

Journal of The Chemical Society, Chemical Communications

NUMBER 1/1976

7 JANUARY

Preparation of $(\text{Ph}_3\text{P})_4\text{Ru}(\pi\text{-MeCN})\cdot\text{MeCN}$

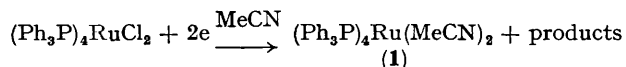
By E. O. SHERMAN, Jr.† and P. R. SCHREINER

(Shell Development Company, Emeryville, California, 94608)

Summary Electrochemical reduction of $(\text{Ph}_3\text{P})_4\text{RuCl}_2$ in acetonitrile yields the zero-valent ruthenium complex, $(\text{Ph}_3\text{P})_4\text{Ru}(\pi\text{-MeCN})\cdot\text{MeCN}$.

ZERO-VALENT complexes of ruthenium usually contain at least one carbonyl or similar π -acceptor ligand to stabilize the oxidation state. Highly reactive tertiary phosphine complexes of ruthenium(0) have been postulated as tautomers of the isolable complexes, *cis*- $[\text{RuH}(2\text{-C}_{10}\text{H}_7)(\text{PP})_2]$ and $\text{RuH}(\text{CH}_2\text{PMeCH}_2\text{CH}_2\text{PMe}_2)(\text{PP})$ [where PP is bis-(dimethylphosphino)ethane] but have not been isolated.¹ We now report the preparation of the title compound by the electrochemical reduction of $(\text{Ph}_3\text{P})_4\text{RuCl}_2$ in acetonitrile solvent. An electrochemical approach was adopted to avoid the introduction of extraneous ligands which are often inherent in strong chemical reducing agents.

Potentiostatic reduction of $(\text{Ph}_3\text{P})_4\text{RuCl}$ at a potential of -2.25 V *vs.* a Ag/AgNO_3 (0.10 M) reference electrode proceeds with the uptake of two electrons. The reduction was carried out in the presence of 0.10 M tetraethylammonium perchlorate as supporting electrolyte and at a platinum foil cathode. The product is obtained as a diamagnetic ($\chi_g = 0.43 \times 10^{-6}$) yellow powder which precipitates during the course of the electrolysis. Elemental analysis of this product agrees with the formula $(\text{Ph}_3\text{P})_4\text{Ru}(\text{MeCN})_2$, (**1**).



The yield of (**1**) is 54% and a mixture of as yet unidentified ruthenium(0) complexes can also be isolated from the spent

catholyte. The product is stable in the absence of oxygen and only slowly decomposes when exposed to air. It is very sparingly soluble in aromatic solvents and melts with decomposition at 124–131 °C. Molecular weight measurements yield a value of 250 ± 20 suggesting extensive dissociation of the complex in solution.

The i.r. spectrum of (**1**) in Nujol exhibits, in addition to bands readily assigned to triphenylphosphine, characteristic bands at 2254 (w), 1912 (s) and 720 (s) cm^{-1} . The band at 2254 cm^{-1} which is identical with the $\nu(\text{CN})$ frequency of unco-ordinated acetonitrile suggests that one of the acetonitrile molecules is present as a molecule of solvation. The remaining bands at 1910 and 720 cm^{-1} are tentatively assigned to $\nu(\text{CN})$ and $\delta(\text{CH})$ vibrations, respectively, of an acetonitrile molecule co-ordinated to ruthenium(0). The possibility of a hydride ligand which might be expected to give bands at similar frequencies appears unlikely on the basis of the following evidence: (a) reaction of (**1**) with CCl_4 yields no chloroform; (b) reaction of (**1**) with phenol produces no hydrogen gas; (c) synthesis of complexes analogous to (**1**) with $[(2,6\text{-D}_2\text{C}_6\text{H}_3)_3\text{P}]$ or CD_3CN ligands have no effect on the position of the bands at 2254 and 1912 cm^{-1} .

The observed decrease in $\nu(\text{CN})$ for the co-ordinated acetonitrile suggests that this ligand is π -bonded to ruthenium. Similar decreases in $\nu(\text{CN})$ have been observed with other nitrile containing complexes.² The decrease of 337 cm^{-1} for $\nu(\text{CN})$ in (**1**) is larger than that observed with most other metal systems and indicates extensive back-donation from the metal into the nitrile π^* -orbitals. This increased back-donation is consistent with the zero-valence state of ruthenium in this complex. Complex (**1**) can be, therefore, best represented by the structural formula,

† Present address: Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7.

$(\text{Ph}_3\text{P})_4\text{Ru}(\pi\text{-MeCN})\cdot\text{MeCN}$. By analogy with the tertiary phosphine carbonyl complexes of ruthenium(0)³ it may be assumed that (1) is most probably trigonal bipyramidal and the less sterically demanding acetonitrile ligand is situated in the equatorial plane.

The title complex undergoes ligand exchange with both carbon monoxide and other tertiary phosphines. Reaction with CO in excess produced the well-known complex $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_3$.³ The addition of CO appears to proceed in a stepwise manner. When the reacting ratio of carbon monoxide to ruthenium was 2:1 an orange-red complex was isolated which analysed as $(\text{Ph}_3\text{P})_3\text{Ru}(\text{CO})_2$. Addition of a single mole of CO per mole of ruthenium yields a yellow complex which has not been isolated in a pure state but existing analytical data suggest the formula $(\text{Ph}_3\text{P})_4\text{Ru}(\text{CO})$.

Metathesis of (1) in acetonitrile with a four-fold excess of diphenylmethylphosphine at reflux produced a pale yellow powder. Satisfactory elemental analyses have been obtained for the formula $(\text{Ph}_2\text{PMe})_4\text{Ru}$ (2). The i.r. spectrum of (2) exhibits bands at 1951 and 753 cm^{-1} in addition to the expected phosphine bands. Reaction of (2) with carbon tetrachloride produces a quantitative yield of chloroform

(g.l.c. and mass spectrometry). Unfortunately the low solubility of (2) prevented n.m.r. analysis of the compound. On the basis of the i.r. spectrum and the reaction with CCl_4 , (2) appears to contain a hydride ligand which results from insertion of the metal into an *ortho* carbon-hydrogen bond of a phenyl ring of the ligand. However, the existing data do not preclude the insertion of the metal also into a carbon-hydrogen bond of the ligand methyl group as observed with bis-(dimethylphosphino)ethane.¹ A recent X-ray study by Cotton and his co-workers⁴ has shown that $[\text{RuH}(\text{CH}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)(\text{PP})]$ is a binuclear ruthenium species with methylene groups acting as bridges between the ruthenium centres. A similar binuclear structure may also exist for (2) and would rationalize the low solubility of (2) in most solvents.

Studies of the reactions of these carbonyl-free ruthenium(0) complexes with olefins and other donor ligands are in progress. These systems appear particularly promising for determining the role of metal basicity on the insertion of a transition metal into carbon-hydrogen bonds.

(Received, 15th July 1975; Com. 810.)

¹ J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843.

² M. F. Farona and K. F. Kraus, *Inorg. Chem.*, 1970, 9, 1700.

³ J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, 87, 4008.

⁴ F. A. Cotton, B. A. Frenz, and D. L. Hunter, *J.C.S. Chem. Comm.*, 1974, 755