

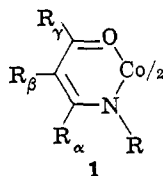
(Grant No. 2445-A1,3 to M. J. J. and Grant No. 383-G to C. H. H.) of this research.

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Received August 2, 1965

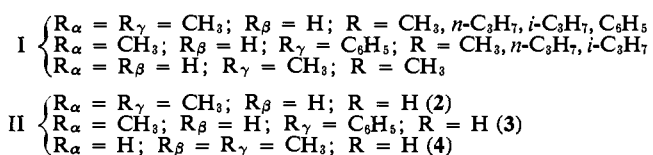
## Existence of the Planar $\rightleftharpoons$ Tetrahedral Equilibrium in Solutions of Cobalt(II) Complexes

Sir:

A problem still largely unsolved in metal complex stereochemistry is that of the preferential stabilization of the planar or the tetrahedral stereoisomer in quadri-coordinate complexes of a given metal or in a series of complexes with the same ligand but different metals. From investigations of nickel(II) complexes it is recognized that the free-energy difference between planar and tetrahedral conformers can be adjusted by appropriate substitution on a parent ligand system to a point at which detectable concentrations of both exist in equilibrium in solutions of noncoordinating solvents.<sup>1-4</sup> Thus far the planar  $\rightleftharpoons$  tetrahedral equilibrium has been detected only in nickel(II) complexes of four general structural types, one of which is a group of bis( $\beta$ -ketoamino) complexes recently studied.<sup>3</sup> We now report the existence of this configurational equilibrium for some bis( $\beta$ -ketoamino)cobalt(II) complexes **1** in solution. Other structural equilibria of cobalt complexes in solution are known<sup>5</sup> but do not involve the planar and tetrahedral forms in equilibrium.



Bis( $\beta$ -ketoamino)cobalt(II) complexes were prepared by a nonaqueous chelation procedure.<sup>3</sup> All are orange crystalline solids which gave satisfactory microanalyses. The complexes may be divided into two groups.



At room temperature crystalline group I complexes

(1) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964); A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010, (1964); A. Chakravorty, J. P. Fennessey, and R. H. Holm, *ibid.*, **4**, 26 (1965); L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963); L. Sacconi and M. Ciampolini, *ibid.*, **85**, 1750 (1963); L. Sacconi, M. Ciampolini, N. Nardi, *ibid.*, **86**, 819 (1964); L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc.*, 255 (1962).

(2) D. R. Eaton, D. J. Caldwell, and W. D. Phillips, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(3) G. W. Everett, Jr., and R. H. Holm, *Proc. Chem. Soc.*, 238 (1964); *J. Am. Chem. Soc.*, **87**, 2117 (1965).

(4) R. H. Holm, A. Chakravorty, and L. J. Theriot, to be published.

(5) (a)  $\text{CoL}_2\text{X}_2 + 2\text{L} \rightleftharpoons \text{CoL}_4\text{X}_2$ ; cf., e.g., H. C. A. King, E. Koros, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963); 4832 (1964); (b) tetrahedral  $\rightleftharpoons$  square pyramidal  $\rightleftharpoons$  octahedral: L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965); (c) low spin (penta-coordinate dimer)  $\rightleftharpoons$  high spin (tetrahedral): M. Nicolini, C. Pecile and A. Turco, *J. Am. Chem. Soc.*, **87**, 2379 (1965).

have magnetic moments in the range 4.22–4.44 B.M., and in solutions of noncoordinating solvents such as chloroform and toluene moments of 4.30–4.50 B.M. The ligand-field spectra of these complexes are identical in the solid and in chloroform solutions, exhibiting bands at 8500 and 10,500  $\text{cm}^{-1}$  and 19,100  $\text{cm}^{-1}$ , which may be assigned as (components of)  $\nu_2$  and  $\nu_3$ , respectively, in idealized tetrahedral symmetry. Both the magnetic moments and optical spectra of these complexes are nearly identical with those of the analogous bis(N-substituted salicylaldimino)cobalt(II) complexes,<sup>6</sup> several of which have been shown by X-ray results to possess a pseudo-tetrahedral configuration.<sup>7</sup> We conclude that all group I complexes, which have for nitrogen substituents methyl or larger groups, are pseudo-tetrahedral in the solid and completely in this form in solution.

Group II complexes exhibit a distinctly different behavior. In the solid these complexes have moments of 2.17–2.33 B.M. indicating low-spin planar Co(II). In chloroform solutions containing  $\sim 15\%$  v/v. TMS and prepared with rigorous exclusion of oxygen and moisture, the following results were obtained at  $\sim 25^\circ$ : **2**, 4.00 B.M.; **3**, 3.60 B.M.; **4**, 2.88 B.M. The moment of each complex increases with increasing temperature (e.g., for **3**, 3.25 B.M. at  $-40^\circ$  and 3.75 B.M. at  $58^\circ$ ) and the magnetic changes have been shown to be reversible with temperature. The ligand-field spectra of the solid complexes (hydrocarbon mull) show a relatively narrow band at 8500  $\text{cm}^{-1}$  ( $\sim 1100\text{-cm}^{-1}$  half-width) and no shoulder at  $\sim 10,500\text{-cm}^{-1}$ , a feature clearly evident in all group I complexes. The narrow 8500- $\text{cm}^{-1}$  absorption must be considered characteristic of low-spin Co-N<sub>2</sub>O<sub>2</sub> complexes inasmuch as it is found in the solid and solution spectra of N,N'-bis-(salicylidene)ethylenediaminocobalt(II)<sup>8</sup> and bis-(benzoylacetone)ethylenediiminocobalt(II). The solution spectra of the group II complexes contain an 8500- $\text{cm}^{-1}$  absorption and the shoulder at 10,500  $\text{cm}^{-1}$ , both of which are reduced in intensity proportionate to the fraction of planar form (obtained from the magnetic data at a given temperature). Associated species are ruled out by the excellent Beer's law dependence<sup>9</sup> of the three group II complexes in chloroform at  $25^\circ$  in the 0.005–0.040 *M* range, which overlaps with that used in the magnetic measurements. We conclude that the data are consistent only with the equilibrium

planar ( $S = 1/2$ ,  $\sim 2.2$  B.M.)  $\rightleftharpoons$  tetrahedral ( $S = 3/2$ ,  $\sim 4.4$  B.M.)

Thermodynamic data for the equilibrium of **2**, **3**, and **4** have been obtained by magnetic susceptibility measurements (n.m.r. method) of chloroform solutions containing 15% v/v. TMS over the range  $-40$  to  $70^\circ$ . Taking  $K_{\text{eq}} = N_t/N_p = [(2.2)^2 - \mu^2_{\text{obsd}}]/[\mu^2_{\text{obsd}} - (4.4)^2]$ , in which 2.2 and 4.4 are the limiting moments of the planar and tetrahedral forms, respectively, the calculated free-energy changes are found to vary linearly with temperature. Least-mean-squares treat-

(6) B. O. West, *J. Chem. Soc.*, 1374 (1962); L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962); H. Nishikawa and S. Yamada, *Bull. Chem. Soc., Japan*, **35**, 1430 (1962).

(7) E. Frasson and C. Panattoni, *Z. Krist.*, **116**, 154 (1961); L. Sacconi and P. L. Orioli, *Ric. sci. rend.*, **32**, 645 (1962).

(8) H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Japan*, **37**, 8 (1964).

(9) Osmometric measurements of molecular weights were vitiated by the extreme sensitivity of the solutions to oxygen.

ment of the results yields  $\Delta F(2) = 829 - 5.42T$ ,  $\Delta F(3) = 1640 - 5.96T$ ,  $\Delta F(4) = 1910 - 4.15T$ , and the following percentages of tetrahedral form at 25°: 79% (2), 56% (3), 24% (4).

The results clearly show that the equilibrium position is dominated by the nature of R such that the planar form is detectable only when R = H. The implication is that a torsional twist induced by steric interaction in the *trans*-planar form destabilizes this configuration, as is believed to be the case for nickel complexes.<sup>1-4</sup> Although no truly quantitative comparisons can yet be made, it is clear that the barrier to distortion from planarity of nickel complexes is much greater than that for cobalt complexes containing the same ligand. Thus, for the *nickel* complexes 2, 3, and 4 no contact shifts are observable at 80° in chloroform ( $K < 0.01$ ,  $\Delta F > 3200$  cal./mole); for the complex with  $R_\alpha = R_\gamma = R = \text{CH}_3$ ,  $R_\beta = \text{H}$ , very small contact shifts are observed,<sup>3</sup> implying  $K \sim 0.02$ ,  $\Delta F \sim 2400$  cal./mole, whereas the cobalt complex is fully tetrahedral. While the greater relative stabilization of tetrahedral Co(II) might be anticipated from CFSE arguments, the present work demonstrates that this stereoisomeric form is not exclusively populated in cobalt complexes which, by virtue of their structural and steric features, are not constrained to be either tetrahedral or planar.<sup>10</sup> A more detailed account of this work will be forthcoming.

**Acknowledgment.** This research was supported by the National Science Foundation under Grants GP-2840 and GP-4899.

(10) The only other example of this type appears to be bis(dipivaloylmethanato)cobalt(II), which is tetrahedral in the solid (F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962)) and apparently fully tetrahedral in benzene (F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964)). The nickel complex is planar in both phases.

(11) N.S.F. Predoctoral Fellow, 1962-1966.

(12) Alfred P. Sloan Foundation Fellow.

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Received October 4, 1965

## Reaction of Triphenylphosphine with Methylmanganese Pentacarbonyl. Structure and Stoichiometry

Sir:

Although the reactions of various amines,<sup>1</sup> phosphines,<sup>2,3</sup> and arsines<sup>3</sup> with  $\text{CH}_3\text{Mn}(\text{CO})_5$  have been reported, the structures and stoichiometry of the products are not well known in each case. Certain of our preliminary results concerned with these aspects have already been mentioned.<sup>2</sup> We now wish to report some important observations on the reaction of triphenylphosphine with  $\text{CH}_3\text{Mn}(\text{CO})_5$ .

When triphenylphosphine reacted with  $\text{CH}_3\text{Mn}(\text{CO})_5$  in a wide selection of organic solvents for 12-24 hr. at 5-10°, a yellow solid (I) was obtained by blowing the solution down to a small volume with a stream of dry nitrogen. These solutions were not allowed to warm

(1) K. A. Keblyns and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

(2) R. J. Mawby, F. Basolo, and R. G. Pearson, *ibid.*, **86**, 5043 (1964).

(3) W. D. Bannister, M. Green, and R. N. Hazeldine, *Chem. Commun.* (London), **1**, 55, 1965.

before the solid was filtered and freed of solvent. An infrared spectrum of I in hexane contained three terminal CO stretching frequencies at 2066 (w), 1995 (m), and 1959 (s)  $\text{cm}^{-1}$ , as well as an acetyl CO stretching frequency near 1631 (w)  $\text{cm}^{-1}$ . The spectrum was identical with that seen when the reaction itself was followed by infrared at temperatures near 5°. The number of carbonyl transitions and their relative intensities were as expected for *trans*- $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$  with localized  $C_{4v}$  symmetry for the metallo-carbonyl groups. Unfortunately, infrared spectral studies do not permit an unequivocal determination of isomeric purity, *i.e.*, *cis* or *trans*, and cannot provide an accurate measure of extent of carbonylation or decarbonylation. Equally misleading are carbon-hydrogen analyses which are not very different for a triphenylphosphine-substituted methyl or acetyl derivative. By contrast, proton magnetic resonance is especially enlightening in both regards. A p.m.r. spectrum of I in benzene taken immediately after mixing revealed two acetyl methyl proton resonances at 161 and 145 c.p.s. relative to tetramethylsilane. These peaks could not be due to  $\text{CH}_3\text{COMn}(\text{CO})_5$  or  $\text{CH}_3\text{Mn}(\text{CO})_5$ , which gave sharp singlets at 136 and -13 c.p.s., respectively. The ratio of the peak heights showed the peak at 145 c.p.s. to be approximately four times that at 161 c.p.s. We believe that these peaks correspond to *trans*- and *cis*- $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ , respectively, since the infrared spectra suggest the predominance of a *trans* complex. After 1 hr. at room temperature, during which the relative intensities of these two peaks had changed, an equilibrium mixture containing approximately 30% *cis* and 70% *trans*- $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$  was obtained. Some decarbonylation also occurred during this period (see below).

When the reaction of triphenylphosphine with  $\text{CH}_3\text{Mn}(\text{CO})_5$  was carried out at room temperature in a closed system, thus preventing extensive decarbonylation of the phosphine-substituted products, the infrared spectrum of the reaction mixture (II) was similar to that seen at the lower temperature, only it was slightly less sharp in the metallo-carbonyl stretching region. The p.m.r. spectrum of such a sample prepared in a closed tube again indicated that an equilibrium mixture containing approximately 70% of the *trans* acetyl species was obtained at room temperature compared to nearly 80% *trans* at 5°. If this same reaction proceeded at room temperature in an open system, decarbonylation occurred and striking changes took place in the infrared spectrum in the metallo-carbonyl stretching region (see below). Other evidences for decarbonylation included diminishment of the intensity of the acetyl stretching mode and appearance of a new proton resonance, indicating formation of *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ .

The formation of pure *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$  (III) was easily achieved by refluxing a benzene solution of equimolar quantities of  $\text{CH}_3\text{Mn}(\text{CO})_5$  and triphenylphosphine for several hours. Recrystallization from ethanol-chloroform yielded gold crystals, m.p. 109.5-111.5°, yield 48%. *Anal.* Calcd.: C, 62.17; H, 4.08. Found: C, 62.17; 61.76; H, 3.90, 4.02. The infrared spectrum of III in hexane contained terminal CO stretching bands at 2055 (m), 1983 (m), 1968 (s), and 1939 (m)  $\text{cm}^{-1}$  and was consistent