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	$\nu(CO)/cm^{-1}$		$\nu(\text{other})/cm^{-1}$	
	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 ν(Mo–H) or ν(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 ν(W–H) and δ(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 ν(W–H) is lower than that normally observed for metal hydrides while δ(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 [(ν(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 *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.

L = N_2, H_2, C_2H_4

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

This work was performed under the auspices of the U.S. Department of Energy, Division of Chemical Sciences.

(*Received, 13th August* 1979; *Com.* 872.)

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† For M = Mo, use of PPr^i_3 gives an apparent N_2-bridged species, for which $\nu(N{\equiv}N)$ 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.

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