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STRUCTURE OF THE PRODUCT FORMED IN THE REACTION OF CARBON DIOXIDE WITH RUTHENIUM HYDRIDE COMPLEXES

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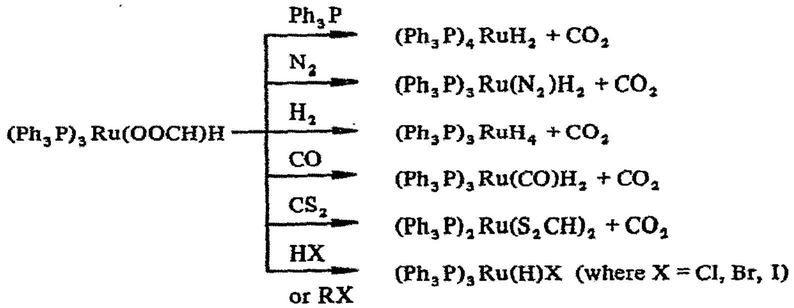
SUMMARY

The structure and chemical properties of the product of the reaction between carbon dioxide with ruthenium hydride complexes have been investigated.

We have found that carbon dioxide reacts readily with the complexes $(Ph_3P)_4RuH_2$, $(Ph_3P)_3Ru(N_2)H_2$ and $(Ph_3P)_3RuH_4$ to give compounds which on the basis of elemental analysis and chemical properties have been assigned the tentative structure $(Ph_3P)_3Ru(CO_2)H_2$[1].

Scheme 1. Reactions of $(Ph_3P)_3Ru(OOCH)H$



The reaction was carried out under CO_2 pressure [13 mmol of $(Ph_3P)_4RuH_2$, 15 ml of benzene, 20 atm CO_2, 20°, 5 h] and the orange crystals formed, after separation from the solution, were found to have m.p. 75–78° (decomp.). (Found: C, 69.30; H, 5.16; P, 9.0. $C_{55}H_{47}P_3RuO_2$ calcd.: C, 70.73; H, 5.04; P, 9.96%.) The same complex may be produced by bubbling CO_2 through a benzene solution of the ruthenium hydride complexes mentioned above.

The complex readily loses carbon dioxide on reaction with different reagents[1,2]. Thus on addition of carbon monoxide, CO_2 is evolved and the complex $(Ph_3P)_3Ru(CO)H_2$ is formed[3]. Bubbling argon through a benzene solution of the complex also results in the evolution of CO_2 and the formation of a compound which has properties similar to those of $(Ph_3P)_3RuH_2$[4]. Carbon dioxide is also evolved in the reactions with Ph_3P, N_2 and H_2 affording respectively $(Ph_3P)_4RuH_2$, $(Ph_3P)_3Ru(N_2)H_2$ and $(Ph_3P)_3RuH_4$, the reaction being reversible in these cases. Carbon dioxide may be also replaced by ethylene and carbon disulfide[5] or transferred to platinum by reaction with the peroxo complex $(Ph_3P)_2PtO_2$ giving the known platinum carbonate $(Ph_3P)_2PtCO_3$.

In contrast, the complex exhibits no chemical reactions typical of formates. Thus, treatment with esterifying agents, *e.g.*, methyl iodide or methanolic BF_3, does not lead to the formation of the formate, and on addition of methyl iodide CO_2 is evolved and the complex $(Ph_3P)_3Ru(H)(I)$ is formed.

A detailed study of the IR spectra has shown, however, that the solid complex is the ruthenium formate complex*. Thus together with bands corresponding to the phosphine ligand, the IR spectrum of the complex contains the following additional absorption bands: 2910 m, 2820 m, 2010 m, 1565 s, 1420 m, 1370 m, 1355 m, 1340 m, 800 s and 690 vs (cm^{-1}). The action of CO_2 on $(Ph_3P)_3RuD_4$ gives the complex $(Ph_3P)_3Ru(OOCD)D$ which exhibits no bands at 2910 and 2820 cm^{-1} but shows a band at 2150 cm^{-1} which from the computed isotopic shift corresponds to a frequency of 2910 cm^{-1}.

The IR spectrum of the deuterated product has no absorption band at 2010 cm^{-1} [ν(Ru–H)] but absorbs at 1450 cm^{-1} [ν(Ru–D)]. The bands at 1355 and 1370 cm^{-1} which correspond to the C–H bending modes are also absent. Other frequencies in the spectrum of the complex $(Ph_3P)_3Ru(OOCD)D$ do not change and may be attributed to the OCO modes.

In order to elucidate the structure of the complex an X-ray study of this material was undertaken. The data obtained show that the complex $(Ph_3P)_3Ru$-

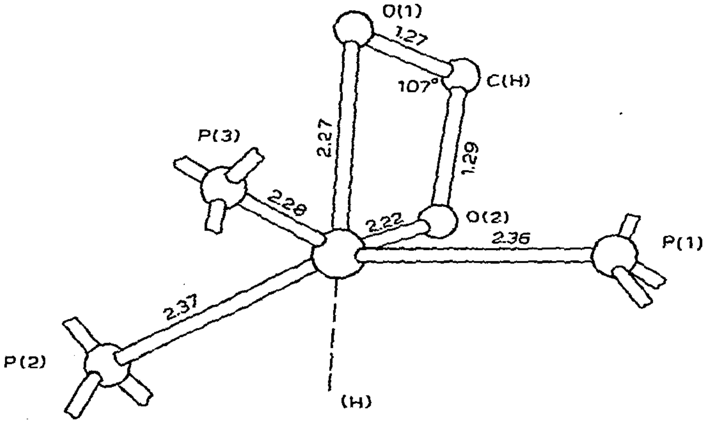


Fig. 1. Coordination of the Ru atom. Bond angles: O(2)–Ru–P(3) = 157°, P(1)–Ru–P(2) = 151°, O(1)–Ru–P(1) = 97°, O(1)–Ru–P(2) = 98°, O(1)–Ru–P(3) = 102°, O(1)–Ru–O(2) = 54°, P(1)–Ru–P(3) = 98°, P(1)–Ru–O(2) = 86°, P(2)–Ru–P(3) = 103°, P(2)–Ru–O(2) = 83°.

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* Recently Yamamoto *et al.*[6] have shown that CO_2 reacts with $(Ph_3P)_4RuH_2$, $(Ph_3P)_3Ru(N_2)H_2$ and $(Ph_3P)_3RuH_4$ to give a complex which on the basis of its IR spectra and chemical reactions has the formate structure $(Ph_3P)_3Ru(OOCH)(H)\cdot$toluene.

(OOCH)H exists as two crystalline modifications, *i.e.* monoclinic and triclinic. At present a detailed X-ray study of the monoclinic form has been completed: $a = 20.272$, $b = 14.260$, $c = 20.944$ Å, $\beta = 122.77$, $Z = 4$, spatial group $P2_1/c$. In order to decode and clarify the structure, 1397 reflections with $F^2 \geqslant 3\ \sigma\ (F^2)$ obtained on a four circular automatic "Hilger Watts" diffractometer with a molybdenum source were employed, the structure being corrected via the isotopic approximation to $R = 15.1\%$. The coordination involving the Ru atom is shown in Fig. 1. Ignoring the position of the H atom, which we failed to elucidate, the observed coordination is essentially distorted tetragonal-pyramidal, the O(1) atom occupying the apex position. The equatorial plane P(1)–P(2)–P(3)–O(2) is essentially tetrahedrally distorted (the sum of the six angles being 677° as against 720° for a square and 657° for the ideal tetrahedron). The H atom probably occupies the sixth coordination place *trans* to the O(1) atom thus providing an octahedral coordination for this atom. The difference between the Ru–O and Ru–P distances may be readily explained by the effect of the *trans* ligands, the C–O bonds in the formate group being practically equivalent.

Thus the solid complex obtained by the reaction of CO_2 with $(Ph_3P)_4RuH_2$, $(Ph_3P)_3Ru(N_2)H_2$ and $(Ph_3P)_3RuH_4$ contains the formate structure. The chemical reactions of this compound which involve the ready elimination of CO_2 may be completely explained by the ready cleavage of the C–H bond in the formate fragment resulting in the following equilibrium in solution:

$$(Ph_3P)_3Ru(OOCH)H \rightleftarrows (Ph_3P)_3Ru(CO_2)H_2$$

REFERENCES

1 I. S. Kolomnikov, T. S. Lobeeva and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1972) 211.
2 M. E. Vol'pin and I. S. Kolomnikov, *Pure Appl. Chem.*, 30 (1972) 607.
3 P. S. Hallman, B. R. McGarvey and G. Wilkinson, *J. Chem. Soc. A*, (1968) 3143.
4 T. I. Elides, R. O. Harris and M. C. Zia, *Chem. Commun.*, (1970) 1709.
5 I. S. Kolomnikov, T. S. Lobeeva and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, in press.
6 S. Komiya and A. Yamamoto, *J. Organometal. Chem.*, 46 (1972) C58.