Journal of Organometallic Chemistry, 408 (1991) 181–192
Elsevier Sequoia S.A., Lausanne
JOM 21669

Molecular orbital study of the bonding and reactivity of the diisocyanide complexes *trans*-$[Mo(CNR)_2(Ph_2PCH_2CH_2PPh_2)_2]$ and derived aminocarbyne compounds

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(Received October 9th, 1990)

Abstract

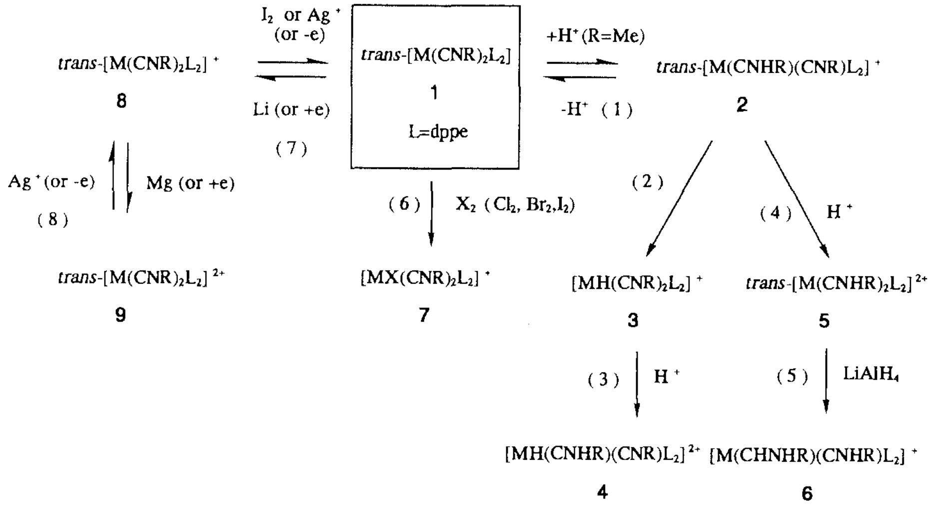
The bonding, structure, properties and reaction patterns of the isocyanide and aminocarbyne-type complexes of molybdenum have been investigated with the aid of EHMO-SCCC calculations and of frontier orbital theory. The results indicate that (i) β-protonation of a ligating isocyanide, in either the *trans*-$[Mo(CNMe)_2(dppe)_2]$ (**1**) or *trans*-$[Mo(CNHMe)(CNMe)(dppe)_2]^+$, is predominantly charge-controlled, whereas the α-nucleophilic attack at the dicarbene-type complex *trans*-$[Mo(CNHMe)_2(dppe)_2]^{2+}$ is orbitally controlled, and (ii) electrophilic attack should preferentially occur at the Mo atom of a molybdenum complex involving linear isocyanide ligands but at the N atoms of a complex with bent isocyanide ligands. The conversion of the hydride into the aminocarbyne complex, the oxidation of **1**, and its oxidative-addition reactions with halogens are interpreted in terms of FMO theory.

Introduction

Quantitative interpretation of the bonding, structure and reactions of organometallic complexes through high-quality *ab initio* quantum-chemical calculations is seldom attempted, owing at least in part, to the complexity of the calculations involved [1,2]. The potential value of such approach to understanding of the activation of unsaturated carbon ligands by their bonding to metal centres has been indicated by the application of semiempirical quantum-chemical calculations to a variety of reactions such as rearrangements of alkynes [3] and nucleophilic or electrophilic additions to ligated acetylides [4], allenes [5], vinylidenes [4], carbenes [4,6], or carbynes [6b,7].

Metal-ligand π-interactions in model Group VI carbyne complexes have been examined by application of extended Hückel calculations to understanding of the nucleophilic or electrophilic character of the ligating carbyne [7b]. In addition, electrophilic addition at the β-position, which is known to occur at vinylidene or alkynyl ligands, has been shown [4] to be charge-controlled. This type of electrophilic attack at a convenient unsaturated ligand may constitute an important reaction mode for carbyne complexes [8,9], which is clearly distinct from that involved in the preparation of Fischer- or Schrock-type carbyne compounds, typically involving an α-abstraction process from a carbene complex precursor. However, there has been only a rather limited number of theoretical studies of the β-electrophilic addition reaction [4,5].

For carbyne complexes the reaction involving β-electrophilic addition has been observed for electron-rich d^6 transition metal isocyanide complexes, typically *trans*-$[M(CNR)_2(dppe)_2]$ (M = Mo or W, R = alkyl or aryl, dppe = $Ph_2PCH_2CH_2PPh_2$) or *trans*-$[ReCl(CNR)(dppe)_2]$, which are satisfactory precursors for aminocarbyne-type species [9]. We thus initiated a systematic qualitative molecular orbital study of these complexes and our preliminary results with the rhenium compounds, already reported [10], indicate, e.g., that β-protonation at the isocyanide ligand is predominantly charge-controlled. We are now examining the more versatile group VI system by investigating the reactions of the carbyne and carbene complexes of molybdenum by the EHMO-SCCC method and in relation to the frontier-orbital theory. In particular, the bonding, structure and properties of the carbyne, carbene, and hydride complexes arising from protonation of the *trans*-$[Mo(CNMe)_2(dppe)_2]$ complex, together with some other related reaction modes are being studied (Scheme 1). To this end we are investigating the electronic structure and bonding characteristics of the reactants, intermediates, and products of the reactions under study as a first step. In order to simplify the study of the bonding of carbyne and carbene ligands, the fragment formalism is used, involving partitioning of the complexes into two closed-shell fragments: a metal-ligand fragment of the type $Mo(CNMe)(dppe)_2$, (C_{2v}), and the free isocyanide, CNMe, and/or $[CNHR]^+$ ligands.



Scheme 1

Results and discussion

Ground-state electronic structure of fragments

The CNMe fragment (C_{lig}–N–C_{term} = 156(1)°; C_{lig} and C_{term} denote the ligating and terminal carbon atoms, respectively), involved in the formation of the complex *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (**1**), being a 16 valence electrons species has the five crucial MO's schematically depicted in the left-hand side of Fig. 1. The $6a$ MO is about 2 eV above the next highest level and $10a$ is far below (ca. 4 eV) the next virtual orbital, so that the set is energetically quite isolated. The $7a$ and $6a$ MO's correspond to the two C_{lig}–N π-bonds. The HOMO ($8a$) is mostly a "lone pair" on the ligating carbon atom and an in-phase $p(C_{lig})$–p(N) σ-combination. About 35% of the HOMO comes also from an in-phase p(N)–$p(C_{ter})$ combination. Both LUMO ($9a$) and $10a$ could be viewed as the virtual counterparts of the π-bonding orbitals $6a$ and $7a$, respectively. Moreover, the slight inequivalence of the two lowest empty levels (ca. 0.19 eV) could account for ability of this ligand to form two non-equivalent π-bonds with the metal fragments [7a].

Inspection of the energies and percentage compositions of the four crucial orbitals ($10a$–$7a$) of the corresponding protonated fragment [CNHR]$^+$ clearly demonstrates their resemblance to those of the original moiety; these crucial FMO's are still well energetically isolated from the others. However, the protonation of the CNR fragment results in (i) a further polarization of the HOMO and LUMO's towards the ligating carbon; $6a$ is still stabilized significantly with respect to the $7a$, and (ii) a more significant destabilization of the $10a$ MO relative to the LUMO ($\Delta E = 1.18$ eV). The larger difference between these two empty MO's further enhances its ability to form two non-equivalent π-bonds with the metal fragments [7a].

Finally, the greater electron localization on the terminal carbon atoms of the two fragments makes them in practice the only ones that can form a bond to the metal, so that they are the ligating carbon atoms of the isocyanide and carbyne ligands.

The most crucial MO's of the metal–ligand fragment Mo(CNMe)(dppe)$_2$, belonging to the C_{2v} point group, are depicted schematically in the orbital energy level diagram shown in the righthand side of Fig. 1. It is evident from this figure that the pair of its $6b_2$ (HOMO) and $6b_1$ MO's is crucial in that it can π-donate to a π-acceptor ligand, such as CNMe or [CNHMe]$^+$, in both yz and xz planes. Furthermore, the $6b_2$, $6b_1$ and $13a_1$ orbital set constitutes the "t_{2g}" set of an octahedron; this orbital set is still well energetically isolated from the others. The LUMO of the fragment, labeled $14a_1$, is a σ-accepting orbital, able to form the sixth coordination bond to the missing isocyanide or carbyne ligand.

From the above discussion of the electronic structures of the fragments it is clear how a triple metal-carbon bond can be formed. In each instance the σ-type HOMO of isocyanide or carbyne ligand donates electron density to the LUMO of the metal fragment while the two empty π-type orbitals ($9a$ and $10a$) of the isocyanide or carbyne ligand accept electron density from the two highest occupied π-orbitals of the metal fragment. With this in mind, we now look more deeply into the ground-state electronic structures and bonding of the complexes under consideration.

Ground-state electronic structure and bonding of complexes

The interaction diagram for [Mo(CNMe)(dppe)$_2$] and CNMe is shown in Fig. 1. On the basis of standard perturbation theoretical arguments [11] the composition of

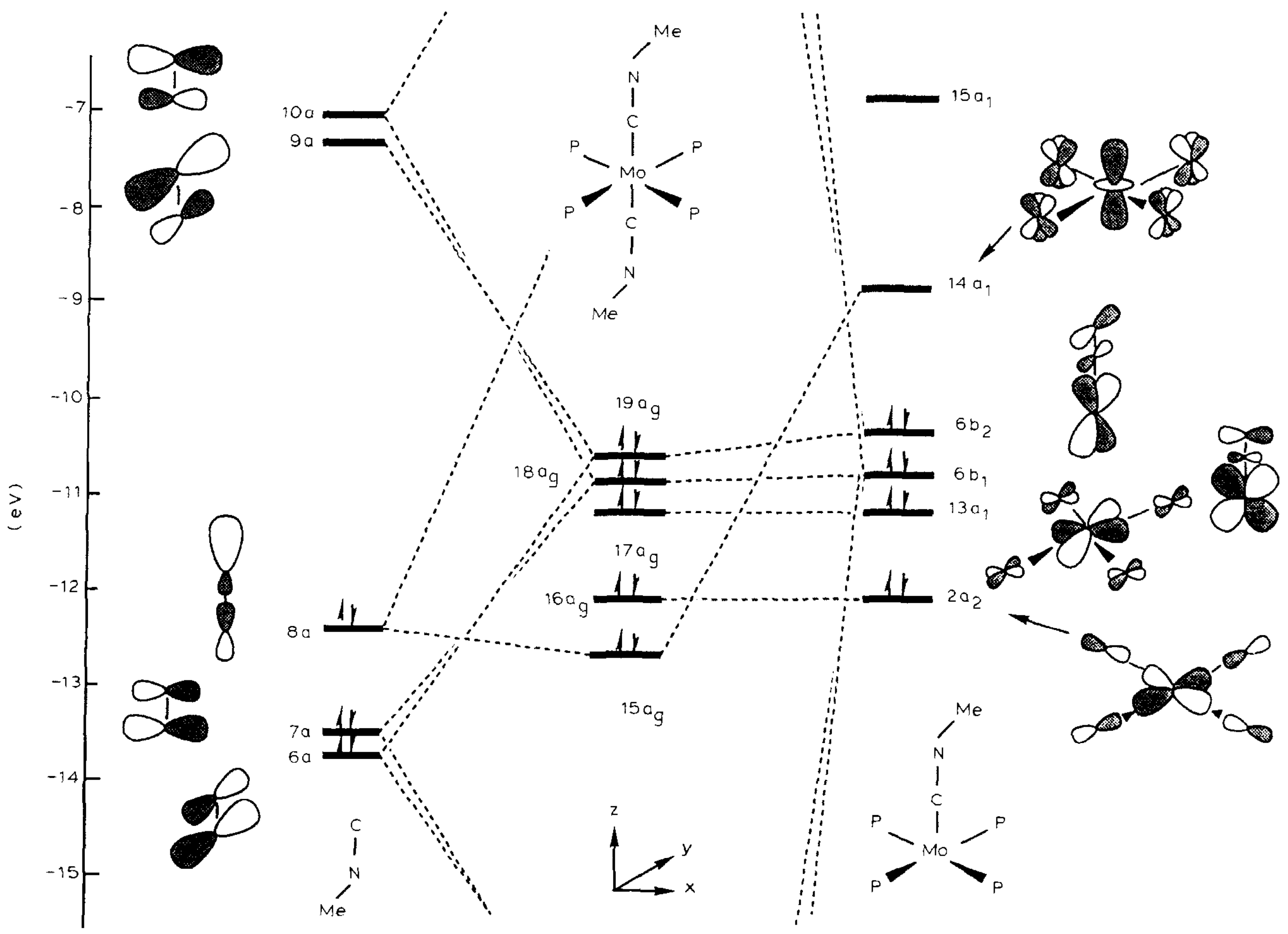
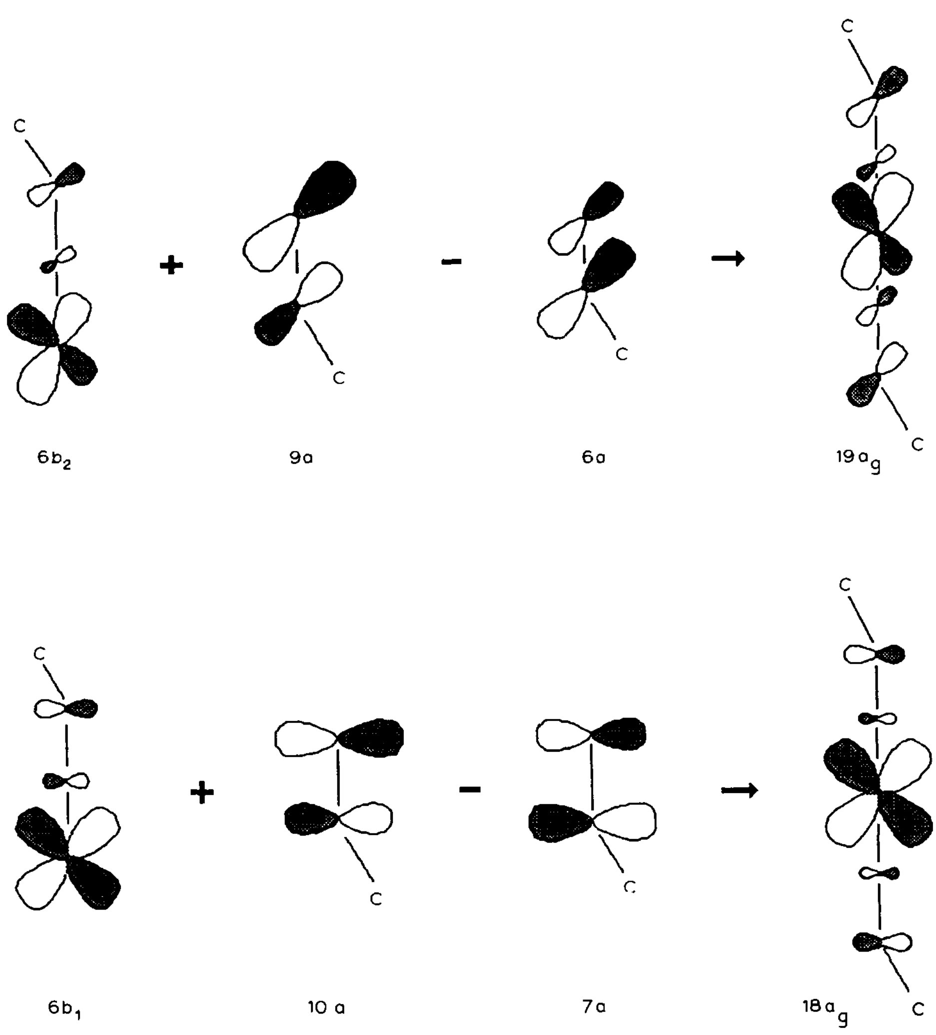
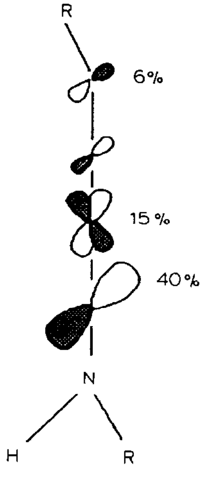


Fig. 1. Diagram showing the interaction of the frontier orbitals of Mo(CNMe)(dppe)$_2$ with those of CNMe in *trans*-[Mo(CNMe)$_2$(dppe)$_2$].



Scheme 2

most of the MO's of complex **1** can be readily understood. Scheme 2 shows the composition of the two highest occupied MO's of **1**, $19a_g$ and $18a_g$, resulting from an intermolecular perturbation. In Scheme 2 the relative phases of the fragment orbitals have been chosen so that the S_{nj} overlap integrals between the corresponding MO's of the fragments Mo(CNMe)(dppe)$_2$, and CNMe, are positive. The third "t_{2g}" orbital ($13a_1$) is unaffected by isocyanide complexation. Both $19a_g$ and $18a_g$ (separated by only 0.17 eV) are formally metal d-centered ($|yz>$ (56%) and $|xz>$ (50%), respectively) the rest being made up of N– $|y>$ or $|x>$ (ca. 7%) and C_{lig}–$|y>$ or $|x>$ (ca. 3%). Due to their energy separation from the LUMO and the $16a_g$ MO (1.86 and 1.69 eV, respectively) these two MO's are energetically well separated from the others. Moreover, they exhibit π-bonding interactions between the Mo and the C_{lig} atoms along with weak π-antibonding ones between the C_{lig} and the N atoms but owing to the small C_{lig} coefficients in these MO's the Mo–C_{lig}



A

π-bonds should not be strong. These conclusions are in agreement with the short Mo–C bond length, indicated by the X-ray analysis [12] of complex **1**, and the low ν(C≡N) value observed [13] in the IR spectrum of this compound; moreover, a strengthening of the C–N bonds of the isocyanide ligands would be expected as a result of electron removal from any of these MO's (see below). Finally, there is a σ-donation of electron density from $8a$ (HOMO) of the isocyanide to $14a_1$ (LUMO) of the $Mo(CNMe)(dppe)_2$ fragment.

The electronic ground state of *trans*-$[Mo(CNHMe)(CNMe)(dppe)_2]^+$ (**2**) is quite analogous to that of **1**, the only differences being (i) the shift of the eigenvalues of **2** towards lower energy values and (ii) the polarization of most of its MO's mainly towards the C_{lig} atom of the protonated CNR group of the complex, this effect being more evident in the LUMO. Actually, the LUMO, (**A**), of **2** is mostly a C_{lig} (the next-neighboring atom to the protonated nitrogen) $|y>$ -centered MO, but about 21% of the LUMO still comes from an in-phase $|yz>(MO)-|y>(C_{lig})$ combination.

On the basis of the present calculations one would expect two inequivalent metal–carbon π-type bonds in the complexes studied. Additional data concerning the overlap population values of the most relevant σ- and π-bonds of the two compounds, summarized in Table 1, clearly show that these expectations are correct.

Table 1

σ- and π-overlap population values for the most relevant coordination bonds of **1** and **2**

Bonds	σ	P^{π}_{xz} [a]	P^{π}_{yz}
Mo–C	0.42 (0.52) [b]	0.05 (0.19)	0.07 (0.22)
C_{lig}–N	0.87 (0.77)	0.37 (0.21)	0.39 (0.29)

[a] P^{π}_{xz} and P^{π}_{yz} stand for the π-overlap population values on the xz and yz planes, respectively. [b] Values in parentheses correspond to the protonated complex **2**.

Moreover, the protonation of the isocyanide complex results in significant changes in the net charges on its most relevant atoms as a result of charge-transfer interactions via the σ-network of the complex. This charge-transfer is consistent with the significant changes observed in the σ-overlap populations of both C–NHMe and Mo–CNHMe bonds. Furthermore, the concomitant changes in the π-populations of the same bonds are also fully consistent with the rehybridization of the nitrogen atom upon ligating of the proton. All these effects could also account for a strengthening of the Mo–C bond with a concomitant weakening of the C–N bond (evidenced by a lowering of the ν(CN) frequency, e.g. to 1518 cm^{-1} in **2**) [14], as a result of β-protonation at the isocyanide ligand (eq. 1a, where **Mo** stands for *trans*-$\mathrm{Mo(dppe)_2}$); moreover, in agreement with the expected decrease of the π-electron acceptance by the isocyanide ligand which did not undergo protonation in this reaction, there is also a strengthening of the corresponding C–N bond, as indicated by IR data (in complex **2**, the ν(CN) frequency of the isocyanide ligand has a value [14] 2163 cm^{-1}, well above that observed [13] for the parent compound **1**, 1862 cm^{-1}).

$$\underset{(\mathbf{1})}{\mathrm{MeN{\equiv}C{=}\mathbf{Mo}{=}C{\equiv}NMe}} \xrightarrow{H^+} \underset{(\mathbf{2})}{[\mathrm{MeN{\equiv}C{-}\mathbf{Mo}{\equiv}C{=}NHMe}]^+} \qquad (1a)$$

FMO's approach to the reactions with electrophiles and / or nucleophiles

From the molecular orbital description of the complexes, the frontier molecular orbital approach [15], and the electrostatic interactions, the following conclusions can be drawn.

The nature of the $19a_g$ and $18a_g$ of **1** (mostly localized (ca. 56%) over the N–C–Mo–C–N nuclear framework) considered along with the high frontier density values, P_r(HOMO) [16] for the Mo (ca. 0.47) and N (ca. 0.1) atoms and the negative net charges, q_r ($q_\mathrm{N} = -0.14e$ and $q_\mathrm{Mo} = -0.13e$) of the same atoms, strongly suggests that these two atoms should be the nucleophilic centers for proton attack of the isocyanide complexes. However despite the high P_r(HOMO) value for molybdenum direct protonation of the Mo atom seems rather unlikely owing to the significant increase in the negative net charge values of the nitrogen atoms upon bending of the -CNMe group (Fig. 2). In this respect, the protonation of **1** seems to be predominantly charge-rather than orbital-controlled. It should also be emphasized here that there is a stabilization of both the HOMO and LUMO's of **1** upon bending of the CNMe group, thereby resulting in a more stable species. All these considerations account well for both the protonation processes that complex **1** is known to undergo [17] and that observed [10] for *trans*-$\mathrm{[ReCl(CNMe)(dppe)_2]}$. They are also in line with the different chemical behavior of the *trans*-$\mathrm{[Mo(CNR)_2(dppe)_2]}$ complex, (where R = Ar) which affords, upon protonation, the $\mathrm{[MoH(CNR)_2(dppe)_2]^+}$ complex, rather than **2**. The inability of the CNR groups (R = Ar), of *trans*-$\mathrm{[Mo(CNR)_2(dppe)_2]}$ to adopt a significantly bent CNR angle (possibly due to both electronic and steric effects) is the most probable reason for the choice of the molybdenum nucleophilic center by the approaching proton. If this is correct, it suggests that the conformation of the isocyanide ligands could play an important role in determining the final products of reactions between Mo isocyanide complexes and electrophiles. As a consequence, the electrophilic attack should prefer-

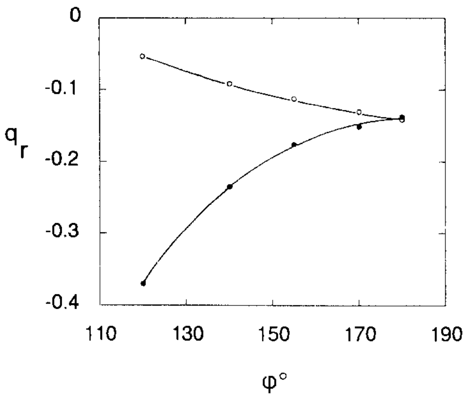
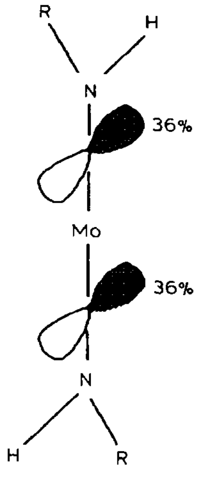


Fig. 2. Variation of the net atomic charge values, q_r, with the CNMe bending angle, φ°, for the Mo (○) and N (●) atoms of the *trans*-[Mo(CNMe)$_2$(dppe)$_2$] complex **1**.

entially occur at the Mo atom of Mo complex involving linear isocyanide ligands and at the N atoms of a complex with bent isocyanides.

Furthermore, possibly due to: (a) the coexistence of two more negative centers (the C_{lig} (-0.14 e) and the Mo (-0.01e) atoms) in the vicinity of the N–H group (negative "channel") of **2**, (b) the opposite net charges of the N and H atoms of the same group, and (c) the favourable character of its crucial MO's ($19a_g$ and $18a_g$), which is also delocalized over these three "channel" atoms, an intramolecular migration (1,3-hydrogen shift) of the H atom of the [CNHMe]$^+$ moiety towards the negatively charged Mo atom (observed in polar solvents) to give the hydride [MoH(CNMe)$_2$(dppe)$_2$]$^+$ species (**3**, eq. 2, Scheme 1) seems probable. The polar solvent could possibly, by solvating the complex, cause a weakening of the N–H bond of **2**, followed by the stabilization of the most polar seven-coordinate structure formed by the 1,3-hydrogen migration. EHMO calculations performed on the three high-symmetry seven-coordinate [MoH(CNMe)$_2$(dppe)$_2$]$^+$ polyhedra (CO, CTP, PB) did, in fact, reveal a positive net charge value of ca. $+0.15$e and a negative one of ca. -0.18e on the Mo and the two N atoms, respectively. However, if the least-motion path for the intramolecular attack of the nitrogen's proton is adopted and considered along with the calculated trend of the total electronic energy derived for the same seven-coordinate polyhedra (CO > CTP > PB), the capped-octahedral structure for **3** seems the most probable, in agreement with observation [18]. The further protonation by acid of this latter complex in solution, to give the seven-coordinate hydride-carbyne [MoH(CNHMe)(CNMe)(dppe)$_2$]$^{2+}$ species (**4**, eq. 3, Scheme 1), can be also accounted for in terms of: (i) the character of the HOMO for the CO structure of **3**, which is formally metal *d*-centered $\{|yz>$ (22%), $|xz>$ (20%) and $|x^2-y^2>$ (15%)$\}$ mostly localized (ca. 79%) over the N–C–Mo–C–N nuclear framework, and (ii) the high negative charge of -0.146 on the N atoms. Hence, this protonation, controlled by both charge- and frontier-orbital interactions, should occur at a N atom of the CO structure of **3**.

Finally, the negative net charges on both nitrogen atoms of **2** also accounts well for a charge- rather than an orbital-controlled second protonation at its isocyanide N to give the [Mo(CNHMe)$_2$(dppe)$_2$]$^{2+}$ (**5**, eq. 4, Scheme 1) complex. Moreover, the LUMO (**B**) of this latter complex is mostly localized on its two C_{lig} atoms,



B

which also exhibit high P_r(LUMO) values (ca. 0.43). Therefore, the nucleophilic attack of the complex, being mostly orbital- rather than charge-controlled, should occur at the C_{lig} atom of the CNHMe group, to give complex **6** (eq. 5, Scheme 1).

Oxidation reactions

As shown above, the two occupied FMO's of **1**, being mostly localized over the N–C–Mo–C–N nuclear framework, are π-bonding and π-antibonding between Mo–C_{lig} and C_{lig}–N, respectively. These findings considered along with (i) the slight inequivalence of these two MO's, which are separated by only 0.17 eV; (ii) their excellent space-orientation towards the vacant coordination sites of the complex; and (iii) the negative net charges on the Mo, C_{lig} and N atoms, make these two occupied FMO's unique candidates for participation in electron-transfer reactions through frontier MO's interactions. Actually, either of these two occupied FMO's can interact with the LUMO of the oxidant molecule, possibly through an S_N2 transition state, to give the final oxidation product. Obviously, these interactions will result in an electron transfer from the $19a_g$ and $18a_g$ of **1** to the oxidant's LUMO, possibly via the molybdenum atom. Such expectations are in excellent agreement with the observed reactions of *trans*-$[Mo(CNR)_2(dppe)_2]$ with the molecular halogens, Cl_2, Br_2 and I_2 [19]. The oxidation of **1** by dichlorine and/or dibromine in polar solvents affords (possibly via an oxidative addition to **1**) the seven-coordinate $[MoX(CNR)_2(dppe)_2]^+$ complexes (**7**, eq. 6, Scheme 1), whereas the analogous treatment of **1** with diiodine gives the monocationic $[Mo(CNR)_2(dppe)_2]^+$ complex (**8**, eq. 7, Scheme 1). It should be also mentioned here that, on the basis of the calculated theoretical trend in the total electronic energies of the three high-symmetry seven-coordinate polyhedra (PB > CO > CTP), a pentagonal bipyramidal structure would be expected for the final seven-coordinate complex, possibly produced by a rehybridization of its oxidized central metal-atom. This is in good agreement with a PB and/or CO structure proposed for the

$[MoBr(CNC_6H_4Me\text{-}4)_4(dppe)_2]Br$ complex on the basis of experimental data [19]. The inability of diiodine to give an analogous seven-coordinate structure might be due to the steric hindrance that would be involved in the PB structure adopted by the seven-coordinated halide complexes.

Finally, the electronic structures of the two oxidized paramagnetic complexes *trans*-$[Mo(CNR)_2(dppe)_2]^+$ (**8**, eq. 7, Scheme 1) and *trans*-$[Mo(CNR)_2(dppe)_2]^{2+}$ (**9**, eq. 8, Scheme 1) have been examined. Calculations showed that the $19a_g$ and $18a_g$ of **1** are the two highest singly- and/or doubly-occupied MO's of complexes **6** and **7**. In each case there is still a significant stabilization of the energies of the two occupied FMO's in both paramagnetic complexes compared with those in **1**. In addition, in view of the significant variation of the net charge on molybdenum, which becomes more and more positive with increase in its oxidation state, it is very probable that this atom is mainly the center of the electron withdrawal upon oxidation. Moreover, the electron withdrawal from the two occupied FMO's of **1** will also result in a weakening of the $Mo-C_{lig}$ π-bonding interactions and a concomitant strengthening of the $N-C_{lig}$ π-bonding interactions. These effects also account well for (a) the increase of the $\nu(C{\equiv}N)$ frequencies for the mono- and dicationic six-coordinate complexes relative to those for their precursor complex **1**, observed experimentally [13,19], (b) the two successive anodic oxidations [13,20] of **1**, the first one being reversible one-electron process, whereas the second one, at a higher potential (which also involves a single-electron transfer) is irreversible in the presence of lithium halides [13], but reversible in a non-coordinating electrolyte, THF/0.2 *M* $[Bu_4N][BF_4]$.

Conclusions

Our results indicate that the β-protonation at a ligating isocyanide, in either *trans*-$[M(CNMe)_2(dppe)_2]$ or *trans*-$[M(CNHMe)(CNMe)(dppe)_2]^+$, is predominantly charge-controlled, as observed for the related *trans*-$[ReCl(CNR)(dppe)_2]$ complexes [10] and for β-electrophilic addition to vinylidene or alkynyl ligands [4]. They also indicate that the electrophilic attack should preferentially occur at the Mo atom of a Mo complex involving linear isocyanide ligands and at the N atoms of a complex with bent isocyanide ligands.

In contrast, α-nucleophilic attack at the dicarbene-type complex *trans*-$[Mo(CNHMe)_2(dppe)_2]^{2+}$ is orbital-controlled, as is known to be the case for other α-additions to carbene [6] or cationic carbyne [6b,7a] complexes.

The conversion of the carbyne into the hydride complex $[MH(CNMe)_2(dppe)_2]$ is accounted for in terms of an intramolecular 1,3-hydrogen shift from the nitrogen to the metal atom along a negative "channel". The oxidative-addition reactions of the diisocyanide complexes by molecular halogens and also their oxidation are interpreted in terms of FMO's, involving electron transfer or removal from the HOMO.

The study also provides a FMO rationalization for the infrared-spectroscopic properties of the complexes, and suggests a CO structure for the hepta-coordinated hydride and a PB structure for the halide compounds.

Calculational details

Calculations were carried out by the extended Hückel LCAO-MO method with self-consistent charge and configuration (EHMO-SCCC) [21], by use of the FORTICON-8 computer program [22]. In these iterative calculations, the modified Wolfsberg–Helmholz formula [23] for the off-diagonal matrix elements (H_{ij}) was used. The value of 1.75 was used throughout for the parameter K. Orbital exponents for carbon, nitrogen, hydrogen, and phosphorus atoms, the basis set of valence AO's of the latter atom consisting of $3s$, $3p$ and $3d$ functions, were those used previously [24,25]. It should be emphasized that inclusion of the phosphorus d AO's in the basis set resulted in more reasonable net charges on the atoms of the neutral complex **1**. The basis set of valence AO's for Mo, consisted of $5s$, $5p$ and $4d$ functions; $4d$ AO's were treated as contracted linear combinations of two Slater-type functions. The exponents of the two d AO's along with their coefficients were also taken from the above references. The parameters used for Cl, were taken from Ref. 26.

The geometry of the complex on which the EHMO calculations were performed was based on the X-ray data available for the *trans*-[Mo(CNMe)$_2$(dppe)$_2$] (C_i) complex [12]. The [CNHMe]$^+$ moiety, used in the construction of both *trans*-[Mo(CNHMe)(CNMe)(dppe)$_2$]$^+$ and *trans*-[Mo(CNHMe)$_2$(dppe)$_2$]$^{2+}$ complexes was that of the complex *trans*-[ReCl(CNHMe)(dppe)$_2$]$^+$ [27]. The Mo–CNHMe bond length was set at 1.945 Å. The three high-symmetry polyhedra of the seven-coordinate [MoH(CNMe)$_2$(dppe)$_2$]$^+$ and [MoCl(CNMe)$_2$(dppe)$_2$]$^+$ structures (capped octahedron (CO), capped trigonal prism (CTP) and pentagonal bipyramid (PB)) were constructed by using the procedure described by Hoffmann et al. [28]; the bond-lengths used were those of the parent *trans*-[Mo(CNMe)$_2$(dppe)$_2$] complex (the Mo–H and Mo–Cl bond-lengths were set at 1.65 and 2.45 Å, respectively). For simplicity, as well as to avoid the use of very large basis sets, all aryl substituents of the dppe ligands were replaced by hydrogen atoms (P–H bond length 1.42 Å).

In all calculations a right-hand Cartesian coordinate system was used, with the z axis pointing toward the vacant coordination site or toward the ligating carbon atom. This facilitates examination of the axial coordination bonds, puts the two dppe ligands of the metal into the xy plane and the metal at the origin.

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