The Photochemistry of $M_3(CO)_{12}$ (M = Ru, Os) with Pyrazole and Its Substituted Derivatives

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The photochemistry of $M_3(CO)_{12}$ [M = Ru (**1a**), Os (**1b**)] with pyrazole, 3,5-dimethylpyrazole, and 3,5-diphenylpyrazole is documented. With **1a**, photolysis with pyrazole leads to the substitution product $HRu_3(CO)_{10}(C_3H_3N_2)$ (**2a**). In the case of **1b**, the initial product is the *ortho*-metallated species $HOs_3(CO)_{10}(C_3H_3N_2)$ (**3b**), heating of which yields $HOs_3(CO)_{10}(C_3H_3N_2)$ (**2b**). Photolysis of **1a** and **1b** with 3,5-dimethylpyrazole yields $HRu_3(CO)_{10}(C_3HMe_2N_2)$ (**4a**) and $HOs_3(CO)_{10}(C_3HMe_2N_2)$ (**4b**), respectively. The molecular structure of **4b** has been determined by X-ray crystallography. There is no reaction on photolysis of **1a** and **1b** with 3,5-diphenylpyrazole.

The reaction chemistry of cluster carbonyl complexes with nitrogen-heterocyclic ligands has received little attention as compared to that of other ligands such as phosphanes[1].This may be attributed in part to the harsh conditions frequently required to prepare N-heterocycle complexes, reactions often resulting in cluster degradation or the formation of complex products[2]. Our research has led us to investigate the photochemistry of ruthenium and osmium complexes with a number of ligand systems[3][4]. Photochemistry offers a simple, and often highly selective, route to organometallic compounds, overcoming large enthalpy barriers. As a consequence, it is often possible to prepare complexes that are otherwise inaccessible by conventional thermochemical routes[3][4][5].

The trinuclear cluster $Ru_3(CO)_{12}$ (**1a**) serves as a prototype for the photoreactivity of more complex examples. Our studies have shown that, by broad-band UV irradiation of a dichloromethane solution of **1a** in the presence of a two-electron donor ligand, high yields of photofragmentation products can be obtained[6]. This opens a route to substituted mononuclear ruthenium and osmium complexes. Although there has been much work on the synthetic potential of the reactive intermediates generated by photofragmentation of **1a**, the corresponding photosubstitution pathway is still relatively unexplored[7]. Our research has shown that, simply by changing the solvent from dichloromethane to ethyl acetate, ether, or acetonitrile, it is possible to prepare photosubstitution products from **1a** this enabling the synthesis of substituted cluster products[8].

A range of trinuclear complexes can be formed on photolysis of **1a** and its osmium analogue $Os_3(CO)_{12}$ (**1b**) with pyridine and bipyridine[9]. The work documented here focuses on the photochemistry of **1a** and **1b** with pyrazole and its substituted derivatives. The aim of the investigation was to prepare photochemically a number of trinuclear carbonyl complexes containing nitrogen heterocycles as ligands since these compounds may well have the ability to act as efficient catalysts for key industrial synthetic transformations[10].

Results and Discussion

The results from the investigations are summarised in Scheme 1 and all spectroscopic data are shown in Table 1.

Photoreactions with Pyrazole

Broad-band UV photolysis of an ethyl acetate solution of **1a** in the presence of an excess of pyrazole leads, within 30 min, to the formation of the substitution product $HRu_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3H_3N_2)$ (**2a**). The ^{1}H-NMR spectrum of **2a** shows a symmetrical arrangement of the pyrazolide group and, in the IR spectrum, the complex does not show any bands assignable to μ-CO groups.

The formation of **2a** from **1a** is a relatively inefficient process, the photoreactions taking some considerable time. To explain this, the mechanism for photosubstitution needs to be considered. By using matrix-isolation and flash-photolysis techniques key intermediates involved in the photosubstitution pathway of **1a** have been generated[11]. The primary photoreaction is the dissociation of CO to form the coordinatively unsaturated fragment $[Ru_3(CO)_{11}]$. This fragment is highly selective in its chemistry, reaction with photoejected CO is eight times faster than with added PPh_3[11]. Therefore, in the case of an added ligand, L, photosubstitution of CO by L is in competition with recombination of the unsaturated triruthenium fragment with photoejected CO.

Due to the increased stability of trinuclear osmium complexes over their ruthenium analogues, different products are often formed. Broad-band UV photolysis of an ethyl acetate solution of **1b** in the presence of an excess of pyrazole leads, within 45 min, to the relatively insoluble *ortho*-

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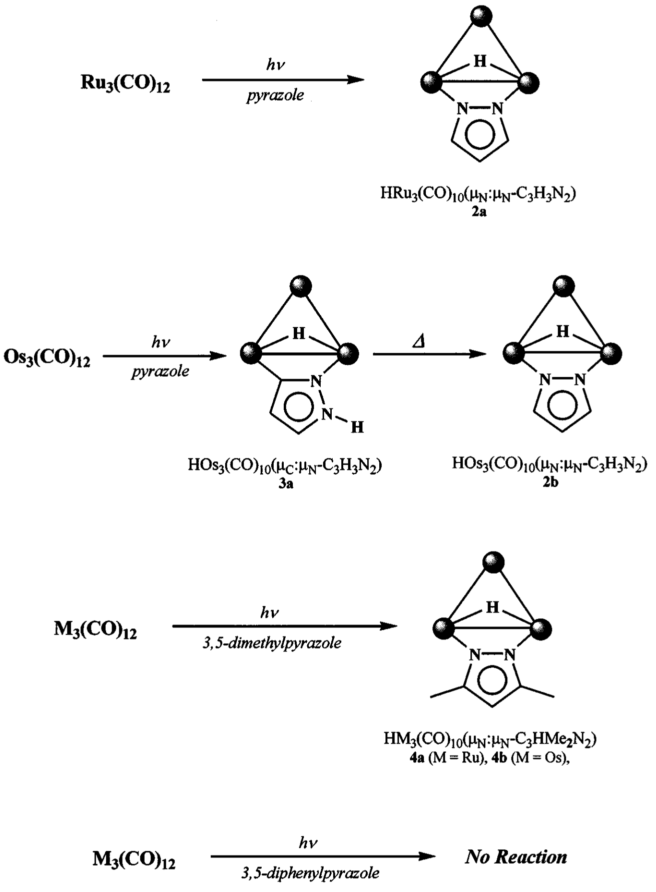
Table 1. Spectroscopic data for the complexes prepared in this study

Compound[a]	IR Spectrum[b]	^{1}H-NMR Spectrum[c]	Mass Spectrum[d]
$Ru_3(CO)_{12}$ (**1a**)	2059(vs), 2027(s), 2007(m)	–	–
$Os_3(CO)_{12}$ (**1b**)	2068(s), 2035(s), 2014(m), 2002(m)	–	–
$HRu_3(CO)_{10}(C_3H_3N_2)$ (**2a**)	2107(m), 2072(s), 2066(vs), 2030(s), 2016(vs), 1999(m), 1984(w)	7.5 (d, 2 H), 6.2 (t, 1 H), −13.45 (s)	653 (653 calcd.)
$HOs_3(CO)_{10}(C_3H_3N_2)$ (**2b**)	2109(m), 2070(s), 2061(vs), 2024(s), 2003(vs), 1994(s), 1979(w)	7.15 (d, 2 H), 5.89 (t, 1 H), −13.49 (s)	923 (924 calcd.)
$HOs_3(CO)_{10}(C_3H_3N_2)$ (**3b**)	2103(m), 2060(s), 2052(vs), 2024(s), 2013(vs), 1999(s), 1979(w), 1956(w)	8.9 (br., 1 H), 7.15 (d, 1 H), 6.22 (d, 1 H), −15.12 (s, 1 H)	924 (924 calcd.)
$HRu_3(CO)_{10}(C_3HMe_2N_2)$ (**4a**)	2108(w), 2074(s), 2064(vs), 2032(m), 2019(s), 1997(m), 1985(w), 1967(w)	5.72 (s, 1 H), 2.04 (s, 6 H), −13.24 (s, 1 H)	680 (681 calcd.)
$HOs_3(CO)_{10}(C_3HMe_2N_2)$ (**4b**)	2107(w), 2067(vs), 2060(vs), 2034(m), 2019(s), 1998(m), 1976(w)	5.29 (s, 1 H), 1.89 (s, 6 H), −13.22 (s, 1 H)	952 (952 calcd.)

[a] Compound numbers refer to text. – [b] In CH_2Cl_2unless stated otherwise. – [c] In $CDCl_3$ unless stated otherwise. – [d] Based on ^{192}Os, ^{101}Ru.

Scheme 1. A summary of the results reported



metallated complex $HOs_3(CO)_{10}(\mu_C{:}\mu_N-C_3H_3N_2)$ (**3b**). Retention of the N–H bond is evident from the spectral data and, because of this and the solubility problem, separation by chromatography is difficult since the acidic amine group interacts with the silica gel surface. Heating **3b** in boiling xylene in the absence of light yields the osmium analogue of **2a**, $HOs_3(CO)_{10}(\mu_N{:}\mu_N-C_3H_3N_2)$ (**2b**). The *ortho*-metallated complex **3b**, has been reported previously, as a minor product in the reaction of the lightly ligated complex $Os_3(CO)_{10}(MeCN)_2$ with pyrazole under reflux in benzene, the major product being **2b**[12]. This shows clearly one of the benefits of photochemistry over conventional thermolytic routes; the reaction conditions being mild and less stable complexes often being formed. This has also been shown in the reaction of **1a** and **1b** with pyridine, photolysis leading initially to the relatively unstable complex $Os_3(CO)_{11}(C_5H_5N)$ before orthometallating to form the more stable $HOs_3(CO)_{10}(C_5H_4N)$, the latter being the only thermolytic product[9].

Of note is that there is no evidence for the formation of the *ortho*-metallated analogue of **3b**, $HRu_3(CO)_{10}(\mu_C{:}\mu_N-C_3H_3N_2)$ (**3a**) in the photochemical reaction of **1a** with pyrazole or in the case of reaction of $Ru_3(CO)_{10}(MeCN)$ with the heterocycle, both routes leading to **2a**.

Photolysis of **2b** and **3b** over a longer time period 1–2 h results in the formation of a black precipitate, this being uncharacterised at present. It is, however, proposed that the black products are charged in nature, due to their insolubility in common organic solvents. This is not wholly unexpected since the photochemistry of $Ru(CO)_5$ with polydentate heterocycles has been show to result in Ru^{III} complexes as a result of a proposed photooxidation process[13]. This occurs regardless of the temperature at which the photolysis is undertaken.

Photoreactions with 3,5-Dimethylpyrazole

With 3,5-dimethylpyrazole, there is no scope for the formation of orthometallated products. Photolysis leads to the $\mu_N{:}\mu_N$ substitution products $HRu_3(CO)_{10}(\mu_N{:}\mu_N-C_3HMe_2N_2)$ (**4a**) and $HOs_3(CO)_{10}(\mu_N{:}\mu_N-C_3HMe_2N_2)$ (**4b**) in the cases of **1a** and **1b**, respectively. Again, prolonged photolysis of the reaction products leads to decomposition and photooxidation.

Photoreactions with 3,5-Diphenylpyrazole

When ethyl acetate solutions of **1a** and **1b** containing 3,5-diphenylpyrazole are irradiated, no net photoreaction is observed. This is attributed to the considerable steric shielding of the nitrogen atom of the pyrazole ring in 3,5-diphenylpyrazole and the concomitant steric hindrance to formation of complexes with the clusters.

The Molecular Structure of $HOs_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3HMe_2N_2)$ (4b)

The molecular structure of $HOs_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3HMe_2N_2)$ (**4b**) has been determined by single-crystal X-ray diffraction studies and is shown in Figure 1. Selected bond lengths and angles are reported in Table 2.

Figure 1. The molecular structure of $HOs_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3HMe_2N_2)$ (**4b**)

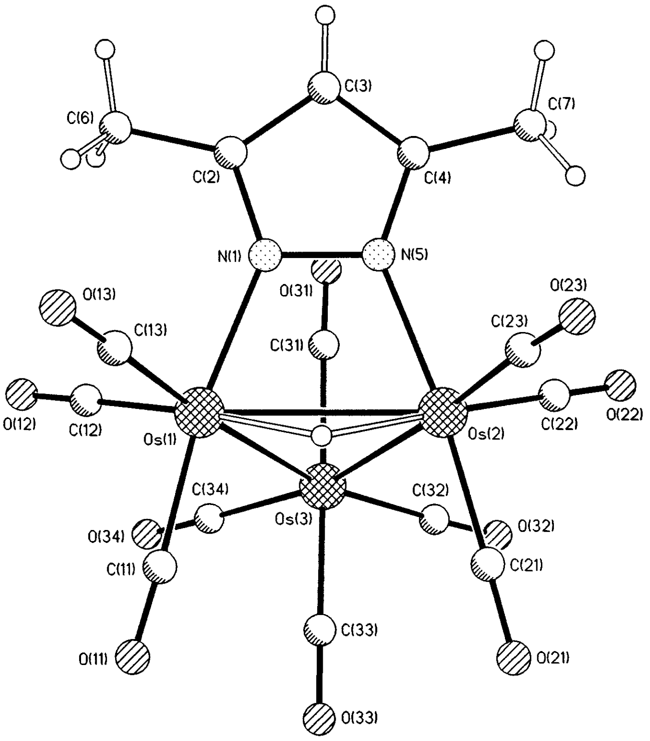


Table 2. Selected bond lengths [Å] and angles [°] for **4b**

Os(1)–Os(3)	2.8704(9)	N(1)–C(2)	1.35(2)
Os(1)–Os(2)	2.9243(13)	N(1)–N(5)	1.38(2)
Os(2)–Os(3)	2.8652(10)	C(2)–C(3)	1.41(2)
Os(1)–N(1)	2.116(11)	C(3)–C(4)	1.38(2)
Os(2)–N(5)	2.114(10)	C(4)–N(5)	1.34(2)
Os(3)–Os(1)–Os(2)	59.26(2)	C(22)–Os(2)–Os(3)	85.1(5)
Os(3)–Os(2)–Os(1)	59.43(3)	C(23)–Os(2)–Os(3)	175.3(4)
Os(2)–Os(3)–Os(1)	61.31(3)	C(22)–Os(2)–Os(1)	139.4(5)
N(1)–Os(1)–Os(3)	87.3(3)	C(23)–Os(2)–Os(1)	116.1(4)
N(1)–Os(1)–Os(2)	68.6(3)	C(32)–Os(3)–Os(2)	98.6(5)
N(5)–Os(2)–Os(3)	88.0(3)	C(34)–Os(3)–Os(1)	97.9(5)
N(5)–Os(2)–Os(1)	68.6(3)	N(5)–N(1)–Os(1)	111.3(8)
C(12)–Os(1)–Os(3)	85.9(4)	N(1)–N(5)–Os(2)	111.5(8)
C(13)–Os(1)–Os(3)	175.9(5)	C(2)–N(1)–N(5)	108.4(11)
C(12)–Os(1)–Os(2)	141.0(4)	C(4)–N(5)–N(1)	108.8(11)
C(13)–Os(1)–Os(2)	117.2(5)		

The solid-state structure of **4b** is consistent with that in solution, the heterocyclic unit bridging one of the Os–Os bonds. The two unbridged Os–Os bond lengths (mean 2.875 Å) in **4b** are very similar to those in $Os_3(CO)_{12}$ **1b** (mean 2.867 Å)[14]. The bridged Os–Os bond is significantly longer at 2.9243 Å. The hydride was not located directly in the Fourier difference map but its position was determined using the program HYDEX[15]. The pyrazolate unit, which is inclined at an angle of 102.4° to the Os_3 plane, coordinates with one nitrogen atom axially bonded to Os(1) and one nitrogen atom axially bonded to Os(2) [Os(1)–N(1) = 2.116(11) Å; Os(1)–N(5) = 2.114(10) Å]. The complex possesses a similar molecular architecture to that of the related complexes $HOs_3(CO)_{10}[\mu_2\text{-}2,3\text{-}\eta^2\text{-}NNN(O)C_6H_4]$[16] (**5b**) and $HOs_3(CO)_{10}(\mu\text{-}\eta^2\text{-}N{=}NPh)$[17] (**6b**) prepared from the reactions of $Os_3(CO)_{10}(MeCN)_2$ and 1-hydroxybenzotriazole and phenyldiazonium tetrafluoroborate, respectively. In both **5b** and **6b**, there is extension of the Os–Os bond bridged by the heterocycle and hydride ligand, as in **4b**. The heterocyclic unit is inclined at an angle of 102.5° in **5b** and at 103.25° in **6b**. In all three structures, a survey of the *cis*-diequatorial angles around the triosmium framework shows that the angles are larger than the remaining *cis*-diequatorial OC–Os–Os angles [for **4b**: C(23)–Os(2)–Os(1) = 116.1(4), C(13)–Os(1)–Os(2) = 117.2(5), C(34)–Os(3)–Os(1) = 97.9(5), C(32)–Os(3)–Os(2) = 98.6(5)]. Compared to the free pyrazole ligand, coordination to **4b** has remarkable little effect, the bond lengths being almost unchanged within the remit of statistical significance[18].

Conclusions

The photolysis of ethyl acetate solutions of $M_3(CO)_{12}$ [M = Ru (**1a**), Os (**1b**)] with pyrazole and 3,5-dimethylpyrazole leads to photosubstitution products. With pyrazole, **1a** forms the substitution product $HRu_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3H_3N_2)$ (**2a**) but, in the case of osmium, the *ortho*-metallated complex $HOs_3(CO)_{10}(\mu_C{:}\mu_N\text{-}C_3H_3N_2)$ (**3b**) can be isolated. Heating **3b** yields the osmium analogue of **2a**, $HOs_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3H_3N_2)$ (**2b**). Photolysis of **1a** and **1b** with 3,5-dimethylpyrazole yields the substitution products $HRu_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3HMe_2N_2)$ (**4a**) and $HOs_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3HMe_2N_2)$ (**4b**), respectively. With 2,6-diphenylpyrazole no net photoreaction is observed.

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Experimental Section

General Experimental: Unless stated otherwise, all syntheses were performed under dry nitrogen using standard Schlenk techniques. All photochemical reactions were performed in a specially designed glass reaction vessel fitted with a nitrogen bubbler, reflux condenser and dry-ice cooling finger. A 125-W mercury arc broad-band UV lamp was used as the irradiation source and reflectors placed around the reaction vessel to maximise efficiency. All reagents were purchased from commercial sources and used as received unless noted otherwise. Literature methods were used to prepare the starting material compounds $Ru_3(CO)_{12}$ (**1a**)[19] and $Os_3(CO)_{12}$ (**1b**)[20]. Purification of the reaction products was by thin layer chromatography (laboratory prepared glass plates coated to a thickness of 1.0 mm with Merck Kieselgel 60 F_{254}) using light petroleum ether as eluent.

Physical Measurements: Infrared (IR) spectra were recorded in NaCl solution cells (path length 0.5 mm) using a Perkin-Elmer PE 1710 Fourier transform infrared spectrometer. All values quoted are in wavenumbers (cm^{-1}). − The ^1H-NMR spectra were recorded using a Bruker AM400, WM250, or WP80SY Fourier transform NMR spectrometer and data reported using the chemical shift scale in units of ppm relative to the solvent resonance. − Fast atom bombardment (FAB) mass spectra were recorded using a KRATOS MS-50 spectrometer, with either 3-nitrobenzyl alcohol or thioglycerol as a matrix and CsI as calibrant. − IR, NMR, and mass spectral data are collected in Table 1.

Photolyses

An Ethyl Acetate Solution of $Ru_3(CO)_{12}$ (**1a**) *with Pyrazole:* An ethyl acetate solution of **1a** (30 mg in 150 ml) containing excess pyrazole (9.6 g) was irradiated using the broad-band UV source. The reaction was deemed complete when there was no further change in the IR spectrum (30 min). From comparison with literature data it was proposed that the yellow-orange cluster formed in 60% yield was $HRu_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3H_3N_2)$ (**2a**)[21]. Prolonged photolysis of the reaction mixture (1 h) led to decomposition.

An Ethyl Acetate Solution of $Os_3(CO)_{12}$ (**1b**) *with Pyrazole:* The photolysis was performed as with **1a** but using **1b** (40 mg in 150 ml) and 16 mg of the heterocycle. The yellow-green *ortho*-metallated cluster $HOs_3(CO)_{10}(\mu_C{:}\mu_N\text{-}C_3H_3N_2)$ (**3b**) was formed in 60% yield after 45 min, as characterised by comparison with literature data[12]. The product is not particularly soluble and sticks to the silica gel surface of TLC plates. As a result, an eluent of 2:1 petroleum ether/dichloromethane was used for purification. Prolonged photolysis of the reaction mixture (1 h) led to decomposition. Heating a solution of **3b** in refluxing xylene for 1 h led to the formation of $HOs_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3H_3N_2)$ (**2b**) in 70% yield.

An Ethyl Acetate Solution of $Ru_3(CO)_{12}$ (**1a**) *with 3,5-Dimethylpyrazole:* The photolysis was performed as with pyrazole but using 3,5-dimethylpyrazole (16 mg) as the heterocycle. The yellow cluster $HRu_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3HMe_2N_2)$ (**4a**) was formed in 60% yield after 30 min. Prolonged photolysis of the reaction mixture (1 h) led to decomposition.

An Ethyl Acetate Solution of $Os_3(CO)_{12}$ (**1b**) *with 3,5-Dimethylpyrazole:* The photolysis was performed as with **1a** but using $Os_3(CO)_{12}$ (**1b**) (40 mg in 150 ml) and 24 mg of the heterocycle. The yellow cluster $HOs_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3HMe_2N_2)$ (**4b**) was formed in 50% yield after 45 min. Prolonged photolysis of the reaction mixture (1 h) led to decomposition.

An Ethyl Acetate Solution of $Ru_3(CO)_{12}$ (**1a**) *and $Os_3(CO)_{12}$* (**1b**) *with 3,5-Diphenylpyrazole:* The photolyses were performed as with pyrazole but using 3,5-diphenylpyrazole (26 mg for **1a**, 35 mg for **1b**) as the heterocycle. No net photoreaction was observed in each case.

Determination of the Molecular Structure of $HOs_3(CO)_{10}(\mu_N{:}\mu_N\text{-}C_3HMe_2N_2)$ (**4b**) *by Single-Crystal X-ray Diffraction*

Crystal Data: $C_{15}H_8N_2O_{10}Os_3$, $M = 946.83$, monoclinic, space group $P2_1/c$ (no. 14), $a = 16.392(3)$, $b = 7.636(2)$, $c = 18.536(4)$ Å, $\beta = 115.53(3)$, $U = 2093.6(8)$ Å^3 (from refinement of 2θ values of 25 independent reflections), $Z = 4$, $D_c = 3.004$ gcm^{-3}, $T = 293$ K, yellow-orange rectangular plate 0.50 × 0.40 × 0.40 mm, μ(Mo-K_α) = 18.216 mm^{-1}, $F(000) = 1680$.

Data Collection and Processing: All X-ray measurements were made with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) with a Stoe-Siemens diffractometer using the ω-θ scan mode, 4994 reflections collected, 3681 independent ($R_{int} = 0.0454$) ($-19 \le h \le 19$, $-8 \le k \le 9$, $-22 \le l \le 22$; $5.5° \le 2\theta \le 50°$). Semi-empirical absorption correction based on ψ-scan data was applied (minimum and maximum transmission factors 0.153 and 0.288, respectively)[22].

Structure Solution and Refinement: The osmium atom positions were determined by direct methods (SHELXTL-PLUS)[23] and all non-hydrogen atoms located by subsequent Fourier difference syntheses. Full-matrix least-squares refinement on F^2 (SHELXL-93)[24] was performed with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. The hydride ligand was located using the program HYDEX. In the final cycles of refinement, a weighting scheme of the form $w^{-1} = [\sigma(F_o^2) + 0.053P^2 + 10.46P]$ [where $P = (F_o^2 + 2F_c^2)/3$] was introduced which produced a flat analysis of variance. At final convergence (max $\Delta/\sigma = 0.001$), $wR(F^2) = 0.1025$ for all data, $R(F) = 0.0865$ for 2801 observed reflections [$I > 2\sigma(I)$] and 188 parameters. The final difference synthesis showed no $\Delta\rho$ above 2.882 or below -1.390 eÅ^{-3}, the major features lying near the osmium atoms.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication no. CCDC-101356. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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