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Reaction of $[M(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ ($M = \text{Fe}, \text{Os}$) with $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$; unexpected substitution of acetylene, formation and molecular structure of $[\text{MW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$

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Abstract

Reaction of $[M(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ ($M = \text{Fe}, \text{Os}$) with $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$ affords the heterobimetallic complexes $[\text{MW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ ($M = \text{Fe}, \mathbf{1}; \text{Os}, \mathbf{2}$). This is contrary to the usual substitution reactions of the former compounds, which proceed by loss of CO and not that of the acetylene ligand. The IR and NMR signatures of the compounds are in accord with their formulation and this has been corroborated by single crystal X-ray crystallography. Each compound contains a d^8 $M(\text{CO})_4$ fragment. The geometry of the Group 8 metal is trigonal bipyramidal (tbp) with a tungsten-carbyne unit, acting as a two-electron pseudo-alkyne ligand, occupying an in-plane equatorial position. In solution the compounds are fluxional. At room temperature, local scrambling at iron averages all four terminal carbonyl ligands, whereas the process is slower for osmium and results only in broadened axial and equatorial CO resonances in the ^{13}C -NMR spectrum. Intermetallic CO exchange is not observed on the NMR time scale. Plausible scenarios for the formation of **1** and **2** are outlined.

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Keywords: Iron; Osmium; Carbonyl; Alkyne; Bridging carbyne; X-ray structure

1. Introduction

The reaction chemistry of transition metal carbonyls with alkynes has a long and rich history. In addition to producing a plethora of mono- and polymetallic complexes containing a variety of hydrocarbon ligands [1], the metal-mediated alkyne–alkyne and/or alkyne–CO coupling reactions have found numerous applications in organic synthesis [2]. Our contribution to the iron-group carbonyl–alkyne chemistry has been the unambiguous identification of $[M(\text{CO})_4(\eta^2\text{-alkyne})]$ ($M = \text{Fe}, \text{Ru}, \text{Os}$) compounds as intermediates in such reactions [3] and to provide benchmark parameters for the enhanced CO lability in these compounds [4]. We have also shown

that, in addition to promoting coupling reactions to produce tropone-, *p*-quinone- and (cyclopentadienone) $M(\text{CO})_3$ molecules, the 18-electron $[M(\text{CO})_4(\eta^2\text{-alkyne})]$ compounds are also valuable building blocks for the directed synthesis of alkyne-bridged heterobimetallic complexes containing Group 8 (Fe, Ru, Os) and Group 9 (Co, Rh, Ir) transition metals [5].

It occurred to us that, on the basis of the above precedents, reaction of $[M(\text{CO})_4(\eta^2\text{-alkyne})]$ compounds with a transition metal–carbyne complex (i.e. an $M\equiv\text{CR}$ triple bond) might result in the formation of heterobimetallic compounds bridged by hydrocarbon ligands arising from alkyne–CR coupling with or without CO incorporation. Indeed, Stone and coworkers have exploited the isolobal analogy [6] between an alkyne ($\text{RC}\equiv\text{CR}'$) and a transition metal carbyne complex ($\text{L}_n\text{M}\equiv\text{CR}$) to successfully prepare a variety of heterometallic transition metal cluster complexes [7]. The compounds $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_4\text{R-4}]$ ($\text{R} = \text{H}, \text{Me}$) are the paradigm for these reactions because the

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$(\eta^5\text{-C}_5\text{R}_5)\text{W}(\text{CO})_2$ fragment is isolobal to CR [8], and these carbyne complexes have consistently shown chemical reactivity that parallels that of organic alkynes.

Here we describe the results of the reactions between $[\text{M}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ ($\text{M} = \text{Fe}, \text{Os}$) and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$.

2. Results

2.1. Synthetic aspects and compound characterization

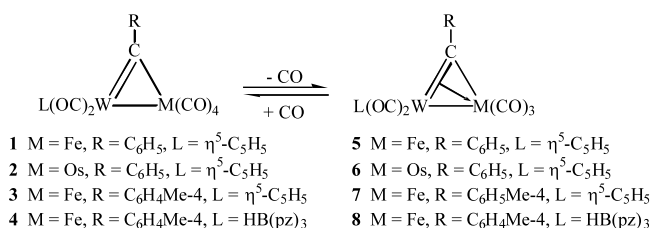
As in previous simple substitution reactions $[\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ reacted readily with $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$ and resulted in complete consumption of the starting material when a 1:1 mixture of the compounds was stirred in pentane at -20°C for 2 h. Simple work-up afforded a deep brown, crystalline material, compound **1**. Spectroscopic characterization of the compound revealed a surprising result. The IR spectrum in hexane showed six bands in the terminal carbonyl stretching region. However, the $^1\text{H-NMR}$ spectrum exhibited resonances due only to the C_6H_5 and C_5H_5 groups, no acetylenic protons were detected. Thus, the reaction proceeded by elimination of the acetylene from $[\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$. These spectroscopic results suggested the product to be $[\text{FeW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$, a compound similar to that obtained by Stone et al. [9] by reacting $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_4\text{Me-4}]$ with $[\text{Fe}_2(\text{CO})_9]$, albeit in much lower yield (10 vs. 62% for **1**). Further corroboration of the nature of **1** came from its $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum which showed a signal at 332.4 ppm, close to the 331.3 ppm reported by Stone et al. [9] and assigned to the bridging carbyne carbon atom. When solvent was removed from solutions of **1** under vacuum and the compound redissolved, the IR and NMR spectra displayed additional signals. A particularly noticeable feature in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum was the appearance of a highly deshielded resonance at 392.3 ppm. In another study Stone et al. reported that complexes of the type $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6\text{L}]$ ($\text{L} = \eta^5\text{-C}_5\text{H}_5$, **3**; $\text{HB}(\text{pz})_3$, **4**, $\text{pz} = \text{pyrazolyl-1-yl}$) exist in equilibrium with $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\text{L}]$ ($\text{L} = \eta^5\text{-C}_5\text{H}_5$, **7**; $\text{HB}(\text{pz})_3$, **8**) [10], the electronic unsaturation created by the loss of a CO ligand is compensated by the bridging carbyne ligand acting as a formal four-electron donor moiety in the latter compounds. The change from two-electron donor in **3** and **4** to four-electron donor $\text{W}\equiv\text{CR}$ in **7** and **8** is accompanied by a downfield shift in the $\mu\text{-CR}$ ^{13}C -NMR signal [9,10], in accord with the empirical correlation established by Templeton between ^{13}C -NMR shifts and electron donation by alkyne ligands [11]. The position of the resonance at 392.5 ppm in **7** is virtually identical to our observation and, in light of these findings, it is reasonable to conclude that $[\text{FeW}(\mu\text{-$

$\text{CC}_6\text{H}_5)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)]$ (**5**) is the source of the extra signals in the IR and NMR spectra of **1**. The relationship between these compounds and their formulation is shown in Scheme 1.

In their studies Stone et al. made several interesting observations concerning the nature of the $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$ containing species. They found that compound **3** was susceptible to further reactions with $[\text{Fe}(\text{CO})_5]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_4\text{Me-4}]$, and gives trinuclear complexes [9]. They also demonstrated that the equilibrium between the $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$ containing species favors the former when $\text{L} = \eta^5\text{-C}_5\text{H}_5$ (i.e. **3**) and the latter when $\text{L} = \text{HB}(\text{pz})_3$ (i.e. **8**) [10]. In light of these observations, it seems clear that the ready reactivity of $[\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$, at low temperature, is responsible for the clean and higher yield production of **1** in our investigation compared with Stone's work with $[\text{Fe}_2(\text{CO})_9]$.

In an attempt to suppress the likelihood of acetylene loss, $[\text{Os}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$, with a stronger $\text{Os-C}_2\text{H}_2$ bond [4a,12], was treated with $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$. The reaction also occurred readily (0°C , 2 h) but again proceeded by acetylene elimination to yield $[\text{OsW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ (**2**). The spectroscopic features of **2** (IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR) are similar to those of **1**. The presence of the two-electron $\mu\text{-CC}_6\text{H}_5$ ligand is indicated by the ^{13}C signal at 332.0 ppm, same as in **1** (332.4 ppm). It is interesting to note that the four high frequency ν_{CO} bands of **2** (2098, 2028, 2010 and 1995 cm^{-1}) are some $10\text{--}20\text{ cm}^{-1}$ higher than the corresponding bands in **1** (2073, 2020, 1995 and 1988), and hence are assigned to CO stretching vibrations localized on the $\text{M}(\text{CO})_4$ fragment. On the other hand, the two lower frequency ν_{CO} bands of **2** (1939 and 1873 cm^{-1}) are $10\text{--}15\text{ cm}^{-1}$ lower than those of **1** (1948 and 1889 cm^{-1}) and indicate enhanced back-bonding to the $\text{W}(\text{CO})_2$ carbonyls in **2** due to the presence of the more electron donating osmium center [13]. As expected, compound **2** is more robust than **1** and this is reflected in the need to heat its solution to 40°C before any indication of the pentacarbonyl, $[\text{OsW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_5(\eta^5\text{-C}_5\text{H}_5)]$ (**6**), is detected by IR spectroscopy.

In their previous study, Stone et al. determined the solid state structure of the $\text{Fe}(\text{CO})_3$ containing compound, $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\text{HB}(\text{pz})_3)]$ (**8**) [10],



Scheme 1.

but not that of the $\text{Fe}(\text{CO})_4$ species **3** or **4**. To confirm the structural predictions presented above and to provide metrical parameters for comparison with **8**, compounds **1** and **2** were subjected to single crystal X-ray structure analysis.

2.2. Solid state structures of $[\text{MW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ ($M = \text{Fe}$, **1**; Os , **2**)

The X-ray analysis showed that crystals of compound **1** contain two crystallographically independent molecules per asymmetric unit (structures **1A** and **1B**) but whose metrical parameters are very similar. When discussing the structural details, the structures will be referred to as **1** and the average value of the structural parameters will be used. The structures of **1A** and **2** are shown in Fig. 1 together with the atom numbering scheme. Important bond distances and angles are listed in Table 1.

As argued above, and shown in Scheme 1, compounds **1** and **2** consist of a $\text{M}(\text{CO})_4$ and $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2$ fragments linked by a bridging carbyne ligand ($\mu\text{-CC}_6\text{H}_5$). The coordination geometry of $\text{Fe}\text{-Os}$ can be described either as distorted trigonal bipyramidal (tbp), with the $\text{W}\equiv\text{CC}_6\text{H}_5$ moiety occupying the normal, in-plane equatorial disposition of the alkyne ligand, as observed in $[\text{M}(\text{CO})_4(\eta^2\text{-alkyne})]$ ($M = \text{Fe}$, Ru , Os) compounds [14], or distorted octahedral when considering the $\text{Fe}\text{-W}\text{-C}7$ core at the dimetallacyclopropene extreme. The tungsten center can be described as distorted octahedral with the $\eta^5\text{-C}_5\text{H}_5$ ligand occupying three facial sites and the opposite three by the two carbonyl groups and the mid-point of the $\text{M}\text{-C}7$ bond. The coordination geometry agrees well with several ‘‘piano stool’’ compounds of the form $[(\eta^5\text{-$

Table 1
Selected bond lengths (Å) and bond angles (°) for **1A**, **1B** and **2**^a

	1A	1B	2
<i>Bond lengths</i>			
M–W	2.833(2)	2.855(2)	2.9141(4)
W–C1	1.96(2)	1.96(2)	1.997(9)
W–C2	1.968(14)	1.99(2)	1.969(8)
W–C7	1.913(12)	1.913(12)	1.955(8)
M–C3	1.80(2)	1.80(2)	1.935(9)
M–C4	1.79(2)	1.79(2)	1.892(11)
M–C5	1.809(14)	1.77(2)	1.970(8)
M–C6	1.83(2)	1.81(2)	1.970(8)
M–C7	2.015(12)	2.018(13)	2.120(7)
C7–C21	1.47(2)	1.49(2)	1.460(11)
<i>Bond angles</i>			
W–C1–O1	172.9(12)	171.9(14)	170.6(9)
W–C2–O2	176.7(13)	176.0(14)	177.0(8)
M–C3–O3	177.3(14)	176.6(14)	178.0(9)
M–C4–O4	179.1(15)	177.1(16)	177.2(8)
M–C5–O5	176.2(13)	176.9(15)	177.9(7)
M–C6–O6	176.8(13)	175.5(13)	177.8(7)
C1–W–C2	90.2(5)	88.2(6)	90.8(4)
C1–W–C7	113.9(5)	115.3(6)	114.9(4)
C2–W–C7	90.3(5)	90.0(5)	88.3(3)
C3–M–C4	103.3(6)	102.9(7)	100.5(4)
C5–M–C6	166.5(6)	168.9(7)	167.5(3)
M–W–C1	70.1(4)	72.2(4)	69.8(3)
M–W–C2	101.8(3)	100.8(4)	100.4(3)
W–M–C7	42.4(3)	42.0(3)	42.1(2)
M–W–C7	45.3(4)	44.9(4)	46.7(2)
M–C7–W	92.3(5)	93.1(5)	91.2(3)
W–C7–C21	141.2(9)	139.7(9)	138.3(6)
M–C7–C21	125.9(9)	126.7(9)	129.8(6)
W–M–C4	142.0(4)	145.7(5)	143.1(3)
C3–M–C7	156.9(6)	153.4(6)	158.3(4)

^a M = Fe (**1A** and **1B**), Os (**2**).

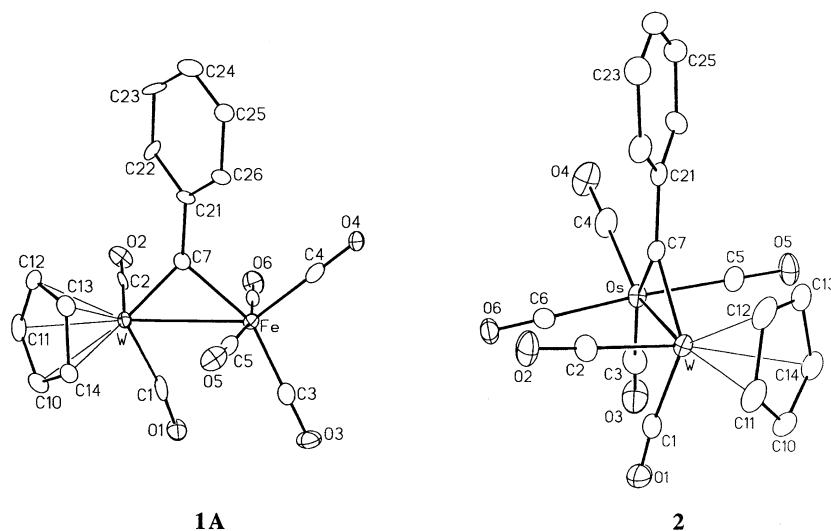


Fig. 1. Perspective views of $[\text{FeW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ (**1A**) and $[\text{OsW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ (**2**) showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

$C_5H_5)W(CO)_2L]$, where, L represents a three-electron donor η^1 - or η^2 -bonded ligand [15].

The most interesting feature of the structures is the three membered $M(\mu-C)W$ ring system. As anticipated, the Fe–W separation in **1** (2.844(11) Å) is much longer than the one observed in the four-electron μ -CR bridged compound $[FeW(\mu-CC_6H_4Me-4)(CO)_5(HB(pz)_3)]$ (**8**) (2.612(2) Å) [10] and even longer than 2.720(1) Å found in $[FeW\{\mu-C(C_6H_4Me-4)C(Me)C(Me)\}(CO)_5(\eta^5-C_5H_5)]$ [16], a compound presumed to have an Fe–W single bond, although the bridging unit in the latter provides a more delocalized bonding framework and probably contributes to the short Fe–W separation. There are no simple bimetallic Os–W compounds that bear similarities to **2**, but the Os–W distance of 2.9141(4) Å lies within the range (2.83–3.01 Å) observed for the vast majority of Os–W single bonds in saturated tri- and tetranuclear cluster compounds [17], and the separation is shorter than the Os→W donor–acceptor bonds of Pomeroy et al. (ave. 3.09 Å) [18].

The μ -C7–Fe distance of 2.017(2) Å is again much longer than the 1.826(6) Å found in **8**, the latter with significant multiple bond character, but close to the μ -C–Fe single bond separation of 1.986(3) Å found in $[Fe_2(\mu-CHMe)(\mu-CO)(CO)_2(\eta^5-C_5H_5)]$ [19]. Similarly the μ -C7–Os distance (2.120(7) Å) is slightly longer than the Os–C(H) separation (2.061(9) Å) in $[Os_2(CO)_8(\mu-\eta^1, \eta^2-CHCH_2)] [BF_4]$ [20], a compound with a σ, π -vinyl bridge, and confirms its single bond formulation. On the other hand the μ -C7–W distances (1.913(12) Å in **1** and 1.955(8) Å in **2**) are significantly shorter than 2.025(7) Å found in **8**, which contains a predominantly singly bonded μ -CR–W unit, but compares favorably with the corresponding distances in a series of similar carbyne bridged bimetallic $MW(\mu-CC_6H_4Me-4)$ (M = Co, Rh, Ti, Pt) complexes (1.91–1.97 Å) [21]. These molecules have considerable μ -CR–W multiple bonding character and have been formulated as having a dimetallacyclopropene core. This is the situation in **1** and **2** also and the asymmetric ligand binding is manifest in the W–C7–C21 angles (140.5(8)° in **1** and 138.3(6)° in **2**) being some 10–15° larger than the Fe–C7–C21 angles (126.3(4)° in **1** and 129.8(6)° in **2**), as observed in the above mentioned complexes. Thus, the structural parameters of the $M(\mu-C)W$ rings nicely complement the corresponding parameters of the previously determined structure $[FeW(\mu-CC_6H_4Me-4)(CO)_5(HB(pz)_3)]$ (**8**) [10]. In **8** the Fe–W and μ -C–Fe separations indicate multiple bonding interaction, consistent with the alkylidyne tungsten fragment functioning as a four-electron donor to the iron center (Scheme 1). Whereas the M–W and μ -C–M separations in **1** and **2** indicate single bonding interaction and suggests a model in which the $W \equiv CC_6H_5$ unit donates two electrons to the Group 8 metal centers

(Scheme 1) and functions as a two-electron pseudo-alkyne ligand.

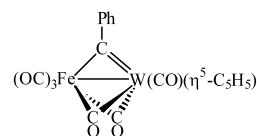
2.3. Solution behavior: VT ^{13}C -NMR spectral studies

On the basis of the solid state structures the ^{13}C -NMR spectrum in the carbonyl regions should exhibit six signals, four for the four different $M(CO)_4$ carbonyls and two for the $W(CO)_2$ fragment. However, the ^{13}C -NMR spectrum of **1** at room temperature showed only one averaged Fe–CO signal at 210.3 ppm and one W–CO resonance at 221.7 ppm, indicating local carbonyl scrambling but no carbonyl exchange between the two metal centers. The spectrum of **2** also showed an averaged $W(CO)_2$ signal at 221.2 ppm and three distinct, but broad signals for the $Os(CO)_4$ moiety at 184.4, 177.0 and 174.9 ppm in a 1:1:2 ratio. Thus, as observed with classical $M(CO)_4(\eta^2$ -alkyne–alkene) compounds [14b,22], carbonyl scrambling at Os is a much slower process than at iron. Upon lowering the temperature the $Fe(CO)_4$ signals decoalesce and emerge as three distinct, sharp peaks at $-90^\circ C$. It only requires $-20^\circ C$ for the three osmium carbonyl peaks to sharpen up. Throughout this process the $W(CO)_2$ signal remains sharp. This indicates that even at the lowest temperature the static solid state structure is not achieved in solution. A rapid oscillation of the $(\eta^5-C_5H_5)W(CO)_2$ group about the M–W vector would result in a time-averaged mirror plane of the molecule and render the two tungsten carbonyls and the two axial $M(CO)_4$ carbonyls (C5O5 and C6O6, Fig. 1) equivalent, in accord with the low temperature ^{13}C -NMR spectra of **1** and **2**.

It is interesting to note that although there is no intermetallic CO exchange between Fe and W in **1** on the NMR time-scale, when **1** was prepared from ^{13}C enriched $[Fe(CO)_4(\eta^2-C_2H_2)]$ and $[(\eta^5-C_5H_5)(CO)_2W \equiv CC_6H_5]$ (natural abundance ^{13}C), enrichment of the tungsten carbonyls also occurred, as demonstrated by $^{13}C\{^1H\}$ -NMR spectroscopy. The most plausible explanation for this is slow carbonyl migration between Fe and W via a higher energy CO bridged intermediate [23], as shown in Scheme 2.

3. Discussion

The reaction of $[M(CO)_4(\eta^2-C_2H_2)]$ (M = Fe, Os) with $[(\eta^5-C_5H_5)(CO)_2W \equiv CC_6H_5]$ resulted in the formation of the carbyne bridged heterobimetallic complexes



Scheme 2.

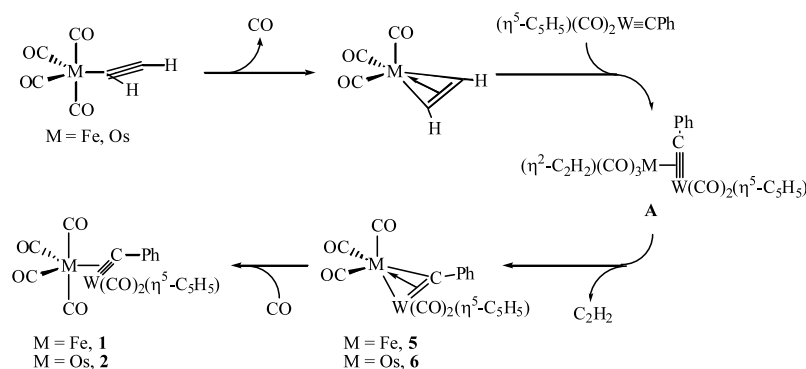
$[\text{MW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Fe}$, **1**; Os , **2**), analogous to the compound obtained by Stone et al. from the reaction of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_4\text{Me-4}]$ and $[\text{Fe}_2(\text{CO})_9]$ [9]. The loss of acetylene in the reaction was unexpected. Since the reaction proceeded in the same temperature regime as the usual dissociative CO substitution reactions [4], it seemed unlikely that the reaction was initiated by loss of the acetylene ligand but that this occurred at some later stage in the reaction. A plausible scenario is depicted in Scheme 3. Initial loss of a CO ligand is followed by coordination of the $\text{W}\equiv\text{CC}_6\text{H}_5$ pseudo-alkyne unit. The presence of the strongly electron donating tungsten-carbyne fragment in intermediate **A** increases the electron density at M (Fe , Os) sufficiently that, in order to reduce the four-electron repulsion [24] between filled metal- d and filled π_{\perp} -alkyne orbitals, instead of carbyne-alkyne coupling the acetylene ligand is eliminated, yielding **5** and **6**. Formation of the final products, **1** and **2**, would then require scavenging of the liberated CO by compounds **5/6**. Although seemingly unlikely, this would be in accord with the observation of Stone et al. [10] that with the cyclopentadienyl ligand the thermodynamically preferred species was the hexacarbonyl.

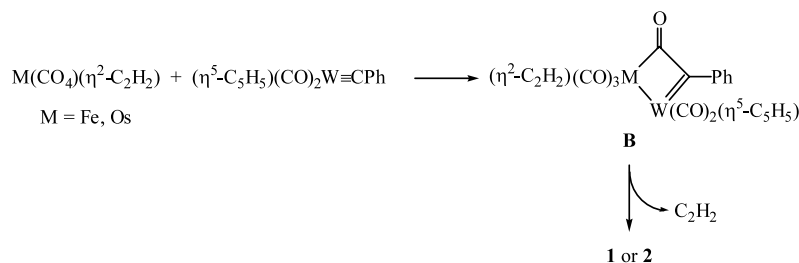
To test this hypothesis the reaction of $[\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ was reinvestigated but this time under a vigorous N_2 purge. Removal of at least some of the liberated CO should reduce the yield of the hexacarbonyl **1** and increase the amount of pentacarbonyl **5**. However, this was not observed. The isolated product was again the hexacarbonyl **1** and careful IR monitoring did not reveal formation of the pentacarbonyl **5** even at the early stages of the reaction. The inescapable conclusion is that the reaction to produce **1** and **2** does not follow the scenario described in Scheme 3.

Although loss of the acetylene ligand from $[\text{M}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ could produce **1** and **2** directly, we are still of the opinion that this is not the way the reaction proceeds. Indeed, prior to this work we have not observed loss of acetylene from $[\text{M}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ ($\text{M} = \text{Fe}$, Os). Loss of alkyne from $[\text{M}(\text{CO})_4(\eta^2\text{-alkyne})]$ has been seen, but this was mostly confined to the

ruthenium derivatives and was attributed to the often observed anomalous behavior of second row transition metals compared with their first and third row congeners and to the attendant weak Ru -alkyne bond [14b, 25]. Loss of bulky, electron donating alkyne ligands from $[\text{Fe}(\text{CO})_4(\eta^2\text{-RC}\equiv\text{CR})]$ ($\text{R} = \text{tBu}$, SiMe_3) were reported by Hübel [1a] and, Pannel and Crawford [26]. The lability could be the result of the combined steric bulk and electron donating ability of the alkyne ligands. However, these reactions could still proceed by initial CO loss. We believe this is a possibility because we have isolated, and structurally characterized $[\text{Fe}(\text{CO})_3(\text{PMe}_3)(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ from the reaction of $[\text{Fe}(\text{CO})_4(\eta^2\text{-Me}_3\text{SiC}\equiv\text{CSiMe}_3)]$ with PMe_3 [27]. Finally, we have observed that $[\text{Fe}(\text{CO})_4(\eta^2\text{-MeC}\equiv\text{CMe})]$ reacts with $[(\text{C}_5\text{Me}_5)\text{Co}(\text{CO})_2]$ to give the alkyne-free heterobimetallic compound $[(\text{C}_5\text{Me}_5)\text{Co-Fe}(\text{CO})_6]$ [28]. Although the mechanism of this transformation is not clear, it appears not to proceed via initial loss of 2-butyne.

Having ruled out the mechanism in Scheme 3 and presented reasonable arguments against initial loss of the acetylene ligand, we propose the mechanism shown in Scheme 4. Inspiration is taken from the recent work of Filippou [29] which, for the first time, demonstrated associative reaction of $[\text{Fe}(\text{CO})_5]$ with the electron-rich alkyne, $\text{Me}_2\text{NC}\equiv\text{CNMe}_2$. The first step of the reaction is nucleophilic attack of a CO ligand by the electron-donating $\text{W}\equiv\text{CR}$ moiety resulting in the formation of the dimetallacyclobutenone intermediate **B**. This is analogous to the ferracyclobutenone intermediate suggested by Filippou in his reaction. However, from here the two reactions follow a different course. Filippou's intermediate is thermolabile, and having only CO ligands, it decarbonylates readily at -30°C . On the other hand, intermediate **B** has a choice and the increased electron density on the M (Fe , Os) results in the preferential loss of the acetylene ligand. Deinsertion of CO from the strained dimetallacyclobutenone gives final products **1** and **2**. In this way formation of the pentacarbonyls **5** and **6** occurs only after subsequent loss of a CO ligand.





Scheme 4.

In conclusion, the reaction between $[\text{M}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$ failed to give the targeted acetylene–carbyne based hydrocarbyl bridged heterobimetallic compounds. Instead, and irrespective of the mechanistic details, the reaction proceeds by facile transfer of a $\text{M}(\text{CO})_4$ fragment and gives the simple carbyne bridged heterobimetallics. Although the use of $\text{Fe}_2(\text{CO})_9$ as a source of the ‘ $\text{Fe}(\text{CO})_4$ ’ fragment is well known and widely used [30], ‘ $\text{Os}(\text{CO})_4$ ’ transfer reagents are virtually unknown [31]. Hence, it is interesting to speculate what other types of electron rich species could react with $[\text{Os}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ with net loss of the acetylene ligand.

4. Experimental

Reactions were carried out using standard Schlenk techniques under a dry and oxygen free nitrogen atmosphere. All solvents were dried over CaH_2 and distilled under nitrogen. $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$ [32] was prepared as described in the literature with the exception that NaC_5H_5 [33] was used in place of LiC_5H_5 and a pentane solution of the product was cold filtered (-20°C) through a sintered glass filter instead of the chromatographic procedure described. $[\text{M}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ ($\text{M} = \text{Fe}$ [3a], Os [5a]) were prepared according to literature methods. IR solution spectra (KBr cell) were recorded on a FTIR Bomem MB-100 spectrometer. NMR samples were prepared under nitrogen atmosphere. The chemical shifts are reported in ppm relative to TMS (^1H , ^{13}C). The NMR spectra were recorded on either a Bruker AM-400 MHz, Varian Inova-300 MHz or Varian Unity 500 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of Alberta.

4.1. Synthesis of $[\text{FeW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ (1)

To a stirred 50 ml pentane solution of $[\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ (102 mg, 0.526 mmol) was added a 20 ml pentane solution of $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$ (207 mg, 0.526 mmol) at -40°C . The mixture was allowed to warm to -20°C and stirred for 1 h. The dark brown solution

was then cannula filtered and the solvent removed in vacuo at -20°C . Recrystallization from cold CH_2Cl_2 –pentane gave a dark brown crystalline solid (183 mg, 62%). IR (hexane, cm^{-1}): 2073, 2020, 1995, 1988, 1948, 1889. $^1\text{H-NMR}$ (CD_2Cl_2 , -20°C , ppm): δ 7.34 (m, 5H, C_6H_5), 5.45 (s, 5H, C_5H_5). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CD_2Cl_2 , -20°C , ppm): δ 332.4 ($\mu\text{-C}$), 221.7 (W-CO , $J(\text{WC})$ 174 Hz), 210.3 (Fe-CO), 162.2, 128.3, 127.6, 125.7 (C_6H_5), 93.2 (C_5H_5); (CD_2Cl_2 , -90°C , ppm): 222.1 (W-CO), 214.7(1), 210.2(1), 207.0(2) (Fe-CO). Anal. Calc. for $\text{C}_{18}\text{H}_{10}\text{FeO}_6\text{W}$: C, 38.47; H, 1.79. Found: C, 37.51; H, 1.76%.

4.2. Synthesis of $[\text{OsW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ (2)

Dark brown crystals of $[\text{OsW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ (276 mg, 40%) were obtained from $[\text{Os}(\text{CO})_4(\eta^2\text{-C}_2\text{H}_2)]$ (278 mg, 0.847 mmol) and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_5]$ (334 mg, 0.848 mmol) by a procedure similar to that described for **1** except that the solution was allowed to warm to 0°C and stirred at this temperature for 1 h. IR (hexane, cm^{-1}): 2098, 2028, 2010, 1995, 1939, 1873. $^1\text{H-NMR}$ (CD_2Cl_2 , 27°C , ppm): δ 7.50 (m, 2H, C_6H_5), 7.34 (m, 3H, C_6H_5), 5.48 (s, 5H, C_5H_5). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (CD_2Cl_2 , 27°C , ppm): δ 332.0 ($\mu\text{-C}$), 221.2 (W-CO , $J(\text{WC})$ 178 Hz), 184.4(1), 177.0(1), 174.9(2) (Os-CO), 164.1, 129.3, 128.5, 127.3 (C_6H_5), 92.7 (C_5H_5). Anal. Calc. for $\text{C}_{18}\text{H}_{10}\text{O}_6\text{OsW}$: C, 31.05; H, 1.45. Found: C, 31.07; H, 1.29%.

4.3. X-ray structure determination of $[\text{FeW}(\mu\text{-CC}_6\text{H}_5)(\text{CO})_6(\eta^5\text{-C}_5\text{H}_5)]$ (1)

Dark brown crystals of **1** were obtained by cooling a CH_2Cl_2 –pentane solution of the compound. Data were collected on a Siemens P4/RA diffractometer [34] using Mo-K_α radiation at -60°C . Unit cell parameters were obtained from a least-squares refinement of 46 reflections with $22.5^\circ < 2\theta < 25.1^\circ$. The space group was determined to be $P2_1/c$ (No. 14). The data were corrected for absorption through the use of semiempirical (ψ scans) methods. See Table 2 for a summary of crystal data, data collection and refinement information.

The structure of **1** was solved using full-matrix methods (SHELXS-86) [35]. Refinement was completed

Table 2
Crystallographic experimental details for **1** and **2**

	1	2
Empirical formula	C ₁₈ H ₁₀ FeO ₆ W	C ₁₈ H ₁₀ O ₆ OsW
Formula weight	561.96	696.31
Crystal dimensions (mm)	0.61 × 0.12 × 0.04	0.36 × 0.10 × 0.04
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
Unit cell dimensions		
<i>a</i> (Å)	8.7058(7)	15.3717(9)
<i>b</i> (Å)	15.0936(13)	9.0149(6)
<i>c</i> (Å)	27.286(2)	14.6851(10)
β (°)	92.484(7)	114.9520(10)
<i>V</i> (Å ³)	3582.1(5)	1845.0(2)
<i>Z</i>	8	4
ρ_{calc} (g cm ⁻³)	2.084	2.507
μ (mm ⁻¹)	7.258	13.14
Diffractometer	Siemens P4/RA	Bruker P4/RA/ SMART 1000 CCD
Radiation (λ (Å))	Graphite-monochromated Mo-K α (0.71073)	Graphite-monochromated Mo-K α (0.71073)
Temperature (°C)	-60	-80
Scan type	θ -2 θ	ϕ rotations (0.3°)/ ω scans (0.3°) (30 s exposures)
Data collection 2 θ limit (°)	50.0	52.78
Total data collected	6764 (-10 ≤ <i>h</i> ≤ 0, -17 ≤ <i>k</i> ≤ 0, -32 ≤ <i>l</i> ≤ 32)	8885 (-19 ≤ <i>h</i> ≤ 7, -11 ≤ <i>k</i> ≤ 11, -17 ≤ <i>l</i> ≤ 18)
Independent reflections	6317	3780
Number of observations	3961 [(<i>F</i> _o ² ≥ 2 σ (<i>F</i> _o ²)]	3145 [(<i>F</i> _o ² ≥ 2 σ (<i>F</i> _o ²)]
Structure solution method	Direct methods (SHELXS-86)	Direct methods/fragment search (DIRDIF-96)
Refinement method	Full-matrix least-squares on <i>F</i> ² (SHELXL-93)	Full-matrix least-squares on <i>F</i> ² (SHELXL-93)
Absorption correction method	Semiempirical (ψ scans)	multi-scan (SADABS)
Range of transmission factors	0.9956–0.5138	0.6028–0.0802
Data/restraints/parameters	6317 [(<i>F</i> _o ² ≥ -3 σ (<i>F</i> _o ²)]/0/469	3780 [(<i>F</i> _o ² ≥ -3 σ (<i>F</i> _o ²)]/0/235
Goodness-of-fit (<i>S</i>) ^a	1.005 [(<i>F</i> _o ² ≥ -3 σ (<i>F</i> _o ²)]	1.013 [(<i>F</i> _o ² ≥ -3 σ (<i>F</i> _o ²)]
Final <i>R</i> indices ^b <i>R</i> ₁	0.0556	0.0384
[<i>F</i> _o ² ≥ 2 σ (<i>F</i> _o ²)]		
<i>wR</i> ₂ [<i>F</i> _o ² ≥ -3 σ (<i>F</i> _o ²)]	0.1022	0.0952
Largest difference peak and hole (e ⁻ Å ⁻³)	1.164 and -0.956	1.524 and -2.244

^a $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (*n* = number of data; *p* = number of parameters varied; for **1**, $w = [\sigma^2(F_o^2) + (0.0241P)^2 + 5.8050P]^{-1}$); for **2**, $w = [\sigma^2(F_o^2) + (0.0585P)^2]^{-1}$); where $P = ([\text{Max}(F_o^2, 0) + 2F_c^2]/3)$.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

using full-matrix least-squares on *F*² (SHELXL-93) [36]. Two crystallographically-independent molecules with essentially identical geometries were found to exist in

the asymmetric unit. Positions of the hydrogen atoms were determined from the geometries of their attached carbon atoms, while their thermal parameters were assigned a value that is 20% greater than those of the attached carbon atoms. The final structure refined to *R*₁ = 0.0556 for 3961 observations with *F*_o² > 2 σ (*F*_o²) and *wR*₂ = 0.1022 for all 6317 independent reflections.

4.4. X-ray structure determination of [OsW(μ -CC₆H₅)(CO)₆(η^5 -C₅H₅)] (**2**)

Dark brown crystals of **2** were obtained by cooling a CH₂Cl₂-pentane solution of the compound. Data were collected on a Bruker P4/RA/Smart 1000 CCD diffractometer [37] using Mo-K α radiation at -80 °C. Unit cell parameters were obtained from a least-squares refinement of 5941 centered reflections. The space group was determined to be *P*2₁/*c* (No. 14). The data were corrected for absorption through the use of SADABS method. See Table 2 for a summary of crystal data, data collection and refinement information.

The structure of **2** was solved using direct methods/fragment search (DIRDIF-96) [38]. Refinement was completed using full-matrix least-squares on *F*² (SHELXL-93) [36]. In contrast to **1** the asymmetric unit of **2** does not contain two independent molecules. Hydrogen atoms were treated in the same manner as for **1**. The final structure refined to *R*₁ = 0.0384 for 3145 observations with *F*_o² > 2 σ (*F*_o²) and *wR*₂ = 0.0952 for all 3780 independent reflections.

5. Supplemental material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 204994 for compound **1** and 204995 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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