# Five-co-ordinate Molybdenum and Tungsten Complexes, $[M(CO)_3(PCy_3)_2]$, which Reversibly add Dinitrogen, Dihydrogen, and Other Small Molecules

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*Summary* New complexes of molybdenum and tungsten with dinitrogen and other small molecules, *trans*-$[M(CO)_3(PCy_3)_2L]$ (L = $N_2$, $H_2$, $C_2H_4$, or $SO_2$), have been synthesized by the reaction of $[M(CO)_3(\text{cycloheptatriene})]$ with $2PCy_3$ in the presence of L; removal of L yields the formally five-co-ordinate species $[M(CO)_3(PCy_3)_2]$.

MOLYBDENUM and tungsten dinitrogen complexes have received much recent attention in regard to nitrogen fixation. However, only two basic types of zerovalent complexes, $[M(N_2)_2P_4]$ and $[M(\text{arene})P_2]_nN_2$ ($n$ = 1,2; P = phosphorus donor, either mono- or bi-dentate phosphine), have been synthesized starting from available reagents, and in all cases the preparations involved relatively difficult reductions of M(II—V) compounds.[1] We have found that a new type of $Mo^0$–$N_2$ complex, as well as other small molecule complexes, can be conveniently synthesized in one step from a commercially available $Mo^0$ compound, $[Mo(CO)_3(C_7H_8)]$ ($C_7H_8$ = cycloheptatriene). Similarly, tungsten analogues can be prepared from $[W(CO)_3(C_7H_8)]$. The complexes, *trans*-$[M(CO)_3(PCy_3)_2L]$ (Cy = cyclohexyl; L = $N_2$, $H_2$, or $C_2H_4$), are formed by the reaction of the olefin complex with $2PCy_3$ in benzene or toluene under nitrogen, hydrogen, or ethylene atmospheres, respectively, and precipitate as yellow microcrystals in 60—70% yield within 2—3 h for M = Mo and 15—30 min for M = W. The binding is reversible and the small molecule ligands can be removed in solution under an argon flush at 40—60 °C to form an apparently five-co-ordinate species, $[M(CO)_3(PCy_3)_2]$. The latter, which can be isolated as a black-purple crystalline solid, will also add CO or $SO_2$ to form the known[2] complex, *trans*-$[M(CO)_4(PCy_3)_2]$, or a new complex, *trans*-$[M(CO)_3(PCy_3)_2(SO_2)]$, respectively, but the reactions are irreversible in these cases. Reversible dioxygen binding was not observed. $[M(CO)_3(PCy_3)_2]$ can also be prepared directly by reaction of $[M(CO)_3(C_7H_8)]$ with $2PCy_3$ under argon in $Et_2O$. The complexes have been characterized by elemental analysis, gas evolution experiments, thermogravimetric analysis, and i.r. spectroscopy (Table). All are moderately air-sensitive in the solid state and may, in some

TABLE. I.r. frequencies (Nujol mull) for $M(CO)_3(PCy_2)_2L$.

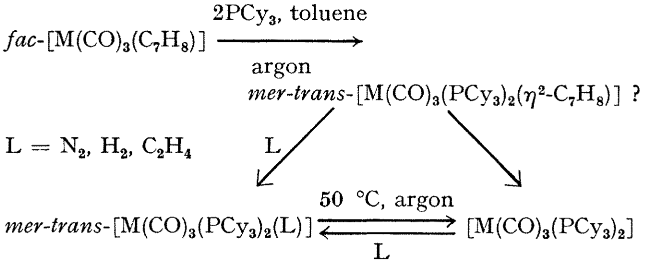
| L | $\nu$(CO)/cm$^{-1}$ | | $\nu$(other)/cm$^{-1}$ | |
|---|---|---|---|---|
| | M = Mo | M = W | M = Mo | M = W |
| — | 1949, 1800—1870[a] | 1946, 1863, 1832, 1811 | | |
| $N_2$ | 1956, 1872, 1841 | 1952, 1863, 1835 | 2159[b] | 2120[b] |
| $C_2H_4$ | 1961, 1869, 1838 | 1962, 1868, 1834 | 1240[c] | 1208[c] |
| $H_2$ | 1966, 1873, 1853 | 1961, 1861, 1843 | | 1568, 951, 464[d] |
| $D_2$ | 1966, 1873, 1853 | 1961, 1861, 1843 | | 1150, 700, 315[e] |
| $SO_2$ | 1996, 1917, 1886 | 1994, 1909, 1873 | 1239, 1070[f] | 1237, 1070[f] |

[a] Unresolvable. [b] $\nu(N\equiv N)$. [c] $\nu(C=C)$. [d] M–H frequencies. [e] M–D frequencies. [f] $\nu$(SO).

cases, retain small amounts of solvent in the crystal lattice [$\nu(C_6H_6) = 673\ cm^{-1}$]. The tungsten complexes are somewhat more stable than the molybdenum analogues to both air and loss of L. The dinitrogen and ethylene adducts are stable *in vacuo* at room temperature, but lose $N_2$ or $C_2H_4$ when heated above *ca.* 80 °C to form [$M(CO)_3(PCy_3)_2$]. However, [$Mo(CO)_3(PCy_3)_2H_2$] readily loses $H_2$ at room temperature and must be stored under an $H_2$ atmosphere. The extreme lability of the hydrogen is remarkable, and neither $\nu$(Mo–H) or $\nu$(Mo–D) could be located in the i.r. spectrum, due to weak intensity, obscuration, or both. For a Nujol mull of [$W(CO)_3(PCy_3)_2H_2$], a broad weak band at 1568 and a medium band at 951 cm$^{-1}$ were observed which can be assigned to $\nu$(W–H) and $\delta$(W–H), respectively, since in [$W(CO)_3(PCy_3)_2D_2$] these shift down to *ca.* 1150 and 700 cm$^{-1}$ ($\nu_H/\nu_D = \delta_H/\delta_D = 1{\cdot}36$). These frequencies are peculiar in that $\nu$(W–H) is lower than that normally observed for metal hydrides while $\delta$(W–H) is higher than usually found. Furthermore, a third band was located at 464 cm$^{-1}$ for the hydride and 315 cm$^{-1}$ for the deuteride which apparently is due to the H or D ligands ($\nu_H/\nu_D = 1{\cdot}47$). These results indicate that the bonding of hydrogen to these metal complexes may be novel, and *X*-ray structural investigations are in progress. Except for L = $SO_2$, [$Mo(CO)_3(PCy_3)_2L$] partially dissociate in solution even in the presence of excess L and are not very soluble in benzene or toluene, making solution i.r. and n.m.r. studies difficult. The tungsten adducts do not dissociate as readily and are somewhat more soluble.

[$W(CO)_3(PCy_3)_2$] is apparently the first example of a formally five-co-ordinate $d^6$ tungsten complex, while [$Mo(CO)_3(PCy_3)_2$] is apparently only the second example of a stable five-co-ordinate $d^6$ molybdenum complex. Their nearly black colour and $N_2$-binding ability closely parallels that of [$Mo(CO)(Ph_2PCH_2CH_2PPh_2)_2$], the first example.[3] I.r. spectral evidence indicates that bridging carbonyls are not present, as in [$Mo(CO)_3D]_2$ (D = bipy, phen), which also was synthesized[4] from [$Mo(CO)_3(C_7H_8)$]. [$Mo(CO)_3(PCy_3)_2$] is air-sensitive and unstable in solution to slow disproportionation to *trans*-[$Mo(CO)_4(PCy_3)_2$], especially above room temperature. The latter [($\nu$(CO) = 2000, 1922, and 1860 cm$^{-1}$] is also present to varying degrees as a minor impurity in the complexes [$Mo(CO)_3(PCy_3)_2L$]. The tungsten analogues are considerably more stable to disproportionation, and deep-purple toluene solutions of [$W(CO)_3(PCy_3)_2$] can be heated to 60 °C with little decomposition occurring. The instability of the molybdenum complex is in harmony with the previously observed formation of the tetracarbonyl by the prolonged reaction of [$Mo(CO)_3(C_7H_8)$] with $3PCy_3$ in benzene at 60 °C.[2]

Key factors in the formation of the new complexes are phosphine size and basicity since $PPh_3$, $PBu^n_3$, $P(PhCH_2)_3$, P(*o*-tolyl)$_3$, and $PBu^t_3$ analogues could not be obtained.† The phosphines must be bulky, but not overly bulky, so that steric constrains allow only *trans* substitution, resulting in carbonyl rearrangement from *facial* to *meridional*. A species with cycloheptatriene weakly occupying the sixth co-ordination site is possibly formed initially.‡ The olefin is then readily dissociable or displaceable to form either [$M(CO)_3(PCy_3)_2$] under argon or [$M(CO)_3(PCy_3)_2(L)$] if the reaction is carried out in the presence of L. The



$$\begin{tikzcd}
 & \textit{fac-}[M(CO)_3(C_7H_8)] \arrow[r, "2PCy_3\text{, toluene}", "\text{argon}"'] & \textit{mer-trans-}[M(CO)_3(PCy_3)_2(\eta^2\text{-}C_7H_8)]\ ? \arrow[dl, "L"'] \arrow[dr] & \\
L = N_2, H_2, C_2H_4 & \textit{mer-trans-}[M(CO)_3(PCy_3)_2(L)] \arrow[rr, shift left, "50\ ^\circ C\text{, argon}"] & & [M(CO)_3(PCy_3)_2] \arrow[ll, shift left, "L"]
\end{tikzcd}$$

*fac* to *mer* carbonyl rearrangement had previously been observed in an analogous reaction with L = $SO_2$, where the product, *mer-trans*-[$Mo(CO)_3(PPr^i_3)_2(SO_2)$], has been structurally characterized by *X*-ray crystallography.[5] We are in the process of obtaining further crystallographic information on the new complexes and assessing the reactivity of the co-ordinated ligands.

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† For M = Mo, use of $PPr^i_3$ gives an apparent $N_2$-bridged species, for which $\nu$(N≡N) could not be located, and an unstable hydride which could not be isolated. Also, the reaction of [Cr(CO)$_3$(cycloheptatriene)] with $2PCy_3$ failed to yield a dinitrogen adduct.

‡ Reaction of [$Mo(CO)_3(C_7H_8)$] with $2PCy_3$ in ether or benzene under argon initially gives a rust-coloured precipitate within 10 min, which slowly redissolves to form eventually [$Mo(CO)_3(PCy_3)_2$]. The complexity of its i.r. carbonyl region indicates that binuclear olefin-bridged species may also be possible intermediates.

[1] T. A. George and M. E. Noble, *Inorg. Chem.*, 1978, **17**, 1678, and references therein; M. L. H. Green and W. E. Silverthorn, *J.C.S. Dalton*, 1973, **301**; 1974, 2164.

[2] F. G. Moers and J. G. A. Reuvers, *Rec. Trav. chim.*, 1974, **93**, 246.

[3] M. Sato, T. Tatsumi, T. Kodama, M. Hidai, T. Uchida, and Y. Uchida, *J. Amer. Chem. Soc.*, 1978, **100**, 4447.

[4] H. Behrens, E. Lindner, and G. Lehnert, *J. Organometallic Chem.*, 1970, **22**, 439.

[5] G. J. Kubas and R. R. Ryan, manuscript in preparation.