Synthesis, characterization, and crystal structure of Os$_3$(CO)$_8$(η^1-C(OMe)Ph)(μ_3-CPh)(μ_3-COMe), a cluster with a carbene and two carbyne ligands

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Abstract

Treatment of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) sequentially with phenyllithium and methyl trifluoromethanesulfonate provides the Fischer-type carbene complex Os$_3$(CO)$_8$(η^1-C(OMe)Ph)(μ_3-CPh)(μ_3-COMe). The complex has been characterized by ^{1}H and ^{13}C NMR spectroscopy and the crystal structure has been determined by X-ray crystallography.

Introduction

Cluster complexes with more than one carbyne or carbene ligand are of interest in regard to possible C–C bond forming reactions [1]. Recently we have investigated the sequential action of phenyllithium and methyl triflate as reagents for synthesis of triosmiun phenyl-carbyne and -carbene complexes [2]. In this paper we report the results of treating the dicarbyne complex Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) [3] with these reagents.

Results and discussion

Sequential Ph$^-$/Me$^+$ treatment of Os$_3$(CO)$_9$(μ_3-CPh)(μ_3-COMe) shows that reaction occurs at a carbonyl ligand, forming a mixed dicarbyne-carbene complex Os$_3$(CO)$_8$(η^1-C(OMe)Ph)(μ_3-CPh)(μ_3-COMe), which is isolated in 66% yield (eq. 1). The compound forms slightly thermally-sensitive, red crystals, and it has been characterized by microanalysis, and by IR, ^{1}H and ^{13}C NMR, and mass spectroscopies together with an X-ray diffraction analysis.

$$ \text{(1)} $$
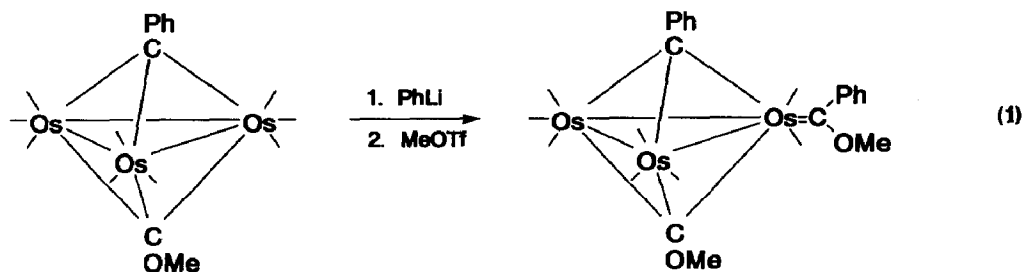
X-ray diffraction study. The molecular structure of $Os_3(CO)_8(\eta^1\text{-}C(OMe)Ph)\mu_3$-CPh$)(\mu_3\text{-}COMe)$ is illustrated in Fig. 1. Table 1 contains selected bonding parameters; Table 2 lists the atomic coordinates and thermal parameters. The overall geometry of the complex is similar to that of the parent compound $Os_3(CO)_9(\mu_3$-CPh$)(\mu_3\text{-}COMe)$ [3]. However, in this case the Os_3 triangle is nearly isosceles, with the Os–Os edge facing the carbene ligand (Os(2)–Os(3) 2.7821(4) Å) slightly, but significantly, shorter than the other two edges (Os(1)–Os(2) 2.8288(4) Å and Os(1)–Os(3) 2.8286(4) Å). The average Os–Os distance in this derivative (2.8132(4) Å) is longer than that in the parent compound (2.805(1) Å) [3].

The μ_3-COMe ligand caps the triosmium core with Os(1)–C(1) 2.081(7), Os(2)–C(1) 2.084(7) and Os(3)–C(1) = 2.088(7) Å (average Os–COMe 2.084(7) Å). The internal bond length of C(1)–O(1) 1.340(8) Å is 0.095 Å shorter than the length
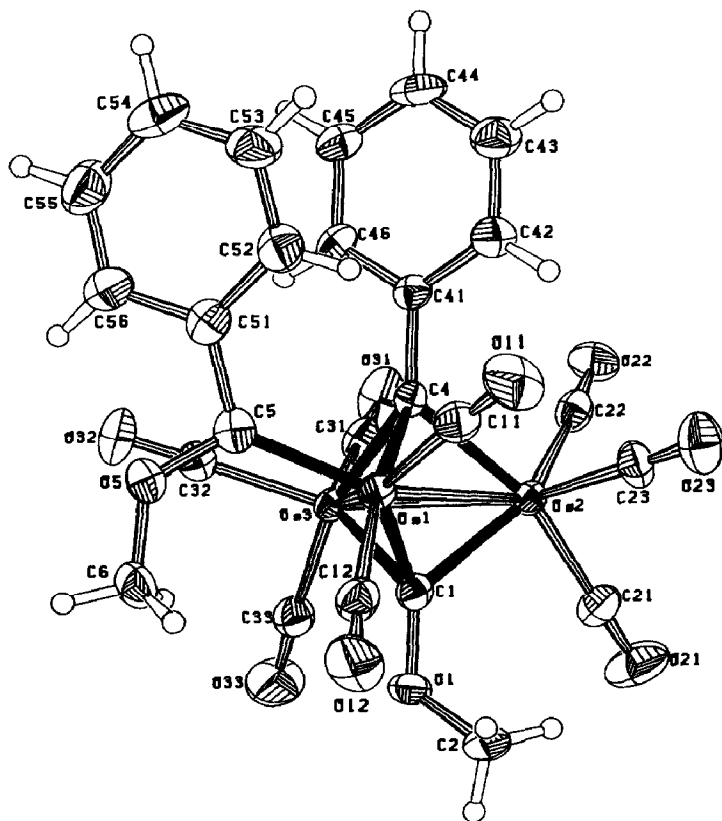

Fig. 1. Geometry and atomic labeling scheme for $Os_3(CO)_8(\eta^1\text{-}C(OMe)Ph)$-$(\mu_3$-CPh$)(\mu_3\text{-}COMe)$.

O(1)–C(2) 1.434(10) Å, suggesting a slight multiple-bond character for the C(1)–O(1) linkage.

The Os–CPh bond lengths are less regular, with Os(1)–C(4) 2.098(7), Os(2)–C(4) 2.137(7) and Os(3)–C(4) 2.144(7) Å, averaging 2.126(7) Å, which is 0.042 Å longer than the average Os–COMe distance. A similar difference was determined for the present compound: avg Os–COMe 2.081(19); avg Os–CPh 2.128(10) Å [3].

The phenylmethoxycarbene group is nearly coplanar and terminally bound to Os(1) in a position approximately *trans* to the Os(1)–Os(2) vector (angle Os(2)–Os(1)–C(5) 143.6(2)°). There is no direct interaction between the carbene carbon and the benzylidyne carbon. The osmium–carbon distance in the carbene, 2.037(4) Å is significantly longer than in the carbonyls (range 1.890(8)–1.934(8) Å). The C–O bond length difference in the C–O–Me moiety is 0.116 Å (C(5)–O(5) 1.314(9) Å and O(5)–C(6) 1.430(10) Å). The angles Os(1)-C(5)-O(5) 124.7°, Os(1)–C(5)–C(51) 127.5(5)° and O(5)–C(5)–C(51) 107.3(6)° are comparable with those previously reported for Fischer-type carbene complexes [4].

Spectroscopic characterization. The IR spectrum in the carbonyl region is very similar to that of $Os_3(CO)_8(PPh_3)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ [3]. Assignments of the phenyl protons in the ^1H NMR spectrum (δ 7.61–7.09) are based on the coupling constants and splitting pattern. A 3H singlet at δ 4.54 is assigned to the methoxy-carbyne protons, since it remains sharp at $-30°C$, whereas the 3H signal at δ 4.32 broadens. The latter effect is attributed to hindered C–OMe bond rotation in the carbene group [5,6].

The ^{13}C NMR spectrum of $Os_3(^{*}CO)_8(\eta^1\text{-}^{*}C(OMe)Ph)(\mu_3\text{-}^{*}CPh)(\mu_3\text{-}^{*}COMe)$ at 17°C shows the resonances for the methoxycarbyne carbon at δ 323.3, the phenylmethoxycarbene carbon at δ 277.3, the benzylidyne carbon at δ 226.6, and the carbonyl carbons at δ 180.7 and 176.9 (ratio of 2/6). Assignments of the alkylidyne carbons are based on the resonances observed for the parent compound $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (δ 319.3, $\equiv COMe$; δ 234.6, $\equiv CPh$) [3]. The 2C signal at δ 180.7, assigned to the two carbonyl in the $Os(CO)_2(C(OMe)Ph)$ moiety, is slightly downfield of the 6C signal at δ 176.9 for the six carbonyls in the $Os(CO)_3$ groups ($\Delta\delta$ 3.8 ppm); this is due to replacement of a carbonyl ligand by the stronger σ-donor carbene ligand and compares with similar shifts in $Os_3(CO)_8(PPh_3)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ ($\Delta\delta$ 8.7 ppm) [3] and in $Os_3(CO)_8(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)_2$ ($\Delta\delta$ 2.8 ppm) [2]. The carbene signal at δ 277.3 is comparable to those measured for $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OEt)Ph)(\mu,\eta^2\text{-}C(O)Me)$ (δ 285.5) [7a] and $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)Me)(\mu,\eta^2\text{-}C(O)Me)$ (δ 282.4) [7b], but significantly downfield of the di-oxycarbene resonances for $Ru_3(CO)_{10}(\eta^1\text{-}C(OCH_2)_2)_2$ (δ 231.8) [8] and $(\mu\text{-}H)Os_3(CO)_9(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)$ (av. δ 219) [9] and $Os_3(CO)_8(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)_2$ (δ 220.4) [2]. This deshielding effect is attributed to decreasing π-electron donating substituents (OR groups) on the carbene carbon; the same behavior has been described in mononuclear carbene-metal systems [10].

On the basis of the solid-state structure (see Fig. 1), a relatively complicated ^{13}C NMR spectrum would be predicted. However, it is likely that several conformational equilibration processes lead to the simple spectrum observed. Local site-exchange in the $Os(CO)_3$ groups (pseudo three-fold rotation) is fast even at $-100°C$ for the parent compound [3], and the same is apparently true for this carbene derivative. Rotation about the Os(1)–C(5) carbene bond should also be relatively unhindered, since there are no obvious strong orientational preferences.

Table 1

Selected bond distances (Å) and angles ($^\circ$) for Os$_3$(CO)$_8$(η^1-C(OMe)Ph)(μ_3-CPH)(μ_3-COMe)

Os(1)-Os(2)	2.8288(4)	Os(1)-Os(3)	2.8286(4)	Os(2)-Os(3)	2.7821(4)
Os(1)-C(1)	2.081(7)	Os(2)-C(1)	2.084(7)	Os(3)-C(1)	2.088(7)
O(1)-C(1)	1.340(8)	O(1)-C(2)	1.435(10)	Os(1)-C(4)	2.098(7)
Os(2)-C(4)	2.137(7)	Os(3)-C(4)	2.144(7)	Os(1)-C(5)	2.034(7)
O(5)-C(5)	1.314(9)	O(5)-C(6)	1.430(10)	Os(1)-C(11)	1.908(8)
O(11)-C(11)	1.13(1)	Os(1)-C(12)	1.934(8)	O(12)-C(12)	1.15(1)
Os(2)-C(21)	1.956(9)	O(21)-C(21)	1.12(1)	Os(2)-C(22)	1.930(8)
O(22)-C(22)	1.121(10)	O(22)-C(23)	1.881(8)	O(23)-C(23)	1.14(1)
Os(3)-C(31)	1.890(8)	O(31)-C(31)	1.16(1)	Os(3)-C(32)	1.915(7)
O(32)-C(32)	1.131(10)	Os(3)-C(33)	1.935(9)	O(33)-C(33)	1.13(1)
C(4)-C(41)	1.485(9)	C(5)-C(51)	1.48(1)		
Os(2)-Os(1)-Os(3)	58.91(1)	Os(2)-Os(1)-C(1)	47.3(2)	Os(2)-Os(1)-C(4)	48.7(2)
Os(2)-Os(1)-C(5)	143.6(2)	Os(2)-Os(1)-C(11)	96.9(2)	Os(2)-Os(1)-C(12)	121.6(3)
Os(3)-Os(1)-C(1)	47.4(2)	Os(3)-Os(1)-C(4)	48.9(2)	Os(3)-Os(1)-C(5)	92.3(2)
Os(3)-Os(1)-C(11)	146.3(2)	Os(3)-Os(1)-C(12)	124.6(2)	C(1)-Os(1)-C(4)	79.7(3)
C(1)-Os(1)-C(5)	129.0(3)	C(1)-Os(1)-C(11)	133.5(3)	C(1)-Os(1)-C(12)	90.0(3)
C(4)-Os(1)-C(5)	96.2(3)	C(4)-Os(1)-C(11)	97.9(3)	C(4)-Os(1)-C(12)	169.4(3)
C(5)-Os(1)-C(11)	97.4(3)	C(5)-Os(1)-C(12)	92.4(3)	C(11)-Os(1)-C(12)	87.2(3)
Os(1)-Os(2)-Os(3)	60.54(1)	Os(1)-Os(2)-C(1)	47.2(2)	Os(1)-Os(2)-C(4)	47.5(2)

Os(1)–Os(2)–C(21)	130.1(2)	Os(1)–Os(2)–C(22)	134.4(2)	Os(1)–Os(2)–C(23)	93.2(3)
Os(3)–Os(2)–C(1)	48.2(2)	Os(3)–Os(2)–C(4)	49.6(2)	Os(3)–Os(2)–C(21)	109.8(3)
Os(3)–Os(2)–C(22)	98.7(2)	Os(3)–Os(2)–C(23)	151.9(3)	C(1)–Os(2)–C(4)	78.7(3)
C(1)–Os(2)–C(21)	88.1(3)	C(1)–Os(2)–C(22)	144.8(3)	C(1)–Os(2)–C(23)	122.0(3)
C(4)–Os(2)–C(21)	159.2(3)	C(4)–Os(2)–C(22)	87.5(3)	C(4)–Os(2)–C(23)	105.9(3)
C(21)–Os(2)–C(22)	94.3(3)	C(21)–Os(2)–C(23)	94.7(4)	C(22)–Os(2)–C(23)	92.9(3)
Os(1)–Os(3)–Os(2)	60.55(1)	Os(1)–Os(3)–C(1)	47.2(2)	Os(1)–Os(3)–C(4)	47.5(2)
Os(1)–Os(3)–C(31)	137.4(2)	Os(1)–Os(3)–C(32)	97.7(2)	Os(1)–Os(3)–C(33)	124.9(3)
Os(2)–Os(3)–C(1)	48.1(2)	Os(2)–Os(3)–C(4)	49.4(2)	Os(2)–Os(3)–C(31)	91.7(2)
Os(2)–Os(3)–C(32)	151.4(2)	Os(2)–Os(3)–C(33)	115.2(3)	C(1)–Os(3)–C(4)	78.5(3)
C(1)–Os(3)–C(31)	134.7(3)	C(1)–Os(3)–C(32)	131.1(3)	C(1)–Os(3)–C(33)	87.1(3)
C(4)–Os(3)–C(31)	90.0(3)	C(4)–Os(3)–C(32)	102.6(3)	C(4)–Os(3)–C(33)	164.0(3)
C(31)–Os(3)–C(32)	94.0(3)	C(31)–Os(3)–C(33)	95.2(3)	C(32)–Os(3)–C(33)	92.2(3)
C(1)–O(1)–C(2)	118.8(5)	C(5)–O(5)–C(6)	125.6(6)	Os(1)–C(1)–Os(2)	85.6(3)
Os(1)–C(1)–Os(3)	85.5(3)	Os(1)–C(1)–O(1)	129.4(5)	Os(2)–C(1)–Os(3)	83.6(2)
Os(2)–C(1)–O(1)	131.8(5)	Os(3)–C(1)–O(1)	125.0(5)	Os(1)–C(4)–Os(2)	83.8(2)
Os(1)–C(4)–Os(3)	83.6(2)	Os(1)–C(4)–C(41)	131.2(5)	Os(2)–C(4)–Os(3)	81.1(2)
Os(2)–C(4)–C(41)	127.9(5)	Os(3)–C(4)–C(41)	131.3(5)	Os(1)–C(5)–O(5)	124.7(5)
Os(1)–C(5)–C(51)	127.5(5)	O(5)–C(5)–C(51)	107.3(6)	Os(1)–C(11)–O(11)	174.3(8)
Os(1)–C(12)–O(12)	173.4(7)	Os(2)–C(21)–O(21)	176.3(8)	Os(2)–C(22)–O(22)	176.7(7)
Os(2)–C(23)–O(23)	178.3(8)	Os(3)–C(31)–O(31)	176.7(7)	Os(3)–C(32)–O(32)	178.2(7)
Os(3)–C(33)–O(33)	178.2(8)	C(4)–C(41)–C(42)	120.1(6)	C(4)–C(41)–C(46)	122.0(6)
C(5)–C(51)–C(52)	122.3(7)	C(5)–C(51)–C(56)	119.9(7)		

Table 2

Atomic coordinates and thermal parameters

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Os(1)	0.81987(3)	0.31336(2)	0.81220(3)	0.0378(2)	0.0296(2)	0.0328(2)	−0.0044(1)	0.0151(1)	−0.0060(1)
Os(2)	1.00661(3)	0.33476(2)	0.67124(3)	0.0387(2)	0.0305(2)	0.0332(2)	0.0032(1)	0.0137(1)	−0.0119(1)
Os(3)	1.01386(3)	0.16078(2)	0.76987(3)	0.0349(2)	0.0261(2)	0.0381(2)	−0.0035(1)	0.0134(1)	−0.0069(1)
O(1)	1.1339(6)	0.2942(3)	1.0238(5)	0.054(3)	0.041(3)	0.031(3)	−0.002(2)	0.001(2)	−0.011(3)
O(5)	0.7138(6)	0.1792(4)	0.9394(6)	0.057(3)	0.057(4)	0.042(3)	0.004(2)	0.022(3)	−0.018(3)
O(11)	0.6034(8)	0.4830(4)	0.6634(7)	0.083(5)	0.041(4)	0.081(4)	0.009(3)	0.015(4)	0.020(4)
O(12)	0.8336(8)	0.4085(5)	1.1156(7)	0.119(6)	0.061(4)	0.056(4)	−0.018(3)	0.046(4)	−0.014(4)
O(21)	1.3037(7)	0.3779(6)	0.8072(8)	0.057(4)	0.127(7)	0.092(5)	−0.031(5)	0.027(4)	−0.048(5)
O(22)	1.0275(6)	0.2775(4)	0.3635(6)	0.062(4)	0.072(4)	0.042(3)	−0.010(3)	0.020(3)	−0.010(3)
O(23)	0.8561(8)	0.5292(4)	0.5692(7)	0.097(5)	0.048(4)	0.086(5)	0.006(3)	0.051(4)	−0.005(4)
O(31)	1.0858(8)	0.0727(4)	0.5020(8)	0.103(6)	0.060(4)	0.100(5)	−0.029(4)	0.076(5)	−0.028(4)
O(32)	0.86711(7)	0.0109(4)	0.8023(7)	0.078(4)	0.048(4)	0.092(5)	−0.001(3)	0.050(4)	−0.025(3)
O(33)	1.29238(8)	0.0751(5)	1.0188(9)	0.060(5)	0.073(5)	0.105(5)	0.022(4)	−0.010(4)	0.002(4)
C(1)	1.0377(8)	0.2852(5)	0.8849(8)	0.039(4)	0.030(4)	0.042(4)	0.000(3)	0.014(3)	−0.005(3)
C(2)	1.156(1)	0.3848(6)	1.0768(8)	0.078(6)	0.054(5)	0.038(4)	−0.012(4)	0.008(4)	−0.028(5)
C(4)	0.8453(7)	0.2558(5)	0.6133(7)	0.034(4)	0.032(4)	0.037(4)	−0.001(3)	0.016(3)	−0.010(3)
C(5)	0.6901(8)	0.2315(5)	0.8221(8)	0.039(4)	0.041(4)	0.051(4)	−0.000(4)	0.027(4)	0.000(4)

C(6)	0.8322(9)	0.1725(6)	1.0800(8)	0.073(6)	0.061(6)	0.042(4)	0.002(4)	0.030(4)	-0.019(5)
C(11)	0.6787(9)	0.4184(6)	0.7204(8)	0.056(5)	0.046(5)	0.041(4)	-0.011(4)	0.018(4)	-0.014(4)
C(12)	0.8325(9)	0.3682(6)	1.0074(9)	0.059(5)	0.042(5)	0.052(5)	-0.007(4)	0.023(4)	-0.016(4)
C(21)	1.1938(10)	0.3646(6)	0.7603(9)	0.056(6)	0.057(5)	0.058(5)	-0.013(4)	0.025(4)	-0.026(5)
C(22)	1.0201(8)	0.3011(5)	0.4758(9)	0.044(5)	0.033(4)	0.056(5)	-0.002(4)	0.021(4)	-0.008(4)
C(23)	0.9144(10)	0.4562(6)	0.6069(8)	0.074(6)	0.039(5)	0.044(4)	0.003(4)	0.029(4)	-0.012(4)
C(31)	1.0602(8)	0.1036(5)	0.6060(9)	0.048(5)	0.032(4)	0.062(5)	-0.011(4)	0.027(4)	-0.017(4)
C(32)	0.9222(8)	0.0657(5)	0.7885(8)	0.049(5)	0.033(4)	0.044(4)	-0.004(3)	0.021(4)	-0.005(4)
C(33)	1.1887(10)	0.1055(6)	0.9273(10)	0.052(6)	0.044(5)	0.060(5)	0.007(4)	0.008(4)	-0.012(4)
C(41)	0.7407(7)	0.2422(5)	0.4598(7)	0.029(4)	0.043(4)	0.038(4)	-0.002(3)	0.016(3)	-0.008(3)
C(42)	0.6691(8)	0.3177(5)	0.3599(8)	0.044(5)	0.042(5)	0.048(4)	-0.006(4)	0.015(4)	-0.004(4)
C(43)	0.5690(9)	0.3076(6)	0.2197(10)	0.048(5)	0.058(6)	0.061(5)	-0.001(4)	0.009(4)	-0.006(4)
C(44)	0.5360(9)	0.2221(7)	0.1723(10)	0.043(5)	0.091(7)	0.045(5)	-0.011(5)	-0.001(4)	-0.025(5)
C(45)	0.6034(9)	0.1480(6)	0.2681(9)	0.058(6)	0.059(6)	0.050(5)	-0.011(4)	0.012(4)	-0.026(5)
C(46)	0.7079(8)	0.1576(5)	0.4119(8)	0.043(4)	0.035(4)	0.048(4)	-0.012(3)	0.017(4)	-0.015(4)
C(51)	0.5651(8)	0.2093(5)	0.6961(9)	0.038(4)	0.051(5)	0.054(5)	-0.004(4)	0.026(4)	-0.007(4)
C(52)	0.4833(8)	0.2702(6)	0.5745(9)	0.041(5)	0.062(6)	0.064(5)	0.008(4)	0.023(4)	-0.007(4)
C(53)	0.3724(9)	0.2451(8)	0.4571(10)	0.038(5)	0.101(8)	0.058(5)	0.009(5)	0.010(4)	-0.014(5)
C(54)	0.3395(10)	0.1611(8)	0.453(1)	0.043(5)	0.090(8)	0.077(7)	-0.022(6)	0.016(5)	-0.027(5)
C(55)	0.420(1)	0.0991(7)	0.571(1)	0.073(7)	0.055(6)	0.102(8)	0.002(6)	0.024(6)	-0.026(5)
C(56)	0.5292(10)	0.1224(7)	0.692(1)	0.058(6)	0.063(6)	0.064(5)	-0.000(4)	0.009(5)	-0.023(5)

Finally, it is interesting that this new compound, $Os_3(CO)_8(\eta^1\text{-}C(OMe)Ph)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$, is a structural isomer of the previously reported, spectroscopically characterized compound, $Os_3(CO)_8(\eta^1\text{-}C(OMe)_2)(\mu_3\text{-}CPh)_2$ [2]. Both compounds result from Ph^-/Me^+ treatments, but only the former is generated by a route that is directly analogous to the formation of Fischer carbenes at mononuclear centers [4]. It appears that two μ_3-carbyne ligands simplify the chemistry that may result from nucleophilic attach at a cluster carbonyl ligand. This parallels the observation that Ph^-/Et^+ treatment of the dinitrene cluster $Fe_3(CO)_9(\mu_3\text{-}NPh)$ also cleanly gives a (phenylethoxy)carbene derivative [11].

Experimental section

General procedures. $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ was prepared as previously described [3]. Phenyllithium (Alfa, 1.8 M in ether/benzene) and methyl trifluoro-methanesulfonate (Aldrich), were used directly as received. Methylcyclohexane, toluene, decane, and dodecane were distilled from sodium, and diethyl ether was distilled from sodium benzophenoneketyl before use. Dichloromethane was dried over phosphorous pentoxide and distilled before use. Preparative thin-layer chromatographic (TLC) plates were prepared from Silica Gel GF (Type 60, E. Merck). Melting points were determined in sealed capillaries. ^1H and ^{13}C NMR spectra were obtained on a Nicolet NT-360 spectrometer at 360 MHz and 90.56 MHz, respectively. IR spectra were taken on a Perkin–Elmer 281B spectrometer and were calibrated with polystyrene film and cyclohexane (2138.5 cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences. Field desorption mass spectra were obtained by the staff of the Mass Spectroscopy Laboratory of the School of Chemical Sciences on a Varian-MAT 731 mass spectrometer.

Sequential Ph^-/Me^+ treatment of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$. An oven-dried, 100 ml Schlenk flask was equipped with a magnetic stir bar and a rubber serum stopper, under a nitrogen atmosphere. A solution of $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (76 mg, 0.080 mmol) in diethyl ether (25 ml) was introduced by cannula. The flask was placed in an ice bath at $0\,^\circ C$ and phenyllithium (140 μl, 0.2 mmol) added via a syringe over a period of 5 min. The mixture was stirred for 30 min and methyltrifluoromethanesulfonate (100 μl, 0.88 mmol) added via a syringe. The solution was concentrated to ca. 5 ml under vacuum at $0\,^\circ C$, then placed under nitrogen and stirred for 30 min at $0\,^\circ C$. The volatile materials were removed under vacuum, and the residue subjected to TLC, eluting with n-pentane/dichloromethane (9/1). $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (15 mg, 20%) was recovered from the first, orange band. Crystallization of the second, red band from n-pentane yielded slightly thermally sensitive, red crystals of $Os_3(CO)_8(\eta^1\text{-}C(OMe)Ph)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (54 mg, 0.052 mmol, 66%). Anal. Found: C, 28.77; H, 1.52. $Os_3C_{25}H_{16}O_{10}$ calcd.: C, 28.66; H, 1.53%. Mass spectrum: m/z 1052 (M^+, ^{192}Os). IR (C_6H_{12}): $\nu(CO)$ 2076(m), 2048(s), 2013(s), 2003(m), 1984(m, br), 1953(w) cm^{-1}. ^1H NMR (CD_2Cl_2, $17\,^\circ C$): δ 7.60 (d, 2H, J 7.2 Hz), 7.42 (t, 1H, J 7.6 Hz), 7.30 (d, 2H, J 7.6 Hz), 7.22–7.10 (m, 5H), 4.54 (s, 3H), 4.32 (s, 3H). ^{13}C NMR (THF-d_8/diethyl ether (1/1), $17\,^\circ C$): δ 323.3 (s, C-OMe), 277.3 (s, $=C(OMe)Ph$), 226.6 (s, $\equiv C$–Ph), 180.7 (s, $2CO$), 176.9 (s, $6CO$).

The crystal of $Os_3(CO)_9(\eta^1\text{-}C(OMe)Ph)(\mu_3\text{-}COMe)$ found suitable for the X-ray diffraction study was grown from dichloromethane/methanol at $-20\,^\circ C$.

Crystal data: $C_{25}H_{16}O_{10}Os_3$, triclinic, $P\bar{1}$, a 10.491(s), b 14.834(6), c 9.461(3) Å, α 94.02(3), β 112.12(2), γ 78.03(3)°, V 1334(1) Å^3, $Z = 2$, ρ(calc) 2.606 g cm^{-3}, μ(Mo-K_α) 143.2 cm^{-1}, temp. 297 K. Enraf–Nonius CAD-4 diffractometer, crystal transparent red (0.12 × 0.20 × 0.27 mm), 3959 data collected (shell 1, 2° < 2θ < 36°, for $\pm h$, $+k$, $\pm l$; shell 2, 36° < 2θ < 46°), 3713 data unique, and 3286 observed, $I_0 \geq 2.58\sigma(I_0)$; $R_i = 0.0155$. The data were corrected for Lorentz and polarization effects, anomalous dispersion, extinction, and absorption (numerical; max, min transmission factors: 0.262, 0.100).

Structure solution and refinement. The structure was solved by direct methods (MULTAN 80); correct positions for the osmium atoms were deduced from an E-map. The remaining nonhydrogen atoms were located by weighted difference Fourier techniques. Hydrogen atoms were included in idealized positions, with d(C–H) 0.95 Å, in either trigonal or tetrahedral geometries. In the final cycle of least squares, all non-hydrogen atoms were refined independently with anisotropic thermal coefficients and a group isotropic thermal parameter was varied for the hydrogen atoms. Convergence was indicated by the maximum shift/error for the last cycle; $R_F = 0.023$, $R_{wF} = 0.031$. The final difference Fourier had a large number of peaks located near the osmium atoms, indicating an insufficient absorption correction; however, this was not considered a major problem, due to the low intensity of these peaks (approximately 1.5 eÅ^{-3}). There were no apparent systematic errors among the final observed and calculated structure factors.

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