Fifty-Electron $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]^-$ Clusters Derived from Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with $[(PPh_3)_2N]X$ Salts. Structural Characterization of the X = I and NCO Derivatives

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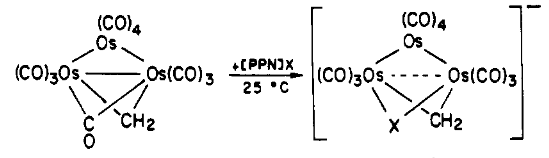
Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$, **1**, with $[(Ph_3P)_2N]X$ salts gives the new $[(Ph_3P)_2N][Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]$ clusters with X = Cl (**2**), Br (**3**), I (**4**), and NO_2 (**5**) in high yields. Likewise reaction of **1** with $[(Ph_3P)_2N]N_3$ yields the μ-NCO cluster $[(Ph_3P)_2N][Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}NCO)]$, **6**. The isomorphous clusters **4** and **6** have been crystallographically characterized. **4**: $P\bar{1}$, a = 12.978 (3) Å, b = 13.131 (3) Å, c = 14.074 (4) Å, α = 90.21 (2)°, β = 96.40 (2)°, γ = 90.63 (2)°, V = 2383 (1) Å^3, Z = 2, R_F = 0.041, R_{wF} = 0.038 for 4229 reflections with $F_o \geq 3\sigma(F_o)$. **6**: $P\bar{1}$, a = 12.874 (3) Å, b = 13.291 (3) Å, c = 13.976 (3) Å, α = 89.07 (2)°, β = 83.39 (2)°, γ = 89.51 (2)°, V = 2374.9 (9) Å^3, Z = 2, R_F = 0.050, R_{wF} = 0.054 for 5167 reflections with $F_o \geq 2.5\sigma(F_o)$. Both structures are similar with the X and CH_2 ligands bridging the same metal–metal bond, and all CO's are terminally bound. Although these are 50-electron clusters with two more than the 48 electrons needed for a closed structure, structural parameters indicate some degree of metal–metal interaction between all the osmium atoms.

Osmium carbonyl clusters are in general relatively unreactive because of the high Os–Os and Os–carbonyl bond strengths.[1] A notable exception is $H_2Os_3(CO)_{10}$ which has a high reactivity because of its coordinative unsaturation.[2] A *coordinatively saturated* osmium cluster that also appears to be unusually reactive is $Os_3(CO)_{11}(\mu\text{-}CH_2)$, **1**, a compound that also bears the interesting methylene ligand.[3] We have shown that **1** readily reacts with CO at 1 atm, 25 °C, to give the μ-ketene cluster $Os_3(CO)_{12}(\mu\text{-}CH_2CO)$[4] and it likewise reacts with SO_2 to give an analogous μ-CH_2SO_2 cluster.[5] Herein we describe its rapid reactions with anions to give a series of $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]^-$ clusters (eq 1). Complete details of the X-ray diffraction studies of **4** and **6** are reported. The latter are particularly interesting since these are 50-electron clusters with two more electrons than required to give closed triangular structures,[6] yet the structural parameters imply some degree of metal–metal interaction between all osmium atoms.



(1)

2, X = Cl
3, X = Br
4, X = I
5, X = NO_2
6, X = NCO

Experimental Section

Literature procedures were followed for preparation of $Os_3(CO)_{11}(\mu\text{-}CH_2)$, **1**,[13a] and the various [PPN]X[7] salts (PPN = $[Ph_3P]_2N$). Unless otherwise specified all manipulations were carried out in air, although the slightly air-sensitive products were stored under N_2. Infrared spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorbance mode. Elemental analyses were obtained by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Synthesis of PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}Cl)$], 2. A solution of **1** (0.414 g, 0.464 mmol) in 3.0 mL of CH_2Cl_2 in a 25-mL round-bottom flask was treated dropwise with a solution of [PPN]Cl (0.259 g, 0.452 mmol) in 1.0 mL of CH_2Cl_2. The solvent was removed from the resultant homogeneous dark orange solution by rotary evaporation to give a thick orange oil. Trituration with n-pentane to remove excess **1** gave **2** (0.576 g, 0.401 mmol) as an orange powder in 89% yield: IR (CH_2Cl_2) 2072 (w), 2030 (s), 2016 (ms), 1977 (s), 1949 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.70 (d, 1 H, J_{HH} = 8.60 Hz), 2.92 (d, 1 H). Anal. Calcd for $C_{47}H_{32}ClNO_{10}P_2Os_3$: C, 39.21, H 2.25. Found: C, 38.91, H, 2.35.

Synthesis of PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}Br)$], 3. Addition of [PPN]Br to **1** in a manner analogous to that used above gave orange [PPN][$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}Br)$] in 92% yield: IR ($CH_2Cl_2$) 2070 (w), 2029 (s), 2018 (ms), 1979 (s), 1950 (m), 1933 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.81 (d, 1 H, J_{HH} = 8.55 Hz), 3.19 (d, 1 H). Anal. Calcd for $C_{47}H_{32}BrNO_{10}Os_3P_2$: C, 38.04; H, 2.18. Found: C, 38.37, H, 2.30.

Synthesis of PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}I)$], 4. A solution of [PPN]I (0.366 g, 0.550 mmol) in 2.0 mL of CH_2Cl_2 was added dropwise to a solution of **1** (0.501 g, 0.562 mmol) in 4.0 mL of CH_2Cl_2 in a 25-mL round-bottom flask. The solvent was immediately removed from the homogeneous dark orange solution by rotary evaporation. The residue was redissolved and the solvent rotary evaporated twice, giving a red-orange oil. Trituration with n-pentane (4 × 5-mL portions) gave **4** as a red-orange powder in 97% yield (0.816g, 0.533 mmol): IR (CH_2Cl_2) 2072 (mw), 2027 (s), 2018 (ms), 1979 (s), 1950 (m), 1933 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (d, 1 H, J_{HH} = 8.01 Hz), 3.58 (d, 1 H). Anal. Calcd for $C_{47}H_{32}O_{10}NP_2IOs_3$: C, 36.87; H, 2.11. Found: C, 36.72; H, 1.86.

Preparation of PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}NO_2)$], 5. A solution of [PPN]NO_2 (0.0953 g, 0.163 mmol) in 2 mL of CH_2Cl_2 was added dropwise to a stirred solution of **1** (0.150 g, 0.168 mmole) in 15 mL of CH_2Cl_2. Solvent was removed by rotary evaporation and the orange oil redissolved and rotary evaporated twice from

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[1] Conner, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

[2] (a) Adams, R. D.; Selegue, J. P. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 4, p 1032. (b) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225.

[3] (a) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559. (b) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975. (c) Johnson, B. F. G.; Lewis, J.; Raithby, T. R.; Sankey, S. W. *J. Organomet. Chem.* **1982**, *231*, C65. (d) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 364.

[4] (a) Morrison, E. D.; Steinmetz, G. R.; Geoffroy, G. L.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 4104. (b) *Ibid.* **1984**, *106*, 4783.

[5] Morrison, E. D. Ph.D. Dissertation, The Pennsylvania State University, University Park, PA, 1985

[6] Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.

[7] Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 645.

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Table I. Crystallographic Data for PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)$] (X = I and NCO)

	6, X = NCO	4, X = I
	Crystal Data	
mol formula	$C_{48}H_{32}NO_{11}Os_3P_2$	$C_{47}H_{32}INO_{10}Os_3P_2$
cryst system	triclinic	triclinic
cryst dimens, mm	0.08 × 0.24 × 0.26	0.22 × 0.26 × 0.32
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.874 (3)	12.978 (3)
b, Å	13.291 (3)	13.131 (3)
c, Å	13.976 (3)	14.074 (4)
α, deg	89.07 (2)	90.21 (2)
β, deg	83.39 (2)	96.40 (2)
γ, deg	89.51 (2)	90.63 (2)
V, Å^3	2374.9 (9)	2383 (1)
Z	2	2
ρ(calcd), g cm^{-3}	2.00	2.13
μ(abs coeff), cm^{-1}	86.1	87.52
T, °C	22	23
	Measurement of Intensity Data	
diffractometer	Nicolet R3	
radiatn	Mo Kα (λ = 0.710 73 Å)	
monochromator	graphite crystal	
scan type	$\omega/2\theta$	ω
scan speed	variable 5°–20° min^{-1}	variable 4°–20° min^{-1}
scan width	[1.6 + $\Delta(\alpha_2 - \alpha_1)$]°	[1.6 + $\Delta(\alpha_2 - \alpha_1)$]°
std reflctns	3 every 197 reflns	3 every 197 rflns
data limits	$4 < 2\theta \leqslant 45°$	$4 \leqslant 2\theta \leqslant 45°$
unique data	6186	6121
obsvd data	5167 ($F_o > 2.5\sigma(F_o)$)	4229 ($F_o > 3\sigma(F_o)$)
weighting factor g^a	0.000 79	0.000 10
$R_F{}^b$	0.050	0.041
$R_{wF}{}^c$	0.054	0.038
GOF^d	1.21	1.56

[a] Weight = $1/[\sigma^2(F) + |g|(F^2)]$. [b] $R_F = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $R_{wF} = [\Sigma w^{1/2}(|F_o| - |F_c|)]/\Sigma w^{1/2}(F_o)$. [d] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obsd} - N_{par})]^{1/2}$.

CH_2Cl_2. Addition of diethyl ether to the oil produced a yellow-orange precipitate which was washed with 3 × 15-mL portions of n-pentane to give 5 as a yellow-orange powder in 92% yield (0.216 g, 0.149 mmol): IR (CH_2Cl_2) 2076 (w), 2037 (s), 2020 (ms), 1986 (s), 1956 (sh) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.84 (d, 1 H, J_{HH} = 10.05 Hz), 2.66 (d, 1 H). Anal. Calcd for $C_{47}H_{32}N_2O_{12}Os_3P_2$: C, 38.93; H, 2.23. Found: C, 38.54; H, 2.24.

Preparation of PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}NCO)$], 6. A solution of [PPN]N_3 (0.0964 g, 0.166 mmol) in 5 mL of acetone was added dropwise to a stirred solution of 1 (0.152 g, 0.171 mmol) in 10 mL of THF to give an immediate deep red to orange color change. The THF/acetone was removed by rotary evaporation and the residue dissolved in 5 mL of CH_2Cl_2. Removal of solvent followed by washing with 3 × 15-mL portions of n-pentane gave 6 as a bright orange microcrystalline solid in 92% yield (0.221 g, 0.153 mmole): IR (CH_2Cl_2) 2207 (s (sharp)), 2070 (w), 2031 (s), 2016 (ms), 1977 (s), 1948 (m), 1930 (sh) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.83 (d, 1 H, J_{HH} = 8.06 Hz), 2.79 (d, 1 H). Anal. Calcd for $C_{48}H_{32}N_2O_{11}Os_3P_2$: C, 39.86; H, 2.24; N, 1.94. Found: C, 39.61; H, 2.34; N, 2.53.

Crystal Structure of PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}I)$], 4, and PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}NCO)$], 6. Crystals of 4 and 6 were obtained by slow evaporation of diethyl ether solutions of each under a partial N_2 atmosphere. Suitable crystals were mounted in arbitrary orientations on glass fibers which were then fixed onto aluminum pins on a eucentric goniometer. Lattice parameters were obtained from the least-squares fit of angular settings of 25 well-centered reflections, 25° < 2θ < 30°. Data collection and refinement procedures used were as previously reported;[8] pertinent details are provided in Table I. Lorentz and polarization corrections were applied to the data, as were empirical (ψ scan) absorption corrections (4, I_{min}/I_{max} = 0.064/0.098; 6, I_{min}/I_{max} = 0.118/0.051).

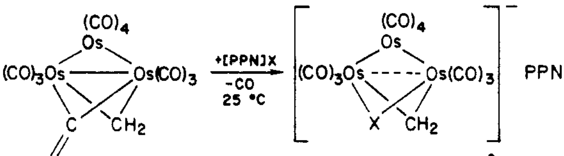
In each case the three Os atoms were located by an automated Patterson interpretation procedure,[9] and the remaining non-hydrogen atoms were obtained from difference maps phased by the three Os atoms. With the incorporation of hydrogen atoms in fixed, idealized positions (d(C–H) = 0.96 Å) and rigid bond constraints on the six cation phenyl rings (d(C–C) = 1.395 Å), the blocked-cascade least-squares refinement process smoothly converged to the residuals reported in Table I. The final difference map revealed no unusual or chemically relevant features (4, highest peak = 0.95 e Å^{-3}; 6, highest peak = 1.42 e Å^{-3}). The unit-cell dimensions and metal atom coordinates reveal that these compounds crystallize isomorphously.

During all calculations for both molecules the analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i\Delta f''$ terms.[10] Final positional parameters are collected in Tables II (4) and III (6); thermal parameters appear in the supplementary material which also contains the structure factors and full bond length and angle data. Relevant bond angles and bond distances are presented in Table IV.

Results and Discussion

Synthesis and Spectroscopic Characterization of PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)$] (X = Cl, Br, I, NCO, and NO_2).

Addition of [PPN]X (X = Cl, Br, I, and NO_2) to room-temperature solutions of the methylene-bridged cluster $Os_3(CO)_{11}(\mu\text{-}CH_2)$, 1, gives an immediate reaction to form the dibridged clusters 2–5 (eq 2). Cluster 1 reacts



(2)

1

2, X = Cl (89%)
3, X = Br (92%)
4, X = I (97%)
5, X = NO_2 (92%)

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(8) Rheingold, A. L.; Sullivan, P. J. *Organometallics* 1983, 2, 327.

(9) Programs used are part of the SHELXTL (1984, version 4.1) program package distributed by the Nicolet Corp., Madison, WI.

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmlingham, England, 1974; Vol. 4, pp 99–10, 149–150.

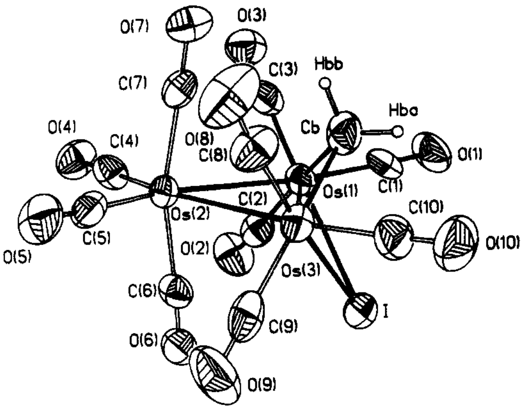


Figure 1. An ORTEP drawing of $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}I)]^-$. Thermal ellipsoids are drawn at the 40% probability level.

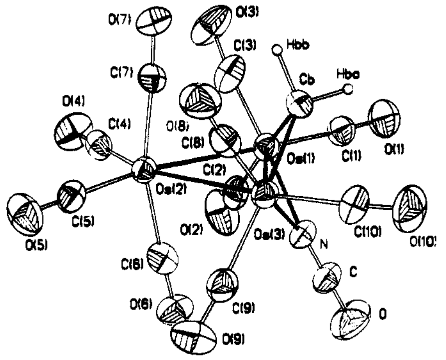
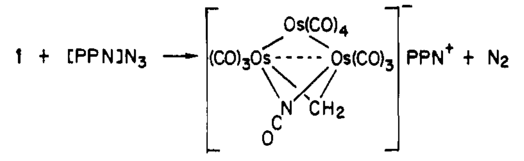


Figure 2. An ORTEP drawing of $[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}NCO)]^-$. Thermal ellipsoids are drawn at the 35% probability level.

with $[PPN]N_3$ in a similar fashion, but loss of N_2 occurs and the isocyanate-bridged cluster **6** is formed (eq 3). The



(3)

6 (92%)

presence of a μ-NCO ligand rather than an μ-N_3 ligand in **6** is indicated by the elemental analysis, IR data, and crystal structure results discussed below. Other workers have observed similar formation of isocyanate ligands upon reaction of azide ion with mononuclear[11] and polynuclear[12] metal carbonyls.

Clusters **2**–**6** have been spectroscopically characterized with **4** and **6** further defined by crystallographic structure determinations (Figures 1 and 2). Spectroscopic data for clusters **2**, **3**, and **5** are sufficiently similar to that for **4** and **6** so as to imply similar structures for all five compounds. Each shows two ^1H NMR doublets in the δ 2.5–4.0 spectral region due to the nonequivalent protons of the methylene group with similar 8–10 Hz coupling between them. It is significant that although the μ-CH_2 resonances for **2**–**6** fall within the range of reported resonances for this ligand, they are substantially upfield of the δ 7.75 and 6.47 resonances of **1**[3a] but are relatively insensitive to the nature of the X ligand. The increased shielding for these protons is presumably due to the overall negative charge on the complex which must in part be delocalized onto the methylene carbon.

Table II. Atomic Positional Parameters (×10⁴) and Equivalent Isotropic Thermal Parameters (Å × 10³) for 4

atom	x	y	z	U_{eq}, Å^2
Os(1)	-341 (1)	3030 (1)	1125 (1)	49 (1)[a]
Os(2)	1406 (1)	2351 (1)	2459 (1)	45 (1)[a]
Os(3)	-485 (1)	2868 (1)	3312 (1)	51 (1)[a]
I	-823 (1)	4718 (1)	2285 (1)	63 (1)[a]
P(1)	5997 (3)	1588 (3)	7591 (3)	43 (1)[a]
P(2)	4423 (3)	3302 (3)	7289 (3)	42 (1)[a]
N	5386 (8)	2608 (8)	7521 (7)	50 (4)[a]
O(1)	-2288 (8)	3480 (8)	-220 (8)	100 (5)[a]
O(2)	1245 (9)	4347 (9)	197 (8)	88 (5)[a]
O(3)	82 (8)	1211 (7)	-39 (7)	79 (4)[a]
O(4)	2989 (8)	2021 (8)	1064 (7)	82 (5)[a]
O(5)	2603 (9)	1758 (8)	4360 (7)	90 (5)[a]
O(6)	1907 (7)	4635 (7)	2586 (7)	73 (4)[a]
O(7)	395 (8)	251 (7)	2074 (7)	76 (4)[a]
O(8)	-281 (10)	785 (8)	4167 (8)	108 (6)[a]
O(9)	827 (9)	3986 (11)	4966 (8)	119 (6)[a]
O(10)	-2507 (9)	3226 (9)	4084 (9)	100 (6)[a]
Cb	-1292 (11)	2199 (11)	2013 (9)	67 (6)[a]
Hba	-2014	2364	1907	72
Hbb	-1214	1475	1973	72
C(1)	-1568 (10)	3333 (10)	298 (10)	60 (6)[a]
C(2)	668 (13)	3894 (12)	534 (10)	59 (6)[a]
C(3)	-73 (11)	1905 (11)	428 (11)	66 (6)[a]
C(4)	2353 (11)	2177 (11)	1579 (9)	57 (6)[a]
C(5)	2169 (11)	2000 (10)	3637 (10)	63 (6)[a]
C(6)	1691 (10)	3799 (10)	2561 (9)	54 (5)[a]
C(7)	768 (11)	1037 (9)	2226 (9)	55 (5)[a]
C(8)	-330 (12)	1588 (11)	3846 (11)	73 (7)[a]
C(9)	352 (11)	3581 (11)	4326 (10)	66 (6)[a]
C(10)	-1737 (11)	3127 (11)	3766 (12)	73 (7)[a]
C(11)	7685 (7)	2692 (6)	7182 (6)	75 (5)
C(12)	8603 (7)	2853 (6)	6771 (6)	90 (5)
C(13)	8992 (7)	2086 (6)	6229 (6)	88 (5)
C(14)	8464 (7)	1156 (6)	6097 (6)	71 (5)
C(15)	7546 (7)	994 (6)	6508 (6)	59 (4)
C(16)	7157 (7)	1762 (6)	7050 (6)	43 (3)
C(21)	7288 (6)	782 (7)	9120 (6)	70 (4)
C(22)	7493 (6)	462 (7)	10066 (6)	85 (5)
C(23)	6754 (6)	596 (7)	10702 (6)	78 (5)
C(24)	5809 (6)	1049 (7)	10392 (6)	81 (5)
C(25)	5604 (6)	1368 (7)	9446 (6)	69 (4)
C(26)	6343 (6)	1235 (7)	8810 (6)	45 (3)
C(31)	5447 (7)	-449 (7)	7377 (6)	75 (5)
C(32)	4866 (7)	-1262 (7)	6951 (6)	107 (6)
C(33)	4138 (7)	-1094 (7)	6162 (6)	94 (6)
C(34)	3991 (7)	-112 (7)	5800 (6)	92 (6)
C(35)	4572 (7)	701 (7)	6227 (6)	76 (5)
C(36)	5300 (7)	533 (7)	7015 (6)	47 (3)
C(41)	3925 (5)	5212 (7)	7947 (6)	59 (4)
C(42)	4151 (5)	6111 (7)	8464 (6)	72 (5)
C(43)	5111 (5)	6240 (7)	9006 (6)	67 (4)
C(44)	5845 (5)	5470 (7)	9032 (6)	70 (4)
C(45)	5619 (5)	4571 (7)	8516 (6)	56 (4)
C(46)	4660 (5)	4442 (7)	7974 (6)	42 (3)
C(51)	3372 (6)	4154 (6)	5657 (6)	54 (4)
C(52)	3262 (6)	4438 (6)	4697 (6)	63 (4)
C(53)	4035 (6)	4203 (6)	4120 (6)	59 (4)
C(54)	4916 (6)	3685 (6)	4503 (6)	65 (4)
C(55)	5026 (6)	3401 (6)	5463 (6)	54 (4)
C(56)	4254 (6)	3636 (6)	6040 (6)	44 (3)
C(61)	2636 (7)	2158 (7)	6876 (5)	64 (4)
C(62)	1755 (7)	1640 (7)	7108 (5)	79 (5)
C(63)	1458 (7)	1721 (7)	8028 (5)	75 (5)
C(64)	2042 (7)	2319 (7)	8715 (5)	76 (5)
C(65)	2923 (7)	2837 (7)	8483 (5)	66 (4)
C(66)	3221 (7)	2757 (7)	7564 (5)	45 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

IR spectra in the metal carbonyl region are nearly superimposable for all the compounds with only slight shifts

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(11) (a) Beck, W.; Smedal, H. S. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 253. (b) Beck, W.; Werner, H.; Engelmann, H.; Smedal, H. S. *Chem. Ber.* **1968**, *101*, 2143. (c) Angelici, R. J.; Busetto, L. *J. Am. Chem. Soc.* **1969**, *91*, 3197. (d) Werner, H.; Beck, W.; Engelmann, H. *Inorg. Chim. Acta* **1969**, *3*, 331. (e) Kruse, A. E.; Angelici, R. J. *J. Organomet. Chem.* **1970**, *24*, 231. (f) Angelici, R. J.; Kruse, A. E. *Ibid.* **1970**, *22*, 461. (g) Angelici, R. J.; Faber, G. C. *Inorg. Chem.* **1971**, *10*, 514.

(12) Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1774.

Table III. Atomic Positional Parameters (×10^4) and Equivalent Isotropic Thermal Parameters (Å × 10^3) for 6

atom	*x*	*y*	*z*	U_{eq}, Å^2
Os(1)	5432 (1)	2820 (1)	3172 (1)	48 (1)[a]
Os(2)	3510 (1)	2356 (1)	2352 (1)	42 (1)[a]
Os(3)	5301 (1)	2980 (1)	1007 (1)	45 (1)[a]
P(1)	995 (3)	8389 (2)	2432 (2)	41 (1)[a]
P(2)	−641 (2)	6737 (2)	2774 (2)	38 (1)[a]
N	5610 (8)	4064 (7)	2095 (7)	49 (4)[a]
O(1)	7509 (9)	3181 (9)	3907 (9)	104 (5)[a]
O(2)	4221 (9)	4031 (10)	4809 (9)	110 (6)[a]
O(3)	5146 (11)	830 (8)	4222 (8)	114 (6)[a]
O(4)	2302 (9)	1772 (8)	4294 (7)	90 (5)[a]
O(5)	1863 (8)	2114 (8)	963 (7)	81 (4)[a]
O(6)	3216 (8)	4652 (6)	2475 (7)	74 (4)[a]
O(7)	4462 (8)	238 (6)	2014 (7)	70 (4)[a]
O(8)	4939 (8)	1193 (7)	−194 (7)	75 (4)[a]
O(9)	3744 (9)	4307 (7)	−1 (7)	83 (4)[a]
O(10)	7260 (8)	3484 (8)	−322 (8)	94 (5)[a]
O	5913 (11)	5748 (7)	2417 (10)	121 (6)[a]
N(10)	362 (8)	7385 (7)	2528 (7)	49 (4)[a]
Cb	6199 (11)	2089 (9)	1925 (10)	50 (5)[a]
Hba	6995 (99)	2091 (82)	1839 (82)	59
Hbb	6124 (89)	1208 (88)	1947 (79)	59
C	5758 (11)	4897 (10)	2244 (10)	61 (5)[a]
C(1)	6723 (11)	3076 (10)	3612 (10)	62 (5)[a]
C(2)	4620 (11)	3623 (11)	4187 (10)	67 (6)[a]
C(3)	5202 (12)	1629 (11)	3854 (9)	68 (6)[a]
C(4)	2758 (10)	1990 (9)	3562 (9)	53 (5)[a]
C(5)	2488 (10)	2188 (9)	1440 (9)	52 (5)[a]
C(6)	3311 (10)	3792 (10)	2450 (9)	55 (5)[a]
C(7)	4137 (9)	1041 (10)	2146 (8)	46 (4)[a]
C(8)	5051 (10)	1896 (9)	242 (10)	56 (5)[a]
C(9)	4328 (11)	3861 (9)	399 (10)	59 (5)[a]
C(10)	6527 (11)	3322 (10)	177 (9)	59 (5)[a]
C(41)	2558 (7)	8961 (5)	3520 (6)	55 (3)
C(42)	3482 (7)	8792 (5)	3933 (6)	75 (4)
C(43)	4009 (7)	7874 (5)	3804 (6)	82 (5)
C(44)	3613 (7)	7126 (5)	3262 (6)	93 (5)
C(45)	2689 (7)	7295 (5)	2849 (6)	79 (4)
C(46)	2162 (7)	8213 (5)	2978 (6)	42 (3)
C(51)	2292 (6)	9192 (6)	888 (5)	54 (3)
C(52)	2502 (6)	9519 (6)	−68 (5)	75 (4)
C(53)	1756 (6)	9396 (6)	−705 (5)	67 (4)
C(54)	801 (6)	8946 (6)	−387 (5)	77 (4)
C(55)	592 (6)	8619 (6)	569 (5)	59 (4)
C(56)	1337 (6)	8742 (6)	1206 (5)	40 (3)
C(61)	452 (7)	10410 (6)	2598 (5)	71 (4)
C(62)	−121 (7)	11217 (6)	3018 (5)	77 (4)
C(63)	−843 (7)	11056 (6)	3829 (5)	84 (5)
C(64)	−992 (7)	10089 (6)	4220 (5)	93 (5)
C(65)	−419 (7)	9282 (6)	3800 (5)	74 (4)
C(66)	303 (7)	9442 (6)	2989 (5)	47 (3)
C(71)	494 (5)	5419 (5)	1560 (6)	54 (3)
C(72)	661 (5)	4533 (5)	1042 (6)	73 (4)
C(73)	−148 (5)	3842 (5)	1033 (6)	80 (4)
C(74)	−1123 (5)	4038 (5)	1541 (6)	79 (4)
C(75)	−1290 (5)	4925 (5)	2059 (6)	71 (4)
C(76)	−481 (5)	5615 (5)	2069 (6)	42 (3)
C(81)	−6 (5)	6586 (6)	4594 (5)	59 (4)
C(82)	−101 (5)	6267 (6)	5555 (5)	57 (3)
C(83)	−985 (5)	5737 (6)	5946 (5)	64 (4)
C(84)	−1774 (5)	5527 (6)	5374 (5)	67 (4)
C(85)	−1679 (5)	5846 (6)	4412 (5)	55 (3)
C(86)	−795 (5)	6376 (6)	4022 (5)	39 (3)
C(91)	−2097 (6)	7366 (6)	1597 (5)	59 (3)
C(92)	−2957 (6)	7932 (6)	1376 (5)	68 (4)
C(93)	−3544 (6)	8482 (6)	2091 (5)	78 (4)
C(94)	−3270 (6)	8467 (6)	3028 (5)	71 (4)
C(95)	−2409 (6)	7901 (6)	3250 (5)	54 (3)
C(96)	−1823 (6)	7350 (6)	2535 (5)	42 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

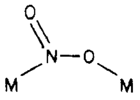
Table IV. Relevant Bond Lengths (Å) and Bond Angles (deg) in PPN[$Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)$]

	6, X = NCO	4, X = I
	Bond Lengths	
Os(1)–Os(3)	3.053 (1)	3.112 (1)
Os(1)–Os(2)	2.911 (1)	2.927 (1)
Os(2)–Os(3)	2.914 (1)	2.934 (1)
Os(1)–X	2.213 (9)	2.863 (1)
Os(3)–X	2.183 (10)	2.844 (1)
Os(1)–Cb	2.144 (13)	2.145 (14)
Os(3)–Cb	2.157 (14)	2.180 (13)
N–C	1.152 (16)	
C–O	1.183 (17)	
P(1)–N′[a]	1.565 (10)	1.561 (11)
P(2)–N′[a]	1.561 (10)	1.562 (10)
	Bond Angles	
Os(2)–Os(1)–Os(3)	58.4 (1)	58.0 (1)
Os(1)–Os(3)–Os(2)	58.3 (1)	57.8 (1)
Os(1)–Os(2)–Os(3)	63.2 (1)	64.1 (1)
Os(2)–Os(1)–Cb	84.7 (4)	85.5 (4)
Os(2)–Os(3)–Cb	84.4 (3)	84.7 (4)
Os(2)–Os(1)–X	85.7 (3)	94.7 (1)
Os(2)–Os(3)–X	86.2 (2)	94.9 (1)
Os(1)–Cb–Os(3)	90.5 (5)	92.0 (5)
Os(1)–X–Os(3)	88.0 (3)	66.1 (1)
Cb–Os(1)–X	77.6 (4)	83.2 (4)
Cb–Os(3)–X	78.0 (4)	83.1 (4)
N–C–O	178.5 (17)	
P(1)–N′–P(2)[a]	154.6 (7)	156.2 (7)

[a] N′ = N10 for **6** and N for **4**.

in peak positions. The isocyanate-bridged cluster **6** shows a ν(NCO) band at 2207 cm^{-1} which falls within the 2180–2230 cm^{-1} spectral region found for other NCO-bridged complexes.[12,13] Gladfelter et al.[12] have pointed out that bridging NCO ligands generally show strong, sharp ν(NCO) bands whereas broad bands are found when these ligands are bound in a terminal fashion. Consistent with the μ-NCO structure for **6** is the sharpness of the band at 2207 cm^{-1}.

The identity of **5** is less certain than **2**–**4** and **6**. In general, when [PPN]NO_2 has been allowed to react with metal carbonyl clusters, *nitrosyl*-substituted clusters have been formed.[14] For example, the reaction of $Os_3(CO)_{12}$ with [PPN]NO_2 gives the μ-NO cluster PPN[$Os_3(CO)_{10}(\mu\text{-}NO)$].[14] Such could also occur during reaction of **1** with [PPN]NO_2 to give a μ-NO cluster ([PPN][$Os_3(CO)_{10}(\mu\text{-}NO)(\mu\text{-}CH_2)$]) instead of the μ-NO_2 formulation suggested for **5**. Carbon and hydrogen analyses, ^{1}H NMR, and IR spectra in the ν(CO) region are not sufficient to distinguish between these two formulations. However, IR bands in the 1700–400 cm^{-1} infrared spectral region should be more useful in this regard. Bridging nitrosyl ligands generally show a ν(NO) stretch in the 1600–1450 cm^{-1} spectral region (e.g., ν(NO) 1460 cm^{-1} for $HOs_3(CO)_9\{P(OMe)_3\}_3(NO)$[15]). Bridging nitro ligands, of which there are the two types illustrated



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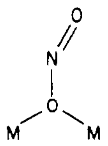

II

typically show *two* ν(NO) bands in the 1550–1400 and 1250–1000 cm^{-1} spectral regions. However, IR spectral

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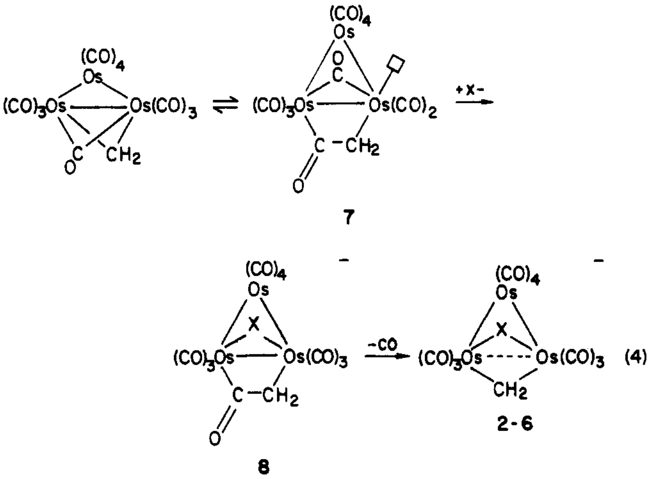
(13) (a) Saillant, R. B. *J. Organomet. Chem.* **1972**, *39*, C71. (b) Mastropasqua, P.; Riemer, A.; Kisch, H.; Kruger, C. *J. Organomet. Chem.* **1978**, *148*, C40. (c) Deeming, A. J.; Ghatak, I.; Owen, D. W.; Peters, R. *J. Chem. Soc., Chem. Commun.* **1982**, 392. (d) Nelson, J.; Nelson, S. M. *J. Chem. Soc. A* **1968**, 1597.

(14) Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 4981.

(15) Johnson, B. F. G.; Raithby, P. R.; Zuccaro, C. *J. Chem. Soc., Dalton Trans.* **1980**, 99.

data does not unambiguously distinguish between these two types, although tentative band assignments have been made.[16-18] Also, a δ (ONO) bend in the 800–900 cm^{-1} spectral region appears characteristic of type II μ-NO_2 ligands.[18] The presence of the PPN cation interferes with the IR analysis of **5**, but careful computer subtraction of the [PPN]I spectrum from that of **5** showed the presence of weak bands at 1445, 1175, 1024, and 847 cm^{-1}. Thus, although not conclusive, the IR data appear more consistent with the presence in **5** of a μ-NO_2 ligand of type II rather than a bridging nitrosyl. Such a μ-NO_2 ligand with a single atom bridge, in contrast to I, is more in accord with the single-atom-bridged structures established for **4** and **6**.

An important aspect of the results reported herein concerns the rate at which $Os_3(CO)_{11}(\mu\text{-}CH_2)$ reacts with the various [PPN]X salts to give clusters **2**–**6**. As noted in the Introduction, osmium clusters do not typically react rapidly with substrates because of the high Os–CO and Os–Os bond strengths. The notable exception is $H_2Os_3(CO)_{10}$ which exhibits high reactivity because of its formal unsaturated character.[2] Even though $Os_3(CO)_{11}(\mu\text{-}CH_2)$ is coordinatively saturated, its reactivity is more akin to $H_2Os_3(CO)_{10}$ than to other saturated Os_x clusters. The reason for this is unknown, although we suspect that it may be due to the facility with which a cluster carbonyl inserts into an Os–methylene bond in $Os_3(CO)_{11}(\mu\text{-}CH_2)$ to give a coordinated ketene ligand.[4] Thus, if this insertion were to occur in the presence of the [PPN]X salts, an open coordination site would be created for the X ligands to add (eq 4). Subsequent loss of CO from the initial product **8** would give **2**–**6**. In support of this suggestion, we have independently shown that clusters **2**–**6** reversibly react with CO to give ketene clusters of type **8** and these reactions occur with half-lives of less than 0.5 min.[19] In the absence of added CO, clusters **8** are not stable and extrude CO to give **2**–**6**. Such facile conversion of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ into coordinatively unsaturated **7** suggests a rich derivative chemistry for this cluster which we are just beginning to elaborate.



7

(4)

8

2-6

Structural Characterization of $PPN[Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}X)]$ (X = I and NCO). Clusters **4** (X = I) and **6** (X = NCO) are isomorphous and crystallize in the centrosymmetric space group $P\bar{1}$ with well-separated anions and cations. ORTEP drawings of the anionic clusters are shown in Figures 1 and 2. As typically found in dibridged Os_3 clusters,[20] the methylene and X ligands bridge the same pair of osmium atoms with dihedral angles between the [Os(1)–X–Os(3)] (X = I, N) and [Os(1)–Cb–Os(3)] planes of 120.4° (**4**) and 123.8° (**6**). If we for the moment neglect the Os(1)–Os(3) vector, each Os atom in these clusters has an approximately octahedral arrangement of ligands. The structures of the PPN cations are unexceptional, both being bent with P–N–P angles of 156.2 (7)° (**4**) and 154.6 (7)° (**6**). In **6**, the μ-NCO ligand is linear with an N–C–O angle of 178.5 (17)°, similar to the other two μ-NCO complexes which have been structurally characterized.[12,13b]

The significant structural differences between these two molecules occur in the dibridged unit. The Os(1)–Cb and Os(3)–Cb distances in the two structures are similar, but due to the larger atomic radius of iodine compared to nitrogen, the Os(1)–X and Os(3)–X distances in **4** are 0.631–0.680 Å longer than in **6** (X = N). This difference is also reflected in the Os(1)–X–Os(3) angles which increase from 66.1 (1)° for **4** to 88.0 (3)° for **6** (X = N). Both of these angles are within normal ranges for μ-I[20e,21] and μ-NCO[12,13b] ligands. However, the Os(1)–Cb–Os(3) angles of 92.0 (5)° for **4** and 90.5 (5)° for **6** are slightly outside the 74.0–87.4° range tabulated by Herrmann[22] for the methylene ligand when it bridges two metals joined by a metal–metal bond.

That brings us to the question of the metal–metal bonding in these two clusters. Both **4** and **6** have a total of 50 valence electrons which is two more than required by the cluster counting rules for a closed triangular cluster.[6] Therefore, open structures with only two metal–metal bonds would have been the predicted result. The structural results clearly show that metal–metal bonds exist in **4** and **6** between the nonbridged Os(1)–Os(2) and Os(3)–Os(2) osmium atoms. The metal–metal distances between the dibridged osmium atoms Os(1) and Os(3) (**4**, 3.112 (1) Å; **6**, 3.053 (1) Å) are longer than the others and are slightly outside the normal unbridged Os–Os single bond value (e.g., Os–Os in $Os_3(CO)_{12}$ average 2.877 Å).[23] However the acute internal angles for the bridging methylene ligands and the bridging iodide in **4** clearly indicate some degree of metal–metal interaction. Halides can certainly bridge two nonbonded metal atoms, and in such compounds M–X–M angles greater than 100° have been reported.[21c,d] Likewise, several compounds have been prepared in which methylene ligands are unsupported by metal–metal bonds,[24] and these have M–CH_2–M angles as large as

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[16] Wieghardt, K.; Siebert, H. *Z. Anorg. Allg. Chem.* **1970**, *374*, 186.

[17] Goodgame, D. M. L.; Hitchman, M. A.; Marsham, D. F.; Phavanantha, P.; Rogers, D. *J. Chem. Soc. D* **1969**, 1383.

[18] Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; Wiley-Interscience: New York, 1978; pp 220–226.

[19] Morrison, E. D.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 254.

[20] (a) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314. (b) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Ibid.* **1977**, *16*, 2697. (c) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297. (d) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1980**, *19*, 2391. (e) Churchill, M. R.; Lashewycz, R. A. *Ibid.* **1979**, *18*, 1926. (f) Churchill, M. R.; Lashewycz, R. A. *Ibid.* **1979**, *18*, 3261. (g) Einstein, F. W. B.; Jones, T.; Tyers, K. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1272. (h) Aleksandrov, G. G.; Zol'nikova, G. P.; Krickaja, I. I.; Struchkov, Ju. T. *Koord. Khim.* **1980**, *6*, 626.

[21] (a) Howard, J. A. K.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 366. (b) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wong, K. *J. Chem. Soc. Dalton Trans.* **1980**, 1248. (c) Kampe, C. E.; Boag, N. M.; Knobler, C. B.;= Kaesz, H. D. *Inorg. Chem.* **1984**, *23*, 1390. (d) Colombo, A.; Allegra, G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 1653.

[22] Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

[23] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

[24] (a) Lin, Y. C.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.* **1983**, *105*, 1679. (b) Jandik, P.; Schubert, U.; Schmidbauer, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73. (c) Azam, K. A.; Frew, A. A.; Lloyd, B. R.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 614. (d) McKeer, I. R.; Cowie, M. *Inorg. Chim. Acta* **1982**, *65*, L107.

123°.[24a] Furthermore, similar $Os_3(CO)_{10}(\mu\text{-}X)_2$ compounds are known in which the dibridged Os–Os separation is as great as 3.29 Å.[20h] Thus there must be some residual metal–metal interaction in 4 and 6 that hold the metals as close together as they are. These structural data also indicate that a continuum of $M\text{–}CH_2\text{–}M$ angles and metal–metal distances exist between the strictly metal–metal nonbonded[24] and unambiguously metal–metal bonded[22] $\mu\text{-}CH_2$ complexes.

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Registry No. **1**, 77208-32-3; **2**, 96897-74-4; **3**, 96897-75-5; **4**, 96897-76-6; **5**, 96897-77-7; **6**, 96897-78-8; [PPN]Cl, 21050-13-5; [PPN]Br, 20545-30-6; [PPN]I, 38011-33-5; $[PPN]NO_2$, 38011-35-7; $[PPN]N_3$, 38011-36-8; Os, 7440-04-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, complete lists of bond angles and bond lengths, calculated positions of hydrogen atoms, and the structure factors for 4 and 6 (65 pages). Ordering information is given on any current masthead page.

Binuclear Tungsten–Rhenium Alkyl–Acyl and Alkyl–Carbene Complexes. Crystal and Molecular Structure of $(CO)_4W(\mu\text{-}PPh_2)_2Re(CO)_3CH_3$

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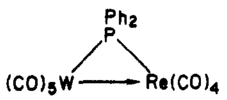
Reaction of $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4$ with PPh_2H gives $(CO)_5W(\mu\text{-}PPh_2)Re(CO)_4(PPh_2H)$ which upon thermolysis yields $(CO)_4W(\mu\text{-}PPh_2)_2Re(CO)_3H$, 3. Abstraction of hydride from 3 with BuLi gives the anion $[(CO)_4W(\mu\text{-}PPh_2)_2Re(CO)_3]^-$, 4. Treatment of the latter with CH_3I, $EtOSO_2CF_3$, phosgene, and PhC(O)Br leads to formation of the new complexes $(CO)_4W(\mu\text{-}PPh_2)_2Re(CO)_3X$ with X = CH_3 (**5**), Et (**6**), Cl (**7**), PhC(O) (**8**), and Br (**9**). Complex **5** has been crystallographically characterized: $P2_1/c$, $a = 9.766$ (3) Å, $b = 19.659$ (4) Å, $c = 17.212$ (4) Å, $\beta = 103.06$ (3)°, $V = 3219$ (2) Å^3, $Z = 4$, $R_F = 0.047$, $R_{wF} = 0.047$, 3693 reflections with $F_o \geq 2.5\sigma(F_o)$. Both the W and Re centers have octahedral coordination geometries with the W ligated by four CO's and two $\mu\text{-}PPh_2$ ligands and Re by three CO's, two $\mu\text{-}PPh_2$ ligands, and the methyl ligand. The W–Re bond distance of 3.015 (1) Å implies a single metal–metal bond between these atoms. Treatment of complexes **5** and **6** with RLi and then $EtOSO_2CF_3$ reagents gives first formation of acyl and then Fischer-type carbene ligands on tungsten. No interaction of the organic ligands on the different metals occurs in these binuclear alkyl–acyl and alkyl–carbene complexes.

In an earlier publication we described the preparation and derivative chemistry of the *monophosphido-bridged* WRe complex 1.[1] Complex 1 contains a weak donor–acceptor bond which is easily displaced by better donor ligands and which provides easy access to an open coordination site for deinsertion reactions of formyl and acyl ligands.[1] Other work in these laboratories has shown that such metal–metal bond cleavage does not occur nearly so readily in *bis(phosphido)-bridged* heterobinuclear complexes.[2,3] We thus sought a corresponding $WRe(\mu\text{-}PPh_2)_2$ complex with which to compare the derivative chemistry of complex 1, and a suitable species 3 has been found to derive in good yield by the reactions of eq 1. Complex 3 has proven to be a versatile precursor to a number of unusual binuclear alkyl, acyl, alkyl–acyl, and alkyl–carbene complexes and these are described herein. Binuclear complexes such as these with organic ligands on adjacent



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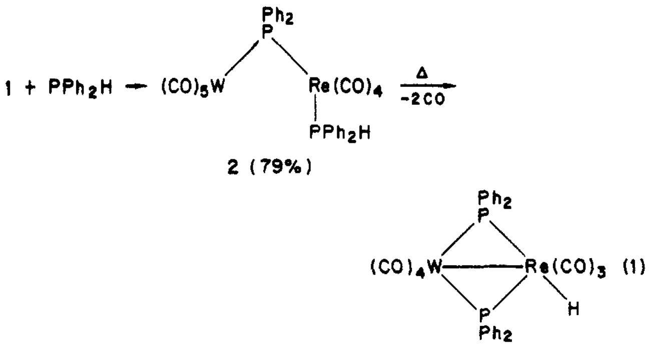

2 (79%)

3 (84%)

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(1) Mercer, W. C.; Whittle, R. R.; Burkhardt, E. W.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 68.

(2) Breen, M. J.; Shulman, P. M.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 782–793.

(3) Morrison, E. D.; Harley, A. D.; Marcelli, M. A.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *Organometallics* **1984**, *3*, 1407–1413.

0276-7333/85/2304-1418$01.50/0