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Conversion of the clusters $[Os_3(1,3\text{-diyne})(CO)_{10}]$ into bis(alkynyl) clusters by carbon–carbon bond cleavage

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Abstract

The symmetrical 1,3-diynes, RC_2C_2R (R = Me, Et, Ph, Bu^t, $SiMe_3$), react with $[Os_3(CO)_{10}(MeCN)_2]$ to give the clusters $[Os_3(\mu_3,\eta^2\text{-}RC_2C_2R)(\mu\text{-}CO)(CO)_9]$. The μ_3,η^2-coordinated alkyne group does not exchange with the non-coordinated one. As a consequence the unsymmetrical diyne, $PhC_2C_2SiMe_3$, gives non-interconverting and separable isomers of $[Os_3(\mu_3\eta^2\text{-}PhC_2C_2SiMe_3)(\mu\text{-}CO)(CO)_9]$ which differ only in which of the two alkyne groups is coordinated. Thermal decarbonylations of the compounds containing RC_2C_2R (R = Ph, Bu^t or $SiMe_3$) and the isomers containing the unsymmetrical diyne, $PhC_2C_2SiMe_3$, lead by carbon–carbon bond cleavage to bis(alkynyl) clusters of the type $[Os_3(\mu,\eta^1\text{-}C_2R^1)(\mu_3,\eta^2\text{-}C_2R^2)(CO)_9]$ where $R_1 = R_2 =$ Ph, Bu^t $SiMe_3$ and only one isomer from the mixed diyne with R^1 = Ph and $R^2 = SiMe_3$. XRD studies on this isomer established that C_2SiMe_3 is in the triply-bridging position and C_2Ph in the doubly-bridging position. Although the C_2Ph ligand is only bonded through the α-carbon atom, we consider it to be σ, π-bonded and a three-electron donor. It spans two osmium atoms that are not bonded (Os...Os = 3.297(2) Å). Thermolysis of the EtC_2C_2Et complex leads to carbon–hydrogen rather than carbon–carbon cleavage to give the allenyl cluster $[Os_3H(\mu_3,\eta^2,\eta^2\text{-}MeCH{=}C{=}C{-}C_2Et)(CO)_9]$, while the MeC_2C_2Me cluster decarbonylates to $[Os_3(C_4Me_2)(CO)_9]$ of unknown structure but which may be $[Os_3(CMe)(CC_2Me)(CO)_9]$.

Introduction

1,4-Disubstituted buta-1,3-diynes have been used previously as ligands with transition metals with the idea of linking metal or metal cluster fragments by forming separate η^2-interactions to more than one of these. For example, PhC_2C_2Ph reacts with $[Pt(C_2H_4)(PPh_3)_2]$ to give $[Pt(\eta^2\text{-}PhC_2C_2Ph)(PPh_3)_2]$ which reacts further with the platinum ethene complex to give $[Pt_2(\mu,\eta^2,\eta^2\text{-}PhC_2C_2Ph)(PPh_3)_4]$ [1]. The diyne is believed to bridge two $Pt(PPh_3)_2$ units. Likewise hexa-2,4-diyne (MeC_2C_2Me) and other diynes link two $Co_2(CO)_6$ units in $[Co_4(CO)_{12}(\mu_4,\eta^2,\eta^2\text{-}MeC_2C_2Me)]$ and related complexes [2]. Sometime ago we reported in a communication the reaction of RC_2C_2R (R = Ph, Bu^t or $SiMe_3$) with $[Os_3(CO)_{10}(MeCN)_2]$ to give the cluster $[Os_3(CO)_{10}(\mu_3,\eta^2\text{-}RC_2C_2R)]$ in which only one of the two alkyne groups is coordinated [3]. We were unable to link another Os_3 cluster to the free alkyne but reported that thermal decarbonylation leads to cleavage of the central carbon–carbon bond to give the bis(alkynyl) clusters $[Os_3(C_2R)_2(CO)_9]$. The X-ray structure when R = Ph showed that one C_2R ligand is μ_3,η^2 coordinated and the other μ_2,η^1 coordinated. In this paper we give a full account of our results and describe the use of the unsymmetrical diyne, $PhC_2C_2SiMe_3$, in an attempt to identify the sites into which the alkyne groups migrate after carbon–carbon bond cleavage has occurred.

Results and discussion

Decarbonyl clusters

Reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with the diynes $R^1C_2C_2R^2$ ($R^1 = R^2 =$ Me, Et, Ph, Bu^t, $SiMe_3$ or $R^1 = SiMe_3$ and R^2 = Ph or Pr^i) occur to give low to moderate yields of the clusters $[Os_3(R^1C_2C_2R^2)(CO)_{10}]$. These were isolated by TLC on silica, some as yellow or orange crystals, others as oils. Elemental analysis confirmed the stoichiometry in several cases and they were shown to belong to a single class of compounds containing a μ_3,η^2 alkyne [4]. Only one alkyne group is coordinated in each case. The IR spectra around 2000 cm^{-1} for these compounds are closely similar and

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all show ν(CO) absorptions in the region 1844 to 1849 cm^{-1} (Table 1) consistent with structures having bridging carbonyl ligands. Two extreme structures (Fig. 1(a) and (b)) have been characterised for alkyne complexes of this kind, although some compounds lie between the extremes and some give isomers in solution [4]. The diyne complexes described here appear to be close to type (a).

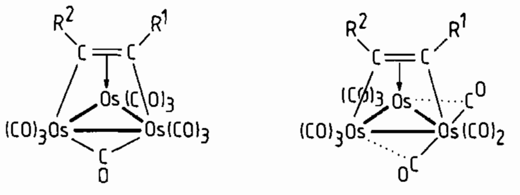
The complexes $[Os_3(RC_2C_2R)(CO)_{10}]$ (R = Me, Et, Bu^t, $SiMe_3$) show separate ^1H NMR signals for the non-equivalent R groups (Table 1) so that there is no dynamic exchange between the free and coordinated alkyne groups. For R = Et the free ethyl group appears as a simple quartet and triplet even though the methylene protons are diastereotopic, whereas the CH_2 group bonded to the metal-bound alkyne contains clearly diastereotopic protons. At −50 °C an AB quartet of 1:3:3:1 quartets at δ 2.70 and 2.23 (AB component of an ABX_3 system) is observed. These signals broaden considerably at 20 °C as dynamic mobility of the alkyne is rapid enough to have an effect. A rotation-flipping process as described for simple monoyne clusters of this type [5] would exchange the diastereotopic methylene protons.

Consistent with the lack of exchange of the free and the coordinated alkynes in these compounds, two isomers of the cluster $[Os_3(PhC_2C_2SiMe_3)(CO)_{10}]$ were obtained and easily separated by TLC on silica; isomer 1 has coordinated PhC_2R and isomer 2 has coordinated Me_3SiC_2R (Fig. 2). Although the IR spectra of these isomers around 2000 cm^{-1} are similar, they are easily distinguishable. Since these compare closely with the spectra of the $Me_3SiC_2C_2SiMe_3$ and PhC_2C_2Ph clusters, respectively (Fig. 3), we can identify the alkyne which is coordinated in each case. ^1H NMR evidence confirmed the assignments of structure because there are small but distinct coordination shifts. Thus free $Me_3SiC_2C_2SiMe_3$ gives a singlet at δ 0.08 close to that observed in isomer 1 (δ 0.07), whereas isomer 2 has a singlet at δ 0.20. The cluster $[Os_3(Me_3SiC_2C_2SiMe_3)(CO)_{10}]$ has two singlets at δ 0.09 (uncoordinated alkyne) and 0.15 (coordinated alkyne). There was no evidence for the interconversion of isomers 1 and 2 in solution at room temperature.

TABLE 1. Spectroscopic data (IR, ^1H NMR) for decarbonyl clusters of the type $[Os_3(CO)_{10}(\mu_3\text{-diyne})]$

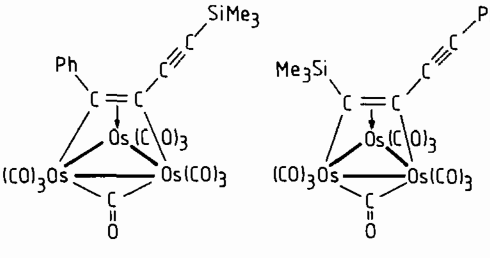
Diyne	ν(CO)[a] (cm^{-1})	^1H NMR[b]
MeC_2C_2Me	2089m 2058vs 2023vs 2006s 1999vs 1985sh 1844br	2.54 (s, Me) 2.01 (s, Me)
EtC_2C_2Et	2097m 2062vs 2056vs 2024vs 2006s 1999s 1985sh 1966sh 1845br	2.70 (m, 1H, CH_2) 2.23 (m, 1H, CH_2) 2.33 (q, 2H, CH_2) 1.18 (t, CH_3) 1.07 (t, CH_3)
PhC_2C_2Ph	2098m 2064vs 2051vs 2027vs 2007s 1984sh 1968sh 1848br	7.1–7.3 (m, Ph)
$Me_3SiC_2C_2SiMe_3$	2097m 2058br 2021vs 2007s 2000s 1987sh 1849br	0.15 (s, Me) 0.09 (s, Me)
$Bu^tC_2C_2Bu^t$	2096m 2060vs 2054vs 2021s 2004s 1998s 1843br	1.27 (s, Me) 1.13 (s, Me)
$PhC_2C_2SiMe_3$ Isomer 1	2100m 2068vs 2054vs 2029vs 2009s 1982sh 1965sh 1848br	7.15–7.35 (m, Ph) 0.07 (s, $SiMe_3$)
$PhC_2C_2SiMe_3$ Isomer 2	2097m 2059vs 2057vs 2022vs 2007s 2000s 1987sh 1849br	7.30 (m, Ph) 0.20 (s, $SiMe_3$)
$Pr^iC_2C_2SiMe_3$	2097m 2062vs 2056vs 2024s 2006s 2000s 1980sh 1848br	2.30 (sept, $CHMe_2$) 1.16 (d, $CHMe_2$) 0.88 (d, $CHMe_2$) 0.08 (s, $SiMe_3$)

[a] Recorded in n-hexane. [b] Recorded at 200 MHz at 20 °C for the MeC_2C_2Me, PhC_2C_2Ph and $Me_3SiC_2C_2SiMe_3$ compounds; at 200 MHz at −50 °C for the EtC_2C_2Et and $Pr^iC_2C_2SiMe_3$; at 400 MHz at 20 °C for the two isomers containing $PhC_2C_2SiMe_3$ ligands.



(a) (b)

Fig. 1. Two extreme structures found for clusters of the type $[Os_3(CO)_{10}(\mu_3\text{-}R^1C_2R^2)]$.



isomer 1 isomer 2

Fig. 2. Two separated isomers of the unsymmetrical alkyne clusters $[Os_3(CO)_{10}(\mu_3\text{-}Me_3SiC_2C_2Ph)]$.

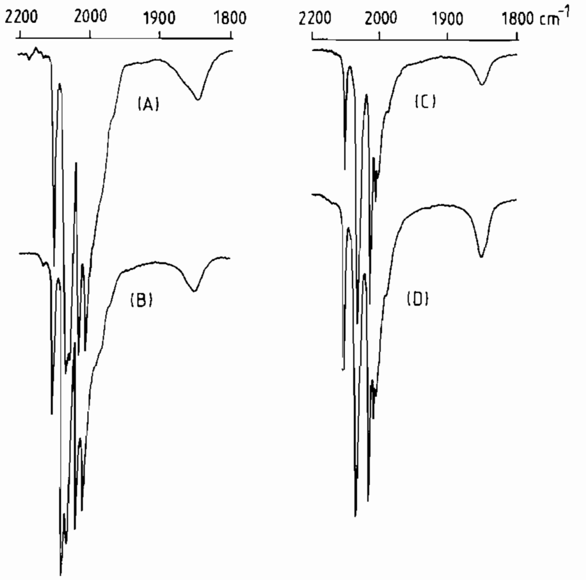


Fig. 3. IR spectra in the CO stretching region of cyclohexane solutions. (A) Isomer 1 of $[Os_3(CO)_{10}(\mu_3\text{-}PhC_2C_2SiMe_3)]$, (B) $[Os_3(CO)_{10}(PhC_2C_2Ph)]$, (C) isomer 2 of $[Os_3(CO)_{10}(\mu_3\text{-}PhC_2C_2SiMe_3)]$ and (D) $[Os_3(CO)_{10}(Me_3SiC_2C_2SiMe_3)]$, showing that, although the IR spectra are very similar, there are small distinct differences depending upon the alkyne which is coordinated.

Attempting to link two Os_3 clusters through the diyne, we dissolved the clusters $[Os_3(RC_2C_2R)(CO)_{10}]$ (R = Et or Ph) and $[Os_3(CO)_{10}(MeCN)_2]$ in dichloromethane, but observed no change in the IR spectrum even after several days at room temperature. We recovered the starting diyne complexes in essentially quantitative yield. Likewise the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 0.5 mol equivalent of PhC_2C_2Ph gave only $[Os_3(PhC_2C_2Ph)(CO)_{10}]$. It is very likely that it is excessive crowding that prevents two $Os_3(CO)_{10}$ units being bonded to the diyne ligand rather than electronic deactivation of the free triple bond towards coordination.

Nonacarbonyl clusters

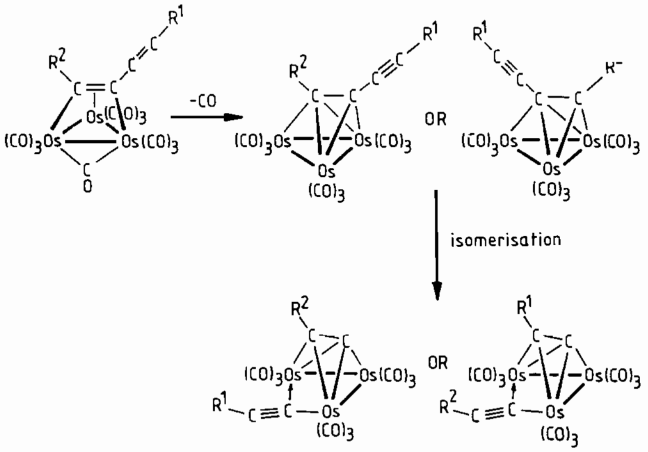
All the decacarbonyl clusters described above decarbonylate in refluxing octane. Except when R = Me or Et, the central carbon–carbon bond is cleaved to give the bis(alkynyl) clusters $[Os_3(C_2R)_2(CO)_9]$. The two C_2R ligands are non-equivalent which is clear from the NMR spectra (Table 2) and all these clusters appear to be isostructural. The X-ray structure of the bis(phenylethynyl) cluster, $[Os_3(\mu,\eta^1\text{-}C_2Ph)(\mu_3,\eta^2\text{-}C_2Ph)(CO)_9]$, was reported in our initial communication of this chemistry [3]. A similar thermal treatment of the two decacarbonyl isomers (1 and 2) of $[Os_3(PhC_2C_2SiMe_3)(CO)_{10}]$ gave a related bis(alkynyl) cluster. These reactions were carried out to establish whether it is the alkyne coordinated in the μ_3 position in the diyne cluster that remains in the μ_3 position in the cleaved product. The simplest process seemed to be for the non-coordinated alkyne group to migrate into the μ_2-position. Loss of CO from the decacarbonyl should initially give the intermediate $[Os_3(R^1C_2C_2R^2)(CO)_9]$ in which the parallel alkyne of the decacarbonyl has rotated into the perpendicular mode (Scheme 1). Such clusters have been structurally characterised for iron [6] and for mixed iron–ruthenium compounds [7]. $[Os_3(PhC_2Ph)(CO)_9]$ has been obtained but its structure is unknown [8] while the substituted derivative of this, $[Os_3(PhC_2Ph)(CO)_7(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$), was found to adopt the perpendicular geometry [9]. Subsequent isomerisation of the intermediate shown in Scheme 1 would require a transfer of the RC_2 group to the metal centre but since we obtain the same product from both isomers it is not clear which C_2R group migrates. The molecule is not ideally set up for conversion to $[Os_3(R^1C_2)(R^2C_2)(CO)_9]$ since either the transferred RC_2 group must migrate around the Os_3 cluster to find the Os–Os edge along which it is finally located in a μ_2 manner, or the $\mu_3\text{-}RC_2$ ligand must rotate with respect to the Os_3 triangle after cleavage has occurred. μ_3-Alkynyl ligands have been shown to rotate easily in this way [10]. Unfortunately we were unable to establish the details of the transformation because *both* isomers of the $PhC_2C_2SiMe_3$ cluster gave the same bis(alkynyl) isomer of $[Os_3(C_2Ph)(C_2SiMe_3)(CO)_9]$ and therefore we were unable to map out the course of the reaction. We were unable to show whether alkyne exchange occurred before or after the C–C bond cleavage. It would seem that there is a preference for Me_3SiC_2 to be triply-bridging or for PhC_2 to be doubly-bridging.

TABLE 2. Spectroscopic data (IR, ^{1}H and ^{13}C{^{1}H} NMR) for the nonacarbonyl clusters

Cluster	ν(CO)[a] (cm^{-1})	^{1}H NMR[b]	^{13}C NMR[c] (hydrocarbyl)	J_{HC}
$Os_3(C_2Ph)_2(CO)_9$	2092w 2072vs	7.84(m, *ortho*)	136.7 (μ_2-C_α)	
	2046vs 2011vs	7.49(m, *meta*)	136.2 (μ_2-*meta*)	
	2001s 1976m	7.45(m, *ortho*)	131.8 (μ_2-*para*)	
	1943vw	7.40(m, *meta*)	130.5 (μ_3-*ortho*/*meta*)	
		7.40(m, *para*)	129.6	
		7.34(m, *para*)	129.2 (μ_3-*meta*/*ortho*)	
			128.7 (μ_2-*ortho*)	
			128.4	
			128.2	
			118.7 (μ_2-*ipso*)	
			53.8 (μ_3-C_β)	
$Os_3(C_2SiMe_3)_2(CO)_9$	2092m 2067vs	0.50(s, Me)	133.1 (s, μ_2-C_α)	
	2045vs 2010vs	0.17(s, Me)	106.9 (m, μ_2-C_β)	
	2001vs 1978vs		51.5 (s, μ_3-C_α)	
	1972vs 1940w		35.1 (m, μ_3-C_β)	
			0.93 (q, $SiMe_3$)	120
			0.58 (q, $SiMe_3$)	120
$Os_3(C_2Bu^t)_2(CO)_9$	2089w 2067vs	1.57(s, Me)		
	2044vs 2010vs	1.13(s, Me)		
	1997vs 1973m			
	1942w			
$Os_3(C_2Ph)(C_2SiMe_3)(CO)_9$	2090w 2070vs	7.34(m, Ph)	136.9 (s, μ_2-C_α)	
	2043vs 2010vs	0.54(s, Me)	136.1 (dt, *meta*)	160, 6.3
	2002s 1998s		131.7 (dt, *para*)	162, 6.3
	1973m 1942w		128.7 (dd, *ortho*)	163, 6.5
			123.8 (m, μ_2-C_β)	
			118.8 (t, *ipso*)	6.3
			36.0 (m, μ_3-C_α)	
			29.8 (m, μ_3-C_β)	
			1.2 (q, $SiMe_3$)	142
$Os_3H(EtC_2{-}C{=}C{=}CHMe)(CO)_9$	2095s 2070vs	3.25(q, C*H*Me)		
	2040vs 2022vs	2.40(q, C*H*$_2$Me)		
	2011s 2002s	2.05(d, CH*Me*)		
	1992m 1982m	1.14(t, CH$_2$*Me*)		
	1952vw			
$Os_3(C_4Me_2)(CO)_9$	2097w 2071vs	3.67(s, Me)		
	2045vs 2038vs	2.11(s, Me)		
	2014s 2001s			
	1973m			
$Os_3H(C_2SiMe_3)(CO)_9$	2102w 2076vs	0.37(s, Me)		
	2053vs 2021vs	−24.7(OsH)		
	2015vs 1984s			
	1952w			

[a]Recorded in n-hexane. [b]Recorded in $CDCl_3$ at 200 MHz at 20 °C. [c]Recorded in $CDCl_3$ at 400 MHz.

We determined the X-ray structure of this mixed bis(alkynyl) cluster to confirm fully which alkynyl ligand was in which site. Although we could not grow a very good crystal, we went ahead with the determination because even a poorly refined structure would establish the overall geometry which we needed to confirm. Figure 4 shows the molecular structure and Table 3 gives selected bond lengths and angles for the mixed compound **A** together with corresponding data for $[Os_3(C_2Ph)_2(CO)_9]$ (**B**) [3]. The structures are very similar. The clusters contain only two osmium–osmium bonds (2.873(2) and 2.861(2) Å for **A**; 2.865(4) and 2.846(4) Å for **B**) while the pair of Os atoms bridged by the μ,η^1-C_2Ph ligand are considered to be non-bonded (3.261(2) Å for **A** and 3.257(4) Å for **B**). We had initially expected that the doubly-bridging ligand would behave as a 3-electron donor and coordinate in a μ,η^2-manner as found, for example, in $[Os_3(\mu,\eta^2$-



Scheme 1.

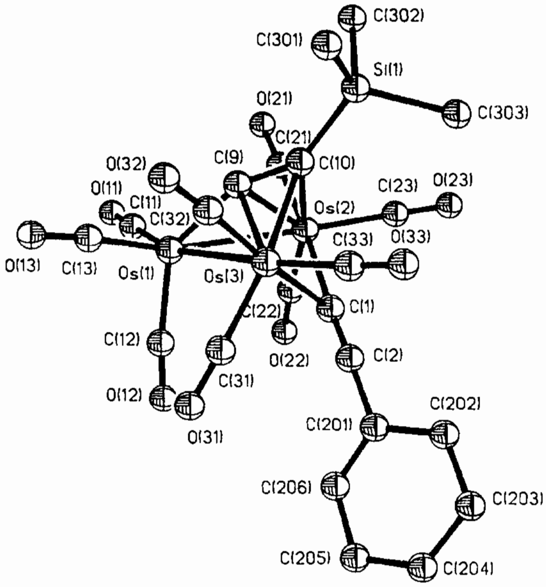


Fig. 4. Molecular structure of the mixed alkynyl cluster $[Os_3(\mu_3\text{-}C_2SiMe_3)(\mu_2\text{-}C_2Ph)(CO)_9]$.

would behave as a 3-electron donor and coordinate in a μ,η^2-manner as found, for example, in $[Os_3(\mu,\eta^2\text{-}C_2Ph)(AuPMe_2Ph)(CO)_{10}]$ [11]. However, alkynyl bridges are known to bridge two metal atoms in the geometries X, Y and Z (Fig. 5) [11, 12]. In the cluster $[Ru_3(\mu,\eta^1\text{-}C_2Bu^t)(\mu,\eta^2\text{-}C_2Bu^t)(PPh_2)_2(CO)_5(PPh_2Bu^t)]$ there is a normal 3-electron donor of type X and a 1-electron donor of type Z and the cluster is thereby electron-precise [12]. Figure 6 shows examples of the geometries X, Y and Z. Symmetrical alkynyl bridges are rare, indeed the only reported examples other than the triruthenium cluster are found for Be and Cu [13, 14]. The geometry Y found in the cluster $[Os_3(\mu,\eta^1\text{-}C_2Ph)(\mu_3,\eta^2\text{-}C_2Ph)(CO)_9]$ is reminiscent of the type of alkynyl bridge found in di-aluminium systems such as $[Al_2Me_4(\mu\text{-}C_2Me)_2]$ [15] and $[Al_2Ph_4(\mu\text{-}C_2Ph)_2]$ [16].

TABLE 3. Selected bond lengths and interatomic distances (Å) and bond angles (°) for the clusters $[Os_3(\mu\text{-}C_2Ph)(\mu_3\text{-}C_2R)(CO)_9]$ (R = Ph or $SiMe_3$)

	A R = $SiMe_3$	**B** R = Ph
Os(1)–Os(2)	2.873(2)	2.865(4)
Os(1)–Os(3)	2.861(2)	2.846(4)
Os(2)...Os(3)	3.297(2)	3.257(4)
Os(1)–C(9)	1.94(3)	1.92(2)
Os(2)–C(9)	2.25(3)	2.24(2)
Os(3)–C(9)	2.22(3)	2.25(2)
Os(2)–C(10)	2.28(3)	2.28(2)
Os(3)–C(10)	2.37(3)	2.30(2)
Os(2)–C(1)	2.08(3)	2.11(2)
Os(3)–C(1)	2.35(3)	2.25(2)
Os(3)...C(2)	2.66(3)	2.77(2)
C(1)–C(2)	1.17(4)	1.20(2)
C(9)–C(10)	1.29(3)	1.33(2)
Os(1)–C(9)–C(10)	156(2)	152(1)
C(9)–C(10)–Si(1)/C(11)	147(2)	142(2)
Os(2)–C(1)–C(2)	172(1)	161(1)
C(1)–C(2)–C(201)/C(3)	171(3)	177(4)
Os(1)–C(1)–Os(3)	96(1)	96.5(6)
Os(3)–C(1)–C(2)	92(2)	103(1)
Os(1)–C(9)–Os(2)	86(1)	86.8(8)
Os(1)–C(9)–Os(3)	87(1)	85.8(7)

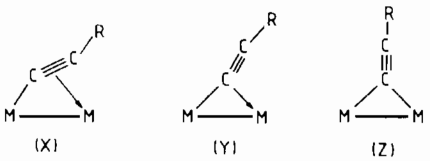


Fig. 5. Modes of μ_2-alkynyl bridging that have been identified in transition metal clusters: (X) μ_2,η^2 3-electron donor, (Y) μ_3,η^1 3-electron donor, (Z) μ_2,η^1 1-electron donor.

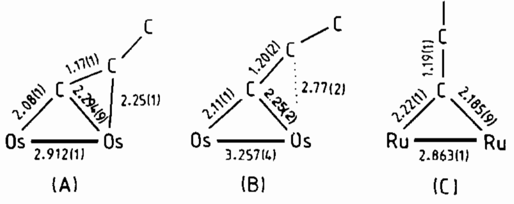
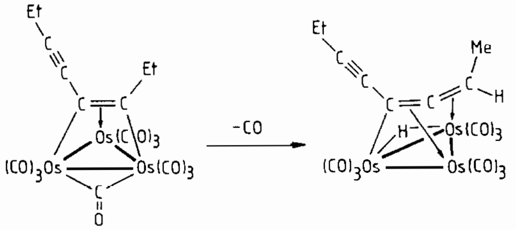


Fig. 6. Three examples of the bonding modes, X, Y, and Z, respectively: structure (A) is found in $[Os_3(\mu_2\text{-}C_2Ph)(AuPMe_2Ph)(CO)_{10}]$, structure (B) in $[Os_3(C_2Ph)_2(CO)_9]$ and structure (C) in $[Ru_3(C_2Bu^t)_2(PPh_2)(CO)_6(PPh_2C_2Bu^t)]$ (distances in Å). The M–M distance in (B) almost certainly means that there is no direct M–M bond.

We believe that the bridges in compounds **A** and **B** should be considered to be a σ,π-bonded but with an interaction with the π carbon–carbon orbital occurring through only one carbon atom. The closest distances of the β-carbon atoms C(2) to the metal atoms in **A** and **B** are 2.66(3) and 2.77(2) Å, respectively. We do not understand clearly the factors controlling the adoption of the geometries X or Y in these systems.

Decarbonylation of the ethyl-substituted cluster $[Os_3(CO)_{10}(EtC_2C_2Et)]$ under similar conditions gave



Scheme 2.

a 78% conversion to a species in which a C–H rather than a C–C bond had been cleaved. The ^1H NMR spectrum showed that there is a hydride ligand and that one of the ethyl groups has been transformed into a $CHCH_3$ group. The structure of $[Os_3(\mu\text{-}H)(EtC_2C{=}C{=}CHMe)(CO)_9]$ shown in Scheme 2 is largely based on a comparison with the chemistry of monoalkyne clusters of the type $[Os_3(CO)_{10}(RCH_2C_2R')]$ which decarbonylate to the μ_3,η^2,η^2-allenyl clusters $[Os_3(\mu\text{-}H)(RCH{=}C{=}CR')(CO)_9]$ and similar chemistry for ruthenium [17, 18]. The IR and NMR characteristics of the cluster are totally consistent with this formulation. Hence it would be easy to conclude that C–C bond cleavage of the diyne ligands occurs in the absence of available H atoms but that C–H cleavage is favoured if suitable groups are present. Although one might expect the cluster $[Os_3(CO)_{10}(MeC_2C_2Me)]$ to behave like the EtC_2C_2Et complex, decarbonylation of the hexa-2,4-diyne cluster does not yield the hydrido cluster $[Os_3(\mu\text{-}H)(MeC_2C{=}C{=}CH_2)(CO)_9]$. But neither does it give $[Os_3(C_2Me)_2(CO)_9]$. The product appears to be an isomer of these two complexes. The IR spectrum is not as expected for these and the ^1H NMR is also inconsistent with either. The spectrum contains only two equal intensity singlets at δ 2.11 and 3.67. The first of these could be compatible with a $C{\equiv}CMe$ group. The parent decacarbonyl has singlets at δ 2.54 and 2.01. However, the singlet at δ 3.67 is a long way from the expected shift for a cluster like any other in this paper. The signal is at exceptionally low field and seems only to be consistent with a ethylidyne ligand (CMe). The cluster $[Os_3H_3(\mu_3\text{-}CMe)(CO)_9]$ gives a singlet at δ 4.45 [19]. We might speculate that the cluster is $[Os_3(CMe)(CC_2Me)(CO)_9]$ but we could not grow suitable crystals for X-ray structure determination and have no other evidence to establish its structure. Why the chemistry in this case is so different from that of the other diynes is also unknown.

Experimental

The cluster $[Os_3(CO)_{10}(MeCN)_2]$ was synthesised as reported [20]. The diynes hexa-2,4-diyne and octa-3,5-diyne were prepared by a method similar to that given earlier [21]. The unsymmetrical diyne, 1-phenyl-4-trimethylsilylbutadiyne, was prepared from Me_3SiC_2Br [22], itself prepared from bis(trimethylsilyl)acetylene, by coupling with phenyl acetylene.

Synthesis of $[Os_3(CO)_{10}(MeC_2C_2Me)]$

Hexa-2,4-diyne (0.025 g, 0.32 mmol) was added to a solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.241 g, 0.258 mmol) in dried dichloromethane (30 cm^3) and the solution changed in colour within 15 min from yellow to dark red. An IR spectrum showed that the starting cluster had been consumed. The solvent was removed and TLC (SiO_2, eluant: light petroleum (b.p. 30–40 °C)) gave an orange oil characterised as $[Os_3(MeC_2C_2Me)(CO)_{10}]$ (0.038 g, 16%).

Synthesis of $[Os_3(CO)_{10}(EtC_2C_2Et)]$

A similar reaction between $[Os_3(CO)_{10}(MeCN)_2]$ and an excess of freshly distilled octa-3,4-diyne in dichloromethane at room temperature for 90 min gave one major TLC band yielding yellow crystals of the product (36%). *Anal.* Found: C, 22.6; H, 1.1; O, 17.5. Calc. for $C_{18}H_{10}O_{10}Os_3$: C, 22.6; H, 1.1; O, 16.7%.

Synthesis of $[Os_3(CO)_{10}(PhC_2C_2Ph)]$

Reaction between $[Os_3(CO)_{10}(MeCN)_2]$ (0.311 g, 0.334 mmol) and 1,4-diphenylbutadiyne (0.135 g, 0.67 mmol) in dichloromethane at room temperature for 48 h gave after work-up as above an uncharacterised pink material (0.0064 g) and a green material (0.0035 g) and a major bright yellow band which gave red crystals (0.168 g, 48%) of the product from a hexane/dichloromethane mixture. *Anal.* Found: C, 29.5; H, 1.0; O, 15.1. Calc. for $C_{20}H_{10}O_{10}Os_3$: C, 29.7; H, 1.0; O, 15.2%.

Syntheses of $[Os_3(CO)_{10}(Me_3SiC_2C_2SiMe_3)]$, $[Os_3(CO)_{10}(Bu^tC_2C_2Bu^t)]$ and $[Os_3(CO)_{10}(Pr^iC_2C_2SiMe_3)]$

A similar treatment gave these products as yellow oils (34, 27 and 24%, respectively) which were characterised spectroscopically.

Synthesis of $[Os_3(CO)_{10}(PhC_2C_2SiMe_3)]$, isomers 1 and 2

A solution of $[Os_3(CO)_{10}(MeCN)_2]$ (0.104 g, 0.112 mmol) and freshly distilled $PhC_2C_2SiMe_3$ (0.020 cm^3) in dichloromethane was kept at room temperature for 5 days. TLC (SiO_2; eluant, light petroleum (b.p. 30–40 °C)) gave two red bands which each yielded red oils characterised as isomer 1 (0.023 g, 20%) (*Anal.* Found: C, 26.55; H, 1.35. Calc. for $C_{23}H_{14}O_{10}SiOs_3$: C, 26.3; H, 1.35%) and isomer 2 (0.023 g, 20%) (Found: C, 29.0; H, 1.95%). Isomer 2 is contaminated with a trace of hydrocarbon, difficult to remove from the oil.

Reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with $[Os_3(CO)_{10}(RC_2C_2R)]$ (R=Ph or Et)

Reactions of the alkyne clusters with a 1.5 to 2.0 excess of the bis-acetonitrile complex in dichloromethane were allowed to stand for 5 days over which time the bis-acetonitrile complex decomposed or reacted with the solvent. TLC of the resulting mixtures gave the starting PhC_2C_2Ph cluster (92%) and the EtC_2C_2Et cluster (80%) as the only alkyne containing compounds.

Synthesis of $[Os_3(C_2Ph)_2(CO)_9]$

The IR spectrum was recorded periodically of a solution of $[Os_3(CO)_{10}(PhC_2C_2Ph)]$ (0.098 g) in refluxing n-octane (30 cm^3) under nitrogen. All the starting material had been consumed after 90 min and the colour had changed from orange to almost colourless. The solvent was removed and TLC (SiO_2; eluant, light petroleum (b.p. 30–40 °C)/CH_2Cl_2 (8:1 vol./vol.) gave a single band which yielded the product as pale yellow crystals (0.0664 g, 69%). *Anal.* Found: C, 29.55; H, 1.0; O, 15.05. Calc. for $C_{25}H_{10}O_9Os_3$: C, 29.65; H, 0.95; O, 15.2%.

Synthesis of $[Os_3(C_2SiMe_3)_2(CO)_9]$

A similar reaction of the $Me_3SiC_2C_2SiMe_3$ complex (0.039 g) in refluxing n-octane was complete within 10 min. The orange solution became almost colourless but a slight deposit was formed. Work-up as above using light petroleum (b.p. 30–40 °C) as eluant gave a single product as a pale yellow oil (0.0265 g, 70%).

Synthesis of $[Os_3(C_2Bu^t)_2(CO)_9]$

In this case reflux for 3 h in n-octane was necessary and the product was obtained as a pale yellow oil (49%).

Thermolysis of $[Os_3(CO)_{10}(PhC_2C_2SiMe_3)]$, isomer 1

Reflux in n-octane of isomer 1 (0.045 g) for 3 h was necessary to decarbonylate the complex (IR evidence). Work-up as above gave $[Os_3(C_2Ph)(C_2SiMe_3)(CO)_9]$ (0.027 g, 62%) as a pale yellow oil.

Thermolysis of $[Os_3(CO)_{10}(PhC_2C_2SiMe_3)]$, isomer 2

A similar treatment of isomer 2 gave decarbonylation within 15 min. The single product was shown to be identical spectroscopically to that formed from isomer 1.

Synthesis of $[Os_3(\mu\text{-}H)(EtC_2C{=}C{=}CHMe)(CO)_9)]$

A solution of the cluster $[Os_3(CO)_{10}(EtC_2C_2Et)]$ (0.043 g) in n-heptane (30 cm^3) was refluxed for 40 min. Work-up as above using light petroleum (b.p. 30–40 °C)/dichloromethane (9:1 vol./vol.) as eluant gave two yellow bands. The first yielded starting material (0.011 g) and the second the product as a pale yellow solid (0.025 g, 78% conversion).

Thermolysis of $[Os_3(CO)_{10}(MeC_2C_2Me)]$

Reflux for 4 h of a heptane solution (20 cm^3) of the cluster (0.031 g) gave a colour change from clear orange to cloudy brown. Work-up as above gave a single orange band which resulted in a orange oil of $[Os_3(CO)_9(MeC_2C_2Me)]$ (0.011 g, 38%). *Anal.* Found: C, 19.7; H, 0.8. Calc. for $C_{15}H_6O_9Os_3$: C, 20.0; H, 0.65%. Crystals could not be obtained so the compound was only characterised spectroscopically and not crystallographically.

Crystal structure determination of the cluster $[Os_3(C_2Ph)(C_2SiMe_3)(CO)_9]$

The structure determination of $[Os_3(C_2Ph)_2(CO)_{10}]$ was described briefly [3], and that of the mixed compound was carried out for comparison. Bond lengths and angles for both compounds are given in Table 3. Pale yellow crystals of $[Os_3(\mu\text{-}C_2Ph)(\mu_3\text{-}C_2SiMe_3)(CO)_9]$ were obtained by evaporation of a mixed hexane/dichloromethane solution. Since it was difficult to find a good crystal, a structure determination was carried out on a fairly poorly diffracting platelet, molecular formula $C_{22}H_{14}O_9Os_3Si$, $M = 1021.05$ g mol^{-1}, of size $0.12 \times 0.30 \times 0.04$ mm, using a Nicolet R3v/m diffractometer. A monoclinic cell, $a = 17.763(4)$, $b = 9.864(2)$, $c = 31.08(1)$ Å, $\beta = 102.07(2)°$, $U = 5224(3)$ $Å^3$, was determined from 25 orientation reflections in the range $12 < 2\theta < 25°$. Intensity data were collected at 20 °C using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), omega scan mode, $5 < 2\theta < 50°$. 6017 data were merged to give 4685 unique data. Intensities were corrected for Lorentz and polarisation effects and the intensities of three standard reflections measured periodically allowed the data to be corrected for the small variations observed. An empirical absorption correction (psi-scans) was carried out; μ(Mo Kα) = 143.6 cm^{-1}.

The structure was solved by direct methods: $C2/c$, $Z = 8$, $F(000) = 3679$, $D_c = 2.55$ g cm^{-3}. A model with 246 parameters was refined to $R = 0.098$ and $R_w = 0.068$, where $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ and $w = 1/[\sigma^2(F_o) + 0.000075F_o^2]$, using 3002 intensity data with $I_o > 1.5\sigma(I_o)$. The Os and Si atoms were refined anisotropically, and all others isotropically. H atoms were not included in the model. The largest shift-to-error in the final refinement was 0.003 and the largest peak in the final difference Fourier map was 2.9 e $Å^{-3}$.

All calculations were carried out using a MicroVax II computer running SHELXTL-PLUS [23].

Supplementary material

Additional material comprising the remaining bond lengths and angles, thermal parameters, and observed and calculated structure factors are available from the author A.J.D. on request.

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