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Decarbonylation Reaction of Dimethylformamide (DMF) with trans-$[W(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$). Preparation and Characterization of $[WH(\eta^2\text{-}CONMe_2)(dpe)_2]$ and $[W(CO)(DMF)(dpe)_2]$[1)]

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When treated with dimethylformamide (DMF) in benzene at reflux, trans-$[W(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) afforded $[WH(\eta^2\text{-}CONMe_2)(dpe)_2]$ and $[W(CO)(DMF)(dpe)_2]$. The structure of the former was fully characterized by X-ray crystallography. The latter reacted with N_2 to give trans-$[W(CO)(N_2)(dpe)_2]$.

During the course of our studies on the decarbonylation reactions of aldehydes and aldehydic compounds promoted by Mo complexes,[2)] we have recently found that trans-$[Mo(N_2)_2(dpe)_2]$ (1, dpe = $Ph_2PCH_2CH_2PPh_2$) smoothly reacts with excess dimethylformamide (DMF) in benzene under refluxing conditions to give a carbonyl complex $[Mo(CO)(DMF)(dpe)_2]$.[3)] The carbonyl complex is readily converted into a carbonyl-dinitrogen complex trans-$[Mo(CO)(N_2)(dpe)_2]$ and then into a coordinatively unsaturated complex $[Mo(CO)(dpe)_2]$(2).[3)] It is noteworthy that the latter unsaturated complex binds a series of electron-donationg ligands including olefins, CO, N_2,[3, 4)] and H_2.[5)] We wish here to describe the results of the reaction of the tungsten analogue trans-$[W(N_2)_2(dpe)_2]$(3) with DMF.

When complex 3 was treated with excess DMF in benzene under refluxing conditions for 2 h under Ar, red crystals of $[W(CO)(DMF)(dpe)_2]$ (4) were isolated in 52% yield after addition of hexane to the product solution.[6)] The IR spectrum of complex 4 shows two characteristic bands assignable to $\nu(C\equiv O)$ and $\nu(C=O)$ at 1680 and 1638 cm^{-1}, respectively.[7)] If the reaction was performed only for 20 min, a hydrido-η^2-carbamoyl complex $[WH(\eta^2\text{-}CONMe_2)(dpe)_2]$ (5) was able to be isolated in 16% yield as dark red crystals in addition to complex 4.[8)] The

$$\text{trans-}[W(N_2)_2(dpe)_2] \xrightarrow[\text{reflux}]{\text{DMF/PhH}} [WH(\eta^2\text{-}CONMe_2)(dpe)_2] \xrightarrow[\text{reflux}]{\text{DMF/PhH}} [W(CO)(DMF)(dpe)_2]$$

complex 5 unambiguously represents the intermediate stage of the conversion of complex 3 into complex 4, since complex 5 isolated in a pure form can be converted into complex 4 accompanied by the formation of $HNMe_2$, when treated with DMF in hot benzene.

The ^{1}H NMR spectrum of complex **5** shows the quintet resonance at -4.1 ppm assignable to a hydride proton ($^{2}J_{PH}$ = 33 Hz) together with two singlet peaks at 3.14 and 2.45 ppm due to the N-methyl protons, whereas weak W-H and strong C=O stretching bands appear in its IR spectrum at 1952 and 1545 cm^{-1}, respectively. These spectroscopic data are indicative of the hydrido-carbamoyl structure of complex **5**, which was fully characterized by X-ray crystallography as shown in Fig. 1.[9)] The essentially planar N, N-dimethylcarbamoyl group coordinates to the tungsten atom at both carbon and oxygen atoms. Interestingly, the C-O bond length of 1.43(4) Å observed for complex **5** is estimated to be that of C-O single bond and is much longer than that of the molybdenum complex $[Ph_4P]_2[Mo(NO)(\eta^2\text{-}CONMe_2)(NCS)_4]$ previously reported (1.322(7) Å).[10)] The long C-O bond length as well as the double bond character between W and C atoms in complex **5** are indicative of considerable perturbation of the η^2-carbamoyl ligand toward the resonance structure II. This may be caused by a stronger back-bonding ability

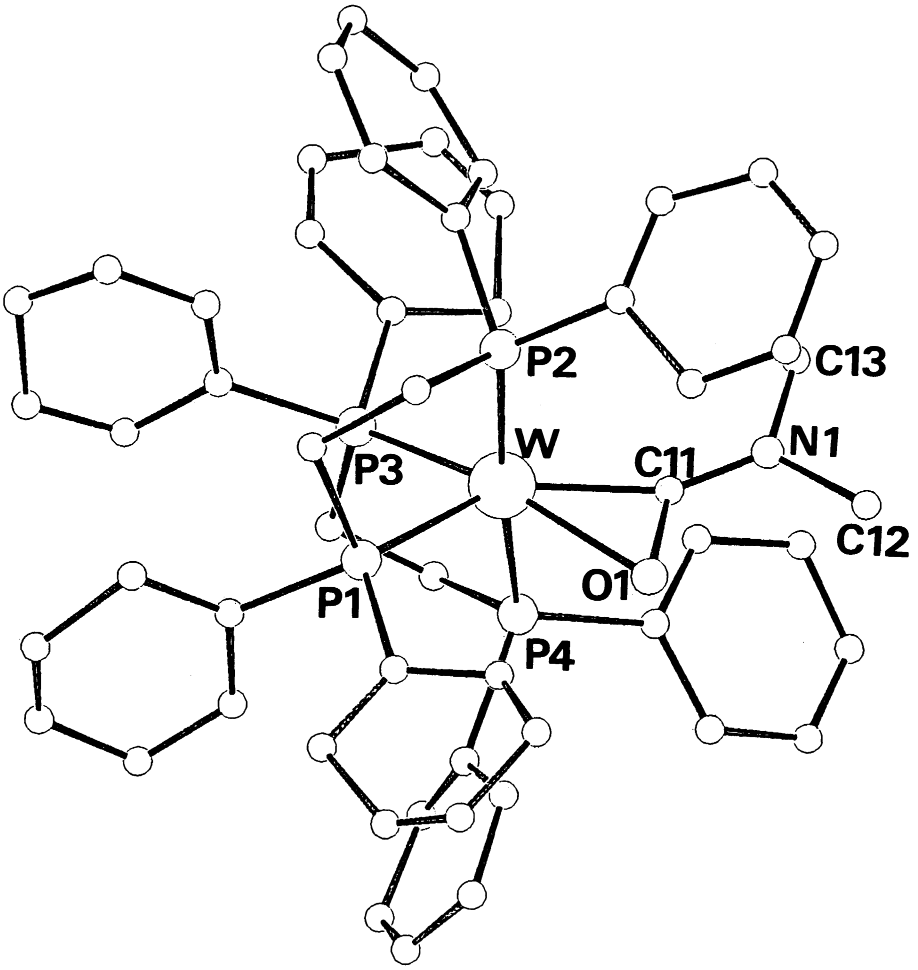

Fig. 1. View of $[WH(\eta^2\text{-}CONHMe_2)(dpe)_2]$(**5**). Selected bond lengths and angles: W-C(11) = 2.07(3), W-O(1) = 2.37(2), C(11)-O(1) = 1.43(4), C(11)-N(1) = 1.33(4) Å; P(2)-W-P(4) = 175.6(2), C(11)-W-P(3) = 140.1(10), P(1)-W-P(3)= 86.7(2), P(1)-W-O(1)= 97.1(5), W-C(11)-N(1) = 155.2(39), W-C(11)-O(1) = 83.0(16)°.

of the low valent metal in complex $\underset{\sim}{5}$ compared with that of the high valent metal in the latter molybdenum complex. To our knowledge, complex $\underset{\sim}{5}$ is the first example of hydrido-carbamoyl complexes, although many carbamoyl complexes are known. This complex may be considered as the model complex of the intermediate in transition metal-catalyzed synthesis of DMF from CO and dimethylamine.[11)]

In contrast to the trans structure of the parent complex $\underset{\sim}{3}$, the tungsten atom in complex $\underset{\sim}{5}$ is surrounded by two axial and two equatorial phosphorus atoms as well as the C(11) and O(1) atoms of carbamoyl ligand at equatorial sites. Although the hydride atom could not be located by the X-ray analysis, the equatorial site adjacent to the C(11) and P(3) atoms is presumably occupied by the hydride atom, since the C(11)-W-P(3) angle of 140.1(10)° is unusually wider than any other angles between two adjacent atoms around the tungsten. Therefore complex $\underset{\sim}{5}$ possibly has a pentagonal bipyramidal structure, consisting of hydride and η^2-carbamoyl ligands produced by the oxidative addition of DMF after the cleavage of the aldehydic C-H bond together with two dpe ligands with pseudo-cis configuration. The resonance pattern of the simple quintet observed for this hydride proton in the ^{1}H NMR spectrum can be explained by the fluxional character of complex $\underset{\sim}{5}$ at ambient temperature that is commonly observred for the molybdenum and tungsten hydride complexes of this type. Thus ^{31}P NMR spectrum of complex $\underset{\sim}{5}$ shows only one broad singlet resonance at 58.5 ppm relative to H_3PO_4 at room temperature, whereas it separates into four resonances at -78°C, indicating the rigid structure at this temperature.

When complex $\underset{\sim}{4}$ was recrystallized from benzene/hexane under N_2, orange crystals of trans-[W(CO)(N_2)(dpe)$_2$] ($\underset{\sim}{6}$) was isolated in 36% yield.[12)] The IR spectrum of complex $\underset{\sim}{6}$ well corresponds to that of the molybdenum analogue which has been fully characterized.[13)] However, synthesis of a five-coordinate complex [W(CO)(dpe)$_2$] from complex $\underset{\sim}{6}$ was not successful under the same reaction conditions as those employed for preparation of [Mo(CO)(dpe)$_2$]. Although dissociation of the dinitrogen ligand in complex $\underset{\sim}{6}$ proceeded by bubbling Ar gas through a solution of complex $\underset{\sim}{6}$ in benzene, the product isolated from the reaction mixture was cis-[W(CO)$_2$(dpe)$_2$] probably formed by disproportionation reaction of the initially formed five-coordinate complex. It seems that even a

$$[\mathrm{W(CO)(DMF)(dpe)_2}] \xrightarrow[\mathrm{PhH}]{N_2} \text{trans-}[\mathrm{W(CO)(N_2)(dpe)_2}] \xrightarrow[\mathrm{PhH}]{\mathrm{Ar}} \begin{array}{l}\text{cis-}[\mathrm{W(CO)_2(dpe)_2}] \\ \\ +\ \text{other W compounds}\end{array}$$

slight change in the electron density at the central metal or the structure around it caused by the nature of the metals and phosphines remarkably affects the stability of five-coordinate complexes [M(CO)(L)$_4$] (L = phosphine). Thus, [Mo(CO)(N_2)(dpe)(dpm)] (dpm = $Ph_2PCH_2PPh_2$),[14)] which was readily derived from trans-[Mo(N_2)$_2$(dpe)(dpm)][15)] and DMF via [Mo(CO)(DMF)(dpe)(dpm)],[16)] did not give a stable five-coordinate complex but cis-[Mo(CO)$_2$(dpe)(dpm)]. Further investigations on the reactivities of complexes **4** and **6** especially toward H_2 gas are in progress.

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6) Found: C, 61.99; H, 5.17; N, 1.53%. Calcd: C, 62.17; H, 5.13; N, 1.30%.
7) Molybdenum analogue [Mo(CO)(DMF)(dpe)$_2$] shows ν(C≡O) and ν(C=O) at 1690 and 1630 cm^{-1}, respectively.
8) Freshly distilled benzene and DMF must be used to obtain complex **5** in this yield. Found: C, 61.94; H, 4.93; N, 0.79%. Calcd: C, 62.68; H, 5.27; N, 1.34%.
9) MW 1053.84, monoclinic, space group Cc, a = 19.722(5), b = 16.067(4), c = 21.949(10) Å, = 135.96(2)°, V = 4834.9 Å^3, Z = 4, d_{calcd} = 1.448 g cm^{-3}. Data were collected on a Rigaku automatic four-circle diffractometer with graphite-monochromatized Mo Kα radiation using $\omega(2<2\theta<30°)$ and ω-2θ $(30<2\theta<60°)$ scans. For 5733 unique reflections with $|Fo| > 3\sigma(|Fo|)$, the structure was solved with use of Patterson and difference Fourier methods and refined by block-diagonal least-squares. Final least-squares refinement gave R = 0.059 and Rw = 0.070.
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11) R. A. Sheldon, "Chemicals from Synthesis Gas," D. Reidel Publishing Co., Dordrecht (1983), p. 174 and references therein.
12) Found: C, 61.70; H, 4.89; N, 2.62%. Calcd: C, 61.40; H, 4.68; N, 2.70%.
13) M = W: ν(N≡N) = 2070m, 2030w, ν(C≡O) = 1817s, 1795vs; M = Mo: ν(N≡N) = 2110m, 2080m, ν(C≡O) = 1812s, 1791s cm^{-1}.
14) trans-[Mo(CO)(N$_2$)(dpe)(dpm)].2PhH: Found: C, 70.11; H, 5.42; N, 2.14%. Calcd: C, 70.45; H, 5.37; N, 2.57%. ν(N≡N) = 2100, ν(C≡O) = 1820 cm^{-1}.
15) Found: C, 65.43; H, 4.84; N, 5.82%. Calcd: C, 65.52; H, 4.97; N, 5.99%. ν(N≡N) = 2050w, 1990vs cm^{-1}.
16) Found: C, 67.23; H, 5.35; N, 1.10%. Calcd: C, 67.42; H, 5.45; N, 1.43%. ν(C≡O) = 1715, ν(C=O) = 1640 cm^{-1}.

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