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Ligand substitution reaction of $(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-COMe})$ with 1,1′-bis(diphenylphosphino)ferrocene

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Abstract

Reaction of $(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-COMe})$ with 1,1′-bis(diphenylphosphino)-ferrocene (dppf) produces $(\mu\text{-H})\mathrm{Os_3(CO)_8}(\mu\text{-COMe})\{\mu\text{-}\eta^2\text{-}(\eta^5\text{-C_5H_4PPh_2})_2\mathrm{Fe}\}$ (1) and $(\mu\text{-H})_2\mathrm{Os_3(CO)_7}(\mu\text{-COMe})\{\mu\text{-}\eta^3\text{-}(\eta^5\text{-C_5H_3PPh_2})\mathrm{Fe}(\eta^5\text{-C_5H_4PPh_2})\}$ (2). Thermolysis of 1 leads quantitatively to 2. These compounds have been characterized by ^{1}H, ^{31}P, and ^{13}C NMR, IR, and mass spectroscopies. Compound 2 crystallizes in space group $P\ 2_1/c$ with $a = 11.898(2)$, $b = 21.266(3)$, $c = 18.262(3)$ Å, $\beta = 104.71(1)°$, $V = 4469(1)$ Å^3, $Z = 4$, and $R_F = 0.029$.

Key words: Osmium; Iron

1. Introduction

The use of ferrocenylphosphines as ligands in organometallic and transition metal complexes has received much attention recently owing to its possible relevance to the catalytic activities of many of their complexes, such as, in asymmetric hydrogenation of olefin substrates [1], aldol condensation [2], hydrosilation [3], and cross-coupling reactions [4]. Although a wide range of mono- and di-metal complexes [5] has been synthesized from these ligands, particularly 1,1′-bis(diphenylphosphino)-ferrocene (dppf), relatively few studies have been carried out on the preparation and structure of their metal cluster complexes [6]. Arising from our interest in alkylidene, alkylidyne, and alkyne triosmium clusters [7], we report that reaction of $(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-COMe})$ with dppf affords cluster compounds featuring a bridging dppf ligand as well as the C–H activation of dppf ligand on the triosmium framework.

2. Experimental section

2.1. General procedures

$(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-COMe})$ was prepared from $\mathrm{Os_3(CO)_{12}}$ as described in the literature [8]. 1,1′-bis(diphenylphosphino)-ferrocene (dppf) was purchased from Aldrich and used as received. Benzene was distilled from sodium benzophenone ketyl immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck, GF 254). ^{1}H, ^{31}P, and ^{13}C NMR spectra were obtained on a Varian VXR-300 spectrometer at 300, 121.4, and 75.4 MHz, respectively. IR spectra were taken on a Hitachi-2001 spectrometer. Fast atom bombardment (FAB) mass spectra were obtained on a VG Blotch-5022 mass spectrometer. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan.

2.2. Reaction of $(\mu\text{-H})\mathrm{Os_3(CO)_{10}}(\mu\text{-COMe})$ with 1,1′-bis(diphenylphosphino)ferrocene

An oven-dried, 100 ml three-necked round bottomed flask was equipped with a magnetic stir bar, a

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rubber serum stopper, a reflux condenser and a nitrogen inlet. The stopper was briefly removed, and (μ-H)$Os_3(CO)_{10}$(μ-COMe) (100 mg, 0.112 mmol), 1,1'-bis(diphenylphosphino)ferrocene (68 mg, 0.123 mmol), and benzene (10 ml) were added against a nitrogen flow. The solution was refluxed under nitrogen for 2.5 h. After cooling to room temperature, the solvent was removed under vacuum, and the residue subjected to TLC, eluting with n-hexane/dichloromethane (5:1, v/v). The material forming the first, yellow band yielded (μ-H)$Os_3(CO)_{10}$(μ-COMe) (31 mg, 31%). Crystallization from dichloromethane-methanol of the material forming the second, orange band, produced air-stable, orange crystals of (μ-H)$_2$$Os_3(CO)_7$($\mu$-CO-Me){$\mu$-$\eta^3$-($\eta^5$-$C_5H_3PPh_2$)Fe($\eta^5$-$C_5H_4PPh_2$)} (**2**) (15 mg, 0.11 mmol, 10%). Crystallization of the material forming the third, yellow band from dichloromethane-hexane produced air-stable, yellow crystals of (μ-H)$Os_3(CO)_8$(μ-COMe){μ-η^2-(η^5-$C_5H_4PPh_2$)$_2$Fe} (**1**) (39 mg, 0.28 mmol, 25%).

2.2.1. Characterization of 2

Mass spectrum: m/z 1370 (M^+, ^{192}Os, ^{56}Fe). IR (C_6H_{12}): ν (CO) 2060m, 2036s, 1992vs, 1980m, 1966m, 1942m cm^{-1}. ^{1}H NMR (CD_2Cl_2, 20°C): δ 7.84–7.13 (m, 20H, Ph), 4.59 (s, 3H, OMe), 4.44 (m, 1H), 4.32 (1H), 4.11 (3H), 3.51 (1H), 2.88 (1H, Cp), −12.50 (m, μ-H), −15.42 (d, μ-H; $^2J_{P-H} = 17$ Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C): δ 357.0 (μ-COMe), 183.5 (1 CO), 179.8 (1 CO), 176.5 (1 CO), 176.0 (1 CO), 175.1 (1 CO), 173.9 (1 CO), 160.3 (1 CO), 140–125 (m, Ph), 100–70 (m, Cp). ^{31}P{^{1}H} NMR ($CDCl_3$, 20°C): δ −5.02 (d; $^2J_{P-P}$ = 9 Hz), −22.4 (d; $^2J_{P-P} = 9$ Hz). Anal. Calcd. for $C_{43}H_{32}FeO_8Os_3P_2$: C, 37.83; H, 2.36. Found: C, 37.35; H, 2.62%.

2.2.2. Characterization of 1

Mass spectrum: m/z 1398 (M^+, ^{192}Os, ^{56}Fe), 1398–28n (n = 1–8). IR (C_6H_{12}): ν (CO) 2078m, 2001s, 1997s, 1993s, 199sh, 1987m, 1969w, 1951w cm^{-1}. ^{1}H NMR ($CDCl_3$, 20°C): δ 7.80–7.12 (m, Ph), 4.80 (1H, Cp), 4.37 (s, 3H, OMe), 4.19 (1H, Cp), 4.12 (1H, Cp), 4.09 (1H, Cp), 3.89 (1H, Cp), 3.53 (1H, Cp), 3.39 (2H, Cp), −15.55 (dd, μ-H; $^2J_{P-H}$ = 5.5 and 6.4 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 20°C): δ 366.1 (μ-COMe), 187.6 (1 CO), 186.0 (1 CO), 183.4 (1 CO), 181.2 (1 CO), 180.0 (1 CO), 178.6 (1 CO), 177.2 (1 CO), 176.7 (1 CO), 135.1-127.9 (m, Ph), 83–70 (m, Cp). ^{31}P{^{1}H} NMR ($CDCl_3$, 20°C): δ −5.41 (s, br), −7.42 (s, br). Anal. Calcd. for $C_{44}H_{32}FeO_9Os_3P_2$: C, 37.93; H, 2.32. Found: C, 37.68; H, 2.57%.

TABLE 1. Experimental data for the X-ray diffraction study of compound 2

Formula	$C_{43}H_{32}O_8P_2FeOs_3$
Crystal solvent	CH_2Cl_2
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	11.898(2)
b (Å)	21.266(3)
c (Å)	18.262(3)
β (degrees)	104.71(1)
V (Å^3)	4469(1)
Z	4
D_c (g cm^{-3})	2.154
F (000)	2711
Diffractometer	Nonius (CAD-4)
Radiation (λ, Å)	Mo Kα_1 (0.70930)
Temp. (K)	298
Crystal size (mm)	0.05 × 0.10 × 0.50
Scan method	$\theta/2\theta$ scan mode
$2\theta_{max}$ (degrees)	45.0
Scan parameters	$2(0.65 + 0.35 \tan \theta)$
Scan speed (deg min^{-1})	2.06 to 8.24
h, k, l (range)	−12 to 12, 0 to 22, 0 to 19
μ (cm^{-1})	90.711
Transm. factors: max; min	1.000; 0.622
Standard reflections (No. 3)	decay 4%; every 3600 s
No. of unique data	5822
No. of data with $I > 2\sigma(I)$	4200
Refinement program and no. of params. refined	NRCVAX; 545
Max Δ/σ ratio	0.0394
R_F; R_w [a]	0.029; 0.023
Goodness of fit	1.44
Max/min resid. electron density, e Å^{-3}	−1.010/1.120

[a] $R_F = \Sigma||F_0|-|F_0||/\Sigma|F_0|$; $R_w = \{\Sigma[\omega(|F_0|-|F_c|)^2]/\Sigma|F_0|^2]\}^{1/2}$

2.2.3. Thermolysis of compound 1

(μ-H)$Os_3(CO)_8$(μ-COMe) {μ-η^2-(η^5-$C_5H_4PPh_2$)$_2$ Fe} (**1**) (20 mg) and chloroform-d (1 ml) were placed in an oven-dried NMR tube under an atmosphere of nitrogen in a glove bag. The tube was sealed and heated in an oil bath at 80°C for 10 h, cooled to ambient temperature, and then detected by ^{1}H NMR, showing the quantitative formation of compound **2**.

2.2.4. Structure determination for compound 2

A single crystal of (μ-H)$_2$$Os_3(CO)_7$($\mu$-COMe) {$\mu$-$\eta^3$-($\eta^5$-$C_5H_3PPh_2$)Fe($\eta^5$-$C_5H_4PPh_2$)} (**2**) was mounted in a thin-walled glass capillary and aligned on the Nonius CAD-4 diffractometer. Diffraction data were collected with Mo Kα radiation using $\theta/2\theta$ scan mode. The structure was solved by direct methods and refined by least-square cycles. The bridging hydride ligand (H) was located from a Fourier map and positional refined. All non-hydrogen atoms were refined with anisotropic thermal parameters. Empirical absorption correction was applied on all data sets. The data collection and refinement parameters are given in Table 1. Atomic positional parameters and selected interatomic dis-

TABLE 2. Atomic coordinates for compound **2**

	x	y	z	B_{iso} (Å^2)
Os1	0.65702(4)	0.22216(2)	0.13226(2)	2.62(2)
Os2	0.76336(4)	0.23093(2)	0.29219(2)	2.70(2)
Os3	0.82229(4)	0.32352(2)	0.17948(2)	2.51(2)
Fe	1.0233(1)	0.15026(6)	0.22066(8)	2.82(7)
P1	1.0303(2)	0.3105(1)	0.2011(2)	2.9(1)
P2	0.7384(2)	0.1181(1)	0.1399(2)	2.6(1)
O1	0.5668(8)	0.2372(5)	−0.0391(4)	8.8(6)
O2	0.4280(7)	0.1759(4)	0.1516(5)	7.4(6)
O3	0.613(1)	0.1263(4)	0.3263(6)	10.0(7)
O4	0.9001(8)	0.2369(4)	0.4568(4)	6.5(5)
O5	0.5817(7)	0.3237(4)	0.3174(4)	6.2(5)
O6	0.8399(7)	0.4496(3)	0.2578(4)	5.5(5)
O7	0.7995(8)	0.3865(4)	0.0280(4)	6.4(5)
O8	0.5719(6)	0.3554(3)	0.1563(4)	4.0(4)
C1	0.604(1)	0.2289(5)	0.0232(6)	4.9(6)
C2	0.5173(9)	0.1923(5)	0.1438(6)	4.2(6)
C3	0.671(1)	0.1653(5)	0.3109(6)	4.6(6)
C4	0.8547(9)	0.2359(5)	0.3945(5)	3.7(6)
C5	0.650(1)	0.2899(4)	0.3069(5)	4.0(6)
C6	0.8345(9)	0.4019(5)	0.2279(5)	3.3(6)
C7	0.8093(9)	0.3629(5)	0.0844(6)	4.0(6)
C8	0.6470(9)	0.3106(5)	0.1566(5)	3.4(6)
C9	0.449(1)	0.3398(6)	0.1310(7)	6.0(7)
C11	1.0863(8)	0.3611(4)	0.1377(5)	2.8(5)
C12	1.1329(9)	0.3393(5)	0.0815(6)	4.2(6)
C13	1.165(1)	0.3790(6)	0.0318(6)	5.5(7)
C14	1.155(1)	0.4422(6)	0.0398(7)	6.0(7)
C15	1.109(1)	0.4660(5)	0.0937(7)	5.1(7)
C16	1.074(1)	0.4272(5)	0.1447(6)	5.0(7)
C21	1.1256(8)	0.3284(4)	0.2951(5)	2.9(5)
C22	1.091(1)	0.3158(6)	0.3599(6)	5.2(7)
C23	1.164(1)	0.3242(6)	0.4310(6)	5.5(7)
C24	1.274(1)	0.3439(5)	0.4386(6)	5.4(7)
C25	1.311(1)	0.3580(6)	0.3776(7)	6.1(7)
C26	1.2373(9)	0.3507(5)	0.3033(6)	4.8(7)
C31	0.7825(8)	0.0829(4)	0.0588(5)	2.7(5)
C32	0.8055(9)	0.0190(4)	0.0577(6)	3.2(5)
C33	0.845(1)	−0.0066(5)	0.0005(6)	4.2(6)
C34	0.8578(9)	0.0305(5)	−0.0583(6)	4.0(6)
C35	0.8333(9)	0.0935(5)	−0.0591(5)	3.6(6)
C36	0.7950(8)	0.1195(4)	−0.0015(5)	2.8(5)
C41	0.6415(9)	0.0577(4)	0.1576(6)	3.3(5)
C42	0.662(1)	0.0247(5)	0.2267(7)	5.0(7)
C43	0.580(1)	−0.0161(5)	0.2403(8)	6.9(9)
C44	0.478(1)	−0.0263(6)	0.1868(9)	8.0(10)
C45	0.461(1)	0.0018(6)	0.1190(8)	7.2(9)
C46	0.540(1)	0.0434(5)	0.1053(7)	4.8(7)
C51	1.0772(8)	0.2329(4)	0.1850(5)	3.1(5)
C52	1.0193(9)	0.1945(4)	0.1219(5)	3.2(5)
C53	1.082(1)	0.1385(5)	0.1263(6)	4.0(6)
C54	1.1776(9)	0.1400(5)	0.1908(6)	4.3(6)
C55	1.1737(9)	0.1989(4)	0.2271(6)	3.6(6)
C61	0.8652(8)	0.1131(4)	0.2180(5)	2.6(5)
C62	0.8854(8)	0.1612(4)	0.2753(5)	2.8(5)
C63	0.9920(9)	0.1418(4)	0.3259(6)	3.6(6)
C64	1.0334(9)	0.0841(4)	0.3021(6)	3.6(6)
C65	0.9535(9)	0.0660(4)	0.2349(5)	3.0(5)
H	0.799(7)	0.251(4)	0.134(5)	5.(3)
C	0.551(3)	0.5625(9)	0.094(2)	31.(4)
Cl1	0.6174(6)	0.6343(3)	0.0934(4)	17.9(6)
Cl2	0.6333(7)	0.5072(3)	0.0933(5)	21.2(7)

TABLE 3. Selected bond distances (Å) and angles (°) for compound **2**

Bond distances			
Os(1)–Os(2)	2.8792(8)	Os(1)–Os(3)	2.8976(7)
Os(2)–Os(3)	3.0558(7)	Os(1)–H	1.79(8)
Os(3)–H	1.75(8)	Os(1)–C(1)	1.94(1)
Os(1)–C(2)	1.84(1)	Os(2)–C(3)	1.86(1)
Os(2)–C(4)	1.91(1)	Os(2)–C(5)	1.91(1)
Os(3)–C(6)	1.87(1)	Os(3)–C(7)	1.90(1)
C(1)–O(1)	1.13(1)	C(2)–O(2)	1.16(1)
C(3)–O(3)	1.15(1)	C(4)–O(4)	1.13(1)
C(5)–O(5)	1.14(1)	C(6)–O(6)	1.15(1)
C(7)–O(7)	1.12(1)	Os(1)–C(8)	1.94(1)
Os(3)–C(8)	2.04(1)	C(8)–O(8)	1.31(1)
O(8)–C(9)	1.45(1)	Os(1)–P(2)	2.406(3)
Os(3)–P(1)	2.421(3)	Os(2)–C(62)	2.152(9)
P(1)–C(11)	1.826(9)	P(1)–C(21)	1.84(1)
P(1)–C(51)	1.79(1)	P(2)–C(31)	1.85(1)
P(2)–C(41)	1.81(1)	P(2)–C(61)	1.798(9)
Fe–C(51)	2.03(1)	Fe–C(52)	2.02(1)
Fe–C(53)	2.04(1)	Fe–C(54)	2.06(1)
Fe–C(55)	2.04(1)	Fe–C(61)	2.03(1)
Fe–C(62)	2.14(1)	Fe–C(63)	2.06(1)
Fe–C(64)	2.03(1)	Fe–C(65)	2.020(9)
Bond Angles			
Os(2)–Os(1)–Os(3)	63.87(2)	Os(2)–Os(1)–P(2)	86.24(6)
Os(2)–Os(1)–C(1)	169.5(3)	Os(2)–Os(1)–C(2)	94.8(3)
Os(2)–Os(1)–C(8)	75.1(3)	Os(2)–Os(1)–H	77(3)
Os(3)–Os(1)–P(2)	115.76(7)	Os(3)–Os(1)–C(1)	105.7(3)
Os(3)–Os(1)–C(2)	141.9(3)	Os(3)–Os(1)–C(8)	44.6(3)
Os(3)–Os(1)–H	34(3)	C(8)–O(8)–C(9)	117.8(8)
C(1)–Os(1)–C(8)	98.1(4)	Os(1)–C(1)–O(1)	174(1)
Os(1)–C(2)–O(2)	177.3(9)	Os(2)–C(3)–O(3)	176.1(9)
Os(2)–C(4)–O(4)	174(1)	Os(2)–C(5)–O(5)	177.6(9)
C(8)–Os(1)–H	77(3)	Os(1)–Os(2)–Os(3)	58.36(2)
Os(3)–C(6)–O(6)	178.7(9)	Os(3)–C(7)–O(7)	179(1)
Os(1)–Os(2)–C(3)	90.5(3)	Os(1)–Os(2)–C(4)	171.8(3)
Os(1)–Os(2)–C(5)	92.3(3)	Os(1)–C(8)–Os(3)	93.3(4)
Os(1)–Os(2)–C(62)	87.1(3)	Os(1)–C(8)–O(8)	141.9(8)
Os(3)–C(8)–O(8)	124.5(7)	Os(3)–Os(2)–C(3)	148.6(3)
Os(3)–Os(2)–C(4)	116.9(3)	Os(3)–Os(2)–C(5)	87.8(3)
Os(3)–Os(2)–C(62)	93.9(3)	Os(1)–Os(3)–Os(2)	57.77(2)
Os(1)–Os(3)–P(1)	123.48(6)	Os(1)–Os(3)–C(6)	140.1(3)
Os(1)–Os(3)–C(7)	99.5(3)	Os(1)–Os(3)–C(8)	42.0(3)
Os(1)–Os(3)–H	35(3)	Os(2)–Os(3)–P(1)	102.48(7)
Os(2)–Os(3)–C(6)	105.0(3)	Os(2)–Os(3)–C(7)	157.1(3)
Os(2)–Os(3)–C(8)	69.7(3)	Os(2)–Os(3)–H	73(3)
P(1)–Os(3)–C(8)	165.5(3)	P(1)–Os(3)–H	90(3)
C(8)–Os(3)–H	75(3)	Os(1)–H–Os(3)	110(4)

tances and angles are collected in Table 2 and 3, respectively.

3. Results and discussion

Treatment of (μ-H)$Os_3(CO)_{10}$(μ-COMe) with 1,1'-bis(diphenylphosphino)ferrocene (dppf) in refluxing benzene for 2.5 h affords (μ-H)$Os_3(CO)_8$(μ-COMe){μ-η^2-(η^5-$C_5H_4PPh_2)_2Fe$} (**1**) and (μ-H)$_2Os_3(CO)_7$(μ-COMe)[μ-η^3-4-(η^5-$C_5H_3PPh_2$)Fe(η^5-$C_5H_4PPh_2$)] (**2**) in 25% and 10% yield, respectively. The starting material is recovered in 31% yield together with six uncharacterized coproducts (each < 2%). The reaction was monitored by IR and TLC to optimize the yields of **1** and **2**. Prolonging the reaction to 6 h shows exhaustion of the starting material but forming a complex mixture.

The molecular structure of compound **2** is illustrated in Fig. 1. It is based upon a triangular array of osmium atoms in which the individual bond lengths are Os(1)–Os(2) = 2.8792(8), Os(1)–Os(3) = 2.8976(7), and Os(2)–Os(3) = 3.0558(7) Å. One hydride ligand bridges the Os(1)–Os(3) edge. The other hydride ligand is not located directly, but the distribution of the carbonyl groups and lengthened Os(2)–Os(3) bond distance relative to Os(1)–Os(2) length indicates that it probably spans the Os(2)–Os(3) edge. The methoxycarbyne ligand adopts an asymmetrically bridging configuration, with C(8) interacting strongly with Os(1) (1.94(1) Å) and weakly with Os(3) (2.04(1) Å). Furthermore the C–OMe bond length of 1.31(1) Å is intermediate between the values expected for single (1.40–Å; *i.e.* O(8)–C(9) = 1.45(1) Å) and double (1.20 Å) C–O bonds [9]. This is clearly indicative of substantial multiple-bond character delocalized in the Os(1)–C(8)–O(8) linkage [10]. The dihedral angle between the triosmium plane and the Os(1)–C(8)–Os(3) plane is 85.0(4)°. The two diphenylphosphino groups in dppf ligand take up essentially axial positions on Os(1) and Os(3), with Os(1)–P(2) = 2.406(3) and Os(3)–P(1) = 2.421(3) Å. The *ortho* carbon C(62) in cyclopentadienyl moiety is metallated on Os(2), Os(2)–C(62) = 2.152(9) Å in an axial position. Finally, we note that the two cyclopentadienyl rings are not parallel, being tilted outwards by 7.2(4)° [5c].

The ^{1}H NMR spectrum of compound **2** shows the phenyl protons as a complex multiplet in the range δ

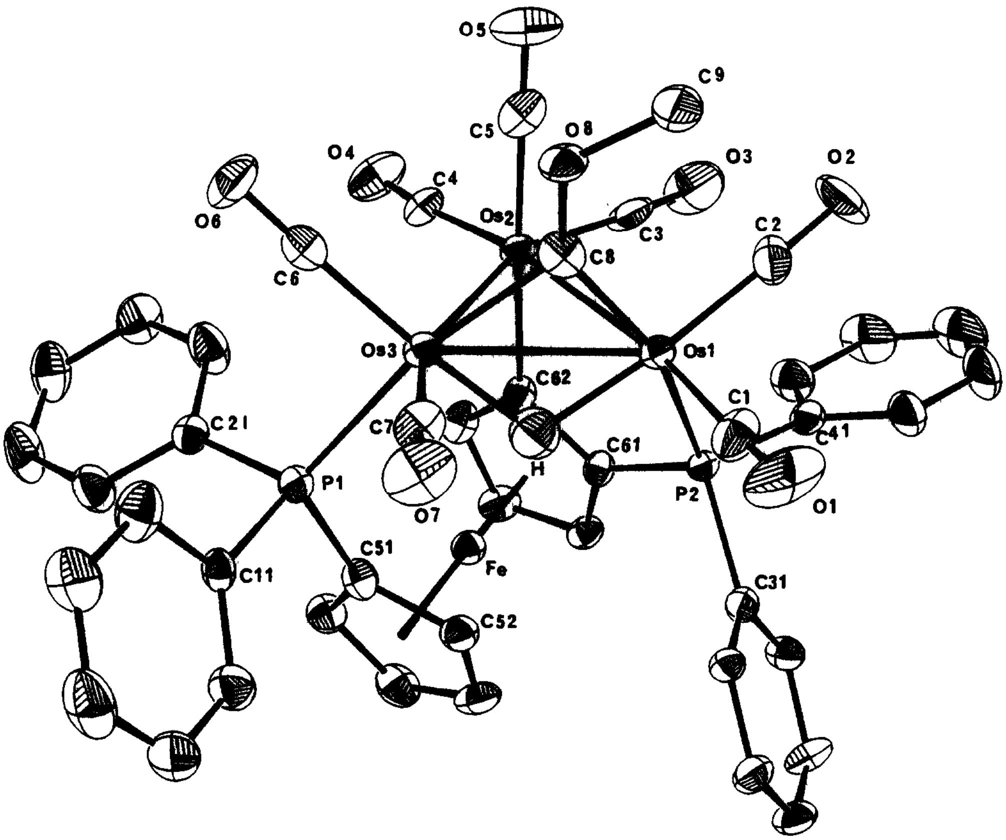
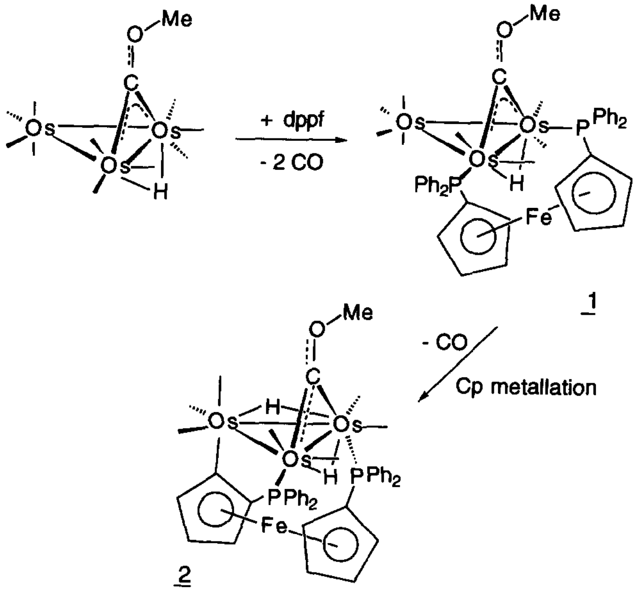


Fig. 1. Molecular structure of (μ-H)$_2Os_3(CO)_7$(μ-COMe){μ-η^3-(η^5-$C_5H_3PPh_2$)Fe(η^5-$C_5H_4PPh_2$)} (**2**), showing the atomic labelling scheme used in the text.

7.84–7.13 (20H), the methoxy protons at δ 4.59 (3H), and the cyclopentadienyl protons (7H) as a 1 : 1 : 3 : 1 : 1 pattern in the range of δ 4.44–2.88. The multiplet at δ -12.50 and doublet at δ -15.42 can be assigned to the hydrides bridging the Os(1)–Os(3) and Os(2)–Os(3) edges, respectively, based on their $^{1}H-^{31}P$ coupling patterns. The ^{13}C NMR spectrum of **2** shows the methoxycarbyne carbon resonance at δ 357.0, which is comparable with that of the parent complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ (δ 352.2) [8]. The ^{31}P NMR spectrum of **2** illustrates two resonances at δ -5.02 and δ -22.4, corresponding to the two non-equivalent phosphorus atoms.

The FAB mass spectrum of compound **1** gives the molecular ion peak at $m/z = 1398$ (^{192}Os) and ion multiplets corresponding to loss of eight carbonyls. The ^{1}H NMR spectrum shows a complicated multiplet in the range of δ 7.80–7.12 for the phenyl protons, a sharp singlet at δ 4.37 for the methoxy protons, seven broad signals ranging from δ 4.80 to δ 3.39 in a ratio of 1 : 1 : 1 : 1 : 1 : 1 : 2, assigned to the protons in the cyclopentadienyl groups, and a doublet of doublets at δ -15.55, assigned to the bridging hydride which is coupled to two non-equivalent phosphorus atoms with $^{2}J_{P-H} = 5.5$ and 6.4 Hz, respectively. The C–OMe ligand is best described as a doubly-bridging carbyne based on its ^{13}C resonance at δ 366.1. Since thermolysis of **1** leads exclusively to **2**, the two phosphine groups in **1** seem likely to span the Os–Os edge bridged by the methoxycarbyne and the hydride ligands to account for the final geometry found in **2**. The ^{31}P NMR spectrum shows broad signals at δ -5.41. and δ -7.42, suggesting a different coordination environment for the two phosphorus atoms, presumably with one phosphine ligand in an equatorial position, and the other in a pseudo-axial position to minimize steric interactions with the methoxycarbyne group. For comparison, we note that both ferrocenylphosphine ligands take up the eq-eq position in $Os_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}(\eta^5\text{-}C_5H_4P^iPr_2)_2Fe\}$ [6e] and $Ru_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}(\eta^5\text{-}C_5H_4PPh_2)_2Fe\}$ [11], and show only one ^{31}P resonance signal.



Scheme 1.

Routes are proposed in Scheme 1. Apparently, replacement of a CO ligand from each of the $Os(CO)_3$ unit in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe)$ by dppf ligand would afford compound **1**. Subsequent thermolysis of **1** results in metallation of the P-substituted C_5 ring, accompanied by loss of a CO ligand, to give compound **2**. Although orthometallation of both the phenyl and the cyclopentadienyl rings has been observed for $Ru_3(CO)_{10}\{\mu\text{-}\eta^2\text{-}(\eta^5\text{-}C_5H_4PPh_2)_2Fe\}$ [11], it is probable that in compound **1** a cyclopentadienyl group is placed under the $Os(CO)_4$ unit to facilitate its C–H activation. Nevertheless, metallation of ferrocene derivatives is not unusual and has been well documented [12].

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