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Acetylenic Derivatives of Metal Carbonyls. Part XV. Reaction of Dodecacarbonyltriosmium with unsymmetrically Substituted Alkynes

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Dodecacarbonyltriosmium and phenylacetylene (L) in refluxing benzene give $Os_3(CO)_{10}L$, $Os_3(CO)_{10}L_2$, $Os_3(CO)_9L$ *and* $HOs_3(CO)_9(L–H)$ *as primary products. Reactivity of these complexes is investigated and formation of 1,2,4-triphenylbenzene in a sequence starting from* $Os_3(CO)_{10}L$ *is described. Corresponding reactions with propyne and 1-butyne exhibit a close analogy with those of phenylacetylene. A partially different behaviour is shown by methylphenylacetylene (L'), which reacts with dodecacarbonyltriosmium to give two isomers of molecular formula* $HOs_3(CO)_8(L'–H)L'$ *as main products. These complexes are suggested to be isostructural with an analogous compound obtained from diphenylacetylene. The main factors affecting the reaction trends are considered.*

Introduction

Diphenylacetylene reacts with docecacarbonyltriosmium to give trinuclear complexes of formula $Os_3(CO)_8[C_2(C_6H_5)_2]_2$, $Os_3(CO)_9[C_2(C_6H_5)_2]_2$ and $Os_3(CO)_7[C_2(C_6H_5)_2]_3$, whose properties and structures have been reported previously.[1–4] The catalytic activity of dodecacarbonyltriosmium in the cyclic trimerization of diphenylacetylene has also been investigated and the reaction mechanism suggested.[1] In this paper we report about reactions of dodecacarbonyltriosmium with some asymmetric alkynes of formula HC≡CX, where X = C_6H_5, CH_3, C_2H_5, with the object of determining the effect of the acetylenic hydrogen on the formation and structure of triosmium complexes and the cyclotrimerization reaction. Reactivity of methylphenylacetylene with dodecacarbonyltriosmium is also discussed herein.

Experimental

I.r. spectra were recorded on a Beckman Model IR 12 double-beam spectrophotometer with KBr optics. ^1H nmr spectra were obtained with a Jeol 60 HL spectrometer and mass spectra with a Hitachi RMU 6H mass spectrometer using an ionizing energy of 50 eV.

All reactions were carried out under nitrogen unless stated otherwise.

The reaction products were separated by TLC, using as absorbent Kieselgel $PF_{254+336}$. The petroleum ether used in elutions had b.p. 40–70° C.

Reaction of Dodecacarbonyltriosmium with Phenylacetylene

A n-heptane solution of dodecacarbonyltriosmium (0.300 g) and phenylacetylene (0.05 ml) was heated under reflux for 1 hour. The solvent was removed from the orange–red solution under reduced pressure. The residue, extracted with chloroform, was separated by TLC, eluent petroleum ether and 3% diethyl ether, to give three main bands, the first containing (Ia) and (IIIa), the second (IIa) and (IVa) and the third (III'a). Subsequently the yellow mixture of (Ia) and (IIIa) was separated by TLC, eluent petroleum ether and carbon sulphide (1:1) and the red mixture of (IIa) and (IVa) by TLC, eluent petroleum ether and 7% diethyl ether. Thus the overall yields were: (Ia), 0.005 g; (IIa), 0.003 g; (IIIa), 0.001 g; (III'a), 0.010 g; (IVa), 0.006 g. All these compounds were crystallized from n-heptane at 0° C. *Anal.* Calcd. for $C_{18}H_6O_{10}Os_3$: C, 22.69; H, 0.63; O, 16.80; Os, 59.88. Found for (Ia): C, 22.40; H, 1.0; O, 16.93; Os, 59.5%. Calcd. for $C_{26}H_{12}O_{10}Os_3$: C, 29.60; H, 1.15; O, 15.17; Os, 54.09. Found for (IIa): C, 29.82; H, 1.3; O, 15.48; Os, 54.8%. Mass spectra: (Ia), m/e 958 $[M]^+$, followed by loss of ten carbonyl groups; (IIa), m/e 1060 $[M]^+$, followed by loss of ten carbonyl groups; (IIIa) and (III'a), m/e 930 $[M]^+$, followed by loss of nine carbonyl groups; (IVa), m/e 1032 $[M]^+$, followed by loss of nine carbonyl groups.

Reaction of $Os_3(CO)_{10}C_2HC_6H_5$ *(Ia) with Phenylacetylene*

0.030 g of (Ia) and 0.01 ml of phenylacetylene dissolved in n-heptane (50 ml) were refluxed for 15 minutes. The red solution was evaporated under vacuum and the residue extracted with chloroform. Separation by TLC, eluent petroleum ether and 3% diethyl ether gave (III'a) (0.004 g), (IVa) (0.005 g) and very low yields of (IV'a) and (IV''a). Mass spectra of (IV'a) and (IV''a): m/e 1032 $[M]^+$, followed by loss of nine carbonyl groups.

Action of Heat on $Os_3(CO)_{10}C_2HC_6H_5$ (Ia)

A solution of (Ia) (0.015 g) in n-hexane (50 ml) was refluxed for 3 hours. The solution concentrated under vacuum was separated by TLC, eluent petroleum ether and 3% diethyl ether, to give (III'a) (0.003 g) as the only product.

Reaction of $Os_3(CO)_9(C_2HC_6H_5)_2$ (IVa) with Phenylacetylene

(IVa) (0.040 g) and phenylacetylene (0.02 ml) were heated in refluxing n-heptane (50 ml) for 30 minutes. After cooling, the solvent was removed under reduced pressure and the residue extracted with benzene. Separation by TLC, using as eluent to get the best movement of bands petroleum ether and 7% diethyl ether, did not give pure products, except 1,2,4-triphenylbenzene (0.003 g). The most abundant complex was however identified by its mass spectrum as $Os_3(CO)_7(C_2HC_6H_5)_3$ (m/e 1078 $[M]^+$, followed by loss of seven carbonyl groups). Other carbonyl compounds in low yields were not characterized.

Action of Carbon Monoxide on $Os_3(CO)_9(C_2HC_6H_5)_2$ (IVa)

Carbon monoxide was bubbled through a n-heptane solution (30 ml) of (IVa) (0.020 g) at room temperature for 7 hours. (IVa) was converted in good yield to a colourless product (Va), isolated by TLC, eluent petroleum ether. *Anal.* Calcd. for $C_{22}H_{12}O_6Os_2$: C, 35.10; H, 1.61; O, 12.75; Os, 50.54. Found for (Va): C, 34.87; H, 1.9; O, 12.93; Os, 50.7%. Mass spectrum: m/e 756 $[M]^+$, followed by loss of six carbonyl groups.

Reaction of Dodecacarbonyltriosmium with Propyne

A slow stream of propyne was slowly bubbled through a refluxing solution of dodecacarbonyltriosmium for 6 hours. After cooling the solvent was removed under reduced pressure and the residue separated by TLC (using as eluent petroleum ether and 2% ethyl ether) into two main bands. One contained (IIb) and traces of a compound shown by mass spectrometry to be $Os_3(CO)_{10}C_2HCH_3$, and the other (IIIb).

After a similar experiment carried on at higher temperature (refluxing n-heptane for 3 hours), the separation of the residue by TLC (eluent as above) yielded three bands, the first containing (IIb) and (IVb), the second (IIIb) and the third (Vb). (IIb) and (IVb) were separated by TLC using as eluent petroleum ether and 8% diethyl ether. *Anal.* Calcd. for $C_{15}H_8O_9Os_3$: C, 19.95; H, 0.89; O, 15.95; Os, 63.2. Found for (IVb): C, 19.15; H, 1.1; O, 16.05; Os, 62.7%. Mass spectrum of (IIb): m/e 936 $[M]^+$, followed by loss of ten carbonyl groups; mass spectrum of (IIIb): m/e 868 $[M]^+$, followed by loss of nine carbonyl groups; mass spectrum of (IVb): m/e 908 $[M]^+$, followed by loss of nine carbonyl groups; mass spectrum of (Vb): m/e 632 $[M]^+$, followed by loss of six carbonyl groups.

Reaction of Dodecacarbonyltriosmium with 1-butyne

A n-heptane solution of dodecacarbonyltriosmium was reacted with 1-butyne (molar ratio 1 : 2) for 3 hours at 120° C in a sealed tube. After removal of the solvent and separation by TLC (eluent petroleum ether and 3% diethyl ether) four compounds were obtained: (IIc), (IIIc), (III'c) and (Vc). *Anal.* Calcd. for $C_{13}H_6O_9Os_3$: C, 17.81; H, 0.69; O, 16.42; Os, 65.08. Found for (III'c): C, 17.58; H, 0.9; O, 16.24; Os, 65.6%. Mass spectra of (IIc): m/e 964 $[M]^+$, followed by loss of ten carbonyl groups; mass spectra of (IIIc): m/e 882 $[M]^+$, followed by loss of nine carbonyl groups; mass spectra of (Vc): m/e 660 $[M]^+$, followed by loss of six carbonyl groups.

Reaction of Dodecacarbonyltriosmium with Methylphenylacetylene

Dodecacarbonyltriosmium (0.300 g) and methylphenylacetylene (0.84 ml), dissolved in n-heptane, were refluxed for 5 hours. After removal of the solvent, the residue was extracted with chloroform and separated by TLC (eluent petroleum ether and 2% diethyl ether) to give four main bands. The first band yielded (III'd) and (IIId); the second a little amount of a compound characterized by its mass spectrum as $Os_3(CO)_9(CH_3C_2C_6H_5)_2$; the third (IId) and (VId); the fourth (VI'd). The mixture of (III'd) and (IIId) was then separated using as eluent petroleum ether and the mixture of (IId) and (IVd) using as eluent petroleum ether and 8% diethyl ether. The overall yields were: (IId), 0.003 g; (VId), 0.008 g; (VI'd), (0.010 g). All the products were crystallized from n-heptane at 0° C. *Anal.* Calcd. for $C_{26}H_{16}O_8Os_3$: C, 30.41; H, 1.57; O, 12.46; Os, 55.56. Found for (VI'd): C, 30.91; H, 1.7; O, 11.78; Os, 54.4%. Mass spectra: (IId), m/e 1088 $[M]^+$, followed by loss of ten carbonyl groups; (IIId) and (III'd), m/e 944 $[M]^+$, followed by loss of nine carbonyl groups; (VI'd) and (VId), m/e 1032 $[M]^+$, followed by loss of eight carbonyl groups.

Action of Carbon Monoxide on $Os_3(CO)_8(CH_3C_2C_6H_5)_2$ (VId)

Carbon monoxide was bubbled through a n-heptane solution (30 ml) of (VId) at room temperature for 2 hours. (VId) was converted in good yield to a colourless product (Vd), which was purified by TLC, eluent petroleum ether and 8% diethyl ether. *Anal.* Calcd. for $C_{24}H_{16}O_6Os_2$: C, 36.92; H, 2.06; O, 12.29; Os, 48.71. Found for (Vd): C, 37.15; H, 2.7; O, 12.05; Os, 48.3%. Mass spectrum of (Vd); m/e, 784 $[M]^+$, followed by loss of six carbonyl groups.

Results and Discussion

Phenylacetylene Complexes

Dodecacarbonyltriosmium and phenylacetylene react in n-heptane under reflux to give three trinuclear primary products of molecular formula $Os_3(CO)_{10}C_2HC_6H_5$ (Ia), $Os_3(CO)_{10}(C_2HC_6H_5)_2$ (IIa) and $Os_3(CO)_9C_2HC_6H_5$ (IIIa), as shown in the Scheme 1. The proton nmr spectrum of (Ia) (Table I) exhibits two singlets at τ –0.06 and 2.77, in the ratio 1:5, and its i.r. spectrum both terminal and bridging carbonyl stretching bands. The high stability of osmium–osmium bonds suggests that a simple substitution reaction takes place in the formation of (Ia) with simultaneous shifting of a number of carbonyl groups from terminal to bridging positions. The phenylacetylene ligand acts as a four-electron donor and is thought to be in a bridging arrangement. Analogous arrangements of ligands in trinuclear osmium complexes have been reported.[7–9] The suggested bonding scheme of (Ia), consisting of two σ bonds to Os(1) and Os(2) with a two π-type electrons donation to Os(3), is shown in Figure 1. This assumption is consistent with the downfield shift of the H-C proton, in accordance with figures reported for complexes containing ligands σ–π bonded to metal atoms.[10,11] The effective atomic number rule is satisfied only if two carbonyl groups bridge Os(1)–Os(3) and Os(2)–Os(3) bonds, or one bridges Os(1)–Os(2) bond.

As shown in the Scheme 1, (IIa) ejects one ligand molecule upon heating in refluxing n-heptane to yield (III'a). This suggests that the two phenylacetylene moieties are not linked together in (IIa). In the proton nmr spectrum the two hydrogen atoms appear as two singlets at τ 1.20 and 2.15 and the aromatic signals in the range τ 2.25–3.00. In the i.r. spectrum absorption bands due to terminal and bridging carbonyl groups are present. Moreover a preliminary X-ray analysis has demonstrated the presence of the metal cluster in (IIa).[5] Therefore it is reasonable to assume that the 2-electron donor ligand molecules are in bridging positions with the hydrogen atoms in non-equivalent environments.

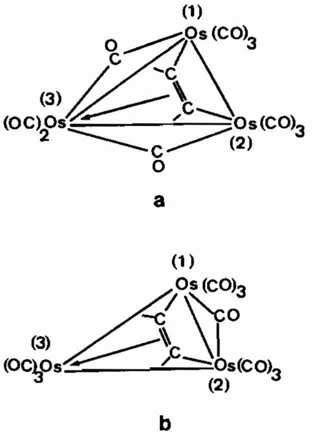
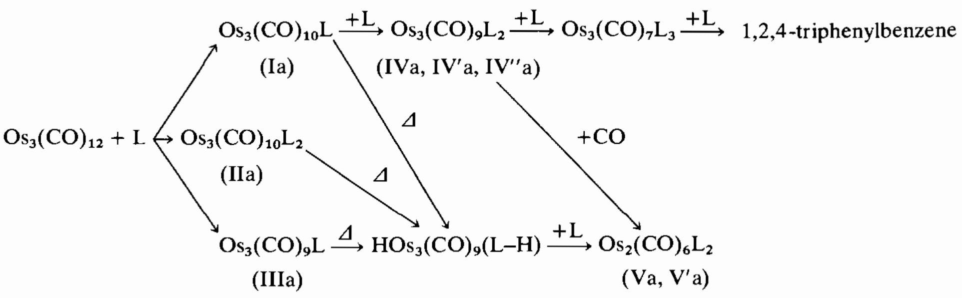


Figure 1. Suggested structures of $Os_3(CO)_{10}C_2HC_6H_5$ (I).

(IIIa) and its isomer (III'a), which is obtained from (IIIa) on heating in n-heptane, exhibit apparent formula $Os_3(CO)_9C_2HC_6H_5$ and similar i.r. spectra with absorption bands assignable to only terminal carbonyl groups. The proton nmr spectrum of (III'a) gives a highfield signal at τ 32.9 assignable to an Os–H bond in addition to a broad multiplet in the range τ 2.46–2.68 due to the phenyl group. Therefore (III'a) is to be reformulated as $HOs_3(CO)_9C_2C_6H_5$. On the basis of these data we assume that (IIIa) and (III'a) display the same simmetry, but different bonding of the organic moiety to the metal cluster. (IIIa) is suggested to be isostructural with $Fe_3(CO)_9C_2(C_6H_5)_2$[12], and (III'a) with $HRu_3(CO)_9C_2(t\text{-}C_4H_9)$,[13] where the formation of a σ carbon–metal bond occurs with migration of a hydrogen atom to the cluster. The thermal stability of (III'a) is rather high, but it reacts in refluxing n-heptane with an excess of phenylacetylene and mixtures of compounds of formula $Os_2(CO)_6(C_2HC_6H_5)_2$ are formed.

More interesting features are observed in the reaction of (Ia) with excess ligand because organic cyclotrimers are isolated as final step. The intermediate products are mixtures of isomers having hydrogen atoms and phenyl groups in different relative positions.



Scheme 1 $L = C_2HC_6H_5$

TABLE I. Carbonyl Stretching Frequencies and Proton Nmr Spectra.

Complex	Colour	ν (CO)[a] cm^{-1}	Chemical Shift[b,c]
(Ia) $Os_3(CO)_{10}C_2HC_6H_5$	Pale yellow	2101m 2066vs 2055s 2027s 2009s 2003shm 1948w 1847w	–0.06s(1) 2.77bs(5)
(IIa) $Os_3(CO)_{10}(C_2HC_6H_5)_2$	Yellow	2096m 2060vs 2026s 2018m 2004m 1996shw 1965shw 1855w	1.20s(1) 2.15s(1) 2.25–3.00bm(10)
(IIIa) $Os_3(CO)_9C_2HC_6H_5$	Colourless	2104m 2082s 2060vs 2029s 2018s 1999w 1987m	
(III'a) $HOs_3(CO)_9C_2C_6H_5$	Colourless	2102m 2077vs 2054vs 2022s 2016m 1985m 1953w	2.46–2.67m(5) 32.9s(1)
(IVa) $Os_3(CO)_9(C_2HC_6H_5)_2$	Red	2106m 2060vs 2031s 2026s 2012s 2000m 1992m 1970shm 1946m	2.27d(1) 2.3–2.9m(10) 3.00d(1)
(IV'a) $Os_3(CO)_9(C_2HC_6H_5)_2$	Pink	2107m 2060vs 2032s 2028s 2012vs 2000s 1989m 1936w	
(IV''a) $Os_3(CO)_9(C_2HC_6H_5)_2$	Pink	2108m 2060vs 2034shs 2028s 2012vs 2000s 1991m 1972w 1943w	
(Va) $Os_2(CO)_6(C_2HC_6H_5)_2$	Colourless	2085s 2054vs 2018s 2007s 1989m 1976s	
(V'a) $Os_2(CO)_6(C_2HC_6H_5)_2$	Pink	2089s 2054vs 2049vs 2016vs 2001w 1986m	2.39–2.72m(10) 3.27s(2)
(IIb) $Os_3(CO)_{10}(C_2HCH_3)_2$	Yellow	2097m 2058vs 2026s 2017m 2002m 1997w 1970shw 1852w	
(IIIb) $Os_3(CO)_9C_2HCH_3$	Yellow	2102m 2074s 2054vs 2023s 2013s 2006w 1983m	
(III'b) $HOs_3(CO)_9C_2CH_3$	Colourless	2102m 2075vs 2054vs 2022s 2017m 2004m 1985m	
(IVb) $Os_3(CO)_9(C_2HCH_3)_2$	Red	2107m 2059vs 2032s 2029s 2012s 1997m 1986m 1939m	2.96d(1) 3.68d(1) 7.38s(3) 7.51s(3)
(Vb) $Os_2(CO)_6(C_2HCH_3)_2$	Colourless	2082s 2048vs 2011s 2001s 1980m 1969s	
(IIc) $Os_3(CO)_{10}(C_2HC_2H_5)_2$	Pale yellow	2097m 2057vs 2025s 2016m 2002m 1999w 1976shw 1852w	
(IIIc) $Os_3(CO)_9C_2HC_2H_5$	Yellow	2100m 2073s 2052vs 2020s 2011s 1997w 1981m 1967shw	
(III'c) $HOs_3(CO)_9C_2C_2H_5$	Colourless	2100m 2074vs 2052vs 2020s 2010m 1983m 1953w	6.65q(2) 8.35t(3) 33.1s(1)
(Vc) $Os_2(CO)_6(C_2HC_2H_5)_2$	Colourless	2083s 2051vs 2015s 2001s 1983m 1972s	
(IId) $Os_3(CO)_{10}(C_2CH_3C_6H_5)_2$	Yellow	2095m 2055vs 2026s 2017m 2001m 1994w 1968shw 1850w	
(III'd) $HOs_3(CO)_9C_2CH_2C_6H_5$	Yellow	2100s 2072s 2048vs 2024s 2018shm 2002s 1995m 1983m 1948w	
(Vd) $Os_2(CO)_6(C_2CH_3C_6H_5)_2$	Colourless	2080s 2049vs 2010s 1999s 1986m 1967s	2.56–2.84m(10) 7.51s(3) 8.11s(3)
(V'd) $Os_2(CO)_6(C_2CH_3C_6H_5)_2$	Colourless	2079s 2053vs 2012m 2002s 1991shm 1975m	2.54–2.94m(10) 7.78s(6)
(VId) $HOs_3(CO)_8(C_2CH_3C_6H_4)(C_2CH_3C_6H_5)$	Yellow	2094s 2056s 2030vs 2018m 2012m 1995m 1986w 1975m	2.1–3.4m(9) 7.58s(3) 7.95s(3) 24.8s(1)
(VI'd) $HOs_3(CO)_8(C_2CH_3C_6H_4)(C_2CH_3C_6H_5)$	Yellow	2096s 2060s 2030vs 2020m 2014m 1999m 1990shw 1972m	2.1–3.4m(9) 7.37s(3) 7.56s(3) 24.9s(1)

[a] Carbon tetrachloride solution, except for (IIIa), (Va) and (V'a) (n-heptane). [b] Carbon tetrachloride solution, except for (Ia), (V'a), (Vd) (deuteroacetone), and (III'a), (Vd), (V'd) (deuterochloroform). [c] Relative intensities in parentheses.

This caused difficulties in the purification step and the very small amounts of some of these isomers were often insufficient to enable any nmr data to be obtained. Treatment of (Ia) with phenylacetylene in refluxing n-heptane gives three isomers of molecular formula $Os_3(CO)_9(C_2HC_6H_5)_2$ (IVa), (IV'a) and (IV''a), which, on the basis of analytical data and reactivity with carbon monoxide, are considered isostructural with $Os_3(CO)_9[C_2(C_6H_5)_2]_2$.[2] The proton nmr absorption bands of (IVa) allow one to suggest a non-symmetric arrangement of hydrogen atoms and phenyl groups on the osmiacyclopentadiene moiety as shown in Figure 2. Insufficient (IV'a) and (IV''a) were available for proton nmr spectra, but the similarity of mass and i.r. spectra can be interpreted as indicating an identical molecular skeleton. The isomerism is due to the relative positions of substituents on the ligand. (IVa) and (IV'a) react in very mild conditions with CO to give the binuclear complexes $Os_2(CO)_6(C_2HC_6H_5)_2$ (Va) and (V'a) respectively, analogous to $Os_2(CO)_6[C_2(C_6H_5)_2]_2$.[2,3] The amount of (IV''a) was insufficient to carry out the reaction with CO. The proton nmr spectrum of (Va) is very complex as phenyl and hydrogen signals are overlapped. As shown in Table I, hydrogen atoms and phenyl groups are in equivalent environments in (V'a) and consequently in (IV'a) too.

Reaction of (IVa) and phenylacetylene in refluxing n-heptane yields a number of complexes, which were found not to be completely pure even after successive chromatographic separations. In addition triphenylbenzene is obtained in this reaction, the 1,2,4-isomer being by far the most abundant. Several i.r. and mass spectra of the complexes with different purity degree showed the presence of a complex of molecular formula $Os_3(CO)_7(C_2HC_6H_5)_3$ (VIa). The analogous $Os_3(CO)_7[C_2(C_6H_5)_2]_3$ has been obtained in the reaction of $Os_3(CO)_{12}$ and $C_2(C_6H_5)_2$ and shown to be involved in the cyclotrimerization of diphenylacetylene to hexaphenylbenzene.[1] A similar reaction sequence could not be proved here for the reasons mentioned above, and the cyclotrimerization mechanism was not demonstrated on experimental basis. However, analogous complexes being involved, we think it is reasonable to suggest that 1,2,4-triphenylbenzene is formed by phenylacetylene in the presence of $Os_3(CO)_{12}$ through the same path as described previously for the cyclotrimerization of diphenylacetylene.

Propyne Complexes

On bubbling propyne through a refluxing benzene solution of dodecacarbonyltriosmium three complexes of molecular formula $Os_3(CO)_{10}C_2HCH_3$ (Ib), $Os_3(CO)_{10}(C_2HCH_3)_2$ (IIb) and $Os_3(CO)_9C_2HCH_3$ (IIIb) are obtained. The amount of (Ib) is very low and its presence was revealed by a mass spectrum, in admixture with (IIb). Attempts to increase the quantity of (Ib) were unsuccessful, because all these compounds seem to be formed at about the same time.

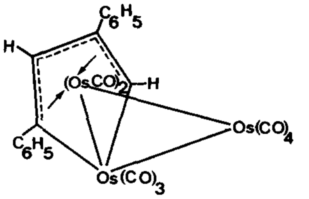


Figure 2. Suggested structure of $Os_3(CO)_9(C_2HC_6H_5)_2$ (IVa).

When the same reaction is carried on in refluxing n-heptane, compounds of molecular formula $HOs_3(CO)_9CCH_3$ (III'b), $Os_3(CO)_9(C_2HCH_3)_2$ (IVb) and $Os_2(CO)_6(C_2HCH_3)_2$ (Vb) are the main products. No isomer due to different position of substituents on the ligand was observed, but their presence in very little quantities is of course not to be excluded. Detailed suggestions can be proposed only for the structure of (IVb), where the ^1H nmr spectrum shows a distribution of substituents on the osmiacyclopentadiene ring identical to that of (IVa). (IIIb) is converted to (III'b) on heating in refluxing n-heptane for 5 hours and (IVb) reacts with CO at room temperature to yield (Vb). These results and the close resemblance of i.r. spectra indicate that propyne and phenylacetylene give similar complexes with $Os_3(CO)_{12}$.

A complete reaction sequence could not be demonstrated here, but the several products obtained under different experimental conditions are consistent with the previous deductions. Milder reaction conditions give (Ib), (IIb) and (IIIb), which are likely to be the primary products also in this case, while higher temperature leads to formation of prevailing quantities of (III'b), (IVb) and (Vb).

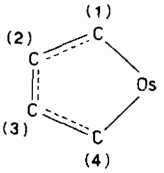
1-Butyne Complexes

The reaction of dodecacarbonyltriosmium and 1-butyne in a sealed tube at 120° C affords as main products $Os_3(CO)_{10}(C_2HC_2H_5)_2$ (IIc), $HOs_3(CO)_9C_2C_2H_5$ (III'c) and $Os_2(CO)_6(C_2HC_2H_5)_2$ (Vc), analogous to the final terms of the sequences shown in the Scheme 1 for phenylacetylene.

Methylphenylacetylene Complexes

A rather different reaction trend is observed when methylphenylacetylene is used as ligand. Two isomers of molecular formula $Os_3(CO)_9C_2CH_3C_6H_5$ (IIId) and (III'd) were isolated, but their very low amounts were insufficient to enable any nmr data to be obtained. (IIId) was characterized only by its mass spectrum, while the i.r. spectrum around 2000 cm^{-1} of (III'd) exhibits a close resemblance with that of $HOs_3(CO)_9C_6H_9$,[14] prepared from $Os_3(CO)_{12}$ and 3-hexyne, and of $HRu_3(CO)_9C_6H_9$,[11] obtained from $Ru_3(CO)_{12}$ and 2,4-hexadiene. (III'd) is therefore considered analogous to these compounds with the ligand $-CH_2-C\equiv C-C_6H_5$ linked to the cluster by a σ Os–C bond involving the methylene group and π bonds from the C≡C moiety. The little yields of (IIId) and (III'd) prevent one from verifying whether they are the only primary products. In addition three other compounds, whose apparent formulae contain two ligand molecules, are obtained: $Os_3(CO)_{10}(C_2CH_3C_6H_5)_2$ (IId), which can be considered isostructural to (IIa), (IIb) and (IId) and two isomers of molecular formula $Os_3(CO)_8(C_2CH_3C_6H_5)_2$ (VId) and (VI'd), which are the major products of this reaction. A high-field signal at about τ 25 and very broad absorption bands in the aromatic region of the ^1H nmr spectrum suggest to assume for (VId) and (VI'd) a structure analogous to that of $HOs_3(CO)_8(C_2C_6H_5C_6H_4)[C_2(C_6H_5)_2]$. A close similarity of the i.r. spectra and the behaviour of (VId) and (VI'd) in the reaction with CO confirm this hypothesis. (VId) and (VI'd) do react with CO under very mild conditions to give as final products $Os_2(CO)_6(C_2CH_3C_6H_5)_2$ (Vd) and (V'd). Trinuclear complexes of type $Os_3(CO)_9[C_2(C_6H_5)_2]_2$[2] are not isolated as intermediate products, but this might be easily explained on taking into account the steric hindrance of the organic substituents on the osmiacyclopentadiene ring – main factor affecting the addition rate of carbon monoxide.

The isomerism of (VId) and (VI'd) is likely to be due to the relative positions of substituents on the osmiacyclopentadiene moiety. In both complexes one phenyl group must be linked to one of the carbon atoms adjacent to the osmium, C(1) in the scheme below,



while the arrangement of the other groups is deduced from the chemical shifts of the CH_3 signals in the proton nmr spectra. The higher τ values and their larger separation in the spectrum of (VId) suggest that the second phenyl group is bonded to C(3) in this isomer. Consequently (VI') should display a symmetric arrangement with the phenyl groups linked to C(1) and C(4) and the methyl groups to C(2) and C(3). Proton nmr data of (Vd) and (V'd) support these assignments.

Conclusions

A comparison of the results described herein with those reported previously[1–5] permits us to draw some conclusions on the behaviour of dodecacarbonyltriosmium with respect of the alkynes. Diphenylacetylene reacts with $Os_3(CO)_{12}$ to give as primary major product $Os_3(CO)_8[C_2(C_6H_5)_2]_2$ containing a bond between a phenyl group and a metal atom. It reacts with carbon monoxide to give $Os_3(CO)_9[C_2(C_6H_5)_2]_2$ and $Os_2(CO)_6[C_2(C_6H_5)_2]_2$ in successive steps and with diphenylacetylene (excess) to give $Os_3(CO)_7[C_2(C_6H_5)_2]_3$ and subsequently hexaphenylbenzene. A part of this sequence is followed by methylphenylacetylene, which yields (VId) and (VI'd). Addition of CO to these isomers takes place under about the same experimental conditions to give the binuclear complexes (Vd) and (V'd) in an apparently single step. The bulkiness of the organic groups on the osmacyclopentadiene ring is considered to be responsible for this different behaviour. Moreover a little amount of the monoligand compound $HOs_3(CO)_9C_2CH_2C_6H_5$ (III'd) is isolated, whilst the absence in diphenylacetylene of a hydrogen atom in α position to the triple bond prevents the formation of an analogous compound.

Phenylacetylene was expected to give with $Os_3(CO)_{12}$ a compound analogous to $Os_3(CO)_8[C_2(C_6H_5)_2]_2$, but surprisingly it was not observed. Instead, the complex $Os_3(CO)_{10}C_2HC_6H_5$ (Ia), isolated in rather good yield, appears to be the initial product of the sequence shown in the Scheme 1 with $Os_2(CO)_6(C_2HC_6H_5)_2$ and 1,2,4-triphenylbenzene as final terms. In particular, the high yield and the good stability of (III'a) demonstrate the ability of a hydrogen atom directly linked to an unsatured carbon to migrate to the cluster. An accompanying formation of a σ C–Os bond must occur. This is confirmed by the reaction of $Os_3(CO)_{12}$ with propyne and 1-butyne, where compounds similar to those described for phenylacetylene are encountered.

Two factors seem to be prevalent in influencing the reaction trends. The former is the rupture of a hydrogen–carbon bond with transfer of the hydrogen to the cluster, the carbon atom involved being one of the C≡C moiety, as in $C_2HC_6H_5$, C_2HCH_3 and $C_2HC_2H_5$, or a carbon in α position to the C≡C moiety as in $C_2CH_3C_6H_5$. The latter is the alternative formation of compounds of type $Os_3(CO)_8L_2$, where $L = C_2(C_6H_5)_2$, $C_2(p\text{-}ClC_6H_4)_2$, $C_2(p\text{-}CH_3C_6H_4)_2$ and $C_2CH_3C_6H_5$, and compounds of type $Os_3(CO)_{10}L'$, where $L' = C_2HC_6H_5$, C_2HCH_3 and $C_2HC_2H_5$.

At this stage no clear-cut explanation can be proposed to justify the different behaviour of these two groups of ligands, the substituent bulkiness being the only apparent and significant difference in these molecules.

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