New Ruthenium Carbonyl Complexes Containing Triphenylphosphine and Triphenylarsine

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The reaction between triphenylphosphine and Ru$_3$(CO)$_{12}$ has been reported by several groups$^{2-4}$ to give the purple-red complex (Ph$_3$P)$_2$Ru$_3$(CO)$_{10}$. However, the several reports vary in detail, and in particular, in the accounts of the infrared spectra in the carbonyl stretching region.

We have found that the carbonyl infrared spectrum of this complex varies according to the conditions of preparation, and quite markedly depends on the solvent used. It seems reasonable to postulate that it is the presence of isomeric mixtures which causes these variations. We have been unable to prepare a product that corresponds to any one isomer, however.

Reaction of the complex with chlorinated solvents such as CHCl$_3$ or CCl$_4$ gives (Ph$_3$P)Ru(CO)$_4$Cl$_2$, which is also formed as an isomeric mixture, since the carbonyl infrared spectrum is complex. The isolation of this complex in high yield from this reaction indicates that the carbonyl complex of the larger arsine molecule being easier peripheral to the Ru$_3$ plane.

In contrast, the reaction between triphenylarsine and Ru$_3$(CO)$_{12}$ gives (Ph$_3$As)$_2$Ru$_3$(CO)$_{10}$ (1). Treatment with CHCl$_3$ or CCl$_4$ resulted in an immediate reaction to form the known$^5$ complex, (Ph$_3$As)$_2$Ru$_3$(CO)$_{10}$ (2).

The stereochemistry of the chlorinated product suggests that the structure of complex (1) is as shown in the Figure, assuming that no rearrangement occurs in the mild reaction with CCl$_4$. An explanation of the different products formed in the reactions between Ru$_3$(CO)$_{12}$ and triphenylphosphine and -arsine may be found in the relative sizes of the donor ligands, approach of the larger arsine molecule being easier peripheral to the Ru$_3$ plane.

A similar case of disubstitution of the Ru$_3$ cluster is to be found in the reaction between 1,3-cyclooctadiene and Ru$_3$(CO)$_{12}$, which is reported$^6$ to give the complex (C$_8$H$_{12}$)Ru$_3$(CO)$_{10}$.

A second product from the chlorination reaction is presumably Ru$_3$(CO)$_{10}$Cl$_2$; however, we were not able to find this compound, nor any [Ru(CO)$_4$Cl$_2$], which is easily formed from the tetracarbonyl chloride.

Experimental

Triphenylphosphine (110 mg, 0.42 mmol) and Ru$_3$(CO)$_{12}$ (100 mg, 0.16 mmol) were refluxed in CHCl$_3$ (25 ml); after 2 hrs, the purple colouration of the trinuclear complex had appeared. Further heating resulted in the colour fading, and after 12 hrs, there was no further change. The pale yellow solution was evaporated, and the residue was recrystallised from light petroleum-benzene to give pale yellow crystals of (Ph$_3$P)$_2$Ru$_3$(CO)$_{10}$, which turned red at 160$^\circ$C, and decomposed at 209 to 215$^\circ$C.

Calc. for C$_{66}$H$_{30}$As$_2$O$_{10}$Ru$_3$:

Found: C, 49.20; H, 2.61; As, 12.52; Ru, 25.55.

A mixture of triphenylarsine (270 mg, 0.35 mmol) and Ru$_3$(CO)$_{12}$ (200 mg, 0.31 mmol) in n-hexane (25 ml) was refluxed for 12 hr. The brown solution was filtered and evaporated, and the residue was recrystallised from benzene-light petroleum-give reddish-purple (Ph$_3$As)$_2$Ru$_3$(CO)$_{10}$ (100 mg, 27.5%), m.p. 158 to 160$^\circ$C (decomp.).

Calc. for C$_{46}$H$_{19}$As$_2$O$_{10}$Ru$_3$:

Found: C, 46.10; H, 2.51; As, 12.52; Ru, 25.55.

A similar preparation, using chloroform (25 ml) as solvent, was refluxed for 136 hrs. Evaporation of the orange solution, and recrystallisation of the residue from benzene-light petroleum gave (Ph$_3$As)$_2$Ru$_3$(CO)$_{10}$, identified by analysis and its carbonyl infrared spectrum. A second product from the reaction between benzene and Ru$_3$(CO)$_{12}$ was also formed, which is a yellow oil and has a carbonyl infrared spectrum [v$_{CO}$: 2053 vs, 1993 vs cm$^{-1}$ (CHCl$_3$)].

Treatment of either trinuclear complex with chloroform or CCl$_4$ gave the same chlorinated complexes.

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