non-H atoms with anisotropic thermal parameters led to an *R* value of 0.035. Conversion to the inverse configuration led to final values of *R* = 0.025 and $R_w$ = 0.028. A final difference Fourier showed no feature greater than 0.3 e/Å$^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

**X-ray Data Collection, Structure Determination, and Refinement for Mo(COCH$_3$)(S$_2$CNMe$_2$)(CO)(PMe$_3$)$_2$.** Data collection was carried out as for complex **1**. Final lattice constants and a summary of the data collection parameters are given in Table I.

The structure was solved by a combination of Patterson and Fourier techniques. Least-squares isotropic refinement of the non-hydrogen atoms led to an *R* value of 0.081 at convergence. The methyl hydrogen atoms were located with the aid of a difference Fourier map, but only the hydrogens on C(3) (H(1)-H(3)) were varied. Refinement of the non-hydrogen atoms with anisotropic temperature factors and of the positional and isotropic thermal parameters of the three hydrogens atoms on C(3) led to final *R* values of 0.029 (*R*) and 0.034 ($R_w$). A final difference Fourier map showed no feature greater than 0.3 e/Å$^3$. The weighting scheme was based on unit weights and no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table IV.

**Acknowledgment.** This work was supported by the Spanish Comisión Asesora de Investigación Científica y Técnica, CAICYT (to E.C.) and the U.S. National Science Foundation (J.L.A.).

**Supplementary Material Available:** Thermal parameters and observed and calculated structure factor amplitudes for Mo($\eta^2$-COCH$_2$SiMe$_3$)Cl(CO)(PMe$_3$)$_3$ and Mo($\eta^2$-COCH$_3$)(S$_2$CNMe$_2$)(CO)(PMe$_3$)$_2$ (Tables A-D), and analytical and spectroscopic data for the new compounds Mo($\eta^2$-COCH$_2$R)X(CO)$_n$(PMe$_3$)$_{4-n}$ and Mo($\eta^2$-COCH$_2$R)(S$_2$CNMe$_2$)(CO)$_n$(PMe$_3$)$_{3-n}$ ($n$ = 1,2) (Tables 1 and 2) (24 pages). Ordering information is given on any current masthead page.

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# Oxidative Addition of Nitrosobenzene Fragments across the Triply Bonded Ditungsten Hexa-*tert*-butoxide Molecule. The Preparation and Structure of [W(OCMe$_3$)$_2$(NPh)]$_2$($\mu$-O)($\mu$-OCMe$_3$)$_2$

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**Abstract:** W$_2$(OCMe$_3$)$_6$ reacts with nitrosobenzene in toluene at 45 °C over a period of 12 h to give [W(OCMe$_3$)$_2$(NPh)]$_2$($\mu$-O)($\mu$-OCMe$_3$)$_2$ in 55–60% yield. The molecule consists of face-sharing octahedra with two *tert*-butoxide units and an oxygen atom as the bridging groups. The tungsten-to-tungsten distance is 3.059 (0) Å. The W–O distances for $\mu$-O are 1.937 (4) and 1.937 (4) Å, while the W–O distances for the oxygen atoms of the bridging *tert*-butoxide groups are W(1)–O(6) = 2.078 (4) Å, W(2)–O(6) = 2.269 (4) Å and W(1)–O(7) = 2.264 (4) Å, W(2)–O(7) = 2.092 (4) Å. The W–N distances are 1.737 (5) and 1.738 (5) Å, and the W–N–C angles have an average value of 164.7 [3]°. The compound crystallizes in space group *C*2/*c* with *a* = 27.57 (1) Å, *b* = 18.09 (1) Å, *c* = 18.36 (1) Å, $\beta$ = 115.97°, *V* = 8231 (8) Å$^3$, and *Z* = 8. The tungsten atoms have formal oxidation numbers of VI and no W–W bond exists, the relatively short W–W separation being attributable to the presence of bridging ligands and the role of the ligated oxygen and nitrogen atoms in reducing the effective charge on the metal atoms through extensive $\pi$ donation. From the bond lengths and angles it is concluded that the W–N bonds have an order of ca. 2.5, which includes about one-half of a N → W $\pi$ donor bond over and above the basic W=N double bond. The oxygen atoms, especially those of the terminal alkoxy ligands, also contribute significant $\pi$ density to the metal atoms.

The chemistry of compounds containing both metal–metal bonds and metal alkoxide groups, particularly their reactions with unsaturated or oxidizing organic groups to form new metal–carbon or metal–nitrogen bonds, is currently in a phase of extremely rapid growth.[1] In these reactions the metal atoms generally go to a higher formal oxidation state although there are a few cases where this is not so, or ambiguity arises depending on the sort of assumptions made about bonding. Several Mo$_2$(OR)$_6$ compounds are known and have been studied, but for tungsten work has necessarily been restricted to W$_2$(OCMe$_3$)$_6$ which is the only known W$_2$(OR)$_6$ compound.[1] Schrock, Listerman, and Sturgeoff,[2] Chisholm et al.,[3] and Cotton, Schwotzer, and Shamshoum[4] have found many diverse reactions of W$_2$(OCMe$_3$)$_6$ with C≡C and C≡N bonds, and for Mo$_2$(OCMe$_3$)$_6$ interesting reactions occur with CO.[5] Two of the most recently reported studies are those of Chisholm, Huffman, and Marchant,[6] who have observed the reaction of dimethylcyanamide, Me$_2$NCN, with W$_2$(OCMe$_3$)$_6$ and Mo$_2$(OCH$_2$CMe$_3$)$_6$, and of Cotton and Schwotzer, who studied the reaction of CO with Mo$_2$(O-*i*-Pr)$_6$ in pyridine.[7]

In this paper we report the first reaction of a nitroso compound, nitrosobenzene (C$_6$H$_5$NO), with W$_2$(OCMe$_3$)$_6$. This gives a product in which a remarkable double oxidative addition has occurred leading to the formation of W=N double bonds with concomitant loss of the W≡W bond.

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[2] Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291.

[3] (a) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratterman, A. L. *J. Chem. Soc., Chem. Commun.* **1981**, 1229.

[4] (a) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1983**, *2*, 1167. (b) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics*, in press.

[5] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 7645.

[6] Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *J. Am. Chem. Soc.* **1983**, *105*, 6162.

[7] Cotton, F. A.; Schwotzer, W. *Inorg. Chem.* **1983**, *22*, 387.

0002-7863/84/1506-3222$01.50/0

**Table I**

| | |
|---|---|
| formula | $[W(OCMe_3)_2(Nph)_2]-(\mu\text{-}O)(\mu\text{-}OCMe_3)_2$ |
| formula weight | 1004.6 |
| space group | $C2/c$ |
| systematic absences | $hkl$: $h + k = l = 2n$, $h0l$: $l = 2n$ |
| $a$, Å | 27.589 (1) |
| $b$, Å | 18.075 (1) |
| $c$, Å | 18.393 (1) |
| $\beta$, deg | 116.0 (1) |
| $V$, Å$^3$ | 8243 (8) |
| $Z$ | 8 |
| $d_{calcd}$, g/cm$^3$ | 1.619 |
| crystal size, mm | 0.2 × 0.2 × 0.3 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 52.09 |
| data collection instrument | CAD-4 |
| radiation (monochromated in incident beam) | Mo K$\alpha$ |
| orientation reflections, no., range ($2\theta$) | 25, $9° \leq 2\theta \leq 15°$ |
| temp, °C | −104 |
| scan method | $\theta$–$2\theta$ |
| data collect. range, $2\theta$, deg | 0–50 |
| no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$ | 5925 |
| no. of parameters refined | 414 |
| trans. factors, max, min | 99.896, 78.053 |
| $R^a$ | 0.0384 |
| $R_w{}^b$ | 0.0531 |
| quality-of-fit indicator$^c$ | 1.5 |
| largest shift/esd, final cycle | 0.13 |
| largest peak, e/Å$^3$ | 0.7 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

## Experimental Section

Ditungsten hexa-*tert*-butoxide, $W_2(OCMe_3)_6$, was prepared[2] by the reduction of $WCl_4$ with sodium amalgam in THF, in the presence of $LiOCMe_3$, followed by recrystallization from hexane at −20 °C. All reactions were done under an argon atmosphere.

**Reaction of $W_2(OCMe_3)_6$ with Nitrosobenzene.** A weighed amount of $W_2(OCMe_3)_6$ (500 mg, 0.60 mmol) was dissolved in 20 mL of toluene. Nitrobenzene (130 mg, 1.20 mmol) was added to the solution at room temperature. The reaction mixture was heated slowly to approximately 45 °C and then stirred at this temperature for 12 h. After the solvent was removed under vacuum the residue was extracted with 10 mL of hexane and the extract concentrated to ca. 3.0 mL. Yellow needles were isolated after 2 days of cooling at −20 °C. The reaction gives reproducible yields of 55–60%.

**X-ray Crystallography.** The crystal used for data collection was mounted in a capillary tube. Data were collected on an Enraf-Nonius CAD-4F diffractometer with the crystal maintained at −104 °C. The general procedure used in determining the structure has already been described elsewhere.[7] A detailed description is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I.

The atomic positional parameters are listed in Table II, and Table III gives a selected list of bond distances and bond angles. The anisotropic thermal parameters, the structure factors, and a complete list of bond lengths and bond angles are all available as supplementary material.

**Other Physical Measurements.** The $^1H$ NMR spectrum of **1** was measured on a Varian XL-200 PFT spectrometer in $CD_2Cl_2$. The chemical shifts are as follows: $\delta$ 1.224 (bridging $OCMe_3$), $\delta$ 1.428 (terminal $OCMe_3$), and a complex multiplet between $\delta$ 7.0 and 8.2 ($NC_6H_5$) with approximate ratios of 1:2:0.6 (calcd 1:2:0.56).

## Results and Discussion

**The Synthetic Reaction.** In a formal sense the preparative reaction involves the oxidative addition of two molecules of PhNO to one of $W_2(OCMe_3)_6$ with concomitant loss of one atom of oxygen. We have not been able to determine the fate of this "missing" oxygen atom, but presumably it participates in some additional oxidation of $W_2(OCMe_3)_6$, although we have not isolated a second product. This assumption is consistent with the fact that yields of the isolated product do not exceed 60% on the basis of $W_2(OCMe_3)_6$.

**Table II.** Positional Parameters and Their Estimated Standard Deviations[a]

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| W(1) | 0.10100 (1) | 0.24059 (2) | 0.03244 (2) | 1.797 (6) |
| W(2) | 0.16902 (1) | 0.22229 (2) | 0.21479 (2) | 1.748 (6) |
| O(1) | 0.1743 (2) | 0.2485 (3) | 0.1164 (3) | 1.8 (1) |
| O(2) | 0.1185 (2) | 0.1734 (3) | −0.0301 (3) | 2.8 (1) |
| O(3) | 0.1332 (2) | 0.1992 (3) | 0.2797 (3) | 2.2 (1) |
| O(4) | 0.1969 (2) | 0.3135 (3) | 0.2645 (3) | 2.1 (1) |
| O(5) | 0.0272 (2) | 0.2126 (3) | −0.0116 (3) | 2.7 (1) |
| O(6) | 0.0947 (2) | 0.2867 (3) | 0.1315 (3) | 1.9 (1) |
| O(7) | 0.1183 (2) | 0.1496 (3) | 0.1252 (3) | 2.0 (1) |
| N(1) | 0.2276 (2) | 0.1696 (4) | 0.2581 (3) | 2.2 (1) |
| N(2) | 0.1001 (2) | 0.3220 (4) | −0.0184 (3) | 2.2 (1) |
| C(1) | 0.0546 (3) | 0.3323 (4) | 0.1418 (4) | 2.3 (2) |
| C(2) | 0.0828 (3) | 0.3781 (5) | 0.2173 (4) | 2.9 (2) |
| C(3) | 0.0289 (3) | 0.3847 (5) | 0.0675 (5) | 3.2 (2) |
| C(4) | 0.0131 (3) | 0.2831 (5) | 0.1494 (5) | 3.1 (2) |
| C(5) | 0.0964 (3) | 0.0768 (4) | 0.1250 (4) | 2.6 (2) |
| C(6) | 0.0898 (4) | 0.0370 (5) | 0.0491 (5) | 4.1 (2) |
| C(7) | 0.1358 (3) | 0.0336 (5) | 0.2001 (5) | 3.3 (2) |
| C(8) | 0.0416 (3) | 0.0855 (5) | 0.1289 (5) | 3.5 (2) |
| C(11) | 0.1114 (3) | 0.3907 (4) | −0.0412 (4) | 2.5 (2) |
| C(12) | 0.0703 (3) | 0.4362 (5) | −0.0954 (5) | 3.7 (2) |
| C(13) | 0.0844 (3) | 0.5067 (6) | −0.1137 (5) | 4.5 (2) |
| C(14) | 0.1371 (4) | 0.5305 (5) | −0.0815 (5) | 4.9 (2) |
| C(15) | 0.1790 (4) | 0.4854 (5) | −0.0265 (6) | 4.8 (2) |
| C(16) | 0.1653 (3) | 0.4157 (5) | −0.0056 (5) | 3.2 (2) |
| C(21) | 0.2766 (3) | 0.1353 (4) | 0.2751 (5) | 2.5 (2) |
| C(22) | 0.2968 (3) | 0.1344 (5) | 0.2166 (5) | 3.3 (2) |
| C(23) | 0.3465 (3) | 0.1038 (5) | 0.2339 (5) | 3.5 (2) |
| C(24) | 0.3778 (3) | 0.0731 (5) | 0.3094 (6) | 4.0 (2) |
| C(25) | 0.3580 (3) | 0.0725 (6) | 0.3686 (5) | 4.0 (2) |
| C(26) | 0.3080 (3) | 0.1037 (6) | 0.3511 (5) | 3.8 (2) |
| C(31) | 0.2454 (3) | 0.3557 (5) | 0.2950 (5) | 3.3 (2) |
| C(32) | 0.2683 (5) | 0.3574 (9) | 0.2374 (7) | 13.7 (4) |
| C(33) | 0.2867 (5) | 0.3154 (7) | 0.370 (1) | 8.8 (5) |
| C(34) | 0.2340 (4) | 0.4276 (6) | 0.3271 (7) | 5.8 (3) |
| C(36) | 0.1424 (3) | 0.1811 (5) | 0.3614 (4) | 2.9 (2) |
| C(37) | 0.1955 (3) | 0.1375 (6) | 0.4041 (5) | 4.1 (2) |
| C(38) | 0.1450 (3) | 0.2537 (5) | 0.4046 (5) | 3.1 (2) |
| C(39) | 0.0933 (3) | 0.1345 (5) | 0.3546 (5) | 3.6 (2) |
| C(41) | 0.1476 (3) | 0.1641 (6) | −0.0780 (5) | 3.8 (2) |
| C(42) | 0.2075 (9) | 0.165 (1) | −0.021 (1) | 15.4 (8)* |
| C(43) | 0.1325 (8) | 0.090 (1) | −0.118 (1) | 13.7 (7)* |
| C(44) | 0.1346 (5) | 0.2218 (7) | −0.1371 (6) | 9.8 (3) |
| C(46) | −0.0214 (3) | 0.2137 (5) | −0.0876 (5) | 3.7 (2) |
| C(47) | −0.0227 (5) | 0.1375 (6) | −0.1266 (7) | 6.3 (3) |
| C(48) | −0.0692 (4) | 0.2240 (8) | −0.0665 (7) | 6.4 (4) |
| C(49) | −0.0203 (4) | 0.2750 (5) | −0.1441 (5) | 3.9 (2) |

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $^4/_3[a2B(1,1) + b2B(2,2) + c2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)*B(1,3) + bc(\cos\alpha)*B(2,3)]$.

According to the excellent review of Nugent and Haymore[8] many reagents of the type RNX can serve as the source of an RN moiety upon reaction with either M or MO, viz.,

$$RNX + MO \rightarrow M(NR) + XO \quad (X = CO, R_3P, \text{etc.})$$

$$RNX + M \rightarrow M(NR) + X \quad (X = N_2)$$

There does not, however, appear to be any prior example of a nitrosyl compound, RNO, serving as the source of RN. There is, in fact, no prior example of the reaction of a nitroso compound with any multiple M–M bond to generate any product. The reaction proceeds smoothly under rather mild conditions.

**Structure and Bonding.** The crystals of the title compound, $[W(OCMe_3)_2(NPh)]_2(\mu\text{-}O)(\mu\text{-}OCMe_3)_2$, consist of discrete dinuclear molecules, each having the structure shown in Figure 1.

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(8) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

**Table III.** Selected Bond Lengths and Bond Angles

| bond distances, Å | | bond angles, deg | |
|---|---|---|---|
| W(1)–W(2) | 3.059 (0) | W(1)–W(2)–O(1) | 37.8 (1) |
| –O(1) | 1.937 (4) | –O(3) | 118.3 (1) |
| –O(2) | 1.876 (4) | –O(4) | 111.2 (1) |
| –O(5) | 1.901 (4) | –O(6) | 42.8 (1) |
| –O(6) | 2.078 (4) | –O(7) | 47.7 (1) |
| –O(7) | 2.264 (4) | –N(1) | 124.2 (2) |
| –N(2) | 1.737 (5) | W(2)–W(1)–O(1) | 37.8 (1) |
| W(2)–O(1) | 1.937 (4) | –O(2) | 113.8 (1) |
| –O(3) | 1.899 (4) | –O(5) | 117.7 (1) |
| –O(4) | 1.878 (4) | –O(6) | 47.9 (1) |
| –O(6) | 2.269 (4) | –O(7) | 43.1 (1) |
| –O(7) | 2.092 (4) | –N(2) | 112.6 (2) |
| –N(1) | 1.738 (5) | W(1)–O(1)–W(2) | 104.3 (2) |
| O(1)–O(6) | 2.429 (5) | –O(6)–W(2) | 89.4 (1) |
| –O(7) | 2.413 (6) | –O(7)–W(2) | 89.1 (1) |
| O(6)–O(7) | 2.577 (5) | –O(2)–C(41) | 144.5 (5) |
| O(2)–C(41) | 1.437 (8) | –O(5)–C(46) | 140.4 (4) |
| O(3)–C(36) | 1.449 (8) | –O(6)–C(1) | 134.4 (4) |
| O(4)–C(31) | 1.423 (7) | –O(7)–C(5) | 135.1 (4) |
| O(5)–C(46) | 1.452 (8) | –N(2)–C(11) | 165.3 (5) |
| O(6)–C(1) | 1.458 (7) | W(2)–O(3)–C(36) | 143.2 (4) |
| O(7)–C(5) | 1.449 (7) | –O(4)–C(31) | 140.9 (4) |
| | | –O(6)–C(1) | 135.7 (4) |
| | | –O(7)–C(5) | 135.0 (4) |
| | | –N(1)–C(21) | 164.2 (5) |

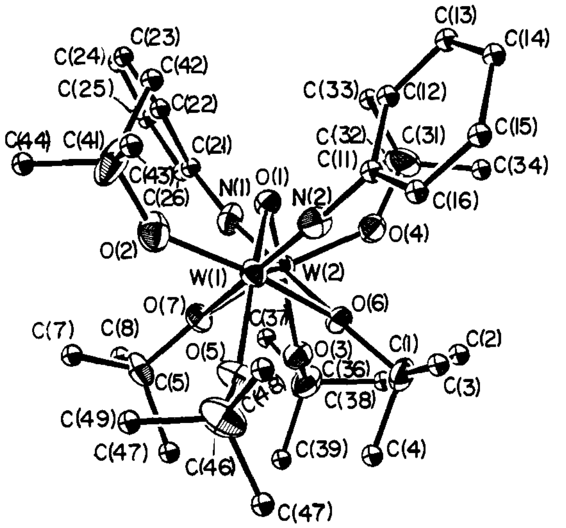

**Figure 1.** An ORTEP drawing of the entire molecule, giving the atomic labeling scheme. The methyl carbon atoms of the *tert*-butyl groups and the carbon atoms of the phenyl groups are represented by arbitrarily small spheres to avoid covering up other atoms. All other atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

In this drawing the methyl carbon atoms of the *tert*-butoxy groups and the carbon atoms of the phenyl groups have been represented by arbitrarily small spheres to avoid having them obscure the more interesting inner parts of the molecule. The molecule as a whole is the crystallographic asymmetric unit and thus has no imposed crystallographic symmetry. However, there is a virtual twofold rotation axis passing through the $\mu$-oxygen atom and perpendicularly bisecting the W(1)–W(2) line.

Each virtually equivalent half of the molecule consists of a six-coordinate tungsten atom, where the arrangement of ligands is that of a very distorted octahedron. The structure will be discussed in more detail shortly. Each tungsten atom is bonded to two terminal $\mathrm{Me_3CO}$— groups and to one terminal PhN= group. In addition these tungsten atoms share two bridging $\mathrm{Me_3CO}$— groups and a bridging oxygen atom. According to normal assumptions about valence numbers, the tungsten atoms must each be assigned a formal oxidation state of VI. There is, then, no formal possibility of W–W bonding, despite the fact that the distance, 3.059 (0) Å, is shorter than those in several cases where bonds of order one have been postulated.[9-11] This close approach of two metal atoms with such high formal charges, even though there is no bond between them, can be attributed to two factors. One is the presence of three bridging groups. In addition, as will be discussed presently, there is a large amount of donor $\pi$ bonding from the nitrogen and oxygen atoms of the terminal ligands, and this lowers the effective charge on the metal atoms to a small value, thus reducing the repulsive force between them.

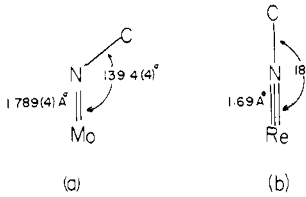

**Figure 2.** Structures from the literature[13,14] exemplifying the closest observed approaches to the limiting cases of M=N double bonding (a) and $\mathrm{N} \overset{\leftarrow}{\equiv} \mathrm{M}$ triple bonding (b).

Let us turn now to a more detailed examination of the structure. The two halves of the molecule share the bridging oxygen atom to which they form W–O bonds that are found to be exactly equal in length, 1.937 (4) Å. Each tungsten atom is bound to two terminal $\mathrm{OCMe_3}$ groups, and these four W–O bond lengths are in the range 1.876 (4) to 1.901 (4) Å, with a mean value of 1.888 [7] Å. There are then two bridging $\mathrm{Me_3CO}$ groups; these form very unsymmetrical bridges with a relatively short bond (2.078 (4) Å, 2.092 (4) Å) and an appreciably longer bond (2.264 (4) Å, 2.269 (4) Å) to each metal atom. The bonds around the bridging alkoxide oxygen atoms are nearly coplanar. The sums of the angles at O(6) and O(7) are 359.5 (9)° and 359.2 (9)°, respectively. The carbon atoms C(1) and C(5) lie 0.14 (1) and 0.17 (1) Å from their respective WWO planes. Finally, each metal atom is bounded to a PhN group with W–N distances of 1.737 (5) and 1.738 (5) Å. The structure can be thought of as two square-pyramidal units that have an oxygen atom in common and are further linked by the weaker bridge bonds. The nitrogen atoms are at the apices of the square pyramids. Thus, the base of the pyramid at W(1) is defined by O(1), O(6), O(5), and O(3) and the weak bridge bond trans to the W(1)–N(2) bond is the W(1)–O(7) bond. Similarly, at W(2) the base is defined by O(1), O(7), O(4), and O(3) and the weak bridge bond trans to the W(2)–N(1) bond is the W(2)–O(6) bond. The N–W–O (trans) angles average 166 [1]°.

The various W–O distances (neglecting the long bridging ones) can be interpreted in terms of different degrees of O → W $\pi$ donation. The greatest amount would appear to be in the bonds to the four terminal alkoxides, assuming that bond distance and extent of $\pi$ bonding are inversely related. In accord with this the W–O–C angles are large, lying in the range 140.4 (4) to 144.5 (5)°, with a mean value of 142.3 [2]°. The next strongest W–O $\pi$ bonding would appear to be in the W–O (bridge) bonds which have the next greatest lengths, although this type of comparison may not be entirely justified. Finally, as would be expected, the long bridging alkoxide bonds would appear to have the least W–O $\pi$ bonding; the amount here may be negligible. Nonetheless, the total amount of oxygen atom $\pi$ electron density donated to each tungsten atom by its entire set of oxygen ligand atoms is probably quite significant and will considerably diminish its effective charge as well as making significant use of the orbitals available for $\pi$ bonding. These results of W ← O $\pi$ bonding must be kept in view as the character of the W–N bonds is evaluated, a task to which we now turn.

**Nature of the Tungsten–Nitrogen Bond.** The occurrence of M(NR), organoimido, groups is well documented.[8,12-14] The

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(9) To cite but two, there are the following: $\mathrm{Cp_2W_2(CO)_6}$, 3.222 (1) Å;[10] $\mathrm{W_2(CO)_6}$(guaiazulene), 3.264 (1) Å.[11]

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MNR groups are characterized by varied amounts of $M \leftarrow N$ $\pi$ bonding, over and above the $\pi$ character inherent in the minimal $M{=}N$ double bond.

To place the present work in context we may select from the literature two structures that represent, or at least tend toward, the limits. The key structural features for these compounds of rhenium[13] and molybdenum[14] are shown in Figure 2. The rhenium case is essentially at the limit of bond order 3 with its angle of 180°. Bearing in mind that the radius of the tungsten atom is 0.02 to 0.03 Å greater than that of the rhenium atom, we conclude that a full W—N bond would probably have a length of 1.71-1.72 Å. For the molybdenum compound the bond angle of 139.4° instead of 120° has been interpreted[14] to imply a bond order of about 2.3, and a distance of perhaps 1.84 Å suggested for a pure double bond. The observed angles (ca. 165°) and distances (1.74 Å) in the present case then are closer to the triple bond limit and suggest a bond order of about 2.8. This considerable, but incomplete, formation of the second $\pi$ bond is consistent with our earlier analysis of the W–O bonding, where we drew the conclusion that the tungsten atoms receive a moderate amount of $\pi$ electron density from the oxygen atoms to which they are bonded. However, the oxygen atoms alone only partially satisfy the capacity of the tungsten atom in this respect, and thus the RN group can compete effectively and make about three-quarters of its total possible contribution.

In a recent preliminary publication[15] the preparation and structure of the dinuclear compound $[(PhN)(MeO)_3W]_2(\mu\text{-}OMe)_2$ were reported. The structure is formed by two octahedra sharing an edge, and the W···W distance is given as 3.47 Å. Since there are only two OR bridges in this case, whereas in our compound there is also the bridging oxygen atom, the shorter distance, 3.06 Å, in our compound bears a reasonable relation to this one. The dimensions of this other compound are reported only partially and they have somewhat large esd's, so that further detailed comparison of the two structures would be of uncertain value. The pattern of W–O distances is comparable in the two cases, but the reported W–N distance, 1.65 (2) Å, is considerably shorter than ours. We can see no reason for such a marked difference, and we therefore look forward to a complete report of a fully refined structure to see whether the discrepancy will lessen.

We also note that a reaction in which $CpMo(CO)_2{\equiv}Mo(CO)_2Cp$ reacts with $PhNO_2$ to give a product containing $\mu_2$-PhN and both $\mu_2$-O and terminal O has been reported recently.[16]

**Acknowledgment.** We thank the National Science Foundation for support and Dr. B. L. Haymore for a helpful discussion.

**Registry No.** $[W(OCMe_3)_2(NPh)]_2(\mu\text{-}O)(\mu\text{-}OCMe_3)_2$, 89711-33-1; $W_2(OCMe_3)_6$, 57125-20-9; $C_6H_5NO$, 586-96-9.

**Supplementary Material Available:** Table of observed and calculated structure factors, anisotropic thermal parameters, and bond lengths and bond angles and a more detailed account of the crystallographic work (46 pages). Ordering information is given on any current masthead page.

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# H/D Exchange in the Reaction of $D_2$ with Bis(triphenyl phosphite)(acetylacetonato)rhodium(I), $Rh(P(OPh)_3)_2(acac)$

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**Abstract:** The reaction of $Rh(P(OPh)_3)_2(acac)$ (**1**) with $D_2$ in benzene has been studied by $^1H$ NMR spectroscopy, and complex **1** has been found to undergo H/D exchange at the ortho positions of the coordinated phosphite ligands and at the central methine position of the acetylacetonate ligand. At 75 °C, the exchange reaction proceeds with the extent of deuterium incorporation into $P(OPh)_3$ being the same as that into acac at all stages of the H/D exchange process. At 60 °C, deuterium incorporation into $P(OPh)_3$ is initially more rapid than that into the acac ligand. The initial rate of deuterium incorporation into $P(OPh)_3$ by **1** in benzene-$d_6$ under $D_2$ at 60 °C proceeds with a first-order rate constant of $9.6 \times 10^{-5}$ s$^{-1}$. A mechanism for this exchange process is proposed.

Rhodium(I) complexes containing a single acetylacetonate (acac) ligand of the type RhLL′(acac) (L, L′ = CO, $PPh_3$, $C_2H_4$) were first reported in 1964.[1] Since that time numerous complexes containing different ligands, L, have been reported and studied. Many of these complexes are used as catalyst precursors for industrially important reactions such as olefin hydrogenation[2] and hydroformylation,[3,4] and have appeared in numerous patents.[5] One acac complex recently reported to catalyze arene hydrogenation is the phosphite complex $Rh(P(OPh)_3)_2(acac)$ (**1**).[6] Related rhodium(I) complexes containing phosphite ligands such as $Rh(P(OPh)_3)_3Cl$ and $Rh(P(OPh)_3)_4^+$ have been studied by Barefield and Parshall[7] and have been found to undergo H/D

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