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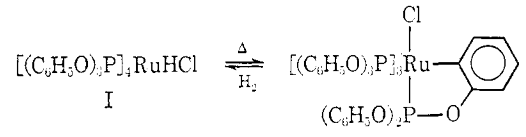
Ligand-Metal Hydrogen Transfer in Phosphite Complexes

Sir:

A number of tertiary phosphine complexes of transition metals have been reported to exhibit interactions between the metal atom and C–H bonds of the phosphine ligand.[1] This communication describes related behavior for *phosphite* complexes. The reaction of tris(triphenylphosphine)ruthenium chlorohydride[2] with triphenyl phosphite in benzene at room temperature forms hydrogen and a mixture of tetrakis (triphenyl phosphite)ruthenium chlorohydride (I)[3] and an *ortho*-phenyl bonded, dehydrogenated derivative, $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4RuCl$ (II).[4] Both I and II are white, air-stable compounds which are soluble in aromatic hydrocarbons; they are readily interconvertible.



I

II

The dehydrogenation proceeds smoothly in refluxing methylcyclohexane from which crystalline II separates on cooling; the reversal occurs readily on exposure of hydrocarbon solutions of II to hydrogen. The ^1H nmr spectrum of I includes a hydride signal at τ 16.8, split into two multiplets. This is consistent with an octahedral structure in which the hydrogen is *trans* to phosphorus ($J_{P-H\ trans} = 176$ cps). The absence of hydrogen bonded to ruthenium in II has been established by nmr and infrared spectroscopy.

The ^{31}P nmr spectrum of II at 40.5 MHz consists of two pairs of overlapping triplets and one pair of overlapping doublets, indicative of an octahedral structure in which the ruthenium–carbon bond is *trans* to phosphorus and the *ortho*-bonded phosphite phosphorus is *trans* to chlorine.[5] The phenyl–ruthenium bond in II is assumed to be at an *ortho* position for steric reasons and by analogy with the deuteration of $[(C_6H_5O)_3P]_4CoH$, discussed below.

The reaction of II with deuterium leads to an *ortho*-deuterated analog of I. Participation of all the *ortho* positions in the equilibrium was demonstrated by an experiment in which 0.26 mmole of II was treated with 7.0 mmoles of deuterium for 2 days at ambient temperature in toluene. Analysis of the recovered gases showed 47.6% D_2, 41.7% HD, and 10.7% H_2, compared to a D_2:HD:H_2 ratio of 48.5:42.2:9.3 calculated for statistical distribution of the deuterium among all the 24 *ortho* positions of I.

The reaction of $[(C_6H_5O)_3P]_4CoH$ with deuterium also results in deuteration of the phenyl rings although no intermediate similar to II has been isolated. At 220 MHz, the spectra of the deuterated and undeuterated complexes are well resolved and permit unambiguous identification of the *ortho* positions as the sole sites of deuteration. Presumably complexes similar to II are involved as reaction intermediates.

Recently the reaction of $[(C_6H_5O)_3P]_3Rh(CO)H$ with triphenyl phosphite was reported to give $[(C_6H_5O)_3P]_4RhH$ in refluxing ethanol[6] and $\{[(C_6H_5O)_3P]_4Rh\}_2$ in refluxing *n*-alkanes.[7] The evidence presented for the dimeric nature of the latter consisted of the observed diamagnetism of the complex and an inability to detect hydride ligands. It is suggested here that "$\{[(C_6H_5O)_3P]_4Rh\}_2$" and the analogous "$\{[(C_6H_5O)_3P]_4Ir\}_2$"[7] are actually *ortho*-phenyl bonded species, $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4M$, analogous to II above. In support of this it was noted that the infrared spectrum of $[(C_6H_5O)_3P]_4RhH$ is virtually identical with that of I, and that refluxing this rhodium complex in *n*-heptane gives a new species with an infrared spectrum very similar to that of II. This transformation is readily reversed by hydrogen at atmospheric pressure, analogous to the transformation of II to I. Additionally, treatment of $[(C_6H_5O)_3P]_4RhH$ with deuterium resulted in extensive deuteration of the *ortho*-phenyl positions.

The mechanism of the reversible hydrogenation and other aspects of this chemistry will be discussed in a forthcoming article.

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[1] J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965); M. A. Bennett and D. C. Milner, *Chem. Commun.*, 581 (1967); G. W. Parshall, *J. Am. Chem. Soc.*, 90, 1669 (1968); A. Sacco and M. Rossi, *Inorg. Chim. Acta*, 2, 127 (1968); W. Keim, *J. Organometal. Chem.*, 14, 179 (1968); G. Hata, H. Kondo, and A. Miyaki, *J. Am. Chem. Soc.*, 90, 2278 (1968); W. H. Knoth, *ibid.*, 90, 7172 (1968); S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968); A. Sacco and M. Aresta, *ibid.*, 1223 (1968).

[2] P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *ibid.*, 305 (1967).

[3] *Anal.* Calcd for $C_{72}H_{61}ClO_{12}P_4Ru$: C, 62.7; H, 4.5; Cl, 2.6; P, 9.0. Found: C, 62.9; H, 4.4; Cl, 2.6; P, 8.4.

[4] *Anal.* Calcd for $C_{72}H_{59}ClO_{12}P_4Ru$: C, 62.8; H, 4.3; Cl, 2.6; O, 14.0; P, 9.0. Found: C, 62.8; H, 4.4; Cl, 2.6; O, 13.8; P, 8.8.

[5] A referee has requested comment on the fact that the ^{31}P nmr pattern of II is also consistent with a structure in which the ruthenium–carbon bond is *trans* to chlorine. We prefer the structure proposed in the text because of the chemical shift and coupling constant data, which will be discussed in detail in a forthcoming paper. Also, the structures proposed for I and II in the text are mutually consistent, whereas the alternate structure for II would require that a rearrangement occur in the equilibrium between I and II.

[6] J. J. Levison and S. D. Robinson, *Chem. Commun.*, 1405 (1968).

[7] S. D. Robinson, *ibid.*, 521 (1968).

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Synthesis of Ethylenediamine-N,N,N′-triacetic Acid and Its Cobalt(III) Complexes

Sir:

Past attempts to prepare ethylenediaminetriacetic acid have been generally unsuccessful and recent reports of the acid's existence could not be confirmed.[1–3]

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[1] K. A. Schroeder and R. E. Hamm, *Inorg. Chem.*, 3, 391 (1964).

[2] R. E. Hamm and M. A. Suwyn, *ibid.*, 6, 139 (1967).

[3] D. L. Venezky and W. B. Moniz, *Anal. Chem.*, 41, 11 (1969).