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ACETYLENIC DERIVATIVES OF METAL CARBONYLS
XII*. DIPHENYLACETYLENIC DERIVATIVES OF DODECACARBONYLTRIOSMIUM

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SUMMARY

The reaction of the complex $(C_6H_5C_2C_6H_5)_2Os_3(CO)_8$ (I) with CO has been investigated and a structure suggested for the compound, $(C_6H_5C_2C_6H_5)_2Os_3(CO)_9$, thus obtained. This consists basically of an Os_3 cluster, in which one of the osmium atoms belongs to a osmacyclopentadiene ring, and to which only terminal carbonyl groups are bonded. The formation of this product from (I) and CO was found to be a second-order process.

The reactions of complex (I) with halogens have also been investigated, and the resulting binuclear derivatives identified.

INTRODUCTION

Several studies have been made of the reactions of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ with various acetylenic derivatives and numerous mono-, bi- and trinuclear compounds have been investigated and characterised[1-6]. Particular interest has been shown in the trinuclear complexes $(RC_2R')_2M_3(CO)_8$ (where M = Fe, Ru), initially obtained with diphenylacetylene, which exists in two isomeric forms. The violet isomers $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$[7-9] and $(C_6H_5C_2C_6H_5)_2Ru_3(CO)_8$[2-3], prepared from carbonyls under mild reaction conditions, contain Fe_3 and Ru_3 clusters, have no bridging carbonyls, and can easily be transformed into more stable isomers having metallacyclopentadiene rings and bridging carbonyl groups.

In a previous note[10], the reaction between $Os_3(CO)_{12}$ and $C_2(C_6H_5)_2$ in n-heptane was considered and the isolation of three acetylenic derivatives was described, one of them being identified as $(C_6H_5C_2C_6H_5)_2Os_3(CO)_8$ (I). From the IR and X-ray-powder spectra it was concluded that this complex may have a structure similar to that of the violet isomers $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$[9] and $(C_6H_5C_2C_6H_5)_2Ru_3(CO)_8$.

The reaction between $Os_3(CO)_{12}$ and $C_2(C_6H_5)_2$, and the behaviour of $(C_6H_5C_2C_6H_5)_2Os_3(CO)_8$ (I) under different temperature conditions and in several solvents has now been investigated; no isomers with bridging carbonyls have been obtained, and $(C_6H_5C_2C_6H_5)_2Os_3(CO)_8$ has been shown to react with CO to give another trinuclear carbonyl complex containing only terminal CO groups.

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* For Part XI, see ref. 18.

EXPERIMENTAL

IR spectra were recorded on a Beckman Model IR12 double-beam spectrophotometer with KBr optics, and ^1H NMR spectra on a Jeol 60HL spectrometer. Mass spectra were recorded on a Perkin–Elmer Hitachi RMU-6H mass spectrometer operated at an ionizing voltage of 70 volts and an ionizing current of 65 μA. The samples were introduced via a direct inlet system.

(a). *Preparation of* $(C_6H_5C_2C_6H_5)_2Os_3(CO)_8$ *(I)*

The complex (I) was prepared under nitrogen from $Os_3(CO)_{12}$ and $C_2(C_6H_5)_2$ in 1/20 ratio using n-heptane as solvent. After 10 h of refluxing the resulting solution was evaporated, the residue was dissolved in CCl_4, and complex (I) was isolated as lemon yellow crystals by TLC (absorbent kieselgel P.F.; eluent, a mixture of petroleum ether b.p. 40–70° and 10% diethyl ether). Complex (I) was recrystallised from n-heptane at −20°. The yield is about 10% (Found: C, 37.1; H, 1.9; O, 11.1; Os, 49.9. $C_{36}H_{20}O_8Os_3$ calcd.: C, 37.54; H, 1.75; O, 11.12; Os, 49.58%.)

The IR spectrum in CCl_4 showed bands at 2096 (s), 2058 (s), 2033 (vs), 2020 (m), 2012 (m), 1997 (m), 1990 (sh), 1977 (m).

The mass spectrum showed peaks at *m/e* 1156 $(M)^+$, 1128 $[(M-CO)]^+$, 1100 $[(M-2\,CO)]^+$, 1072 $[(M-3\,CO)]^+$, 1044 $[(M-4\,CO)]^+$, 1016 $[(M-5\,CO)]^+$, 988 $[(M-6\,CO)]^+$, 960 $[(M-7\,CO)]^+$, and 932 $[(M-8\,CO)]^+$.

(b). *Preparation of* $(C_6H_5C_2C_6H_5)_2Os_3(CO)_9$ *(II)*

Complex (II) was prepared by slowly bubbling CO for a few minutes at room temperature into a previously evacuated toluene or n-heptane solution of (I). The solution, initially yellow, turned violet at the end of the reaction.

The resulting solution was evaporated and the residue was dissolved in CCl_4. Complex (II) was separated both from unreacted complex (I) and possible traces of complex (III) by TLC (absorbent Kieselgel P.F.; eluent, a mixture of petroleum ether b.p. 40–70° and 2% diethyl ether, or a mixture of 50% petroleum ether and carbon sulphide). The product thus obtained was recrystallised from n-heptane at −20°, usually as needles, sometimes as tablets. (Found: C, 37.9; H, 1.9; O, 12.2; Os, 47.9. $C_{37}H_{20}O_9Os_3$ calcd.: C, 37.69; H, 1.71; O, 12.21; Os, 48.39%.)

The IR spectrum, in CCl_4, showed bands at 2113 (m), 2057 (vs), 2042 (s), 2037 (sh), 2011 (s), 1998 (m), 1990 (sh), 1972 (m) and 1927 (m) cm^{-1}.

Its mass spectrum exhibited a molecular ion $(M)^+$ at *m/e* 1184.

The complex (III), formed from complex (II) and CO at room temperature during a few hours, was separated by TLC using the same eluents as above and purified by recrystallisation from n-heptane at −20°. (Found: C, 44.7; H, 2.6; O, 11.0; Os, 42.6. $C_{34}H_{20}O_6Os_2$ calcd.: C, 45.13; H, 2.23; O, 10.61; Os, 42.04%.)

The IR spectrum, in CCl_4, showed bands at 2082 (s), 2051 (vs), 2017 (m), 1999 (s) and 1969 (m) cm^{-1}. Its mass spectrum showed peaks at *m/e* 908 $(M)^+$, 880 $[(M-CO)]^+$, 852 $[(M-2\,CO)]^+$, 824 $[(M-3\,CO)]^+$, 796 $[(M-4\,CO)]^+$, 768 $[(M-5\,CO)]^+$, and 740 $[(M-6\,CO)]^+$. (III) was formulated as $(C_6H_5C_2C_6H_5)_2Os_2(CO)_6$.

(c). *Preparation of halocarbonyls* $(C_6H_5C_2C_6H_5)_2Os_2(CO)_5X_2$ *(where* $X=Cl, Br, I$*)*

A solution of (I) in toluene was treated with Cl_2, Br_2 or I_2, in a molar ratio of 1/2 at 0°, after evacuation of the reaction vessel. The product containing Cl is green-yellow and forms after a few minutes. Compounds containing Br or I are gold-yellow and orange-yellow respectively, and the reaction is complete after about 20 min. The halogenated compounds were separated by TLC using the same eluent as above and subsequently recrystallised from n-heptane at −20°.

$(C_6H_5C_2C_6H_5)_2Os_2(CO)_5Cl_2$. (Found: C, 40.9; H, 1.9; Cl, 7.9; O, 8.1. $C_{33}H_{20}Cl_2O_5Os_2$ calcd.: C, 41.82; H, 2.13; O, 8.44; Cl, 7.48%.) The IR spectrum, in CCl_4, showed bands at 2115 (s), 2068 (vs), 2062 (vs), 2012 (s) and 2001 (m) cm^{-1}. Its mass spectrum showed peaks at *m/e* 950 $(M)^+$, 922 $[(M-CO)]^+$, 894 $[(M-2\ CO)]^+$, 866 $[(M-3\ CO)]^+$, 838 $[(M-4\ CO)]^+$ and 810 $[(M-5\ CO)]^+$.

$(C_6H_5C_2C_6H_5)_2Os_2(CO)_5Br_2$. (Found: C, 38.3; H, 1.7; Br, 14.5; O, 7.8; Os, 37.2. $C_{33}H_{20}Br_2O_5Os_2$ calcd.: C, 38.23; H, 1.94; Br, 15.41; O, 7.72; Os, 36.70%.) The IR spectrum, in CCl_4, showed bands at 2113 (s), 2066 (vs), 2060 (vs), 2010 (s), and 1998 (m) cm^{-1}. Its mass spectrum showed peaks at *m/e* 1038 $(M)^+$, 1010 $[(M-CO)]^+$, 982 $[(M-2\ CO)]^+$, 954 $[(M-3\ CO)]^+$, 926 $[(M-4\ CO)]^+$ and 898 $[(M-5\ CO)]^+$.

$(C_6H_5C_2C_6H_5)_2Os_2(CO)_5I_2$. (Found: C, 36.2; I, 21.6; O, 7.8; Os, 33.2. $C_{33}H_{20}I_2O_5Os_2$ calcd.: C, 35.05; I, 22.45; O, 7.07; Os, 33.64%.) The IR spectrum, in CCl_4, showed bands at 2106 (s), 2061 (vs), 2056 (vs), 2006 (s) and 1995 (m) cm^{-1}. Its mass spectrum showed peaks at *m/e* 1134 $(M)^+$, 1106 $[(M-CO)]^+$, 1078 $[(M-2\ CO)]^+$, 1050 $[(M-3\ CO)]^+$, 1022 $[(M-4\ CO)]^+$ and 994 $[(M-5\ CO)]^+$.

(*d*). *Reduction of complex (II) with $LiAlH_4$*

An ether solution of complex (II) was introduced into a distillation flask, fitted with a reflux condenser and a dropping funnel, containing a suspension of $LiAlH_4$ in anhydrous ether. Moisture was excluded by means of $CaCl_2$ tubes. The mixture was kept at room temperature for 2 h, then heated to boiling for $\frac{1}{2}$ h, and was subsequently treated with water to destroy residual $LiAlH_4$. The ethereal layer was separated, dried with $CaCl_2$, and evaporated; the residue was dissolved in CCl_4 and submitted to TLC analysis. Organic compounds thus obtained were recrystallised from n-heptane at −20° and identified by mass spectrometry.

Kinetics

The kinetics of formation of complex (II) were studied on a point-by-point basis using Pyrex reaction vials of fixed volume. Aliquots of complex (II) in toluene were pipetted into vials, which were connected to a vacuum line and cooled to the reaction temperature. After saturation by slow bubbling of CO the vials were flame-sealed.

After the appropriate time the vials were opened and the reaction quenched by slowly bubbling nitrogen through the solution. The extent of conversion of (I) into (II) was determined from both the decreased absorbance of $(C_6H_5C_2C_6H_5)_2Os_3(CO)_8$ (I) at 2096 cm^{-1} and the increased absorbance of $(C_6H_5C_2C_6H_5)_2Os_3(CO)_9$ (II) at 2113 cm^{-1}. TLC analysis of reaction mixtures showed that up to 40% conversion took place with no formation of complex $(C_6H_5C_2C_6H_5)_2Os_2(CO)_6$ (III). In no case was there any trace of decomposition products. All the runs were pseudo-first-order because of the large excess of CO present. Linear plots of $\log (A_0/A_t)$ *versus* time were obtained (where A_0 is absorbance at zero time and A_t absorbance at time t) from which k_{obs} were calculated.

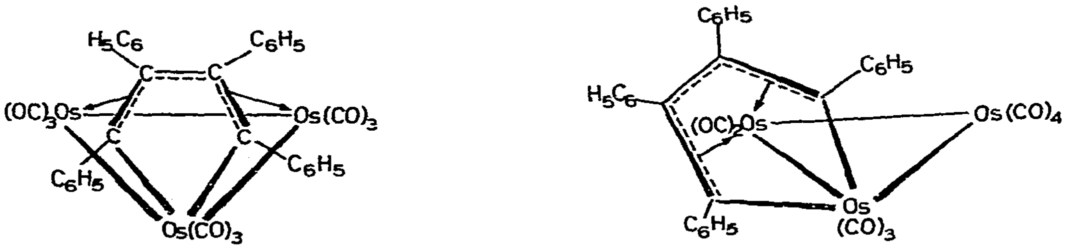
RESULTS AND DISCUSSION

The reaction of $(C_6H_5C_2C_6H_5)_2Os_3(CO)_8$ (I) with CO, in n-heptane or toluene at room temperature, gives an amethyst-violet compound formulated as $C_{37}H_{20}O_9Os_3$ (II). This complex was previously obtained by reaction of $Os_3(CO)_{12}$ with $C_2(C_6H_5)_2$, suggesting that (II) is formed from (I) by reaction of (I) with the CO liberated upon reaction of $Os_3(CO)_{12}$ with $(C_6H_5)_2C_2$.

Complex (II) exhibits low thermal stability, subliming at 10^{-2} mm pressure and 120° to give mainly (I). Its mass spectrum, however, does show a weak molecular ion peak at *m/e* 1184, which confirms the above formula. The more intense peaks correspond either to the molecular ion peak or fragment peaks of complex (I).

The structure of complex (II) was also investigated by $LiAlH_4$ reduction of the organic ligand and by its reaction with CO. In separate experiments, as final products of $LiAlH_4$ reduction, two organic compounds were isolated, *i.e.* 1,2,3,4-tetraphenylbutadiene and 1,2,3,4-tetraphenylbutane, identified by mass spectrometry. This implies that complex (II) contains two diphenylacetylene molecules bonded to each other. Reaction of (II) with CO leads to the formation of $(C_6H_5C_2C_6H_5)_2Os_2(CO)_6$ (III), characterised by mass spectrometry and infrared spectrophotometry. The mass spectrum of complex (III) displays a molecular ion at *m/e* 908 $(M)^+$ and peaks attributable to successive loss of six carbonyl groups. Its IR spectrum suggests a basic structure analogous to complexes $C_6H_8Os_2(CO)_6$[11] and $(CH_3C_2CH_3)_2Os_2(CO)_6$[12], the former containing an osmacyclopentadiene ring coordinated to tricarbonyl moiety as determined by X-ray diffraction methods[13]. Furthermore, the IR spectrum of complex (II) shows that all nine carbonyl groups are terminal, carbonyl stretching absorptions being observed only in the region between 1927 and 2113 cm^{-1}. The ^1H NMR spectrum shows two multiplet absorptions at $\tau = 2.95$ and 3.20, of equal area, attributable to the two different phenyl groups.

The above data suggest that the complex $(C_6H_5C_2C_6H_5)_2Os_3(CO)_9$ has a structure containing an osmacyclopentadiene ring and terminal carbonyl groups. A structure consisting of an osmacyclopentadiene moiety π-bonded to two osmium tricarbonyl groups on each side of the ring, can be proposed by analogy with the structures of the black $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$ and the yellow-orange $(C_6H_5C_2C_6H_5)_2Ru_3(CO)_8$, the only difference in the osmium derivative being the absence of bridging CO groups. However preliminary results of an X-ray diffraction study of (II) indicate the presence of an Os_3 cluster in the complex (II), and so, the above structure must be discarded. Two alternative structures can be suggested for the complex (II), as shown in Figs. 1 and 2, both of which satisfy the effective atomic number rule. Fig. 1 shows



Figs. 1 and 2. Possible structures of $(C_6H_5C_2C_6H_5)_2Os_3(CO)_9$.

TABLE 1

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF $(C_6H_5C_2C_6H_5)_2Os_3(CO)_8$ WITH CO IN TOLUENE

Complex (mmoles/l)	CO[a] (mmoles/l)	Temp. (°C)	$10^5 k_{obs}$ (sec^{-1})	$10^2 k_2$ ($M^{-1} \cdot sec^{-1}$)
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

[a] Concentration of CO in solution.
$\Delta H^{\neq} = 16$ kcal/mole. $\Delta S^{\neq} = -6.5$ e.u.

the three osmium atoms located at the corners of an equilateral triangle. One osmium atom also belongs to an osmacyclopentadiene ring, which is at an angle with the Os_3 cluster plane and coordinates the remaining two osmium atoms through π bonds. Each metal atom is coordinated to three CO groups. In the structure of Fig. 2, the osmacyclopentadiene ring is disposed near one side of the triangle, outside of the Os_3 cluster and coordinating a single osmium atom through two π bonds. The CO groups are distributed as shown in Fig. 2, so that the metal atoms all have closed-shell configurations. Both structures seem equally likely. However, the results of the reaction of $(C_6H_5C_2C_6H_5)_2Os_3(CO)_9$ with CO suggests the structure shown in Fig. 2 as the more likely, since it already contains the skeleton of the compound $(C_6H_5C_2C_6H_5)_2$-$Os_2(CO)_6$.

The kinetics of formation of (II) were also investigated. From Table 1, it can be seen that the reaction follows a second-order rate-law. Therefore, the rate-determining step is the coordination of a CO molecule to complex (I).

Complex (I) is also highly reactive towards halogens, reacting rapidly at 0° with Cl_2, Br_2, I_2 to give binuclear compounds of the type $(C_6H_5C_2C_6H_5)_2Os_2(CO)_5X_2$, (where X=Cl, Br, I), containing five terminal carbonyls. The compounds were identified by elemental analysis, and IR spectrometry. The mass spectra of these derivatives show molecular ion peaks at *m/e* 950 when X=Cl, *m/e* 1038 when X=Br, *m/e* 1134 when X=I, as well as complete range of fragment peaks due to successive loss of five carbonyl groups.

It can be concluded, therefore, that diphenylacetylene carbonyl osmium derivatives behave differently from their Fe and Ru analogues. Complex (I) prefers a non-bridged structure containing an Os_3 cluster to the carbonyl bridged structure of the Fe and Ru compounds. Complex (I) reacts with an additional molecule of CO to give (II) which is also a non-bridged structure and the Os_3 cluster is preserved in complex (II) as well. This is consistent with both increased energies of metal–metal bonds and the decreased tendency to form bridging isomers already known for the parent metal carbonyls as the atomic number is increased. Although (I) and $Os_3(CO)_{12}$ both show a high reactivity towards halogens, $Os_3(CO)_{12}$ gives linear trinuclear halocarbonyls[15-17], while (I) undergoes Os–Os bond cleavage to give binuclear compounds.

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