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Theoretical studies of transition metal complexes with nitriles and isocyanides

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Contents

I.	Introduction	265
II.	Electronic structures of complexes and the nature of coordination bonds	265
III.	Spectroscopic properties of coordinated ligands	274
IV.	Reactivities and mechanisms of reactions with coordinated ligands	276
V.	Conclusion	281

Abstract. Theoretical studies of transition metal complexes with nitriles and isocyanides are reviewed. The electronic structures and the nature of coordination bonds in these complexes are discussed. The correlation between the electronic structures of transition metal complexes with nitriles and isocyanides and their structural properties, spectroscopic characteristics, and reactivities are considered. The bibliography includes 121 references.

I. Introduction

It is known that free nitriles (N≡CR) and isocyanides (C≡NR) containing no strong acceptor substituents R are poorly reactive or even inert in a number of processes, for example, in nucleophilic addition. If these molecules are involved as ligands in transition metal complexes, the situation reverses because complex formation leads to activation of nitrile and isocyanide ligands. Reactions, which proceed under drastic conditions, if at all, with free nitriles and isocyanides, every so often occur under relatively mild conditions with coordinated ligands. In some reactions with coordinated ligands, the rate is increased by a factor of 10^{18} as compared to that in the reaction with the correspodning free ligand.[1–4] Nitriles and isocyanides thus activated can be used in the synthesis of new compounds with the C–O, C–N, C–C, C–S and C–P bonds, which cannot be prepared without resorting to transition metals. Cycloaddition of the corresponding reagents to the inner-sphere nitrile and isocyanide ligands affords tetrazoles and oxadiazolines, respectively, which are widely used in pharmacology.

The design of new antitumour drugs is yet another field of application of nitrile complexes. Thus the imino-ether compounds *trans*-$[PtCl_2\{NH=C(OMe)Me\}_2]$ prepared by the nucleophilic addition of methanol to the $[PtCl_2(NCMe)_2]$ complex exhibited high antitumour activity.[5,6] This result was unexpected because *cis* isomers of platinum complexes with N-donor ligands generally show higher antitumour activity as compared to the corresponding *trans* isomers.

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Coordinated nitriles also find application in catalysis. For example, large-scale production of acrylamide and nicotinamide is based on catalytic (including, catalysis by metal ions[4,7–9]) hydrolysis of nitriles. Metal-promoted hydrolysis of nitriles and isocyanides can be used for detoxication of industrial wastes containing these compounds. Finally, some nitrile complexes of transition metals possess nonlinear-optical properties.[10,11]

Interesting properties of transition metal complexes with nitriles and isocyanides and their wide industrial applications have given impetus to a substantial increase in the number of publications devoted to these compounds. The results of experimental studies of their reactivities have been surveyed in reviews.[1,4,12–17] However, the data from theoretical investigations of nitrile and isocyanide coordination compounds were not systematised. At the same time, transition metal complexes with other ligands have been extensively studied by quantum-chemical methods † in the last decade. These investigations were motivated primarily by the necessity of interpreting and systematising the ever-growing body of experimental information. Besides, theoretical methods are sometimes the only tool in studying unstable compounds and intermediates formed in the course of many chemical reactions.

In this review, the results of theoretical investigations of transition metal complexes with nitriles and isoelectronic isocyanides are generalised. The electronic structures and the nature of coordination bonds in these compounds are discussed. The correlations between the electronic structures of these complexes and their structural characteristics, spectroscopic properties, and reactivities are considered. Studies concerned with analysis of interactions between ligands and some transition metals are partially included for comparison.

II. Electronic structures of complexes and the nature of coordination bonds

Two models, *viz*., the ligand field theory and the Dewar – Chatt – Duncanson (DCD) model, are most commonly used for the qualitative description of the nature of coordination bonds in transition metal complexes. The latter model is applied to complexes containing ligands with multiple bonds. These theories are based on the molecular orbital method and treat the formation of coordination bonds as a result of interactions between the valence

† The results of theoretical studies of transition metal complexes (primarily, carbonyl, carbene, carbyne and π-complexes) are surveyed in reviews.[18–24]

orbitals of the ligand and the metal atom. Of particular interest is the elucidation of the character of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals because they are primarily responsible for the chemical reactions and determine the spectroscopic and other physical properties of compounds.

Systematic studies of nitrile and isocyanide complexes by quantum-chemical methods were started only recently and most of the publications date back to 1990s.‡ The DCD model [25,26] is commonly used for the description of these complexes. According to this model, the metal–ligand coordination bond involves the σ-component, which originates from the transfer (donation) of the electron density from the occupied σ-orbitals of the ligand to the unoccupied *d*-orbitals of the metal atom, and the π-component resulting from π-back donation. By π-back donation is meant the electron density transfer from the highest occupied *d*-orbitals of the metal atom to the free valence antibonding π*-orbitals of the ligand resulting in two-electron stabilisation of the frontier MOs of the complex. In addition, the π-component of the coordination bond often includes the contributions of the highest occupied π-orbitals of the ligand whose interactions with the occupied *d*-orbitals of the metal atom lead to destabilisation of the HOMOs (Fig. 1).

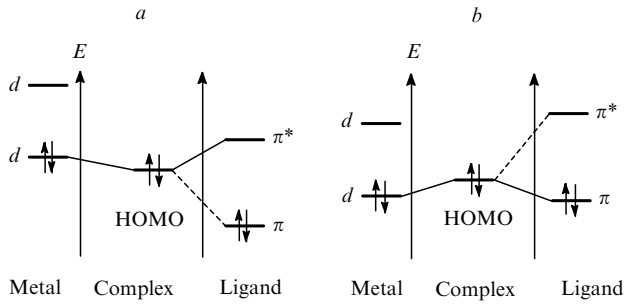


Figure 1. Scheme of formation of the HOMO of complexes containing ligands with multiple bonds .
(*a*) Ligands possessing strong π-acceptor properties, (*b*) ligands possessing weak π-acceptor properties.

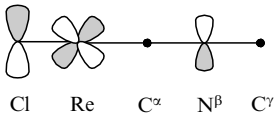
Apparently, the contributions of the π- and π*-MOs of the ligand to the HOMO of the complex are determined by the relative energies of the valence orbitals of the metal atom and the ligand. The *d*(M)–π*-MO(ligand) interaction prevails in the HOMOs of the complexes with ligands possessing strong π-acceptor properties [for example, the carbon(II) oxide or carbyne ligands] because the valence occupied *d*-orbitals of the metal atom are closer in energy to the π*-MOs than to the π-MOs of the ligand (Fig. 1 *a*), whereas the *d*(M)–π-MO(ligand) interaction dominates the HOMOs of the complexes with ligands exhibiting weak π-acceptor properties, such as nitriles, because the energies of the highest occupied *d*-orbitals of the metal atoms are similar to those of the occupied π-MOs of the ligand (Fig. 1 *b*).

Until very recently, the extended Hückel theory (EHMO) was most commonly used in calculations of MOs of nitrile and isocyanide complexes. However, higher-level approximations, *viz*., the Hartree–Fock method (HF), the functional density theory (DFT), the second-order Møller–Plesset theory (MP2), *etc*., have found application in the last few years. The next section covers the results of studies devoted to the electronic structures and the nature of coordination bonds in transition metal complexes with isocyanides and nitriles.

‡ It should be noted that theoretical studies devoted to isocyanide complexes and, particularly, to nitrile complexes are much smaller in number than those dealing with carbonyl compounds or π-complexes.

1. Electronic structures of isocyanide and nitrile complexes

The nature of coordination bonds and reactivities of the molybdenum diisocyanide complex *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) and the rhenium isocyanide complexes *trans*-[Re(CNR)Cl(dppe)$_2$] (R = H, Alk, Ar) were studied.[27,28] It was found that two of the highest occupied MOs of the molybdenum complex and the HOMOs of the rhenium complexes are formed *via* interactions of the *d*-orbitals of the metal atom with the π- and π*-MOs of isocyanide. The HOMO of the molybdenum complex (Fig. 2) is bonding for the Mo–C bond and antibonding for the C≡N bond due to the predominant contribution of the π*-MO of the ligand to the HOMO responsible for the π-back donation effect. However, the π-component of the metal–ligand bond is rather weak because of the small coefficients with which the AOs of the α-carbon atom are included into the HOMO of the complex under consideration. The contributions of the π- and π*-MOs of isocyanide to the HOMOs of the rhenium complexes are approximately equal (the HOMO is a nonbonding orbital with respect to the Re–C bond).



The electronic structures of the [Pd$_2$(CNR)$_2$(μ-η^3-L)$_2$] (L is indenyl) and [Pd$_4$(μ-CNR)$_4$(μ-OAc)$_4$] complexes, the model compounds $[Pd_2(\mu\text{-}CNH)_2(OH)_4]_2^{4-}$ and $[Pd_2(\mu\text{-}CNH)_2(OH)_4]^{2-}$ and the [Ni$_2$(CNH)(PH$_2$CH$_2$PH$_2$)$_2$] complex were examined at the EHMO level of theory.[29,30] The highest occupied MOs of the last two mentioned complexes consist of the π_d^*-orbitals of the $\{Pd_2(OH)_4\}^{2-}$ or {Ni$_2$(PH$_2$CH$_2$PH$_2$)$_2$} fragment and the π*-MO of isocyanide. It was noted that the interaction between these orbitals in the former complex is rather weak. The lowest unoccupied MO of the nickel complex is a purely π*(CNH)-orbital. For the indenyl complexes, the energy gap between the HOMO and LUMO was demonstrated to be rather large. As a consequence, these complexes exist in the singlet state, which accounts for the formation of the Pd–Pd bond.

The MOs of the model binuclear complex [Pd$_2$(CNMe)$_4$Cl$_2$] were calculated by the extended Hückel method [31] with the aim of obtaining qualitative information on the nature of the frontier MOs and examining the dependence of the compositions of the MOs on the internuclear Pd–Pd distance and the torsion angle θ between the planes of two {Pd(CNMe)$_2$Cl} fragments. The orbitals of the metal atom make the major contribution to the HOMO and LUMO, the orbitals of the Cα atom of isocyanide also making a particular contribution (the antibonding character of the Pd–C bond), whereas the AOs of the Nβ and Cγ atoms of the isocyanide ligand contribute insignificantly to these orbitals. The composition of the MOs is virtually insensitive to variations in the torsion angle θ and the internuclear Pd–Pd distance.

The electronic structures and the nature of the coordination bonds in the isocyanide complexes M(CNBu^t)Me(CO)$_2$.(η^5-C$_5$R$_5$)] and the isomeric compounds [M(η^2-CMe=NR′).(CO)$_2$(η^5-C$_5$R$_5$)] and [M{η^3-CH$_2$=CHNBu^t}(CO)$_2$(η^5-C$_5$R$_5$)] (M = Mo, W; R = H, Me; R′ = Pr^i, Bu^t) were discussed based on the data from photoelectron spectroscopy and the results of EHMO calculations of the molecular orbitals carried out for model compounds.[32] In the isocyanide complexes, the two highest occupied MOs are centred on the metal atom but the π*-MOs of the carbonyl and isocyanide ligands also make particular contributions to these MOs giving rise to π-back donation [the π-MO(CNR) also makes a certain contribution to these MOs of the complexes].

Although the isocyanide ligands in many complexes possess noticeable π-acceptor properties, the contributions of the π- and π*-MOs of the ligand to the HOMOs of the complex are in some cases insignificant and the HOMOs are centred on the metal atom. Thus calculations for the frontier MOs of the model complexes

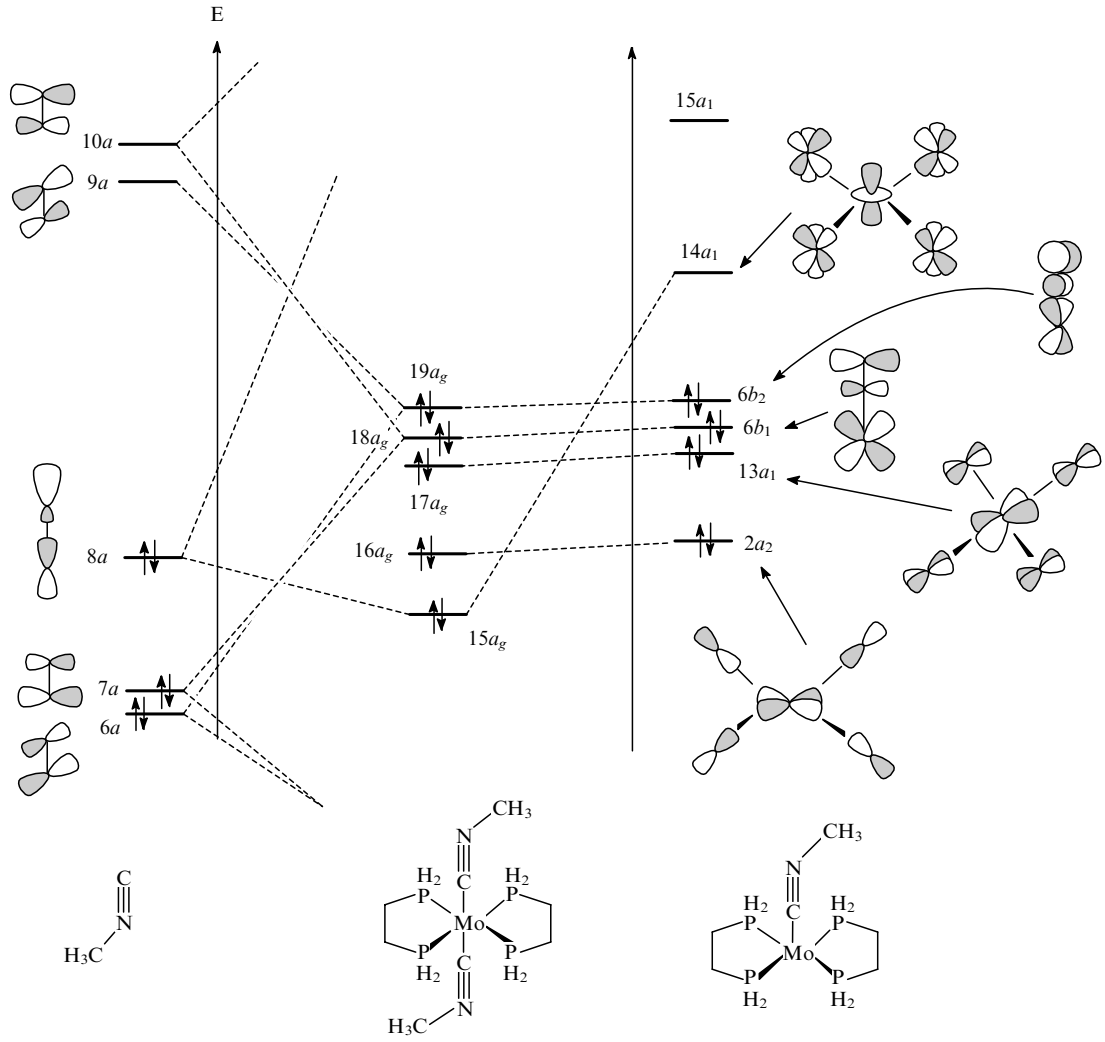


Figure 2. Correlation diagram of the MOs in the *trans*-$[Mo(CNMe)_2(dppe)_2]$ complex.[27]

$[Ag_2(CNMe)_4X_2]$ (X = Cl, Br, I) (**1**),[33] $[PtRh(CNBu^t)_2.(CN)_2(dmpm)_2]^+$ (dmpm = $Me_2PCH_2PMe_2$) (**2**), *trans*-$[Rh(CNBu^t)_2(PPh_3)_2]^+$ (**3**)[34] and $[M(CNH)_4]^+$ (**4**) (M = Cu, Ag)[35] demonstrated that the HOMOs are localised predominantly on the metal atoms. The orbitals of the halogen atoms in the complexes **1** and the *s*-orbitals of the carbon atom of the isocyanide ligand in the complexes **4** also make contributions to the HOMOs of these complexes. The lowest unoccupied MOs of the complexes **1** and **4** are the π*-orbitals of the CNR fragment, whereas the LUMOs of the complexes **2** and **3** consist of the p_z(Rh), π*(CN), p_z, d_{xz}(P) and *p*(Pt) atomic orbitals.

The compositions of the frontier MOs in the tetranuclear linear $[M_4(CNMe)_8(PH_3)_2]^{2+}$ clusters (M = Pd, Pt) were studied by the EHMO method.[36,37] The highest occupied and lowest unoccupied MOs are the σ_d^*-orbitals of the metal atom. The next 18 occupied MOs of the clusters are centred on the metal atom, whereas 4 unoccupied MOs following after the LUMO are the π*-orbitals of CNMe.

The introduction of other ligands exhibiting strong π-acceptor properties into isocyanide complexes often leads to weakening of π-back donation of the electron density from the *d*-orbitals of the metal atom to the π*-orbitals of isocyanide. This weakening is particularly noticeable when a strong π-acceptor is in the *trans* position with respect to the isocyanide ligand, which actually reflects the mutual trans effect of two π-acceptors. In contrast, the introduction of a ligand exhibiting pronounced donor properties (for example, the chloride ligand) in the *trans* position with respect to isocyanide leads to enhancement of the π-acceptor properties of isocyanide and strengthening of π-back donation. Thus several highest occupied MOs in the *trans*- and *cis*-$[(PH_3)_2(CO)_2W.(CNMe)(\equiv CCH=CH_2)]^+$ complexes containing one carbyne ligand and two carbonyl ligands (strong π-acceptors) along with the isocyanide ligand are composed predominantly of the orbitals of the metal atom and the carbonyl and carbyne ligands with a very small contribution of the AOs of the nitrogen atom of isocyanide (Figs 3 and 4).[38]

The nature of the coordination bond in the isocyanide complexes $[Cp_2Ta(CNMe)(\eta^2\text{-}CH_2=CH-CH=CH_2)]^+$ (Cp is the cyclopentadienyl ligand) (**5**), $[Cp_2Ta(CNMe)_2]^+$ (**6**) and $[Cp_2M(CNMe)]^{0/+}$ (M = Ta, Zr) was examined based on the results of DFT calculations[39] with full geometry optimisation of different isomers of these complexes. Analysis of the theoretical and experimental structural data (the linearity of the isocyanide molecule, the equal CN bond lengths in free and coordinated isocyanides) and examination of the energy components of the coordination bond showed that π-back donation is of secondary importance in the interaction between isocyanide and tantalum in the complex **5**, which contains other strong π-acceptors. In this case, the interaction between the metal atom and the ligand is predominantly Coulombic in character. In the complex **6**, which contains no other π-acceptor ligands except for isocyanide, the Ta → CNR π-back donation becomes essential.

Three orbitals, *viz*., the *d*-orbital of the metal atom and the π- and π*-orbitals of isocyanide, contribute to the π-component of the coordination bond between the metal atom and the isocyanide ligand. The interactions between these orbitals give rise to three

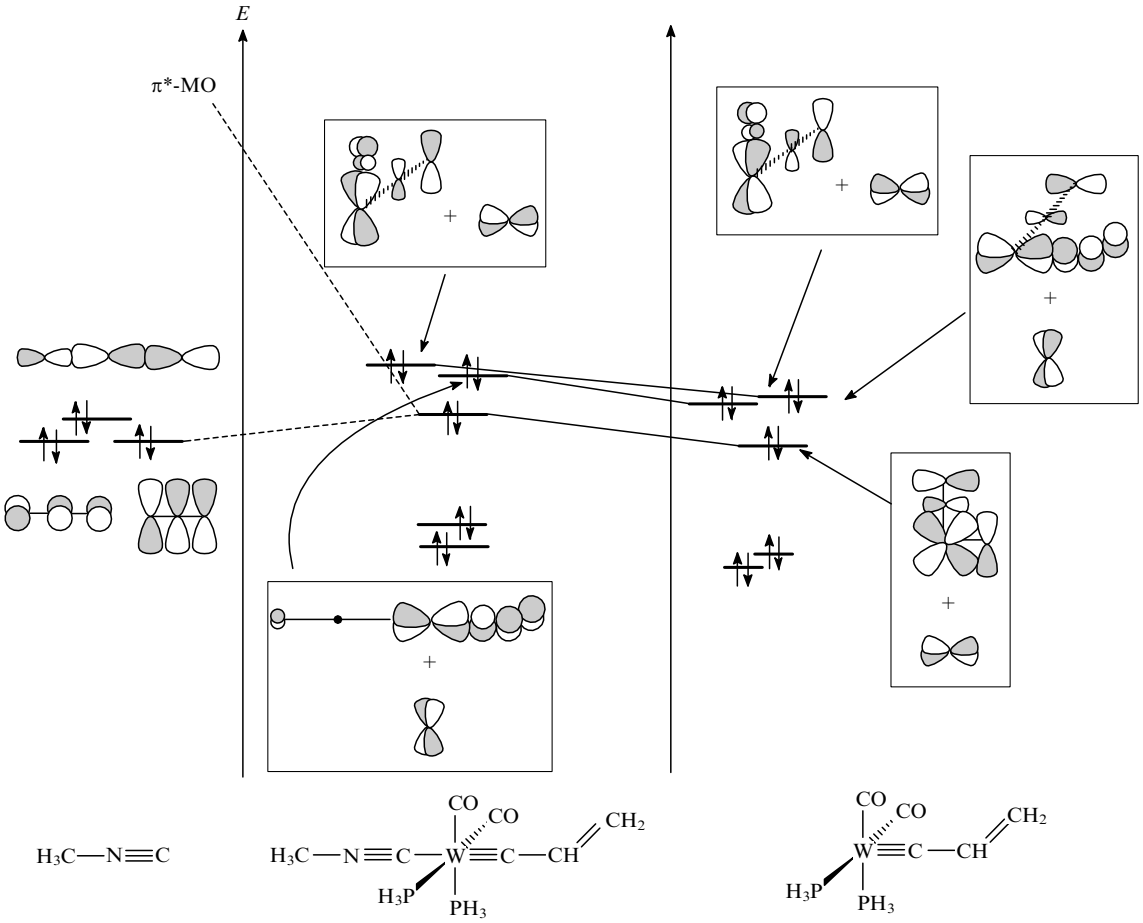


Figure 3. Correlation diagram of the MOs in the *trans*-$[(PH_3)_2(CO)_2W(CNMe)(\equiv CCH=CH_2)]^+$ complex.[38]

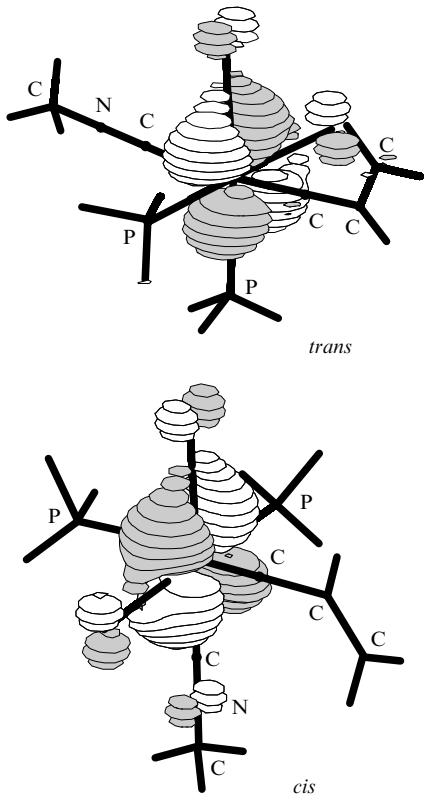


Figure 4. Composition of the HOMOs in the tungsten isocyanide complexes *trans*- and *cis*-$[(PH_3)_2(CO)_2W(CNMe)(\equiv CCH=CH_2)]^+$.[38]

molecular orbitals two of which, *viz*., $\pi_{d-\pi(L)}$ (MO1) and $\pi^*_{d-\pi^*(L)}$ (MO3), are formed primarily from the *d*-orbitals of the metal atom and the π- or π*-orbitals of the ligand. These MOs produce the bonding and antibonding combinations for the metal–ligand bond, respectively (Fig. 5). In some cases, the third orbital (MO2) is the HOMO of the complex derived from a linear combination of the $\pi^*_{d-\pi(L)}$- and $\pi_{d-\pi^*(L)}$-orbitals. The contribution of the unoccupied π*-orbital of the ligand to the MO2 of the isocyanide complexes is often larger than the contributions of the occupied π-MOs of the ligand although the participation of the latter remains essential. As a result, the MO2 orbital either remains nonbonding with respect to the metal–ligand bond or becomes weakly bonding. Actually, as can be seen from Fig. 6, the formation of the MO2 leads to a substantial decrease in the electron density on the C^α and C^γ atoms, whereas the electron

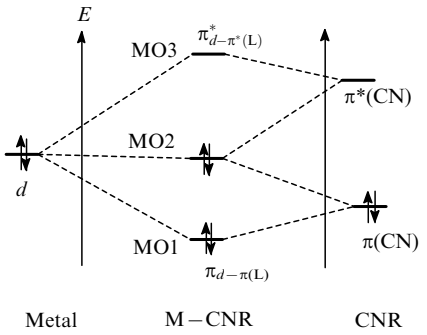


Figure 5. Three-orbital interaction between the frontier MOs of the metal atom and the ligand.

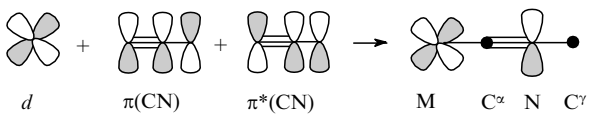


Figure 6. Polarisation effect of the nonbonding HOMO.

density on the nitrogen atom increases resulting in polarisation of the corresponding MO. This polarisation of orbitals in cyanide, carbonyl and nitrogen complexes was described by R Hoffmann[40] as early as 1977. At the same time, the contributions of the π- and π*-MOs of isocyanide to the HOMO are very small in the presence of other (in addition to CNR) ligands possessing strong π-acceptor properties. In the latter case, the properties of such complexes are not always correctly interpreted in terms of the qualitative DCD model.

On the whole, the compositions of frontier MOs determining the π-component of the coordination metal–ligand bond in nitrile complexes is similar to those in isocyanide compounds. The EHMO calculations were carried out for the model nickel nitrile complex $[Cp(PH_3)Ni(N{\equiv}CC_6H_4NH_2)]^+$ (**7**).[10] Figure 7 shows the correlation diagram of the MOs describing interactions between the molecular orbitals of the $[Cp(PH_3)Ni]^+$ fragment and the nitrile ligand upon the formation of the complex **7**. The most important result of this interaction is σ-donation of the electron density from the occupied σ-orbitals of the nitrile ligand (σ_1- and σ_2-MOs), which are bonding with respect to the CN group, to the unoccupied d_{z^2}-orbital of the metal atom. In addition to the above-mentioned two σ-orbitals, the third lower-energy σ-orbital of the nitrile ligand (it is omitted in the figure), which is antibonding with respect to the CN bond, also makes a contribution to this interaction. The authors of the cited study believed that the last-mentioned contribution [which leads to a decrease in occupancy of the σ*(CN)-orbital upon coordination] is mainly responsible for strengthening of the CN bond on going from the free ligand to the complex.

In addition to the σ-component, the coordination bond in the complex **7** also involves the π-component (interactions between the occupied *d*-orbitals of nickel and the π-orbitals of the nitrile ligand). Both π- and π*-MOs contribute to the resulting MOs of the complex. The highest occupied MO derived from a linear combination of three orbitals $a'' + \lambda_1\pi_{\|} + \lambda_2\pi^*_{\|}$ is a nonbonding orbital with respect to the N and C atoms. The contribution of the $\pi_{\|}$-orbital of the ligand to the HOMO only insignificantly overrides the contribution of the $\pi^*_{\|}$-orbital from which it was concluded that the metal–ligand π-interaction has its origin in very weak π-donation of the electron density from the ligand to metal.

In transition metal complexes, nitriles exhibit both weak π-donor and weak π-acceptor properties, which is yet another important characteristic of the electronic structures of this class of

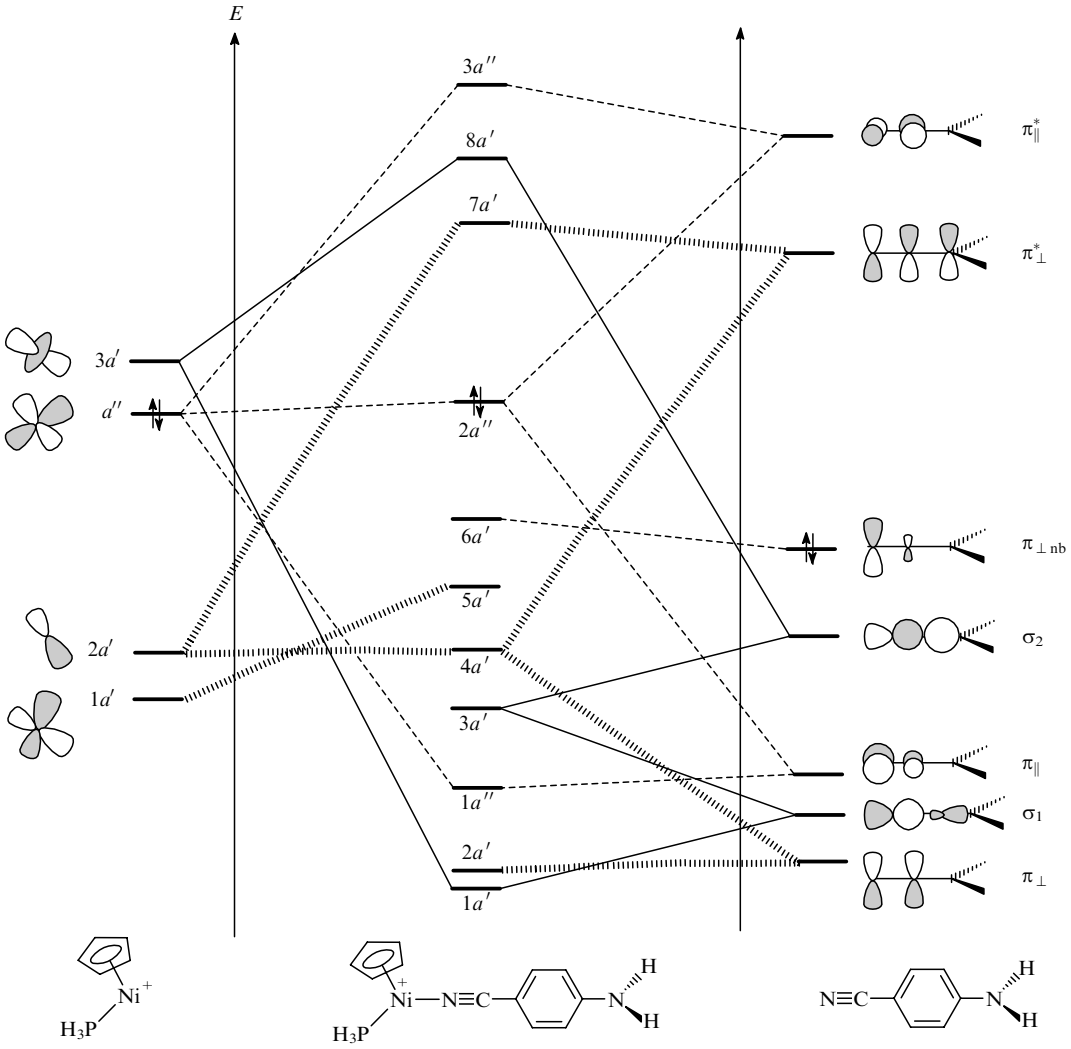
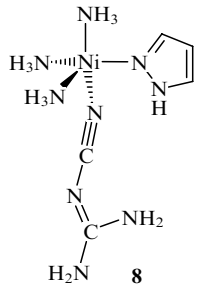
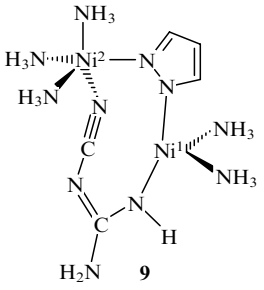


Figure 7. Scheme of the interactions between the MOs of the $[Cp(PH_3)Ni]^+$ and $NCC_6H_4NH_2$ fragments upon the formation of the complex **7**. For the nitrile ligand, only the orbitals belonging to the nitrile group are shown.[10]

coordination compounds. Hence, the total contribution of the π-orbitals of nitrile (both π and π*) to the frontier MOs of the complex is, generally, insignificant and the latter orbitals are often centred on the metal atom. The results of EHMO or HF calculations of the electronic structures of the model nitrile complexes $[CpFe(NCMe)(PH_3)_2]^+$, $[CpFe(N{\equiv}CCH_2C_6H_4O.\{P_3N_3(OH)_5\}\text{-}p)(PH_3)_2]^+$ (see Ref. 41) and $[CpFe(p\text{-}N{\equiv}C.C_6H_4NO_2)(PH_3)_2]^+$ (see Ref. 11) indicate that the HOMOs of all complexes consist predominantly of the *d*-orbitals of the iron atom although the π*-orbitals of the nitrile ligand in the latter compound also make a particular contribution to the MO, which is the closest in energy to the HOMO, thus providing the π-dative interaction. Analogous results were obtained in the DFT calculations of the molecular and electronic structures of the model nickel complexes $[LNi\{N{\equiv}CN{=}C(NH_2)_2\}(NH_3)_3]$ (**8**) and $[(NH_3)_3Ni\{N{\equiv}CN{=}C(NH_2)NHNi(NH_3)_2L\}]$ (**9**) (L is 1,2-diazolidine).[42]



8



9

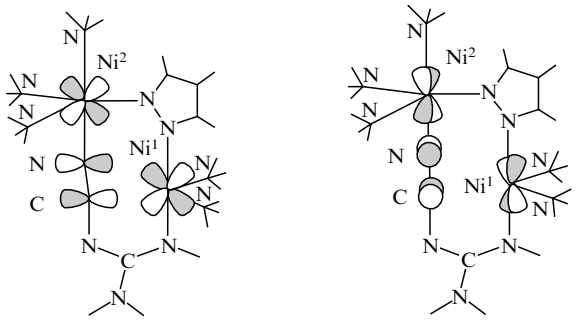


Figure 8. Interactions between the orbitals of the metal atom and the nitrile ligand in the complex **9**.[42]

The ground state of the complex **9** is quintuplet, whereas the energies of the triplet and singlet states are higher by 46.9 and 381.4 kJ mol^{-1}, respectively. The singly occupied MOs are centred on the d_{z^2}- and d_{xy}-orbitals of Ni^1 and the $d_{z^2-y^2}$- and d_{x^2-} orbitals of Ni^2. The lower-energy doubly occupied MOs are composed of the d_{yz}- and d_{xz}-orbitals of the Ni^1 and Ni^2 atoms with a particular contribution of the π*-MO of nitrile. The latter orbital is responsible for insignificant π-back donation of the electron density from the orbitals of the Ni^2 and Ni^1 atoms to the orbitals of the ligand. The side-to-side interaction between the orbitals of the Ni^1 atom and the nitrile ligand (Fig. 8) is rather unusual for the high-spin Ni(II) ion.

Kuznetsov *et al.*[43,44] reported the results of theoretical studies of the platinum nitrile complexes *trans*-$[Pt(NCMe)_2Cl_2]$ (**10**),

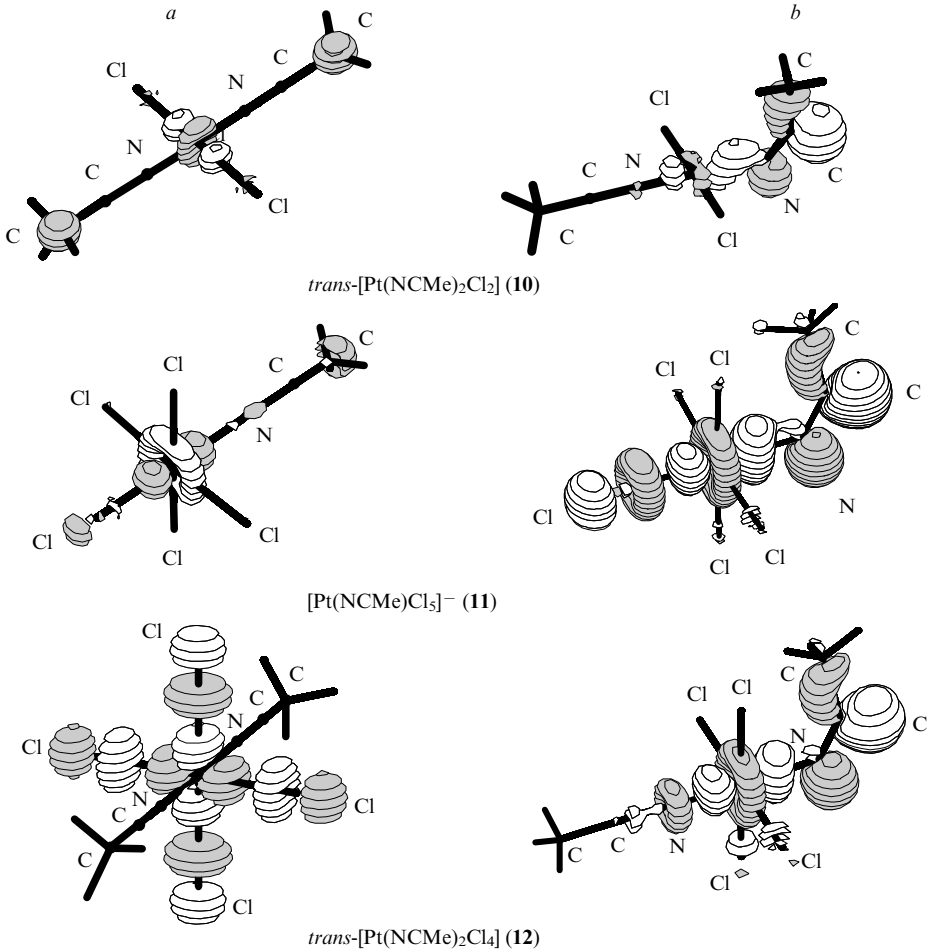


Figure 9. Compositions of the HOMOs in the complexes **10**–**12** when they contain two linear acetonitrile ligands (*a*) and when one of the acetonitrile ligands has an angular sructure (*b*).[44]

$[Pt(NCMe)Cl_5]^-$ (**11**) and *trans*-$[Pt(NCMe)_2Cl_4]$ (**12**). Figure 9 presents the compositions of the HOMOs of the complexes **10**–**12** when they contain two linear acetonitrile ligands (*a*) and when one of the acetonitrile ligands has a bent sructure (*b*). Calculations performed for the complexes **10**–**12** at different levels of theory (HF and MP2) and with different basis sets demonstrated that several of the highest occupied MOs of these complexes are formed from the orbitals of the chlorine atoms or, in the case of *trans*-$[Pt(NCMe)_2Cl_2]$, from the orbitals of the metal atom without a noticeable contribution of the orbitals of acetonitrile.

Recently, similar results were obtained by Pombeiro and co-workers [38] for the tungsten complexes *trans*- and *cis*-$[(PH_3)_2(CO)_2W(NCMe)(\equiv CCH=CH_2)]^+$ (Fig. 10).

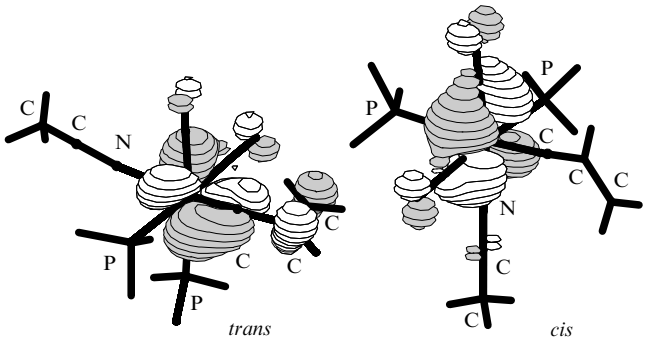


Figure 10. Compositions of the HOMOs in the tungsten nitrile complexes *trans*- and *cis*-$[(PH_3)_2(CO)_2W(NCMe)(\equiv CCH=CH_2)]^+$.[38]

One of the highest occupied MOs of the $\{(PH_3)_2.(CO)_2W(\equiv CCH=CH_2)\}^+$ fragments (the first orbital in the case of the *trans* isomers and the second orbital in the case of the *cis* isomers) is derived from a linear combination of the *d*-orbitals of the metal atom with the π- and π*-MOs of two CO ligands. Due to a large contribution from the π*-orbitals, the HOMO is bonding relative to the W–C bond and antibonding with respect to the C–O bond. This is indicative of the presence of π-back donation from the metal atom to the π*-MO of a strong π-acceptor such as CO. Two other highest occupied MOs of the $\{(PH_3)_2(CO)_2W(\equiv CCH=CH_2)\}^+$ fragments of the *cis* and *trans* isomers are composed of the *d*-orbitals of the metal, which also interact with the π- and π*-MOs of one of the CO ligands and with the orbitals of the carbyne ligand. Upon the formation of the nitrile complex $[(PH_3)_2(CO)_2W(NCMe)(\equiv CCH=CH_2)]^+$ from the $\{(PH_3)_2(CO)_2W(\equiv CCH=CH_2)\}^+$ and {NCMe} fragments, the composition of the highest occupied MOs of the former fragment remains virtually unchanged and the orbitals of the nitrile ligand make an insignificant contribution to the HOMO of the complex (see Fig. 10).

In the study,[45] calixarene complexes of Ta and Nb, including those containing the coordinated acetonitrile molecule, were synthesised, their spectroscopic parameters and structural characteristics were determined, and the molecular orbitals were calculated by the Fenske–Hall method.[46] In the [Cp*Ta(NCMe)(calix[4]arene)] complex (Cp* = η^5-C_5Me_5), the bonding interaction between nitrile and metal involves the d_{z^2}(Ta)- and p_z(N)-orbitals *via* σ-bonding (Fig. 11) and the HOMO of the complex is centred on the atoms of the calixarene ligand.

The *ab initio* calculations for the tetranuclear copper(I) clusters $[Cu_4(NCMe)_2I_4L_2]$ (L is 2,6-dimethylaniline, 6-ethyl-*o*-toluidine or *p*-toluidine) [47] demonstrated that the *p*-orbitals of the iodine atoms make major contribution to the HOMO of the complex, whereas the LUMO is formed from the *p*-orbitals of copper. It was noted that the orbitals of acetonitrile make no substantial contribution to the frontier MOs of the complex.

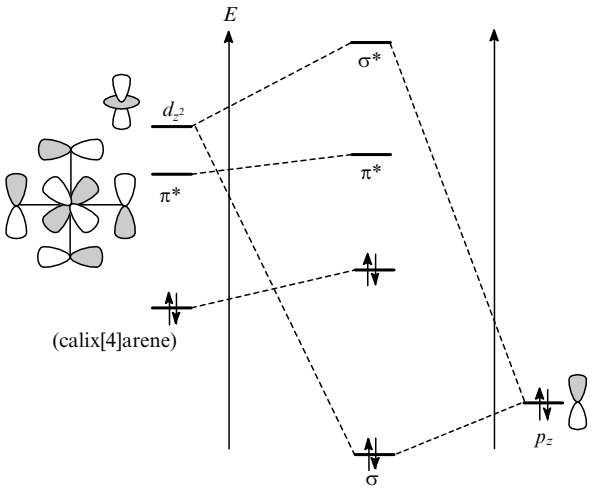


Figure 11. Correlation diagram of the MOs in the nitrile complex [Cp*Ta(NCMe)(calix[4]arene)].[45]

The main difference between the nitrile and isocyanide complexes is associated with weaker π-acceptor properties of nitriles compared to those of isocyanides due to which the contributions of the π- and π*-MOs of the ligand to the MOs of the complex compensate each other and the corresponding molecular orbital is nonbonding.

The total contribution of the π- and π*-orbitals of the ligand to the HOMOs in nitrile complexes is smaller than that in isocyanide complexes, which is also indicative of weaker π-acceptor properties of the nitrile ligands. As a result, the π-component of the coordination bond in nitrile complexes is often negligible as compared to the σ-donor or Coulombic component (see below). Hence, the DCD model must be applied to the description of the properties of the nitrile complexes with caution. Finally, analysis of the compositions of the frontier MOs of acetonitrile and methyl isocyanide [48] demonstrated that nitriles are weaker σ-donors than isocyanides due to substantially lower energy of the valence occupied σ-orbitals of NCR compared to those of CNR.

2. Structural features of metal complexes with nitriles and isocyanides

Back π-donation of the electron density from metal to the ligand has a substantial effect on the geometric parameters of the complexes. Actually, an increase in the occupancy of the π*-antibonding orbitals of the ligand must lead to weakening of the multiple C≡N bond in the ligand and, consequently, its length must slightly increase on going from the free ligand to the complex. To the contrary, the metal–ligand bond becomes stronger due to additional π-interaction resulting in shortening of the metal–ligand bond compared to those in the related complexes in which π-back donation is absent.

In the early studies by Sarapu and Fenske,[49,50] the presence of π-back donation in isocyanide complexes was confirmed by the X-ray diffraction data. The Mn–C(CNMe) bond length in the $[Mn(CNMe)_2(CO)_3Br]$ complex is 0.10–0.14 Å smaller than the sum of the covalent radii of Mn and the *sp*-hybridised carbon atom, which indicates that this bond in the complex is partially double. The results of X-ray diffraction studies are in agreement with the data from theoretical calculations of MOs by the Fenske–Hall method. In particular, the substantial occupancies of the π*-MOs of the isocyanide ligand in the $[Mn(CNMe)_n(CO)_{5-n}Br]$ ($n = 0-4$), $[Mn(CNMe)_n(CO)_{6-n}]^+$ ($n = 0-6$), $[Mn(CN)(CO)_5]$, $[Mn(CN)_6]^{5-}$ and $[Fe(CNMe)_6]^{2+}$ complexes are indicative of the efficient electron density transfer from the *d*-orbitals of metal to the π*-MO of isocyanide in spite of

the presence of such a strong π-acceptor as the CO ligand. A comparison of the occupancies of the π*-MOs of the isocyanide and carbonyl ligands shows that the latter is the stronger π-acceptor than isocyanide and that π-back donation of the electron density from the *d*-orbitals of metal to the π*-MOs of the carbonyl ligand is more pronounced than that to the π*-orbitals of the isocyanide ligand.

It does not always happen that the expected elongation of the C≡N triple bond takes place on going from the free ligand to the complex. For example, the calculated C≡N bond length in the *trans*- and *cis*-[$(PH_3)_2(CO)_2W(CNMe)(\equiv CCH=CH_2)$] complexes (1.145 and 1.147 Å, respectively) is 0.011 – 0.013 Å smaller than that in the free ligand.[38] The interactions of the $[MCp_3]^+$ fragment (M = Ti, Zr, Hf) with such ligands as NCMe, CNMe and CO, which afford the corresponding $[MLCp_3]^+$ complexes, were examined.[51] It was demonstrated that the M – L bond length calculated by the DFT method increases in the series Ti < Hf < Zr and CO < CNMe < NCMe. The authors of the cited study attributed the former tendency to the relativistic effects, which were taken into account for Hf. An increase in the M – L bond length on going from CO to NCMe correlates with weakening of the π-acceptor properties of the ligands in this series.

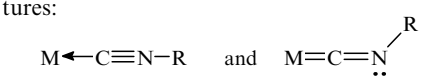
The variations in the C≡O and C≡N bond lengths on going from the free ligand to the complex are less evident. These bond lengths depend on two opposite effects.[52] One effect, *viz*., σ-donation from the ligand to metal L → M, must lead to shortening of the C≡N(O) bond because the corresponding occupied σ-orbital of the ligand, which is involved in the formation of the M – L σ-bond, is antibonding. Consequently, coordination of the ligand must lead to a decrease in the electron density on the σ*-orbital, which is antibonding for the C≡N or C≡O bond, resulting in its strengthening. The opposite effect, *viz*., π-back donation from metal to the ligand, must lead to elongation of the C≡N or C≡O bond due to an increase in the electron density on the π*-MO of the ligand upon coordination. Taking into account weakening of the π-acceptor properties of the ligands (more precisely, a decrease in the ratio between the π-acceptor and σ-donor abilities) on going from CO to NCMe, one would expect a decrease in $\Delta r = r(C\equiv X)_{comp} - r(C\equiv X)_{free}$ (X = O, N) in this series. However, the results of calculations demonstrated that the C≡O bond length increases upon coordination, the C≡N bond length in isocyanide complexes decreases, whereas the corresponding bond length in nitrile complexes remains virtually unchanged (Table 1). To account for this phenomenon, the energy characteristics of the M – L bond were analysed. The energy of this bond (E_{bond}) was divided into three components $E_{bond} = -(\Delta E_{Coul.} + \Delta E_{Pauli} + \Delta E_{oi})$, where $\Delta E_{Coul.}$ characterises the Coulombic component of the M – L interaction, ΔE_{Pauli} represents the exchange repulsion and ΔE_{oi} accounts for the contribution of the bonding orbital interaction. The sum $\Delta E_{Pauli} + \Delta E_{oi}$ represents the orbital energy (ΔE_{orb}). The results of analysis showed that the maximum contribution of $\Delta E_{Coul.}$ to the energy of the bond E_{bond} is observed in the case of isocyanide complexes, whereas this contribution in the case of carbonyl and nitrile complexes is much lower (see Table 1), which is responsible for additional shortening of the C≡N bond in the $[M(CNMe)Cp_3]^+$ complexes. The lowest orbital energies ΔE_{orb} were found for nitrile complexes, which results in intermediate values of Δr.

Table 1. The M – L, C≡N and C≡O bond lengths in the $[MLCp_3]^+$ complexes (M = Ti, Zr, Hf; L = CO, CNMe, NCMe), the energies of the coordination bonds and their components.

Complex	Bond lengths /Å		E /kJ mol^{-1}			
	M – L	C≡N (C≡O)	$\Delta E_{Coul.}$	ΔE_{Pauli}	ΔE_{oi}	E_{bond}
$[Ti(CO)Cp_3]^+$	2.09	(1.15)	−282	476	−302	108
$[Ti(CNMe)Cp_3]^+$	2.15	1.17	−337	414	−246	169
$[Ti(NCMe)Cp_3]^+$	2.18	1.16	−233	261	−164	136
$[Zr(CO)Cp_3]^+$	2.25	(1.14)	−228	365	−247	110
$[Zr(CNMe)Cp_3]^+$	2.30	1.17	−309	345	−218	182
$[Zr(NCMe)Cp_3]^+$	2.32	1.16	−219	223	−155	151
$[Hf(CO)Cp_3]^+$	2.22	(1.15)	−288	448	−294	134
$[Hf(CNMe)Cp_3]^+$	2.25	1.17	−390	457	−274	207
$[Hf(NCMe)Cp_3]^+$	2.28	1.16	−264	186	−192	170

Note. The calculated C≡O and C≡N bond lengths in the free CO, CNMe and NCMe ligands are 1.14, 1.18 and 1.16 Å, respectively.

It should be noted that π-back donation sometimes leads to a bent distortion of the ligand. Thus the geometry of coordinated isocyanide can be described as intermediate between two structures:



Apparently, a predominance of a particular form is determined by the relative contributions of the π-acceptor and σ-donor components to the metal – ligand bond. When the σ-donor (L → M) component substantially dominates over the π-acceptor (M → L) component, the ligand adopts a linear conformation. In contrast, when π-back donation becomes dominant, the multiplicity of the M – L bond increases, whereas the multiplicity of the C≡N bond decreases, which could cause a bent distortion of the isocyanide ligand.[39, 53]

Actually, according to the X-ray diffraction data,[54–58] the isocyanide ligand has a linear structure in most of isocyanide complexes of transition metals in high oxidation states in which π-back donation is manifested to only a small extent, if at all. At the same time, the isocyanide ligand has an angular structure in complexes of transition metals in low oxidation states in which efficient electron density transfer occurs from the *d*-orbitals of metal to the π*-MO of the ligand,[59, 60] the C – N – C angle being contracted to 140°.

The correlation diagrams of the MOs for linear and angular methyl isocyanide[48] show that the bent distortion of the ligand leads to an increase in the energy of the π-MO and this orbital becomes the highest occupied MO, whereas the energy of the π*-MOs decreases (Fig. 12 *a*). Hence, the bent distortion leads to a noticeable enhancement of the π-acceptor properties of the CNMe ligand, its σ-donor properties being virtually unchanged because the energy of the π-MO in the angular ligand is only 0.008 a.u. higher than the energy of the σ-MO in the linear ligand and the π-MO is localised on the terminal carbon atom to a much lesser extent.

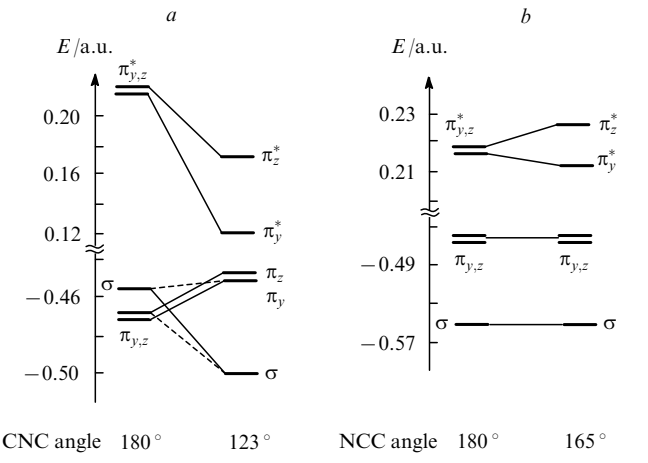


Figure 12. Walsh diagrams for the bent distortions of the methyl isocyanide (*a*) and acetonitrile (*b*) molecules (the data from the study[48]).

Analysis of the linear and angular structures of the nitrile ligand NCMe (Fig. 12 *b*) demonstrated that acetonitrile exhibits very weak π-acceptor properties due to a small degree of localisation of the π*-MO on the terminal N atom although the energy of the π*-MO of the nitrile ligand determined in the study [48] is comparable with the energy of the π*-MO of the isocyanide ligand. The bent distortion of the NCMe ligand must lead to weakening of its acceptor properties due to the total destabilisation of the π*-MO. At the same time, the authors of the cited study [48] believed that essential localisation of the π-MO(NCMe) on the C and N atoms of the C≡N bond makes acetonitrile a potentially strong π-donor ligand. These π-donor properties of the nitrile ligand are responsible for the deviation of the M—N—C fragment from linearity, which is frequently observed in experimental studies. However, as shown in Section II.1, the fact that the contributions of the π-orbitals of nitriles to the HOMOs of the complexes are small refutes this assumption.

Somewhat different distributions of the frontier MOs for acetonitrile and the model NCH structure were found in the study [61] (Fig. 13). The authors believed that the bent distortion of the NCH ligand leads to mixing of the σ- and π_y-orbitals and their reorientation so that overlapping of these orbitals with the orbitals of the metal atom is enhanced in the case of the lateral coordination of the nitrile ligand through the C≡N triple bond. Hence, the bent distortions of the nitrile ligands lead to enhancement both of their donor and acceptor properties. The lateral coordination of nitrile leads to a decrease in the energy of the LUMO of the ligand and, consequently, π-back donation in nitrile π-complexes becomes substantial.

Thus the NCC fragment of the ligand is linear in the case of the standard σ-coordination of nitriles to transition metals, whereas

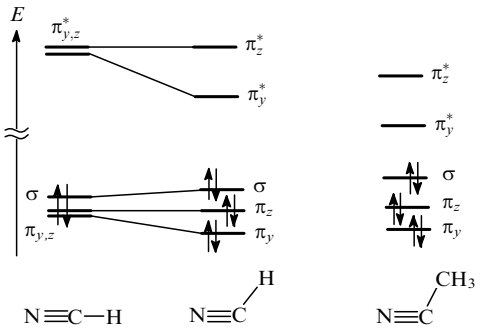


Figure 13. Walsh diagram for the bent distortion of the NCH molecule and the frontier MOs of the angular acetonitrile molecule (the data from the study [61]).

the nitrile ligand undergoes a bent distortion due to substantial π-back donation in the case of the lateral π-coordination through the C≡N triple bond. Actually, geometry optimisation of the model complex [CpW(η²-NCH)(CO)(HC=C=O)] by the DFT method [61] gave the N—C—H angle of 135.6°.

Analysis of the electronic structures of the tungsten complexes [W(NCH)Cl$_2$(PH$_3$)$_3$] and [CpW(NCMe)(CO) {C(SiH$_3$)=C=O}] demonstrated that the π*-MOs of the ligand contribute significantly to the highest occupied MOs of the complexes (in the case of [CpW(NCMe)(CO) {C(SiH$_3$)=C=O}], to the highest occupied MO, which is the closest in energy to the HOMO) (Fig. 14).

The effect of the nature of the ligand, primarily, of its donor and acceptor properties, on the geometric parameters of other

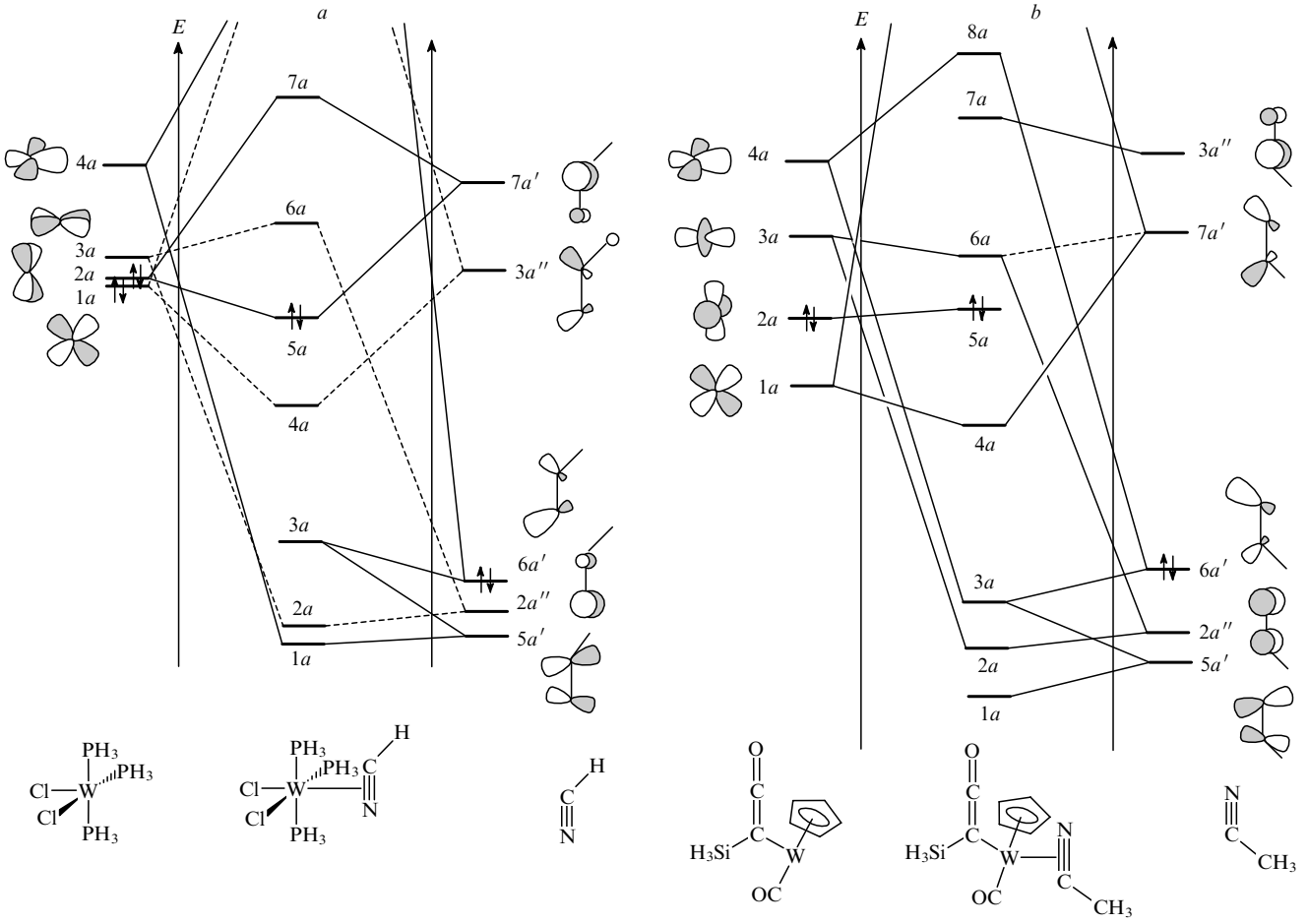
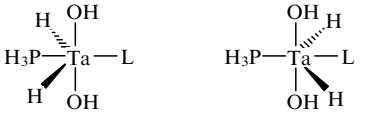


Figure 14. Correlation diagrams of the MOs in the [W(NCH)Cl$_2$(PH$_3$)$_3$] (*a*) and [CpW(NCMe)(CO) {C(SiH$_3$)=C=O}] (*b*) complexes.[61]

fragments in complexes was considered in the study.[62] In the cited study, the results of *ab initio* calculations for a series of $[TaLL'(OH)_2H_2]^+$ complexes with various L and L′ ligands, including NCMe, were discussed (the geometry optimisation was carried out by the MP2 method). The trans effect of the ligand L on the phosphine ligand (the Ta–P distance was used as a measure of the trans effect) was considered using the $[TaL(PH_3)(OH)_2H_2]^+$ complexes as an example.

Depending on the nature of the ligand L, the Ta–P distance was found to decrease in the series CH_3^- > H^- > NH_2^- > BF > CS > PH_3 (**A**) > OH^- > CO > CN^- > F^- > NC^- > Cl^- > Br^- > I^- > NH_3 > NCMe > PH_3 (**B**) > N_2. The relative stabilities of the isomers **A** and **B**



A **B**

($\Delta E_{AB} = E_A - E_B$) change in the following series: F^- < OH^- < Cl^- < Br^- < NC^- < I^- < CH_3^- < CN^- < NCMe < NH_3 < N_2 < H^- < NH_2^- < PH_3 < CO < CS < BF (Table 2). The ligands exhibiting strong π-donor properties reside in the left side of this series, *i.e.*, the π-donor ability of the ligands L decreases from left to right. From the above series it follows that there is no correlation between the σ-donor properties (trans effect) and the π-donor (acceptor) properties of the ligands.

It was found that the hydride atoms in the complexes **A** and **B**, which are located in the *trans* positions with respect to each other, are shifted from the stronger π-donor toward the stronger π-acceptor. If the ligands possess both weak π-acceptor and weak π-donor properties, the bent distortion is caused by the ligand exhibiting the strongest static trans effect and the hydride atoms are shifted toward the weaker σ-donor. It was proposed [62] that the unusual bent distortion of the H–Ta–H fragment is determined by these π-donor and π-acceptor (rather than by σ-donor) properties of the ligands L.

From the above-considered data, it is evident that π-back donation sometimes has a substantial effect on the structural parameters of the complexes. One of the indicators of the efficient π-back donation is the bent distortion of the CNC or NCC fragment. However, in actual practice this distortion is uncommon even in the case of transition metal complexes in low oxidation states and, hence, the linearity of CNC or NCC cannot serve as proof of weak π-acceptor properties of the ligand in the complex.

In the general case, the relative length of the C≡N multiple bond in transition metal complexes with nitriles and isocyanides also cannot be considered as a reliable criterion for the degree or even existence of π-back donation because the length of this bond is substantially influenced not only by two opposite effects, *viz.*, σ-donation and π-back donation, but also by the Coulombic component.[39, 51] A comparison of a series of related complexes showed that the M–L bond length is a more reliable criterion for the degree of π-back donation.

Table 2. Relative energies of the **A** and **B** isomers of the $[TaL(PH_3).(OH)_2H_2]^+$ complexes.

L	ΔE_{AB} /kJ mol^{-1}	L	ΔE_{AB} /kJ mol^{-1}	L	ΔE_{AB} /kJ mol^{-1}
Cl^-	−111.33	CN^-	−57.32	NH_2^-	−19.43
Br^-	−101.24	NCMe	−36.84	PH_3	0.00
NC^-	−90.43	NH_3	−35.21	CO	10.76
I^-	−89.47	N_2	−24.99	CS	16.08
CH_3^-	−68.91	H^-	−19.93	BF	53.55

III. Spectroscopic properties of coordinated ligands

1. Vibrational spectra

Stretching vibrational frequencies of the C≡N and C≡O bonds in transition metal complexes with nitriles and carbonyls§ are influenced by several factors, including σ-donation of the electron density from the ligand to the metal atom, π-back donation from metal to the ligand and the Coulombic component of the coordination bond. σ-Donation from the ligand to metal leads to strengthening of the C≡N and C≡O bonds and, consequently, to an increase in their vibrational frequencies, whereas π-back donation from metal to the ligand causes weakening of these bonds and, hence, a decrease in the corresponding vibrational frequencies. In complexes with strong π-acceptor ligands, such as CO (and in some cases CNR), the latter effect generally dominates over the former as a result of which the ν(CN) and ν(CO) frequencies for the complexes are lower than those for the free ligands.

Actually, lowering of the ν(CO) and ν(CN) vibrational frequencies on going from the free ligand to the complex was predicted theoretically and observed experimentally for many carbonyl complexes as well as for a series of transition metal complexes with isocyanides (predominantly, with metals in low oxidation states).[39, 59, 63, 64] However, complex formation with isocyanides possessing weaker π-acceptor properties as compared to CO often leads to an increase in the ν(CN) frequency. Thus theoretical analysis of the force constants and ν(CN) vibrational frequencies for the $[Mn(CNMe)_n(CO)_{5-n}Br]$ ($n = 0-4$), $[Mn(CNMe)_n(CO)_{6-n}]^+$ ($n = 0-6$) and $[Fe(CNMe)_6]^{2+}$ complexes demonstrated that the ν(CN) frequency for the complexes is higher than that for the free ligand, which indicates that σ-donation dominates over π-back donation.[50]

At the same time, detailed theoretical studies of the nature of coordination bonds in transition metal complexes demonstrated that the ν(CN) and ν(CO) stretching vibrational frequencies generally cannot serve as a reliable criterion for the degree of L → M donation and M → L π-back donation even for complexes with such a strong π-acceptor as carbon(II) oxide. Examples are provided by the so-called 'non-classical' carbonyl complexes, for instance, $[Os(CO)_6]^{2+}$ and $[Ir(CO)_6]^{3+}$. In their spectra, the ν(CO) frequency is higher than that in the spectrum of the free ligand. The reason is that Coulombic interactions are of paramount importance in the formation of coordination bonds in non-classical carbonyl complexes and these interactions ultimately determine the ν(CO) frequency.[65, 66] In transition metal complexes with isocyanides, which are weaker π-acceptors than CO, Coulombic interactions can exert a stronger effect on the ν(CN) frequency compared to that of π-donation, which often leads to an additional increase in this vibrational frequency upon complex formation.

In nitrile complexes, the above-described tendencies are further enhanced because the nitrile ligands exhibit very weak π-acceptor properties and rather weak σ-donor properties. In this case, the Coulombic component of the metal–ligand interaction often exerts primary control over the ν(CN) frequency. This fact is confirmed by the preliminary data from analysis of the natural bond orbitals performed for the *cis*-$[Re(NCMe)Cl(PH_3)_4]$ and *trans*- and *cis*-$[Re(NCMe)Cl(PH_3)_4]^{+/2+}$ complexes.[67] Generally, the ν(CN) vibrational frequencies for nitriles are shifted to the high-frequency region on going from the free ligand to the complex.[68–78] At the same time, there are examples of low-frequency shifts of this band upon coordination of nitriles with metals in the lowest oxidation states [79–81] but these shifts are much smaller than those in the spectra of analogous isocyanide complexes. Finally, it should be noted that the low-frequency

§ Spectroscopic properties of carbonyl compounds are considered for comparison.

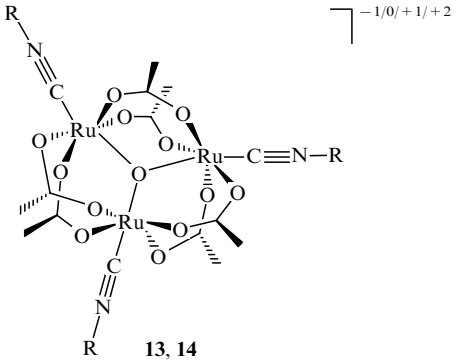
shifts of ν(CN) for nitrile η^2-complexes in which the ligand is coordinated through the C≡N bond are rather high,[82–84] which indicates that this is virtually a double bond.

The spectroscopic properties of nitrile complexes were examined in several theoretical studies. Thus the vibrational spectra of the platinum complex $[Pt(NCMe)Cl_3]^-$ were calculated and described in detail.[69] The ν(CN) band in the spectrum of the complex is shifted by 113 cm^{-1} to the high-frequency region as compared to its position in the spectrum of free acetonitrile. Interestingly, analogous high-frequency shifts of ν(C≡N) (95–117 cm^{-1}) were found for the adducts of acetonitrile with Lewis acids BF_3 and BCl_3 (Ref. 85) in which π-back donation is, in principle, impossible.

It was demonstrated that the calculated ν(CN) frequency decreases from 2209 cm^{-1} for the free N≡C–N=C$(NH_2)_2$ ligand to 2189 and 2143 cm^{-1} upon coordination of the ligand to nickel (complexes **8** and **9**, respectively).[42] The calculated C≡N bond length increases from 1.163 Å (in the free ligand) to 1.178 and 1.187 Å (in the complexes **8** and **9**, respectively), which correlates with a change in the ν(CN) vibrational frequency. However, the order in which the calculated ν(CN) frequencies change is inconsistent with the experimental series **8** > N≡C–N=C$(NH_2)_2$ > **9**.

The vibrational spectra of acetonitrile coordinated to the Li^+ and Na^+ ions were calculated at the HF/6-31G and HF/6-31G** levels of theory.[86] Coordination leads to a substantial increase in the intensities of the ν(C≡N), ν(C–C) and $\delta(CH_3)$ vibrations but calculations demonstrated that their frequencies change only slightly.

Finally, mention may be made of the study[87] in which the vibrational spectra and the nature of the Fermi resonance for ruthenium isocyanide complexes **13** and **14** were analysed by the DFT method.



13, **14**

R = MeC_6H_4 (**13**), Bu^t (**14**).

In the case of the neutral complexes and their reduced forms, Fermi resonance appears due to the interaction between the fundamental frequency ν(C≡N) [2094 (**13**), 2010 (**13**$^-$), 2131 (**14**) and 2028 cm^{-1} (**14**$^-$)] and the vibrational overtone B_2 (**13** and **13**$^-$) or E (**14** and **14**$^-$) involving deformation of the C≡N–C fragment as the major component.

In some experimental studies (see, for example, the review[4]), it was found that the change in the ν(C≡N) frequency correlates with the reactivities of nitrile and isocyanide complexes with respect to nucleophilic and electrophilic addition. It was shown that complexes for which the parameter $\Delta\nu(C{\equiv}N) = \nu(C{\equiv}N)_{comp} - \nu(C{\equiv}N)_{free}$ is negative are readily subjected to electrophilic attack. If $\Delta\nu(C{\equiv}N) > 0$, complexes are involved in nucleophilic addition at the β-carbon atom. If the contribution of π-back donation to the coordination bond is essential, the β-atom of the ligand becomes more nucleophilic due to the electron density transfer from the *d*-orbitals of metal to the π*-MO of the ligand thus facilitating electrophilic attack. In contrast, if π-back donation makes only an insignificant contribution upon the formation of the coordination bond, the electron density transfer from the σ*-orbitals of the ligand to the *d*-orbitals of metal leads to enhancement of electrophilicity of the β-atom of the ligand, which facilitates the nucleophilic attack. However, detailed theoretical studies providing the interpretation of this correlation are lacking.

2. Electronic spectra and excited states

Theoretical and experimental investigations devoted to the electronic spectra and the nature of excited states of nitrile and isocyanide complexes are rather scarce. Most of the calculations were carried out in a one-electron approximation. Several electronic states of the bis(isocyanide) complexes of nickel(II) peroxo $NiO_2(CNH)_2$ were studied by the unrestricted HF and CI methods.[88] It was demonstrated that the singlet state $^1A_1$ is the ground electronic state of the complex. The first excitation state is the triplet $^3B_1$ with the energy parameter $\Delta E(^3B_1 - {}^1A_1)$ = 47.60 kJ mol^{-1}. The authors of the cited study considered the electron density distribution (ρ) and its Laplacian ($\nabla^2\rho$) and analysed the natural orbitals.

Photophysical properties of the model mononuclear copper clusters CuL_n^+ (L = NH_3, NCMe, C_5H_5N; n = 1–4) were described.[89] These properties were interpreted with the use of the Hartree–Fock method. The nature of the low-energy excited states was examined, their energies were determined, and the assignments of the metal-to-ligand charge transfer (MLCT) bands in the spectra of these complexes were made. The first excited state of the $[Cu(NCMe)_4]^+$ complex ($^3B_3$) is formed due to MLCT and the second excited state ($^3B_1$) is formed through electron transfer from the 3*d*- to 4*s*-orbitals of the metal (Table 3). The assignments of these bands in the emission spectra of these complexes were performed.[89]

Table 3. Energies of the first excitation states (ΔE) and changes in the Mulliken electronic populations of the 4*s*-, 4*p*- and 3*d*-orbitals of the copper atom with respect to the ground state for the $[Cu(NCMe)_4]^+$ complex.

State	ΔE /a.u.	ΔCu			
		4*s*	4*p*	3*d*	total
$^3B_3$	0.159	0.062	0.393	−0.786	−0.331
$^3B_1$	0.164	0.900	0.050	−0.796	0.156
$^3A_1$	0.179	0.905	0.056	−0.827	0.135

The nature of the low-energy excited states of the $[Ag_2(dmb)_2X_2]$ complexes (X = Cl, Br, I; dmb is 1,8-diisocyano-*p*-menthane) was discussed based on the experimental data and the results of EHMO calculations.[33] The charge-transfer bands in the electronic absorption spectra were assigned and their nature was studied. The broad band in the region of 250–350 nm was assigned to the electron transfer from the HOMO (HOMO−n) to the LUMO (LUMO + n): $d(Ag_2)/p(X) \rightarrow \pi^*(CNR)$.

A comparison of the photoelectron spectra of the $[CpM(CNBu^t)(CO)_2Me]$ and $[CpM(CO)_3Me]$ complexes (M = Mo or W) showed[32] that the replacement of the carbonyl ligand by isocyanide leads to destabilisation of the *d*-orbitals of the metal atom, which is manifested in shifts of stretching bands in the spectrum of the isocyanide complex to lower energies by 0.73–0.83 eV. An analogous result was obtained in the study[90] dealing with iron pentacarbonyl $Fe(CO)_5$ and the iron isocyanide complexes $Fe(CNR)(CO)_4$ (R = Me, Bu^t, $SiMe_3$, Ph). The higher energies of the occupied π-MOs of the isocyanide ligand compared to those of CO (the electron ionisation energy for the π-MOs of the corresponding free ligands are 12.46 and 16.91 eV) leads to enhancement of the destabilising interaction between the valence occupied *d*-orbitals of metal and the occupied π-MOs of the isocyanide ligand and to weakening of the stabilising d(M)–π*(L) interaction in the pentacarbonyl complexes resulting in an increase in the HOMO energy. Hence, it was concluded that

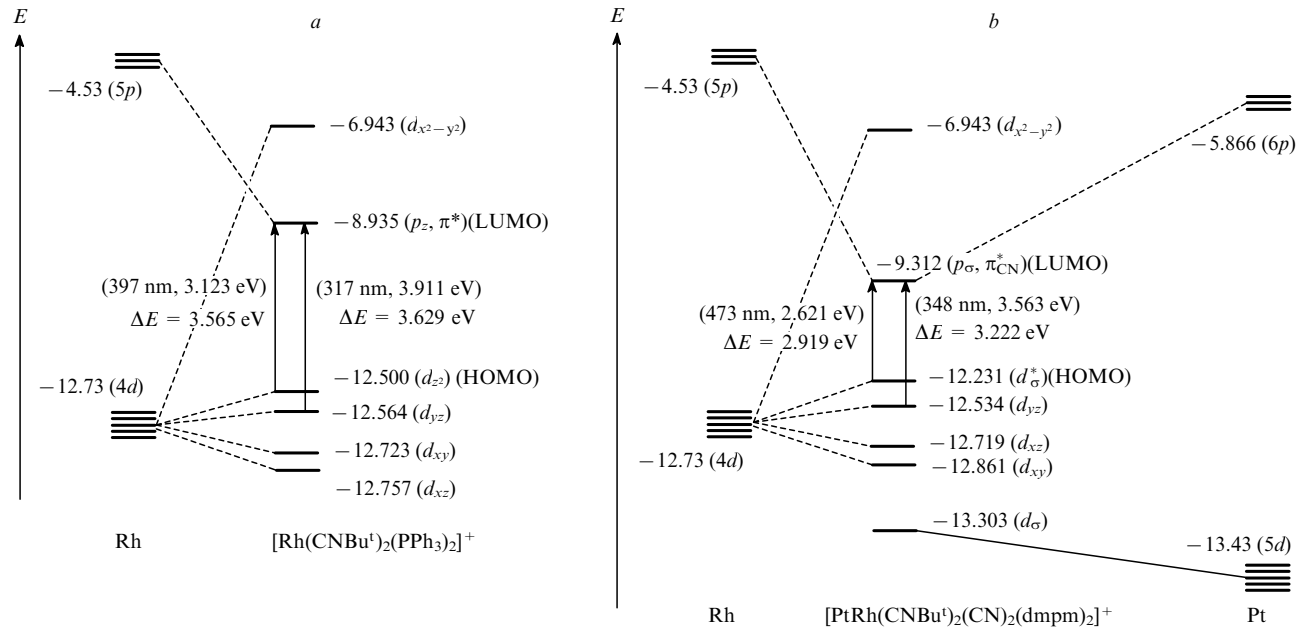


Figure 15. Correlation diagram of the MOs in the *trans*-[Rh(CNBu^t)$_2$(PPh$_3$)$_2$]$^+$ (*a*) and [PtRh(CNBu^t)$_2$(CN)$_2$(dmpm)$_2$]$^+$ (*b*) complexes.[34]

the isocyanide ligand is a better π-donor but a poorer π-acceptor as compared to the carbonyl ligand.

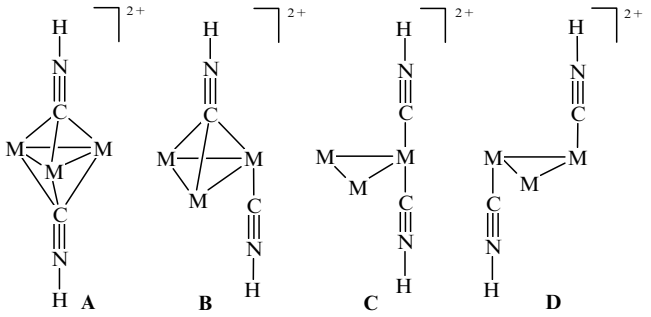
Analysis and the assignments in the electronic spectra of the *trans*-[Rh(CNBu^t)$_2$(PPh$_3$)$_2$]$^+$ and [PtRh(CNBu^t)$_2$(CN)$_2$.(dppm)$_2$]$^+$ complexes (dppm = $Ph_2PCH_2PPh_2$) were carried out based on the results of EHMO calculations for the model compounds *trans*-[Rh(CNBu^t)$_2$(PPh$_3$)$_2$]$^+$ and [PtRh(CNBu^t)$_2$.(CN)$_2$(dmpm)$_2$]$^+$ (Fig. 15).[34] Two intense absorption bands at 397 and 317 nm in the spectrum of the former complex were assigned to the transitions d_{z^2}(Rh) → p_z(Rh)/π*(CNR)/p_z,d_{xz}(P) and d_{yz}(Rh) → p_z(Rh)/π*(CNR)/p_z,d_{xz}(P), respectively. The bands at 473 and 348 nm in the spectrum of the latter compound were assigned to the transitions d_{z^2}(Rh)/d_{z^2}(Pt) → p_y(Rh)/π*(CNR)/p_z,d_{xz}(P) and d_{yz}(Rh) → p_y(Rh)/π*(CNR)/p_z,d_{xz}(P), respectively, the electron transfer from the *d*-orbitals of Rh to the π*-MO of the ligand contributing significantly to the former band.

Among other studies devoted to examination of the spectroscopic properties of the complexes under consideration, noteworthy is the investigation[91] in which the spin-spin coupling constants J_{HD} for the [OsL(NH$_3$)$_4$(η^2-H$_2$)]$^{(z+2)+}$ compounds (where L = Me_2CO, H_2O, $MeCOO^-$, Cl^-, H^-, C_5H_5N, NCMe, NH_3, NH_2OH or CN^-) were calculated by the DFT method. For the acetonitrile complex, the constant J_{HD} is 20.8 Hz. The dependence of J_{HD} on the internuclear H−H distance was discussed.

IV. Reactivities and mechanisms of reactions with coordinated ligands

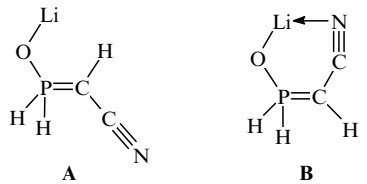
1. Isomerism and coordination modes

The coordination modes of ligands in complexes were discussed in theoretical studies.[38,67,92–94] The relative stabilities of the trinuclear platinum and palladium isocyanide clusters [M$_3$(CNH)$_2$(μ-dppm)$_3$]$^{2+}$ (M = Pt, Pd) with different coordination modes of the CNH ligand (isomers **A**–**D**) were studied based on the results of EHMO calculations:[92]



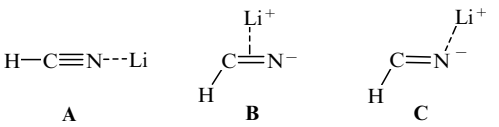
According to these results, the stability of the clusters **A**–**D** changes in the series **A** > **B** > **C** > **D**. This order is inconsistent with the experimental data, which provided evidence that the configuration **C** is most stable for the platinum complex. Apparently, more precise calculation methods are necessary for the correct description of the energy characteristics.

The stabilities of the monodentate (**A**) and chelate (**B**) configurations of the model complex [Li−O−PH$_2$=CH−C≡N] were analysed theoretically (HF/6-31G*).[93]



Calculations demonstrated that the chelate configuration of the complex is 112.6 kJ mol^{-1} more stable than the monodentate form in spite of the fact that it is characterised by the unusual Li−N≡C angle (91°).

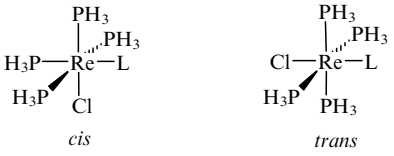
The reactions of the Li^+ ion with the NCH and NCMe molecules were studied by the semiempirical MNDO method and EPR spectroscopy.[94] Geometry optimisation of the LiNCH complexes revealed three minima corresponding to the structures **A**–**C**.



A **B** **C**

The heats of formation of these isomers are 46, 163 and 113 kJ mol^{-1}, respectively. The activation energy of the **C** → **B** conversion is 8 kJ mol^{-1}, which indicates that there is little likelihood that the structure **C** exists under the experimental conditions.

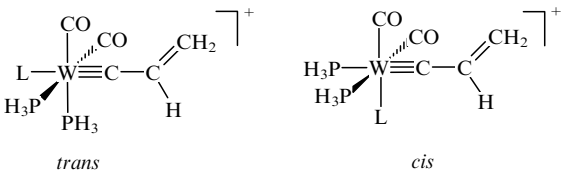
The geometric isomerisation of transition metal complexes was examined in the studies.[38,67] The preliminary study of the rhenium(I) complexes *trans*- and *cis*-[ReLCl(PH$_3$)$_4$] (L = NCMe, CNMe or CO) revealed that the *cis* isomers are more stable in the presence of weak π-acceptor ligands (L = NCMe), whereas the *trans* isomers are more stable in the presence of strong π-acceptor ligands (L = CO and CNMe).[67]



cis *trans*

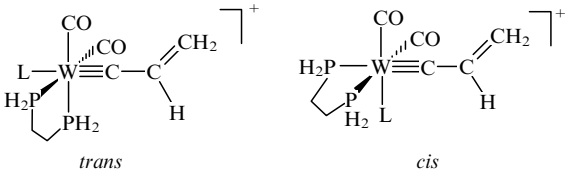
L = NCMe, CNMe, CO.

The opposite tendency was found for the model tungsten complexes [(PH$_3$)$_2$(CO)$_2$WL(≡CCH=CH$_2$)]$^+$ (**15**) and [(H$_2$PCH$_2$CH$_2$PH$_2$)(CO)$_2$WL(≡CCH=CH$_2$)]$^+$ (**16**) (L = Cl$^-$, NCMe, CNMe or CO),[38] which contain such a strong π-acceptor as the carbyne ligand in addition to the nitrile or isocyanide ligands. If the ligand L is a strong π-acceptor (L = CO, CNMe), the *cis* isomers are more stable (L and the carbyne ligands are in the *cis* positions) (Table 4). In contrast, if the ligand L is a weak π-acceptor (L = NCMe) or an efficient σ-donor (L = Cl$^-$), the *trans* isomers become more stable. The relative stabilities of the *cis* isomers compared to those of the *trans* isomers increases in the series Cl$^-$ < NCMe < CNMe < CO in accordance with enhancement of the π-acceptor properties of the ligands (more precisely, with the net π-acceptor minus σ-donor abilities of the ligand). Theoretical predictions about the relative stabilities of the geometric isomers were confirmed by the experimental data on the *trans* → *cis* isomerisation of the tungsten isocyanide complexes.



trans *cis*

L = Cl$^-$, NCMe, CNMe, CO.



trans *cis*

L = NCMe, CNMe, CO.

Based on the results of theoretical investigations[38,67] and experimental studies,[95–98] it can be assumed that configurations with σ-donor ligands and strong π-acceptor (in particular, CNR) ligands or with weak π-acceptor ligands (for example, NCR) and strong π-acceptor ligands in the *trans* positions are thermodynamically more stable for octahedral transition metal complexes in low oxidation states. Structures containing two strong π-acceptors, a weak π-acceptor and a σ-donor or two weak π-acceptors in the *trans* positions are less stable than the corresponding *cis* isomers. In contrast, for complexes with metals in high oxidation states, structures with σ-donor ligands and weak π-acceptor ligands in the *trans* positions or with σ-donor ligands and strong π-acceptor ligands in the *cis* positions appear to be stable. The question of whether these conclusions have a general character calls for further investigations.

Table 4. Relative energies of the *trans*- and *cis* isomers of the complexes **15** and **16**.

L	$\Delta E = E_{trans} - E_{cis}$ /kJ mol^{-1}	
	HF//HF	MP2//HF
[(PH$_3$)$_2$(CO)$_2$WL(≡CCH=CH$_2$)]$^+$		
Cl$^-$	−26.08	−27.05
NCMe	−12.56	−14.49
CNMe	11.60	10.63
CO	35.71	35.71
[(H$_2$PCH$_2$CH$_2$PH$_2$)(CO)$_2$WL(≡CCH=CH$_2$)]$^+$		
NCMe	−18.34	
CNMe	4.81	
CO	36.68	

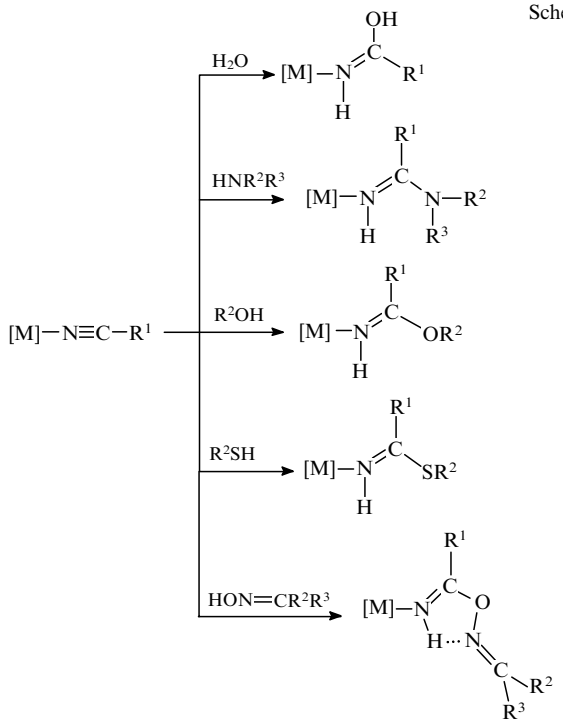
2. Nucleophilic addition reactions

Theoretical studies of the reactivities of compounds, in general, and complexes, in particular, are usually carried out with the use of frontier orbital theory.[99] According to this theory, if the reactivity of the compound is determined predominantly by the energies and compositions of the highest occupied and lowest unoccupied MOs (the so-called frontier orbitals) whose interactions are responsible for the formation of new bonds, the reaction is orbital-controlled. If the reaction (in particular, nucleophilic and electrophilic addition) is determined predominantly by the distribution of the effective charges on the atoms involved in formation of a new chemical bond, the reaction is charge-controlled.

Among various reactions with coordinated nitriles, the nucleophilic addition at the nitrile C≡N group is of paramount importance. These reactions were considered in numerous experimental studies and reviews. The reactions of such nucleophiles as water, amines, alcohols,[4,100–104] thiols,[105,106] phosphines,[107–109] hydrazines[110] and oximes[111–114] with nitrile complexes lead to the addition of the nucleophile at the carbon atom of the C≡N group, which is generally accompanied by migration of the proton from the nucleophile to the nitrile nitrogen atom. Examples of the reactions of coordinated nitriles with a number of nucleophiles are presented in Scheme 1 (all products are arbitrarily shown in the *E* configurations). It was noted that coordinated nitriles are more reactive in nucleophilic addition reactions than the free ligands, the complexes of metals in high oxidation states being more reactive than those bearing metals in low oxidation states.

Theoretical studies concerned with activation of nitriles with metals and the reactivities of coordinated nitriles in nucleophilic addition reactions are few in number. The reactions of oximes with nitriles and hydrolytic processes have received the most study (see Section IV.3). Activation of nitriles upon complex formation is often qualitatively explained by a decrease in the electron density on the carbon atom of nitrile upon its coordination to the metal atom and, as a consequence, by the enhancement of electrophilicity of the β-carbon atom thus facilitating the attack of the nucleophile on this atom. However, theoretical studies[43,44,69] demonstrated that this interpretation is in doubt. Thus it was found[69] that the effective charges on the C and N atoms of the nitrile ligand, which were calculated according to Lowdin scheme, are increased on going from free acetonitrile to the [Pt^{II}(NCMe)Cl$_3$]$^-$ complex (Table 5), *i.e.*, the electron density on these atoms decreases due to which the ligand becomes more accessible to nucleophilic attack. However, calculations of the

Scheme 1



effective charges according to Mulliken gave another charge density distribution and opposite results. Thus the effective charge on the carbon atom of nitrile was found to decrease on going from NCMe to $[Pt^{II}(NCMe)Cl_3]^-$.

The reactivities and activation of platinum nitrile complexes in the nucleophilic addition at the C≡N triple bond were examined.[43,44] The *ab initio* calculations of the effective charge distributions in free acetonitrile and three platinum complexes, *viz*., *trans*-$[Pt^{II}(NCMe)_2Cl_2]$ (**10**), $[Pt^{IV}(NCMe)Cl_5]^-$ (**11**) and *trans*-$[Pt^{IV}(NCMe)_2Cl_4]$ (**12**), by the HF and MP2 methods with different basis sets demonstrated that the effective positive charge on the carbon atom of nitrile calculated according to Mulliken changes only slightly on going from the free ligand to the complex and is virtually independent of both the oxidation state of the metal atom and the total charge on the complex ion (Table 6).

Table 5. Effective charges on the atoms in the NCMe and $[Pt(NCMe)Cl_3]^-$ molecules.

Atom or ligand	NCMe				$[Pt(NCMe)Cl_3]^-$	
	M [a]	L [a]	M [b]	L [b]	M [a]	L [a]
N	−0.09	−0.13	−0.08	−0.10	0.18	0.11
C	−0.05	−0.04	−0.05	−0.05	−0.16	0.13
CMe	0.14	0.17	0.11	0.15	0.10	0.20
NCMe	0	0	0	0	0.12	0.44
Pt					0.43	−1.15
Cl_{trans}					−0.49	−0.05
Cl_{cis}					−0.53	−0.12

Note. M is the analysis of the Mulliken populations, L is the analysis of populations according to Lowdin.
[a] Without considering the electron correlation. [b] Taking into account the electron correlation.

Activation of nitriles in the complexes **10**–**12** can be partially accounted for by the orbital control. In the context of the theory of frontier orbitals, the formation of a new chemical bond upon nucleophilic addition results from the interaction between the HOMO of the nucleophile and the LUMO of nitrile. In this case, the reactivity must depend on the relative energies of these orbitals. If the reaction involves the same nucleophile, the reactivity must be governed by the energy of the LUMO of nitrile. Actually, calculations showed that the energies of the LUMOs of the complexes **10**–**12** are 1.5–3.5 eV lower than the energy of the LUMO (π*-MO) of acetonitrile, which provides an explanation for the activation of MeCN in complexes. At the same time, the energy of the LUMO changes non-monotonically and insignificantly on going from **10** to **12** in spite of the noticeable enhance-

Table 6. Mulliken effective charges on the atoms calculated for the free NCMe ligand and the complexes **10**–**12**.

Atom	ECP [a]	3-21G [b]	6-31G [b]	6-31G(*d*-Cl) [b] HF	6-31G(*d*-Cl) [b] MP2	6-31G* [b]	DH [b]
NCMe							
N	−0.02	−0.51	−0.32	–	−0.25	−0.45	−0.09
C	−0.16	0.31	0.12	–	0.11	0.30	−0.05
trans-$[Pt(NCMe)_2Cl_2]$							
Pt	0.75	0.51	0.59	0.66	0.24	0.62	0.27
Cl	−0.52	−0.44	−0.41	−0.43	−0.31	−0.43	−0.36
N	−0.16	−0.77	−0.39	−0.38	−0.25	−0.45	0.06
C	0.03	0.64	0.18	0.18	0.19	0.34	0.01
$[Pt(NCMe)Cl_5]^-$							
Pt	0.82	0.32	0.09	0.34	−0.18	0.30	0.02
Cl	−0.40; −0.34	−0.33; −0.21	−0.26; −0.14	−0.31; −0.18	−0.22; −0.11	−0.31; −0.18	−0.26; −0.15
N	−0.14	−0.72	−0.36	−0.35	−0.20	−0.42	0.07
C	0.04	0.63	0.17	0.15	0.16	0.32	−0.05
trans-$[Pt(NCMe)_2Cl_4]$							
Pt	0.84	0.59	0.44	0.67	0.07	0.59	0.29
Cl	−0.31	−0.26	−0.19	−0.24	−0.15	−0.23	−0.19
N	−0.17	−0.81	−0.39	−0.39	−0.21	−0.42	0.10
C	0.07	0.69	0.20	0.19	0.20	0.34	−0.03

[a] Stuttgart quasi-relativistic pseudopotentials and the corresponding basis sets on the Pt, C, N and Cl atoms (for the hydrogen atoms, the 6-31G basis set was used). [b] Stuttgart quasi-relativistic pseudopotentials and the corresponding basis sets on the Pt atom.

ment of the reactivity in this series of compounds. In addition, the LUMOs of the starting nitrile complexes do not virtually involve the orbitals of acetonitrile although the nucleophilic attack occurs at the carbon atom of the nitrile group (see Fig. 9 *a*).

The nucleophilic addition reactions of oximes with the complexes **10**–**12** were accompanied by a change in the geometry of the acetonitrile fragment from linear to angular, which corresponds to a change in hybridisation of the β-C atom from *sp* to sp^2. Apparently, the change in hybridisation must cause the rearrangement of the valence molecular orbitals and substantial variations in their composition and energy. Analysis of the Walsh diagrams[44] demonstrated that the change of the conformation of coordinated acetonitrile from linear to angular leads to a decrease in the energy of the LUMOs of the complexes by 0.3–0.8 eV and to variations in the compositions of the lowest occupied MOs such that the orbitals of the carbon and nitrogen atoms of nitrile contribute significantly to the LUMOs (Fig. 9 *b*). According to the theory of frontier orbitals, this bent distortion of acetonitrile facilitates the nucleophilic addition at the β-C atom.

With the aim of providing the more rigorous description of the relative reactivities of nitriles and their platinum complexes **10**–**12**, the activation and reaction energies of the interaction of formaldoxime with these complexes were calculated. It was found that the activation energy decreases and the absolute value of the reaction energy increases in the series NCMe–**10**–**11**–**12** (Table 7), which is consistent with the enhancement of the reactivity of these compounds. Hence, activation of nitriles in complexes and their relative reactivities can be described on the basis of kinetic (a decrease in the activation energy) and thermodynamic (an increase in the reaction energy) factors.

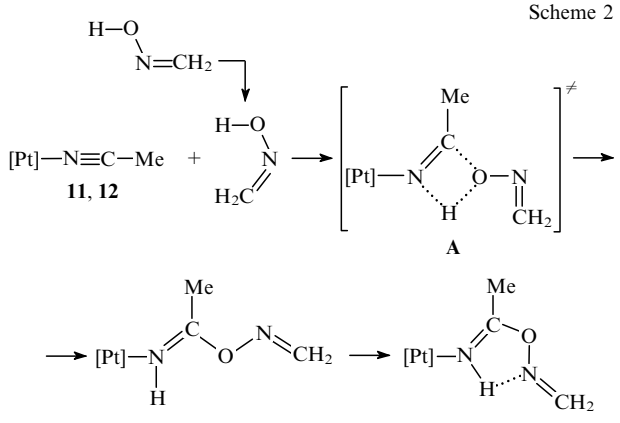
Table 7. Activation energies of the rate-limiting step (E_a /kJ mol^{-1}) and the energy effects (ΔE /kJ mol^{-1}) of the reactions of NCMe and the complexes **10**–**12** with formaldoxime.

Compound	E_a	ΔE
NCMe	275.16	−3.85
10	265.53	−66.61
11	253.93	−75.32
12	237.52	−91.73

The mechanism of nucleophilic addition of oximes to acetonitrile and the complexes **11** and **12** was examined in detail.[43, 115] The possible transition states and the reaction coordinates were calculated. Under non-catalytic conditions, these reactions proceed through the formation of the four-membered cyclic transition state **A** (Scheme 2).

Nucleophilic and electrophilic addition to coordinated nitriles and isocyanides at the C≡N triple bond are of great practical importance because these reactions allow one to prepare compounds possessing valuable properties, which cannot be synthesised without the use of transition metals. Nowadays, these processes call for further extensive theoretical investigations.

Scheme 2



[Pt] = $PtCl_5^-$ (**11**), $PtCl_4$(NCMe) (**12**).

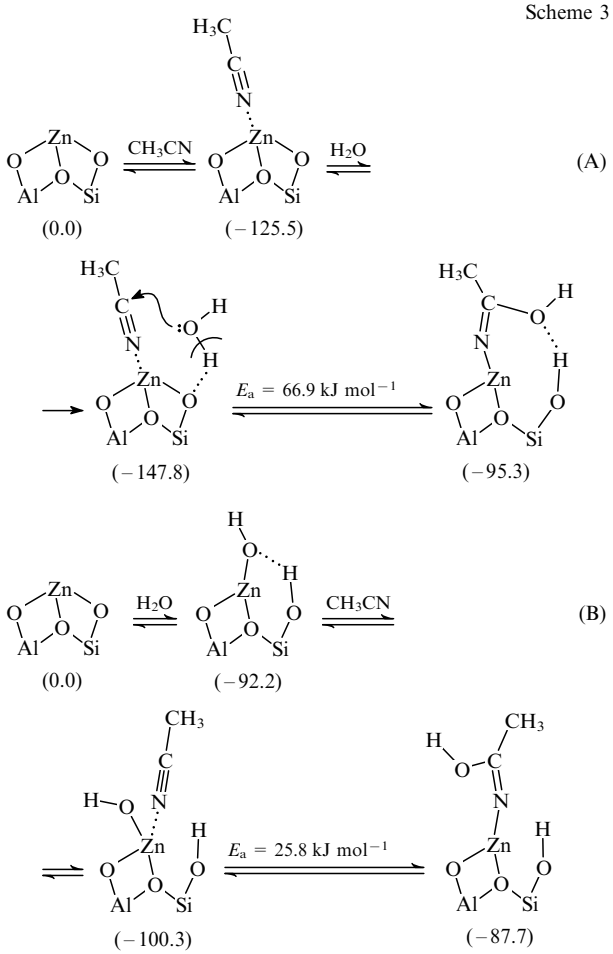
3. Catalytic reactions

One of the most promising and practically important directions in the theoretical chemistry of transition metal complexes is concerned with catalytic reactions whose mechanisms often cannot be studied in detail without application of theoretical methods. Actually, the idea of metal complex catalysis assumes that intermediates formed in the course of the reaction are highly labile due to which they often cannot be detected experimentally.

The mechanisms of catalytic reactions with the use of transition metal complexes have been the subject of much investigation, but the studies devoted to reactions involving nitrile complexes are few in number. Thus the mechanism of hydrolysis of acetonitrile adsorbed on Zn^{2+} ion-exchange zeolite was studied in detail by the DFT method.[116] The reaction involves three main steps, *viz*., hydration, isomerisation and desorption of the product. The first step includes two different processes, *viz*., the initial activation of the reagents and the primary nucleophilic attack of the water molecule on Zn or nitrile. Of eight possible mechanisms of the first step (involving one water molecule), two mechanisms (A and B) shown in Scheme 3 are preferable (in this scheme and in Scheme 4, the calculated heats of formation of intermediates (in kJ mol^{-1}) are given below the formulae in parentheses).[116]

The first mechanism involves activation of nitrile upon coordination followed by the nucleophilic attack of the water molecule on the oxygen atom of zeolite and concerted elimination of the OH group with the simultaneous nucleophilic attack at the carbon atom of nitrile. The second mechanism (in the presence of an excess of water) consists in primary adsorption of the H_2O molecule on zeolite followed by the cleavage of the O—H bond

Scheme 3

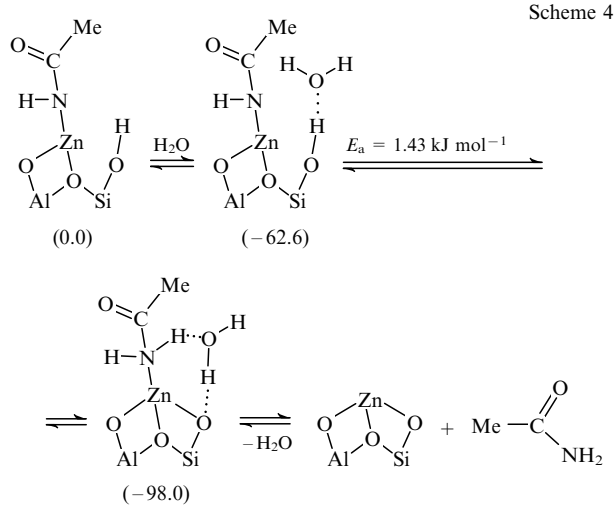


and migration of the proton on the oxygen atom of zeolite, coordination of acetonitrile to the zinc atom and migration of the OH group from metal to the carbon atom of nitrile.

The second step (isomerisation) involves conformational changes of the iminol fragment and migration of the proton from the OH group to the N atom through the formation of a four-membered transition state (or a six-membered state with the participation of the water molecule).

The third step, *viz*., desorption of acetamide, consists in the formation of the hydrogen bond between the hydrogen atom of the OH group and the new water molecule followed by the proton transfer from the water molecule to the nitrogen atom (Scheme 4) and desorption of acetamide by itself, which either occurs directly or proceeds with the participation of acetonitrile or water molecules.

Scheme 4



The mechanism of nickel-catalysed hydrogenation of nitriles giving rise to amines was proposed.[117] According to the results of EHMO calculations, the addition of the first hydrogen atom most probably leads to the attack at the carbon atom of nitrile to produce imidoethylidenes $CH_3CH=N-[Ni]$. Then either the second proton adds to the β-carbon atom to form the nitrene intermediate $CH_3CH_2-N=[Ni]$ or the imidoethylidene products undergo dimerisation.

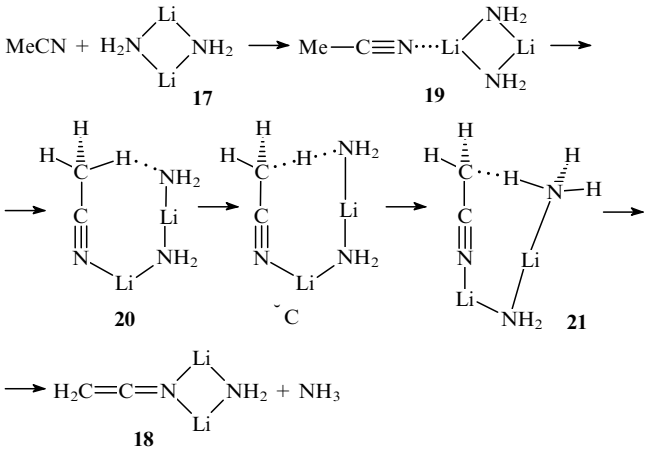
4. Other reactions

Hydrogenation of quinoline (Q) catalysed by $[Ru(NCMe)_2(CO).H(PR_3)_2][BF_4]$ was studied by the CNDO/2 method.[118] The bond between the metal atom and the acetonitrile ligand, which is located in the *trans* position with respect to the hydrogen atom, is weaker than that with another acetonitrile ligand located in the *cis* position with respect to this hydrogen atom. This arrangement facilitates the replacement of the former nitrile ligand in the reaction with Q although the reaction at the latter ligand also can proceed to a considerable extent. Based on the results of calculations and taking into account the data from kinetic and chemical studies,[119] the mechanism of this reaction was suggested.

In the experimental and theoretical investigation of the coordination transformations of the indenyl (Ind) ligand in the $[(\eta^5\text{-Ind})MoL_2(CO)_2]^{0/+}$ complexes (L are various ligands, including NCMe and CNMe),[120] the $\eta^5 \rightarrow \eta^3$-transformation of indenyl due to the addition of one more acetonitrile molecule to the $[(\eta^5\text{-Ind})Mo(NCMe)_2(CO)_2]^+$ complex was considered {this reaction did not proceed with the $[(\eta^5\text{-Ind})Mo(CNMe)_2(CO)_2]^+$ complex}. The driving forces for these processes were discussed based on the results of DFT and EHMO calculations.

The mechanism of the reaction of acetonitrile with dimeric lithium amide $[LiNH_2]_2$ (**17**) was examined by the MP2 and DFT methods and by the semiempirical methods (PM3 and MNDO).[121] The reaction involves deprotonation of acetonitrile accompanied by the formation of the dianionic $[(CH_2CN)/(NH_2)]^{2-} \cdot 2\,Li^+$ complex (**18**) (Scheme 5).

Scheme 5



The first step of the reaction affords the adduct of NCMe with the dimer of lithium amide (adduct **19**). This adduct is transformed into the 'open' dimeric complex **20**, which requires energy consumption of 47.7 kJ mol^{-1} (the MP2/6-31+G*//MP2/6-31+G* level, Table 8). Then, the migration of the proton from the CH_3 group of acetonitrile to the amino group occurs through the formation of a transition state (TS) to produce complex **21**. Finally, elimination of NH_3 gives rise to the reaction product **18**. Calculations by the PM3 method demonstrated that the intramolecular mechanism (including solvation) is 37.7 kJ mol^{-1} energetically more favourable than the intermolecular mechanism involving two dimeric molecules of lithium amide.

The driving forces for the chemical, electrochemical and photochemical activation of CO_2 by transition metal (Ir or Ni) complexes containing the isocyanide ligands were discussed relying on analysis of frontier molecular orbitals.[30]

Table 8. Relative energies of formation of the compounds **17**–**21** and the transition state (TS) (kJ mol^{-1}).

Compound	PM3	6-31G*//6-31G* [a]	6-31+G//6-31+G [a]	MP2/6-31+G*// MP2/6-31+G* [b]	B3LYP/6-311+G*// B3LYP/6-311+G* [b]	DGauss/DZVP A1 [b]
NCMe + **17**	0.0	0.0	0.0	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
19	−107.10	−45.97	−42.96	−49.82 (−51.79)	−42.45 (−44.25)	−42.79 (−47.23)
20	−2.80	10.26	9.42	−4.14 (−4.10)	−4.14 (−3.06)	–
PS	18.92	40.74	46.81	8.37 (0.75)	−1.42 (6.11)	−13.98 (−11.30)
21	−68.08	−40.44	−46.39	−55.43 (−59.62)	−63.81 (−68.75)	−63.60 (−67.70)
18	42.08	51.37	34.29	49.91 (47.90)	23.36 (27.63)	24.24 (29.64)

[a] The Hartree–Fock approximation; [b] the values, which were corrected for the zero-point energy scaled by a factor of 0.91, are given in parentheses.

V. Conclusion

To summarise, theoretical methods can successfully be used for the solution of practically important problems, such as investigations of electronic and geometric structures, spectroscopic properties, reactivities and reaction mechanisms of coordination compounds containing nitrile and isocyanide ligands. However, in spite of the fact that transition metal complexes with nitriles and isocyanides belong to an important class of coordination compounds (from both fundamental and applied standpoints), the theoretical chemistry of these compounds remains a poorly studied field of the modern coordination chemistry and applied quantum chemistry due, apparently, to the difficulties in describing coordination bonds in isocyanide and, particularly, in nitrile complexes.

In most cases, complexes with strong π-acceptor ligands, such as carbonyls, in which π-back donation most often prevails, are successfully described with the use of the Dewar – Chatt – Duncanson (DCD) model. However, this model must be applied to the interpretation of the properties of isocyanide complexes and, particularly, of nitrile complexes with caution because, being weak π-acceptors, nitriles and often isocyanides, form coordination bonds in which π-back donation is of secondary importance. The σ-component and Coulombic interactions make a large (and often the major) contribution to the coordination bonds in these compounds. As a result, there are often no direct correlations of the properties of these complexes with the π-acceptor ability of the ligand or with the difference between the π-acceptor and σ-donor properties.

Studies of the reactivities of coordination compounds are of paramount importance in modern chemistry. This problem is most efficiently solved by the combined employment of experimental and theoretical methods. Early in the development of applied quantum chemistry, theoretical analysis of the reactivities was restricted to examination of the electronic structures of the starting compounds. However, recent studies demonstrated that detailed data on the reaction mechanisms with consideration for all possible transition states and intermediates are necessary for the correct description of the chemical properties. A knowledge of the mechanisms and driving forces for chemical reactions helps essentially in the design of chemical experiments and target-directed syntheses. Modern computation tools and theoretical methods allow one to study the reactivities of complexes using high-level approximations. There is no doubt that theoretical studies of transition metal complexes, including those with nitrile and isocyanide ligands, will attract ever increasing interest in the near future.

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