Acetylenic Derivatives of Metal Carbonyls. Part XIII.[1] Reactions of Dodecacarbonyltriosmium with Aryl Acetylenes

By **R. P. Ferrari, G. A. Vaglio, O. Gambino, M. Valle,** and **G. Cetini,*** Institute of General and Inorganic Chemistry, University of Turin, Corso Massimo d'Azeglio 48, C.A.P. 10125, Turin, Italy

Dodecacarbonyltriosmium reacts with acetylenic ligands L [L = Ph_2C_2, $(p\text{-}ClC_6H_4)_2C_2$, $(p\text{-}CH_3C_6H_4)_2C_2$] in n-heptane under reflux to yield complexes of general formula $L_2Os_3(CO)_8$. Analysis of their n.m.r. and mass spectra indicated the probable existence of a bridging hydrido-ligand. It is suggested that the stability of these compounds is due to a bond between a phenyl group and an osmium atom and the presence of a hydrido-ligand.

Complexes $L_2Os_3(CO)_8$ react with CO to give $L_2Os_3(CO)_9$, following second-order rate laws. Effect of ligand L on the reaction rate is discussed. Further action of CO on $L_2Os_3(CO)_9$ gives binuclear complexes $L_2Os_2(CO)_6$. Ligands L′ such as PF_3, PPh_3, $AsPh_3$, and $SbPh_3$ react with $L_2Os_3(CO)_8$ to give $L_2Os_3(CO)_8L'$, which are considered to be isostructural with $L_2Os_3(CO)_9$.

DIFFERENCES between dodecacarbonyltriosmium and its ruthenium and iron analogues in reaction with diphenylacetylene have been reported.[1]

The initial product of the dodecacarbonyltriosmium reaction, $(Ph_2C_2)_2Os(CO)_8$ (I), was initially considered isostructural with the violet isomers $(Ph_2C_2)_2Fe_3(CO)_8$ [2] and $(Ph_2C_2)_2Ru_3(CO)_8$.[3] However, the ^1H n.m.r. spectrum of a concentrated solution of (I) shows an absorption at τ 25·5, indicating the presence of a metal–hydrogen bond.

X-Ray analysis [4] of (I) has shown a close resemblance between its skeleton and that of $(Ph_2C_2)_2Os_3(CO)_9$ (II).[1] The two ligand molecules that form an osmacyclopentadiene ring in (II) form the same moiety in (I). The most significant feature of the structure (I) is the presence of a bond between the phenyl group (a) and the osmium atom (2), as shown by the broken line in Figure 1. Bond distances and angles suggested two hypotheses, one implying a bond between a phenyl carbon atom and the osmium atom (2) and the presence of a terminal hydrogen on the same osmium atom, the other the existence of a tricentric carbon–hydrogen–osmium bond. However i.r. data would not distinguish between these hypotheses.[5]

More useful information was obtained from the mass spectrum of (I). Eight carbonyl groups were lost from the molecular ion in successive steps, but no sign of the elimination of a hydrogen radical was observed. This fragmentation scheme suggests that the hydrido-ligand is not terminally bonded.[6] The molecular ion with a structure, different from that shown in Figure 1, in which no hydrogen–osmium bond is present and no phenyl group is linked to a metal atom may also be postulated. This would be more compatible with a carbon–hydrogen–osmium tricentric bond.

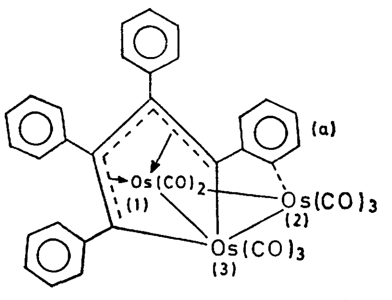

FIGURE 1 Structure of $(Ph_2C_2)_2Os_3(CO)_8$

Besides the singlet at τ 25·5, the ^1H n.m.r. spectrum of (I) also shows bands in the range τ 2·2—4·3. The area values indicate three phenyl groups in similar environments, with hydrogen atoms of the phenyl group (a) giving rise to absorption bands at different τ values.

Analogous results were obtained in the reactions of dodecacarbonyltriosmium with *pp*′-dichloro- and *pp*′-dimethyl-diphenylacetylene. The initial products $[(p\text{-}ClC_6H_4)_2C_2]_2Os_3(CO)_8$ (IV) and $[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_8$ (VII), are shown in the Scheme. The mass spectrum of (IV) does not exhibit any ion of reasonable intensity, because of thermal decomposition in the ionization

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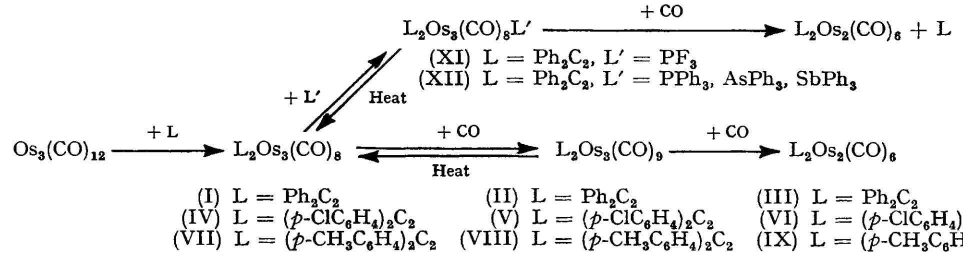
chamber, while (VII) shows a weak molecular ion. However, similarity of (I), (IV), and (VII) was evident from the i.r. (Table 1) and ^1H n.m.r. data and on the positive results of elemental analysis. The ^1H n.m.r. spectra for (IV) and (VII) display characteristic singlets at τ 25·7 and 25·6 respectively, while the aromatic hydrogen absorptions and the τ 7·7 and 7·8 bands (area ratio 3 : 1) seem to support the substituent arrangement suggested above. Moreover, (IV) and (VII) react with CO similarly to (I), *i.e.* they give, in a first step, $[(p\text{-}ClC_6H_4)_2C_2]_2Os_3(CO)_9$ (V) and $[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_9$ (VIII) and, after longer reaction times $[(p\text{-}ClC_6H_4)_2C_2]_2Os_2(CO)_6$ (VI) and $[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_2(CO)_6$ (IX).



SCHEME

TABLE 1

I.r. data (cm^{-1}) for the reported osmium carbonyl compounds (measured in carbon tetrachloride) in the range 2200—1800 cm^{-1}

$[(p\text{-}ClC_6H_4)_2C_2]_2Os_3(CO)_8$	2100s, 2062s, 2038vs, 2024m, 2018m, 2002m, 1995w, 1981m
$[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_8$	2094s, 2056s, 2032vs, 2017m, 2011m, 1996m, 1988sh, 1975m
$[(p\text{-}ClC_6H_4)_2C_2]_2Os_3(CO)_9$	2118s, 2062vs, 2048s, 2040s, 2017s, 2004m, 1995w, 1976s, 1932m
$[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_9$	2113s, 2058vs, 2044s, 2037s, 2011s, 1998m, 1989w, 1972s, 1927m
$(Ph_2C_2)_2Os_3(CO)_8AsPh_3$	2076m, 2042s, 2003vs, 1993m, 1985w, 1960m, 1908w
$(Ph_2C_2)_2Os_3(CO)_8PPh_3$	2074m, 2042s, 2006vs, 1993m, 1985w, 1965m, 1910w
$(Ph_2C_2)_2Os_3(CO)_8SbPh_3$	2074m, 2043s, 2004vs, 1997m, 1984w, 1962m, 1909w
$[(p\text{-}ClC_6H_4)_2C_2]_2Os_3(CO)_8AsPh_3$	2078m, 2046s, 2007vs, 1997m, 1987w, 1965m, 1912w
$[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_8AsPh_3$	2074m, 2042s, 2003vs, 1995m, 1982w, 1961m, 1909w
$(Ph_2C_2)_2Os_3(CO)_8PF_3$	2100m, 2058vs, 2036vs, 2018s, 2004m, 1992sh, 1976s, 1930m
$[(p\text{-}ClC_6H_4)_2C_2]_2Os_2(CO)_6$	2087s, 2057vs, 2024s, 2000s, 1974m
$[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_2(CO)_6$	2081s, 2050vs, 2016s, 1998s, 1967m

The ^1H n.m.r. and i.r. (Table 1) spectra also show that (V) and (VIII) are isostructural with (II), while (VI) and (IX) with $(Ph_2C_2)_2Os_2(CO)_6$ (III).[1] In addition (VI) and (IX) display intense molecular ions and fragments reminiscent of (III).[7]

Analogous binuclear complexes have already been reported.[8,9]

By contrast, dodecacarbonyltriosmium reactions with acetylene and but-2-yne produced[1] complexes of type (II) with no intermediate $L_2Os_3(CO)_8$ stage. This suggests that type (I) complexes are stable only when a substituent group and an osmium atom give a bond of the type present in (I), (IV), and (VII) (Figure 1). Experiments are in progress to determine whether bulkiness and/or the nature of the substituent groups is the major factor controlling stability.

The formation kinetics of (V) and (VIII) were also investigated. The parameters illustrated in Table 2, together with those for the reaction of (I) with CO,[1] show the reactions follow a second-order rate law. The effect of temperature on k_{II} values for the reaction of (VII) with CO could not be investigated, due to poor yield of (VII). The k_{II} values at 0 °C suggest that the reaction rate decreases when the phenyl groups are substituted in the same positions and the effects of a chlorine atom and a methyl group point in the same direction. Substituent bulkiness seems to be a dominant factor in controlling the CO addition rate. Since the steric hindrance of the two substituents is not very different, electrostatic repulsion between phenyl group (a) chlorine and the entering CO may occur; this might explain the larger decrease of the reaction rate for (IV).

Treatment of (I) with PF_3 in toluene yielded $(Ph_2C_2)_2Os_3(CO)_8PF_3$ (X). The reaction rate was not measured, but appeared to be very similar to that between (I) and CO. PF_3 and CO behave, in fact, like similar π acceptor ligands. The i.r. (Table 1) and ^1H n.m.r. spectra are related to those of (II), and the mass spectrum shows an abundant molecular ion. (X) is expected to be isostructural with (II). (X) reacts readily with PF_3 to give one of the possible $(Ph_2C_2)_2Os_3(CO)_7(PF_3)_2$ (XI) isomers, identified solely by observation of the molecular ion. The very low yield prevented a better characterization.

Reactions of (I) with nucleophilic ligands such as triphenylphosphine, triphenylarsine, and triphenylstibine in toluene at room temperature instantaneously give $(Ph_2C_2)_2Os_3(CO)_8L'$ (XII) complexes (Scheme). When heated *in vacuo*, these complexes yielded (I), and

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no information was obtained from their mass spectra. However, elemental analysis results indicated that one ligand molecule is present in (XII) and ^{1}H n.m.r. spectra showed three absorption bands in the aromatic hydrogen region at τ *ca.* 2·5, 3·0, 3·2 (areas in the ratio 1·5 : 1 : 1). Reactions of (XII) with CO gave the free ligand L′ and (III). It can thus be argued that these complexes present a structure similar to that of (II) (Figure 2). Complexes (IV) and (VII) behave like (I) in the reactions with triphenylarsine.

TABLE 2

Second-order rate constants for the reactions of of $L_2Os_3(CO)_8$ with CO in toluene

L	Complex mM	CO [a] mM	Temp. °C	10^5k_{obs} s^{-1}	10^2k M^{-1} s^{-1}
Ph_2C_2	0·716	0·57	0	1·87	3·3
	0·752	1·96	0	6·5	3·3
	0·752	7·2	0	19·6	2·9
	0·544	1·93	0	6·6	3·4
	0·46	1·96	0	6·6	3·4
	0·885	0·54	10·2	5·1	9·5
	0·758	0·51	18	11·0	21·6
$(p\text{-}ClC_6H_4)_2C_2$	0·388	7·0	0	2·8	0·40
	0·791	1·83	0	8·1	0·44
	0·795	7·3	0	3·2	0·44
	0·786	1·72	9·5	2·3	1·34
	0·641	1·70	9·5	2·4	1·42
	0·776	1·65	17·7	6·0	3·6
$(p\text{-}CH_3C_6H_4)_2C_2$	0·861	0·35	0	0·47	1·34
	0·352	1·70	0	2·4	1·42
	0·718	6·5	0	9·6	1·48

[a] Concentration of CO in solution L = Ph_2C_2 : $\Delta H^{\ddagger} = 16$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6·5$ e.u. L = $(p\text{-}ClC_6H_4)_2C_2$: $\Delta H^{\ddagger} = 18·4$ kcal mol^{-1}, $\Delta S^{\ddagger} = -2$ e.u.

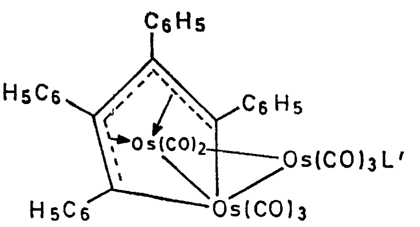

FIGURE 2 Structure of $(Ph_2C_2)_2Os_3(CO)_8L'$; L′ = PF_3, PPh_3, $AsPh_3$, or $SbPh_3$

EXPERIMENTAL

I.r. spectra were recorded on a Beckman IR 12 double-beam spectrophotometer with KBr optics, and ^{1}H n.m.r. spectra on a Jeol 60 HL spectrometer. Mass spectra were obtained with a Perkin-Elmer–Hitachi RMU 6H mass spectrometer using an ionizing energy of 75 eV. All complexes were found to be diamagnetic.

Preparation of $[(p\text{-}ClC_6H_4)_2C_2]_2Os_3(CO)_8$ (IV).—A solution of dodecacarbonyltriosmium (0·300 g) and *pp*′-dichlorodiphenylacetylene (0·250 g) was heated under reflux in n-heptane (300 ml), under nitrogen, for 26 h. The cooled solution was filtered and the solvent removed under reduced pressure. The residue was extracted with carbon tetrachloride (20 ml), and the orange solution separated by t.l.c. [using light petroleum (b.p. 40—70 °C)–diethyl ether (19 : 1) on kieselgel $PF_{254+366}$] to give (IV), as lemon-yellow product (0·010 g). This was recrystallized from n-heptane at −20 °C (Found: C, 34·0; H, 1·95; Cl, 10·30; O, 9·85; Os, 44·8. $C_{36}H_{16}Cl_4O_8Os_3$ requires C, 33·55; H, 1·25; Cl, 11·00; O, 9·95; Os, 44·3%).

Preparation of $[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_8$ (VII).—Dodecacarbonyltriosmium (0·200 g) and *pp*′-dimethyldiphenylacetylene (0·0735 g) were heated under nitrogen in refluxing n-heptane (250 ml) for 24 h. The cooled solution was filtered, n-heptane was removed and the residue was extracted with benzene (20 ml). The orange benzene solution was separated by t.l.c. [using light petroleum (b.p. 40—70 °C)–diethyl ether (49 : 1) on kieselgel $PF_{254+366}$] to give (VII), as yellow product (0·009 g), which was recrystallized from toluene in dry ice. Mass spectrum: *m/e* 1212 $[M]^+$ followed by the loss of eight carbonyl groups.

Preparation of $[(p\text{-}Cl_6H_4)_2C_2]_2Os_3(CO)_9$ (V).—Dodecacarbonyltriosmium (0·300 g) and *pp*′-dichlorodiphenylacetylene (0·250 g) dissolved in n-heptane (300 ml) were heated to reflux for 26 h. When the initially yellow-orange solution was turned violet by slow bubbling of carbon monoxide, complex (V) (0·013 g) was obtained as violet plates, by a similar method to that used for (IV). ^{1}H N.m.r. spectrum (CCl_4): τ 3·0 (8H, C_6H_4) and 3·1 (8H, C_6H_4) (Found: C, 33·0; H, 2·20; Cl, 11·3; O, 10·5; Os, 44·0. $C_{37}H_{16}Cl_4O_9Os_3$ requires C, 33·75; H, 1·20; Cl, 10·8; O, 10·95; Os, 43·35%).

Preparation of $[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_9$ (VIII).—A mixture of dodecacarbonyltriosmium (0·200 g) and *pp*′-dimethyldiphenylacetylene (0·074 g) was heated in refluxing n-heptane (300 ml) for 24 h. Then, carbon monoxide was slowly bubbled through the solution which, initially yellow, turned violet. The cooled filtered solution was separated to give (VIII) (0·008 g), as violet crystals, similar to (VII). ^{1}H N.m.r. spectrum (CCl_4): τ 3·1 (8H, C_6H_4), 3·4 (8H, C_6H_4), 7·7 (6H, CH_3), and 7·8 (6H, CH_3); mass spectrum: *m/e* 1240 $[M]^+$ (Found: C, 38·9; H, 2·55; O, 11·0. $C_{41}H_{28}O_9Os_3$ requires C, 39·85; H, 2·30; O, 11·65%).

Action of L′ [L′ = PPh_3, $AsPh_3$, $SbPh_3$] *on* $(Ph_2C_2)_2Os_3(CO)_8$ (I).—L′ (0·100 g) was added to a solution of (I) (0·020 g) in benzene (50 ml). Instantaneously the yellow solution became black-green; after 10 min it was separated by t.l.c. [using light petroleum (b.p. 40—70 °C)–diethyl ether (19 : 1) on kieselgel $PF_{254+366}$] to give (XII) (0·015 g). The resulting black-green crystals were recrystallized from n-heptane at 0 °C. $(Ph_2C_2)_2Os_3(CO)_8PPh_3$ (Found: C, 46·0; H, 3·05; P, 2·35; O, 8·95; Os, 41·15. $C_{54}H_{35}O_8Os_3P$ requires C, 45·9; H, 2·50; P, 2·20; O, 9·05; Os, 40·35%). $(Ph_2C_2)_2Os_3(CO)_8AsPh_3$ (Found: C, 43·1; H, 2·60; As, 5·55; O, 8·40; Os, 40·0. $C_{54}H_{35}AsO_8Os_3$ requires C, 44·50; H, 2·40; As, 5·15; O, 8·80; Os, 39·1%). $(Ph_2C_2)_2Os_3(CO)_8SbPh_3$ (Found: C, 42·1; H, 2·45; O, 8·45; Os, 38·20. $C_{54}H_{35}O_8Os_3Sb$ requires C, 43·1; H, 2·35; O, 8·50; Os, 37·95%).

Action of $AsPh_3$ *on* $[(p\text{-}ClC_6H_4)_2C_2]_2Os_3(CO)_8$ (IV).—The reaction was similar to that for (III) and gave a black-green complex $[(p\text{-}ClC_6H_4)_2C_2]_2Os_3(CO)_8As_3$ (Found: C, 40·0; H, 2·60; Cl, 9·10; O, 8·25; Os, 34·90; As, 4·55. $C_{54}H_{31}AsCl_4O_8Os_3$ requires C, 40·65; H, 1·95; Cl, 8·90; O, 8·00; Os, 35·75; As, 4·70%).

Action of $AsPh_3$ *on* $[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_8$ (VII).—The reaction was similar to that for (XII) and gave the black-green complex $[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_3(CO)_8AsPh_3$.

Action of PF_3 *on* $(Ph_2C_2)_2Os_3(CO)_8$ (I).—PF_3 (5 ml) was added to a toluene (50 ml) solution of (I) (0·020 g) in an evacuated tube; after 10 min the yellow solution became almost violet. The solvent and unreacted PF_3 were removed *in vacuo* after 1 h, to give a violet residue from which $(Ph_2C_2)_2Os_3(CO)_8PF_3$ (XI) (0·014 g) was isolated as violet crystals. It was crystallised from n-heptane under nitrogen at 0 °C. ^1H N.m.r. spectrum (CCl_4): τ = 3·0 (10H, C_6H_5) and 3·2 (10H, C_6H_5); mass spectrum: *m/e* 1244 $[M]^+$ followed by loss of eight carbonyl groups and PF_3.

Preparation of $[(p\text{-}ClC_6H_4)_2C_2]_2Os_2(CO)_6$ (VI).—(VI) was prepared as white crystals by a similar method to that used for (III). Mass spectrum: *m/e* 1044 $[M]^+$ followed by the loss of six carbonyl groups.

Preparation of $[(p\text{-}CH_3C_6H_4)_2C_2]_2Os_2(CO)_6$ (IX).—(IX) was prepared as white-yellow crystals by a similar method to that used for (III). Mass spectrum: *m/e* 964 $[M]^+$, followed by the loss of six carbonyl groups.

Kinetics.—A previously described method [1] was used for the study of the reaction of (IV) and (V) with carbon monoxide. The extent of conversion of (IV) into (VI) and of (V) into (VII) was determined from decreased absorbance of (IV) at 2100 cm^{-1} and of (V) at 2094 cm^{-1} respectively.

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