agreement with the Zr-H bond lengths found in (η-C_5Me_5)Zr(η-C_8H_8)H (1.81 and 1.78 Å)[2c] and {ZrH(μ-H)(η-C_5H_4Me)$_2$}$_2$ (1.78 Å);[15] it is also consistent with the covalent radii of the elements[16] (the Bragg-Slater radii of hydrogen and zirconium are 0.25 and 1.55 Å, respectively).[17] The Zr-B distance of 2.558 Å is indicative of a bidentate methyltrihydroborato group as compared to 2.335 and 2.31 Å in the triply hydrogen bridged $Zr(BH_3CH_3)_4$[2] and $Zr(BH_4)_4$, respectively.[18]

We have been unable to isolate $Cp_2Zr(BH_3CH_3)_2$ by the synthetic route with which $Cp_2U(BH_3CH_3)_2$ is prepared. This may be due to the smaller ionic radius of Zr(IV) (0.19 Å smaller than that of U(IV)),[19] which results in a larger coordination number about U(IV) as shown by the difference in molecular structure between $Zr(BH_4)_4$ and $U(BH_4)_4$.[20] Moreover, we have also been unable to isolate the compound $Cp_2U(H)BH_3CH_3$.

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Supplementary Material Available: Tables of thermal parameters, additional distances and angles, the least-squares plane, and the calculated powder pattern and additional ORTEP drawings (6 pages); a table of observed structure factors and their discrepancies from the calculated values (6 pages). Ordering information is given on any current masthead page.

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(13) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1971**, 2225.
(14) Ronova, I. A.; Alekseev, N. V.; Gapotchenko, N. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1971**, *25*, 149.
(15) Stones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889.
(16) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.
(17) Slater, J. C. *J. Chem. Phys.* **1964**, *41*, 3199.
(18) (a) Plato, V.; Hedberg, K. *Inorg. Chem.* **1971**, *10*, 590. (b) Spiridonov, V. P.; Mamaeva, G. I. *J. Struct. Chem. (Engl. Transl.)* **1969**, *10*, 120.
(19) Shanon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.
(20) Marks, T. J.; Kolb, J. R. *Chem. Rev.* **1977**, *77*, 263.

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Comparison of Dative and Covalent Metal-Metal Bonds: Structures of the Isomers $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ and $(Br)(Me_3P)(OC)_3OsRe(CO)_5$

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Recent work from this laboratory has demonstrated that neutral 18-electron organometallic compounds can act as ligands.[1-4] Structural studies appeared to indicate that the donor-acceptor metal-metal bonds in the resulting complexes were somewhat longer than the covalent bonds reported in the literature between the same metals. In each case, however, the molecules that were compared were very different and it was not clear if the small differences in the metal-metal bond lengths could be attributed to the electronic nature of the bond or to the various ligand influences within each molecule.

Here we report the synthesis and structure of the isomers $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ and $(Br)(Me_3P)(OC)_3OsRe(CO)_5$. These structures allow for the first time a comparison of a dative and a covalent metal-metal bond in molecules where the changes in ligand influences have been kept to a minimum.

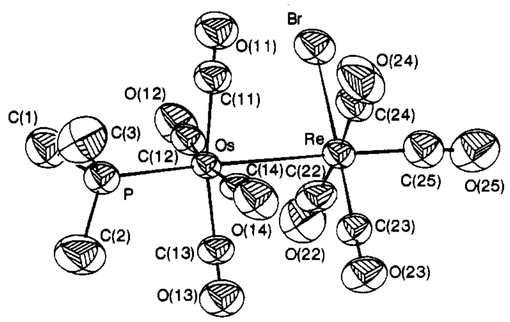

Figure 1. Molecular structure of $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ (**1**). Ellipsoids enclose 50% probabilities; hydrogen atoms are deleted here and in Figure 2.

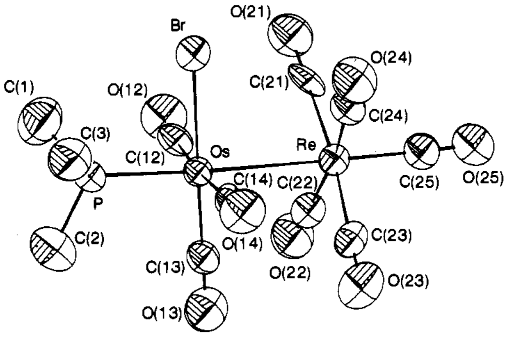

Figure 2. Molecular structure of $(Br)(Me_3P)(OC)_3OsRe(CO)_5$ (**2**).

Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hexane and dichloromethane were distilled under nitrogen from potassium and P_2O_5 respectively, before use. Literature methods were used to prepare $[Re(CO)_4(Br)]_2$[5] and $Os(CO)_4(PMe_3)$.[6] The hydride $Re(CO)_5(H)$ was prepared by the reduction of $Re(CO)_5(Br)$ with powdered zinc in acetic acid; a preparation similar to this has been reported by Shapley and co-workers.[7]

Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer, mass spectra on a Hewlett-Packard 5985 GC-MS spectrometer, and NMR spectra on a Bruker WM400 spectrometer (operating frequencies: 400 MHz for ^1H, 100.6 MHz for ^{13}C, and 161.96 MHz for ^{31}P). In order to obtain a good signal to noise ratio for the ^{13}C NMR spectra, overnight accumulation of transients was employed or ^{13}C-enriched samples were used. (The enrichment by ^{13}CO of $Re(CO)_5(Br)$[8] and $Os(CO)_4(PMe_3)$[2] has been described.) The assignments of ^{13}C NMR resonances reported below are made with reference to Figures 1 and 2. The ^{31}P NMR spectra are referenced to external 85% H_3PO_4 (downfield positive). The microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University.

Preparation of $(Me_3P)(OC)_4OsRe(CO)_4(Br)$. A 100-mL round-bottom flask (fitted with a Teflon valve) charged with $[Re(CO)_4(Br)]_2$ (0.096 g, 0.127 mmol), $Os(CO)_4(PMe_3)$ (0.096 g, 0.254 mmol), and CH_2Cl_2 (15 mL) was cooled to -196 °C and evacuated; the solution was degassed with two freeze-pump-thaw cycles. The solution was then heated, with stirring, at 50 °C for 2.5 h. After this period the solution was cooled, filtered through Celite to a Schlenk flask, and concentrated to ~5 mL. Hexane (10 mL) was added, and the resultant solution stored at -15 °C overnight whereupon pale yellow crystals formed. The mother solution was removed, and the crystals were washed with hexane and dried on the vacuum line.

The air-stable product, $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ (0.15 g, 78%), was pure by infrared spectroscopy. The analytical sample was obtained by recrystallization from CH_2Cl_2-hexane. IR (CH_2Cl_2): ν(CO) 2115

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(1) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854.
(2) Einstein, F. W. B.; Jones, T.; Pomeroy, R. K.; Rushman, P. *J. Am. Chem. Soc.* **1984**, *106*, 2707.
(3) Einstein, F. W. B.; Martin, L. R.; Pomeroy, R. K.; Rushman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 345.
(4) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *Organometallics* **1985**, *3*, 250.
(5) Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844. Abel, E. W.; Hargreaves, G. B.; Wilkinson, G. *J. Chem. Soc.* **1958**, 3149.
(6) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1985**, *24*, 2777.
(7) Urbancic, M. A.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1984**, *23*, 2954.
(8) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.

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Table I. Crystal Data, Data Collection, and Refinement of the Structures

	1	**2**
formula	$C_{11}H_9BrO_8OsPRe$	$C_{11}H_9BrO_8OsPRe$
fw	756.46	756.46
space group	$P\bar{1}$	$P2_1/c$
a, Å	8.014 (2)	8.5737 (13)
b, Å	8.796 (2)	15.130 (3)
c, Å	14.018 (4)	14.745 (3)
α, deg	103.53 (2)	
β, deg	93.19 (2)	105.67 (1)
γ, deg	99.56 (1)	
V, Å^3	942.80	1841.6
Z	2	4
ρ_{calcd}, g cm^{-3}	2.664	2.728
μ, cm^{-1}	154.5	158.2
cryst dimens, mm	0.32 × 0.05 × 0.34	0.11 × 0.06 × 0.15
ω-scan width, deg	$0.80 + 0.35 \tan\theta$	$0.75 + 0.35 \tan\theta$
ω-scan speed, deg min^{-1}	5.49–0.78	4.12–0.72
2θ range	3–50°	3–50°
no. of unique refcns	3323	3224
no. of obsd reflcns	2497 ($I > 3\sigma(I)$)	2139 ($I > 2.3\sigma(I)$)
no. of variables	209	209
final R_F[a]	0.035	0.047
final R_{wF}[b]	0.043	0.043
p in w[b]	0.0004	0.0003
GOF	1.63	1.41

[a] $R_F = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum F_o^2]^{1/2}$, where $w = [(\sigma(F_o)^2 + p(F_o)^2]^{-1}$. [c] GOF $= [\sum w(|F_o| - |F_c|^2/(\text{no. of observns} - \text{no. of variables}))]^{1/2}$.

(w), 2068 (m), 2023 (vs), 1973 (m), 1914 (m). ^{1}H NMR ($CDCl_3$): δ 2.07 (d, $J_{P-H} = 10.3$ Hz) (a very weak doublet was observed at 2.00 ppm, $J_{P-H} = 10.5$ Hz, which may have been due to the presence of a trace of the isomer of **1** with the PMe_3 group cis to the metal–metal bond[2]). $^{13}C\{^1H\}$ NMR (CH_2Cl_2–CD_2Cl_2, 5:1): δ 22.8 ($J_{C-P} = 37.5$ Hz, CH_3), 183.9 (4 C, $J_{C-P} = 3.4$ Hz, Os–C), 186.1 (1 C, $J_{C-P} = 3.6$ Hz, C(25)), 188.7 (1 C, C(23)), 193.1 (2 C, C(22), C(24)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −54.5. Anal. Calcd for $C_{11}H_9BrO_8OsPRe$: C, 17.47; H, 1.20. Found: C, 17.40; H, 1.20. The compound was not sufficiently volatile to obtain an electron-impact mass spectrum below its decomposition temperature.

Preparation of $(H)(Me_3P)(OC)_3OsRe(CO)_5$. A hexane solution (15 mL) of $Re(CO)_5(H)$ (~0.060 g, ~0.18 mmol) and $Os(CO)_4(PMe_3)$ (0.069 g, 0.18 mmol) was degassed and the vessel sealed under vacuum as described above. The solution was stirred at 60 °C for 20 h to give a yellow solution and a small amount of an insoluble material. The solution was filtered through Celite and the solvent removed on the vacuum line. Traces of unreacted $Os(CO)_4(PMe_3)$ were removed from the residue by sublimation at 40 °C (< 0.02 mm). The remaining solid was recrystallized from hexane at −15 °C to afford large, air-stable, yellow-orange needles of $(H)(Me_3P)(OC)_3OsRe(CO)_5$ (estimated yield ~90%). IR (hexane): ν(CO) 2107 (w), 2037 (m), 2007 (s, sh), 2003 (vs), 1987 (w), 1966 (m). MS: m/e 678 (M^+). ^{1}H NMR ($C_6D_5CD_3$): δ 1.10 ($J_{H-P} = 10.3$ Hz, CH_3), −10.38 ($J_{H-P} = 19.4$ Hz, Os–H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 23.2 ($J_{C-P} = 37.7$ Hz, CH_3), 184.5 (1 C, $J_{C-P} = 3.7$ Hz, C(13)), 189.0 (2 C, $J_{C-P} = 6.1$ Hz, C(12), C(14)), 189.7 (vbr, Re–C). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$): δ −48.9. Anal. Calcd for $C_{11}H_{10}O_8OsPRe$: C, 19.50; H, 1.49. Found: C, 19.77; H 1.37.

Preparation of $(Br)(Me_3P)(OC)_3OsRe(CO)_5$. To a solution of $(H)(Me_3P)(OC)_3OsRe(CO)_5$ (0.050 g, 0.074 mmol) in hexane (15 mL) was added CBr_4 (0.17 g, 0.05 mmol). The reaction was complete in 15 min. (In other experiments of this type the rate appeared to depend on the amount of CBr_4 present.) When the conversion of the hydride was complete, the solvent was removed on the vacuum line and the excess CBr_4 removed by sublimation. The residue was recrystallized at −15 °C from CH_2Cl_2–hexane to afford pale yellow, air-stable crystals of (Br)-$(Me_3P)(OC)_3OsRe(CO)_5$ (0.045 g, 81%). IR (hexane): ν(CO) 2117 (m), 2054 (m), 2040 (m), 2012 (vs), 2009 (vs), 1976 (s) MS: m/e 756,758 (M^+). ^{1}H NMR ($C_6D_5CD_3$): δ 1.17 ($J_{H-P} = 10.4$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (CH_2Cl_2–CD_2Cl_2, 5:1): δ 18.9 ($J_{C-P} = 37.8$ Hz, CH_3), 177.0 (1 C, $J_{C-P} = 4.0$ Hz, C(13)), 189.9 (2 C, $J_{C-P} = 5.6$ Hz, C(12), C(14)), 191 (vbr, Re–C). $^{31}P\{^1H\}$ NMR: δ −47.1. Anal. Calcd for $C_{11}H_9BrO_8OsPRe$: C, 17.47; H, 1.20. Found: C, 17.49; H, 1.19.

X-ray Structure Determinations for 1 and 2. Crystals of **1** and **2** were selected and sealed in thin-walled glass capillaries, which were mounted on an Enraf-Nonius CAD4F diffractometer. Mo Kα (Kα_1, λ = 0.709 30 Å; Kα_2, λ = 0.713 59 Å) radiation at 20 °C, monochromated by graphite, was used for the determinations. In each case accurate cell dimensions were obtained by least-squares methods from well-centered reflections widely distributed in reciprocal space: 24 reflections with $30° < 2\theta < 36°$ for **1** and 25 reflections with $23° < 2\theta < 35°$ for **2**.

Table II. Positional and Thermal Parameters of Non-Hydrogen Atoms for $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ (**1**) and $(Br)(Me_3P)(OC)OsRe(CO)_5$ (**2**)

	x	y	z	B_{eq},[a] Å^2
		Compound **1**		
Os	0.58147 (5)	0.50139 (5)	0.76529 (3)	3.08
Re	0.33395 (6)	0.20096 (6)	0.66873 (3)	3.77
Br[b]	0.32461 (21)	0.11629 (21)	0.83693 (11)	5.59
P	0.7843 (4)	0.7333 (4)	0.8364 (3)	4.62
C(11)	0.4297 (17)	0.5233 (17)	0.8719 (10)	5.0
O(11)	0.3467 (13)	0.5386 (14)	0.9278 (7)	6.6
C(12)	0.6966 (15)	0.3618 (15)	0.8259 (8)	3.9
O(12)	0.7633 (12)	0.2855 (11)	0.8616 (7)	5.9
C(13)	0.7010 (16)	0.4424 (15)	0.6470 (8)	4.1
O(13)	0.7665 (13)	0.4410 (12)	0.5802 (7)	6.1
C(14)	0.4386 (15)	0.6126 (15)	0.6981 (8)	4.0
O(14)	0.3547 (12)	0.6744 (12)	0.6594 (7)	6.5
C(22)	0.5340 (20)	0.0924 (18)	0.6416 (9)	5.4
O(22)	0.6448 (16)	0.0363 (14)	0.6275 (9)	8.0
C(23)	0.3406 (16)	0.2687 (15)	0.5487 (9)	4.5
O(23)	0.3434 (14)	0.3070 (12)	0.4770 (7)	6.4
C(24)	0.1431 (17)	0.3160 (18)	0.7103 (10)	5.3
O(24)	0.0450 (15)	0.3849 (18)	0.7311 (9)	9.3
C(25)	0.1785 (19)	0.0109 (18)	0.6036 (11)	5.8
O(25)	0.0902 (17)	−0.1055 (14)	0.5584 (9)	8.4
C(1)	0.935 (2)	0.715 (2)	0.9322 (12)	6.8
C(2)	0.907 (2)	0.811 (3)	0.7511 (13)	9.9
C(3)	0.689 (3)	0.900 (2)	0.8951 (13)	8.1
		Compound **2**		
Os	0.68325 (7)	0.19194 (4)	0.63463 (4)	3.06
Re	0.42865 (7)	0.32832 (5)	0.56526 (5)	3.49
Br[c]	0.89839 (23)	0.28559 (15)	0.58422 (15)	4.97
P	0.8936 (5)	0.0912 (3)	0.6953 (3)	4.20
C(12)	0.7434 (20)	0.2570 (11)	0.7521 (13)	3.9
O(12)	0.7823 (16)	0.2998 (10)	0.8173 (10)	6.6
C(13)	0.5247 (20)	0.1249 (12)	0.6689 (11)	4.2
O(13)	0.4297 (15)	0.0827 (10)	0.6868 (9)	6.6
C(14)	0.6197 (20)	0.1338 (15)	0.5052 (14)	4.6
O(14)	0.5870 (18)	0.1086 (11)	0.4451 (11)	6.4
C(21)	0.5925 (23)	0.4136 (11)	0.6328 (13)	4.3
O(21)	0.6845 (16)	0.4623 (9)	0.6746 (10)	6.5
C(22)	0.3647 (19)	0.3042 (12)	0.6851 (12)	4.1
O(22)	0.3356 (16)	0.2930 (10)	0.7536 (9)	6.7
C(23)	0.2882 (19)	0.2319 (13)	0.4998 (11)	4.2
O(23)	0.2064 (16)	0.1763 (10)	0.4612 (10)	7.4
C(24)	0.5187 (21)	0.3438 (12)	0.4536 (12)	4.3
O(24)	0.5683 (17)	0.3504 (11)	0.3925 (10)	6.8
C(25)	0.2649 (21)	0.4192 (13)	0.5251 (13)	4.8
O(25)	0.1709 (16)	0.4740 (10)	0.5015 (11)	7.4
C(1)	1.058 (3)	0.1356 (19)	0.7850 (18)	9.3
C(2)	0.839 (3)	−0.0018 (17)	0.7475 (19)	8.8
C(3)	0.991 (2)	0.0445 (16)	0.6122 (16)	7.6

[a] $B_{eq} = 8\pi^2(U_1 + U_2 + U_3)/3$ where U_n are the principal axes of the ellipsoid. [b] Occupancy = 0.895 (5). [c] Occupancy = 0.892 (6).

Intensity data sets were measured by using a coupled ω–2θ scan; the background was determined by extending the scan 25% on each side of a reflection. For **1**, $h = -9$ to 9, $k = 0$ to 10, and $l = -16$ to 15; for **2**, $h = -10$ to 10, $k = 0$ to 18, and $l = 0$ to 17. Other details are given in Table I. Two standard reflections were measured at intervals of 1 h of exposure time for each data set. During data collection for **1**, the standards showed a 6% overall intensity decrease, and therefore the data were scaled according to a five-point smoothed curve. Rescaling of the data set of **2** was not performed since the fluctuations about the mean of the standards were <2%. Lorentz polarization and absorption corrections were applied to the data sets. For **1** the absorption correction was an analytical correction[9] (T range 0.38–0.04); for **2** it was an empirical correction[10] (T range 1.00–0.38).

Both structures were solved by heavy-atom methods. All non-hydrogen atoms were located and refined by full-matrix least-squares methods

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(9) DeMeulanaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

(10) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

Table III. Interatomic Distances (Å) and Selected Angles (deg) for $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ (**1**) and $(Br)(Me_3P)(OC)_3OsRe(CO)_5$ (**2**)

	1	**2**		**1**	**2**		**1**	**2**		**1**	**2**
Os–Re	3.006 (1)	2.977 (1)	Os–Br		2.589 (2)	Re–C(22)	2.008 (15)	2.02 (2)	C(22)–O(22)	1.091 (18)	1.12 (2)
Os–P	2.359 (4)	2.347 (5)	Re–Br	2.635 (2)		Re–C(23)	1.912 (13)	1.97 (2)	C(23)–O(23)	1.133 (16)	1.14 (2)
Os–C(11)	1.974 (14)		C(11)–O(11)	1.055 (17)		Re–C(24)	2.010 (14)	2.01 (2)	C(24)–O(24)	1.082 (18)	1.10 (2)
Os–C(12)	1.964 (11)	1.94 (2)	C(12)–O(12)	1.110 (13)	1.13 (2)	Re–C(25)	1.910 (15)	1.94 (2)	C(25)–O(25)	1.165 (19)	1.14 (2)
Os–C(13)	1.969 (12)	1.87 (2)	C(13)–O(13)	1.101 (14)	1.12 (2)	P–C(1)	1.808 (14)	1.78 (2)	P–C(3)	1.818 (16)	1.80 (2)
Os–C(14)	1.959 (11)	2.04 (2)	C(14)–O(14)	1.123 (14)	0.94 (3)	P–C(2)	1.774 (17)	1.73 (3)			
Re–C(21)		1.97 (2)	C(21)–O(21)		1.13 (2)						

	1		**2**		**1**		**2**
Re–Os–P	177.51 (9)	Re–Os–P	176.44 (13)	Br–Re–C(25)	90.8 (4)	C(21)–Re–C(25)	92.8 (7)
Re–Os–C(11)	85.5 (4)	Re–Os–Br	92.02 (5)	C(22)–Re–C(23)	92.5 (5)	C(22)–Re–C(23)	91.2 (7)
Re–Os–C(12)	84.5 (4)	Re–Os–C(12)	87.0 (5)	C(22)–Re–C(24)	174.2 (5)	C(22)–Re–C(24)	172.7 (6)
Re–Os–C(13)	83.6 (4)	Re–Os–C(13)	87.1 (5)	C(22)–Re–C(25)	91.6 (6)	C(22)–Re–C(25)	92.9 (7)
Re–Os–C(14)	86.9 (4)	Re–Os–C(14)	89.5 (5)	C(23)–Re–C(24)	92.2 (5)	C(23)–Re–C(24)	90.3 (7)
P–Os–C(11)	96.9 (4)	P–Os–Br	86.06 (13)	C(23)–Re–C(25)	90.5 (6)	C(23)–Re–C(25)	94.6 (7)
P–Os–C(12)	94.8 (4)	P–Os–C(12)	89.9 (5)	C(24)–Re–C(25)	91.9 (6)	C(24)–Re–C(25)	94.2 (7)
P–Os–C(13)	94.1 (4)	P–Os–C(13)	94.9 (5)	Os–P–C(1)	115.3 (6)	Os–P–C(1)	114.2 (9)
P–Os–C(14)	93.9 (4)	P–Os–C(14)	93.5 (5)	Os–P–C(2)	114.7 (6)	Os–P–C(2)	115.2 (8)
C(11)–Os–C(12)	89.9 (5)	Br–Os–C(12)	86.6 (5)	Os–P–C(3)	112.9 (7)	Os–P–C(3)	116.4 (7)
C(11)–Os–C(13)	169.0 (6)	Br–Os–C(13)	178.9 (5)	C(1)–P–C(2)	106.2 (9)	C(1)–P–C(2)	102.4 (13)
C(11)–Os–C(14)	87.9 (5)	Br–Os–C(14)	89.9 (5)	C(1)–P–C(3)	104.0 (8)	C(1)–P–C(2)	103.5 (11)
C(12)–Os–C(13)	89.2 (4)	C(12)–Os–C(13)	94.1 (7)	C(2)–P–C(3)	102.5 (10)	C(2)–P–C(3)	102.4 (12)
C(12)–Os–C(14)	171.3 (5)	C(12)–Os–C(14)	175.0 (8)	Os–C(11)–O(11)	177.7 (12)		
C(13)–Os–C(14)	91.3 (4)	C(13)–Os–C(14)	89.4 (7)	Os–C(12)–O(12)	178.6 (12)	Os–C(12)–O(12)	175.1 (16)
Os–Re–Br	90.89 (5)	Os–Re–C(21)	85.6 (5)	Os–C(13)–O(13)	178.9 (10)	Os–C(13)–O(13)	177.5 (16)
Os–Re–C(22)	88.0 (5)	Os–Re–C(22)	85.5 (5)	Os–C(14)–O(14)	178.9 (12)	Os–C(14)–O(14)	177.7 (19)
Os–Re–C(23)	87.8 (4)	Os–Re–C(23)	87.1 (5)			Re–C(21)–O(21)	177.3 (16)
Os–Re–C(24)	88.7 (4)	Os–Re–C(24)	87.4 (5)	Re–C(22)–O(22)	178.6 (15)	Re–C(22)–O(22)	176.7 (15)
Os–Re–C(25)	178.3 (5)	Os–Re–C(25)	177.7 (6)	Re–C(23)–O(23)	179.1 (11)	Re–C(23)–O(23)	179.5 (16)
Br–Re–C(22)	88.6 (4)	C(21)–Re–C(22)	90.1 (7)	Re–C(24)–O(24)	176.0 (14)	Re–C(24)–O(24)	178.5 (17)
Br–Re–C(23)	178.3 (4)	C(21)–Re–C(23)	172.5 (7)	Re–C(25)–O(25)	175.3 (14)	Re–C(25)–O(25)	178.6 (16)
Br–Re–C(24)	86.7 (4)	C(21)–Re–C(24)	87.6 (7)				

initially using isotropic temperature factors. In **1**, at this stage, the Br atom had unreasonably large thermal motion. This, coupled with the features of the radial carbonyls on the rhenium, was consistent with a small amount of disorder involving the Br and these coplanar carbonyl ligands. An occupancy factor for the Br site was introduced, and it refined to 0.88 with a corresponding change in R from 0.075 to 0.073. Models involving greater complexity with disordered Br and carbonyl groups at each equatorial site at Re did not refine as successfully. A very similar situation was found for **2**, and it was treated in the same fashion. Anisotropic temperature factors were introduced (after their need was indicated) for the Os, Re, Br, and P atoms, and then for O and C atoms. Hydrogen atom coordinates were calculated with the assumptions that C–H = 0.95 Å, and that the hydrogen atoms adopt staggered conformations; hydrogen atoms were assigned U = average U_{eq}(methyl C). Hydrogen parameters were not refined.

Least-squares refinement was continued until all shift:error ratios were <0.04. The weighting schemes for both **1** and **2** were confirmed to be reasonable as a function of $|F_o|$ and $(\sin\theta)/\lambda$. The major features in the final electron density difference map were close to the Os and Re atoms: the biggest peak in **1** was 1.4 (2) e $Å^{-3}$ and in **2**, 1.8 (3) e $Å^{-3}$. Refinement throughout was by full-matrix least-squares methods, which minimized the function R_{wF} (Table I) where w was initially unity but in the later stages changed to the value shown as footnote b in Table I. Neutral-atom scattering factors with anomalous dispersion corrections were used.[11] Computer programs were run on a VAX 11/750 computer.[12]

Results and Discussion

The compound with the donor–acceptor metal–metal bond, $(Me_3P)(OC)_4OsRe(CO)_4(Br)$ (**1**), was prepared by the reaction of $Os(CO)_4(PMe_3)$ with $[Re(CO)_4(Br)]_2$ in CH_2Cl_2 at 60 °C (eq 1). The isomer with the covalent metal–metal bond, $(Br)(Me_3P)(OC)_3OsRe(CO)_5$ (**2**), was isolated by the sequence of reactions shown as eq 2 and 3.

$$2Os(CO)_4(PMe_3) + [Re(CO)_4(Br)]_2 \rightarrow \underset{\mathbf{1}}{2(Me_3P)(OC)_4OsRe(CO)_4(Br)} \quad (1)$$

$$Os(CO)_4(PMe_3) + Re(CO)_5(H) \xrightarrow{60\ ^\circ C} \underset{\mathbf{3}}{(H)(Me_3P)(OC)_3OsRe(CO)_5} \quad (2)$$

$$(H)(Me_3P)(OC)_3OsRe(CO)_5 \xrightarrow{CBr_4} \underset{\mathbf{2}}{(Br)(Me_3P)(OC)_3OsRe(CO)_5} \quad (3)$$

The substitution of $Re(CO)_5(H)$ by PBu_3 to give $Re(CO)_4(PBu_3)(H)$ is believed to proceed via the radical $[Re(CO)_4(PBu_3)]^\bullet$.[13] The formation of the hydride $(H)(Me_3P)(OC)_3OsRe(CO)_5$ (**3**) could, therefore, involve the intermediate $[(Me_3P)(OC)_4OsRe(CO)_4]^\bullet$ followed by rearrangement to $[(Me_3P)(OC)_3OsRe(CO)_5]^\bullet$ and capture of a hydrogen atom by this radical at the osmium atom. Alternatively, there could be an initial proton transfer from $Re(CO)_5(H)$ to $Os(CO)_4(PMe_3)$ and then replacement of CO in the resulting cation, $[(H)Os(CO)_4(PMe_3)]^+$, by $[Re(CO)_5]^-$. A third possibility is the formation $(Me_3P)(OC)_4OsRe(CO)_4(H)$, analogous to **1**, followed by rapid isomerization to give **3**. We have reported this type of isomerization for $(L)(OC)_4OsRu(CO)_4(SiCl_3)(Br)$ (L = CO, PMe_3) to give $(Br)(L)(OC)_3OsRu(CO)_4(SiCl_3)$.[14] Although we have not observed the isomerization of **1** to **2**, the manganese analogue of **1** does undergo this rearrangement when stirred in CH_2Cl_2 at room temperature.[15]

Complexes **1**–**3** are air-stable crystalline solids. Whereas **2** and **3** are soluble in hexane, **1** is not soluble in this solvent. It is a general observation for the complexes we have prepared with donor–acceptor metal–metal bonds that they are either insoluble or only sparingly soluble in hexane. This is probably a consequence of the polar nature of the bond. The spectroscopic properties of **1** and **2** (Experimental Section) are consistent with the solid-state

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(11) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

(12) (a) Larson, A. C.; Gabe, E. J. *Computing in Crystallography*; Schenk, H.; Olthof-Mazekamp, R.; Van Koningsveld, H.; Bassi, G. C., Eds.; Delft Unversity Press: Holland, 1978; p 81. (b) Davies, E. K. *CHEMGRAF Program Suite*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1983.

(13) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527. See also: Edidin, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 948.

(14) Fleming, M. M.; Pomeroy, R. K.; Rushman, P. *J. Organomet. Chem.* **1984**, *273*, C33.

(15) Jennings, M. C.; Rushman, P.; Pomeroy, R. K. unpublished results.

structures described below. The ^1H and ^{13}C NMR spectra of **3** indicate it has a structure analogous to **2**. For example, the phosphorus–hydrogen coupling observed for the hydride signal in the ^1H NMR spectrum of **3** is typical for a *cis*-$M(H)(PR_3)$ grouping.[16]

Structures of 1 and 2. The structures of **1** and **2** were determined by conventional X-ray crystallographic methods. Views of **1** and **2** are given in Figures 1 and 2 respectively. Final positional and isotropic thermal parameters for **1** and **2** are recorded in Table II; bond lengths and angles for the molecules are collected in Table III. Each structure suffered from minor disorder that involved the bromine ligand and the equatorial carbonyl groups bonded to the same metal atom as the Br. However, this did not unduly limit the accuracy of the structures, especially the bond lengths between the metal atoms.

As can be seen from Figure 1, in **1** the 18-electron complex $Os(CO)_4(PMe_3)$ acts as a two-electron-donor ligand to the 16-electron moiety $Re(CO)_4(Br)$ via an unbridged OsRe donor–acceptor bond. It is the first example of this type of bond between osmium and rhenium to be reported. In **2** (Figure 2) the OsRe bond is best considered as a covalent metal–metal bond in the same manner as the ReRe bond in $Re_2(CO)_{10}$. The difference between the OsRe bond lengths in the two molecules is significant crystallographically: in **1** the length is 3.006 (1) Å whereas in **2** it is 2.977 (1) Å. The only difference between molecules **1** and **2** is an interchange of bromine and carbonyl ligands in positions cis to the metal–metal bond, which should have a negligible steric influence on the length of the metal–metal bond. We, therefore, believe the difference may be reasonably attributed to the different electronic character of each bond. Caution is required with this interpretation since the difference is small and could be influenced by packing forces (**1** and **2** do adopt different space groups). Obviously further studies of this type are necessary to put this observation on a firmer footing. The lengthening of the OsRe bond in **1** compared to that in **2** is, however, consistent with the observations[1–4] that dative metal–metal bonds are weaker than comparable covalent metal–metal bonds in metal carbonyl complexes. It suggests that the weakness may be attributed, in part at least, to a ground-state effect.

The OsRe bond lengths in the present molecules may be compared with 2.959 (1) Å, the Os–Re length found in $Os_3Re(\mu\text{-}H)(CO)_{15}(NCCH_3)$,[17] and with 2.942 (3) and 2.952 (3) Å and 2.969 (3) and 2.983 (3) Å, the values found for the two pairs of chemically different OsRe bond lengths in $Os_3Re_2(\mu\text{-}H)_2(CO)_{20}$.[18] Note these last lengths are shorter than the OsRe distance in **1** but the differences in lengths for the chemically equivalent bonds in $Os_3Re_2(\mu\text{-}H)_2(CO)_{20}$ are comparable to the difference in the OsRe distances in **1** and **2**.

The OsP bond lengths in **1** and **2** are not significantly different, nor are the corresponding ReC bond lengths that are trans to the metal–metal bonds. This indicates that the trans influences of $Os(CO)_4(PMe_3)$ and $Os(CO)_3(PMe_3)(Br)$ are approximately the same, as are the trans influences of $Re(CO)_4(Br)$ and $Re(CO)_5$. The OsP distance of 2.359 (4) Å found for **1** is consistent with other OsP distances we have found for molecules in which $Os(CO)_4(PMe_3)$ (L′) acts as a ligand: 2.351 (2) Å in $L'Cr(CO)_5$,[19] 2.359 (2) Å in $L'W(CO)_5$,[2] and 2.354 (5) and 2.355 (5) Å in $L'Os_3(CO)_{11}$.[3] The ReBr distance in **1** of 2.635 (2) Å may be compared to the ReBr distances of 2.62 (1) Å found for $Re(CO)_5(Br)$[20] and 2.636 (2) Å found for $Re(CO)_3(Me_2NCH_2CH_2NMe_2)(Br)$.[21] Likewise, the OsBr distance in **2** (2.589 (2) Å) may be compared to 2.567 (3) and 2.570 (3) Å, the OsBr distances in $Os(CO)(pdma)_2(Br)_2$ (pdma = *o*-phenylenebis(dimethylarsine)).[22] The small, inward leaning of the radial carbonyls on the osmium atom in **1** (Re–Os–C angles range from 83.6 (4) to 86.9 (4)°) has been observed before in molecules of this type.[1,2,3,19] Although the effect is not quite as large, the radial carbonyls on the Re atom of **1** and the radial carbonyls in **2** also lean toward the metal–metal bond. This inward leaning was also found for $Re_2(CO)_{10}$.[23] In $[Mn_3(CO)_{14}]^-$ this bending has been attributed to a bonding interaction between the π^* orbitals of the carbonyls and the filled d orbitals on the opposite metal atom.[24]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and Simon Fraser University for financial support.

Supplementary Material Available: Tables of hydrogen atom coordinates, final temperature factors, and selected torsion angles for **1** and **2** (4 pages); structure factor listings for **1** and **2** (44 pages). Ordering information is given on any current masthead page.

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(16) (a) *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 119. (b) Pomeroy, R. K.; Hu, X. *Can. J. Chem.* **1982**, *60*, 1279. (c) Liu, D. K.; Brinkley, C. G.; Wrighton, M. S. *Organometallics* **1984**, *3*, 1449.

(17) Churchill, M. R.; Hollander, F. J.; Lashewycz, R. A.; Pearson, G. A.; Shapley, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 2430.

(18) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 3546.

(19) Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P., to be submitted for publication.

(20) Couldwell, M. C.; Simpson, J. *Cryst. Struct. Commun.* **1977**, *6*, 1.

(21) Couldwell, M. C.; Simpson, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1101.

(22) Bottomley, F.; Lin, I. J. B.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1978**, 1726.

(23) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

(24) Bau, R.; Kirtley, S. W.; Sorrell, T. N.; Winarko, S. *J. Am. Chem. Soc.* **1974**, *96*, 988.

Additions and Corrections

1986, Volume 25

Douglas S. Dudis, John D. Corbett,* and Shiou-Jyh Hwu: Synthesis, Characterization, and Crystal Structures of Two Scandium Cluster Carbides and a Boride, $Sc_7X_{12}C$ (X = I, Br) and $Sc_7I_{12}B$.

Page 3437. In Figure 2, I(4) should be labeled I(2), and vice versa.—Douglas S. Dudis