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PREPARATION AND PROPERTIES OF DINITROGENMOLYBDENUM COMPLEXES

IX *. REACTIONS OF *trans*-$Mo(CO)(N_2)(Ph_2PCH_2PPh_2)_2 \cdot \frac{1}{2} C_6H_6$ AND $Mo(CO)(Ph_2PCH_2CH_2PPh_2)_2$ WITH LEWIS BASE LIGANDS

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Summary

The complexes $Mo(CO)L(DPE)_2$ (L = amides, imidazoles, amines, nitriles, pyridines, and olefins; DPE = $Ph_2PCH_2CH_2PPh_2$) have been obtained by the reaction of *trans*-$Mo(CO)(N_2)(DPE)_2 \cdot 1/2\ C_6H_6$ or $Mo(CO)(DPE)_2$ with the corresponding ligand. The C≡O stretching vibrations in the IR spectra of these complexes are found in the range of 1680–1880 cm^{-1}. The variation in ν(C≡O) is interpreted in terms of donor and acceptor properties of the ligands. The exceedingly low ν(C≡O) of the complexes of amides and imidazoles may be due to their strong π-donor property. The complexes containing nitriles, NH_3, and 4-aminopyridine are stable, but the other ligands are readily lost on recrystallization under N_2, affording *trans*-$Mo(CO)(N_2)(DPE)_2 \cdot 1/2\ C_6H_6$. The coordination abilities of the ligands are also greatly affected by their bulk. In the reactions of *trans*-$Mo(N_2)_2(DPE)_2$ with NH_3, one molecule of ligating dinitrogen is replaced to give $Mo(N_2)(NH_3)(DPE)_2$.

Introduction

In the preceding paper [1], we reported the synthesis and structure of the novel mono-dinitrogen complex, *trans*-$Mo(CO)(N_2)(DPE)_2 \cdot 1/2\ C_6H_6$ (I) (DPE = $Ph_2PCH_2CH_2PPh_2$) and the first isolable five-coordinate Mo^0 complex, $Mo(CO)(DPE)_2$ (II). As reflected in the higher energy of $\nu(N_2)$ of I compared with that of *trans*-$Mo(N_2)_2(DPE)_2$, the amount of back-donation from the metal to N_2 decreases due to the presence of a strong π-acceptor CO ligand in the *trans* position, resulting in the weakening of the Mo–N_2 bond. Consequently,

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* For part VIII see ref. 14.

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TABLE 1

CARBONYL COMPLEXES OF π-DONORS

Compound		ν(C≡O) (cm^{-1})	ν(C=O) (cm^{-1})		Color	Yield (%)	Analysis found (calcd.) (%)		
			Coordinated	Free [15]			C	H	N
IIIa	Mo(CO)$\{HCON(CH_3)_2\}$(DPE)$_2$	1687	1638	1716	dark red	77	67.5 (67.7)	5.7 (5.6)	1.3 (1.3)
IIIb	Mo(CO)($HCONH_2$)(DPE)$_2$	1677	1636	1734	dark red	67	67.5 (67.4)	5.5 (5.5)	1.1 (1.4)
IIIc	Mo(CO)$\{HCON(C_2H_5)_2\}$(DPE)$_2$	1693	1628		dark red	75	68.2 (68.2)	5.8 (5.8)	1.3 (1.4)
IIId	Mo(CO)$\{HCON(C_6H_5)_2\}$(DPE)$_2$	1720	1639		dark red	69	71.1 (70.9)	5.5 (5.3)	1.1 (1.3)
IIIe	Mo(CO)($HCONHCH_3$)(DPE)$_2$	1694	1644	1724	dark red	72	67.4 (67.0)	5.4 (5.5)	1.2 (1.4)
IIIf	Mo(CO)$\{CH_3CON(CH_3)_2\}$(DPE)$_2$	1693	1628	1683		3 [a]			
IVa	Mo(CO)(Imidazole)(DPE)$_2$	1678			orange	70	67.5 (68.0)	5.7 (5.3)	2.9 (2.8)
IVb	Mo(CO)(*N*-Methylimidazole)(DPE)$_2$	1705			orange red	78	68.2 (68.2)	5.8 (5.4)	3.0 (2.8)

[a] The yield was estimated from the IR spectrum of the product mixture (see Experimental), since the complex cannot be isolated and was accompanied by II ($CH_3CON(CH_3)_2$/Mo = 130).

the dinitrogen ligand of I is easily released from the metal to afford II. The five-coordinate Mo^0 complex II is a prototype for the potential intermediate in S_N1 processes of six-coordinate Group VI metal complexes. Therefore, I and II are expected to react with Lewis bases which have appropriate electronic and steric properties. In order to gain further knowledge of the character of this dinitrogen-binding site, $Mo(CO)(DPE)_2$, we have now studied the reactions of several Lewis bases with I or II. Here we report the preparation and some chemical properties of a series of $Mo(CO)L(DPE)_2$, where L = amides, imidazoles, amines, nitriles, pyridines, and olefins.

Results and discussion

Coordination of Lewis base ligands to the vacant site of Mo(CO)(DPE)₂

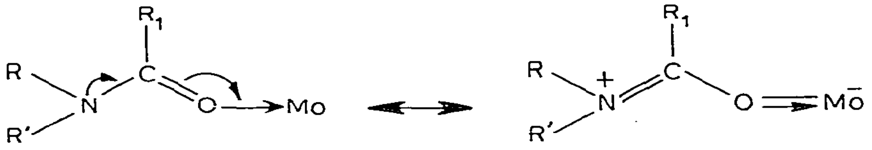
Various kinds of Lewis bases coordinate to the vacant site of the five-coordinate complex II. They may be divided into two groups according to whether or not they are replaced by dinitrogen on recrystallization of their six-coordinate complexes under dinitrogen. The complexes of amides, amines, pyridines, and ethylene are generally converted to I on recrystallization under dinitrogen. The complexes of amides can be prepared under dinitrogen when an excess of the amide is added, whereas the other complexes cannot be obtained under similar conditions. Therefore, reactions under argon are required to obtain the latter complexes. On the other hand, the complexes with carbon monoxide, nitriles, NH_3, and 4-aminopyridine can be recrystallized under dinitrogen. Their preparations are carried out in the presence of an excess of the Lewis base under dinitrogen. Compared with carbon monoxide and nitriles, ammonia and 4-aminopyridine are weaker ligands with respect to the vacant site of $Mo(CO)(DPE)_2$ since ammonia and 4-aminopyridine are slowly replaced by N_2 on bubbling dinitrogen into a solution of the complexes. The complexes of imidazoles are partly converted to I on recrystallization and their coordination abilities, therefore, seems to be between those of two groups. Based on these results, the coordination ability of Lewis bases toward $Mo(CO)(DPE)_2$ is roughly estimated to decrease in the following order: CO>nitriles>NH_3~4-aminopyridine>N_2~imidazoles>amides>amines~pyridines~ethylene.

Reactions with amides

The complex II reacts with several formamides at room temperature under argon to give reddish brown crystals of $Mo(CO)(HCONRR')(DPE)_2$ [R = R' = CH_3 (IIIa), H (IIIb), C_2H_5 (IIIc), C_6H_5 (IIId), or R = H and R' = CH_3 (IIIe)] (Table 1). The striking characteristic of IIIa—e lies in $\nu(C\equiv O)$ in their IR spectra, which is lowered to below 1700 cm^{-1}, except for IIId. The carbonyl oxygen of the formamides seems to be the donor in all these complexes. Coordination through the nitrogen lone pair is excluded since the complex II combines only with small primary amines and secondary amines to give Mo(CO)-(amine)$(DPE)_2$ (see below). It does not combine with tertiary amines such as $N(CH_3)_3$, but, on the other hand, it does undergo complex formation with bulky formamides such as $HCON(C_6H_5)_2$.

The complexes IIIa—e have also a strong IR band assigned to $\nu(C=O)$ of coordinated amides, which show a considerable shift to lower frequency on coordination. The shifts are of the order 70—100 $\mathrm{cm^{-1}}$, compared with unassociated amides in the vapor state. This seems consistent with coordination through oxygen, while coordination through nitrogen would require a shift of $\nu(\mathrm{C{=}O})$ in the opposite direction since the resonance of the carbonyl group with the nitrogen lone pair would be hindered in such a case [2]. One would suppose that H—(C=O) bond cleavage of formamides proceeds to yield carbamoyl complexes. But this is excluded since (1) recrystallization of IIIa—e under dinitrogen atmosphere readily releases the formamides to give I and (2) IR spectra of *N,N*-dimethylcarbamoyl ligands are known to show $\nu(\mathrm{C{=}O})$ in the range of 1565—1615 $\mathrm{cm^{-1}}$ [3].

As described previously [1], the finding that formamides are much more effective in promoting back-donation to CO than is expected from their protonic basicity may arise from their good π-electron donating property (eq. 1). Although ^{31}P NMR spectra were not observable owing to their poor solubility, the complexes IIIa—e are considered to have *trans* configuration (see below). Since ligands coordinated *trans* to CO will compete for π-electron density on the metal, the binding of CO to $\mathrm{MoL(DPE)_2}$ will be sensitive to the π-donating ability of the axial ligand L. Good π-donors will increase the electron density available for metal to CO π-back bonding, resulting in the tight binding of both CO and L.



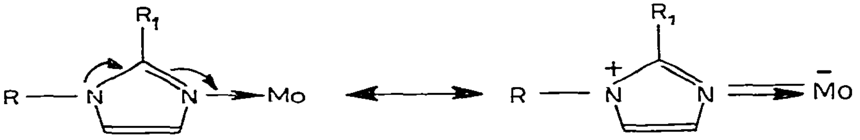
(1)

The series of increasing donor strength of formamides toward $\mathrm{Mo(CO)(DPE)_2}$ derived from $\nu(\mathrm{C{\equiv}O})$ shown in Table 1 is: $\mathrm{HCON(C_6H_5)_2} < \mathrm{HCONHCH_3} < \mathrm{HCON(C_2H_5)_2} < \mathrm{HCON(CH_3)_2} < \mathrm{HCONH_2}$. This is quite different from the series predicted on the basis of inductive effects. The electron release shown in eq. 1 requires coplanarity of the groups attached to nitrogen with the N, C, O and Mo atoms; therefore, $\mathrm{HCONH_2}$ could be a stronger donor than *N*-substituted amides because the coplanarity may be sterically difficult in the complexes of bulky amides.

The reaction of II with a large excess of *N,N*-dimethylacetamide was investigated. The reaction mixture showed weak IR bands at 1693 $\mathrm{cm^{-1}}$ [$\nu(\mathrm{C{\equiv}O})$] and 1628 $\mathrm{cm^{-1}}$ [$\nu(\mathrm{C{=}O})$] indicating the partial formation of the corresponding carbonyl-amide complex IIIf. Attempts to isolate the complex were unsuccessful.

Reactions with imidazoles

Imidazoles are potential π-donors because we can consider the bonding in terms of the resonance between the canonical forms as shown in eq. 2.



(2)

Complex II also reacts with imidazole or *N*-methylimidazole to form the corresponding complex Mo(CO)(Imidazole)(DPE)$_2$ (IVa) or Mo(CO)(*N*-methylimidazole)(DPE)$_2$ (IVb) with very low $\nu(C{\equiv}O)$ (Table 1). Like their formamide analogs, $\nu(C{\equiv}O)$ of IVa is lower than that of its *N*-methyl derivative IVb. The complex II is unreactive to 2-methylimidazole, which is in accord with the poor coordination ability of acetamides. When R_1 is CH_3 instead of H in eqs. 1 and 2, there may be a pronounced increase in steric repulsion between R_1 and the phenyl groups of DPE. Benzimidazole also cannot coordinate to II. The failure to obtain the complexes of pyrazole suggests the importance of the π-donor property.

Reactions with amines

Treatment of I with bubbling NH_3 immediately gives Va. This reaction is reversible and on bubbling N_2 into the solution of Va, I is recovered almost quantitatively (eq. 3) *

$$\underset{\text{(I)}}{\mathrm{Mo(CO)(N_2)(DPE)_2}} \underset{N_2}{\overset{NH_3}{\rightleftharpoons}} \underset{\text{(Va)}}{\mathrm{Mo(CO)(NH_3)(DPE)_2}} \qquad (3)$$

Complex II reacts with several aliphatic primary amines under argon to afford Mo(CO)(RNH$_2$)(DPE)$_2$ [R = CH_3 (Vb), C_2H_5 (Vc), n-C_3H_7 (Vd), i-C_3H_7 (Ve), or n-C_4H_9 (Vf)] (Table 2). On recrystallization under dinitrogen, these complexes are completely converted to I. In contrast, Va can be recrystallized under dinitrogen. In the case of all the normal-chain alkyl amines tested and isopropylamine, the adduct can be isolated. This can be contrasted with the attempted preparation of the corresponding isobutyl- or t-butylamine complex. apparently these ligands are too bulky to fit the crowded site of Mo(CO)(DPE)$_2$. As described below, however, isobutyronitrile, which is sterically similar to isobutylamine, can coordinate to the site, suggesting that electronic effects also are important.

Coordination of secondary amines seems to be difficult. Only in the case of dimethylamine and diethylamine were the adducts detectable by IR, but they could not be isolated. In the case of aliphatic tertiary amines, II was recovered unchanged. It may be concluded that the coordination ability of amines is strongly dependent on their steric bulk; NH_3 is the only successful competitor against N_2.

The fact that the amine ligands, which have no π-electron acceptor capacities, can coordinate to the vacant site of Mo(CO)(DPE)$_2$, is consistent with the proposal that the dinitrogen binding site has a strong σ-acceptor capacity [5]. No clear relationship, however, was observed between $\nu(C{\equiv}O)$ and the σ-donor ability of amines which may be estimated from ionization potentials (Table 2).

Treatment of *trans*-Mo(N$_2$)$_2$(DPE)$_2$ with NH_3 affords a dark red solution, from which dark red needles analyzing as Mo(N$_2$)(NH$_3$)(DPE)$_2$ are obtained. Its IR spectrum shows an exceedingly low $\nu(N{\equiv}N)$ band at 1890 cm^{-1}. In solution

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* Reversible displacement of N_2 by NH_3 has been reported for CoH(N$_2$)(PPh$_3$)$_2$ [4].

TABLE 2

CARBONYL COMPLEXES OF AMINES

Compound	$\nu(C\equiv O)$ (cm^{-1})	Amine I_p [a] (eV)	Color	Yield (%)	Analysis found (calcd.) (%)		
					C	H	N
Va $Mo(CO)(NH_3)(DPE)_2$	1709	0	orange red	82	67.9 (67.8)	5.4 (5.4)	1.2 (1.5)
Vb $Mo(CO)(CH_3NH_2)(DPE)_2$	1707	−1.18	orange red	85	68.1 (68.1)	5.6 (5.6)	1.3 (1.5)
Vc $Mo(CO)(C_2H_5NH_2)(DPE)_2$	1729	−1.29	vermillion	45	68.0 (68.4)	5.3 (5.7)	1.3 (1.5)
Vd $Mo(CO)(n\text{-}C_3H_7NH_2)(DPE)_2$	1720	−1.37	orange	52	68.2 (68.6)	5.8 (5.9)	1.2 (1.4)
Ve $Mo(CO)(i\text{-}C_3H_7NH_2)(DPE)_2$	1711	−1.43	vermillion	43	68.4 (68.6)	5.9 (5.9)	1.3 (1.4)
Vf $Mo(CO)(n\text{-}C_4H_9NH_2)(DPE)_2$	1714	−1.44	orange	50	68.2 (68.9)	5.7 (5.8)	1.4 (1.4)
Vg $Mo(CO)(s\text{-}C_4H_9NH_2)(DPE)_2$	1726	—		2 [b]			
Vh $Mo(CO)\{(CH_3)_2NH\}(DPE)_2$	1691	−1.91		38 [b]			
Vi $Mo(CO)\{(C_2H_5)_2NH\}(DPE)_2$	1723	−2.14		12 [b]			

[a] $I_p = I_p(\text{amine}) - I_p(NH_3)$; I_p = ionization potential energy [16].

[b] Footnote in Table 1 applies ($s\text{-}C_4H_9NH_2/Mo = 10$, $(CH_3)_2NH/Mo = (C_2H_5)_2NH/Mo = 6$).

the NH_3 ligand is quite labile. Dissolved in benzene under dinitrogen, the complex is easily reconverted to *trans*-$Mo(N_2)_2(DPE)_2$. The difference in the affinity of NH_3 for $MoL(DPE)_2$ ($L = CO$ or N_2) can be explained in terms of the π-acceptor property of L. The CO ligand, being a strong π-acceptor, would be expected to facilitate the coordination of a σ-donor, NH_3.

When *trans*-$Mo(N_2)_2(DPE)_2$ was allowed to react with aliphatic amines while bubbling argon gas through it, the original orange solution changed to dark brown. The IR spectra of the solution, however, provided no evidence for the formation of $Mo(N_2)(\text{amine})(DPE)_2$.

Reactions with nitriles

Complex I reacts rapidly with substituted benzonitriles and aliphatic nitriles in benzene under dinitrogen atmosphere to afford $Mo(CO)(RCN)(DPE)_2$ [$R = 4\text{-}XC_6H_4$ ($X = NH_2$ (VIa), CH_3O (VIb), CH_3 (VIc), H (VId), Cl (VIe), or $COCH_3$ (VIf)), CH_3 (VIg), C_2H_5 (VIh), i-C_3H_7 (VIi), or $CH_2{=}CH$ (VIj)]. The complex VIb exhibits a sharp singlet at 68 ppm (positive downfield) relative to 85% H_3PO_4 in the ^{31}P NMR spectrum, which indicates a *trans* configuration. Similar NMR spectra were observed for VIc (68 ppm) and VIe (69 ppm). Although the other complexes were not examined, they are assumed to have *trans* configurations. The coordination of 4-aminobenzonitrile through the amino nitrogen should be excluded since the complex II does not combine with aniline.

The IR spectra of the complexes VIa—j show a strong absorption in the range of 1716—1767 cm^{-1} assignable to $\nu(C{\equiv}O)$ and a sharp absorption in the range of 2160—2241 cm^{-1} assignable to $\nu(C{\equiv}N)$. Pertinent IR data presented in Table 3 show that the $\nu(C{\equiv}O)$ vibration is sensitive to the nature of the *para* substituent of the $p\text{-}XC_6H_4CN$ moiety in the complexes. A plot of $\nu(C{\equiv}O)$ vs. the Hammett substituent parameter, σ_p, shows no clear-cut correlation between these quantities, although $\nu(N{\equiv}N)$ showed a linear dependence on σ_p in the case of a series of $Mo(N_2)(4\text{-}XC_6H_4CN)(DPE)_2$ complexes [6]. The finding that $\nu(C{\equiv}O)$ of VIe is lower than that of VId suggests the contribution of the electron-releasing resonance property of the Cl substituent, which may be enhanced by the strong π-acceptor property of the CO ligand.

Table 3 also shows the value of $\nu(C{\equiv}N)$ and $\Delta\nu(C{\equiv}N)$, where $\Delta\nu(C{\equiv}N)$ is the change on coordination. For the entire series of the carbonyl complexes, $\Delta\nu(C{\equiv}N)$ is smaller than that of the corresponding dinitrogen analogs, $Mo(N_2)(RCN)(DPE)_2$ [6]. An explanation can be made by considering the stronger π-acceptor property of CO than N_2.

Reactions with pyridines

Complex II reacts with several 4-substituted pyridines under argon to give $Mo(CO)(4\text{-}XC_5H_4N)(DPE)_2$ [$X = NH_2$ (VIIa), CH_3 (VIIb), H (VIIc), Cl (VIId), or $COCH_3$ (VIIe)]. The complexes VIIa—e show $\nu(C{\equiv}O)$ bands at 1696—1728 cm^{-1} (Table 4). The 2-substituted pyridines such as 2-methylpyridine do not combine with II, which may be due to a steric effect. On recrystallization under dinitrogen, the complexes VIIb—e are converted to I, whereas IIa is recovered almost quantitatively, suggesting that 4-aminopyridine is a stronger ligand than other pyridines. Competitive reaction of II with a mixture of pyridine and 4-aminopyridine gives only VIIa; electron-releasing substituents favor coordina-

(continued on p. 72)

TABLE 3

CARBONYL COMPLEXES OF ORGANONITRILES

Compound	ν(C≡O) (cm^{-1})	ν(C≡N) (cm^{-1})		$\Delta\nu$(CN) [a]	σ_p	Color	Yield (%)	Analysis found (calcd.) (%)		
		Coordinated	Free					C	H	N
VIa Mo(CO)(4-$NH_2C_6H_4CN$)(DPE)$_2$	1716	2210	2216	−6	−0.65	reddish orange	85	68.8 (69.3)	5.4 (5.2)	2.6 (2.7)
VIb Mo(CO)(4-$CH_3OC_6H_4CN$)(DPE)$_2$	1755	2184	2217	−33	−0.27	orange red	82	69.8 (69.5)	5.7 (5.3)	1.4 (1.3)
VIc Mo(CO)(4-$CH_3C_6H_4CN$)(DPE)$_2$	1757	2181	2230	−49	−0.17	wine red	76	70.6 (70.6)	5.5 (5.3)	1.1 (1.3)
VId Mo(CO)(C_6H_5CN)(DPE)$_2$	1766	2174	2231 [b]	−57	0	maroon	68	70.9 (70.4)	5.5 (5.2)	1.1 (1.4)
VIe Mo(CO)(4-ClC_6H_4CN)(DPE)$_2$	1762	2162	2227	−65	+0.23	dark brown	70	67.2 (68.1)	5.4 (4.9)	1.1 (1.3)
VIf Mo(CO)(4-$CH_3COC_6H_4CN$)(DPE)$_2$	1767	2155	2228	−73	+0.50	green	66	68.9 (69.9)	5.4 (5.2)	1.1 (1.3)
VIg Mo(CO)(CH_3CN)(DPE)$_2$	1738	2241	2254 [b]	−13		vermillion	52	68.7 (68.7)	5.3 (5.3)	1.3 (1.5)
VIh Mo(CO)(C_2H_5CN)(DPE)$_2$	1725	2234	2249 [b]	−15		wine red	54	68.2 (68.9)	5.6 (5.5)	1.3 (1.4)
VIi Mo(CO)(i-C_3H_7CN)(DPE)$_2$	1727	2238	2254 [b]	−16		orange	60	68.6 (69.2)	5.8 (5.6)	1.2 (1.4)
VIj Mo(CO)(CH_2=CHCN)(DPE)$_2$	1749	2160	2227 [b]	−67		dark red	63	68.4 (69.0)	5.8 (5.2)	1.1 (1.4)

[a] Change in ν(CN) on coordination. [b] Neat.

TABLE 4

CARBONYL COMPLEXES OF PYRIDINES AND OLEFINS

Compound	$\nu(C\equiv O)$ (cm^{-1})	Color	Yield (%)	Analysis found (Calcd.) (%)		
				C	H	N
VIIa Mo(CO)(4-$NH_2C_5H_4N$)(DPE)$_2$	1696	orange	67	68.0	5.3	1.2
				(68.6)	(5.3)	(1.4)
VIIb Mo(CO)(4-$CH_3C_5H_4N$)(DPE)$_2$	1718	orange	56	68.9	5.4	1.1
				(69.9)	(5.3)	(1.4)
VIIc Mo(CO)(C_5H_5N)(DPE)$_2$	1718	vermillion	44	69.2	5.4	1.1
				(69.7)	(5.3)	(1.4)
VIId Mo(CO)(4-ClC_5H_4N)(DPE)$_2$	1721	brown	36	66.5	5.0	1.0
				(67.3)	(5.0)	(1.4)
VIIe Mo(CO)(4-$CH_3COC_5H_4N$)(DPE)$_2$	1728	green	23	68.0	5.5	1.0
				(69.1)	(5.3)	(1.3)
VIIIa Mo(CO)(C_2H_4)(DPE)$_2$	1813	orange red	66	69.2	5.8	
				(69.6)	(6.0)	
VIIIb Mo(CO)(CH_2=$CHCOCH_3$)(DPE)$_2$	1885	yellow	47	68.6	5.6	
				(69.1)	(5.5)	
VIIIc Mo(CO)(CH_2=$CHCOOCH_3$)(DPE)$_2$	1775		76 [a]			

[a] Footnote in Table 1 applies ($CH_2CHCOOCH_3$/Mo = 30).

tion of pyridines, which may be interpreted as showing that the coordinate bonding consists mainly of donation of pyridines.

Reactions with olefins

Complex II reacts rapidly with ethylene to give $Mo(CO)(C_2H_4)(DPE)_2$ (VIIIa). The ^1H NMR spectrum of VIIIa in C_6D_6 shows a resonance of coordinated ethylene at δ 4.51 ppm (broad singlet), which is lower than that of $Mo(C_2H_4)(DPE)_2$ [7]. This is consistent with a lower electron density on the metal caused by CO.

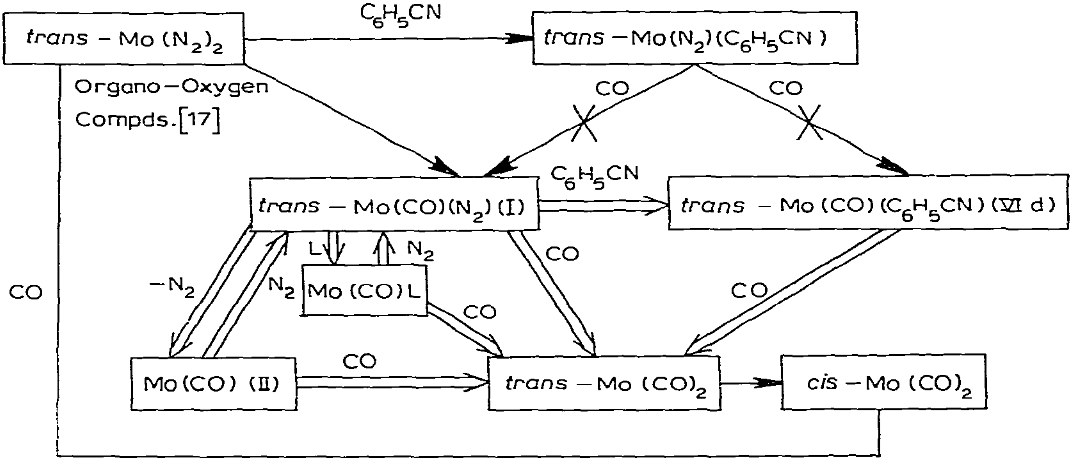
Olefins having electron-withdrawing substituents form $Mo(CO)(CH_2{=}CHR)(DPE)_2$ [R = $COCH_3$ (VIIIb) or $COOCH_3$ (VIIIc)] (Table 4). The electron-withdrawing substituents increase the back-donation from the metal to the olefin, stabilizing the metal—olefin bond. This is contrasted with the lack of coordination ability of propylene, $CH_2{=}CHOC_2H_5$ and $CH_2{=}CHOCOCH_3$. The observed $\nu(C{\equiv}O)$ of VIj, which is 158 cm^{-1} lower than that of VIIIb, suggests that the coordination of acrylonitrile occurs through the nitrogen lone pair.

Replacement reactions by CO

Previously we described the reaction of II with carbon monoxide [1]. In an effort to shed light on this and related reactions, CO displacement reactions were carried out with the derivatives of I, which were summarized in Scheme 1.

Treatment of I with bubbled CO in benzene gives *trans*-$Mo(CO)_2(DPE)_2$ almost instantaneously. In contrast, predominantly *cis*-$Mo(CO)_2(DPE)_2$ was obtained from *trans*-$Mo(N_2)_2(DPE)_2$ after 4 days' reaction, although intermediate formation of the *trans* isomer was confirmed by IR [8—10]. No evidence for the formation of I was presented. Isomerization of *trans*-$Mo(CO)_2(DPE)_2$ to the thermodynamically more stable *cis* isomer proceeds almost com-

SCHEME 1



DPE ligands are omitted. ⟹, rapid reaction; ⟶, slow reaction.

pletely after 1 day. Chatt et al. [11] and Gray et al. [12] recently reported that the common rate-determining step in the substitution reactions of *trans*-$Mo(N_2)_2(DPE)_2$ by nitriles is the dissociation of N_2, resulting in the formation of a coordinatively unsaturated intermediate, $Mo(N_2)(DPE)_2$. These results suggest that *cis*-$Mo(CO)_2(DPE)_2$ is formed from *trans*-$Mo(N_2)_2(DPE)_2$ in successive steps. Thus the behavior of *trans*-$Mo(N_2)_2(DPE)_2$ toward CO would be accounted for on the basis of the observed order of the reaction rates, ii, iii, iv > v > i.

$$\textit{trans}\text{-}Mo(N_2)_2(DPE)_2 \underset{(i)}{\xrightarrow{-N_2}} Mo(N_2)(DPE)_2 \underset{(ii)}{\xrightarrow{CO}} \underset{(I)}{\textit{trans}\text{-}Mo(N_2)(CO)(DPE)_2}$$

$$\underset{(iii)}{\xrightarrow{-N_2}} \underset{(II)}{Mo(CO)(DPE)_2} \underset{(iv)}{\xrightarrow{CO}} \textit{trans}\text{-}Mo(CO)_2(DPE)_2 \underset{(v)}{\rightarrow} \textit{cis}\text{-}Mo(CO)_2(DPE)_2$$

Complexes VIa—j react with CO immediately to give *trans*-$Mo(CO)_2(DPE)_2$, followed by isomerization to the *cis* isomer. This finding suggests that all the organonitrile complexes VIa—j have a *trans* configuration. In contrast, the corresponding dinitrogen analog of VIf, *trans*-$Mo(N_2)(C_6H_5CN)(DPE)_2$ [6], is recovered quantitatively after bubbling CO through its toluene solution for 4 days. The inertness to substitution of C_6H_5CN and N_2 by CO may be due to the strong $Mo—NCC_6H_5$ and $Mo—N_2$ bonds as reflected in the large decrease in $\nu(C\equiv N)$ and $\nu(N\equiv N)$; replacement of either ligand would have led to the biscarbonyl since both *trans*-$Mo(CO)(N_2)(DPE)_2$ (I) and $Mo(CO)(C_6H_5CN)(DPE)_2$ (VIf) react readily with CO. This finding indicates that displacement of one molecule of ligating dinitrogen of *trans*-$Mo(N_2)_2(DPE)_2$ by C_6H_5CN enhances the complex stability constant. On the other hand, the aliphatic nitriles of *trans*-$Mo(N_2)(RCN)(DPE)_2$ ($R = CH_3$ or C_2H_5) can be replaced by CO and N_2. This is due to the weakness of the Mo—NCR bonds as reflected in the small decrease in $\nu(C\equiv N)$ [6].

Treatment of IIIa, IVa, Va, or VIIc with bubbled CO in benzene also gives *trans*-$Mo(CO)_2(DPE)_2$ immediately, suggesting that all these complexes have a *trans* configuration. This finding is in accord with expectations based on the steric and electronic factors of the type $MoLL'(DPE)_2$ [10,13]. In the above complexes with L = CO and L′ = $HCON(CH_3)_2$, imidazole, NH_3, or pyridine, the *trans* configuration would be favored not only sterically but also electronically, since L′ is essentially an electron donor.

It should be noted that I gives *cis*-$Mo(CO)_2(DPE)_2$ slowly in the absence of CO. Disproportionation appears to have occurred, but the other disproportionation product, $Mo(N_2)_2(DPE)_2$, could not be found. In contrast with the reaction with CO, no evidence was found for *trans*-$Mo(CO)_2(DPE)_2$. Complex II shows behavior similar to I.

Experimental

All reactions were carried out under dinitrogen or argon. Solvents were dried and distilled under dinitrogen. The complexes *trans*-$Mo(CO)(N_2)(DPE)_2$ ·

1/2 C_6H_6 (I) and Mo(CO)(DPE)$_2$ (II) were prepared by the published method [2]. Methylamine, ethylamine, and diethylamine were used as aqueous solutions. IR spectra were taken of KBr pellets unless noted, using a Nihon-bunko IRA-2 double beam spectrometer. ^{31}P (40.5 MHz) and ^{1}H (100 MHz) spectra were recorded on a computer-assisted JEOL PS-100 spectrometer.

Preparations of Mo(CO)L(DPE)$_2$. general procedures

The complexes of amides, imidazoles, amines, pyridines, and olefins were prepared from II under argon. The synthesis of II in large quantity, however, is troublesome. Therefore, II is often prepared in situ from I [2], thereafter it was allowed to react with the substrates. The complexes of CO, nitriles, NH_3, and 4-aminopyridine were prepared from I.

Mo(CO){HCON(CH$_3$)$_2$}(DPE)$_2$ (IIIa). To a solution of II prepared in situ from 0.049 g (0.050 mmol) of I in 4 ml of benzene was added 39 μl (0.50 mmol) of *N,N*-dimethylformamide. The mixture turned reddish brown immediately and addition of n-hexane (6 ml) deposited dark red crystals after 1 day. These were filtered, washed with n-hexane (3 × 5 ml) and dried in vacuo.

The complexes of amides, imidazoles, amines, pyridines, and olefins were prepared in similar manner.

Reaction of II with N,N-dimethylacetamide. To a solution of II prepared in situ from 0.049 g (0.050 mmol) of I in 4 ml of benzene was added 0.6 ml (6.5 mmol) of *N,N*-dimethylacetamide. The solution was concentrated in vacuo to give a yellow brown solid, which showed weak IR bands at 1693 [ν(C≡O)] and 1628 cm^{-1} [ν(C=O)], attributable to Mo(CO){$CH_3CON(CH_3)_2$}(DPE)$_2$ (IIIf), in addition to the bands of II. The product yield was estimated to be 3% from IR ν(C≡O) intensities when the molar extinction coefficient of ν(C≡O) of IIIf is assumed to be equal to that of II. Several attempts to obtain a crystalline sample of IIIf have failed.

Although the complexes Vg, Vh, Vi, and VIIIc were similarly confirmed by IR, they were always contaminated by II; no analytically pure sample was obtained. Product yields were estimated from IR data (see Tables 2 and 4).

Mo(CO)(NH$_3$)(DPE)$_2$ (Va). Ammonia gas was bubbled through a solution of I (0.049 g, 0.050 mmol) in benzene (5 ml) at room temperature. The original orange color changed rapidly to orange red. On addition of n-hexane (10 ml) to the resulting solution under ammonia atmosphere, orange-red crystals were formed after 1 day. These were filtered off, washed with n-hexane (3 × 10 ml), and dried in vacuo.

Mo(N$_2$)(NH$_3$)(DPE)$_2$. Ammonia gas was bubbled through a solution of *trans*-Mo(N$_2$)$_2$(DPE)$_2$ (0.250 mg, 0.26 mmol) in benzene (20 ml) at room temperature for 12 h. The original orange color changed gradually to dark red. On addition of n-hexane (35 ml) to the solution under ammonia, dark red needles were formed after 1 day, which were filtered off under argon, washed with n-hexane (3 × 10 ml), and dried in vacuo.

Mo(CO)(4-NH$_2$C$_6$H$_4$CN)(DPE)$_2$ (VIa). Benzene (4 ml) was added to the mixture of 0.049 g (0.050 mmol) of I and 12 mg (0.10 mmol) of 4-aminobenzonitrile. Immediate reaction took place, affording an orange-red solution. Addition of n-hexane (10 ml) deposited reddish-orange crystals after 1 day, which were filtered, washed with ether (3 × 5 ml), and dried in vacuo.

The complex of nitriles and 4-aminopyridine were prepared in similar manner.

Reaction of I with carbon monoxide. Carbon monoxide was bubbled through a solution of 0.099 g (0.10 mmol) of I in benzene (10 ml) at room temperature for 3 min. The solvent was removed in vacuo to give an orange powder, which showed ν(C≡O) at 1812 cm^{-1} of *trans*-$Mo(CO)_2(DPE)_2$ in its IR spectrum. No evidence for the formation of the *cis* isomer was found. When the powder was recrystallized from benzene (10 ml)/n-hexane (15 ml), yellowish-orange crystals of *trans*-$Mo(CO)_2(DPE)_2$ (25 mg, 26%) were obtained with concomitant formation of a yellow powder of *cis*-$Mo(CO)_2(DPE)_2$. Anal. Found: C, 68.3; H, 5.1. Calcd for $C_{54}H_{48}O_2P_4Mo$: C, 68.4; H, 5.1%.

When the above solution was allowed to stand for 1 day and then n-hexane was added, the *cis* isomer was obtained exclusively.

Reaction of IIIa, IVa, Va, VIa—j, VIIc, *trans*-$Mo(N_2)(C_6H_5CN)(DPE)_2$, or *trans*-$Mo(N_2)(CN_3CN)(DPE)_2$ with carbon monoxide was carried out in similar manner.

Conversion of I to cis-Mo(CO)$_2$(DPE)$_2$. A benzene solution (15 ml) of 0.200 g (0.203 mmol) of I was allowed to stand under dinitrogen for 1 week and then n-hexane (20 ml) was added to give a yellow powder of *cis*-$Mo(CO)_2(DPE)_2$ (57 mg, 30%). Only trace amounts of I remained unchanged.

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