Note

Syntheses, structures and redox properties of {Os(PPh₃)₂Cp}₂{μ-(C≡C)ₓ} (x = 2, 3, 4): Comparisons with the Ru analogues

Michael I. Bruce [a,*], Kathy A. Kramarczuk [a], Brian W. Skelton [b], Allan H. White [b]

[a] School of Chemistry and Physics, University of Adelaide, Adelaide, SA 5005, Australia
[b] Chemistry M313, SBBCS, University of Western Australia, Crawley, WA 6009, Australia

ABSTRACT

The syntheses of {Os(PPh₃)₂Cp}₂{μ-(C≡C)ₓ} (x = 2, 3, 4) from reactions between OsBr(PPh₃)₂Cp* and Me₃Si(C≡C)ₓSiMe₃ in the presence of KF/NaBPh₄ are described. The molecular structure of x = 3 has been determined by a single-crystal XRD study. Comparison of the redox properties of {M(PPh₃)₂Cp}₂{μ-(C≡C)ₓ} (M = Ru, Os) shows that the oxidation potentials of the osmium complexes are invariably lower (by between 0.16 and 0.64 V) than those of the Ru analogues.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Continuing interest in the chemistry of complexes containing redox-active metal–ligand fragments end-capping carbon-rich linking groups stems from their potential as components in molecular scale electronics. In particular, complexes containing rigid π-conjugated chains of C(sp) atoms linking transition metal centres have been considered as models of "molecular wires" [1–3]. This chemistry encompasses a desire to rationalise the observed electrochemical behaviour and, if possible, to determine the effects of various changes to the linker groups on the electronic interaction between the end-groups [4–9].

Many studies have been carried out with complexes containing chains of carbon atoms, C₂ₓ, linking metal centres such as Mn(dppe)Cp′ (Cp′ = Cp, Cp^Me) [10], Re(NO)(PPh₃)Cp* [11], Fe(dppe)Cp* [12], Ru(PP)Cp′ [(PP)Cp′ = (PPh₃)₂Cp, (dppe)Cp*] [13], Os(dppe)Cp* [14], Ru₂(LL)₄ [15,16], and Pt(Ar)(PAr′₃)₂ (Ar = tol, C₆F₅, Ar′ = tol) [17]. Recent reviews of this chemistry are available [18–21]. Earlier structural and electrochemical studies of {M(dppe)Cp*}₂{μ-(C≡C)ₓ} (M = Fe [12], Ru [13c], Os [14]) and the ruthenium analogues of the present complexes, {Ru(PPh₃)₂Cp}₂{μ-(C≡C)ₓ} [13b] have been interpreted in terms of a series of 1-e redox processes which interconnect several species [{M(PP)Cp′}₂{μ-(C≡C)ₓ}]ⁿ⁺ (n = 0–4). It was therefore of interest to make related osmium–PPh₃ complexes and to compare their redox behaviour with the ruthenium analogues.

2. Results and discussion

2.1. Synthesis of {Cp(PPh₃)₂Os}₂(C≡C)ₓ (x = 2, 3, 4)

The most accessible precursor to Os(PPh₃)₂Cp complexes is OsBr(PPh₃)₂Cp which is readily obtained from OsO₄ via H₂OsBr₆ and OsBr₂(PPh₃)₃ [22]. Subsequent reactions of the bromo complex with Me₃Si(C≡C)ₓSiMe₃, carried out in the presence of KF as a desilylating agent and Na[BPh₄] to labilise the Os–Br bond, following previous results obtained with the analogous Ru systems [13a], afforded the desired complexes {Cp(PPh₃)₂Os}₂(C≡C)ₓ (x = 2 (**1**), 3 (**2**), 4 (**3**)). For osmium, the yields were considerably lower than those found for ruthenium, no doubt in part due to the well-established kinetic stability of the osmium systems, together with the lability of the silylated poly-ynes under the reaction conditions employed. In the absence of Na[BPh₄], the yield of the C₄ complex was <10%, deep blue products (presently unidentified) being obtained. Attempts to prepare the ruthenium complex {Cp*-(dppe)Ru}₂(μ-C≡CC≡C) via this method also afforded similar products [23]. Further, reactions carried out using NEtCy₂ or 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) also failed to give substantial amounts of the desired product, although a pale yellow precipitate formed during these reactions was identified spectroscopically as OsH(PPh₃)₂Cp, probably formed via an intermediate methoxy derivative formed from the MeOH solvent; in the absence of the poly-ynes, this is the only product obtained.

The complex {Cp(Ph₃P)₂Os}₂(μ-C≡CC≡C) **1** was obtained as a yellow powder in 10% yield. As with the other two complexes reported here, **1** was characterised by elemental microanalyses and

spectroscopically. Spectroscopic properties include a single $v(C\equiv C)$ absorption at 1972 cm^{-1}, while the NMR spectra contained resonances at δ_H 4.45, δ_C 81.69 (Cp) and signals between δ_H 6.91–7.78, δ_C 127.45–128.83 (Ph), with a singlet at δ_P 0.9 (PPh$_3$). Signals from the C$_4$ chain were not observed. The electrospray mass spectrum (ES-MS) contained M$^+$ at m/z 1608.

The C$_6$ complex {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_3$} **2** was similarly obtained in 60% yield from the reaction between OsBr(PPh$_3$)$_2$ and Me$_3$Si(C≡C)$_3$SiMe$_3$ and KF in MeOH. Crystallisation from CHCl$_3$ afforded the 2CHCl$_3$ solvate. As found for the Ru analogue, this derivative has extremely limited solubility in the usual organic solvents. The IR spectrum of **2** has one strong and two weak $v(C\equiv C)$ bands at 2063, 2111 and 1987 cm^{-1}, respectively. The NMR spectra contain singlets at δ_H 4.40, δ_C 81.91 (Cp) and resonances between δ_H 7.11–7.40, δ_C 127.40–139.30 (Ph), the PPh$_3$ ligands appearing at δ_P 3.55. For **2**, two of the C$_6$ resonances were found at δ_C 56.76 and 53.68. The ES-MS contains [M+H]$^+$ at m/z 1633.

Significant decomposition was observed during the reaction between OsBr(PPh$_3$)$_2$Cp and Me$_3$Si(C≡C)$_4$SiMe$_3$ to give the C$_8$ complex, {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_4$} **3**. The silylated tetrayne is significantly less stable than the shorter chain analogues and, like the product, does not survive lengthy heating. The thermal instability of poly-ynes with longer carbon chains is well documented [24,25]. The crude C$_8$ product was isolated as a black powder (ca. 40%), purification by flash chromatography giving pure **3** as a yellow powder, but in only 9% isolated yield. The IR spectrum of **3** contained two $v(C\equiv C)$ bands at 2102s and 1953w cm^{-1}. In the NMR spectra, only the Cp (δ_H 4.06, δ_C 82.42), Ph (δ_H 6.59–7.27, δ_C 127.45–139.17) and PPh$_3$ resonances (δ_P 1.6) were found. The ES-MS contained [M+H]$^+$ at m/z 1657.

2.2. Molecular structure of {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_3$}

The X-ray determined structure of **2**·2CHCl$_3$ is shown in Fig. 1, from which it can be seen that each of the two independent molecules adopts a *trans* conformation about a crystallographic inversion centre. Overall, the geometry of **2** is similar to that of its ruthenium analogue [13a], selected structural parameters of the two compounds being listed in Table 1. The M(PPh$_3$)$_2$Cp fragments have the usual pseudo-octahedral geometry, with no significant differences between the M–P and M–C(cp) bonds as a result of the similar atomic radii of the two metals. The M–C(1) separations are experimentally indistinguishable at 2.001(6) (Ru) and 1.997(3), 2.013(3)Å (Os).

Along the C$_6$ chain, alternate short [C(1)–C(2), C(3)–C(4), C(5)–C(6)] and long [C(2)–C(3), C(4)–C(5)] separations confirm the triyndiyl nature of the bridge. Bond angles along the Os–C$_6$–Os chain are quasi-linear, with the most pronounced bending being at C(1) [165.4(2), 171.7(3)°] [cf. Ru, 172.2(4)° [13a]]. Non-linear M–C$_{2x}$–M chains are generally found for {ML$_n$}$_2${μ-(C≡C)$_x$} complexes [11c]. This feature may be accommodated by a sigmoidal arrangement, particularly for centrosymmetric molecules, or by distinct bending of the chain, the angles at each carbon atom in **2** ranging between 165.4(3)° and 177.9(4)°, i.e., somewhat greater than those found for the C$_4$ complexes [176.2(3)–177.4(3)°]. The solvent molecules, although well-ordered, have no close interactions with the molecular cores.

2.3. Electrochemistry of {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_x$} (x = 2, 3, 4)

Limited solubility of **2** in CH$_2$Cl$_2$ necessitated carrying out the electrochemical studies in thf, rather than CH$_2$Cl$_2$ used previously. Comparative studies of OsBr(PPh$_3$)$_2$Cp (E = +0.49 V) and **2** showed that there are no significant differences in redox potentials measured in these two solvents. The solution contained 0.1 M [NBu$_4$]BF$_4$ as supporting electrolyte. Table 2 summarises some electrochemical properties of complexes {M(PP)Cp'}$_2${μ-(C≡C)$_x$} [M = Ru, Os, (PP)Cp' = (PPh$_3$)$_2$Cp, (dppe)Cp*, x = 2–4].

Table 1
Selected bond parameters (Å, °) for {M(PPh$_3$)$_2$Cp}$_2${μ-(C≡C)$_3$} (M = Ru [13a], Os).

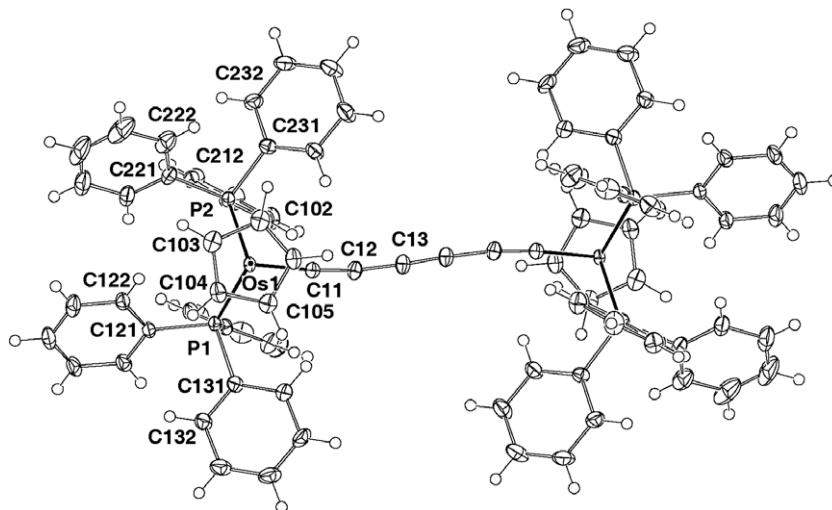| M	Ru	Os (molecules 1; 2)
Bond lengths (Å)		
M–P(1,2)	2.297(2), 2.301(1)	2.2848(8), 2.2982(8); 2.2858(8), 2.2858(7)
M–C(cp)	2.216(6)–2.261(6)	2.217–2.257(3); 2.238–2.261(3)
M–C(1)	2.001(6)	1.997(3); 2.013(3)
C(1)–C(2)	1.210(8)	1.216(4); 1.231(4)
C(2)–C(3)	1.382(8)	1.371(5); 1.363(4)
C(3)–C(3')	1.212(8)	1.228(6); 1.231(5)
Bond angles (°)		
P(1)–M–P(2)	99.02(5)	98.67(3); 99.02(3)
P(1,2)–M–C(1)	87.8(2), 95.1(2)	92.87(8), 91.31(8); 91.48(9), 89.96(8)
M–C(1)–C(2)	172.2(4)	165.4(2); 171.7(3)
C(1)–C(2)–C(3)	178.8(6)	171.2(3); 177.4(3)
C(2)–C(3)–C(3')	177.3(6)	176.9(4); 177.9(4)

Fig. 1. Plot of molecule 1 of {Cp(Ph$_3$P)$_2$Os}{μ-(C≡C)$_3$}{Os(PPh$_3$)$_2$Cp} **2**. Molecule 2 is similar.

Table 2
Oxidation potentials (V) of the series $\{Cp'(PP)M\}_2\{\mu\text{-}(C\equiv C)_x\}$ [M = Ru, Os; $Cp'(PP)$ = $Cp(Ph_3P)_2$, $Cp^*(dppe)$; $x = 2$–4].

C_{2x}	M	$Cp'(PP)$	$E_1°$	$E_2°$	ΔE_{12}	K_C	$E_3°$	$E_4°^a$	References
C_4	Ru	$Cp(Ph_3P)_2$	−0.23	+0.41	0.64	6.6×10^{10}	+1.03	+1.68	[13b]
		$Cp^*(dppe)$	−0.43	+0.22	0.65	9.7×10^{10}	+1.04	+1.51	[13c]
	Os **1**	$Cp(Ph_3P)_2$	−0.33	+0.16	0.49	1.9×10^8	+0.75		This work
		$Cp^*(dppe)$	−0.62	−0.01	+0.61	2.05×10^{10}	+1.20		[14]
C_6	Ru	$Cp(Ph_3P)_2$	+0.06	+0.52	0.46	6.0×10^7	+1.07		[13a]
		$Cp^*(dppe)$	−0.15	+0.33	0.48	1.3×10^8	+1.05	+1.33	[30]
	Os **2**	$Cp(Ph_3P)_2$	−.06	+0.31	0.37	1.8×10^6	+0.52		This work
C_8	Ru	$Cp(Ph_3P)_2$	+0.24	+0.58	0.34	5.6×10^5	+1.07		[13a]
		$Cp^*(dppe)$	+0.08	+0.43	0.35	8.3×10^5	+1.07	+1.27	[30]
	Os **3**	$Cp(Ph_3P)_2$	+0.14	+0.35	0.21	3.5×10^3	+0.51		This work

For conditions, see Section 4.
  a Irreversible.

The CVs of complexes **1**, **2** and **3** (Table 2) each show three reversible, 1-e oxidation waves, consistent with the formation of the respective mono-, di- and tri-cations.

Values of the oxidation potentials (E^1, E^2, E^3) of these complexes increase in the sequence $C_4 < C_6 < C_8$ in both ruthenium and osmium series while replacement of $(PPh_3)_2Cp$ with the more electron-rich $(dppe)Cp^*$ ligand combination results in more ready oxidation of **1** and of the three ruthenium complexes. Osmium complexes, regardless of chain length, are more readily oxidised than the ruthenium analogues, all the oxidation steps of the osmium complexes with $x = 2$, 3 and 4 being thermodynamically *more* favourable than those of the three ruthenium analogues. For the Ru complexes, $E_3°$ falls within a small range (+1.03 to +1.07 V), whereas for Os derivatives, the range extends from +0.51 to +0.75 V for the PPh_3 derivatives. Only for the dppe-C_4 complex is a higher value (+1.20 V) found. The osmium complexes do not display the further, irreversible, process found at higher potentials ($E_4°$ between +1.27 and +1.68 V) for the Ru complexes. The distribution of potentials follows the usual pattern of higher oxidation states becoming more stable on going down a group.

The CVs show that *increasing* the length of the carbon chain results in a *decrease* of potential separation ΔE_{12} between two successive oxidation processes. The comproportionation constants, K_C = $\exp(\Delta E/25.69)$, which are related to the thermodynamic stability of the monocations, are lower for Os than for Ru. This trend correlates very closely with those observed for the analogous ruthenium series [13], the Group 8 series $\{Cp^*(dppe)M\}_2\{\{\mu\text{-}(C\equiv C)_x\}$ (M = Fe, Ru, Os; $x = 2$, 3, 4) [12–14] and the rhenium series $\{Cp^*(NO)(PPh_3)Re\}_2\{\mu\text{-}(C\equiv C)_x\}$ ($x = 2$, 3, 4) [11].

We have previously discussed the electronic structures of $\{M(dppe)Cp^*\}_2\{\mu\text{-}(C\equiv C)_x\}$ [13,14] and the comments made therein are also relevant to the present discussion. The highest lying orbitals in these complexes are derived from overlap of metal d and C_x π-type orbitals and are delocalised over the M–C_x–M chain. The relative contributions of metal and carbon to these orbitals depend upon the nature of the metal and the length of the carbon chain. In particular, the carbon-character increases with the length of the carbon chain [12–14,20]. This feature results in an increase in the redox potentials and decrease in the separations between them.

3. Conclusions

The osmium analogues of known ruthenium-C_4, -C_6 and -C_8 complexes in the $\{M(PPh_3)_2Cp\}_2\{\mu\text{-}(C\equiv C)_x\}$ series have been prepared and characterised, including a single-crystal X-ray structure determination of the C_6 compound. The similar sizes of Ru and Os result in there being few significant differences from the structure of the Ru derivative. In contrast, and in agreement with observa-

tions with $\{M(dppe)Cp^*\}_2\{\mu\text{-}(C\equiv C)_4\}$ (M = Ru, Os) [14], the redox potentials of the three single-electron oxidation processes of the Os complex are significantly lower than those of the lighter congener, probably because of increased repulsion of the electrons in the HOMOs by the larger electron core in the heavier element.

4. Experimental

4.1. General experimental conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques, unless otherwise stated, although no special precautions to exclude air were taken during subsequent workup. Solvents were dried and distilled under nitrogen before use.

4.2. Instruments

IR spectra were recorded with a Perkin–Elmer Spectrum BX FT-IR. Solution spectra were obtained using a 0.5 mm path-length cell fitted with NaCl windows. Nujol mull spectra were collected from samples mounted between NaCl discs. NMR spectra were recorded using either a Varian ACP-300 [300.145 MHz (^{1}H), 75.47 MHz (^{13}C), 121.105 MHz (^{31}P)], Varian Gemini 200 [199.98 MHz (^{1}H), 50.29 MHz (^{13}C)] or Inova 600 [599.957 MHz (^{1}H), 150.87 MHz (^{13}C), 242.21 MHz (^{31}P)] instruments. Solutions were contained in standard 5 mm sample tubes. Chemical shifts are reported in δ, relative to internal TMS (^{1}H and ^{13}C) or external H_3PO_4 (^{31}P). Electrospray mass-spectrometry was carried out at the University of Waikato, Hamilton, New Zealand. Cyclic voltammograms were recorded at 298 K from solutions in CH_2Cl_2 (Ru) or thf (Os) ca 10^{-4} M in analyte, also containing 10^{-1} M [NBu$_4$]BF$_4$. A single-compartment three-electrode cell equipped with Pt working, coiled Pt wire auxiliary and Pt wire pseudo-reference electrodes was used, with scan rates of 50–800 mV s^{-1}. Redox potentials are reported vs SCE, with internal reference FeCp$_2$/[FeCp$_2$]$^+$ (+0.46 V vs. SCE). Data were collected with a computer-interfaced PAR Model 263A potentiostat. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, BC, or Chemical and MicroAnalytical Services, Belmont, Victoria.

4.3. Reagents

The compounds OsBr(PPh$_3$)$_2$Cp [22], Me$_3$Si(C$\equiv$C)$_x$SiMe$_3$ ($x = 2$ [26], 3 [27], 4 [28]) were prepared by standard literature methods. Cyclopentadiene was freshly distilled prior to use. All other reagents were used as received without further purification.

4.4. Precautionary warning

OsO$_4$ is extremely toxic. The yellow solid melts at 31 °C and has an appreciable vapour pressure even at r.t. The compound is often liberated when solutions of osmium compounds are treated with oxidising agents. Ample precautions to protect eyes, nose and mouth are essential.

4.5. {Cp(PPh$_3$)$_2$Os}$_2${μ-C≡C C≡C} 1

OsBr(PPh$_3$)$_2$Cp (100 mg, 0.116 mmol) and Me$_3$SiC≡CC≡CSiMe$_3$ (11.5 mg, 0.06 mmol), were suspended in THF (0.5 mL) and methanol (10 mL). NaBPh$_4$ (43.9 mg, 0.13 mmol, 1.1 eq) was added to the suspension, followed by KF (6.9 mg, 0.12 mmol) and the mixture was heated at reflux point for 18 h. After this time the solution was deep blue over a dull yellow precipitate. The precipitate was removed by filtration and washed with cold methanol (3 × 5 mL) to give {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_2$} 1 as a yellow powder (9.5 mg, 10%). Anal. Calc. for C$_{86}$H$_{70}$Os$_2$P$_4$: C, 64.24; H, 4.36; *M*, 1606. Found: C, 63.75; H, 4.12%. IR (CH$_2$Cl$_2$): ν(C≡C) 1972 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ_H 4.45 (s, 10H, Cp), 6.91–7.78 (m, 60H, Ph). ^{13}C NMR (C$_6$D$_6$): δ_C 81.69 (s, Cp), 127.45–140.21 (Ph). ^{13}P NMR (C$_6$D$_6$): δ_P 0.9 (s, PPh$_3$). ES-MS (*m/z*): 1608, M$^+$.

4.6. {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_3$} 2

OsBr(PPh$_3$)$_2$Cp (100 mg, 0.116 mmol), Me$_3$Si(C≡C)$_3$SiMe$_3$ (12.7 mg, 0.06 mmol), and KF (6.8 mg, 0.12 mmol) were suspended in methanol (10 mL) and the mixture was heated at reflux point for 18 h to give a pale brown solution over a mustard yellow precipitate. The solid was removed by filtration and washed with cold methanol (3 × 5 mL) and cold CH$_2$Cl$_2$ (3 × 5 mL) to give {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_3$} 2 as a yellow powder (57.3 mg, 53%). The analytical and X-ray sample was obtained as crystals of the 2CHCl$_3$ solvate from hexane/CHCl$_3$. Anal. Calc. for C$_{88}$H$_{70}$-Os$_2$P$_4$.2CHCl$_3$: C, 57.77; H, 3.85; *M* (unsolvated), 1630. Found: C, 58.61; H, 3.82%. IR (CHCl$_3$): ν(C≡C) 2111 cm^{-1} (w), 2063 cm^{-1} (s), 1987 cm^{-1} (w). ^{1}H NMR (CDCl$_3$): δ_H 4.40 (s, 10H, Cp), 7.11–7.40 (m, 60H, Ph). ^{13}C NMR (CDCl$_3$): δ_C 53.68, 56.76, (2 × s, C$_\alpha$, C$_\beta$, or C$_\gamma$), 81.91 (s, Cp), 127.40–139.43 (Ph). ^{31}P NMR (CDCl$_3$): δ_P 3.4 (s, PPh$_3$). ES-MS (*m/z*): 1632, [M+H]$^+$.

4.7. {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_4$}{Os(PPh$_3$)$_2$Cp} 3

OsBr(PPh$_3$)$_2$Cp (120 mg, 0.140 mmol), Me$_3$Si(C≡C)$_4$SiMe$_3$ (16.2 mg, 0.07 mmol) and KF (16.3 mg, 0.28 mmol) were suspended in methanol (20 mL) and the mixture was heated at reflux point for 18 h. After this time the solution was black-brown over a black solid. The precipitate was removed by filtration and washed with cold methanol (3 × 5 mL) to give crude 3 (44.8 mg). The crude product was purified by flash chromatography on basic alumina (CH$_2$Cl$_2$-hexane, 1/1) to give pure {Cp(PPh$_3$)$_2$Os}$_2${μ-(C≡C)$_4$}3 as a yellow powder (9.8 mg, 9%). Anal. Calc. for C$_{90}$H$_{70}$Os$_2$P$_4$: C, 65.28; H, 4.23; *M*, 1654. Found: C, 66.10; H, 4.52%. IR (CH$_2$Cl$_2$): ν(C≡C) 2102 cm^{-1} (s), 1953 cm^{-1} (w). ^{1}H NMR (C$_6$D$_6$): δ_H 4.06 (s, 10H, Cp), 6.59–7.27 (m, 60H, Ph), ^{13}C NMR (C$_6$D$_6$): δ_C 82.42 (s, Cp), 127.45–139.17 (Ph), ^{13}P NMR(C$_6$D$_6$): δ_P 1.6 (s, PPh$_3$). ES-MS (*m/z*): 1656, M$^+$; 828, M^{2+}.

4.8. Structure determination

A full sphere of diffraction data was measured at ca 150 K using a Bruker AXS CCD area-detector instrument. 78 253 reflections were merged to 39 001 unique (R_{int} 0.031) after "empirical"/multi-scan absorption correction (proprietary software), 25 137 with $F > 4\sigma(F)$ were considered observed and used in the full matrix least squares refinement on F^2. All data were measured using monochromatic Mo Kα radiation, $\lambda = 0.71073$ Å. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Conventional residuals R_1, wR_2 are 0.039, 0.093 [weights: $(\sigma^2(F_o^2) + (0.045P)^2)^{-1}$ $[P = (F_o^2 + 2F_c^2 + 2F_c^2)/3]]$. Neutral atom complex scattering factors were used; computation used the SHELXL 97 program [29]. Pertinent results are given in the figure (which shows non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in Table 1.

{Os(PPh$_3$)$_2$Cp}$_2${μ-(C≡C)$_3$}·2CHCl$_3$ ≡ C$_{88}$H$_{70}$Os$_2$P$_4$·2CHCl$_3$, *M* = 1870.46. Triclinic, space group P$\bar{1}$, *a* = 14.083(1), *b* = 15.935(2), *c* = 17.449(2) Å, α = 83.118(2)°, β = 81.917(2)°, γ = 80.953(2)°, *V* = 3809.5(7) Å^3, *Z* = 2. Crystal: 0.35 × 0.30 × 0.13 mm, 2θ = 75°, ρ_c = 1.631 g cm^{-3}, μ(Mo Kα) = 3.67 mm^{-1}, $T_{min/max}$ = 0.68. R_1 0.039, wR_2 0.093.

Appendix A. Supplementary material

CCDC 743261 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.ca-m.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.043.

References

[1] R.L. Carroll, C.B. Gorman, Angew. Chem. Int. Ed. 41 (2002) 4378.
[2] (a) A. Nitzan, M.A. Ratner, Science 300 (2003) 1384;
(b) C. Joachim, M.A. Ratner, Proc. Natl. Acad. Sci. USA 102 (2005) 8801.
[3] D.K. James, J. Tour, Chem. Mater. 15 (2004) 4423.
[4] K.D. Demadis, C.M. Hartshorn, T.J. Meyer, Chem. Rev. 101 (2001) 2655.
[5] B.S. Brunschwig, C. Creutz, N. Sutin, Chem. Soc. Rev. 31 (2002) 168.
[6] A. Ceccon, S. Santi, L. Orian, A. Bisello, Coord. Chem. Rev. 248 (2004) 683.
[7] D.M. Alessandro, F.R. Keene, Dalton Trans. (2006) 424.
[8] M.H. Chisholm, N.J. Patmore, Acc. Chem. Res. 40 (2007) 19.
[9] W. Kaim, G.K. Lahiri, Angew. Chem. Int. Ed. 46 (2007) 1778.
[10] S. Kheradmandan, K. Venkatesan, O. Blacque, H.W. Schmalle, H. Berke, Chem. Eur. J. 10 (2004) 4872.
[11] (a) T. Bartik, B. Bartik, M. Brady, R. Dembinski, J. Gladysz, Angew. Chem., Int. Ed. Engl. 35 (1996) 414;
(b) M. Brady, W. Weng, Y. Zhou, J.W. Seyler, A.J. Amoroso, A.M. Arif, M. Bohme, G. Frenking, J.A. Gladysz, J. Am. Chem. Soc. 119 (1997) 775;
(c) R. Dembinski, T. Lis, S. Szafert, C.L. Mayne, T. Bartik, J.A. Gladysz, J. Organomet. Chem. 578 (1999) 229;
(d) R. Dembinski, T. Bartik, B. Bartik, M. Jaeger, J.A. Gladysz, J. Am. Chem. Soc. 122 (2000) 810.
[12] (a) N. Le Narvor, L. Toupet, C. Lapinte, J. Am. Chem. Soc. 117 (1995) 7129;
(b) F. Coat, C. Lapinte, Organometallics 15 (1996) 477;
(c) F. Coat, M.-A. Guillevic, L. Toupet, C. Lapinte, Organometallics 16 (1997) 5988;
(d) N. Le Narvor, C. Lapinte, C.R. Acad. Sci., Ser. IIc: Chim. 1 (1998) 745;
(e) M. Guillemot, L. Toupet, C. Lapinte, Organometallics 17 (1998) 1928.
[13] (a) M.I. Bruce, B.C. Hall, B.D. Kelly, P.J. Low, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1999) 3719;
(b) M.I. Bruce, P.J. Low, K. Costuas, J.-F. Halet, S.P. Best, G.A. Heath, J. Am. Chem. Soc. 122 (2000) 1949;
(c) M.I. Bruce, B.G. Ellis, P.J. Low, B.W. Skelton, A.H. White, Organometallics 22 (2003) 3184.
[14] M.I. Bruce, K. Costuas, T. Davin, J.-F. Halet, K.A. Kramarczuk, P.J. Low, B.K. Nicholson, G.J. Perkins, R.L. Roberts, B.W. Skelton, M.E. Smith, A.H. White, Dalton Trans. (2007) 5387.
[15] T. Ren, G. Zou, J.C. Alvarez, Chem. Commun. (2000) 1197.
[16] K.-T. Wong, J.-M. Lehn, S.-M. Peng, G.-H. Lee, Chem. Commun. (2000) 2259.

[17] (a) T.B. Peters, J.C. Bohling, A.M. Arif, J.A. Gladysz, Organometallics 18 (1999) 3261;
     (b) W. Mohr, J. Stahl, F. Hampel, J.A. Gladysz, Inorg. Chem. 40 (2001) 3263;
     (c) G.R. Owen, J. Stahl, F. Hampel, J.A. Gladysz, Organometallics 23 (2004) 5889;
     (d) G.R. Owen, F. Hampel, J.A. Gladysz, Organometallics 23 (2004) 5893;
     (e) Q. Zheng, F. Hampel, J.A. Gladysz, Organometallics 23 (2004) 5896;
     (f) Q. Zheng, J.A. Gladysz, J. Am. Chem. Soc. 127 (2005) 10508;
     (g) L. de Quadras, F. Hampel, J.A. Gladysz, Dalton Trans. (2006) 2929.
[18] F. Paul, C. Lapinte, Coord. Chem. Rev. 178–180 (1998) 431.
[19] N.J. Long, C.K. Williams, Angew. Chem. Int. Ed. 42 (2003) 2586.
[20] M.I. Bruce, P.J. Low, Adv. Organomet. Chem. 50 (2004) 179.
[21] T. Ren, Organometallics 24 (2005) 4854.
[22] (a) M.I. Bruce, N.J. Windsor, Aust. J. Chem. 30 (1977) 1601;
     (b) M.I. Bruce, P.J. Low, B.W. Skelton, E.R.T. Tiekink, A. Werth, A.H. White, Aust. J. Chem. 48 (1995) 1887.
[23] M.I. Bruce, B.G. Ellis, B.W. Skelton, A.H. White, J. Organomet. Chem. 690 (2005) 1772.
[24] T.R. Johnson, D.R.M. Walton, Tetrahedron 28 (1972) 5221.
[25] E. Kloster-Jensen, Angew. Chem., Int. Ed. Engl. 11 (1972) 438.
[26] G.E. Jones, D.A. Kendrick, A.B. Holmes, Org. Synth. Coll. Vol. VIII (1993) 63.
[27] Y. Rubin, S.S. Lin, C.B. Knobler, J. Anthony, A.M. Boldi, F. Diederich, J. Am. Chem. Soc. 113 (1991) 6943.
[28] D.R.M. Walton, F. Waugh, J. Organomet. Chem. 37 (1972) 45.
[29] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.
[30] B.G. Ellis, unpublished work.