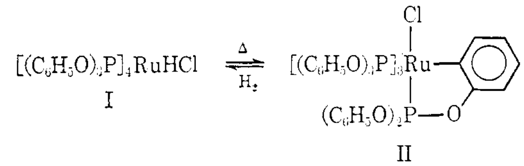
Acknowledgment. We thank the National Air Pollution Control Administration, Public Health Service, for support of this work through Grant AP 00580.

Paul R. Story, W. Herbert Morrison, III, James M. Butler
Department of Chemistry, The University of Georgia
Athens, Georgia 30601
Received December 30, 1968

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, $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4Ru}Cl$ (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, $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4M}$, 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.

---

[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).

W. H. Knoth, R. A. Schunn
Contribution No. 1552, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898
Received February 6, 1969

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]

---

[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).

The most significant contribution to report in this communication is that we have synthesized cobalt(III) complexes containing the ligand ethylenediamine-N,N,N′-triacetic acid (ED3A). The uniqueness of this pentadentate ligand renders it essential to cobalt(III) chemistry. First, it completes the series of cobalt(III) complexes of N-substituted ethylenediaminepolycarboxylic acids from ethylenediaminetetraacetic acid (EDTA) to ethylenediaminediacetic acid (EDDA). Secondly, the cobalt(III) complexes of ED3A act as models for the other cobalt(III) complexes containing EDTA-type pentadentate ligands.

The method used to prepare the acid, ED3A, was similar to that of Dwyer and Garvan[4] in their preparation of 1,2-propylenediaminetetraacetic acid.

When ethylenediamine is allowed to react with monochloroacetic acid, in a 1:3 mole ratio in basic solution at 10° for 24 hr, a solution results which is thought to contain a mixture of EDTA, ED3A, and EDDA.

The acid ED3A was separated from the other acid products of the reaction in complexed form with cobalt(III). The desired product, $Co(ED3A)(H_2O)$, was isolated from the other cobalt(III) species by passing the solution containing the cobalt(III) complexes through Dowex 1-X8 and Dowex 50W-X8 ion-exchange resins in the Cl^- and K^+ forms, respectively. Only the zero charged $Co(ED3A)(H_2O)$ species passed through both columns. The complex was collected and purified: yield, before final purification, 36% based on cobalt(II) added. *Anal.* Calcd for $[Co(ED3A)(H_2O)] \cdot 1.5H_2O$: C, 28.67; H, 4.81; N, 8.37. Found: C, 28.61; H, 4.70; N, 8.64.

The aquo complex was used to prepare $K[Co(ED3A)X]$ where X^- is Cl^-, NO_2^-, or ONO^-. The nitro and nitrito species were prepared by the addition of $NaNO_2$ to a solution of the aquo complex. The nitro and nitrito complexes were easily separated and purified by ion-exchange chromatography. Analysis of the two compounds proved to be nearly identical. *Anal.* Calcd for $K[Co(ED3A)X] \cdot H_2O$ where X is NO_2 or ONO: C, 24.43; H, 3.33; N, 10.68; K, 9.94. Found: C, 24.48; H, 3.35; N, 10.57; K, 9.94.

The chloro complex was prepared by dissolving the aquo complex in a saturated NaCl solution, acidifying with HCl, and evaporating to dryness on a steam bath. The blue complex that resulted was also purified by ion-exchange chromatography. *Anal.* Calcd for $K[Co(ED3A)Cl] \cdot 0.5H_2O$: C, 23.69; H, 2.98; N, 6.91; K, 9.64; Cl, 8.74. Found: C, 23.66; H, 3.15; N, 6.98; K, 10.04; Cl, 8.92

The colors of the complex salts in this study were found to be identical with those of the related series[5,6] of cobalt(III) complexes containing similar pentadentate ligands. The nitrito complex was found to be bluish purple in color. This color slowly changed to the brick red color of the nitro species when allowed to remain on the resin for several days. This observation reflects the possibility of linkage isomerization of the $-NO_2$ ligand.

The infrared absorption bands for the compounds under current investigation are in accord with those reported previously for similar compounds.[6,7]

The absence of the three absorptions typically associated with an uncoordinated carboxylic acid group, namely the absorptions at 2600–2800, 1700–1750, and 1228 cm^{-1}, rules out the possibility of an uncoordinated carboxylic acid group in the ED3A complexes. An absorption at 1648–1658 cm^{-1} arising from the complexed carboxyl group appears throughout the series of cobalt(III) complexes of ED3A. The nitro complexes show the characteristic bands associated with the coordinated nitro ligand, namely 1408, 1342, and 830 cm^{-1}. The nitrito complex gives two additional absorptions occurring at 1460 and 1065 cm^{-1} which have been assigned to the two ONO stretching vibrations.[8] The hydrogen, bound to the nitrogen atom of the ED3A ligand, gives rise to a N–H stretching frequency at 3150 cm^{-1}. This absorption was observed in all of the ED3A complexes. The occurrence of this absorption substantiates the existence of the ED3A ligand.

The visible spectra of the cobalt(III) complexes of ED3A are very similar to the related complexes reported previously.[5,9,10] The absorption curve for the nitrito species has two low-energy maxima of nearly equal intensity occurring at 17,800 and 21,000 cm^{-1}. Upon rearrangement of the nitrito species the spectrum of the nitro complex is obtained which has a maximum absorption at 20,300 cm^{-1} and a shoulder at 17,100 cm^{-1}.

The absorption curves for the nitro and chloro complexes of cobalt(III) EDTA, HEDTA, and MEDTA[5] are all seen to be very similar to that of their model $Co(ED3A)NO_2^-$ and $Co(ED3A)Cl^-$.

Previous studies[5,9] as well as this investigation have shown no evidence for geometrical isomerism with respect to the ligand even though the possibility of such isomerism exists.

---

(4) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, 81, 2955 (1959).

(5) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, 7, 1393 (1968).

(6) M. L. Morris and D. H. Busch, *J. Am. Chem. Soc.*, 78, 5178 (1956).

(7) K. Nakamoto, J. Fujita, and H. Murata, *ibid.*, 80, 4817 (1958).

(8) R. B. Penland, T. J. Lane, and J. V. Quagliano, *ibid.*, 78, 887 (1956).

(9) R. A. Haines and B. E. Douglas, *Inorg. Chem.*, 4, 452 (1965).

(10) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *ibid.*, 2, 1194 (1963).

Gary L. Blackmer, Randall E. Hamm
Department of Chemistry, Washington State University
Pullman, Washington 99163

Received February 3, 1969

A Contribution to the Chemistry of Stannane

Sir:

We wish to report the results of recent work in our laboratory which considerably expands the chemistry of stannane, SnH_4. The development of the chemistry of stannane[1] has been hampered by its instability which complicates the experimental situation and leads at best to low yields of products. The only reactions of stannane, besides its decomposition, which have been described are its conversion into the highly unstable compound SnH_3Cl[2] and some of its monoalkali metal derivatives.[3]

---

(1) For a review of stannane chemistry, see F. G. A. Stone, "Hydrogen Compounds of the Group IV Elements," Prentice-Hall, Inc., New York, N. Y., 1962, p 79.

(2) E. Amberger, *Angew. Chem.*, 72, 78 (1960).