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Acetylenic Derivatives of Metal Carbonyls. XIV. Cyclotrimerization of Diphenylacetylene with Dodecarbonyltriosmium[1]

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$L_2Os_3(CO)_8$ complexes, where L = $(C_6H_5)_2C_2$, $(p\text{-}ClC_6H_4)_2C_2$, $(p\text{-}CH_3C_6H_4)_2C_2$, react with excess of ligand to yield compounds of general formula $L_3Os_3(CO)_7$. On the basis of chemical and physical chemical data, a structure is suggested in which only two ligand molecules are linked together. $[(C_6H_5)_2C_2]_3Os_3(CO)_7$ reacts with more diphenylacethylene to form hexaphenylbenzene. In the course of this process $[(C_6H_5)_2C_2]_3Os_3(CO)_6$ can be isolated. This seems to be the last stable trinuclear intermediate in the cyclotrimerization reaction and seems to contain the three ligand molecules joined together. It does in fact give hexaphenylbenzene readily by thermal decomposition.

Introduction

Reactions of alkynes with metalcarbonyls have shown that formation of complexes is sometimes accompanied by cyclic trimerization of alkynes to benzene derivatives.[2] Phosphine substituted nickel carbonyls, octacarbonyldicobalt and the alkyne complexes $RC_2R'Co_2(CO)_6$ and $RC_2R'Co_4(CO)_{10}$ have been particularly studied.[2]

Two of us reported that dodecarbonyltriosmium could also be used as catalyst to prepare hexaphenylbenzene (HPB) from diphenylacetylene (DPA).[3]

In this paper we describe the results of investigation of the cyclotrimerization path and the properties of some complexes isolated in the reaction of DPA with $Os_3(CO)_{12}$.

Experimental Section

I.r. spectra were recorded on a Beckman Model IR 12 double beam Spectrophotometer with KBr optics. ^{1}H n.m.r. spectra were obtained with a Jeol 60 HL Spectrometer and mass spectra with a Perkin-Elmer Hitachi RMU 6H mass Spectrometer using an ionizing energy of 75 ev.

Preparation of $[(C_6H_5)_2C_2]_3Os_3(CO)_7$ (II). A solution of $[(C_6H_5)_2C_2]_2Os_3(CO)_8$ (I) (0.050 g) and DPA (0.25 g) was heated in refluxing n-heptane (100 ml) under nitrogen for 18 hours. The cooled orange solution was filtered and solvent removed under vacuum. The residue was dissolved in carbontetrachloride and the solution separated by TLC (absorbent Kieselgel $PF_{254+336}$, eluent petroleum ether b.p. 40°-70°C and 3% diethyl ether) to give (II) (0.035 g) as main product. The resulting orange crystals were recrystallized from n-heptane at O°C. (II) was found to be diamagnetic.

Anal. Calcd. for $C_{49}H_{30}O_7\,Os_3$: C, 45.02; H, 2.30; O, 8.57; Os, 44.10. Found: C, 45.48; H, 3.00; O, 8.57; Os, 43.02%. $\nu(CCl_4)$: 2092vs, 2029s, 2024s, 2008vs, 1995m, 1959m and 1948w cm^{-1}; mass spectrum: m/e 1306 [M$^+$], followed by the loss of seven carbonyl groups; ^{1}H n.m.r. spectrum (CCl_4): complex pattern in the range τ 2.2–3.4.

Reaction of $[(C_6H_5)_2C_2]_3Os_3(CO)_7$ (II). (a) *with carbon monoxide.* A solution of (II) (0.030 g) in n-heptane (20 ml) was treated with carbon monoxide (750 mm Hg) at 90°C for 3 hours in a sealed tube. Then the solution was dried under reduced pressure and the residue extracted with carbontetrachloride and separated by TLC (absorbent and eluent as above). Diphenylacetylene (0.005 g) and $[(C_6H_5)_2C_2]_2Os_2(CO)_6$ (III)[4] were the main products. (b) *with diphenylacetylene (DPA).* A n-heptane solution of (II) (0.035 g) and DPA (0.200 g) was heated under reflux under nitrogen for 10 hours. The solvent was evaporated and the residue extracted with carbontetrachloride and separated by TLC (absorbent and eluent as above). HPB, in very small amount, and a yellow compound $[(C_6H_5)_2C_2]_3Os_3(CO)_6$ (V) (0.010 g) were isolated. (V) was recrystallized from n-heptane at 0°C. $\nu(CCl_4)$: 2088s, 2052vs, 2018s, 2009m, 1996m and 1983w cm^{-1}; mass spectrum: m/e 1278 [M$^+$], followed by the loss of six carbonyl groups; ^{1}H n.m.r. spectrum (CCl_4): bands in the range τ 2.7–3.4.

When (II) (0.035 g) and DPA (0.200 g) were reacted in refluxing n-heptane for 2 days, HPB (0.044 g), $[(C_6H_5)_2C_2]_2Os_2(CO)_6$ (III) (0.007 g) and $[(C_6H_5)_2C_2]_2Os(CO)_3$ (IV) 0.005 g) were obtained. (IV) was characterized by i.r. and mass spectra. $\nu(CCl_4)$: 2054s, 1985m; mass spectrum: m/e 632 [M$^+$], followed by the loss of three carbonyl groups. (c) *with phenylacetylene.* Phenylacetylene (0.50 ml) and (II) (0.045 g) dissolved in n-heptane were heated under reflux for 20 hours. The solvent was removed in vacuum and the residue dissolved in carbontetrachloride and separated by TLC (absorbent and eluent as above) to give pentaphenylbenzene (0.005 g) and

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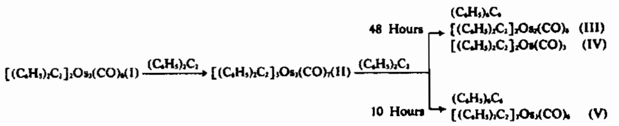
(3) M. Valle, G. Cetini, O. Gambino, and E. Sappa, *Atti Accad. Sci. Torino, 105*, 913 (1969).

uncharacterized carbonyl compounds.

Thermal decomposition of $[(C_6H_5)_2C_2]_3Os_3(CO)_6$ (V). (V), at solid form, was heated for 1 hours in a sealed evacuated tube at 100°C and gave HPB in good yield.

Results and Discussion

The reaction between DPA and dodecarbonyltriosmium gives, in a first step, a complex $[(C_6H_5)_2C_2]_2Os_3(CO)_8$ (I),[1,5] where two ligand molecules are joined together to form an osmacyclopentadiene ring. Treatment of (I) with the free ligand gives a compound of formula $[(C_6H_5)_2C_2]_3Os_3(CO)_7$ (II) which, by reacting with an excess of DPA, forms HPB (yield 22%), $[(C_6H_5)_2C_2]_2Os_2(CO)_6$ (III)[4] and $[(C_6H_5)_2C_2]_2Os(CO)_3$ (IV) (Scheme 1). (IV) is thought to be tetraphenylcyclobutadiene-tricarbonylosmium, similar to $[(C_6H_5)_2C_2]_2Fe(CO)_3$.[6,7]



Scheme 1

Thermal decomposition of (II) gives (III) as main product. The presence of an osmacyclopentadiene ring in (III) suggests that also in (II) two ligand molecules are linked together in a ring. This fact has been confirmed by reaction of (II) with carbon monoxide, where DPA and (III) are isolated together with uncharacterized products. Thus a six carbon ring system seems not to be preformed in (II). Moreover a preliminary X-ray analysis[8] has demonstrated the presence of the Os_3 cluster in (II), while its i.r. spectrum indicates all carbonyl groups are in terminal positions and its ^1H n.m.r. spectrum shows bands only in the aromatic region. These data permit one to argue that the structure of (II) is strictly related to that of (I),[1,5] the main difference being both the absence of a hydrido ligand and the presence of a third readily displaceable ligand molecule in (II). Therefore one can suggest that the skeleton of (II), without the third DPA molecule, is that shown in Figure 1. The effective atomic number rule is satisfied if the carbonyl groups are distribuited as shown in the figure and the third ligand molecule acts as a four-electron donor in a bridging position between Os(2) and Os(3), or bonded to the cluster considered as a whole.

However not all the three ligand molecules of (II) can be involved in the formation of HPB, because this is readily formed only when (II) reacts with excess DPA. Moreover heating of (II) does not give HPB until partial decomposition has taken place and free DPA has been formed.

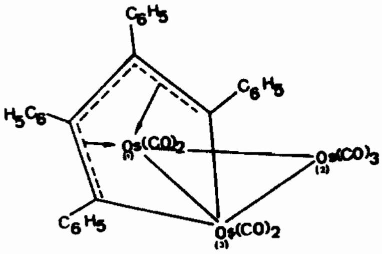


Figure 1. Skeleton of $[(C_6H_5)_2C_2]_3Os_3(CO)_7$ without the third ligand molecule.

Reaction of (II) with phenylacetylene gave some evidence about the mechanism of the cyclotrimerization process, pentaphenylbenzene being the main product. One can assume the first step is the displacement of carbonyl groups by a molecule of the acetylenic compound, which gives, in turn, the cyclic compound by bonding with two other acetylenic fragments originally present in (II). It is very probable these are the two fragments in the osmacyclopentadiene ring of (II).

This scheme seems to be reasonable. In reaction of (II) with DPA a compound of formula $[(C_6H_5)_2C_2]_3Os_3(CO)_6$ (V) can be isolated, when the amount of HPB formed is still very small. (V) gives HPB readily and in good yield when heated. Therefore it may be suggested that the three ligand molecules are already linked together. (V) is thought to be formed when substitution of a carbonyl group on Os(3) or Os(1) with DPA occurs, probably followed by ejection of the third ligand molecule of (II) and subsequent rearrangement. (V) seems to act like $(RC_2R')_3Co_2(CO)_4$ in cyclotrimerization of acetylenic compounds with cobalt carbonyl complexes.[9]

Finally, it is noteworthy that direct formation of (V) from (I) does not occur. This can be explained if the most labile coordination site for a four-electron donor in (I) must already be occupied as in (II), for a further ligand molecule to be coordinated in such a position as to give (V) and then the benzene derivative.

$L_2Os_3(CO)_8$ complexes, where L = $(p\text{-}ClC_6H_4)_2C_2$ and $(p\text{-}CH_3C_6H_4)_2C_2$, with excess of ligand give $L_3Os_3(CO)_7$, which present a close similarity to (II). However only hexa-(*p*-chlorophenyl)benzene has been isolated. Attempts to trimerize bis(*p*-methylphenyl)acetylene were unsuccessful.

Note added in proof: Structure of Figure 1, with the third DPA molecule bonded to the whole cluster has been established for (II) by X-ray analysis (G. Ferraris and G. Gervasio, private communication).

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