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A Tungsten Carbonyl Complex $[W(CO)(Ph_2PCH_2CH_2PPh_2)_2]$ Present as a Mixture of Two Species Having Agostic Interaction or Ortho-Metallation and Its Reaction with Hydrogen Gas[1)]

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A tungsten carbonyl complex $[W(CO)(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) exists in solution as a mixture of two species, one of which has an agostic interaction and the other has an ortho-metallation between one ortho hydrogen of the dpe ligand and the tungsten atom. This carbonyl complex reacted with H_2 gas to give a dihydrido complex $[WH_2(CO)(dpe)_2]$.

We have already reported that a dinitrogen complex trans-$[Mo(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) reacts with N,N-dimethylformamide (DMF) in benzene at reflux to give trans-$[Mo(CO)(DMF)(dpe)_2]$ and this corbonyl complex is readily converted into a carbonyl-dinitrogen complex trans-$[Mo(CO)(N_2)(dpe)_2]$ (**1**) by recrystallization under N_2.[2)] If complex **1** is heated at 50 °C in benzene under Ar, a five coordinate complex $[Mo(CO)(dpe)_2]$ (**2**) is obtained. This coordinatively unsaturated complex can bind a wide range of molecules such as Lewis bases, ethylene, CO, N_2,[3)] and H_2[4)] at its vacant site. The X-ray crystallographic analysis of complex **2** showed that an agostic interaction is present between one ortho hydrogen of the dpe ligand and the molybdenum atom at the trans position to the CO ligand.[2)] More recently we have reported that a tungsten complex trans-$[W(CO)(N_2)(dpe)_2]$ (**3**) can be derived from trans-$[W(N_2)_2(dpe)_2]$ according to the same reaction pathway as that for the molybdenum analogue **1**.[5)] However, a five coordinate complex $[W(CO)(dpe)_2]$ (**4**) could not be prepared by the analogous treatment of complex **3** to that for the molybdenum analogue.

Now we have found that complex **4** can be isolated as very air-sensitive dark

$$\text{trans-}[W(N_2)_2(dpe)_2] \xrightarrow[C_6H_6/\text{reflux}]{\text{DMF}} \text{trans-}[W(CO)(DMF)(dpe)_2] \xrightarrow[C_6H_6]{N_2}$$

$$\underset{\mathbf{3}}{\text{trans-}[W(CO)(N_2)(dpe)_2]} \xrightarrow[C_6H_6/\text{reflux}]{\text{Ar}} \underset{\mathbf{4}}{[W(CO)(dpe)_2]}$$

green crystals[6)] in 81% yield by refluxing a benzene solution of complex **3** for 1 h under Ar, followed by the addition of hexane to the solution. Interestingly the

^{1}H NMR spectrum of complex 4 recorded at 400 MHz in C_6D_6 shows two resonances in the high field at -2.68 ppm (broad singlet) and -5.56 ppm (quintet, J_{P-H} = 28 Hz), which is shown in Fig. 1.$^{7)}$ The intensity ratio of these two resonances is about 1:1 and the integrated value combined corresponds to one proton. These two resonances smoothly disappeared after treatment of the sample solution with N_2 and complex 3 was formed. The variable temperature ^{1}H NMR spectra from -80 °C to +80 °C in $C_6D_5CD_3$ have revealed that these two resonances appear with the same intensities in this whole region. The saturation transfer experiment on these two resonances demonstrated that the exchange between these two protons was not taking place on the NMR timescale. The presence of two different species for complex 4 in a solution state was also confirmed by its IR spectrum in C_6D_6, which showed two ν(C≡O) bands with approximately same intensities at 1771 and 1735 cm^{-1}.$^{8)}$ On the other hand, the ^{1}H NMR spectrum of complex 2 in C_6D_6 shows only one broad singlet at -0.25 ppm with the intensity corresponding to one proton (Fig. 1), which broadens gradually as the temperature is raised and disappears at around +80 °C. Based on these observations, we have concluded that the broad singlet can be assigned to the agostic ortho hydrogen of the dpe ligand occupying the vacant site in complexes 2 and 4, whereas the quintet observed for complex 4 is assignable to the ortho-metallated hydrogen of the dpe ligand. Thus although only the agostic interaction is present in the molybdenum complex 2, the tungsten complex 4 exists as a mixture of two different species, one of which has the agostic hydrogen and the other has the ortho-metallated hydrogen.$^{8)}$ At present the most reliable indication of the presence of the agostic C-H→M system in a solution state is the substantially diminished value of J_{C-H} measured by ^{13}C NMR spectra,$^{9)}$ but we could not determine these values for complexes 2 and 4 because of the low solubility of these complexes in unreactive solvents.

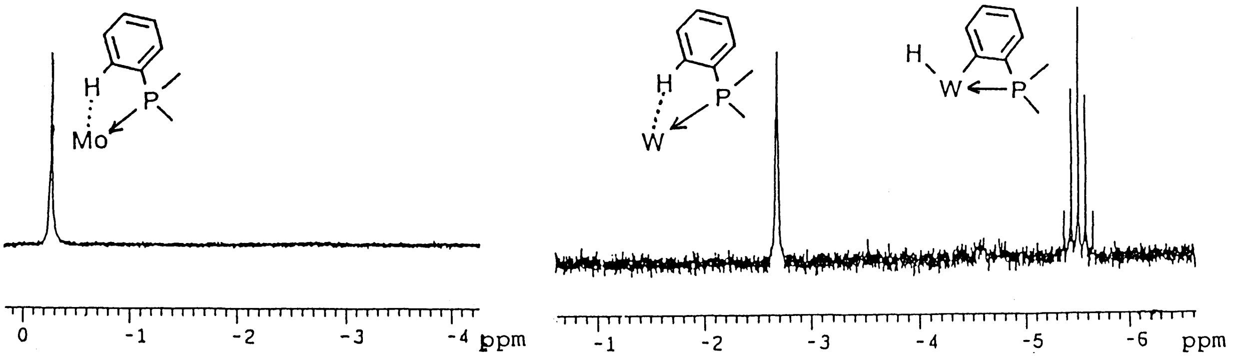
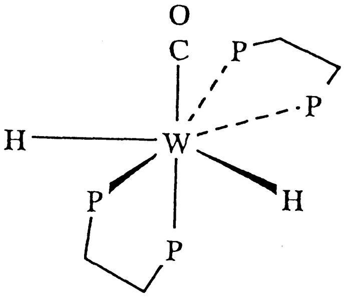


Fig. 1. Characteristic ^{1}H NMR resonances for [Mo(CO)(dpe)$_2$] (2) (left) and for [W(CO)(dpe)$_2$] (4) (right).

When treated with H_2 gas in benzene for 0.5 h, complex 4 gives a dihydrido complex [WH_2(CO)(dpe)$_2$] (5) in 42% yield as yellow crystals.$^{10)}$ Complex 5 can also be prepared by the reaction of trans-[W(CO)(DMF)(dpe)$_2$] with H_2 gas in benzene for 1 h in 81% yield. Complex 5 shows a strong ν(C≡O) band at 1777 cm^{-1} and a medium ν(W-H) band at 1726 cm^{-1} in its IR spectrum (KBr disk). The latter band shifts to 1235 cm^{-1} in [WD_2(CO)(dpe)$_2$]. In the ^{1}H NMR spectrum of complex 5, a quintet with W satellites appears at -3.70 ppm (J_{P-H} = 34 Hz, J_{W-H} = 34 Hz).

When recorded at -78 °C, this quintet changes to a slightly broadened multiplet which can be interpreted as a A_2BCX_2 pattern and simulated by taking the coupling constants of J_{P-H} with 18, 47, and 47 Hz. In the ^{31}P NMR spectrum of complex 5 in $C_6D_5CD_3$, one broad singlet appears at 58.3 ppm at room temperature (relative to H_3PO_4), which separates into three broad singlet bands at 64.5, 63.6, and 39.4 ppm with the intensity ratio of 2:1:1 at -78 °C. These NMR data for complex 5 are indicative of the rigid pentagonal bipyramidal structure shown below at low temperatures, which was already clarified for a closely relating complex [$MoH_2(CO)(Et_2PCH_2CH_2PEt_2)_2$] by an X-ray crystallography.11) The T_1 value measured by the inversion-recovery pulse sequence (0.52 s at room temperature and 1.7 s at -78 °C) is also consistent with the dihydrido character for complex 5. This presents a sharp contrast to the fact that the molybdenum complex 2 gives a η^2-dihydrogen complex trans-[$Mo(\eta^2-H_2)(CO)(dpe)_2$] by the reaction with H_2 gas.4)



5

The fate of hydrogen addition, η^2-H_2 or dihydride, is now known to be controlled by the electronic and steric factors12) and as for the d^6 ML_5 fragment it is predicted by the Extended Huckel calculations that the formation of the dihydride is much easier for a metal with high lying d orbitals than for a metal with low lying d orbitals.13) The result described above is consistent with this theoretical prediction. Morris et al have quantified the trend that poor π-donor metal sites favor η^2-H_2 and good π-donor sites favor dihydride structures by using $\nu(N\equiv N)$ of the corresponding octahedral d^6 N_2 complexes and found that H_2 binds as a η^2-H_2 ligand where $\nu(N\equiv N)$ is in the range of about 2060 - 2150 cm^{-1}, while a dihydride structure is adopted if $\nu(N\equiv N)$ is less than 2050 cm^{-1}.14) The fact that complex 3 shows $\nu(N\equiv N)$ band at 2050 cm^{-1} and complex 1 at 2095 cm^{-1} is consistent with this relationship. Since the $\nu(N\equiv N)$ value for complex 3 is located in the border region to separate the coordination mode, preparation of the Lewis acid adducts of complex 5 was carried out to decrease the π-donating ability of the tungsten center. Thus the reactions of complex 5 with excess AlR_3 were undertaken in NMR sample tubes and the ^1H NMR spectra of the mixtures were recorded directly. For the adducts of $Al(i\text{-}Bu)_3$, $AlEt_3$, $AlEt_2Cl$, and $AlEtCl_2$, the hydride resonances

$$[WH_2(CO)(dpe)_2] \xrightarrow[C_6D_6 \text{ or } C_6D_5CD_3]{AlR_3} [WH_2(CO\rightarrow AlR_3)(dpe)_2]$$

appear as broad multiplets and shift to the lower field in this order (-1.88, -1.85, -1.39, and -1.22 ppm, respectively). By the reaction with $AlCl_3$ the hydride resonance disappeared and H_2 gas was evolved (0.70 mol/W atom). However, the T_1 values of the adducts with $Al(i\text{-}Bu)_3$ and $AlEt_3$ measured at room temperature were 0.36 and 0.43 s, respectively,15) which indicates that the hydrogen atoms attached to the tungsten have still dihydride character in these complexes.16)

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6) Found: C, 62.17; H, 4.95; N, 0%. Calcd: C, 63.10; H, 4.81; N, 0%.

7) ^{31}P NMR (ppm, relative to H_3PO_4, C_6D_6/C_6H_6 solution). Complex 2: 77.8 (s); complex 3: 50.0 (s, J_{W-P} = 302 Hz); complex 4: 78.5 (s, J_{W-P} = 314 Hz), 43.0 (s, J_{W-P} = 254 Hz). In the spectrum of complex 4 recorded at -80 °C also appeared two singlets almost in the same manner as those observed at room temperature. A singlet nature of the ^{31}P resonance for the ortho-metallated species presumably results from the fluxional rotation of dpe ligands present even at low temperatures. This is consistent with the fact that the hydride resonance is observed as a quintet in this temperature region. The J_{P-H} value observed for this hydride resonance (28 Hz) well corresponds to those for the classical hydrides of this type such as [WH_2(CO)(dpe)$_2$] (34 Hz).

8) In a solid state, complex 4 also shows only one strong $\nu(C\equiv O)$ band at 1716 cm^{-1} (Nujol). Since complex 2 also shows one similar $\nu(C\equiv O)$ band at 1721cm^{-1} (Nujol), complex 4 in a solid form presumably has only an agostic hydrogen.

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