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The reaction of triphenylphosphine selenide with triosmium clusters: a facile cluster coupling through a selenium atom

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The room temperature reactions of Ph_3PSe with the triosmium clusters $Os_3(CO)_{11}(CH_3CN)$, $Os_3(CO)_{10}(CH_3CN)_2$ and $Os_3(\mu\text{-}H)_2(CO)_{10}$ have been investigated. The reaction with an equimolar amount of $Os_3(CO)_{11}(CH_3CN)$ afforded the known clusters $Os_3(\mu_3\text{-}Se)_2(CO)_9$, **1**, and $Os_3(CO)_{11}(PPh_3)$, **2**, and the new cluster $Os_3(\mu_3\text{-}Se)(CO)_9(PPh_3)$, **3**. The analogous reaction with $Os_3(CO)_{10}(CH_3CN)_2$ gave **1** and **2**; reaction with 0.5 equivalent of the cluster gave **1** quantitatively. The reaction with $Os_3(\mu\text{-}H)_2(CO)_{10}$ gave two new clusters, *viz.* $Os_3(\mu_3\text{-}Se)(\mu\text{-}H)_2(CO)_8(PPh_3)$, **4a**, and $Os_6(\mu_3\text{-}Se)(H)(\mu\text{-}H)_3(CO)_{18}(PPh_3)_2$, **5a**. Single crystal structures of **3**, **4a** and **5a** have been obtained. Cluster **3** possesses bridging carbonyls; these appear to have been lost on elongation of the osmium–osmium bonds by bridging hydrides in **4a**. The structure of **5a** is novel and comprises a naked μ_3-Se atom bridging two triosmium moieties; an $Os_3(\mu\text{-}H)(CO)_{10}$ unit and an $Os_3(H)(\mu\text{-}H)_2(CO)_8(PPh_3)_2$ unit.

Introduction

For some time now we have been interested in the synthesis and reactivity of main group–transition metal cluster compounds. These compounds are expected to show structural and reactivity patterns that may be quite unlike those of the homometallic main group or transition metal clusters. From a synthetic point of view it is highly desirable to have mild and specific methods of synthesis for such clusters. We have recently reported our investigations into the synthesis and reactivity of some osmium–tellurium clusters using Ph_2Te_2 as the tellurium precursor.[1] We naturally carried out similar investigations into osmium–selenium clusters. Specifically, we wanted to explore approaches to the synthesis of such clusters as well as the structural diversity that they can afford. For the synthesis of such clusters selenium precursors that have been employed include elemental selenium,[2] selenol,[3] diorgano diselenides,[4] selenophene,[5] organoselenium halides,[6] tetraselenostannolanes,[7] and even $Fe_2(\mu\text{-}Se)_2(CO)_6$.[8] One class of reagent that caught our attention was the organophosphine selenides; this has been demonstrated to be a convenient synthon for the introduction of selenido and phosphine moieties into iron and ruthenium clusters.[9,10] We were thus interested in exploring the possibilities that this synthon may offer towards osmium–selenium cluster chemistry.

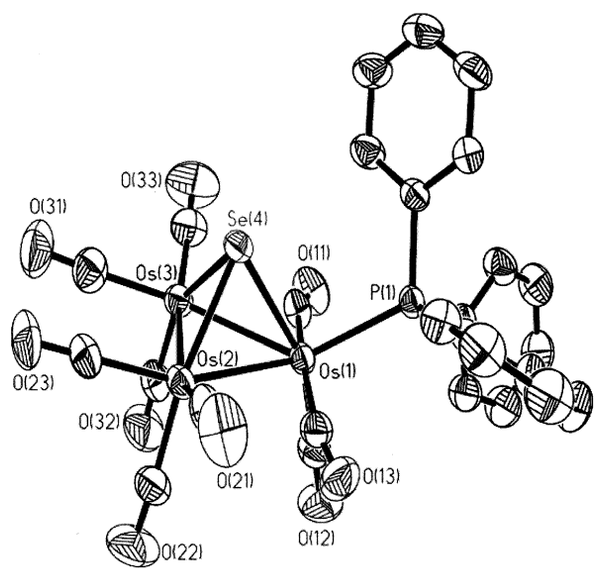
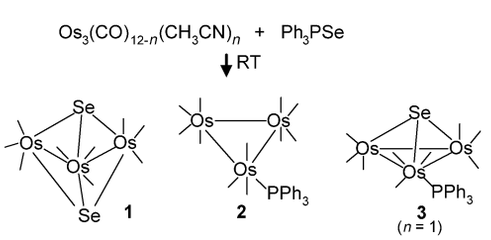


Fig. 1 ORTEP[11] diagram of compound **3** (50% thermal ellipsoids, as in all the structures shown).

Results and discussion

The reaction of the substitutionally labile triosmium clusters $Os_3(CO)_{12-n}(CH_3CN)_n$ (n = 1 or 2) with Ph_3PSe is summarised in Scheme 1. The reaction of an equimolar amount of Ph_3PSe with $Os_3(CO)_{11}(CH_3CN)$ proceeded rapidly under ambient conditions to afford three clusters in fairly similar, moderate, yields. Two of these were the known clusters $Os_3(\mu_3\text{-}Se)_2(CO)_9$, **1**, and $Os_3(CO)_{11}(PPh_3)$, **2**, which were identified primarily *via* their IR spectroscopic characteristics. The third was a novel cluster, $Os_3(\mu_3\text{-}Se)(CO)_9(PPh_3)$, **3** (Fig. 1).

The reaction with $Os_3(CO)_{10}(CH_3CN)_2$ under similar conditions gave mainly compound **1** and a little **2** but no **3**; the formation of **2** in this reaction was probably the result of the inevitable presence of small amounts of $Os_3(CO)_{11}(CH_3CN)$. When the amount of $Os_3(CO)_{10}(CH_3CN)_2$ was reduced to half a molar equivalent a higher yield of **1** was obtained; the IR spectrum of the reaction mixture indicated that the formation of **1** was essentially quantitative.



Scheme 1 Reaction scheme for $Os_3(CO)_{12-n}(CH_3CN)_2$ + Ph_3PSe.

These observations suggest that the reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with an excess of Ph_3PSe offers a mild and high-yielding route to compound **1**; this is to be contrasted with the need for refluxing octane starting from elemental selenium,[2] or high pressure and temperature (160 °C, 3000 psi of CO) by

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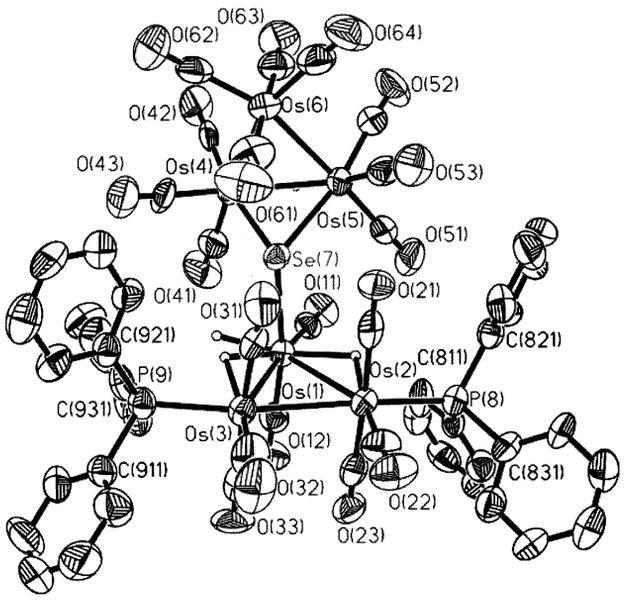

Fig. 2 ORTEP diagram of compound **5a**. Os(1)–Os(2) 3.1111(10); Os(2)–Os(3) 2.9663(9); Os(3)–Os(1) 3.1084(10); Os(4)–Os(5) 2.8552(9); Os(5)–Os(6) 2.8557(11); Os(6)–Os(4) 2.8616(11); Os(1)–Se(7) 2.6026(17); Os(4)–Se(7) 2.5591(16); Os(5)–Se(7) 2.5735(17); Os(2)–P(8) 2.366(4) and Os(3)–P(9) 2.378(4) Å.

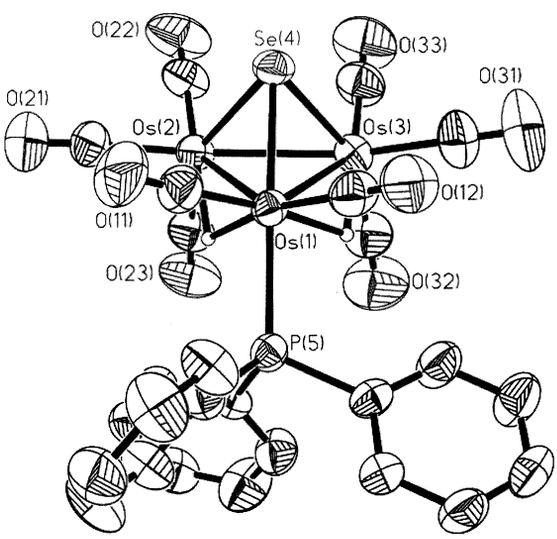

Fig. 3 ORTEP diagram of compound **4a**.

thermolysis of $Os_3(\mu\text{-SePh})(\mu\text{-H})(CO)_{10}$.[3] It has been suggested that in the iron and ruthenium systems the reaction involved initially oxidative transfer of the selenido ligand, together with the triphenylphosphine;[10] this was reasonable as the products formed all contained selenido and triphenylphosphine ligands. The isolation of **3** from the reaction with $Os_3(CO)_{11}(CH_3CN)$ initially suggested to us that a similar mechanism may be operating here, *i.e.* oxidative addition of Se and Ph_3P to an "$Os_3(CO)_{11}$" fragment to give **3** followed by attack of another mole of Ph_3PSe leading to displacement of the first phosphine ligand by the second selenium atom. However, we have found that **3** failed to react with Ph_3PSe even at 45 °C after 5 h. This clearly indicates that the formation of **1** and **3** followed different pathways. We have also verified by ^{31}P NMR spectroscopy that PPh_3 was indeed released in the reaction involving $Os_3(CO)_{10}(CH_3CN)_2$. Thus in our case the Ph_3PSe seems to function primarily as a selenium transfer reagent; incorporation of the triphenylphosphine is only incidental. The reaction of Ph_3PSe with $Os_3(\mu\text{-H})_2(CO)_{10}$ led to a rapid change in colour and precipitation of a yellow powder which has been identified as the novel cluster $Os_6(\mu_3\text{-Se})(H)(\mu\text{-H})_3(CO)_{18}(PPh_3)_2$, **5a** (Fig. 2).

Table 1 Selected bond lengths (Å) and angles (°) for compounds **3** and **4a**

	3	**4a**
Os(1)–Os(2)	2.8528(3)	2.9440(4)
Os(1)–Os(3)	2.8308(3)	2.9961(4)
Os(2)–Os(3)	2.7703(3)	2.8054(4)
Os(1)–Se(4)	2.5548(6)	2.5190(8)
Os(2)–Se(4)	2.5161(6)	2.5061(7)
Os(3)–Se(4)	2.5315(7)	2.5065(8)
Os(1)–P(1)	2.3875(15)	2.3682(8)
Os(2)–Os(1)–P(1)	137.95(4)	113.92(5)
Os(3)–Os(1)–P(1)	133.78(4)	114.56(4)
d(Os–C) + *d*(C–O)	3.01 to 3.12	3.04 to 3.07

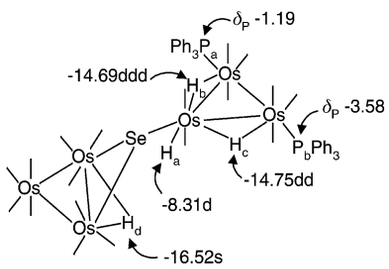

Fig. 4 ^1H NMR assignments for compound **5a** (metal hydrides).

From the supernatant was obtained, after chromatographic separation, another novel cluster, $Os_3(\mu_3\text{-Se})(\mu\text{-H})_2(CO)_8(PPh_3)$, **4a** (Fig. 3). A similar reaction starting from $(p\text{-MeC}_6H_4)_3PSe$ gave the corresponding $(p\text{-MeC}_6H_4)_3P$-substituted analogues **4b** and **5b**. Cluster **5a** is interesting not least in that it comprises a naked μ_3-Se atom bridging two triosmium moieties. It is the first example of such a structural type in osmium–selenium chemistry; related examples containing a heavier main group element bridging two osmium clusters can be found for tin,[12] arsenic[13] and antimony.[14] The Os–Se bond lengths are all fairly long, ranging from 2.5591(16) to 2.6026(17) Å, as compared to 2.5061(7) to 2.5548(6) Å for those in **3** and **4a**. All the Os–Os bonds in the triosmium unit bearing the two phosphines are significantly longer that those in the other triosmium unit. From the electron count, **5a** is expected to have four metal hydrides, and one might expect that all the Os–Os edges in the Os(1)Os(2)Os(3) unit are bridged by hydrides. However, potential energy calculations with XHYDEX suggested that three of the hydrides were on this triosmium unit and they shared a common osmium atom, with one of them terminally bonded;[15] the fourth hydride was calculated to be bridging the Os(4)–Os(5) edge. As to be expected, the ^1H NMR spectrum of **5a** in the metal hydride region was quite complicated due to the large number of NMR-active nuclei and second-order effects. We were, however, able to assign the signals as shown (Fig. 4) from a series of NOE and selective decoupling experiments, together with NMR simulations;[16] the assignments were thus consistent with the positions of the hydrides suggested by XHYDEX. The assignments for **5b** were made by comparison with those for **5a**.

The general structural features of compounds **3** and **4a** are very similar (Table 1); the two bridging hydrides in **4a** are replaced by an additional carbonyl on Os(1) in **3**. Besides the well-established elongation of the hydride-bridged Os–Os bonds in **4a** (2.9440(4) and 2.9661(4) Å for Os(1)–Os(2) and Os(1)–Os(3), respectively, compared to 2.7703(3) to 2.8528(3) Å for all the other Os–Os bonds), the presence of the additional CO seems to have resulted in the phosphine occupying a position more nearly equatorial with respect to the triosmium plane in **3** than in **4a**. The most interesting feature, however, is the presence of two semibridging carbonyls in **3**; CO(11) and CO(13) in cluster **3** are both disposed towards the neighbouring

Table 2 Crystal data for $Os_3(\mu_3\text{-Se})(CO)_9(PPh_3)$ **3**, $Os_3(\mu_3\text{-Se})(\mu\text{-H})_2(CO)_8(PPh_3)$ **4a** and $Os_6(\mu_3\text{-Se})(H)(\mu\text{-H})_3(CO)_{18}(PPh_3)_2$ **5a**

	3	**4a**	**5a**
Empirical formula	$C_{27}H_{15}O_9Os_3PSe$	$C_{26}H_{17}O_8Os_3PSe$	$C_{54}H_{34}O_{18}Os_6P_2Se$
Formula weight	1163.92	1137.93	2252.91
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a/Å	14.9599(3)	13.6945(7)	14.049(2)
b/Å	9.7844(1)	14.1174(7)	14.093(2)
c/Å	20.7467(4)	15.9671(7)	19.876(3)
α/°			69.815(13)
β/°	99.703(1)	98.124(1)	80.778(11)
γ/°			72.182(13)
V/Å^3	2993.33(9)	3056.0(3)	3509.9(9)
Z	4	4	2
μ/mm^{-1}	14.022	13.729	11.444
Reflections collected	19312	36482	25625
Independent reflections	7395 (R_{int} = 0.0361)	7433 (R_{int} = 0.0315)	16474 (R_{int} = 0.0610)
Final R [$I > 2\sigma(I)$]	0.0322	0.0360	0.0626
$wR2$ (all data)	0.0843	0.0987	0.1850

osmium atoms (the Os(2)···C(13) and Os(3)···C(11) distances are 2.697 and 2.627 Å, respectively, compared to 3.857 and 3.824 Å for the corresponding distances from C(12)), and their Os–C–O angles also deviate significantly from linearity (Os(1)–C(11)–O(11) 160.4(6) and Os(1)–C(13)–O(13) 163.6(5)°, *cf*. 176.6(7) to 179.4(9)° for all the other carbonyls in **3**). A bridging carbonyl should behave more like a ketone and hence have a lower C–O bond order. As expected, therefore, the sum of the Os–C and C–O bond lengths for CO(11) and CO(13) in **3** are longer (3.12 and 3.11 Å, respectively) than the others, which average 3.06 Å; the values for CO(23) and CO(31), at 3.02 and 3.01 Å, respectively, are in that respect short although we have no ready explanation for this.† The absence of semibridging carbonyls in **4a** may be attributed to the elongation of the Os–Os bonds by the bridging hydrides.

Experimental

General procedures

All reactions and manipulations were carried out under nitrogen by using standard Schlenk techniques. Solvents were purified, dried, distilled, and stored under nitrogen prior to use. NMR spectra were recorded on a Bruker ACF-300 FT-NMR spectrometer; chemical shift and coupling information from complex spectra were obtained with the aid of the software gNMR.[16] Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in an *m*-nitrobenzyl alcohol matrix. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The clusters $Os_3(CO)_{11}(CH_3CN)$,[17] $Os_3(CO)_{10}(CH_3CN)_2$[18] and $Os_3(\mu\text{-H})_2(CO)_{10}$,[19] and the triarylphosphine selenides,[20] were prepared by published methods; all other reagents were from commercial sources and used as supplied.

Reactions of Ph_3PSe

With $Os_3(CO)_{11}(CH_3CN)$. $Os_3(CO)_{11}(CH_3CN)$ (50.9 mg, 0.0544 mmol) and Ph_3PSe (18.5 mg, 0.0542 mmol) were stirred in dichloromethane (8 ml) at room temperature for 30 min. Removal of the solvent followed by TLC separation using hexane as eluent gave clusters **1** (18.9 mg, 35.6%), **2** (10.1 mg, 16.3%) and **3** (16.8 mg, 26.6%) as yellow bands. **1** (Found: C, 11.53. Calc. for $C_9O_9Os_3Se_2$: C, 11.01%). ν_{max}/cm^{-1} (hexane) 2076s, 2056s and 2015s, br (CO) (lit.[2,3] (hexane) 2075s, 2055s, 2015s and 2009sh cm^{-1}). **2**: ν_{max}/cm^{-1} (hexane) 2108m, 2056s, 2037s, 2020s, 2004m, 1992m and 1980m (CO) (lit.[21] (cyclohexane) 2109m, 2057s, 2038s, 2022s, 2004m, 1992w and 1980w cm^{-1}). **3**: (Found: C, 27.78; H, 1.29. Calc. for $C_{27}H_{15}O_9Os_3PSe$: C, 27.86; H, 1.29%): ν_{max}/cm^{-1} (CH_2Cl_2) 2079m, 2069vw, 2039s, 2019m, 1990m and 1975sh (CO); ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 6.59(s).

With $Os_3(CO)_{10}(CH_3CN)_2$. $Os_3(CO)_{10}(CH_3CN)_2$ (50.1 mg, 0.0533 mmol) and Ph_3PSe (18.2 mg, 0.0533 mmol) were stirred in dichloromethane (8 ml) at room temperature for 3 h. Removal of the solvent followed by TLC separation using hexane as eluent gave clusters **1** (29.5 mg, 56.4%) and **2** (6.7 mg, 11.0%), which were identified by their IR spectra. An analogous reaction with 0.5 equivalent of $Os_3(CO)_{10}(CH_3CN)_2$ gave a 78.7% yield of **1**.

With $Os_3(\mu\text{-H})_2(CO)_{10}$. $Os_3(\mu\text{-H})_2(CO)_{10}$ (50 mg, 0.059 mmol) and Ph_3PSe (20 mg, 0.059 mmol) were stirred in hexane (8 ml) at room temperature. A yellow solid precipitated after about 30 min. The reaction was allowed to continue until the IR spectrum showed no further change (≈4 h). The precipitate was decanted and recrystallised from CH_2Cl_2–hexane to afford a yellow crystalline sample of compound **5a** (33 mg, 67%). TLC separation of the supernatant gave **4a** (1.9 mg, 2.8%): ν_{max}/cm^{-1} (CH_2Cl_2) 2080m, 2045s, 1994ms, 1987sh and 1962sh (CO); ^{1}H NMR (d_8-toluene) δ −21.52 (s, OsHOs) and −20.38 (d, $^2J_{HP}$ = 45.0 Hz, OsHOs); ^{31}P-{^{1}H} NMR (d_8-toluene) δ 0.50 (s); MS *m*/*z*: 1137.0 (M^+), calculated for $C_{26}H_{17}O_8Os_3PSe$ 1137.9. **5a** (Found: C, 28.76; H, 1.94. Calc. for $C_{54}H_{34}O_{18}Os_6P_2Se$: C, 28.79; H, 1.52%): ν_{max}/cm^{-1} (CH_2Cl_2) 2094w, 2061w, 2049ms, 2046sh, 2025m, 2006s, 1980w, sh, 1960w and 1927w (CO); ^{1}H NMR (d_8-toluene) δ −8.31 (d, H_a, $^2J_{HaHb}$ = 11.0), −14.69 (ddd, H_b, $^2J_{HbPa}$ = 11.0, $^2J_{HbHc}$ = 2.3), −14.75 (dd, H_c, $^2J_{HcPb}$ = 13.4 Hz) and −16.52 (s H_d); ^{31}P-{^{1}H} NMR (d_8-toluene) δ −1.19 (s, P_a) and −3.58 (s, P_b).

An analogous reaction using (p-MeC_6H_4)$_3$PSe gave the (p-MeC_6H_4)$_3$P substituted analogues **4b** (4.5%) and **5b** (60.7%). **4b**: ν_{max}/cm^{-1} (hexane) 2080m, 2045s, 1999w and 1966m (CO); ^{1}H NMR (d_8-toluene) δ −21.51 (s, OsHOs) and −20.22 (d, $^2J_{HP}$ = 9.0 Hz, OsHOs); ^{31}P-{^{1}H} NMR (d_8-toluene) δ −2.07 (s); MS *m*/*z*: 1180.0 (M^+), calculated for $C_{29}H_{23}O_8Os_3PSe$ 1181.0. **5b** (Found: C, 34.83; H, 2.79. Calc. for $C_{60}H_{46}O_{18}Os_6P_2Se$: C, 34.45; H, 2.95%): ν_{max}/cm^{-1} (CH_2Cl_2) 2093w, 2048ms, 2023m, 2005s, 1965w and 1927w (CO); ^{1}H NMR (d_8-toluene) δ −8.20 (d, H_a, $^2J_{HaHb}$ = 10.3), −14.63 (ddd, H_b, $^2J_{HbPa}$ = 11.1, $^2J_{HbHc}$ = −1.8), −14.68 (dd, H_c, $^2J_{HcPb}$ = 13.0 Hz) and −16.50 (s, H_d); ^{31}P-{^{1}H} NMR (d_8-toluene) δ −2.07 (s, P_a) and −3.30 (s, P_b).

† We have argued in earlier work for the use of the sum of Os–C and C–O bond lengths rather than either of the individual parameters for the purpose of assessing stereoelectronic effects on carbonyls in heavy atom structures. See, for example, reference 12.

Crystal structure determinations

Crystals were grown from dichloromethane–hexane solutions and mounted on quartz fibres. X-Ray data were collected on a Siemens SMART CCD system, using Mo-Kα radiation, at ambient temperatures (293(2) K). Data were corrected for Lorentz and polarisation effects with the SMART suite of programs,[22] and for absorption effects with SADABS.[23] The final unit cell parameters were obtained by least squares on 6133, 6500 and 157 strong reflections for compounds **3**, **4a** and **5a**, respectively. Structural solution and refinement were carried out with the SHELXTL suite of programs.[24] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. For **5a** the phenyl rings of one of the phosphines were constrained to be regular hexagons and pivoted about the *ipso* carbons. All phenyl H atoms were placed in calculated positions and given isotropic thermal parameters 1.5 times those of the C atoms to which they were attached. Metal hydrides were placed in calculated positions with the program XHYDEX,[15] given fixed isotropic thermal parameters of 0.05 Å^2, and allowed to ride on the osmium atoms that they were bonded to. All non-hydrogen atoms were given anisotropic thermal parameters in the final model.

CCDC reference numbers 155039–155041.

See http://www.rsc.org/suppdata/dt/b0/b010043i/ for crystallographic data in CIF or other electronic format.

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References

1 J. Zhang and W. K. Leong, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 1249.
2 B. F. G. Johnson, J. Lewis, P. G. Lodge, P. R. Raithby, K. Hendrick and M. McPartlin, *J. Chem. Soc.*, *Chem. Commun.*, 1979, 719.
3 R. D. Adams and I. T. Horvath, *Inorg. Chem.*, 1984, **23**, 4718.
4 P. V. Broadhurst, B. F. G. Johnson and J. Lewis, *J. Chem. Soc.*, *Dalton Trans.*, 1982, 1881; A. J. Arce, P. Arrojo, A. J. Deeming and Y. De Sanctis, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 1491; A. J. Arce, P. Arrojo, A. J. Deeming and D. J. West, *Polyhedron*, 1992, **11**, 1013.
5 A. J. Arce, A. J. Deeming, Y. De Sanctis, R. Machado, J. Mansur and C. Rivas, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 1568; A. J. Arce, R. Machado, C. Rivas, Y. De Sanctis and A. J. Deeming, *J. Organomet. Chem.*, 1991, **419**, 63; A. J. Arce, Y. De Sanctis, L. Hernandez, M. Marquez and A. J. Deeming, *J. Organomet. Chem.*, 1992, **436**, 351.
6 T. M. Layer, J. Lewis, A. Martín, P. R. Raithby and W.-T. Wong, *J. Organomet. Chem.*, 1993, **444**, C57.
7 N. Tokitoh, Y. Matsuhashi and R. Okazaki, *Organometallics*, 1993, **12**, 2894; Y. Matsuhashi, N. Tokitoh and R. Okazaki, *Organometallics*, 1994, **13**, 4387.
8 P. Mathur, I. P. Mavunkal and V. Rugmini, *Inorg. Chem.*, 1989, **28**, 3616.
9 F. Van Gastel, L. Agnes, A. A. Cherkas, J. F. Corrigan, S. Doherty, R. Ramachandran, N. J. Taylor and A. J. Carty, *J. Cluster Sci.*, 1991, **2**, 131.
10 P. Baistrocchi, D. Cauzzi, M. Lanfranchi, G. Predieri, A. Tiripicchio and M. T. Camellini, *Inorg. Chim. Acta*, 1995, **235**, 173; P. Baistrocchi, M. Careri, D. Cauzzi, C. Graiff, M. Lanfranchi, P. Manini, G. Predieri and A. Tiripicchio, *Inorg. Chim. Acta*, 1996, **252**, 367; D. Cauzzi, C. Graiff, G. Predieri, A. Tiripicchio and C. Vignali, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 237.
11 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
12 W. K. Leong, F. W. B. Einstein and R. K. Pomeroy, *J. Cluster Sci.*, 1996, **7**, 211.
13 K. Guldner, B. F. G. Johnson, J. Lewis, A. D. Massey and S. Bott, *J. Organomet. Chem.*, 1991, **408**, C13.
14 W. K. Leong and G. Chen, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 4442.
15 A. G. Orpen, XHYDEX: A Program for Locating Hydrides in Metal Complexes, School of Chemistry, University of Bristol, 1997.
16 P. H. M. Budzelaar, gNMR, Adept Scientific plc, Letchworth, UK, 1999.
17 J. N. Nicholls and M. D. Vargas, *Inorg. Synth.*, 1989, **28**, 232.
18 J. N. Nicholls and M. D. Vargas, *Inorg. Synth.*, 1989, **28**, 234.
19 H. D. Kaesz, *Inorg. Synth.*, 1989, **28**, 238.
20 H. J. Reich, J. M. Renga and I. L. Reich, *J. Am. Chem. Soc.*, 1975, **97**, 5434.
21 M. Castiglioni, R. Giordano and E. Sappa, *J. Organomet. Chem.*, 1988, **342**, 97; B. F. G. Johnson, J. Lewis and D. A. Pippard, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 407.
22 SMART, version 4.05, Siemens Energy & Automation Inc., Madison, WI, 1996.
23 G. M. Sheldrick, SADABS, University of Göttingen, 1996.
24 SHELXTL, version 5.03, Siemens Energy & Automation Inc., Madison, WI, 1995.