ELSEVIER

Journal of Organometallic Chemistry 578 (1999) 103–114

Journal of Organo metallic Chemistry

Synthesis and structure of metallocarbon clusters bearing pendant ethynyl ligands. X-ray crystal structures of $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$, $Os_3Ru(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$, $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ and $\{Ru_4(CO)_{12}\}\{Co_2(CO)_6\}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2{:}\mu\text{-}\eta^2,\eta^2\text{-}Me_3SiC_2C{\equiv}CC_2SiMe_3)$

Paul J. Low [a], Konstantin A. Udachin [a], Gary D. Enright [a], Arthur J. Carty [a,b,*]

[a] *Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, K1A 0R6 Ontario, Canada*
[b] *Ottawa–Carleton Research Institute, Department of Chemistry, University of Ottawa, 1125 Colonel By Drive, Ottawa, K1S 5B6 Ontario, Canada*

Received 21 July 1998

Abstract

The reaction of 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne (**1**) with $Os_3(CO)_{10}(NCMe)_2$ yields $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**2**), which on treatment with $Ru_3(CO)_{12}$ gives $Os_3Ru(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**3**). In the case of the reaction between **1** and $Ru_3(CO)_{12}$ the major products are the butterfly cluster $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**4**) and the ruthenole complex $Ru_2(CO)_6\{\mu\text{-}\eta^2,\eta^5\text{-}C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C\text{-}(C{\equiv}CSiMe_3)\}$ (**5**). Cluster **4** reacts with $Co_2(CO)_8$ to give $\{Ru_4(CO)_{12}\}\{Co_2(CO)_6\}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2{:}\mu\text{-}\eta^2,\eta^2\text{-}Me_3SiC_2C{\equiv}CC_2SiMe_3)$ (**6**) in which the butterfly cluster core has slipped along the hexatriyne chain. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hexatriyne; Ethynyl cluster; Ruthenium; Osmium

1. Introduction

The statement that transition metal compounds containing carbon-rich ligands are currently the subject of an intensive research effort around the world probably requires no further justification than the publication of this special issue of the *Journal of Organometallic Chemistry* devoted to the subject. Polyynediyl bridging ligands have been shown to be especially efficient in allowing the passage of electronic effects between redox active centres [1] while clusters bearing exposed C_n ligands possess reactive sites for functionalisation, oligomerisation or metal attachment [2,3]. The presence of multiple, reactive C≡C alkynyl moieties on a cluster surface raises intriguing possibilities for the generation of wire-like polyynyl materials with electronic properties tuned by both the end-capping and π-bound metal fragments and large dimensional multimetallic arrays [4].

One synthetic approach to metal complexes bearing polyynyl ligands involves the coupling of unsaturated carbon ligands, such as acetylides and alkynylalkylidynes, bound to smaller metal complexes [5]. For example we have recently demonstrated the high-yield synthesis of the butadiynyl complex $Ru_4(CO)_8(\mu\text{-}PPh_2)_2\text{-}(Bu^tC{\equiv}CC{\equiv}CBu^t)$ in which the butadiyne ligand is derived from a specific head-to-head intermolecular coupling of $\mu\text{-}\eta^1,\eta^2$-alkynyl ligands from $Ru_2(CO)_6(\mu\text{-}$

---

* Corresponding author.

PII: S0022-328X(98)01112-7

$PPh_2)(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CBu^t)$ molecules [6]. Extension of this reaction to the related iron complex $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CPh)$ afforded $Fe_4(CO)_8(\mu\text{-}PPh_2)_2(\mu_4\text{-}\eta^2,\eta^2,\eta^2,\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)$ in which a similar head-to-head interaction of the acetylide moieties has generated a 'through-the-cluster' carbon–carbon bond [7], while similar treatment of the analogous ruthenium complex $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CPh)$ yielded electronically unsaturated tetra-nuclear clusters via head-to-head or head-to-tail coupling reactions of the acetylide ligands [8]. Clusters containing longer polyalkynyl ligands are also available via this approach and thermolysis of the diynyl complex $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CC{\equiv}CBu^t)$ yielded a number of higher nuclearity clusters including $Ru_4(CO)_9(\mu\text{-}PPh_2)\{\mu_4\text{-}\eta^1,\eta^2,\eta^2,\eta^1\text{-}C{\equiv}CC{=}C(Bu^t)C{\equiv}CC{\equiv}CBu^t\}$ [9].

An alternative method of preparing polyynyl clusters involves the co-ordination of metal fragments to preformed polyalkyne reagents $R(C{\equiv}C)_nR'$ bearing readily replaced R and R′ groups such as $SiMe_3$ or $SnMe_3$ followed by substitution of the labile groups with appropriate metal fragments. However, while the cluster chemistry of mono-alkynes has been widely studied, the reactions of conjugated polyalkynes remains relatively unexplored. As symmetrical 1,3-diynes, $RC{\equiv}CC{\equiv}CR$, are readily available from the corresponding terminal mono-alkynes and are usually stable, crystalline materials [10], the reactions of these compounds with cluster species have been the most widely examined [11–13]. It has been frequently observed that steric constraints restrict co-ordination about the diyne reagent and only one alkynyl moiety will co-ordinate to the metal cluster. Consequently, the product complexes obtained from these reactions often resemble ethynyl-substituted alkynyl clusters. Subsequent reactions may result in either fragmentation of the diynyl ligand by cleavage of the central C–C single bond [12], C–C bond formation during reactions with other alkyne substrates [14], or incorporation of the pendant ethynyl moiety into the cluster co-ordination environment [15].

In the case of reactions with mono- or bi-nuclear metal reagents the pendant group may also be used to sequester other metal species to give compounds which resemble linked alkynyl cluster units [3,11a,11b]. Larger clusters bearing pendant ethynyl ligands may also undergo more complicated rearrangement reactions giving complexes containing new cluster core geometries [16], or exhibit limited co-ordination chemistry due to excessive crowding about the pendant alkyne [12].

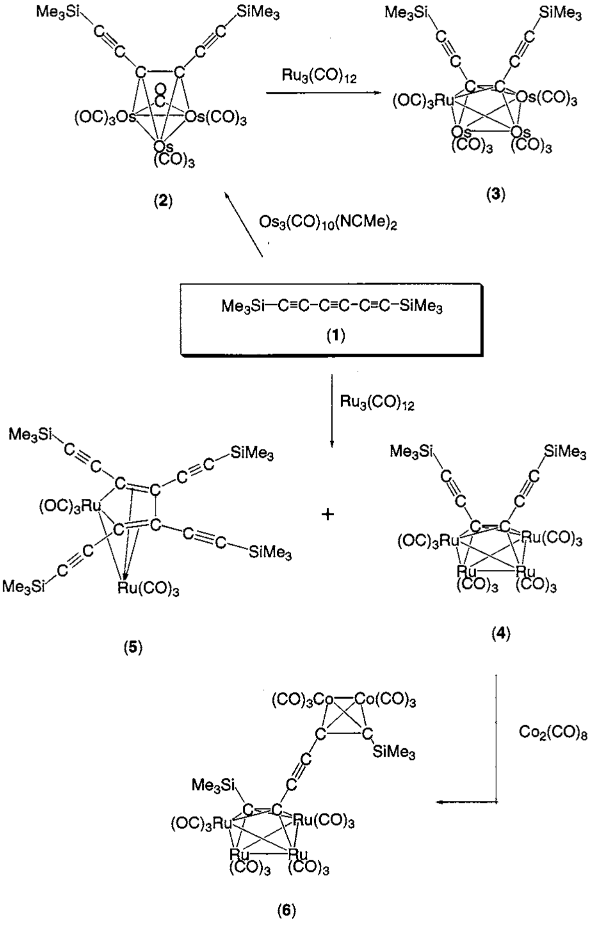
We are currently exploring the cluster chemistry associated with 1,3,5-hexatriynes such as bis(trimethylsilyl)hexa-1,3,5-triyne, $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ (**1**). The potentially rich co-ordination chemistry associated with the three alkynyl moieties, in addition to the steric flexibility afforded by the six carbon chain, should not only provide a base for an extensive new cluster chemistry but also provide a useful entry point for the assembly of complexes containing linked organometallic fragments. Diederich and co-workers have used a similar silyl-protected hexatriyne reagent in the preparation of dicobalt–triyne complexes which could be deprotected and coupled to afford cobalt stabilised cyclo-C_{18} and cyclo-C_{24} [17]. Some heterometallic clusters bearing 2,2,9,9-tetramethyl-octa-3,5,7-triyne ($Bu^tC{\equiv}CC{\equiv}CC{\equiv}CBu^t$) as a ligand have been obtained by Stone and colleagues from the reactions of $M({\equiv}CC{\equiv}CBu^t)(CO)_2(\eta\text{-}C_5H_5)$ with $Fe_2(CO)_9$ and $Rh(CO)_2(\eta\text{-}C_5H_5)$ [5e]. To the best of our knowledge these compounds are the only examples of compounds containing π-co-ordinated conjugated hexatriyne ligands. This contribution is the first in a series of full papers describing the synthesis and reactivity of cluster derivatives of bis(trimethylsilyl)hexa-1,3,5-triyne.

2. Results and discussion

2.1. Reaction of **1** with $Os_3(CO)_{10}(NCMe)_2$

The bis-acetonitrile complexes $M_3(CO)_{10}(NCMe)_2$ have been established as a convenient entry point into Group 8 trinuclear carbonyl alkyne clusters [18]. Thus reaction of $Os_3(CO)_{10}(NCMe)_2$ with **1** gave $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**2**) in 80% yield following filtration and crystallisation (Scheme 1). The cluster is a typical M_3-alkyne cluster [19,20], with the triyne ligand co-ordinated to the metal triangle via the central C≡C triple bond as established by both NMR data and a single crystal structural study. The bridging CO ligand found in the solid state structure, persists in solution as evidenced by the low frequency $\nu(CO)$ band at 1844 cm^{-1}. The fast atom bombardment mass spectrum (FAB-MS) contained the molecular ion at m/z 1070, which fragmented by loss of all ten CO groups. In addition, a secondary series of fragments of general form $[M{-}SiMe_3{-}n CO]^+$ ($n = 4$–8) was observed. The $SiMe_3$ groups gave rise to a single sharp singlet in both the ^1H- and ^{13}C-NMR spectra, while the carbon nuclei of the symmetrically co-ordinated triyne ligand gave only three singlet resonances at 118.18, 114.48 and 99.58 ppm. The CO resonances were not observed in the room temperature spectra, presumably due to the long T_1 relaxation times and chemical exchange processes associated with these ligands.

A perspective view of a molecule of **2** is shown in Fig. 1, and selected bond parameters are included in Table 1. Crystallographic details are summarised in Table 2. The compound is another example of the well known $M_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}RC_2R')$ clusters. A triangle of Os atoms supports the triynyl ligand, which is co-ordinated through the central C(3)≡C(4) moiety in the usual $\mu_3\text{-}\eta^1,\eta^1,\eta^2$ (or $\mu_3\text{-}\eta^2\text{-}\|$) fashion. The alkyne sits parallel to the Os(1)–Os(3) bond, which is also supported by a bridging carbonyl ligand [C(19)–O(19)]. Within the Os_3 triangle, metal–metal separations are normal [Os(1)–Os(2) 2.7553(3), Os(1)–Os(3) 2.8336(3), Os(2)–Os(3) 2.7689(3) Å], with the longest separation being found between Os(1)–Os(3). The bridging carbonyl moiety is co-ordinated in a somewhat asymmetric fashion, and is found closer to Os(3) than Os(1) in the solid state [Os(1,3)–C(19) 2.225(5), 2.104(6) Å]. There appears to be a corresponding degree of asymmetry in the co-ordination of the C(3)–C(4) alkyne moiety [Os(2)–C(3,4) 2.249(5), 2.273(5); Os(1)–C(4) 2.115(5); Os(3)–C(3) 2.123(5) Å] although it may be argued that these differences are not significant within the precision of the structure determination. A similar, but more pronounced asymmetric arrangement has been observed in $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}RC_2R')$ ($R = R' = Et$ [21a], Ph [21b], CO_2Me [21c]; $R = Ph$, $R' = C{\equiv}CPh$ [13]). Since the asymmetry is not preserved in solution, as evidenced by the NMR data, it seems likely that packing forces are responsible for these distortions. The bonding parameters of the pendant ethynyl moieties are equivalent within error [Si(1,2)–C(1,6) 1.822(6), 1.830(5); C(1)–C(2) 1.210(7); C(5)–C(6) 1.205(7) Å; C(1)–C(2)–C(3) 176.9(5)°, C(4)–C(5)–C(6) 179.3(5)°]. Bend-back angles at C(3) and C(4) are 123.3(4)° and 122.3(4)°, respectively.



Scheme 1.

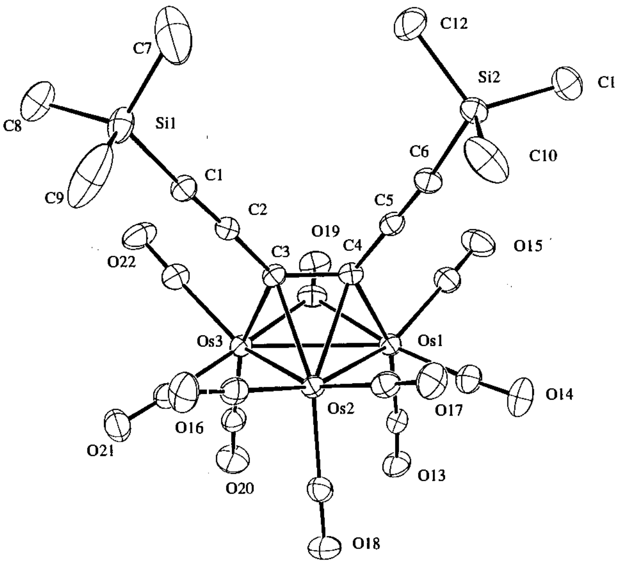


Fig. 1. The molecular structure of $Os_3(\mu\text{-}CO)(CO)_9(\mu_3\text{-}\eta^1,\eta^1\text{-}\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**2**) showing the atom labeling scheme.

The selective co-ordination of the central C≡C moiety of **1** is a recurring theme in the complexes prepared in this study and deserves some comment. While acetylene HC≡CH and diacetylene HC≡CC≡CH have been subjected to numerous theoretical studies [22], similar investigations of the structure and electronic properties of the higher polyynes $H(C{\equiv}C)_nH$ ($n > 2$) are rare. In 1966 Hoffmann reported the results of extended Hückel type calculations for $H(C{\equiv}C)_nH$ (n even, 2–16) and found that the atomic charges and overlap populations varied only slightly in the chain interior [23]. A decade later Moffat used ab initio calculations at the STO-3G level to examine the variations of C–C bond distances with chain length for some polyynes and related cyano- and lithio-derivatives [24]. While the magnitude of the variations were small, the central carbon atoms in hexa-1,3,5-triyne were found to carry a larger negative atomic charge than the others. More recently, Fan and Pfieffer have used RHF ab initio methods, with DZ and DZP basis sets, to calculate the electronic and geometric structures of the linear molecules HC_nH ($n = 2–10$) [25]. In keeping with the conclusions reached in Moffat's study a significant portion of the HOMO of HC_6H was found to reside on the central carbon atoms, with bond length alternation consistent with a polyyne structure.

The ^{13}C-NMR shifts of the triynyl carbon atoms in substituted hexatriynes such as **1** have been measured and have also been taken as an indication that the central triple bond is likely the most electron rich alkyne moiety [26].

Table 1
Selected bond lengths (Å) and angles (°) for clusters **2**, **3**, **4** and **6**

	2	**3**	**4**	**6**	**$Ru_4(CO)_{12}(PhC_2Ph)$**
Bond lengths (Å)					
M(1)–M(2)	2.7553(3)	2.7611(8)	2.7492(4)	2.7801 (11)	2.74(1)
M(2)–M(3)	2.7689(3)	2.7441(8)	2.7204(5)	2.7035 (10)	2.71(1)
M(1)–M(3)	2.8336(3)	2.8533(7)	2.8348(4)	2.8148 (10)	2.85(1)
M(1)–M(4)		2.7388(9)	2.7182(4)	2.7471 (11)	2.71(1)
M(3)–M(4)		2.7758(9)	2.7582(5)	2.7319 (11)	2.74(1)
M(1)–C(4)	2.115(5)	2.12(1)	2.133(3)	2.139(8)[a]	2.16(1)
M(3)–C(3)	2.123(5)	2.13(2)	2.145(3)	2.194(9)[b]	2.16(1)
M(2)–C(3)	2.249(5)	2.23(2)	2.242(4)	2.229(9)[b]	2.24(1)
M(2)–C(4)	2.273(5)	2.22(1)	2.215(3)	2.215(8)[a]	2.24(1)
M(4)–C(3)		2.52(1)	2.206(4)	2.245(9)[b]	2.25(1)
M(4)–C(4)		2.23(1)	2.233(3)	2.228(8)[a]	2.26(1)
C(1)–C(2)	1.210(7)	1.19(2)	1.204(5)	1.473(12)	
C(2)–C(3)	1.439(7)	1.41(2)	1.433(5)	1.420(13)	1.53(2)
C(3)–C(4)	1.409(7)	1.52(2)	1.471(5)	1.200(12)	1.46(2)
C(4)–C(5)	1.443(7)	1.46(2)	1.440(5)	1.425(13)	1.52(2)
C(5)–C(6)	1.205(7)	1.19(2)	1.197(5)	1.337(12)	
Bond angles (°)					
M(1)–M(2)–M(3)		62.43(2)	62.43(1)	61.75(3)	63.1(1)
M(2)–M(1)–M(3)		58.49(2)	58.29(1)	57.79(3)	57.9(1)
M(1)–M(3)–M(2)		59.07(2)	59.282(9)	60.46(3)	92.3(1)
M(1)–M(4)–M(3)		62.31(2)	62.34(1)	61.83(3)	63.0(1)
C(4)–C(3)–M(3)	109.7(3)	107.3(9)	108.5(2)	104.1(6)[a,b]	109.0(7)
C(2)–C(3)–C(4)	123.3(4)	125(1)	125.3(3)	177.8(9)	125.8(9)
C(3)–C(4)–C(5)	122.3(4)	123(1)	124.8(3)	177.5(9)	127.9(10)

[a] For C(4) read C(2).

[b] For C(3) read C(1).

Diederich and co-workers have prepared a number of $Co_2(CO)_n(dppm)_m$ ($n = 6, m = 0$; $n = 4, m = 1$) complexes of $Pr^i_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiPr^i_3$, an analogue of **1** which is capped by sterically demanding $SiPr^i_3$ end caps, and found the metal fragment co-ordinated exclusively to the central triple bond [27]. While on the basis of electronic arguments selective co-ordination of the binuclear cobalt fragment may be anticipated to occur at the least electron rich alkyne moiety, the steric influence of the end caps was cited as the most likely factor in determining the site of co-ordination.

Deeming and co-workers have described the synthesis of a number of diynyl complexes of general form $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}RC_2C{\equiv}CR')$, which were obtained in modest (16–48%) yields [12]. In the case of the asymmetric ligand $PhC{\equiv}CC{\equiv}CSiMe_3$ both regio isomers were isolated in a 1:1 ratio, and no evidence of interconversion of the isomers in solution at room temperature was observed. The related 1,3-diyne $Pr^iC{\equiv}CC{\equiv}CSiMe_3$ was apparently found to co-ordinate to the Os_3 framework exclusively through the $C{\equiv}C^iPr$ fragment. It would therefore appear that the selective co-ordination of the central triple bond in **1** to the Os_3-core to give **2** is a result of both the electronic properties of the alkyne moieties in **1** and the steric influence of the $SiMe_3$ end-caps.

As indicated above, cluster compounds such as **2** are well known and their structures are often described in terms of a triangular cluster core, with the μ_3-alkyne ligand acting as a four-electron donor. In terms of the simple 18-electron rule, this approach leads to a perfectly satisfactory description of **2** as a 48-e cluster. However, the carbon–carbon separation of the co-ordinated alkyne is much shorter than would be expected for a C–C single bond [C(3)–C(4) 1.409(7) Å], which suggests that a degree of multiple bond character still exists between these centres. Cluster **2** may also be described using PSEP theory [28] as a 7-pair, 5-vertex Os_3C_2 *nido*-octahedron, or square-based pyramid [19b]. In this description the carbon atoms of the co-ordinated alkyne moiety are considered to be an integral part of the polyhedral cluster core and the pendant $C{\equiv}CSiMe_3$ ligands each act as a 1-e donor.

From this latter point of view, it seemed likely that subjecting **2** to a source of a suitable mono-nuclear capping fragment would lead to the formation of an $M_3M'C_2$ *closo*-octahedon. However, such a fragment might also be expected to interact with the pendant ethynyl groups. The Ru–Ru bonds in $Ru_3(CO)_{12}$ are prone to cleavage under thermal conditions to generate smaller reactive fragments which are particularly susceptible to condensation reactions in the presence of alkynes [19a]. This cluster was therefore regarded as a

Table 2
Crystallographic data for **2**, **3**, **4**, and **6**

	2	**3**	**4**	**6**
Formula	$Os_3Si_2O_{10}C_{22}H_{18}$	$Os_3RuSi_2O_{12}C_{24}H_{18}$	$Ru_4Si_2O_{12}C_{24}H_{18}$	$Ru_4Co_2Si_2O_{18}C_{30}H_{18}$
fw	1069.14	1198.22	958.84	1244.76
Crystal size (mm)	0.30 × 0.25 × 0.25	0.30 × 0.30 × 0.25	0.30 × 0.50 × 0.50	0.30 × 0.06 × 0.01
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pna2_1$	$Pna2_1$	$P2_1/c$
a (Å)	15.619(9)	22.9610(10)	22.9665(10)	17.2744(8)
b (Å)	13.2812(8)	14.6531(6)	14.7199(7)	9.7298(5)
c (Å)	15.3282(9)	9.9448(4)	9.9204(4)	24.8760(12)
α (°)	90	90	90	90
β (°)	105.747(5)	90	90	105.520 (5)
γ (°)	90	90	90	90
V (Å^3)	2970.8(3)	3345.9(2)	3353.7(3)	4028.6(3)
Z	4	4	4	4
D_c, (g cm^{-3})	2.390	2.379	1.899	2.052
$F(000)$	1935.40	2176	1829.46	2400
μ (mm^{-1})	12.92	11.918	1.89	2.397
2θ range (°)	3.00–57.5	3.30–57.5	3.00–57.5	3–57.5
No. of reflections measured	34469	38070	37436	27330
No. of unique reflections	7704	8598	8652	5270
No. of observed reflections	6373	8598	8508	4925
No. of parameters refined	334	402	379	512
Final R, R_w	0.024, 0.024	0.0542, 0.1506	0.020, 0.026	0.0492, 0.0901
GOF	2.27	0.942	2.53	1.014
Max, min residual density (e Å^{-3})	+1.030, −1.170	+6.685, −4.280	+0.890, −0.540	+0.731, −0.528

suitable reagent to compare the reactivity of the metallocarbon core versus the pendant ethynyl ligands in **2**.

2.2. Reaction of 2 with $Ru_3(CO)_{12}$

The reaction of **2** with $Ru_3(CO)_{12}$ was performed in refluxing heptane for 10 h, giving a dark red solution from which bright red $Os_3Ru(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**3**) was isolated in good (63%) yield following preparative TLC and crystallisation from hexane (Scheme 1). Cluster **3** was characterised by the usual solution spectral techniques and a single crystal diffraction study. The IR spectrum of **3** contained a weak broad ν(C≡C) band at 2145, and a pattern of six strong terminal ν(CO) bands similar to that of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}PhC_2Ph)$ [29–31]. There was no evidence of a bridging carbonyl. The FAB-MS contained a molecular ion at m/z 1227, and fragments formed by the sequential loss of up to six CO ligands. The high symmetry in the molecule was once again apparent from the simplicity of both the ^{1}H- and ^{13}C-NMR spectra, with a single $SiMe_3$ resonance being observed in each case and only three sharp singlet resonances for the triynyl carbons at δ 123.13, 119.79 and 92.62. The spectral data were consistent with the substitution of the μ-CO ligand in **5** by an $Ru(CO)_3$ fragment to give an $RuOs_3$ butterfly cluster, with the heteroatom in a wing-tip position. This assumption was verified by a single crystal X-ray structural analysis.

A molecule of **3** is shown in Fig. 2 and selected bond lengths and angles are listed in Table 1, with relevant crystallographic details summarised in Table 2. The molecule is derived from the addition of an $Ru(CO)_3$ fragment to the Os(1)–Os(3)–C(3)–C(4) plane of **2**, and the cluster core may be considered as either an $RuOs_3$ butterfly cluster or as an $RuOs_3C_2$ distorted

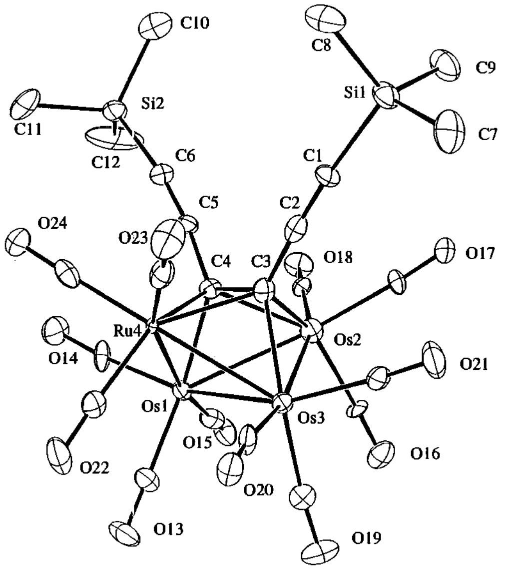


Fig. 2. The molecular structure of $RuOs_3(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**3**) showing the atom labeling scheme.

octahedron. The co-ordination sphere about each metal atom is completed by three terminal CO ligands. The wingtip Ru(4) sits slightly closer to Os(1) than does Os(3) [Ru(4)–Os(1,3) 2.7388(9), 2.7758(9) Å]. In light of the synthetic approach employed in the preparation of **3** it is interesting to note the increased C(3)–C(4) separation in **3** [C(3)–C(4) 1.52(2) Å] compared with that in **2** [C(3)–C(4) 1.409(7) Å] which is consistent with a decrease in the formal bond order between these atoms following co-ordination of Ru(4). Within the butterfly framework, the longest M–M distance is found between the hinge atoms Os(1)–Os(3) [2.8533(7) Å], which is entirely consistent with the other structurally characterised examples of this type of cluster. The butterfly is characterised by a dihedral angle of 113.5(3)°, which is similar to angles in other examples of this cluster type [30]. The geometry of the pendant ethynyl fragments is very similar to that described for **2**, with C(1)–C(2)–C(3) [175.4(15)°] and C(4)–C(5)–C(6) [173.8(14)°] nearly linear, and the C–C separations of C(1)–C(2) and C(5)–C(6) both 1.19(2) Å as expected for an uncoordinated triple bond.

The CO region of the ^{13}C-NMR spectrum of **3** consists of three sharp singlet resonances at room temperature (δ 188.37, 180.47, 175.96) in approximately a 1:2:1 ratio. This is indicative of a fluxional mechanism based on rapid rotation of the $M(CO)_3$ wingtip fragments, and possibly CO exchange between the Ru(1) and Ru(3) atoms in the hinge positions of the butterfly. There is apparently no exchange of CO ligands between the wingtip and hinge metals. A similar process has been observed for $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}PhC_2Ph)$ [31].

The electron counting schemes that may be applied to M_4C_2 clusters have been well documented and deserve no further comment here, except to say that **3** may be satisfactorily described as a 7-pair, 6-vertex M_4C_2 octahedral cluster [30,32].

Metal fragment condensation reactions are often used in the synthesis of larger metal clusters [20,33]. Indeed, the idea of cluster assembly via the addition of mono-metallic fragments to vacant vertex points in *nido* and *arachno* type clusters is implicit in both the Wade–Mingos approach to cluster structure and bonding [28,32,34] and Hoffmann's isolobal principle [35].

Other established, rational syntheses of heterometallic examples of $M_3M'C_2$ clusters involve the addition of alkynes to tetranuclear $M_nM'_{4-n}$ cluster frameworks [36]. For example, $Ru_2Co_2(CO)_{13}$ and $NEt_4[RuCo_3(CO)_{12}]$ react with PhC≡CPh to give $Ru_2Co_2(\mu\text{-}CO)_2(CO)_9(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}PhC_2Ph)$ [36a] and $NEt_4[RuCo_3(\mu\text{-}CO)_2(CO)_8(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}PhC_2Ph)$ [36b], respectively. It is also worth noting that upon treatment of $NEt_4[RuCo_3(\mu\text{-}CO)_2(CO)_8(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}PhC_2Ph)$ with HCl, the cluster extrudes a mononuclear fragment to give the trinuclear μ_3-alkyne cluster $RuCo_2(CO)_9(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}PhC_2Ph)$ [36b].

The clusters $FeRu_3(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}RC_2R')$ (R = R′ = Ph, Me; R = Ph, R′ = Me) have been prepared by insertion of alkynes into one Ru–Ru bond in $H_2FeRu_3(CO)_{13}$, followed by elimination of H_2 to give the kinetic products in which the heteroatom was located in a hinge position [36c]. Upon mild thermolysis, the metal framework rearranged to give the thermodynamically preferred isomer in which the iron atom occupies a wingtip position. The location of the ruthenium atom in **3** at a wingtip position is therefore not surprising as this isomer might be expected to be both the thermodynamically preferred form as well as the kinetic product.

There are also several reports of more serendipitous syntheses of compounds with the $M_3M'C_2$ octahedral cluster core, such as the preparation of $RuCo_3(\mu\text{-}CO)_2(CO)_7(\mu\text{-}PPh_2)$ ($\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Bu^tC_2H$) from $RuCl_2$(*p*-cymene)($Ph_2PC{\equiv}CBu^t$) and $Co_2(CO)_8$ [37].

2.3. Reaction of 1 with $Ru_3(CO)_{12}$

The reactions of $Ru_3(CO)_{12}$ with mono-alkynes [19a] and 1,3-diynes [38,39] are known to give a plethora of reaction products, the nature of which is highly dependent on the reaction conditions employed. For example, the reaction of 1,4-diphenylbuta-1,3-diyne with $Ru_3(CO)_{12}$ has been reported by Bruce and co-workers to yield $Ru_2\{\mu\text{-}\eta^2,\eta^5\text{-}C(C{\equiv}CPh){=}C(Ph)C(C{\equiv}CPh){=}CPh\}(CO)_6$ from a reaction initiated by Me_3NO and carried out in THF [38b], while Tunik and colleagues obtained $Ru_2\{\mu\text{-}\eta^2,\eta^5\text{-}C(Ph)C(C{\equiv}CPh)C(C{\equiv}CPh)CPh\}(CO)_6$ directly from a reaction in hexane [38a]. A similar thermal reaction between 1,4-bis(ferrocenyl)buta-1,3-diyne and $Ru_3(CO)_{12}$ gave a mixture of each of the three isomers of the bimetallic metallacyclopentadienes as well as metallacycloheptadienone complexes [39].

As has been discussed previously, the electronic and steric properties of the central and terminal C≡C moieties in **1** are quite distinct. We were curious as to whether or not this distinction in the electronic properties of the C≡C units would lead to a more selective reaction between $Ru_3(CO)_{12}$ and **1** when compared to the reactions of symmetrical 1,3-diynes in which each C≡C fragment exhibits identical reactivity.

The reaction between **1** and $Ru_3(CO)_{12}$ was carried out in refluxing hexane for 3 h. Precipitation of the un-reacted $Ru_3(CO)_{12}$ followed by purification of the filtrate by column chromatography on Florisil gave two compounds which were identified as the red tetranuclear butterfly cluster $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**4**) and the yellow ruthenole complex $Ru_2(CO)_6\{\mu\text{-}\eta^2,\eta^5\text{-}C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)\}$ (**5**) (Scheme 1) [40].

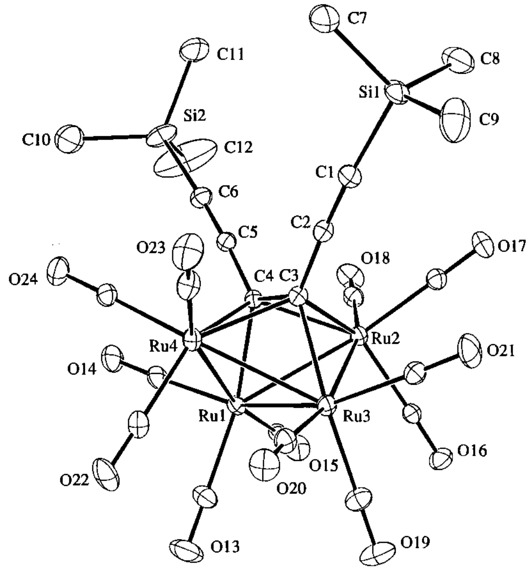


Fig. 3. The molecular structure of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**4**) showing the atom labeling scheme.

The reaction was followed by infrared spectroscopy and only bands due to $Ru_3(CO)_{12}$, **4** and **5** could be detected. Only one regio-isomer of **4** or **5** was observed.

The complexes **4** and **5** were identified by the usual spectroscopic techniques and the structures confirmed by single crystal X-ray studies (see below). Structural analogues of both compounds are known and the $\nu(CO)$ pattern in the IR spectra of **4** [19,29] and **5** [19,41] are comparable with these examples. The FAB-MS of **4** contained a molecular ion at *m/z* 960 which fragmented by loss of all twelve CO ligands. A symmetrical structure, with the triyne ligand co-ordinated through the central C≡C triple bond, was indicated by the observation of only three carbon resonances for the triyne ligand and a single $SiMe_3$ resonance in the ^{13}C-NMR spectrum and confirmed by the single crystal study (vide infra). The carbonyl ligands gave rise to two singlet resonances of equal intensity in agreement with the fluxional process described for **3** above.

A plot of a molecule of **4** is given in Fig. 3, and selected bond parameters are given in Table 1, along with those of $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}PhC_2Ph)$ [29] for comparison. Details of the crystallography are given in Table 2. The gross features of the molecule are obviously analogous to those of **3** and a closer examination of the crystallographic parameters indicates that **3** and **4** are isomorphous (Table 2). The four ruthenium atoms are found in the usual butterfly arrangement with a dihedral angle of 113.78(2)°. The triyne ligand is attached to the cluster through the central C(3)–C(4) triple bond, and lies parallel to the hinge formed by the Ru(1)–Ru(3) vector. The ligand sphere of each Ru atom is completed by three CO ligands. Within the Ru_4C_2 pseudo octahedral core the Ru–Ru separations range between 2.7182(4) and 2.8348(4) Å, the longest of these being the hinge bond. Along the C_6 chain the Si(1)–C(1) and Si(2)–C(6) separations are identical [1.834(4) and 1.834(4) Å], as are the C(1)–C(2) and C(5)–C(6) separations in the pendant ethynyl groups [1.204(5) and 1.197(5) Å] and the bonds these pendant groups make to the Ru_4C_2 core [C(2)–C(3) 1.433(5), C(4)–C(5) 1.440(5) Å]. The C(3)–C(4) separation is the longest C–C distance in the chain [1.4712(5) Å]. The pendant ethynyl groups are essentially linear, and are bent back about C(3) and C(4) by ca. 125°.

Complex **5** was similarly identified and found to be another member of the known binuclear metallocyclopentadiene series. The simple NMR spectral data was indicative of the symmetrical isomer, as shown in Scheme 1, and confirmed by a structural study. The $SiMe_3$ fragments gave rise to a sharp singlet resonance in both the ^1H- and ^{13}C-NMR spectra. In addition, the ^{13}C spectrum also contained six signals arising from the pendant ethynyl ligands and metallocyclopentadienyl ring carbons, and three CO resonances. The FAB-MS contained a molecular ion at *m/z* 808, which fragmented by loss of up to five carbonyl ligands. The IR $\nu(CO)$ spectrum consisted of six strong bands, similar to that reported for other examples of complexes of this type [19a,41].

The complex forms fine bright yellow crystalline needles. A preliminary X-ray structure determination confirmed the structure of **5** with a metallocyclopentadiene ligand constructed from the central triple bonds of two molecules of **1**. However, the crystals of **5** were twinned and this coupled with extensive disorder prevented satisfactory refinement of the structure.

The yield of each complex was found to depend on the stoichiometry of the reagents employed. However, while the use of a larger molar ratio of Ru with respect to the triyne reagent resulted in the formation of smaller amount of **5**, in no case could the yield of **4** be improved much above 30%. Conversely, higher yields of **5** were obtained from reaction mixtures containing a large excess of **1**, although this led to a decrease in the isolated yield of **4**. The optimised reaction conditions which are reported below, gave **4** and **5** in approximately 30% and 35% yields, respectively.

2.4. *Reaction of* **4** *with* $Co_2(CO)_8$

We were interested in probing the reactivity of the pendant ethynyl ligands in these compounds. In an effort to minimise the potential for spurious side reactions we chose to examine the reaction of the homometallic, *closo*-octahedral cluster **4** with the alkyne scavenger $Co_2(CO)_8$.

Reaction of **4** with $Co_2(CO)_8$ in benzene afforded $\{Ru_4(CO)_{12}\}\{Co_2(CO)_6\}$ $(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2{:}\mu\text{-}\eta^2,\eta^2\text{-}Me_3\text{-}$

$SiC_2C{\equiv}CC_2SiMe_3$) (**6**) in good (60%) yield as a brown crystalline material. The ν(CO) region of the IR spectrum contained at least twelve bands, which roughly approximated the superposition of the spectrum of **4** with that of $Co_2(\mu\text{-}\eta^2,\eta^2\text{-}RC_2R)(CO)_6$ [11e]. The FAB-MS contained a parent ion centred on *m/z* 1161 ([M−3CO]$^+$) which fragmented by loss of up to eleven CO ligands. The inequivalent $SiMe_3$ groups gave rise to two singlet resonances in the ^{1}H- (δ 2.69, 3.07) and ^{13}C- (δ 0.49, 5.37) NMR spectra. The ^{13}C spectrum contained six weak signals which were assigned to the carbon centres of the Ru_4C_2 pseudo octahedral core (δ 171.09, 169.62), an uncoordinated C≡C alkyne moiety (δ 112.82, 90.84) and the Co_2C_2 pseudo tetrahedral fragment (δ 83.16, 53.65). In the carbonyl region, three sharp resonances were observed. By comparison with the spectrum obtained for **4** these were assigned to the CO ligands on the Ru_4C_2 (δ 198.89, 196.05) and Co_2C_2 (δ 191.01) cores. The carbonyl ligands on both cores are obviously fluxional at this temperature, with the usual fluxional mechanism being observed for the Ru_4C_2 core and a rapid exchange process rendering all CO ligands on the Co_2C_2 core equivalent.

The spectral data clearly suggested an addition of a $Co_2(CO)_n$ fragment to **4**, although it was not possible to ascertain the exact structure of the product. A single crystal X-ray structure determination was therefore carried out. Fig. 4 illustrates the molecular structure of cluster **6**, selected bond lengths and angles are collected in Table 1 and crystal data are given in Table 2. The structure demonstrates that the dicobalt reagent has added to the C(5)–C(6) C≡C triple bond to give the expected $Co_2(CO)_6$(alkyne) adduct. The Ru_4C_2 octahedral cluster core from **4** has been preserved, but has been displaced along the hexatriyne chain and is now located on C(1)≡C(2). The previously co-ordinated C(3)–C(4) atoms are free of any adorning metal fragments and as a result the C(3)–C(4) separation has shortened to 1.20(1) Å, which is consistent with an uncoordinated acetylene. This unusual slipping of the Ru_4 core along the hexatriyne chain most likely results from the steric interactions between the metal fragments, and may be likened to pulling a thread from a piece of cloth. This contrasts strongly with the reactions of $M_3(CO)_8(L_2)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}PhC_2C{\equiv}CPh)$ with $Co_2(CO)_8$ in which the dicobalt reagent was found to insert into an M–M bond (M = Ru, $L_2 = (CO)_2$ [16a]), add to the pendant alkyne moiety followed by cleavage of the diyne C–C single bond (M = Ru, L_2 = dppm [16b]) or abstract the diyne ligand (M = Os, $L_2 = (CO)_2$ [13]).

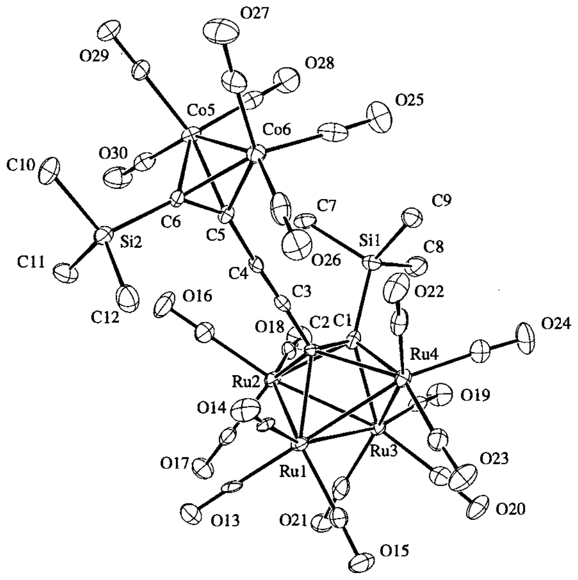


Fig. 4. The molecular structure of $\{Ru_4(CO)_{12}\}\{Co_2(CO)_6\}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{:}\mu\text{-}\eta^2,\eta^2\text{-}Me_3SiC_2C{\equiv}CC_2SiMe_3)$ (**6**) showing the atom labeling scheme.

The connection of the Ru_4C_2 and Co_2C_2 cluster moieties in **6** through the C(3)≡C(4) alkyne moiety raised several questions about the degree of intramolecular electronic interaction between these metallocarbon cores. In the ^{13}C-NMR spectrum of **6**, C(1) and C(2), which are attached to the Ru_4 butterfly core, are found at significantly lower field than the corresponding atoms in **4**, suggesting that the electron density at this centre in **6** may be lower than in the un-substituted cluster **4**. Conversely, the δ 53.65 resonance of the Co_2C_2 core is at a higher field than the corresponding resonance in simple $Co_2(CO)_6$(polyalkyne) complexes, which might indicate a relative increase in electron density at this site in **4**. The cluster units are joined through the C(3)≡C(4) moiety via C(2)–C(3) [1.42(1) Å] and C(4)–C(5) [1.43(1) Å]. These values suggest that a degree of conjugation exists between the metallocarbon cores and the C(3)≡C(4) alkyne moiety.

The bonding parameters in the Co_2C_2 core of $Co_2(\mu\text{-}\eta^2,\eta^2\text{-}RC_2R)(CO)_6$ alkyne complexes are known to vary with the electronic nature of the R substituent [11e,38]. One of the more important stabilising factors in the bonding of these cobalt alkyne complexes comes from the back-donation from the Co d-orbitals to a π^*-MO of the alkyne. Thus, as the electron-donating character of the R group increases, and the Co-alkyne bonding is weakened, there is a corresponding decrease in the alkyne C–C and Co–Co distances and an increase in the Co–C distance. Thus, in a series of complexes the Co–C distances were found to vary from 1.97(2) Å ($R = Bu^t$) to 1.987(2) Å (R = Ph) to 1.92(1) Å ($R = CO_2Me$). The same trend was observed in the C–C and Co–Co separations, although the accuracy of the data is limited [42].

Within the Co_2C_2 tetrahedral core of **6** the Co(5)–Co(6) separation is within the normal range (2.467(2) Å) and Co–C distances [Co(5,6)–C(5) 1.972(9), 1.965(9); Co(5,6)–C(6) 1.972(9), 1.991(9) Å] are comparable with the dimensions of the R = Bu^t complex, as is the C(5)–C(6) separation [1.34(1) Å]. The bend back angles at C(5) and C(6) are 144.6(9)° and 140.2(7)° in keeping with the observations made on the R = Bu^t complex [144.4°] [42].

The Ru_4C_2 pseudo-octahedral cluster core in **6** exhibits some minor structural variations when compared with the analogous fragment in **4** or $Ru_4(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}PhC_2Ph)$ [31]. As can be seen from the data collected in Table 1, the Ru(1)–Ru(3) hinge of the Ru_4 butterfly is significantly shorter than has been observed in other examples of this cluster motif. The Ru(2) wingtip sits closer to Ru(3) than Ru(1) [Ru(2)–Ru(1,3) 2.780(1), 2.704(1) Å], while Ru(4) is displaced toward Ru(1) [Ru(4)–Ru(1,3) 2.747(1), 2.732(1) Å] without displaying the same degree of asymmetry. There appears to be a related distortion in the contacts from C(1) and C(2) to the hinge atoms Ru(3) and Ru(1) [C(1,2)–Ru(3,1) 2.194(9), 2.139(8) Å]. An examination of Table 1 indicates that the η^2 contacts from C(1)–C(2) to the butterfly wingtips Ru(2,4) in **6** [C(1)–Ru(2,4) 2.229(9), 2.216(8); C(2)–Ru(2,4) 2.216(8), 2.229(8) Å] are relatively short in comparison to $Ru_4(CO)_{12}(PhC_2Ph)$ [2.25(1) Å]. The C(1)–C(2) separation [1.47(1) Å] is comparable with the related values in Table 1. The bend back angles at C(1) and C(2) are 120.6(8) and 125.0(8)°, respectively and the dihedral angle is 113.0°.

While distortions are evident in the Ru_4C_2 and Co_2C_2 cluster cores, it is difficult to be confident in ascribing these structural variations to electronic interactions between the cluster cores. An electrochemical and theoretical study on a series of related compounds is underway to probe this question in more detail and these results will form the subject of a future report [43].

3. Conclusion

In conclusion we have observed that 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne undergoes facile reactions with ruthenium and osmium carbonyls to afford products of similar structure to those obtained from the reactions with simple mono-alkynes. These reactions are remarkable for the regio-specificity observed in the co-ordination of the triyne ligand, with only one isomer being formed in each case. The pendant alkyne ligands are attractive sites for the attachment of further metal groups offering great potential for the synthesis of a wide range of mixed metal species, including molecules with linked metallocarbon cluster cores.

4. Experimental

All reactions were carried out under dry high purity nitrogen using standard Schlenk techniques. Solvents were dried, distilled and degassed prior to use. Preparative TLC was performed on 20 × 20 cm glass plates coated with silica gel (CAMAG DSF-5, 0.5 mm thick). Instrumental conditions: Infrared spectra were recorded on a BioRad FTS-40A spectrometer, using calcium fluoride cells of 0.5 mm path length; NMR spectra were recorded on a Bruker DRX-400 (^1H 400.13 MHz, ^{13}C 100.61 MHz) in $CDCl_3$ and referenced against the solvent resonances; FAB-MS spectra were obtained on a JEOL AX505 spectrometer, using Xe as the exciting gas, FAB gun voltage 6 kV, accelerating potential 3 kV, and *m*-nitrobenzylalcohol matrix. The compounds $Ru_3(CO)_{12}$ (Strem) and $Co_2(CO)_8$ (Fluka) were purchased and used as received. Literature methods were used to prepare $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ [26a] and $Os_3(CO)_{10}(NCMe)_2$ [44].

4.1. $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (2)

A solution of $Os_3(CO)_{10}(NCMe)_2$ (975 mg, 1.05 mmol) in CH_2Cl_2 (75 ml) was treated with $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ (**1**) (300 mg, 1.38 mmol) and allowed to stir for 1 h. After this time, the reaction was judged to be complete (TLC, IR). The solution was filtered through a silica gel plug and the plug washed with CH_2Cl_2. The yellow–orange filtrate was diluted with hexane (ca. 20 ml), concentrated to ca. 40 ml and stored at −30°C overnight to afford large block shaped crystals of **5** (900 mg, 80%). Calculated for $Os_3Si_2O_{10}C_{22}H_{18}$: C 24.72, H 1.70%. Found C 24.52, H 1.60%. IR (CH_2Cl_2): ν(C≡C) 2128 vw; ν(CO) 2104 m, 2071 vs, 2066 sh, 2029 s, 2009 s, 1844 w, br cm^{-1}. ^1H-NMR: δ 0.17 (s, $SiMe_3$). ^{13}C-NMR: δ −0.09 (s, $SiMe_3$), 99.58, 114.48, 118.178 (3 × s, $CC{\equiv}CSiMe_3$). FAB-MS (*m*/*z*): 1069 $[M]^+$, 1041–789 $[M{-}nCO]^+$ ($n = 1–10$).

4.2. $Os_3Ru(CO)_{12}(\mu_4\text{-}\eta^1,\eta^2,\eta^1,\eta^2\text{-}Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (3)

A solution of **2** (70 mg, 0.057 mmol) and $Ru_3(CO)_{12}$ (45 mg, 0.070 mmol) in heptane (10 ml) was heated at reflux for 8 h. Removal of the solvent and purification of the residue by TLC (5% CH_2Cl_2 in hexane) afforded two orange compounds. The first band yielded **3** after crystallisation (CH_2Cl_2–MeOH) (35 mg, 76% based on **2** consumed) while the second contained unreacted **2** (30 mg). Calculated for $RuOs_3Si_2O_{12}C_{24}H_{18}$: C 23.51, H 1.48%. Found C 23.34, H 1.54%. IR (cyclohexane): ν(C≡C) 2145 w, br; ν(CO) 2101 m, 2076 vs, 2051 s, 2043 vs, 2019 s, 2015 sh, 1975 m cm^{-1}. ^1H-NMR: δ 0.20 (s, $SiMe_3$). ^{13}C-NMR: δ 0.00 (s, $SiMe_3$), 92.62, 119.79, 122.13 (3 × s, $CC{\equiv}CSiMe_3$), 175.96, 180.47, 188.37 (3 × s, 3 × CO). FAB-MS (*m*/*z*): 1227 $[M]^+$, 1199–1059 $[M{-}nCO]^+$ ($n = 1–6$).

4.3. *$Ru_4(CO)_{12}(\mu_4$-$\eta^1,\eta^2,\eta^1,\eta^2$-$Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$* ***(4)***

A hexane solution (40 ml) of $Ru_3(CO)_{12}$ (400 mg, 0.626 mmol) and **1** (120 mg, 0.550 mmol) was heated at reflux for 8 h resulting in a colour change from orange to dark red. The solution was cooled, concentrated and filtered to remove precipitated $Ru_3(CO)_{12}$ (200 mg). The filtrate was purified by column chromatography on Florisil. Elution of the column with a CH_2Cl_2/hexane gradient afforded a dark red band (5% CH_2Cl_2) containing $Ru_4(CO)_{12}(\mu_4$-$\eta^1,\eta^2,\eta^1,\eta^2$-$Me_3SiC{\equiv}CC_2C{\equiv}CSiMe_3)$ (**4**) (80 mg, 35%) and a yellow band (25% CH_2Cl_2) containing $Ru_2(CO)_6\{\mu$-η^2,η^5-$C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)\}$ (**5**) (70 mg, 20%). **4**: red prisms from CH_2Cl_2/MeOH. Calculated for $Ru_4Si_2O_{12}C_{24}H_{18}$: C 30.06, H 1.89%. Found C 30.29, H 1.76%. IR (cyclohexane): $\nu(C{\equiv}C)$ 2140 vw; $\nu(CO)$ 2098 w, 2075 vs, 2050 s, 2044 vs, 2021 m, 1977 w cm^{-1}. ^{1}H-NMR: δ 0.19 (s, SiMe$_3$). ^{13}C-NMR: δ −0.35 (s, SiMe$_3$), 96.00 (s, C≡*C*SiMe$_3$), 116.30 (s, *C*≡CSiMe$_3$), 153.84 (s, *C*–C≡CSiMe$_3$), 190.57, 197.12 (2 × s, CO). FAB-MS (*m*/*z*): 960 [M]$^+$, 932–624 [M−*n*CO]$^+$ (*n* = 1–12).

4.4. *$Ru_2(CO)_6\{\mu$-η^2,η^5-$C(C{\equiv}CSiMe_3)$-$C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)\}$* ***(5)***

A solution of $Ru_3(CO)_{12}$ (690 mg, 1.08 mmol) and **1** (700 mg, 3.2 mmol) was heated in refluxing hexane (300 ml) for 8 h. The solution was concentrated and chilled to precipitate any unreacted $Ru_3(CO)_{12}$ and the filtrate purified as described for **4** above to give **4** (100 mg, 13%) and $Ru_2(CO)_6\{\mu$-η^2,η^5-$C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)C(C{\equiv}CSiMe_3)\}$ (**5**) (400 mg, 33%). **5**: yellow needles from CH_2Cl_2/MeOH. Calculated for $Ru_2Si_4O_6C_{30}H_{36}$: C 44.65, H 4.50%. Found C 44.55, H 4.45%. IR (cyclohexane): $\nu(C{\equiv}C)$ 2159 vw, 2133 w; $\nu(CO)$ 2089 s, 2064 vs, 2027 vs, 2009 s, 1997 m, 1984 w cm^{-1}. ^{1}H-NMR: δ 0.17, 0.28 (2 × s, SiMe$_3$). ^{13}C-NMR: δ −0.49, −0.46 (2 × s, SiMe$_3$), 97.94, 100.39, 107.23, 108.59, 111.85, 137.58 (6 × s, C≡C–C=C–C≡C), 193.34, 194.02, 195.21 (3 × s, CO). FAB-MS: (*m*/*z*) 808 [M]$^+$, 780–696 [M−*n*CO]$^+$ (*n* = 1–4).

4.5. *$\{Ru_4(CO)_{12}\}\{Co_2(CO)_6\}(\mu_4$-$\eta^1,\eta^2,\eta^1,\eta^2$:$\mu$-$\eta^2,\eta^2$-$Me_3SiC_2C{\equiv}CC_2SiMe_3)$* ***(6)***

A solution of **4** (70 mg, 0.073 mmol) and $Co_2(CO)_8$ (35 mg, 0.10 mmol) in benzene (15 ml) was stirred at room temperature for 3 h. The solvent was removed and the residue purified by TLC (hexane). Repeated development resolved two bands. The upper dark red band contained a small amount of unreacted **1** (10 mg) while the lower dark brown band yielded **6** (55 mg, 60%) following crystallisation from hexane at −30°C. Calculated for $Ru_4Co_2Si_2O_{18}C_{30}H_{36}$: C 28.53, H 2.87%. Found C 28.67, H 2.79%. IR (cyclohexane): $\nu(CO)$ 2097 w, 2088 m, 2067 vs, 2059 m, 2046 m, 2038 m, 2033 s, 2029 s, 2015 m, 2007 m, 1980 w cm^{-1}. ^{1}H-NMR: δ 0.29, 0.46 (2 × s, 2 × SiMe$_3$). ^{13}C-NMR: δ −0.12, 5.37 (2 × s, 2 × SiMe$_3$), 53.65, 83.16 (2 × s, Co$_2$C$_2$), 90.84, 112.82 [2 × s, C(3)≡C(4)], 169.62, 171.09 (2 × s, Ru$_4$C$_2$), 191.01, 196.05, 198.89 (3 × s, CO). FAB-MS: (*m*/*z*) 1162–826 [M−*n*CO]$^+$ (*n* = 3–11).

5. Crystallography

Data was collected on a Siemens SMART CCD diffractometer. Unique diffractometer data sets (monochromic Mo–K$_\alpha$ radiation, $\lambda = 0.7107_3$ Å; ω scan mode; $T = 173$ K) were measured within the specified $2\theta_{max}$ limit yielding N independent reflections, N_o of these with $I = 2.5\ \sigma\ (I)$ being considered observed and used in the block = full-matrix least squares refinement after an empirical absorption correction utilising the SADABS routine associated with the Siemens diffractometer. Anisotropic thermal parameters were refined for the non-hydrogen atoms. In the final cycles of refinement hydrogen atoms were placed in calculated positions and constrained with a riding model. For structures **2** and **4** the function minimised in the least-squares calculation was $\Sigma\, w(|F_o| - |F_c|)^2$. For **3** and **6**, the minimised function was $\Sigma\, w(F_o^2 - F_c^2)^2$. Computations were performed using either the NRCVAX [45] or SHELXTL [46] suite of programs.

Cluster **3**: The SiMe$_3$ group associated with Si(2) was found to be disordered over two sites, which were satisfactorily modeled as 54 and 46% occupancy following trial refinement. Although the compound crystallised in a non-centrosymmetric space group, there was evidence of racemic twinning [Flack parameter 0.28(1) [47]]. The poor quality of the data, a result of the poor crystal specimen, did not support meaningful resolution of the absolute structure.

Cluster **4**: In the case of **4**, which also crystallised in a polar space group, the absolute crystal configuration was determined following refinement of the Flack parameter [−0.007(40)].

6. Supplementary information

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. CCDC No.'s: 103072 (**2**), 103073 (**3**), 103074 (**4**), 103075 (**6**). Tables of structure factors are available from the authors upon request.

Acknowledgements

The authors gratefully acknowledge financial support from the National Research Council of Canada (NRC) and the Natural Sciences and Engineering Research Council (NSERC). P.J. Low holds a NSERC-NRC Canadian Government Laboratories Visiting Fellowship.

References

[1] (a) T. Bartik, B. Bartik, M. Brady, R. Dembinski, J.A. Gladysz, Angew. Chem. 108 (1996) 467; Angew. Chem. Int. Ed. Engl. 35 (1996) 414. (b) N. Le Narvor, L. Toupet, C. Lapinte, J. Am. Chem. Soc. 117 (1995) 7129. (c) F. Coat, C. Lapinte, Organometallics 15 (1996) 477. (d) M.I. Bruce, L.I. Denisovich, P.J. Low, S.M. Peregudova, N.A. Ustynyuk, Mendeleev. Commun. (1996) 200.

[2] M.I. Bruce, J. Cluster Sci. 8 (1997) 293.

[3] P. Blenkiron, J.F. Corrigan, D. Pilette, N.J. Taylor, A.J. Carty, Can. J. Chem. 74 (1996) 2349.

[4] For lead references see (a) H. Lang, Angew. Chem. 106 (1994) 569; Angew. Chem. Int. Ed. Engl. 33 (1994) 547. (b) W. Beck, B. Neimer, M. Wieser, Angew. Chem. 105 (1993) 969; Angew. Chem. Int. Ed. Engl. 32 (1993) 923. (c) N.J. Long, Angew. Chem. 107 (1995) 37; Angew. Chem. Int. Ed. Engl. 34 (1995) 21. (d) D. Astruc, Electron Transfer and Radical Processes in Transition Metal Chemistry, VCH, New York, Part I. (e) N. Duffy, J. McAdam, C. Nervi, D. Osella, M. Ravera, B. Robinson, J. Simpson, Inorg. Chim. Acta. 247 (1996) 99. (f) G. Frapper, M. Kertesz, Inorg. Chem. 32 (1993) 732. (g) M. Akita, M.-C. Chung, A. Sakurai, S. Sugimoto, M. Terada, M. Tanaka, Y. Moro-oka, Organometallics 16 (1997) 4882. (h) F. Coat, A.-A. Guillevic, L. Toupet, F. Paul, C. Lapinte, Organometallics 16 (1997) 5988.

[5] (a) H. Lang, S. Blau, G. Rheinwald, L. Zsolnai, J. Organomet. Chem. 494 (1995) 65. (b) H.J. Heeres, J. Nijhoff, J.H. Teuben, R.D. Rogers, Organometallics 12 (1993) 2609. (c) W.J. Evans, R.A. Keyer, J.W. Ziller, Organometallics 9 (1990) 2628. (d) S. Jeannin, Y. Jeannin, F. Robert, C. Rosenberger, Inorg. Chem. 33 (1994) 243. (e) S.J. Etches, I.J. Hart, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1989) 2281.

[6] Y. Chi, A.J. Carty, P. Blenkiron, G.D. Enright, W. Wang, S.-M. Peng, G.-H. Lee, Organometallics 15 (1996) 5269.

[7] (a) A.J. Carty, G. Hogarth, G.D. Enright, G. Frapper, Chem. Commun. (1997) 1883. (b) J.E. Davies, M.J. Mays, P.R. Raithby, K. Sarveswaren, Angew. Chem. 109 (1997) 2784; Angew. Chem. Int. Ed. Engl. 36 (1997) 2668.

[8] E. Delgado, Y. Chi, W. Wang, G. Hogarth, P.J. Low, G.D. Enright, S.-M. Peng, G.-H. Lee, A.J. Carty, Organometallics 17 (1998) 2936.

[9] P. Blenkiron, G.D. Enright, P.J. Low, J.F. Corrigan, N.J. Taylor, Y. Chi, J.-Y. Saillard, A.J. Carty, Organometallics 17 (1998) 2447.

[10] L. Brandsma, Preparative Acetylenic Chemistry, Second Edition, Elsevier Science Publishers, New York, 1988.

[11] For examples see (a) M.I. Bruce, P.J. Low, A. Werth, B.W. Skelton, A.H. White, J.Chem. Soc. Dalton Trans. (1996) 1551. (b) F. Schager, W. Bonrath, K.-R. Pörschke, M. Kessler, C. Krüger, K. Seevogel, Organometallics 16 (1997) 4276. (c) J. Lewis, B. Lin, M.S. Khan, M.R.A. Al-Manhury, P.R. Raithby, J. Organomet. Chem. 484 (1994) 161. (d) K.H. Pannell, G.M. Crawford, J. Coord. Chem. 2 (1973) 251. (e) R.S. Dickson, P.J. Fraser, Adv. Organomet. Chem. 12 (1974) 323 and references therein.

[12] A.J. Deeming, M.S.B. Felix, D. Nuel, Inorganica Chimica Acta. 213 (1993) 3.

[13] M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, Aust. J. Chem. 49 (1996) 155.

[14] (a) J.F. Corrigan, S. Doherty, N.J. Taylor, A.J. Carty, Organometallics 13 (1994) 3778. (b) M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, J. Organomet. Chem. 558 (1998) 197.

[15] J.F. Corrigan, S. Doherty, N.J. Taylor, A.J. Carty, Organometallics 12 (1993) 1365.

[16] (a) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, Polyhedron 14 (1995) 2647. (b) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, J. Cluster Sci. 7 (1996) 109.

[17] F. Diederich, Y. Rubin, O.L. Chapman, N.S. Goroff, Helv. Chim. Acta. 77 (1994) 1441.

[18] (a) G.A. Foulds, B.F.G. Johnson, J. Lewis, J. Organomet. Chem. 296 (1985) 147. (b) B.F.G. Johnson, J. Lewis, D.A. Pippard, J. Organomet. Chem. 160 (1978) 263.

[19] (a) M.I. Bruce , in: G. Wilkinson, F.G.A. Stone, E. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, Exeter, 1982, vol. 4, Ch 32.5.2.9. (b) J.-F. Halet, J.-Y. Saillard, R. Lissillour, M. McGlinchey, G. Jaouen, Inorg. Chem. 24 (1985) 218. (c) F.W.B. Einstein, K.G. Tyers, A.S. Tracey, D. Sutton, Inorg. Chem. 25 (1986) 1631 and references therein.

[20] E. Sappa, A. Tirripicchio, P. Braunstein, Chem. Rev. 83 (1983) 203.

[21] (a) E. Rosenberg, J. Backer-Novak, R.W. Gellert, S. Aime, R. Gobetto, D. Osella, J. Organomet. Chem. 364 (1989) 163. (b) C.G. Pierpoint, Inorg. Chem. 16 (1977) 636. (c) A.J. Deeming,, A.M. Senior, J. Organomet. Chem. 439 (1992) 177.

[22] For a recent review see D.A. Plattner, Y. Li, K.N. Houk, in: P.J. Stang, F. Diederich (Eds.), Modern Acetylene Chemistry, VCH Publishers Inc., New York, 1995.

[23] R. Hoffmann, Tetrahedron 22 (1966) 521.

[24] J.B. Moffat, J. Mol. Struct. 42 (1977) 251.

[25] Q. Fan, G.V. Pfeiffer, Chem. Phys. Lett. 162 (1989) 472.

[26] (a) Y. Rubin, S.S. Lin, C.B. Knobler, J. Anthony, A.M. Boldi, F. Diederich, J. Am. Chem. Soc. 113 (1991) 6943. (b) D.G. Morris, in: S. Patai, Z. Rappoport (Eds.), The Chemistry of the Triple-Bonded Functional Groups (Supp. C), Part 2, Chapter 25, Wiley, Chichester, 1983.

[27] F. Diederich, Y. Rubin, O.L. Chapman, N.S. Goroff, Helv. Chim. Acta. 77 (1994) 1441.

[28] (a) K. Wade, Adv. Inorg. Chem. Radiochem. 18 (1976) 1. (b) K. Wade, in: B.F.G.Johnson (Ed.), Transition Metal Clusters, Wiley, New York, 1981, p. 193. (c) D.M.P. Mingos, Acc. Chem. Res. 1 (1984) 311. (d) D.M.P. Mingos, D.J. Wales, Introduction to Cluster Chemistry, Prentice Hall Publishers, Eaglewood Cliffs, NJ, 1990.

[29] J. Wang, M. Sabat, L.J. Lyons, D.F. Shriver, Inorg. Chem. 30 (1991) 382 and references therein.

[30] E. Sappa, A. Tiripicchio, A.J. Carty, G.E. Toogood, Prog. Inorg. Chem. 35 (1987) 437.

[31] B.F.G. Johnson, J. Lewis B.E. Reichert, K.T. Schorpp, G.M. Sheldrick, J. Chem. Soc. Dalton Trans. (1977) 1470.

[32] D.M.P. Mingos, A.S. May, in: D.F. Shriver, H.D. Kaesz, R.D. Adams (Eds.), The Chemistry of Metal Cluster Complexes, VCH Publishers, New York, 1990, Ch. 2.

[33] (a) H. Vahrenkamp, Adv. Organomet. Chem. 22 (1983) 169. (b) R.D. Adams, in: D.F. Shriver, H.D. Kaesz, R.D. Adams (Eds.), The Chemistry of Metal Cluster Complexes, VCH Publishers, New York, 1990, Ch. 3.

[34] (a) K. Wade, Electron Deficient Compounds, Nelson, London, 1971. (b) K. Wade, Inorg. Nucl. Chem. Lett. 8 (1972) 559. (c) K. Wade, Adv. Inorg. Chem. Radiochem. 18 (1976) 1. (d) D.M.P.

Mingos, Nat. Lond. 236 (1972) 99. (e) D.M.P. Mingos, J. Chem. Soc. Chem. Commun. (1985) 1352 (f) D.M.P. Mingos, R.L. Johnson, Struct. Bond. 68 (1987) 29.
[35] R. Hoffmann, Angew. Chem. Int. Ed. Engl. 21 (1982) 711.
[36] (a) E. Roland, H. Vahrenkamp, Organometallics 2 (1983) 183. (b) P. Braunstein, J. Rose, O. Bars, J. Organomet. Chem. 252 (1983) C101. (c) J.R. Fox, W.L. Gladfelter, G.L. Geoffroy, I. Tavanaiepour, S. Abdel-Mequid, V.W. Day, Inorg. Chem 20 (1981) 3230.
[37] D.F. Jones, P.H. Dixneuf, A. Benoit, J.-Y. Le Marouille, J. Chem. Soc. Chem. Commun. (1982) 1217.
[38] (a) S.P. Tunik, E.V. Grachova, V.R. Denisov, G.L. Starova, A.B. Nikol'skii, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, J. Organomet. Chem. 536–537 (1997) 339. (b) M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, Inorg. Chim. Acta. 250 (1996) 129.
[39] A.A. Kordize, V.I. Zdanovich, N.V. Andrievskayam Yu. Siromakhova, P.V. Petrovskii, M.G. Ezernitskaya, F.M. Dolgushin, A.I. Yanvsky, Yu.T. Struchkov, Russ. Chem. Bull. 45 (1996) 1200.
[40] P.J. Low, G.D. Enright, A.J. Carty, J. Organomet. Chem. 1998, in press.
[41] See examples in (a) M.I. Bruce, J.G. Matisons, B.W. Skelton, A.H. White, J. Organomet. Chem. 251 (1983) 249. (b) A. Astierm J.-C. Daran, Y. Jeannin, C. Rigault, J. Organomet. Chem. 241 (1983) 53. (c) A.A. Koridze, A.I. Yanovsky, Yu. T. Struchkov, J. Organomet. Chem. 441 (1992) 277.
[42] D. Gregson, J.A.K. Howard, Acta. Crystallogr. C39 (1983) 1024.
[43] P.J. Low, R. Rousseau, A.J. Carty, unpublished results.
[44] S.R. Drake, R. Khattar, Organomet. Synth. 4 (1988) 234.
[45] E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, S.P. White, J. Appl. Crystallogr. 22 (1989) 384.
[46] (a) G.M. Sheldrick, Acta Crystallogr. A46 (1990) 467. (b) G.M. Sheldrick, Acta. Crystallogr. A49 (1993) C53.
[47] H.D. Flack, Acta Crystallogr. A39 (1983) 876.