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Preliminary communication

PREPARATION AND PROPERTIES OF DINITROGEN—MOLYBDENUM COMPLEXES

IV*. *trans*-$Mo(CO)(N_2)(Ph_2PCH_2CH_2PPh_2)_2$ AND RELATED COMPLEXES

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Summary

The reaction of *trans*-$Mo(N_2)_2(DPE)_2$ [DPE = 1,2-bis(diphenylphosphino)-ethane] with dimethylformamide (DMF) gives the carbonyl complex, $Mo(CO)(DMF)(DPE)_2$, which reacts readily with nitrogen gas forming the dinitrogen complex, *trans*-$Mo(CO)(N_2)(DPE)_2$; the dinitrogen ligand is so labile as to be displaced to afford the complexes, $[Mo(CO)(DPE)_2]_n$ and $Mo(CO)L(DPE)_2$ (L = donor compounds).

In the course of investigating the reactions of the molybdenumdinitrogen complexes [1-3], we have found that *trans*-$Mo(N_2)_2(DPE)_2$ reacts with DMF in benzene at reflux to yield $Mo(CO)(DMF)(DPE)_2$. The only other reported example of carbon monoxide abstraction from amides was found in a rhodium complex [4]. The complex, $Mo(CO)(DMF)(DPE)_2$, is an air-stable, dark-red crystalline solid, the IR spectrum of which (KBr) shows intense bands at 1690 cm^{-1} [$\nu(C{\equiv}O)$] and 1630 cm^{-1} [$\nu(C{=}O)$]. It can be recrystallized from benzene under an argon atmosphere, but is completely converted to *trans*-$Mo(CO)(N_2)(DPE)_2$ on recrystallization under nitrogen. Dinitrogen complexes of rhenium having strongly π-bonding carbon monoxide groups as co-ligands have been reported [5,6].

The reaction of *trans*-$Mo(N_2)_2(DPE)_2$ with carbon monoxide has been reported to give *trans*-$Mo(CO)_2(DPE)_2$, which isomerizes to the *cis* isomer [1,

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7,8]. However, there appears to be no indication of the intermediate formation of the mixed species $Mo(CO)(N_2)(DPE)_2$. The complex *trans*-$Mo(CO)(N_2)(DPE)_2$ reacts rapidly with carbon monoxide to give *trans*-$Mo(CO)_2(DPE)_2$, which is slowly converted to the *cis* isomer. Interestingly, when the benzene solution of *trans*-$Mo(CO)(N_2)(DPE)_2$ is allowed to stand for a long time under nitrogen, *cis*-$Mo(CO)_2(DPE)_2$ is formed, which is considered to be a disproportionation product.

The IR spectrum of *trans*-$Mo(CO)(N_2)(DPE)_2$ shows medium strong bands at 2110 and 2080 cm^{-1} and strong bands at 1812 and 1791 cm^{-1}. The ^{15}N-labeled derivative shows bands at 2036, 2009, 1812 and 1789 cm^{-1}. Therefore, the two higher frequency vibrations are assigned to $\nu(N{\equiv}N)$ and the lower ones to $\nu(C{\equiv}O)$. The splittings of $\nu(N{\equiv}N)$ and $\nu(C{\equiv}O)$ seem to be due to a crystal effect, since such splitting was not observed in solution. The ^{31}P NMR spectrum of *trans*-$Mo(CO)(N_2)(DPE)_2$ shows a sharp singlet at -69 ppm (relative to 85% H_3PO_4) for the four equivalent phosphorus nuclei, indicating a *trans* configuration similar to the bis-dinitrogen complex, $Mo(N_2)_2(DPE)_2$.

As reflected in the high frequencies of $\nu(N{\equiv}N)$, the dinitrogen ligand of *trans*-$Mo(CO)(N_2)(DPE)_2$ is very labile in solution. When nitrogen is removed in vacuo or with a stream of argon, the original orange solution (benzene) changes rapidly to dark brown. From the resulting solution black crystals analyzing as $[Mo(CO)(DPE)_2]_n$ can be obtained. The IR spectrum of $[Mo(CO)(DPE)_2]_n$ shows a band at 1807 cm^{-1} ascribable to $\nu(C{\equiv}O)$. If $n = 1$, this complex is formally a coordinatively unsaturated 16-electron species, but its structure remains uncertain. Dissolved in benzene under nitrogen, this complex can be reconverted to *trans*-$Mo(CO)(N_2)(DPE)_2$.

TABLE 1

IR SPECTRA OF $Mo(CO)L(DPE)_2$ COMPLEXES [a]

L	$\nu(CO)$ (cm^{-1})	Other bands
N≡N	1812, 1791	$\nu(N{\equiv}N)$ 2080, 2110
C_2H_4	1813	
4-ClC_6H_4CN	1762	$\nu(C{\equiv}N)$ 2162
PhCN	1766	$\nu(C{\equiv}N)$ 2175
Pyridine	1724	
N-MeIm [b]	1705	
DMF	1690	$\nu(C{=}O)$ 1630

[a] KBr disk; in cm^{-1}. [b] *N*-Methylimidazole.

We have studied also the reaction of *trans*-$Mo(CO)(N_2)(DPE)_2$ with several substrates. The dinitrogen ligand is easily displaced by these substrates, yielding the complexes of the type $Mo(CO)L(DPE)_2$ (Table 1). These complexes also can be prepared from $[Mo(CO)(DPE)_2]_n$. The $\nu(C{\equiv}O)$ of the complexes of DMF and *N*-methylimidazole is unusually low, which may be due to the strong π-donor properties of these ligands [9,10].

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