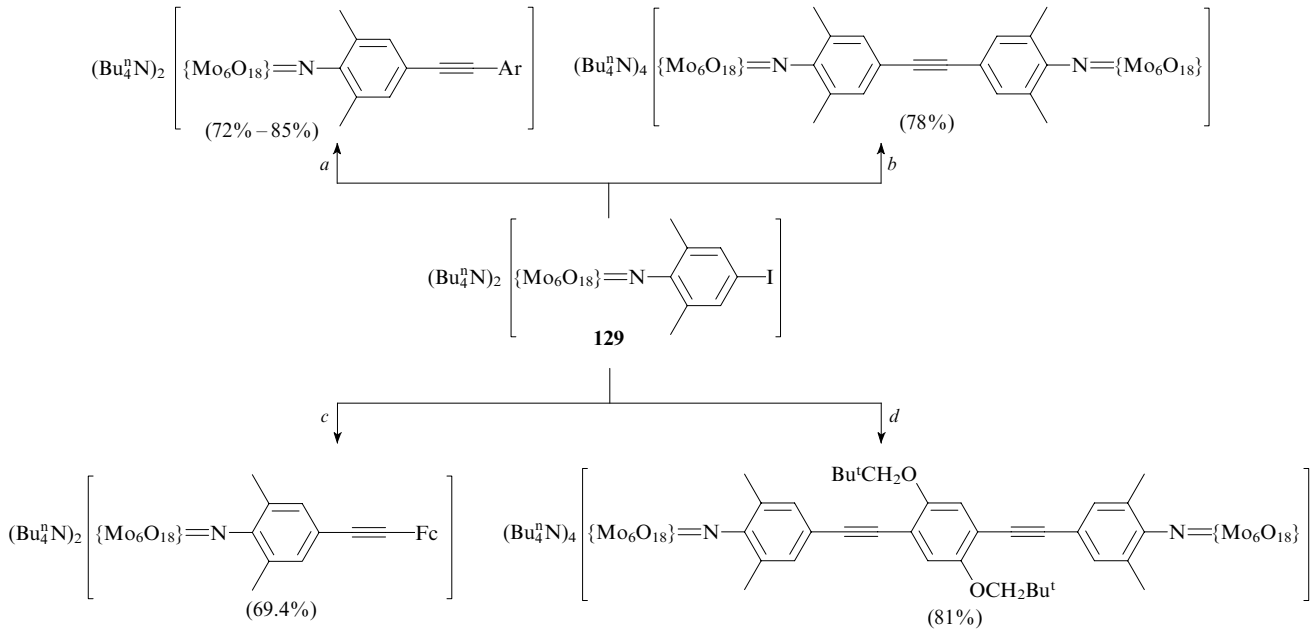
Recently, the possibility of elongation of the carbon chain in the alkylimido group by one methylene unit as a result of consecutive deprotonation and alkylation of the cationic methylimido complex **130** was demonstrated. It was shown that the complex can be deprotonated to the ketimido derivative **131**, which, in turn, is readily alkylated with methyl iodide to give compound **132**, a homologue of the starting complex.[369]



130 **131** (62%) **132** (96%)

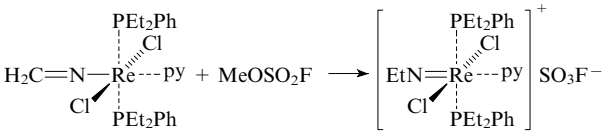
Ar = 3,5-$Me_2C_6H_3$.

Scheme 14



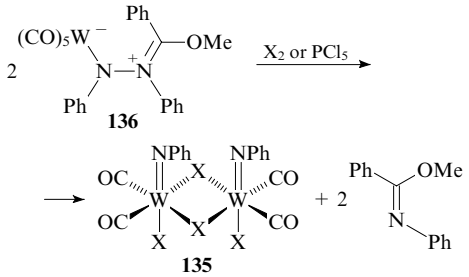
(*a*) HC≡CAr–Pd(PPh$_3$)$_2$Cl$_2$ (Ar = 3,5-Bu$^t_2$C$_6$H$_3$, 4-MeC$_6$H$_4$), CuCl, Et$_3$N; (*b*) (Bu$^n_4$N)$_2$[{Mo$_6$O$_{18}$}=N(4-HC≡C-2,6-Me$_2$C$_6$H$_2$)]–Pd(PPh$_3$)$_2$Cl$_2$, CuI, Et$_3$N, K$_2$CO$_3$; (*c*) HC≡CFc–Pd(PPh$_3$)$_2$Cl$_2$, CuI, Et$_3$N; (*d*) 3,6-(HC≡C)$_2$-1,4-(Bu^{t}CH$_2$O)$_2$C$_6$H$_2$–Pd(PPh$_3$)$_2$Cl$_2$,CuI, Et$_3$N, K$_2$CO$_3$.

We would like to add that the possibility of converting metal ketimides into imido complexes was first demonstrated for complex **133**. In particular, this was found to be readily methylated with methyl fluorosulfate to give cationic complex **134**.[411]



133 **134** (62%)

For the synthesis of tungsten imido carbonyls **135**, zwitterionic complex **136** can be used. The latter is smoothly oxidised with iodine, bromine or phosphorus pentachloride with N–N bond cleavage to give binuclear complexes **135** with bridging halogen atoms.[412–415]



136 **135**

X = I (76%), Br (13%), Cl (63%).

IV. Conclusion

The chemistry of transition metal imido complexes has long aroused particular interest owing to the remarkable ability of imido ligands to stabilise transition metals in higher oxidation states. The introduction of imido ligands into the coordination environment allowed, for example, preparation and characterisation of organic derivatives of chromium(VI) and manganese(VII), *i.e.*, the elements the oxides of which are classical oxidants used in organic chemistry.

Over the last 15 years, the focus has moved toward the application of transition metal imides, which has, in turn, stimulated the development of new methods for the synthesis of metal imido complexes of diverse structural types. Currently, the reactions of a broad range of nitrogen-containing reagents with transition metal compounds have been studied in sufficient detail, the features of these reactions were revealed and their synthetic potential was demonstrated.

A wide diversity of imido complexes was attained, first of all, owing to the use of intermolecular imidation methods. Currently, it can hardly be expected that the range of imidating reagents would be extended; further development of intermolecular imidation methods is possible, most of all, through the use of new transition metal-containing substrates and new types of imido ligands, in particular, heteroarylimido ligands. The progress in this field may also be connected with modern quantum-mechanical calculations of potential energy surface fragments. Such calculations are now virtually missing, and detailed structures of the transition states often remain obscure.

The methodology of intramolecular imidation has been developed less extensively than the intermolecular imidation strategy; therefore, there are grounds for expecting fruitful development of this line of research. In our opinion, the most interesting prospects are related to selective inner-sphere modification of the imido ligands, for example, functionalisation, elongation of the organic group, design of polymeric or dendrimeric molecules. Examples of such modifications are still few, but further development of this field would favour the synthesis of new promising compounds and material based on them.

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