

Preliminary communication

Butadienic derivatives of metal carbonyls

I. Reactions of dodecacarbonyltriruthenium with arylbutadienes

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Reactions between $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ with diphenylacetylene have been previously reported¹. It is not known that these reactions often give complexes in which the organic portion is a heterocyclic five-membered ring system with metal-carbon σ bonds. Furthermore it has been shown that two alkyne ligands join to form metal-cyclopentadiene rings which then constitute the organic moieties. This suggested that the same complexes could be prepared from metal carbonyls and organic ligands, such as butadienes. Here we report the first results of reactions between $\text{Ru}_3(\text{CO})_{12}$ and 1,2,3,4-tetraphenyl-1,3-butadiene, and 1,4-*trans,trans*-diphenyl-1,3-butadiene. Comparison of the products showed that only the orange isomer^{1f} $\text{L}_2\text{Ru}_3(\text{CO})_8$ (where L is C_2Ph_2 or C_2HPh) can be obtained from both diphenylacetylene and arylbutadiene ligands. A number of other compounds were also isolated, including $\text{C}_7\text{H}_{12}\text{Ru}_3(\text{CO})_9$ (I), $\text{C}_6\text{H}_{10}\text{Ru}_3(\text{CO})_9$ (II), $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (III), $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ (IV), $\text{C}_4\text{H}_4\text{Ph}_2\text{Ru}_3(\text{CO})_9$ (V).

Bi- and mono-nuclear complexes were also formed as byproducts. All the compounds were separated by TLC plates. The only reaction between $\text{Ru}_3(\text{CO})_{12}$ and $\text{C}_4\text{H}_4\text{Ph}_2$ yielded (V). High field signals (τ 25–30) characteristic of transition metal hydrides were observed in the NMR spectra for (I) to (V). The IR, NMR and mass spectrometry data for (III) and (IV) agreed with those in the literature². Parent molecular ions $[\text{C}_7\text{H}_{12}\text{Ru}_3(\text{CO})_9]^+$, $[\text{C}_6\text{H}_{10}\text{Ru}_3(\text{CO})_9]^+$, $[\text{C}_4\text{H}_4\text{Ph}_2\text{Ru}_3(\text{CO})_9]^+$, together with peaks corresponding to the stepwise loss of nine carbonyl groups giving $[\text{C}_7\text{H}_{12}\text{Ru}_3]^+$, $[\text{C}_6\text{H}_{10}\text{Ru}_3]^+$, $[\text{C}_4\text{H}_4\text{Ph}_2\text{Ru}_3]^+$ are readily identifiable. A product (VI) of the same empirical formula as (II) was isolated as the major product of the reaction of *trans,trans*- and *cis,trans*-1,3-hexadiene and $\text{Ru}_3(\text{CO})_{12}$. The mass, ¹H NMR and IR spectra of (II) and (VI) were identical, and we conclude that (II) and (VI) are the same compound. The IR spectrum in the carbonyl stretching region of $\text{C}_6\text{H}_{10}\text{Ru}_3(\text{CO})_9$, in carbon tetrachloride, exhibited several bands at 2097 vs, 2070 vs, 2043 vs, 2028 vs, 2016 vs, 1998 (sh) and 1975 w cm^{-1} . All of them are assignable to terminal carbonyl groups. The ¹H NMR spectrum of (II) showed a doublet at τ 3.36, a rather complicated multiplet at τ 7.21, a singlet at τ 7.16, a triplet at τ 8.58 and a doublet at τ 30.1. Integration showed that the areas associated with the particular resonance signals were in the ratio of 1/5/3/1.

The absence of phenyl groups is thus certain and the data suggest that $C_6H_{10}Ru_3(CO)_9$ should be considered as a π -1,3-methylethylallyl compound. The formation of (II) points out that the presence of $Ru_3(CO)_{12}$ causes a noteworthy change in the molecule of the organic ligand. On the other hand a number of π -enyl complexes of transition metals were prepared from diene olefins³. The hydrido ligand⁴ is also believed to interact with the enyl proton and the proton doublet at τ 30.1 supports this view. A detailed analysis of the mass spectra of (II) and (VI) showed that elimination of H_2 molecules from the ligand accompanies the loss of carbonyl groups. Furthermore the isotopic peaks of $[C_6H_{10}Ru_3]^+$ are superimposed to those of $[C_6H_8Ru_3]^+$, $[C_6H_6Ru_3]^+$ and $[C_6H_4Ru_3]^+$. The fragmentation of the organic ligand proceeds with the loss of an ethyl and a methyl radical to give abundant $[C_3HRu_3]^+$, $[C_3Ru_3]^+$ and $[C_2Ru_3]^+$. Trinuclear doubly-charged ions are also present in good intensity. The only binuclear $[C_2Ru_2]^+$ ion is observed and accounts about for 0.5% of metal-containing fragments, while no mononuclear species are present. These results, when compared with the intensities of the ions in the spectrum of $Ru_3(CO)_{12}^{2c}$, suggest that the $Ru_3(CO)_9$ moiety contains the Ru_3 cluster. $C_6H_{10}Ru_3(CO)_9$ is a diamagnetic compound, so on the basis of the effective atomic number we suggest that the allyl ligand is coordinated to the $Ru_3(CO)_9$ moiety by one π and two σ bonds. At the moment we have no data to distinguish the three possible types of metal-hydrogen linkages, *i.e.* with H as a terminal, edge bridging or face bridging group. However, the hydrido ligand must give one electron to the cluster considered as a whole.

A detailed analysis of the 1H and ^{13}C NMR spectra of this compound and an X-ray crystallographic study of VI is presently under way⁵.

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