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Metal-carboxylic Acids and Their Derivatives

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Questions connected with the synthesis of metal-carboxylic acids, compounds incorporating [M] -COOH fragments with a metal-carbon bond in which M is a transition metal complex, and their derivatives (salts, esters, and amides) are considered. The bibliography includes 189 references.

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I. INTRODUCTION

Metal-carboxylic acids (MCA) [M]−COOH constitute a new type of organometallic compound. The interest in complexes of this type is associated with studies on the formation of complexes by carbon dioxide with transition metal compounds.[1-7] The formation of MCA and their derivatives is also encountered in the study of various reactions in the presence of transition metal complexes. A review on MCA and their derivatives appeared in 1972.[8]

In the present review, covering the literature up to 1985, attention has been concentrated on the preparation of MCA and their derivatives and the literature on catalytic processes with the intermediate formation of [M]−COOH, [M]−COOR, or [M]−$CONR_2$ groups is covered only fragmentarily. The review also hardly reflects data on the synthesis of unstable MCA esters and amides by the usual methods.

The formation of MCA and their derivatives (esters and amides) in intermediates has been postulated in various catalytic processes with participation of carbon monoxide and carbon dioxide, although their involvement in the catalytic step has not been rigorously demonstrated. At any rate, one of the possible pathways in the majority of these processes may involve the intermediate formation of [M]−COOH, [M]−COOR, or [M]−$CONR_2$. The synthesis of higher carboxylic acids and their esters from unsaturated compounds, carbon monoxide, and an alcohol (or water) in the presence of transition metal compounds (the Reppe synthesis) can also be assigned to reactions of this type:[9-15]

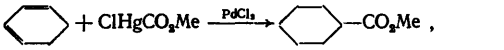
$$H_2O + [M] \rightleftarrows H[M]OH ,$$
$$H[M]OH + CO \rightleftarrows H[M]CO_2H ,$$
$$H[M]CO_2H + \underset{|\ |}{C{=}C} \rightarrow \underset{|\ |}{HC{-}CCO_2H} + [M] ,$$
$$\text{or } H[M]OR + CO \rightleftarrows H[M]COOR ,$$
$$H[M]COOR + \underset{|\ |}{C{=}C} \rightleftarrows \underset{|\ |}{HC{-}CCOOR} + [M] ,$$

where [M] is a fragment of the transition metal complex.

The formation of MCA esters as intermediates has been put forward also in the reaction involving the carbonylation of alkyl halides by carbon monoxide in the presence of transition metal complexes (see Fracalanci et al.[16] and the literature quoted therein). Although the metal-carboxylic acid can be isolated in a pure state from the reaction mixture under the conditions of the reaction involving the addition of formic acid and its esters to unsaturated compounds,[1,17] the question of the character of the transfer of the carboxy-group to the olefin with formation of H[M]COOH remains open; one of the possible pathways is as follows:

$$HCO_2H + [M] \rightarrow H[M]CO_2H ,$$
$$H[M]CO_2H + \underset{|\ |}{C{=}C} \rightarrow \underset{|\ |}{HC{-}CCO_2H} + [M] .$$

It is entirely possible that the esters of palladium-carboxylic acid are formed as intermediates in the carboxylation of unsaturated compounds in the presence of palladium salts[18] and in the synthesis of oxalic and carbonic acid esters by the reaction of carbon monoxide with alcohols:[19-21]



$$2CO + 2ROH \xrightarrow{PdCl_2} RCO_2CO_2R .$$

One cannot rule out the possibility that the electrocatalytic carboxylation of olefins in alcohols in the presence of platinum complexes proceeds, as postulated by Inoue and Tsutsumi,[22] with formation of a platinum-carboxylic acid ester, while the electro-chemical reduction of carbon dioxide at a platinum electrode results in the formation of the $[Pt]CO_2H$ fragment.[23] A reaction mechanism involving stages with participation of metal-carboxylic acids has been proposed for the electrocatalytic reduction of CO_2 to carbon monoxide in the presence of cobalt and nickel complexes:[24]

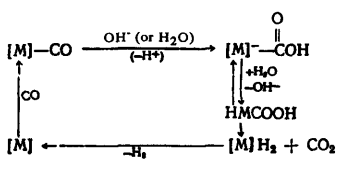
$$[L_nM^{III}CO_2Na]^{n+} + H_2O \overset{fast}{\rightleftarrows} [L_nM^{III}CO_2H]^{n+} + NaOH ,$$
$$[L_nM^{III}CO_2H]^{n+} + e \rightarrow [L_nM^{II}CO_2H]^{(n-1)+} ,$$
$$[L_nM^{II}CO_2H]^{(n-1)+} \xrightarrow{slow} [L_nM^{II}]^{n+} + CO + OH^- .$$

where M is the metal and L an N-containing ligand.

In connection with this study, one should note that much attention has been devoted recently to the investigation of the reactions involving the oxidation of CO by water in the presence of transition metal complexes:[25-32]

$$CO_2 + H_2O \overset{[M]}{\rightleftarrows} H_2 + CO_2 .$$

This reaction takes place via a general mechanism involving as one of the stages the formation of an unstable metal-carboxylic acid[31] (see also Vol'pin and Kolomnikov[25] and the literature quoted therein):



There is no doubt that metal-carboxylic acids or their esters are formed in all the reactions quoted above, although the transfer of the carboxy-group to the olefin remains in many respects obscure. Therefore the synthesis and study of the properties of metal-carboxylic acids and their derivatives will promote in many ways the elucidation of this complex process.

A fair amount of attention has also been devoted in the literature to the synthesis of carbamoyl compounds of transition metals (metal-carboxylic acid amides), which are intermediates in catalytic processes.[8] The synthesis of metal-carboxylic amides and the study of their properties are of undoubted interest for the understanding of the mechanism of carbonylation of amines in the presence of transition metal complexes.[33,34]

To conclude this, by no means complete, list of reactions in which the formation of metal-carboxylic acids and their derivatives as intermediates plays a major role, one must emphasise the importance of the chemistry of these compounds, because they constitute an independent class of organometallic compounds. Syntheses based on them extend the possibilities of coordination and organometallic chemistry. On the other hand, platinum(or gold)-carboxylic acids and their derivatives can be of interest from the practical point of view as antitumour medicinal preparations.[35]

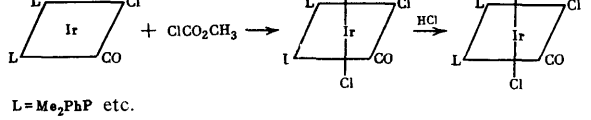
II. METAL-CARBOXYLIC ACIDS

1. Stable Metal-carboxylic Acids

Although the intermediate formation of MCA is frequently postulated, their preparation in a pure state involves considerable difficulties. The number of stable metal-carboxylic acids described in the literature is small. The synthesis of such acids would make it possible to obtain their various derivatives by analogy with the chemistry of carboxylic acids. On the other hand, as already mentioned above, metal-carboxylic acids are of great interest for preparative coordination chemistry, because specific synthesis of transition metal complexes with carbon dioxide via the following pathways is possible with their aid:

$$[M]OH + [M']CO_2H \rightarrow [M']CO_2[M] + H_2O\ ,$$
$$[M]HCO_3\ (\text{or}\ [M]_2CO_3) + [M']CO_2H \rightarrow [M']CO_2[M] + CO_2 + H_2O\ .$$

A stable metal-carboxylic acid was first described in 1969:[36]



L = Me_2PhP etc.

According to the data of these workers, the iridium-carboxylic acid is formed as colourless crystals stable in air. The IR spectrum of the resulting compound contains the intense ν(CO) = 1663 cm^{-1} (KBr) absorption band as well as the distinct ν(OH) = 3313 cm^{-1} (dry deuteriochloroform) absorption band. Titration of the iridium-carboxylic acid in aqueous acetone after the addition of one equivalent of alkali led to the observation of the evolution of carbon dioxide and the formation of the initial complex $L_2Ir(CO)Cl$. Carbon dioxide is also evolved on thermolysis of the acid with formation of the iridium hydride complex $L_2Ir(CO)HCl_2$.

The question of the formation of an iridium-carboxylic acid on hydrolysis of the complex $L_2Ir(CO)Cl_2(COOCH_3)$ has been investigated using the methods proposed by Deeming and Shaw;[36] when gaseous HCl is passed through a benzene solution of the iridium-carboxylic acid ester, only a mixture of the acid with the initial ester can be isolated from the reaction mixture in all cases.[37] The lack of information about this acid in later literature is probably associated with this finding.

Iridium-carboxylic acids of the above type have also been obtained on treating phosphine complexes of tervalent iridium with formic acid.[38] However, in view of the insignificant yields of the acids, this procedure cannot be regarded as preparative.

The preparation of a platinum-carboxylic acid via the mechanism

$$\text{dppe Pt(R)OH} + CO \rightarrow \text{dppe Pt(R)}CO_2H$$
$$R = Me,\ C_6H_5;\ \text{dppe} = Ph_2PCH_2CH_2PPh_2$$

has been reported.[39] However, this communication contains no data on IR spectroscopy, elemental analysis, etc. Analogous platinum-carboxylic acids were obtained later: $(Ph_2PCH{=}CHPPh_2)Pt(CO_2H).(CH_3CN)$ with m.p. 177–179 °C [ν(OCO) = 1604 cm^{-1} (v.s.) and ν(OH) = 2680 cm^{-1} (v.w.)] and $(Ph_2PCH{=}CHPPh_2)Pt(CO_2H).(CH_3CF_3)$ with m.p. 188–190 °C [ν(OCO) = 1610 cm^{-1} (v.s.) and ν(OH) = 2685 cm^{-1} (v.w.)].[40] The platinum-carboxylic acid *trans*-$(Et_3P)_2Pt(CO_2H)Cl$, which is unstable in air, has been obtained recently by treating the cationic complex $[(Et_3P)_2Pt(Cl)CO][BF_4]$ with water;[41] the IR spectrum contains the ν(OCO) = 1595 cm^{-1} (v.s.) and 1150 (s.) as well as the ν(OH) = 3140 cm^{-1} (v.w.) absorption bands; the last band shifts to ν(OD) = 2240 cm^{-1} (v.w.) when hydrogen is replaced by deuterium. According to NMR data, the spin–spin coupling constant $J^{195}_{Pt-}{}^{13}_{C}$ = 1337. It is noteworthy that this method of synthesis of metal-carboxylic acid is the easiest among all those available.

The comparatively stable rhenium-carboxylic acid of the type η^5-CpRe(CO)(NO)COOH has been obtained by treating the cationic complex $[\eta^5\text{-CpRe(CO)NO}]^+$ with aqueous solutions of triethylamine or alkali.[42–44]

The rhenium-carboxylic acid is quantitatively converted into the hydride complex CpRe(CO)(NO)H in absolute tetrahydrofuran (THF). The IR spectrum of the acid in THF contains the 2960 (s., br.) and 1631 (m.) absorption bands, while the ^1H NMR ($CDCl_3$) spectrum contains the δ = 9.47 p.p.m. signal. According to Sweet and Graham,[43] the interaction of a dialkylamine with the rhenium-carboxylic acid in solution results in the formation of the metal complex of carbon dioxide:

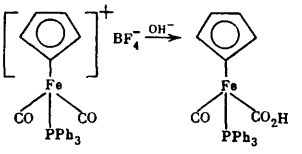
$$[Re]COOH + R_2NH \rightarrow [Re]COO^- \ldots H_2NR_2^+\ ,$$
$$[Re]COO^- \rightarrow [Re] + CO_2\ .$$

A rhenium-carboxylic acid of the type $CpRe(CO)(N_2Ar)COOH$ has been obtained recently.[45] The authors failed to observe the ν(OH) frequency both in fluorinated oil and in CH_2Cl_2. However, on treatment with NaOD in D_2O the exchange of hydrogen for deuterium was observed—an absorption band at 2240 cm^{-1} appeared in the IR spectrum.

The rhenium complexes $[\eta^5\text{-CpRe(CO)}_2(p\text{-}N_2C_6H_4R)COOH]$, where R = Me, OMe, or NEt_2, have been obtained in the same way, i.e. by treating cationic rhenium complexes with alkali.[45] A band with δ = 8.9 p.p.m., corresponding to the proton in the carboxy-group, has been observed in the ^1H NMR ($CDCl_3$) spectrum. The IR spectrum (CH_2Cl_2) also contains absorption bands at 1954 (v.s.), 1643 (v.s.), and 1596 (v.s.) cm^{-1}. A rhenium hydride complex as well as $[CpRe(CO)_2(N_2Ar)(CO_2^-)]$ are formed in the presence of an excess of alkali as a consequence of the deprotonation of the metal-carboxylic acid. After the irradiation of rhenium carbonyl with UV light in THF in the presence of cyclo-octatetraene, an insignificant amount of a trirhenium-carboxylic acid having the composition $Re_3(CO)_{14}CO_2H$ was detected among the reaction products.[46] The colourless "$Re(CO)_5OH$" complex, which becomes coloured in the light, has been obtained in a quantitative yield by treating the

cationic complex $(CO)_5ReBF_4$ with alkali.[47] Subsequently, this intermediate, which may be a rhenium-carboxylic acid, is converted into a rhenium complex of carbon dioxide. In comparing the results of the synthesis of the rhenium-carboxylic acid obtained by different workers, one must note that the spectroscopic data for the identification of the rhenium-carboxylic acid quoted by Casey et al.[42] agree qualitatively with the spectroscopic data for the rhenium complex of carbon dioxide.[47] It has therefore been suggested[47] that the adduct having the composition "$(CO)_5ReOH$" is the protonated form of the rhenium complex of carbon dioxide formed ultimately: "$(CO)_5$. .ReOH" $\leftrightarrows$ $(CO)_4ReCO_2H$.

There are also literature data concerning the synthesis of stable iron-carboxylic acids.[48] Thus the interaction of aqueous solutions of alkalies with cationic iron complexes made it possible to obtain an iron-carboxylic acid in a pure state:



The compound synthesised is a yellow substance, fairly stable in the presence of atmospheric oxygen, which decomposes on heating above 130 °C. The IR spectrum contains the ν(OCO) = 1565 (m.) and 2700 (m.) cm^{-1} absorption bands. Treatment of the iron-carboxylic acid with potassium hydroxide leads to the formation of the corresponding potassium salt, which can be converted into the iron-carboxylic acid on acidification with hydrochloric acid.

2. Unstable Metal-carboxylic Acids

As can be seen from the foregoing, the problem of the synthesis in one way or another of stable metal-carboxylic acids has been solved in principle, which made it possible to investigate their chemical and physicochemical properties. On the other hand, the hypotheses concerning the existence of unstable metal-carboxylic acids as intermediates had been put forward even earlier. Studies in which the formation of unstable metal-carboxylic acids as intermediates has been claimed can be divided into two groups:

(a) Oxidation of carbon monoxide with water in the presence of transition metal salts. Only hypotheses concerning the formation of metal-carboxylic acids in one of the stages were put forward in these investigations.

(b) The formation of metal-carboxylic acids in the presence of ligands stabilising the metal–carbon σ-bond, such as CO, phosphines, cyclopentadiene (Cp), and others. Under these conditions, it is sometimes possible to obtain an unstable metal-carboxylic acid or at least to achieve the confirmation of its formation by spectroscopic methods.

The existence of metal-carboxylic acids in aqueous solutions was first reported in 1961.[49,50] The authors suggested the formation of a mercury-carboxylic acid as one of the stages in the oxidation of carbon monoxide by water in the presence of mercury salts:[49]

$$Hg^{2+}OH_2 + CO \rightarrow [-Hg-\overset{\overset{O}{\|}}{C}-OH] + H^+ .$$

By analogy with this reaction, the formation of carbon dioxide and hydrogen when carbon monoxide is passed through a solution of univalent thallium hydroxide permitted the conclusion that unstable thallium-carboxylic acid is formed in aqueous solution:[51]

$$TlOH + CO \rightarrow [TlCO_2H] .$$

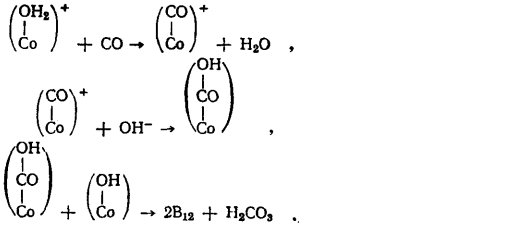
It is also stated in the literature that nickel-carboxylic,[48] silver-carboxylic,[50], and copper-carboxylic[52] acids are formed under analogous conditions. It has been shown in relation to iron-carboxylic acids that the nature of the ligand determines in many respects the stability of these derivatives.[48] The formation of unstable iron-carboxylic acids has also been indicated in other investigations.[53,54] When a cationic platinum complex was treated with water, a platinum hydride complex was obtained as an intermediate.[55] The authors suggest that the reaction proceeds via the formation of a platinum-carboxylic acid:

$$[(Et_3P)_2Pt(Cl)CO]BF_4 \xrightarrow[-HBF_4]{H_2O} [(Et_3P)_2Pt(Cl)CO_2H] \rightarrow [(Et_3P)_2Pt(Cl)H] + CO_2 .$$

The interaction of carbon monoxide with water in the presence of phosphine complexes of zerovalent platinum has been studied in fair detail.[26] The complex $[(iso\text{-}Pr)_3P]_3Pt$ proved to be the most active in this process; a hydroxoplatinum complex is formed on treatment with water in the course of the reaction and interacts further with carbon monoxide, being converted into a platinum-carboxylic acid [ν(OCO) = 1575 cm^{-1}].

There are data on the synthesis of unstable manganese- and rhenium-carboxylic acids on interaction of water with the corresponding metal carbonyl derivatives.[56,57] Derivatives labelled with ^{13}C and ^{18}O were used to identify the intermediates in spectroscopic studies.[57] For example, the interaction of the cationic manganese complex $[dppeMn(CO)_4]^+$ (see Table 1 below) with $H_2{}^{18}O$ results in the formation of the manganese-carboxylic acid $dppeMn(CO)_3.CO^{18}OH$ according to spectroscopic data.

Much attention has been devoted in the literature to the formation of cobalt-carboxylic acids in connection with the modelling of the reactions of vitamin B_{12} by various cobalt chelate complexes.[1,56] Thus the formation of a unstable cobalt-carboxylic acid can be represented schematically in the following way:[58]



The study of processes involving the oxidation of $[Co^I(CN)_2(Et_3P)_2.CO]^-$ by hexacyanoferrate(III) $[Fe(CN)_6]^{3-}$ led to the conclusion that the unstable cobalt-carboxylic acid $[(CN)_5Fe^{II}CNCo^{III}(CN)_2(Et_3P)_2.CO_2H]^{4-}$ is formed in solution.[59]

The formation of unstable rhodium-, iridium- and platinum-carboxylic acids has been postulated in the synthesis by indirect methods of transition metal complexes of carbon dioxide involving treatment of the corresponding hydroxo-complexes of the transition metals with carbon monoxide.[60–63] Thus a familiar carbon dioxide complex has been obtained from the complex $(Ph_3P)_2Rh(CO)OH$:[63]

$$(Ph_3P)_2Rh(CO)OH \xrightarrow{CO+C_6H_6} [(Ph_3P)_2Rh(CO)CO_2H] \rightarrow (Ph_3P)_3Rh_2(CO)_2 \cdot CO_2 \cdot C_6H_6 .$$

The formation of unstable rhodium-carboxylic acids has also been indicated in other communications.[64,65]

An unstable palladium-carboxylic acid is apparently formed on carboxylation of aromatic compounds to the corresponding acids with the aid of palladium acetate in a mixture of glacial acetic acid and its anhydride.[20,21] In this connection, we may note that numerous reactions involving the oxidation of carbon monoxide by water to CO_2 in the presence of palladium salts also probably proceed with formation of a palladium-carboxylic acid.[20]

The synthesis of metal-carboxylic acids from CO_2 and transition metal hydride complexes is a fundamentally new procedure.[1,66] Thus, when a cobalt hydride complex is treated with carbon dioxide, an "anomalous" insertion of a CO_2 molecule in the CO–H bond takes place with formation of an unstable cobalt-carboxylic acid, which was identified by means of chemical reactions.[66]

Table 1. Metal-carboxylic acid esters.

Compound*	Colour	M.p., °C	IR spectrum ν(CO), cm^{-1}	Refs.
$ClHgCO_2Me$	white	109—110	—	[83]
$ClHgCO_2Et$	»	87—88	—	[83]
$MeCO_2HgCO_2Me$	»	109—110	—	[83]
$MeCO_2HgCO_2Et$	»	125	—	[83]
$MeCO_2HgSHgCO_2Me$	»	—	—	[83]
$C_6H_5HgCO_2Me$	»	68—69	—	[84]
p-$MeOC_6H_4HgCO_2Me$	»	89	—	[84]
$Hg(CO_2Me)_2$	»	84	—	[84]
$CpMo(CO)_3CO_2Me$	yellow	47—49	1708	[85]
$(CO)_5MnCO_2Et$	pale-yellow	59,5	1644	[86]
$(Ph_3P)_2Mn(CO)_3CO_2Me$	»	150	1612	[86]
$(Ph_3P)_2Mn(CO_3)CO_2Et$	»	—	1606	[86]
$(Ph_3P)_2Mn(CO)_3CO_2C_5H_{11}$	»	—	1611	[86]
$(Ph_3P)_2MnCO_2CH_2Ph$	»	—	1607	[86]
$CpMn(CO)(NO)CO_2Me$	»	55—57	1650	[87, 88]
$(CO)_5ReCO_2Et$	colourless	69	1635	[89—90]
$(Ph_3P)_2Re(CO)_3CO_2Me$	»	—	1613	[86]
$(CO)_5Re(bipy)CO_2Me$	»	—	1621	[86]
$CpRe(CO)(NO)CO_2Me$	yellow	92—94	1620	[87]
$CpFe(CO)_2CO_2Me$	—	34—36	1665	[85, 88, 91]
$Cp(Ph_3P)Fe(CO)CO_2Me$	yellow	—	1605	[48]
$CpRu(CO)_3CO_2Me$	—	—	—	[92]
$(Ph_3P)_2Ru(CO)_2(I)CO_2Me$	—	—	1651	[92]
$[(C_6H_{11})_3P]Ru(CO)_3CO_2Me$	—	—	1657	[92]
$(Ph_3P)_2Os(CO)_2(Cl)CO_2Me$	—	272—274	1641	[93]
$(Ph_3P)_2Os(CO)_2(Cl)CO_2Et$	—	254—256	1639	[93]
$[(C_6H_{11})_3P]_2Os(CO)_3(Cl)CO_2Me$	—	350	1655	[93]
$[(C_6H_{11})_3P]_2Os(CO)_2(Cl)CO_2Et$	—	—	1652	[93]
$HOs_3C(CO)_{14}CO_2Et$ **	—	—	—	[94]
$IOs_3C(CO)_{14}CO_2Me$ **	—	—	—	[94]
$Ph_3PCo(CO)_3CO_2Et$	yellow	100	1647	[95, 96]
$(PhO)_3PCo(CO)_3CO_2Et$	»	70	1666	[95, 96]
$(Ph_3P)_2Co(CO)_2CO_2Me$	pale-yellow	100	1633	[95, 96]
$(Ph_3P)_2Co(CO)_2CO_2Et$	yellow	90	1627	[95, 96]
$(Salen)_2CoCO_2Me$	—	—	—	[97—99]
$(Salen)_2CoCO_2Me\cdot H_2O$	orange-yellow	—	1716	[97, 98]
$(Salen)_2CoCO_2Et\cdot H_2O$	»		—	[97, 98]
$(Salen)_2CoCO_2Me\cdot Py$ ***	—		—	[97—99]
$RhCl_2(CO)_2CO_2Et$	yellow	—	1705	[100]
$(Ph_3Sb)_3Rh(CO)CO_2Me$	yellow-brown	144	1621	[101]
$(Ph_3P)_2Rh(CO)_2CO_2Me$	yellow	—	1637	[102]
$Rh_4(CO)_{11}CO_2Me$ ****	»	—	1629	[103]
$[Rh_6(CO)_{15}CO_2Et]^-$	—	—	—	[104]
$[(Ph_3P)Rh_6(CO)_{15}CO_2Me]^-$	—	—	—	[104]
$(Me_2PhP)_2IrCl_2(CO)CO_2Me$	white	139—144	1677	[36]
$(Me_2PhP)_2Ir(CO)(Cl_2)CO_2Et$	»	97—100	1663	[36]
$(Me_2PhP)_2IrCl_2(CO)CO_2Ph$	»	167—170	1701	[36]
$(Me_2PhAs)_2IrCl_2(CO)CO_2Me$	»	121—133	1672	[36]
$(Me_2PhAs)_2IrCl_2(CO)CO_2Et$	»	70—72	1664	[36]
$(Me_3P)_2IrCl_2(CO)CO_2Me$	»	159—162	1672	[36]
$(Ph_3P)_2Ir(CO)_2CO_2Me$	»	124—125	1655	[105, 106]
$(Ph_3Sb)_3Ir(CO)CO_2Me$	yellow	156	1612	[101]
$(Ph_3Sb)_3Ir(CO)CO_2Et$	»	148	1608	[101]
$Ir(CO)I_2(bipy)CO_2Me$	»	260	1670	[106]
$Ir(CO)I_2(bipy)CO_2Et$	»	250	1645	[106]
$Ir(CO)I_2(bipy)CO_2Pr\text{-}iso$	»	224	1640	[106]
$Ir(CO)I_2(bipy)CO_2CH_2CH{=}CH_2$	»	178—180	1660	[106]
$Ir(CO)I_2(phen)CO_2Me$	»	300	1654	[106]
$Ir(CO)I_2(Py)CO_2Me$	»	180	1660	[106]
$(Ph_3P)_2Ir(CO)(I_2)CO_2Me$	»	160	1650	[106]
$(Ph_3P)_2Ir(CO)(I_2)CO_2Et$	»	174	1700	[106]
$(Ph_3P)_2Ir(CO)_2(I)CO_2Me$	»	166	1650	[106]
$(Ph_3P)_2Ir(CO)_2(I)CO_2Et$	»	146	1660 1610	[106]
$(Ph_3P)_2Ir(CO)_2(Br)CO_2Et$	»	128—130	1670	[106]
$(Ph_3P)_2Ir(CO)_2(Cl)CO_2Et$	green	110—115	1650	[106]
$(Me_2PhP)_2Ir(CO)Cl_2CO_2Me$	—	—	1677	[106]
$(Me_2PhP)_2Ir(CO)Cl_2CO_2Et$	—	—	1663	[106]
$(Ph_3P)_2\overline{IrCO_2CH_2CH{=}}CH_2(CO)$	colourless	164—166	1662	[107]
$(Ph_3P)_2\overline{IrCO_2CH_2CH{=}}CHMe(CO)_2$	»	146—147	1666	[107]
$(Ph_3P)_2IrCO_2CH_2CH_2OH(CO)_2$	»	135—140	1639	[107]
$(Ph_3P)_2\overline{IrCO_2CH_2CH{=}}CH_2(CO)$	»	160	1660	[108]
$(Ph_3P)_2\overline{IrCO_2CH{=}CH}{=}CHPh(CO)$	»	159	1660	[108]
$(Ph_3P)_2Ir(CO)CO_2Pr\text{-}n$	»	137	1640	[108]
$[(Me_2PhP)_2IrH(CO)(Cl)(HgCl)CO_2Me]^+$	»	165—167	1623	[109]
$[(dmpe)_2Ir(Cl)CO_2Me][FSO_3]$	»		1630	[110]

Table 1 (continued).

Compound*	Colour	M.p., °C	IR spectrum ν(CO), cm^{-1}	Refs.
$[(dmpe)_2IrHCO_2Me][BPh_4]$	»	180	1625	[111]
$[(dmpe)_2Ir(H)CO_2Et][BPh_4]$	»	184	1610	[111]
$[(dmpe)_2Ir(D)CO_2C_2D_5][BPh_4]$	»	182	1598 1610	[111]
$[(Me)_2(CH_2Ph)_2N][Ir_4(CO)_{11}CO_2Me]$	—	—	1645	[112]
$[Ph_4P][Ir_4(CO)_{11}CO_2Me]$	—	—	1650	[112]
Other Ir_4 clusters	—	—	—	[112]
trans-$(Ph_3P)_2Ni(Cl)CO_2Me$	yellow	150—153	1629	[113]
trans-$(Ph_3P)_2Ni(Cl)CO_2Et$	»	134—138	1630	[113]
$(Ph_3P)_2Pd(CO_2Me)_2$	—	118—134	1630	[114]
$(Ph_3P)_2Pd(OCOMe)CO_2Me$	—	129—136	1655	[114]
$(Ph_3P)_2Pd(OCOCF_3)CO_2Me$	—	—	1667	[114]
$(Ph_3P)_2Pd(Cl)CO_2Me$	colourless	190—192	1656, 1672	[21, 80, 113—115]
$(Ph_3P)_2Pd(Cl)CO_2Et$	»	170—190	1633, 1645	[113, 116]
$[(PhO)_3P]_2Pd(Cl)CO_2Et$	»	128—136	1670	[113]
$(t\text{-}C_4H_9NC)_2Pd(Cl)CO_2Me$	»	106—108	1680	[113]
$(t\text{-}C_4H_9NC)_2Pd(Cl)CO_2Et$	»	98—100	1670	[113]
$(t\text{-}C_4H_9NC)_2Pd(Cl)CO_2CH_2Ph$	pale-yellow	137—139	1675	[113]
$(Ph_3P)_2Pd(NCO)CO_2Me$	colourless	225—228	1668, 1653	[117]
$(Ph_3P)_2Pd(NCO)CO_2Et$	»	162—163	1668	[117]
$[(Ph_3P)_2Pd(CO)CO_2Me][BF_4]$	—	—	1668	[117]
$(Ph_3P)_2Pt(CO_2Me)_2$	yellow	178—183	1632	[80, 118]
$(Ph_3P)Pt(OCOCF_3)CO_2Me$	white	188—195	1710, 1692	[119, 120]
$(Ph_3P)_2Pt(OCOCF_3)CO_2Et$	»	185—187	—	[120]
$(Ph_3P)_2Pt(OCOMe)CO_2Me$	»	224—227	—	[120]
$(Ph_3P)_2Pt(Cl)CO_2Me$	»	222—227	1664	[21, 80, 121]
$(Ph_3P)_2Pt(Br)CO_2Me$	»	226—231	1665	[121]
$(Ph_3P)_2Pt(I)CO_2Me$	»	226—229	1655	[121]
$(Ph_3P)_2Pt(Cl)CO_2Et$	»	215—217	1638	[117, 121]
$(Ph_3P)_2Pt(Br)CO_2Et$	»	226—231	1638	[121]
$(Ph_3P)_2Pt(I)CO_2Et$	»	221—229	1638	[121]
$(Ph_3As)_2Pt(Cl)CO_2Me$	»	234—236	1658	[122]
$(Ph_3As)_2Pt(Cl)CO_2Et$	yellow	214—216	1632	[122]
$(Ph_3P)_2Pt(Cl)CO_2Ph$	white	—	1646	[123]
$(Ph_3P)_2Pt(SCN)CO_2Me$	»	230—233	1645	[124]
$(Ph_3P)_2Pt(NO_3)CO_2Me$	»	215—218	1642	[124]
$(Ph_3P)_2Pt(C_6F_5)CO_2Me$	cream	242—245	1660	[124]
$(Ph_3P)_2Pt(C_6H_5)CO_2Me$	white	—	1646	[124]
$(Ph_3P)_2Pt(CH_3)CO_2Me$	»	180—183	1650	[125]
trans-$(Ph_3P)_2Pt(CF_3)CO_2Me$	—	186—188	1655, 1632	[40]
$Pt(CH_2CN)(Ph_2PCH{=}CHPPh_2)CO_2Me$	—	190—192	1639	[40]
$Pt(CF_3)(Ph_2PCH{=}CHPPh_2)CO_2Me$	—	206—209	1657, 1643	[40]
$Pt(CH_2CN)(Ph_2PCH{=}{=}CHPPh_2)CO_2CMe_3$		205—208	1638	[40]
$Pt(CH_2CN)(Ph_2PCH{=}CHPPh_2)CO_2CHMe_2$		191—193	1633	[40]
$[(Ph_3P)_2Pt(CO)CO_2Me][BF_4]$	white	184—185	1661	[117]
$[(Ph_3P)_2Pt(CO)CO_2Et][BF_4]$	»	149	1660	[117]
$[(Ph_3P)_2Pt(CO)CO_2Me][BF_4]$	»	186—188	1667	[117]
$[(Ph_3P)_2Pt(CO)CO_2Et][BF_4]$	»	182—183	1661	[117]
$(Ph_3P)_2Pt(NCO)CO_2Et$	»	228—230	1656	[117]
$(Ph_3P)_2Pt(Cl)HgCO_2Me_2$	»	185—192	1670	[80]
$(COD)Pt(Cl)CO_2Me$	—	—	1665	[126]
$(Ph_3P)_2Pt(Cl)CO_2CHMe$	—	—	1615	[127]
$(dppe)Pt(OMe)CO_2Me$	—	—	1690	[128]
$(dppe)Pt(CO_2Me)_2$	—	—	1650, 1680	[128, 129]

*Salen = salicylidene-ethylenediamine; bipy = 2,2-bipyridyl; phen = 1,1-phenanthroline; dmpe = dimethylphosphinoethane; dppe = diphenylphosphinoethane; COD = cyclo-octa-1,5-diene; Py = pyridine.

**Characterised by X-ray diffraction.

***The esters of cobalt-carboxylic acids with other *N*-containing ligands have also been obtained.

****Other esters of rhodium-carboxylic acids of the type $[Rh(NO).(Ph_3P)_2(ROH)CO_2R]^+$ as well as rhodium clusters of the type $[Rh_6(CO)_{14}(CO_2Me)_2]^{2-}$ have also been obtained.

Data on the synthesis of a fairly stable chromium-carboxylic acid on radiolysis of tervalent chromium salts in the presence of formic acid in aqueous solutions are also of fundamental importance:[67]

$$[\cdot COOH] + [Cr^{3+}] \rightarrow [CrCO_2H]^{3+} .$$

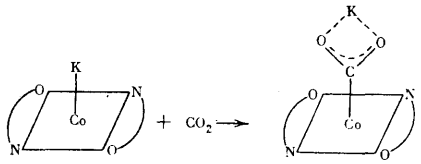
The radical-anion CO_2^- is apparently formed under these conditions and can be stabilised at the metallic centre with subsequent protonation to .COOH. A titanium-carboxylic acid may be formed under analogous conditions.[1] These results are important for the

understanding of the mechanism of the reduction of carbon dioxide to organic compounds in aqueous solutions in the presence of transition metal compounds.

III. METAL-CARBOXYLIC ACID SALTS AND POLYNUCLEAR TRANSITION METAL COMPLEXES OF CARBON DIOXIDE

As already mentioned above, treatment of a platinum-carboxylic acid with potassium hydroxide can yield an equivalent amount of the potassium salt of the platinum-carboxylic acid,[26] which has been characterised by IR and NMR spectroscopic methods.

There have been reports of attempts to obtain salts of metal-carboxylic acids by inserting carbon dioxide in the transition metal–alkali metal (or alkaline earth metal) bond. Thus treatment of the organometallic analogue of a Grignard reagent $C_6H_5(Ph_3P)NiMgBr$ with CO_2 results in the formation of the unstable $Cp(Ph_3P)NiCO_2.MgBr$, the complex $Cp_2Ni(CO)_2$ being formed as the final product on hydrolysis.[68] When carbon dioxide was passed through a solution of the potassium salts of complexes of the type $K(Co)(Salen)_2$ (where Salen = silicylidene-ethylenediamine), the insertion of a CO_2 molecule in the cobalt–potassium bond was observed:[69,70]



When sodium salts of manganese and rhenium hydride carbonyls are treated with carbon dioxide, a CO_2 molecule is also inserted in the transition metal–sodium bond.[71] The product of the interaction of carbon dioxide with the sodium salt of the rhenium compound was then characterised spectroscopically and with the aid of chemical reactions as the sodium salt of a rhenium-carboxylic acid. However, in the light of latest data concerning the synthesis of trirhenium-carboxylic acids,[46,47] further studies on these lines are essential in order to elucidate the question whether or not the compound obtained by Lysak et al.[71] is a rhenium cluster with CO_2.

It has been shown recently that carbon dioxide can be inserted also in the iron–magnesium bond:[72]

$$[(\eta\text{-CpFe(CO)}_2]_2Mg + CO_2 \rightarrow [(\eta\text{-Cp})(CO)_2FeCO_2]_2Mg\,.$$

Alkylation of this salt with methyl iodide yielded the methyl ester of the iron-carboxylic acid.

When aluminium halides interact with the iridium-carboxylic acid ester $(Ph_3P)_2Ir(CO)_2CO_2Me$ in the presence of traces of moisture, a complex of carbon dioxide coordinated simultaneously to iridium and aluminium atoms is formed.[73,74] It has been shown that carbon dioxide is displaced from this compound by triphenylphosphine and carbon monoxide and that, following the replacement of $^{12}CO_2$ by $^{13}CO_2$, the 1725, 1375, and 1220 cm^{-1} bands are displaced to 1700, 1340, and 1210 cm^{-1} respectively.

Overall, the study of reactions in which compounds of CO_2 coordinated to a transition metal atom and to alkali or alkaline earth metals are formed is important for the solution of problems associated with the introduction of CO_2 molecules into catalytic processes (bifunctional catalysis).[75–77]

Considerable difficulties arise in the interpretation of experimental data concerning the nature of these products. It has been shown by X-ray diffraction that the product of the insertion of the CO_2 molecule in the cobalt–potassium bond is in reality not a salt of a cobalt-carboxylic acid but a complex of carbon dioxide.[70] On the other hand, the insertion of a CO_2 molecule in the rhenium–sodium bond is irreversible. Depending on the nature of the metal and the ligand, one can probably expect the formation of metal-carboxylic acid salts in some cases and of transition metal complexes of carbon dioxide in others.

One can assume that the formation of metal-carboxylic acids on interaction of hydroxo-complexes with carbon dioxide can lead to the formation of transition metal complexes of carbon dioxide, for example via the mechanism

$$[M]OH + [M']CO_2H \rightarrow [M']CO_2[M] + H_2O$$

In this case the dinuclear (polynuclear) complexes formed can be regarded as derivatives (salts) of the corresponding metal-carboxylic acids. Indeed, it has been found that the interaction of carbon monoxide with the hydroxorhodium complex $(Ph_3P)_2Rh(CO)OH$ leads to the formation of a rhodium complex of carbon dioxide: $(Ph_3P)_3Rh_2(CO)_2CO_2C_6H_6$.[63] Analogous reactions occur also when hydroxo-complexes of transition metals, namely $[Me_3PtOH]_4$, $(Ph_3P)_2Ir(CO)OH$, etc., are treated with carbon monoxide.[60–62] The formation of the rhenium complex of carbon dioxide $(CO)_5ReCO_2.[Re(CO)_4]_2$ also probably proceeds via the formation of an unstable rhenium-carboxylic acid.[47] The IR spectrum of the resulting compound contains absorption bands characteristic of transition metal complexes of CO_2 [1458 (s.), 1165 (br.), and 1150 (s.) cm^{-1}]. According to X-ray diffraction data, the CO_2 molecule is coordinated to three metal atoms. We may note that the IR spectra of metal-carboxylic acids usually contain one ν(CO) absorption band, while in the case of carbon dioxide complexes the spectra show three absorption bands.[1,2] The data of Casey et al.,[42] demonstrating that the IR spectrum (nujol) of the rhenium-carboxylic acid $CpRe(CO)(NO)CO_2H$ which they obtained contains three intense absorption bands near 1585 (s.), 1145 (s.), and 1135 (s.) cm^{-1}, correspond better to a rhenium complex of carbon dioxide, although they observed also absorption bands corresponding to the vibrations of the hydroxy-group near 2960 (w.), 2860 (w.), 2705 (w.), and 2690 (w.) cm^{-1}.

The ruthenium and osmium complexes of carbon dioxide are probably formed on treatment of the corresponding metal carbonyls with alkalies also via the intermediate formation of metal-carboxylic acids.[78,79] According to X-ray diffraction data, the CO_2 molecule in the osmium complex $[HOs_3(CO)_{10}CO_2Os_6(CO)_{17}]^-$ is linked to three metal atoms.[79]

IV. ESTERS OF METAL-CARBOXYLIC ACIDS (ALKOXY-CARBONYL COMPLEXES OF TRANSITION METALS)

1. Synthesis

The most widely used and convenient methods from the preparative point of view are as follows:[8]

(1) Treatment of the carbonyl group coordinated to the metal with solutions of alkalies in alcohol:

$$[M]CO + OR^- \rightarrow \{[M]CO_2R\}^-\,,$$

Treatment of cationic complexes of metal carbonyl derivatives with alcohols is a modification of this method.

(2) Treatment of halogeno-derivatives of transition metal complexes with alcoholic alkalies in the presence of carbon monoxide, for example:

$$(Ph_3P)_2PtCl_2 + CO + NaOH/ROH \rightarrow (Ph_3P)_2Pt(CO_2R)_2\,,$$

Treatment of alkoxo-complexes of transition metals directly with carbon monoxide leads to the same results.

(3) Exchange reactions between chloroformic acid esters and transition metal hydride salts, for example:

$$NaMn(CO)_5 + ClCO_2CH_3 \rightarrow (CO)_5MnCO_2CH_3 .$$

(4) Reactions involving the oxidative addition of chloroformic acid esters to transition metal complexes, for example:

$$(Ph_3P)_3Pt + ClCO_2R \rightarrow (Ph_3P)_2Pt(Cl)CO_2R .$$

(5) Treatment of transition metal isocyanate complexes with carbon monoxide and alcohol:

$$(Ph_3P)_2Pd(NCO)_2 \xrightarrow{ROH;CO} (Ph_3P)_2Pd(CO_2R)_2 ,$$

(6) Alkylation of metal-carboxylic acid salts:[72]

$$[(\eta\text{-Cp})Fe(CO)_2CO_2]_2Mg + CH_3I \rightarrow (\eta\text{-Cp})Fe(CO)_2CO_2CH_3 .$$

(7) Transfer of the CO_2R group from an organomercury derivative to a transition metal complex via the oxidative addition mechanism:[80,81]

$$(Ph_3P)_4Pd + ClHgCO_2R \rightarrow (Ph_3P)_2Pd(Cl)CO_2R + Hg .$$

(8) Direct action of carbon dioxide on transition metal complexes containing a metal–carbon σ-bond:[82]

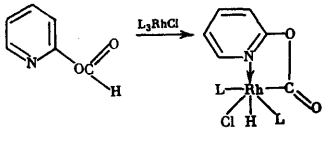
$$M^{\delta-}—R^{\delta+} + CO_2 \rightarrow MCO_2R .$$

(9) Esters of metal-carboxylic acids can be obtained also by esterifying the carbamoyl complexes of transition metals. Table 1 lists the metal-carboxylic acid esters described in the literature.

Esters of metal-carboxylic acids are also formed on decomposition of keto-acids in solution or on their thermolysis:[130]

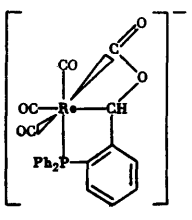
$$(Ph_3P)_2Pd(Cl)COCO_2R \rightarrow (Ph_3P)_2Pd(Cl)CO_2R + CO .$$

Yet another method of synthesis of metal-carboxylic acid esters is *ortho*-metallation. Thus the interaction of α-pyridyl formate with the complex $[Rh(Ph_3P)_3Cl]$ can yield the ester of a rhodium-carboxylic acid:



The disproportionation of CpRe(CO)(NO)CHO results in the formation of the complex $Cp(CO)(NO)ReCO_2CH_2Re(CO)(NO)Cp$, which can be regarded as a rhenium-carboxylic acid ester.[132] Treatment of the ester with methanol results in the formation of CpRe.(CO)(NO)CO_2Me (m.p. 105–115 °C; IR spectrum: 1626 and 1010 cm^{-1} in nujol).

A rhenium-carboxylic acid ester has been obtained to which the following structure was attributed on the basis of IR and ^1H NMR spectroscopic data:[133]



After alkylating an iridium complex of carbon dioxide with $MeSO_3F$, the methyl ester of an iridium-carboxylic acid was isolated:[110]

$$(dmpe)_2Ir(Cl)CO_2 + MeSO_3F \rightarrow [(dmpe)_2Ir(Cl)CO_2Me][SO_3F],$$

dmpe = dimethylphosphinoethane

The IR spectrum contains absorption bands at 1630 and 1065 cm^{-1}.

2. Investigation by Physicochemical Methods

As can be seen from Table 1, the IR spectroscopic method yields an extremely large amount of information in the study of metal-carboxylic acid esters. The MCA esters have characteristic absorption bands, as a rule with appreciable intensity, corresponding to the ν(OCO) frequencies of the ester group in the range 1600–1700 cm^{-1} and the ν(OR) frequencies in the range 1000–1070 cm^{-1}. A fairly large number of metal-carboxylic acid esters, which cannot be isolated as pure compounds from the reaction mixture, were characterised by this method.

There exist also data obtained by investigating metal-carboxylic acid esters in solutions by UV spectroscopy. Thus studies have been made of the UV spectra of complexes of the type $(Ph_3P)_2Pt(Cl)CO_2.CH_2R$, where R = H, Me, or Ph.[123] The following values of 10^{-4} ε (λ_{max}, nm) were found for R = H: 2.3 (257); 1.6 (268); 1.1 (275). The corresponding values for the ethyl and benzyl esters are close to those for the methyl ester.

The ^1H NMR method is used widely for the identification of metal-carboxylic esters. Data obtained by determining the dipole moments permitted the conclusion that platinum-dicarboxylic acid esters of the type $(Ph_3P)_2Pt(CO_2Me)_2$ have the *trans*-structure.[118]

It is noteworthy that metal-carboxylic acid esters are the *C*-isomers of the corresponding carboxylate complexes of transition metals (*O*-isomers),[134] for example: $Hg(CO_2R)_2$ and $Hg(OCOR)_2$; $(CO)_5ReCO_2R$ and $(CO)_5ReOCOR$; $(Ph_3P)_2Pt(CO_2R)_2$ and $(Ph_3P)_2.Pt(OCOR)_2$; $(Ph_3P)_2Pd(CO_2R)_2$ and $(Ph_3P)_2Pd(OCOR)_2$. The method of X-ray electron spectroscopy has been applied successfully in the solution of the problem of the mode of coordination of carbon dioxide in the complex $(Ph_3P)_2PtCO_2$.[135]

Table 2 lists the bond lengths in metal-carboxylic acid esters determined by X-ray diffraction.

Table 2. X-Ray diffraction data for metal-carboxylic acid esters.

Compound	Bond length, Å			O–C–O angle, deg	Refs.
	M–C	C=O	C–O		
$ClHgCO_2Me$	1.96	1.24	1.26	114	[136]
trans-$(Ph_3P)_2Pt(CO_2Et)_2$	2.059 (7)	1.228 (7)	1.351 (7)	119.5 (6)	[137]
$[(dmpe)_2Ir(Cl)CO_2Me][FSO_3]$	2.073 (8)	1.151 (10)	1.366 (10)	123.0 (8)	[110]
(bipy)$Ir(I_2)(CO)CO_2Me$	2.05 (2)	1.18 (2)	1.28 (2)	120.6	[138]
$[NMe_2(CH_2Ph)_2][Ir_4(CO)_{11}CO_2Me]$	2.20 (4)	1.13 (6)	1.27 (6)	—	[112]
$HOs_3C(CO)_{14}CO_2Et$	2.028 (15)	1.28 (2)	1.34 (3)	—	[94]
$IOs_3C(CO)_{14}CO_2Me$	2.02 (4)	1.28 (5)	1.29 (5)	—	[94]
$[Rh_6(CO)_{15}CO_2Me]^-$	1.96 (2)	1.18 (3)	1.31 (3)	109.2	[139]

3. Reactions

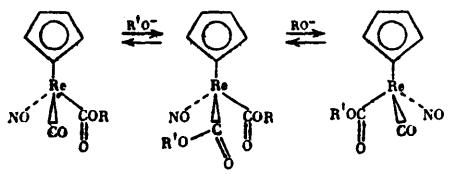
(a) Transesterification. One of the widely investigated reactions of metal-carboxylic acid esters is transesterification:

$$[M]CO_2R + R'OH \rightleftarrows [M]CO_2R' + ROH .$$

It has been shown for an iron-carboxylic acid ester that the ease of this reaction is due to the existence in solution of the equilibrium:[42]

$$Cp(Ph_3P)Fe(CO)CO_2Me \rightleftarrows Cp(Ph_3P)Fe(CO)_2^+ + OMe^- .$$

The existence of such equilibrium has been confirmed by IR and ^1H NMR spectroscopic methods. The compound $CpFe(CO)(Ph_3P).CO_2Me$ [ν(OCO) = 1630 cm^{-1}] has been obtained in an optically inactive form by the transesterification of the (-)$CpFe(CO)(Ph_3P).CO_2C_{10}H_{19}$ [ν(OCO) = 1615 cm^{-1}] diastereoisomers with methyl alcohol.[140] The following mechanism has been proposed for the transesterification of rhenium-carboxylic acid esters:[132]



The interaction of the allyl alcohols $H_2C=C(R)CH_2OH$ with the methyl ester of an iridium-carboxylic acid leads to the formation of cyclic esters of the type $(Ph_3P)_2COIrCO_2CH_2C(R)=CH_2$ as a result of transesterification (Table 1).

Metal-carboxylic acid esters are formed readily also when carbamoyl complexes of transition metals are treated with alcohols, which can also be regarded as a method of their synthesis. On the other hand, when metal-carboxylic acid esters are treated with amines, the reverse reaction is observed, i.e. metal-carboxylic acid esters are formed.[141,142]

(b) Reactions with alkyl halides. When metal-carboxylic acid esters interact with alkyl halides, the corresponding new esters are formed:[82]

$$[M]CO_2R + R'X \rightarrow R'CO_2R + [M]X .$$

(c) Interaction with acids. In acid hydrolysis of the esters, one observes as a rule the decomposition of the metal-carboxylic ester to the corresponding alcohol and carbon monoxide. As mentioned above, an iridium-carboxylic acid may be obtained by treating the iridium-carboxylic acid $(Me_2PhP)_2Ir(CO)Cl_2(CO_2Me)$ with hydrogen chloride.[36]

The reactions of cationic complexes with the various reagents, leading to the formation of metal-carboxylic acid esters, have been briefly characterised.[117]

(d) Hydrolysis. When metal-carboxylic acid esters interact with water, carbon dioxide is evolved and a hydride complex is formed. This reaction probably proceeds via the intermediate formation of a metal-carboxylic acid:[143]

$$(Ph_3P)_2Pt(Cl)CO_2R + H_2O \rightarrow [(Ph_3P)_2Pt(Cl)CO_2H] \rightarrow (Ph_3P)_2Pt(H)Cl + CO_2 .$$

(e) Thermal decomposition. Carbon dioxide is evolved in the thermolysis of the methyl ester of an iridium-carboxylic acid and an iridium hydride complex is formed:[36]

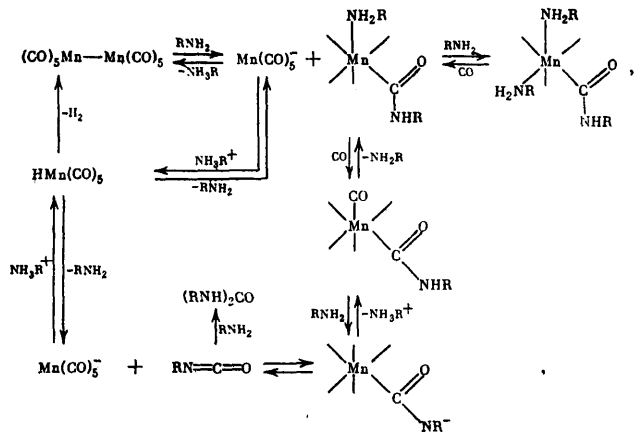
$$(Me_2PhP)_2Ir(CO)Cl_2(CO_2Me) \rightarrow (Me_2PhP)_2Ir(CO)(H)Cl_2 + CO_2 .$$

(f) Other reactions. Among other reactions, the interaction of cationic complexes containing the CO_2R group various reagents, leading to the substitution or modification of the ligand, is of some interest:[117]

$$[(Ph_3P)_2Pt(CO)CO_2R]BF_4 \xrightarrow{Ph_3P} [(Ph_3P)_3PtCO_2R]\cdot BF_4 ,$$
$$[(Ph_3P)_2Pt(CO)CO_2R]BF_4 \xrightarrow{N_3^-} (Ph_3P)_2Pt(NCO)CO_2R .$$

V. AMIDES OF METAL-CARBOXYLIC ACID (CARBAMOYL COMPLEXES OF TRANSITION METALS)

As already mentioned above, the formation of MCA amides as intermediates is observed in the reactions involving the carbonylation of amines by carbon monoxide in the presence of catalysts. According to Dombek and Angelici,[144] the mechanism of this reaction can be represented schematically in the following manner:



The study of the carbonylation of amines in the presence of iron[145,146] and manganese[144] carbonyls led to the conclusion that the corresponding carbamoyl derivatives are formed in the course of the process, for example, *cis*-$Mn(CO)_4(NH_2R)CONHR$ on carbonylation of n-butylamine.[144] A series of amides of a nickel-carboxylic acid (carbamoyl derivatives) having the general formula $(PNP)Ni(Cl).CONHR$, where PNP is the ligand and R = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, n-Bu, etc., have been obtained in a study of the carbonylation of amines with carbon monoxide in the presence of nickel chloride and 2,6-bis(diphenylphosphinomethyl)pyridine (PNP) as the ligand.[147]

The alkoxycarbonylation reactions of the amines probably proceed via the intermediate formation of carbamoyl complexes.[148,149]

1. Methods of Synthesis of Metal-carboxylic Acid Amides

The general methods of synthesis of MCA amides (carbamoyl complexes of transition metals) have been described.[8,142] Among the methods of preparation of carbamoyl derivatives, the following may be noted:

(1) Exchange reactions of the type

$$(CO)_nMnNa + ClCONR_2 \rightarrow (CO)_nMnCONR_2 + NaCl .$$

(2) Oxidative addition reactions:

$$(Ph_3P)_3Pd + ClCONR_2 \rightarrow (Ph_3P)_2Pd(Cl)CONR_2 + Ph_3P .$$

(3) Syntheses via mercury-carboxylic acid amides[80] of the oxidative addition type.

(4) Interaction of metal carbonyls or their derivatives with primary and secondary amines:

$$Mn(CO)_5 + RNH_2 \rightarrow Mn(CO)_4(CONHR)(RNH_2) \text{ etc.}$$

In terms of their reactivity, metal carbonyls can be divided into three groups.[8] It was found that the reactivity can be related to the M–CO bond force constant, which can be obtained from spectroscopic data. Such correlation permits the prediction of the course of these reactions via one pathway or another: the formation of stable carbamoyl complexes, the establishment of equilibrium, and, finally, the absence of any interaction.

(5) Interaction of cationic complexes of transition metals with NaNRR′, isocyanates or quaternary ammonium salts.[142]

(6) Aminolysis of metal-carboxylic acid esters. The rate of this reaction diminishes with increase in the size of the group at the nitrogen atom:[142] $MeNH_2 \gg EtNH_2 \gg Me_2NH > Me(CH_2)_3NH_2 > Me_2CHNH_2 \geqslant Me_3CNH_2$.

(7) Insertion of alkyl isocyanates in a metal–hydrogen bond, for example:

$$CpFe(CO)_2H + MeNCO \rightarrow CpFe(CO)_2CONHMe \ .$$

(8) Interaction of isonitrile complexes of transition metals with alkalies:[150]

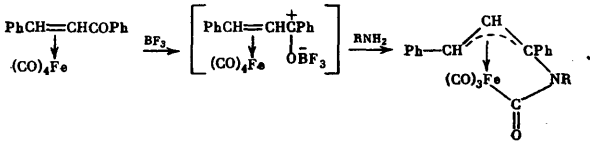
$$(Ph_3P)_3Pt(CNMe)_2^{2+} + OH^- \rightarrow (Ph_3P)_2Pt(CNMe)CONHMe^+ \ .$$

(9) Insertion of carbon monoxide in the $M-NR_2$ bond. This reaction proceeds under mild conditions in the case of coordination compounds of the actinides:[151]

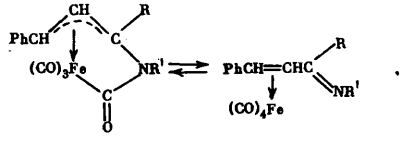
$$M(\eta\text{-}C_5Me_5)_2NR_2(Cl) + CO \rightarrow M(\eta\text{-}C_5Me_5)_2(\eta^2\text{-}CONR_2)Cl \ .$$

The reaction is extremely important as one of the stages in the carbonylation of amines by carbon monoxide in the presence of catalysts.

Stable carbamoyl complexes of iron are formed from the adduct of (*C*-chalcone)$Fe(CO)_4$ with boron trifluoride, its formation being followed by treatment with primary amines:[152–154]



The carbamoyl derivatives with the R = Me and C_6H_{11} groups obtained in this way consist of yellow crystals which are extremely stable in air and have distinct melting points. The equilibrium



has been investigated by IR spectroscopy.[154] It was shown that, when the group R is large, the equilibrium is displaced to the left, while in the case where the group R′ at the nitrogen atom is large the equilibrium is displaced to the right.

Anionic complexes constitute a special type of compound incorporating the carbamoyl group. Thus the interaction of tetrakis(dimethylamino)methane with iron or nickel carbonyl [155] results in the formation of stable carbamoyl complexes:

$$M(CO)_n + C(NMe_2)_4 \rightarrow [C(NMe_2)_3][(CO)_{n-1}MCONMe_2] \xrightarrow{R_2NH} [C(NMe_2)_3][(CO)_{n-1}MCONR_2]$$

M=Fe, Ni

When an anionic iron complex containing the carbamoyl group is treated with a nickel salt, a complex is formed in which the carbamoyl group plays the role of the bridging ligand (η^2-coordination):[156]

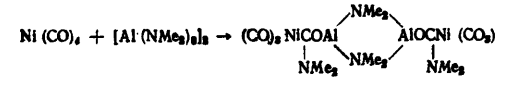
$$[C(NMe_2)_4][(CO)_4FeCONR_2] + NiBr_2 \rightarrow [(CO)_4FeCONR_2]_2Ni \ .$$

R=Me_2, $(CH_2)_4$, $(CH_2)_5$

The interaction of nickel carbonyl with lithium dimethylamide leads to the formation of a carbamoyl complex of nickel:[157]

$$Ni(CO)_4 + LiNMe_2 \rightarrow Li[(CO)_3NiCONMe_2] \ .$$

An analogous reaction takes place also between nickel carbonyl and $[Al(NMe_2)_3]_2$ [158] or $Ti(NMe_2)_4$:[159]



The results obtained in the syntheses of stable metal-carboxylic acid amides are summarised in Table 3.

Table 3. Stable metal-carboxylic acid amides.

Compound	Colour	M.p., °C	ν(CO), cm^{-1}	Refs.
$ClHgCONEt_2$	white	66–68	1575	[80]
$Hg(CONMe_2)_2$	»	148–149	1555	[33]
$Hg(CONEt_2)_2$	»	138–139	1575	[33]
$Hg(CONMeCH_2Ph)_2$	»	138	1560	[33]
$Hg(CON(CH_2)_4]_2$	»	96	1530	[33]
$Hg[CON(CH_2)_5]_2$	»	102	1555	[33]
$Hg[CON(CH_2)_4O]_2$	»	196	1560	[33]
$CpMo(CO)_3CONMe_2$	—	—	1594	[160]
$CpMo(CO)_3CONHMe$	—	—	1614	[160]
$CpMo(CO)_3CON(CH_2)_5$	orange-yellow	70	1590	[160]
$CpW(CO)_3CONHMe$	yellow	122–124	1597	[160]
$CpW(CO)_3CONHCMe_3$	orange	—	1627	[160]
$CpW(CO)_3CONMe_2$	yellow	117–119	1576	[160]
$CpW(CO)_3CON(CH_2)_5$	orange-yellow	110	1571	[160]
η^5-$CpW(CO)_3(MeNH_2)CONHMe$	orange	100–115	1600	[161]
η^5-$CpW(CO)_3(Ph_3P)CONHMe$	yellow	186	1550	[161]
η^5-$CpW(CO)_3(MeCN)CONHMe$	brown	164	1575	[161]
$Mn(CO)_4(NH_3)CONH_2$	—	—	1518, 1501	[162]
$Mn(CO)_3(Ph_3P)(NH_3)CONH_2$	pale-yellow	140	1520, 1508	[162]
$Mn(CO)_4(MeNH_2)CONHMe$	—	75	1605	[163]
$Mn(CO)_4(EtNH_2)CONHEt$	—	105	—	[163]
$Mn(CO)_4CON(p\text{-}MeOC_6H_4)CHN(p\text{-}MeOC_6H_4)$	—	111–112	1693	[164]
$Mn(CO)_4CON(p\text{-}Me_6H_4)CHN(p\text{-}MeC_6H_4)$	—	119–120	1697	[164]
$Mn(CO)_4CONPh(CHNPh)$	—	118–119	1699	[164]
$Mn(CO)_4CON(p\text{-}ClC_6H_4)CHN(p\text{-}ClC_6H_4)$	—	122–125	1703	[164]
$Mn(CO)_4CON(p\text{-}FC_6H_4)CHN(p\text{-}FC_6H_4)$	—	115–116	1704	[164]
$Mn(CO)_4(Ph_3P)CONH_2$	pale-yellow	—	1605, 1580, 1553	[165]
$Mn(CO)_3(Ph_3P)_2CONH_2$	»	—	—	[165]
$Mn(CO)_3(Et_3P)_2CONH_2$	»	—	1600, 1572	[165]
$Mn(CO)_3(bipy)CONH_2$	orange-red	—	1598, 1543	[165]
$Mn(CO)_3(phen)CONH_2$	»	—	1602, 1580, 1550	[165]
$Mn(CO)_3(Ph_3P)_2CONHMe$	yellow	—	—	[166]
η^5-$CpMn(CO)(NO)CONH_2$*	—	—	—	[167]
$Me_4C_4Mn(CO)_3CONH_2$	yellow	—	1546	[168]
$Me_4C_4Mn(CO)_3CONC_6H_{11}$	»	—	1589	[168]
$Re(CO)_4(MeNH_2)CONHMe$	colourless	—	1610, 1511, 1486	[169]
$Re(CO)_4(NH_3)(CONH_2)$	»	—	1640, 1618, 1497	[169]
cis-$Re(CO)_4(Me_2CHNH_2)CONHCHMe_2$	—	—	—	[170]
$Re(CO_4)CON(p\text{-}MeOC_6H_4)CHN(p\text{-}MeOC_6H_4)$	—	115–117	1696	[164]

Table 3 (continued).

Compound	Colour	M.p., °C	ν(CO), cm^{-1}	Refs.
$Re(CO)_4CON(p\text{-}MeC_6H_4)CHN(p\text{-}MeC_6H_4)$	—	119—121	1703	[164]
$Re(CO)_4CONPh(CHNPh)$	—	114—116	1708	[164]
$Re(CO)_4CON(p\text{-}ClC_6H_4)CHN(p\text{-}ClC_6H_4)$	—	180—182	1711	[164]
$Re(CO)_4CON(p\text{-}FC_6H_4)CHN(p\text{-}FC_6H_4)$	—	125—127	1709	[164]
$CpFe(CO)_2CONH_2$	—	—	1593	[92]
$CpFe(CO)_2CONHC_6H_{11}$	yellow	116—117	1635	[171]
$CpFe(CO)_2CONHMe$	—	118	1625	[91]
$CpFe(CO)_2CONHEt$	—	97	1622	[91]
$CpFe(CO)_2CONHCHMe_2$	—	78—80	1620	[91]
$CpFe(CO)_2CON(CH_2)_5$	—	70	1560	[91]
$CpFe(CO)(Ph_2P)CONHMe$	—	114	1558	[91]
$CpFe(CO)_2CONMe_2$	—	111—112	1545, 1530	[172]
$CpFe(CO)_2CONEt_2$	—	75—76,5	1534	[172]
$CpFe(CO)_2CONHCMe_3$	yellow	95—97	1633	[173]
$CpFe(CO)(CNCMe_3)CONHCMe_3$	pale-yellow	—	1609	[173]
$Fe(CO)_2(Ph_3P)_2(Br)CONH_2$	—	—	1565, 1558, 1532	[174]
$Ru(CO)_2(Ph_3P)_2(Cl)CONH_2$	—	—	1575, 1568, 1545	[174]
$CpRu(CO)(Et_3P)CONH_2$	—	—	—	[175]
$CpRu(CO)(Ph_3P)CONH_2$	—	—	—	[175]
$CpRu(CO)(CNMe)CONH_2$	—	—	—	[175]
$CpRu(CO)_2CONH_2$	—	—	—	[175]
$CpRu(CO)_2CONHMe$	—	—	1631	[92]
$CpRu(CO)_2CONHC_6H_{11}$	—	—	1621	[92]
$CpRu(CO)_2CONHBu\text{-}n$	—	—	1626	[92]
$CpRu(CO)_2CONHCHMe_2$	—	—	1628	[92]
$Os(CO)_3(Ph_3P)_2(Cl)CONH_2$	—	—	1575, 1530	[174]
$Os(CO)_3[P(C_6H_{11})_3]_2(Cl)CONH_2$	—	—	1567, 1529	[174]
$Co(CO)_3(Ph_3P)CON(CH_2)_5$	yellow	—	1591	[176]
$Co(CO)_3(Ph_3P)CON(Pr\text{-}n)_2$	»	—	1598	[176]
$Rh_6(CO)_{16}CONH(CHMe_2)$	—	—	1630	[104]
$(Ph_3P)_2Pd(Cl)CONHMe$	white	—	1628	[177]
$(Ph_3P)_2Pd(Cl)CONMe_2$	»	—	1598	[177]
$(Ph_3P)_2Pd(Cl)CONMeEt$	»	—		[177]
$(MePh_2P)_2Pd(Cl)CONMe_2$	yellow-orange	—		[177]
$(Ph_3P)_2Pd(Cl)CONEt_2$	white	164	1590	[80]
$(Ph_3P)_2Pt(Cl)CONMe_2$	»	—	1586	[177]
$(Ph_3P)_2Pt(I)CONMe_2$	pale-orange	—	1570	[177]
$(Ph_3As)_2Pt(Cl)CONMe_2$	white	—	1585	[177]
$(MePh_2P)_2Pt(Cl)CONMe_2$	»	—	1565	[177]
$(Me_2PhP)_2Pt(Cl)CONMe_2$	»	—		[177]
$(Ph_3P)_2Pt(Cl)CONMeEt$	»	—		[177]
$(Ph_3P)_2Pt(Cl)CONHMe$	»	—	1600	[177]
$(Ph_3P)_2Pt(Cl)CONHEt$	»	—	1601	[177]
$(Ph_3P)_2Pt(Cl)CONEt_2$	»	237	1580	[80, 177]
$(Ph_3As)_2Pt(Cl)CONEt_2$	»			[177]
$(Ph_3As)_2Pt(Cl)CONHCHMe_2$	»	—	1616	[177]
$(Ph_3P)_2Pt(NCO)CONMe_2$	—	—	1580	[177]
$(Ph_3P)_2Pt(CONEt_2)_2$	—	134	—	[80]
$(Ph_3P)_2Pt(CONEt_2)HgCONEt_2$	—	70	1690, 1650	[80]
$[NH_2(CHMe_2)_2]$ [cis-$Pt(CO)Cl_2CON(CHMe_2)_2$]	—	—	—	[178]
$[(Ph_3P)_2Pt(NCMe)CONHMe][BF_4]$	pale-yellow	183—185	—	[179]
$(\eta\text{-}C_5Me_5)Th(\eta^2\text{-}CONMe_2)Cl$	—	—	1548	[151]
$(\eta\text{-}C_5Me_5)Th(\eta^2\text{-}CONEt_2)Cl$	—	—	1516	[151]
$(\eta\text{-}C_5Me_5)Th(\eta^2\text{-}CONMe_2)NMe_2$	—	—	1521	[151]
$(\eta\text{-}C_5Me_5)Th(\eta^2\text{-}CONMe_2)_2$	—	—	1523	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONMe_2)Cl$	—	—	1559	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONEt_2)Cl$	—	—	1537	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONMe_2)NMe_2$	—	—	1521	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONMe_2)_2$	—	—	1529	[151]
$(\eta\text{-}C_5Me_5)U(\eta^2\text{-}CONEt_2)_2$	—	—	1499	[151]

*Characterised by X-ray diffraction analysis.

2. Investigation of Metal-Carboxylic Acid Amides by Physicochemical Methods

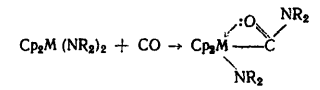
One of the principal physicochemical methods used to study MCA amides is IR spectroscopy. With the aid of this method, it is possible to identify in most cases the CO and NH groups, although in many instances the identification of the vibration frequencies of the carbonyl group may be difficult owing to the superposition of the broad band due to the deformation vibrations of the NH group.[8] The bands of the carbonyl group are observed over a fairly wide range and are sensitive to the solvent employed in the measurement.[163]

The ^{1}H NMR methods yields much information for the identification of substituents at the nitrogen atom (see, for example, Refs.147, 165, and 179). This method has been used successfully also in the study of the reactions involving the transformation of the carbamoyl group into the amidine group.[163] The signal of the carbon atom of the carbamoyl group can also be identified by NMR. In the case of cobalt-carboxylic acid amides it is located within a fairly wide range of values of δ (183—213 p.p.m).[180]

The mass-spectrometric method has also been used to identify metal-carboxylic amides (see, for example, Angelici and Blacik[168]).

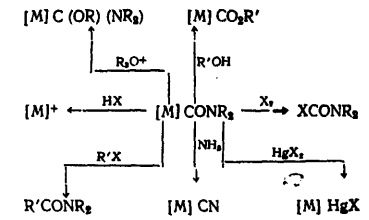
A study in which the structure of the complex $Mn(CO)_4(MeNH_2)$. .CONHMe had been established by X-ray diffraction[8] was for a long time the only structural study available. However, recently X-ray diffraction data have been published on the coordination of the carbamoyl group with other metals. It has been established that the carbamoyl group can function both as a monodentate ligand, for example, in *trans*-$(Et_3P_2)Ni(I)CONEt_2$,[181] and a bidentate ligand. In the latter case, the carbon and oxygen atoms of the carbamoyl group can be linked to a single metal atom, for example, in $(\eta\text{-}C_5Me_5)_2Th$. .$(\eta^2\text{-}CONEt_2)Cl$ [151] or can function as a bridge between two metal atoms as in $HRu_3(CO)_{10}CONMe_2$.[182] It has been noted[151] that on η^2-coordination the C—O bond is lengthened compared with the usual coordination of this group to a metal. The pronounced shortening of the metal—oxygen bond in the uranium complex compared with the uranium—carbon bond was attributed by the authors to the high affinity of uranium for oxygen. Table 4 presents data obtained in X-ray diffraction studies on the carbamoyl complexes.

Clearly the results of X-ray diffraction analysis have posed a number of problems in this field which can be solved with the aid of IR and NMR spectroscopic methods. Indeed, data concerning the mode of coordination of the carbamoyl group can be obtained with the aid of IR spectra. Furthermore, it is apparently possible to estimate by NMR the contribution of a particular structure in the reaction, as shown by Fagan et al.:[151]



3. Reactions of Metal-Carboxylic Acid Amides (Carbamoyl Derivatives)

The chemical reactions of carbamoyl complexes of transition metals have been considered in a review:[8]



The thermal stability of the isostructural iron, ruthenium, and osmium carbamoyls has been investigated.[184] The authors showed that the stability of these compounds increases in the sequence Fe < Ru < Os. A study,[185] in which the interaction of a cationic manganese complex with amines, namely

$$Mn(CO)_4(MeCN)_2^+ + MeNH_2 \rightarrow Mn(CO)_3(CONHMe)(MeCN)_2 ,$$

was investigated, should also be mentioned. It is remarkable that, after a long reaction time, the amidine complex (CO_4). .$\overline{MnC(R'NMeCNHR)}$ is formed; the course of this reaction depends on the nature of the amine.

A comparatively stable carbamoyl complex of nickel, active in the carbonylation reaction, has been obtained recently:[186]

$$(Et_3NH)_2NiI_2 + CO \xrightarrow[THF]{Et_2NH} (Et_2NH)_2Ni(I)CONEt_2$$

It has been suggested that an unstable biscarbamoyl complex of nickel is formed on further treatment of the above compound with CO and Et_2NH.

Other questions associated with the formation and chemical reactions of carbamoyl complexes (metal-carboxylic acid amides) have been examined in reviews[187–189] (see the references therein); in the last study, certain aspects of the formation of alkoxycarbonyl complexes (metal-carboxylic acid esters) are examined in addition.

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As can be seen from the present review, metal-carboxylic acids and their derivatives constitute a fairly broad class of organometallic compounds. The interest in the synthesis of these complexes has increased still further in connection with the advances made in the field of the fixation of carbon dioxide in the presence of transition metal compounds. One of the aims of the present review was to attempt to demonstrate as far as possible the relation between these two trends in modern coordination chemistry.

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Table 4. Some X-ray diffraction data for metal-carboxylic acid amides.

Compound	Bond lengths, Å				OCN angle, deg	Refs.
	C=O	C–N	M–C	M–O		
$Mn(CO)_4(MeNH_2)CONHMe$	1.251	1.345	2.072	—	121.2	[8]
η^5-$CpMn(CO)(NO)CONH_2$	1.222 (6)	1.346 (6)	2.026 (4)	—	119.4 (3)	[167]
η^5-$CpW(CO)_3(MeNH_2)CONHMe$	1.25 (3)	1.41 (3)	—	—	113 (2)	[161]
$[NH_2(CHMe_2)_2][cis\text{-}PtCl_2(CO)CON(CHMe_2)_2]$	1.36 (3)	1.30 (3)	1.96 (2)	—	118 (4)	[178]
trans-$(Et_3P)_2Ni(I)CONEt_2$	1.237 (4)	1.359 (7)	1.882 (7)	—	120.7 (4)	[181]
$(Et_2NH)Ni_2I_2(\mu\text{-}CONEt_2)_4$	1.260 (6)	1.343 (8)	1.887 (5)	2.045 (4)	118.7 (5)	[181]
$HRu_3(CO)_{10}(\mu\text{-}CONMe_2)$	1.287 (4)	1.340	2.098 (8)	2.100 (5)	115.2 (7)	[182]
$Fe_2(CO)_6(\mu\text{-}AsMe_2)(\mu\text{-}CONMe_2)$	1.26 (2)	1.35 (2)	2.00 (1)	2.00 (1)	115.9 (11)	[183]
$[Fe(CO)_4(\mu\text{-}CONMe_2)]_2Ni$	1.285 (3)	1.334 (3)	2.001 (2)	1.855 (1)	115.8 (2)	[156]
$Fe(CO)_2CON(C_6H_{11})CPh{\cdots}CH{\cdots}CHPh$	1.22 (1)	1.39 (1)	1.978 (7)	—	124.5 (6)	[152]
$Mo(NO)(NCS)_4(\eta\text{-}CONMe_2)$	1.322 (7)	1.240 (10)	2.029	2.078	123.96	[184]
$Th(\eta\text{-}C_5Me_5)_2(Cl)(\eta^2\text{-}CONEt_2)$	1.44 (3)	1.34 (2)	2.418 (20)	2.460 (16)	108.9	[151]
$U(\eta\text{-}C_5Me_5)_2(\eta^2\text{-}CONEt_2)_2$	1.273	1.321	2.405 (8)	2.370 (5)	120.2	[151]

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