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Reactivity of bridging phosphido ligands in WOs binuclear complexes. Crystal and molecular structure of (CO)5W(.mu.-PPh2)Os(H)(CO)2(PMePh2)(PPh2H)

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$(\eta^5\text{-}C_5H_5)(PPh_3)Cl]$, 31904-79-7; $[NiCp(CO)]_2$, 12170-92-2; $[NiCp(CO)I]$, 55046-35-0; $[NiCp(PPh_3)CN]$, 42378-02-9; $ClCH_2SCH_3$, 2373-51-5; $LiCH_2SCH_3$, 286-60-2; CH_3I, 74-88-4; $LiCH_2CN$, 20428-58-4; dimethylsulfonium methylide, 6814-64-8; cyclooctene, 931-88-4; bicyclo[6.1.0]nonane, 286-60-2.

Supplementary Material Available: Tables of thermal parameters for non-hydrogen atoms, positional and thermal parameters of hydrogen atoms, and observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Reactivity of Bridging Phosphido Ligands in WOs Binuclear Complexes. Crystal and Molecular Structure of $(CO)_5W(\mu\text{-}PPh_2)Os(H)(CO)_2(PMePh_2)(PPh_2H)$

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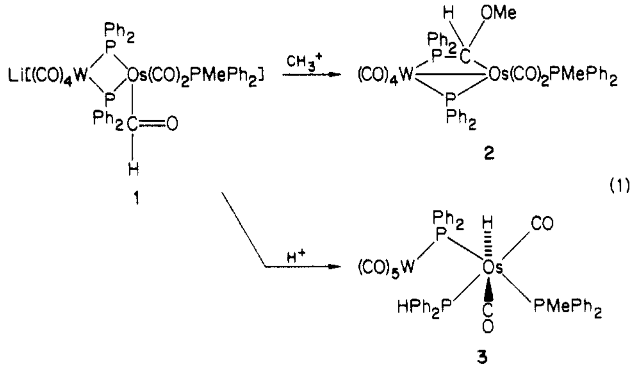
The binuclear complex $(CO)_5W(\mu\text{-}PPh_2)Os(H)(CO)_2(PMePh_2)(PPh_2H)$, **3**, is obtained from protonation of the formyl compound $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(CHO)(CO)_2(PMePh_2)]$. Complex **3** has been characterized by a complete single-crystal X-ray diffraction study. It crystallizes in the space group *C*2/*c* with $a = 35.172$ (9) Å, $b = 11.045$ (3) Å, $c = 25.275$ (6) Å, $\beta = 105.89$ (2)°, $V = 9444$ (3) Å^3, and $Z = 8$. The structure has been refined for the 5365 reflections with $F_o \geq 3\sigma(F_o)$ to $R_F = 0.036$ and $R_{wF} = 0.041$. The two nonbonded metal atoms are bridged by the μ-PPh_2 ligand with the W further coordinated by five CO's and the Os by two CO's, the hydride, PPh_2H, and $PMePh_2$ ligands. Both the Os hydride and the hydrogen on phosphorus were located and refined. The W–P$_\mu$–Os angle of 116.2 (1)° is the largest yet reported for this structural unit and illustrates the tremendous flexibility of this bridging ligand. Thermolysis of **3** leads to CO and H_2 loss with formation of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Os}(CO)_2(PMePh_2)$, **4**, which involves formation of a second phosphido bridge. A second phosphido bridge also forms upon reaction of **3** with MeLi to give $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_2(PMePh_2)]$, **5**, after loss of CO. If MeI is added immediately after addition of MeLi, the product is instead the monophosphido-bridged complex $(CO)_5W(\mu\text{-}PPh_2)Os(H)(CO)_2(PMePh_2)_2$, **6**, formed as a mixture of two isomers. Protonation of **5** leads to the bridge cleavage product $(CO)_5\overline{W(\mu\text{-}PPh_2)Os}(H)(CO)(PMePh_2)(PPh_2H)$, **7**, while methylation with $[(CH_3)_3O]BF_4$ leads to formation of **4**. Complex **4** is also obtained when solutions of **7** are heated to 55 °C.

Bridging phosphido ligands have recently been shown to participate in a number of interesting chemical transformations.[1-16] These include conversion of bridging phosphido ligands into bridging phosphinidene,[6,8] phosphine oxide,[9] and diphosphene ligands[10] and coupling of bridging phosphido ligands with alkyl,[1,3] alkyne,[11,16] vinyl,[12] hydride,[1,13] carbene,[1,2,14] and phosphide ligands.[14] An understanding of the types of reactions that these ligands undergo and the conditions under which they occur will be necessary for polynuclear reactivity and catalytic studies of phosphido-bridged complexes.

We recently reported that methylation and protonation of the phosphido-bridged WOs formyl complex **1** led to the phosphido rearrangements given in eq 1.[1,2] Particularly



interesting was complex **2** which apparently arose via coupling of a phosphido ligand with a carbene, the latter generated by methylation of the formyl ligand. Protonation of **1** led cleanly to complex **3** in which one μ-PPh_2 ligand had been converted into a terminal PPh_2H ligand. We have since investigated the derivative chemistry of **3**

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and these results are reported herein, including a complete crystallographic characterization of this complex.

Experimental Section

The complex $(CO)_4W(\mu\text{-}PPh_2)OsH(CO)_2(PMePh_2)(PPh_2H)$, **3**, was prepared by the literature procedure.[2] MeLi, $[(CH_3)_3O]BF_4$, and MeI (Aldrich) were used as received without further purification. Unless otherwise specified, all operations were performed under a prepurified N_2 atmosphere by using rigorously dried and deoxygenated solvents and standard Schlenk techniques. The spectroscopic instruments employed in this research have been previously described[3] except that some IR spectra were recorded on an IBM IR-32 FT/IR spectrometer. Field desorption (FD) mass spectra were recorded by Robert Hale at the Tennessee Eastman CO., Kingsport, TN. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Synthesis of $(CO)_4\overline{W(\mu\text{-}PPh_2)_2Os}(CO)_2PMePh_2$, 4. A solution of **3** (200 mg, 0.175 mmol) in 20 mL of toluene was heated at reflux for 12 h. During this time the orange solution turned purple. Removal of solvent by rotary evaporation (MeOH azeotrope) afforded an air-stable, purple oil. This oil was supported on 1 g of SiO_2 by rotary evaporation of a CH_2Cl_2 solution. The SiO_2 was then loaded midway down a 12-in. chromatography column. Elution with 10% CH_2Cl_2/hexane gave a red band of **4**. Removal of solvent from this band yielded **4** as air-stable, purple microcrystals in 92% yield (184 mg, 0.161 mmol): MS, *m/e* (EI) 1112 (M^+), 1084 ($M^+ - CO$), 1056 ($M^+ - 2CO$), 1028 ($M^+ - 3CO$), 1000 ($M^+ - 4CO$), 972 ($M^+ - 5CO$), 944 ($M^+ - 6CO$); IR ν_{CO} (CH_2Cl_2) 2040 (m), 2010 (m), 1955 (s), 1935 (sh), 1910 (m) cm^{-1}. Anal. Calcd for $C_{43}H_{33}O_6OsP_3W$: C, 46.40; H, 2.97. Found: C, 46.17; H, 2.95.

Synthesis of $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_2(PMePh_2)]$, 5. To a solution of **3** (200 mg, 0.175 mmol) in 30 mL of THF was added MeLi (146 μL of a 1.2 M THF solution). The solution was stirred for 16 h during which time the color changed from orange to brown. Evaporation of solvent afforded an orange-brown oil. $^{31}P\{^1H\}$ and ^1H NMR data were identical with those reported previously for **5**, prepared by a different procedure.[2] IR: ν_{CO} (THF) 2022 (w), 1987 (m), 1970 (m), 1914 (m), 1873 (s), 1857 (ssh), 1813 (m) cm^{-1}.

Synthesis of $(CO)_5W(\mu\text{-}PPh_2)Os(H)(CO)_2(PMePh_2)_2$, 6a and 6b. To a solution of **3** (200 mg, 0.175 mmol) in 20 mL of THF was added MeLi (146 μL of a 1.2 M THF solution) which gave a rapid orange to brown color change. To this solution was immediately added MeI (80 μL, 0.982 mmol) which then gave a brown to yellow color change. Evaporation of solvent gave a yellow oil. Recrystallization from CH_2Cl_2/hexane afforded yellow crystals of a 50/50 mixture (by ^1H NMR integration) of the CH_2Cl_2 solvate of isomers **6a** and **6b** in 61% yield (132 mg, 0.06 mmol): MS, *m/e* (FD) 1156 (M^+); IR ν_{CO} (CH_2Cl_2) 2060 (m), 2033 (w), 1999 (w), 1965 (m), 1918 (s), 1894 (ssh) cm^{-1}. Anal. Calcd for $C_{45}H_{37}O_7OsP_3W\cdot CH_2Cl_2$: C, 44.80; H, 3.14. Found: C, 44.83; H, 3.29.

Synthesis of $(CO)_5\overline{W(\mu\text{-}PPh_2)Os}(H)(CO)(PPh_2H)(PMePh_2)$, 7. To a THF solution of **5**, generated from **3** (200 mg, 0.175 mmol) and MeLi (146 μL of a 1.2 M THF solution), was added 1 mL of glacial acetic acid. This solution was allowed to stir for 0.5 h. Evaporation of solvent at 0 °C gave a brown oil. This oil was dissolved in 10 mL of CH_2Cl_2 and extracted with 2 × 10 mL portions of H_2O. The CH_2Cl_2 was then filtered through a medium porosity fritted funnel containing $MgSO_4$ followed by rotary evaporation to leave a brown oil. Addition of 10 mL of pentane to this oil followed by rotary evaporation at 22 °C afforded $\mathbf{7}\cdot CH_2Cl_2$ as an air-stable, brown solid (189 mg, 0.158 mmol) in 90% yield: MS, *m/e* (FD) 1114 (M^+); IR ν_{CO} (CH_2Cl_2) 2047 (m), 2000 (s), 1978 (m), 1940 (m), 1890 (ssh), 1873 (s), 1845 (ssh) cm^{-1}. Anal. Calcd for $C_{44}H_{37}Cl_2O_6OsP_3W$: C, 44.04; H, 3.08. Found: C, 44.00; H, 2.91.

Deuterium Labeling Experiments. Complex **3** with a deuterium label at the hydride position was prepared via the same procedure as unlabeled **3**[2] by substituting $Li[BEt_3D]$ for $Li[BEt_3H]$ followed by protonation with CH_3CO_2H. **3**-d_1: IR, ^{31}P, and ^1H NMR spectra were identical with those of **3** except that no hydride resonance was observed and the δ 7.1 (ddd) resonance of the PPh_2H ligand did not show metal–hydride coupling. Complex **5** was then prepared by treatment of **3**-d_1 with MeLi as described above. Reaction of this product with CH_3CO_2H gave complex **7** with the deuterium label in the hydride position. **7**-d_1: IR, ^{31}P, and ^1H NMR spectra were identical with those of **7** except that no hydride resonance was observed in the ^1H NMR spectrum.

Reaction of 5 with $[(CH_3)_3O]BF_4$. A THF solution of **5**, prepared as described above, was added via cannula to a 100-mL Schlenk flask containing $[(CH_3)_3O]BF_4$ (27 mg, 0.185 mmol). The solution was stirred at 22 °C for 45 min during which time the brown solution turned purple. Removal of solvent by rotary evaporation afforded a purple oil. Chromatography on SiO_2 in the manner described above for compound **4** gave a red band of an unidentified compound and then a red band of **4**. Removal of solvent from this second band afforded **4** in 75% yield (146 mg, 0.131 mmol).

Thermolysis of 7. A solution of **7** (102 mg, 0.092 mmol) in 20 mL of CH_2Cl_2 was heated to 55 °C for 5 min. During this time the color changed from brown to purple. Rotary evaporation afforded pure **4** in 97% yield (99 mg, 0.089 mmol).

X-ray Diffraction Study of 3. Pale yellow crystals of **3** were obtained by recrystallization from CH_2Cl_2/hexane. A suitable crystal was coated with epoxy cement to provide a barrier to the atmosphere and affixed to a glass fiber. Systematic absences in the intensity data indicated either of the monoclinic space groups *Cc* or *C*2/*c*. The initial supposition, based on *E* statistics and $Z = 8$, that the centrosymmetric alternative was correct was affirmed by the chemically and crystallographically sensible solution and refinement of the structure. Crystal parameters and details of data collection are given in Table I. The intensity data were corrected for *Lp* effects, decay (11%), and absorption (empirical psi scan method).

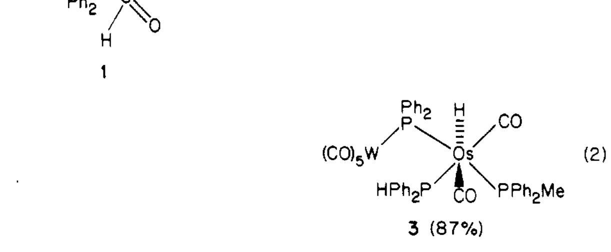
The positions of the metal and phosphorus atoms were determined by using a Patterson interpretation program contained in the SHELXTL (version 4.0) program package (G. Sheldrick, Nicolet Corp.). All remaining non-hydrogen atoms and the hydrogen atoms bonded to Os and P(3) were located in subsequent difference Fourier maps. A severely disordered molecule of CH_2Cl_2 was found in at least two sites with a total site occupation of approximately 1.0. The seven highest peaks on the final difference map (0.97–0.62 e $Å^{-3}$) were contained within these sites. In the final cycles of blocked-cascade refinement, all non-hydrogen atoms were refined with anisotropic temperature factors, hydrogen atoms H(P3) and H(Os) were refined isotropically, phenyl rings were constrained as rigid planar groups (d(C–C) = 1.395 Å), and the remaining hydrogen atoms were placed in idealized, updated positions (d(C–H) = 0.95 Å).

Final positional parameters are given in Table II and selected bond distances and angles in Table III. A listing of observed and calculated structure factors and a computer listing of bond distance and angles, anisotropic temperature factors, and hydrogen atom coordinates are available as supplementary material.

Results

Synthesis and Structural Characterization of $(CO)_5W(\mu\text{-}PPh_2)Os(H)(CO)_2(PPh_2H)(PMePh_2)$, 3.

Complex **3** was prepared by protonation of the binuclear formyl complex $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(CHO)(CO)_2(PMePh_2)]$, **1**[2] (eq 2), with complete details of its synthesis given in ref 2. An ORTEP drawing of **3** is shown in Figure 1. The W and Os atoms are bridged by a μ-PPh_2 ligand with W further coordinated by five CO's and the Os by



1

(2)

3 (87%)

Table I. Crystallographic Summary for $(CO)_5W(\mu\text{-}PPh_2)Os(H)(CO)_2(PPh_2H)(PPh_2Me)\bullet CH_2Cl_2$, 3

Crystal Data	
mol formula	$C_{44}H_{35}O_7OsP_3W\cdot CH_2Cl_2$
cryst dimens, mm	0.17 × 0.26 × 0.31
space group	$C2/c$
a, Å	35.172 (9)
b, Å	11.045 (3)
c, Å	25.275 (6)
β, deg	105.89 (2)
V, $Å^3$	9444 (13)
Z	8
ρ(calcd), g cm^{-3}	1.63
abs coeff μ, cm^{-1}	55.8
T, °C	23
Measurement of Intensity Data	
diffractometer	Nicolet R3
radiation	Mo Kα
monochromator	graphite crystal
scan type	ω
std reflctns	3 monitored every 97 reflctns (corrected for 11% obsd linear decay)
scan range	$3.2° < 2\theta < 44.4°$
reflctns measd	6842
unique data	6165
obsd data $[F_o \geq 3\sigma(F_o)]$	5365
transmission factors	0.15–0.27
R_F	0.036
R_{wF}	0.041
no. of parameters	478
GOF	1.385
highest peak in final difference map, $Å^{-3}$	0.97 e (located in solvent molecule)
mean shift/esd max	0.093

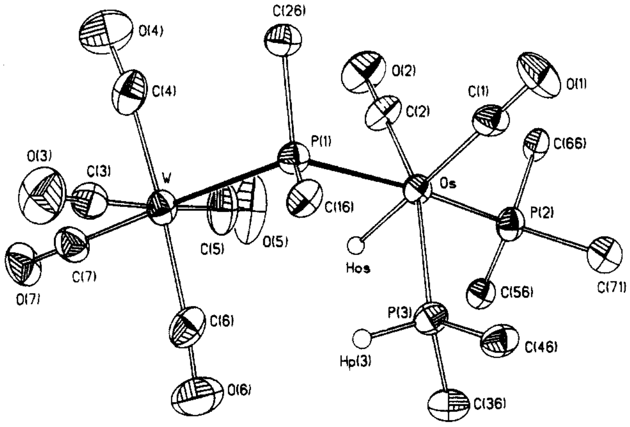


Figure 1. An ORTEP drawing of $(CO)_5W(\mu\text{-}PPh_2)OsH(CO)_2(PPh_2H)(PPh_2Me)$, 3. Thermal elipsoids are drawn at the 40% probability level and only the ligand carbon atoms attached to phosphorus are included for clarity. Hydrogen atoms H(Os) and Hp(3) have arbitrary radii.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) in 3

atom	x	y	z	U,[a] $Å^2$
Os[b]	10786 (1)	46532 (3)	20430 (1)	31 (0)
W[b]	13179 (1)	25069 (4)	35324 (1)	38 (0)
P(1)	1512 (1)	4311 (2)	2984 (1)	33 (1)
P(2)	596 (1)	4729 (2)	1177 (1)	38 (1)
P(3)	1502 (1)	3367 (2)	1706 (1)	37 (1)
HP(3)	1697 (18)	2724 (63)	2092 (26)	35 (20)
O(1)	1421 (2)	7119 (6)	1872 (3)	66 (3)
O(2)	447 (2)	5504 (7)	2567 (3)	70 (3)
O(3)	2827 (2)	7431 (7)	637 (3)	77 (3)
O(4)	3932 (2)	9186 (8)	601 (3)	98 (4)
O(5)	4565 (2)	7591 (8)	2211 (3)	98 (4)
O(6)	3469 (2)	5518 (7)	2238 (3)	85 (4)
O(7)	3948 (2)	5322 (6)	854 (3)	66 (3)
C(1)	1305 (2)	6182 (8)	1942 (3)	39 (3)
C(2)	687 (2)	5206 (8)	2374 (3)	41 (3)
C(3)	1870 (2)	2463 (8)	4057 (3)	46 (3)
C(4)	1158 (3)	3637 (10)	4071 (4)	58 (4)
C(5)	753 (3)	2584 (10)	3042 (4)	66 (4)
C(6)	1457 (2)	1268 (9)	3026 (3)	52 (4)
C(7)	1150 (2)	1114 (9)	3924 (4)	49 (4)
C(11)	2207 (1)	5243 (4)	2786 (2)	45 (3)
C(12)	2591 (1)	5184 (4)	2730 (2)	48 (4)
C(13)	2802 (1)	4100 (4)	2833 (2)	48 (4)
C(14)	2629 (1)	3076 (4)	2993 (2)	45 (3)
C(15)	2246 (1)	3135 (4)	3050 (2)	36 (3)
C(16)	2035 (1)	4219 (4)	2946 (2)	35 (3)
C(21)	1810 (2)	5614 (5)	3952 (2)	59 (4)
C(22)	1837 (2)	6579 (5)	4317 (2)	68 (5)
C(23)	1614 (2)	7624 (5)	4149 (2)	68 (5)
C(24)	1363 (2)	7703 (5)	3616 (2)	71 (5)
C(25)	1336 (2)	6737 (5)	3252 (2)	42 (3)
C(26)	1559 (2)	5693 (5)	3420 (2)	39 (3)
C(31)	1291 (2)	2263 (6)	666 (2)	60 (4)
C(32)	1119 (2)	1343 (6)	301 (2)	80 (5)
C(33)	926 (2)	387 (6)	480 (2)	98 (6)
C(34)	905 (2)	351 (6)	1023 (2)	90 (6)
C(35)	1078 (2)	1272 (6)	1388 (2)	64 (4)
C(36)	1271 (2)	2228 (6)	1209 (2)	45 (4)
C(41)	2229 (2)	3121 (5)	1511 (3)	62 (4)
C(42)	2546 (2)	3475 (5)	1315 (3)	79 (5)
C(43)	2539 (2)	4597 (5)	1059 (3)	81 (6)
C(44)	2216 (2)	5365 (5)	999 (3)	78 (5)
C(45)	1898 (2)	5011 (5)	1195 (3)	57 (4)
C(46)	1905 (2)	3889 (5)	1451 (3)	39 (3)
C(51)	174 (2)	2737 (5)	1369 (2)	48 (4)
C(52)	−60 (2)	1704 (5)	1226 (2)	56 (4)
C(53)	−163 (2)	1289 (5)	684 (2)	61 (4)
C(54)	−32 (2)	19059 (5)	285 (2)	69 (5)
C(55)	202 (2)	2937 (5)	429 (2)	54 (4)
C(56)	305 (2)	3353 (5)	970 (2)	37 (3)
C(61)	337 (1)	7102 (6)	1207 (2)	57 (4)
C(62)	58 (1)	8019 (6)	1167 (2)	61 (4)
C(63)	−342 (1)	7729 (6)	1063 (2)	65 (5)
C(64)	−463 (1)	6521 (6)	100 (2)	76 (5)
C(65)	−183 (1)	5604 (6)	1041 (2)	58 (4)
C(66)	216 (1)	5894 (6)	1144 (2)	38 (3)
C(71)	771 (3)	5175 (8)	594 (3)	50 (2)
Cl(1)	2104 (1)	10167 (6)	250 (2)	180 (3)
Cl(2)	1650 (2)	8138 (5)	433 (2)	174 (3)
Cl(3)	4583 (2)	4186 (6)	2426 (2)	228 (4)
C(99)	1985 (5)	9418 (20)	720 (6)	165 (11)
C(100)	5000	3327 (2)	2500	137 (12)
Hosa	887 (15)	3305 (57)	2144 (22)	15 (16)

[a] Equivalent isotropic U defined as $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Atom coordinates $\times 10^5$.

two CO's, $PMePh_2$, PPh_2H, and a hydride ligand. The W and Os atoms are clearly nonbonding with a W–Os separation of 4.332 (1) Å. The W–P(1)–Os angle of 116.2 (1)° is the largest yet reported for such an M–P_μ–M angle. This illustrates the impressive structural flexibility of this μ-PPh_2 ligand as it can also comfortably bridge two metals separated by as little as 2.343 (2) Å and a M–P_μ–M angle as small as 65.23 (5)°.[17] Both metal atoms of 3 show nearly perfect octahedral coordination geometries with bond angles and distances in the coordination spheres within normal ranges. Of particular interest is the location of the terminal PPh_2H ligand on Os. Its cis relationship to the μ-PPh_2 ligand and close proximity to W facilitates conversion of this ligand into a second phosphido bridge as will be demonstrated below.

A curious feature of the structural data for 3 is the significant lengthening of *both* the W–P(1) and Os–P(1) bonds as compared to other related compounds. In 3, the W–P(1) bond length is 2.623 (2) Å whereas it averages 2.502 Å with a range of 2.435–2.538 Å in the five compounds $WIr(\mu\text{-}PPh_2)_2(CO)_5H(PPh_3)$,[3] $WIr(\mu\text{-}PPh_2)_2(CO)_4H(PPh_3)\{C(OMe)Ph\}$,[3] $WPt(\mu\text{-}PPh_2)_2(CO)_4(PPh_3)$,[18]

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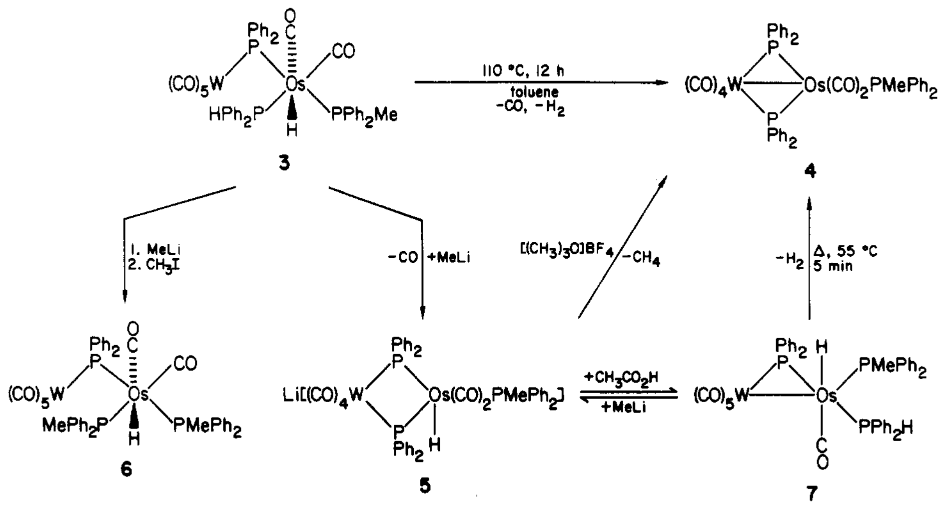
[17] Harley, A. D.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 60.

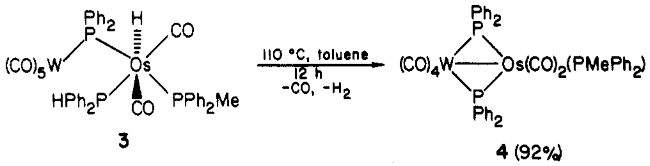
Scheme I



$WPt(\mu\text{-}PPh_2)_2(CO)_4(PhC{\equiv}CPh)$,[18] and $WOs(\mu\text{-}PPh_2)(\mu\text{-}PPh_2CH(OMe))(CO)_6(PMePh_2)$.[2] Likewise, the Os–P(1) bond length of 2.478 (2) Å is significantly larger than the Os–P(2) (2.376 (2) Å) and Os–P(3) (2.377 (2) Å) bond lengths to the terminal phosphines in **3** and is also longer than the 2.314 (3) Å Os–P_μ bond length in $WOs(\mu\text{-}PPh_2)(\mu\text{-}PPh_2CH(OMe))(CO)_6(PMePh_2)$.[2] We do not understand the cause for this unusual lengthening of the two bonds, but it certainly does not reflect an inherent weakness of the W–P_μ–Os structural unit since compound **3** does not readily fragment (see below).

Spectroscopic data for complex **3** are consistent with the determined structure. NMR data for **3** and all the new complexes described herein are given in Table IV. Complex **3** shows a ^{31}P NMR resonance at δ −64.9 (dd) attributed to the μ-PPh_2 ligand with its upfield position consistent with the absence of a metal–metal bond. It is now well established that when μ-PPh_2 ligands bridge two metals joined by a metal–metal bond, their resonances appear downfield (δ 300–δ 50), whereas when no metal–metal bond is present, upfield resonances (δ 50 – δ −300) are found.[16,19] However, there are exceptions to this correlation, so caution must be exercised in its use.[20] Separate resonances are observed for the PPh_2Me and PPh_2H ligands with the latter showing a 396-Hz ^{31}P–^{1}H coupling. The hydride ligand appears at δ −3.6 (dddd) in the ^{1}H NMR spectrum of **3**.

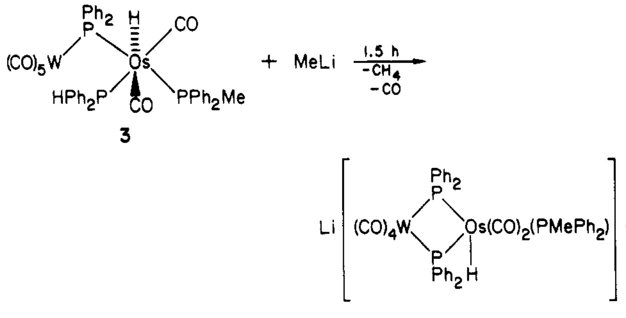
Conversion of 3 into $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_2(PMePh_2)$, 4. When complex **3** was heated in refluxing toluene, CO and H_2 were evolved and the bis(phosphido)-bridged complex $(CO)_4W(\mu\text{-}PPh_2)_2Os(CO)_2(PMePh_2)$, **4**, was formed in near-quantitative yield (eq 3).



(3)

The $^{31}P\{^{1}H\}$ NMR spectrum of **4** shows a doublet at δ 139.1 assigned to the two equivalent μ-PPh_2 ligands and a triplet at δ −4.9 attributed to the terminal $PMePh_2$ ligand on Os. The downfield position of the μ-PPh_2 resonance implies the presence of a metal–metal bond in **4**,[16,19] and the absence of ^{183}W satellites on the ^{31}P NMR resonance of the $PMePh_2$ ligand argues for its position on Os. The EI mass spectrum of **4** is consistent with its given formulation, showing a parent ion at *m*/*e* 1112 and stepwise loss of six carbonyl ligands.

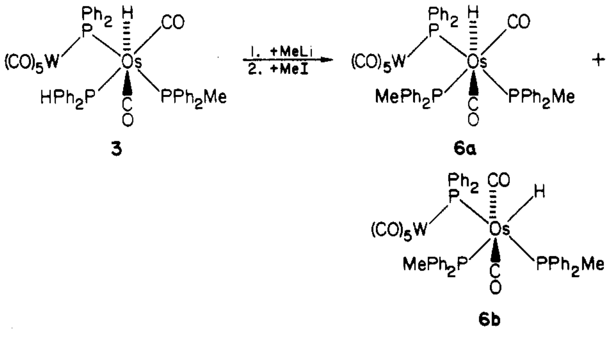
Reaction of 3 with MeLi. Treatment of a THF solution of **3** with MeLi results in abstraction of the PPh_2H hydrogen and CO loss to give near quantitative formation of $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(H)(CO)_2(PMePh_2)]$, **5** (eq 4).



(4)

Complex **5** was previously prepared by deinsertion of the formyl complex $Li[(CO)_4W(\mu\text{-}PPh_2)_2Os(CHO)(CO)_2(PMePh_2)]$, **1**.[2] Complete characterization details of complex **5** are given in ref 2.

When complex **3** was deprotonated with MeLi and then immediately treated with MeI, the phosphide generated in situ was alkylated and isolated as a terminal PPh_2Me ligand in complex **6** (eq 5). Complex **6** exists as an equal



(5)

mixture of two inseparable isomers, to which we tentatively

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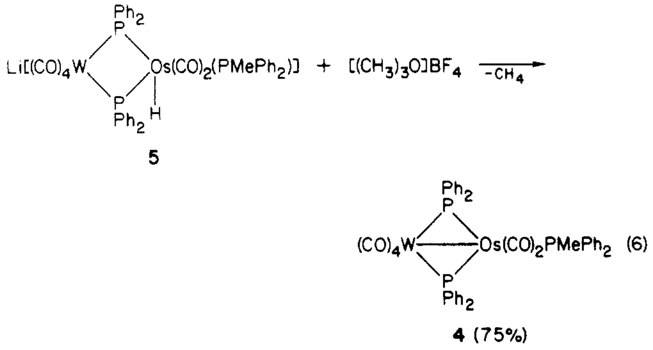
Table III. Selected Bond Distances (Å) and Angles (deg) in 3

	Bond Lengths		
Os–P(1)	2.478 (2)	W–P(1)	2.623 (2)
Os–P(2)	2.376 (2)	W–C(3)	2.031 (7)
Os–P(3)	2.377 (2)	W–C(4)	2.037 (10)
Os–C(1)	1.914 (8)	W–C(5)	2.036 (8)
Os–C(2)	1.897 (9)	W–C(6)	2.024 (10)
Os–H(Os)	1.68 (6)	W–C(7)	2.003 (10)
	Bond Angles		
P(1)–Os–P(2)	170.6 (1)	P(1)–W–C(4)	92.3 (3)
P(1)–Os–P(3)	88.4 (1)	P(1)–W–C(5)	89.9 (3)
P(1)–Os–C(1)	95.3 (2)	P(1)–W–C(6)	92.1 (3)
P(1)–Os–C(2)	87.5 (2)	P(1)–W–C(7)	177.6 (2)
P(1)–Os–H(Os)	83.5 (2)	C(3)–W–C(4)	88.2 (3)
P(2)–Os–P(3)	92.9 (1)	C(3)–W–C(5)	176.8 (4)
P(2)–Os–C(1)	93.7 (2)	C(3)–W–C(6)	92.5 (3)
P(2)–Os–C(2)	88.5 (2)	C(3)–W–C(7)	91.0 (3)
P(2)–Os–H(Os)	87.5 (2)	C(4)–W–C(5)	88.8 (4)
C(1)–Os–C(2)	98.8 (4)	C(4)–W–C(6)	175.2 (4)
C(1)–Os–H(Os)	178.8 (6)	C(4)–W–C(7)	88.2 (4)
C(2)–Os–H(Os)	81.3 (2)	C(5)–W–C(6)	90.5 (4)
W–P(1)–Os	116.2 (1)	C(5)–W–C(7)	87.8 (4)
C(16)–P(1)–C(26)	98.4 (2)	C(6)–W–C(7)	87.0 (4)
P(1)–W–C(3)	91.3 (3)		

assign the structures **6a** and **6b**. Both show upfield resonances due to the μ-PPh$_2$ ligands and separate resonances for the PMePh$_2$ ligands. The observed ^{31}P–^{31}P couplings (Table IV) imply that all three phosphorus nuclei are in cis positions in both isomers. The hydride ligands appear at δ −5.27 (ddd) and δ −7.38 (ddd) in **6a** and **6b** and have similar ^{1}H–^{31}P coupling constants, except that **6b** shows one coupling of 41.3 Hz, larger than any of the rest, which may be attributed to coupling of the hydride to a trans PPh$_2$Me ligand, as drawn in **6b**.

Methylation and Protonation of 5. Addition of [(CH$_3$)$_3$O]BF$_4$ to THF solutions of **5** results in hydride abstraction and formation of complex **4** in 75% yield (eq 6).

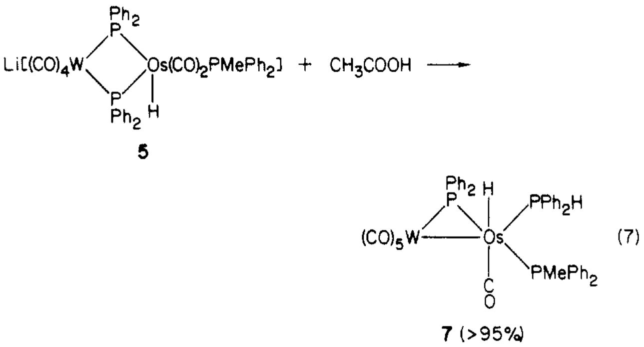


5

4 (75%)

(6)

In contrast, reaction of **5** with CH$_3$COOH results in protonation of one μ-PPh$_2$ ligand and formation of the monophosphido-bridged complex **7** (eq 7). The downfield μ-PPh$_2$ ^{31}P NMR resonance of **7** at δ 53.3 (d) implies the presence of a metal–metal bond[16,19] and the absence of ^{183}W satellites on the PPh$_2$H and PMePh$_2$ resonances argue for their location on Os.



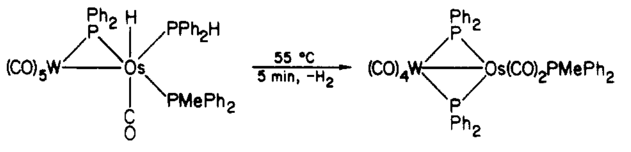
5

7 (>95%)

(7)

When complex **5**, labeled with deuterium at the hydride position (see Experimental Section), was treated with CH$_3$CO$_2$H, complex **7** was formed with the deuterium label still at the hydride position. This implies that the PPh$_2$*H* hydrogen derives from the added acid. This reaction could occur via initial protonation at W followed by phosphide–hydride coupling or via direct protonation at the phosphorus ligand.

Complex **7** is thermally unstable and decomposes via H$_2$ loss when warmed to 55 °C for 5 min to quantitatively form the bis(phosphido)-bridged complex **4** (eq 8).



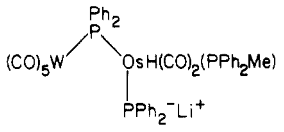
7

4 (97%)

(8)

Discussion

Scheme I summarizes the series of bridge-cleavage/formation reactions observed in this study. Deprotonation of **3** apparently generates the terminal phosphide complex **8**. This species can be alkylated at phosphorus to give **6** if CH$_3$I is rapidly added after deprotonation. If an alkylating agent is not added, complex **8** is unstable, and the terminal phosphide ligand displaces CO on W to give the bis(phosphido)-bridged complex **5**. The formation of bridging phosphido ligands by deprotonation of terminal PR$_2$H ligands has precedent,[14,15] although this is a rare example of intramolecular ligand displacement by a



8

Table IV. ^{31}P and ^{1}H NMR Data[a]

compd	δ (P$_\mu$)	δ (P$_{Os}$)	$J_{P_\mu-P_\mu}$, Hz	$J_{^{31}P_\mu-^{31}P_{Os}}$, Hz	$J_{^{31}P_{Os}-^{31}P_{Os}}$, Hz	$J_{^{31}P_\mu-^{183}W}$, Hz	δ (H)	$J_{^1H-^1H}$, Hz	$J_{^1H-^{31}P}$, Hz
3	−64.9 (dd)	−11.2 (dd, PPh$_2$H)		9.6	22.9	205.2	6.6 (dddd, PPh$_2$H)	3.6	396, 12.4, 10.8
		−20.5 (dd, PPh$_2$Me)		122.0			−3.6 (dddd, H)		31.3, 16.2, 12.5
4	139.1 (d)	−4.9 t		41.0		142.0			
5	−119.4 (dd)	−3.5 dd	45.5	142.2		173.2	−3.7 (ddd)		225, 17.6, 11.5
	−128.7 (dd)			15.0		165.45			
6a	−79.1 (dd)	−22.7 (dd)		101.2	4.7	203.5	−5.27 (ddd)		31.2, 15.3, 11.6
		−26.7 (dd)		11.7					
6b	−67.2 (dd)	−16.0 (dd)		19.5	23.0	202.5	−7.38 (ddd)		41.3, 23.6, 22.0
		22.3 (dd)		130.4					
7	53.3 (d)	−13.9 (d, PPh$_2$H)		88.4	25.3	250.0	7.4 (ddd)		415, 11.9, 7.8
		−35.0 (dd, PPh$_2$Me)					−12.8 (t)		15.4

[a] Solvents used were C$_6$D$_6$ (**3**, **4**, **6**, **7**) and (CD$_3$)$_2$SO and (**5**).

phosphide anion. The phosphido bridge of **5** can be opened again by protonation with CH_3CO_2H to give complex **7**. Note that **7** differs from **3** only by loss of a CO from Os and formation of the W–Os bond. However, complex **7** cannot be directly formed from **3** since heating the latter induces CO *and* H_2 loss to give **4**.

Complex **7** can be converted back to **5** by deprotonation with MeLi. However, note that a CO ligand must migrate from one metal to the other as these reactions occur. The hydride ligand of **5** can be removed by addition of $[(CH_3)_3O]BF_4$ to yield **4**, and this latter complex is also produced by heating **7** to induce H_2 loss. Complex **4** is the thermodynamic sink in this series of complexes, and once formed it does not convert into the other derivatives under any conditions that we have explored. Particularly interesting would be hydrogenation of **4** to give **7** or **3** (in the presence of CO), but neither of these reactions occur. Complex **4** was recovered unchanged when heated under 1000 psi of CO/H_2 (1:1) at 110 °C for 24 h or 1000 psi of CO at 110 °C for 24 h.

Protonation of **5** could occur at the metal or directly at phosphorus. Protonation at Os seems unlikely on two grounds. First, an $Os-PPh_2H$ ligand is produced whereas the most reasonable consequence of Os protonation followed by $(\mu\text{-}PPh_2)$–H coupling would be a PPh_2H ligand on W. Also, recall that the deuterium labeling study showed that the initial Os hydride ligand remains on Os and does not participate in the bridge elimination. If protonation occurred at Os, some interchange between the two hydride ligands would seem likely and the isotopic purity of the labeled product would be lost. Our data do not allow us to distinguish between protonation at W followed by hydride–phosphide coupling or direct protonation at phosphorus.

In summary, the results reported herein further demonstrate the facility with which phosphido ligands can be generated and eliminated in bimetallic complexes. These ligands are not inert and their chemistry must be considered in reactivity studies of such bridged complexes.[1–16]

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Registry No. **3**, 96393-02-1; **3**-d_1, 96393-04-3; **4**, 88904-57-8; **5**, 88904-60-3; **6a**, 96348-81-1; **6b**, 96393-03-2; **7**, 96348-82-2; **7**-d_1, 96348-83-3; W, 7440-33-7; Os, 7440-04-2.

Supplementary Material Available: Table of anisotropic thermal parameters, complete lists of bond angles and bond lengths, calculated hydrogen atom positions, and structure factors (35 pages). Ordering information is given on any current masthead page.

Preparation of Anionic Tungsten(VI) Alkyl Complexes Containing Oxo or Sulfido Ligands and the X-ray Structure of $[N(C_2H_5)_4]\{WO_2[OC(CH_3)_2C(CH_3)_2O][CH_2C(CH_3)_3]\}$

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$W(CCMe_3)(OCMe_3)_3$ reacts with 1 equiv of $[NEt_4][OH]$ in water to give colorless $[NEt_4][WO_3(CH_2CMe_3)]$ in high yield. $[NEt_4][WO_3(CH_2CMe_3)]$ is stable in air and is hydrolyzed only by strong acid or base. A similar reaction between $W(CSiMe_3)(OCMe_3)_3$ and $[NEt_4][OH]$ gives $[NEt_4][WO_3(CH_2SiMe_3)]$. $[NEt_4][WO_3(CH_2CMe_3)]$ reacts with 1 equiv of pinacol to give $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$. $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$ crystallizes in the space group $I2/c$ where $a = 21.294$ (3) Å, $b = 10.175$ (1) Å, $c = 22.331$ (3) Å, $\beta = 90.97$ (1)°, $V = 4837.7$ Å^3, and $Z = 8$. It is approximately a trigonal-bipyramidal molecule in which the two oxo ligands lie in the equatorial plane (W=O = 1.712 (5) and 1.720 (5) Å; O—W—O = 110.4 (3)°), the O—W—O angle is 75.6 (2)° in the pinacolato ligand, and W—C = 2.170 (6) Å and W—C_α—C_β = 123.1 (5)° in the neopentyl ligand. $[NEt_4][WO_3(CH_2CMe_3)]$ reacts with $S(SiMe_3)_2$ in acetonitrile to give $[NEt_4][WS_3(CH_2CMe_3)]$ as yellow-orange needles.

Introduction

In general d^0 transition-metal alkyl complexes are either thermally or hydrolytically unstable.[1] Some notable exceptions are members of the small family of d^0 oxo alkyl complexes. Examples are ReO_3Me,[2] $V(O)(CH_2SiMe_3)_3$,[3] and ReO_2Me_3.[4] Complexes of the type $MoO_2R_2(bpy)$ have been prepared where R = methyl, benzyl, or neopentyl,[5] and complexes of the type $MoO_2(R)(Br)(bpy)$[6a] (R = Me, Et, etc.) hydrolyze to give species that have been formulated as $[MoO_3R]^-$ on the basis of ^1H NMR and hydrolysis studies;[6b] the $[MoO_3R]^-$ species are hydrolyzed relatively

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