(Fig. 1) was performed, which confirmed the 1:1 stoichiometry. The compound may be conveniently prepared in benzene or toluene since biscyclopenta-dienyltungsten dihydride is soluble in such hydrocarbons but the BF_3 adduct is not. This adduct does not have an appreciable BF_3 dissociation pressure.

Infrared spectra were obtained on Nujol mulls using a prism-grating Beckman IR9: $(C_5H_5)_2WH_2$, 601 (m), 776 (s), 822 (s), 876 (w), 906 (m), 985 (s), 1004 (s), 1053 (w), 1097 (m), 1252 (w), 1415 (m), 1921 (m) cm.; $(C_5H_5)_2WH_2 \cdot 0.95\ BF_3$, 602 (m), 777 (s), 823 (s), 906 (m), 1005 (s), 1053 (s), 1095 (s), 1286 (w), 1917 (m), 1922 (sh) cm.$^{-1}$. The W–H stretching frequency 1921 cm.$^{-1}$ is shifted to 1917 cm.$^{-1}$ upon complex formation (the shoulder at 1922 cm.$^{-1}$ is attributed to the small amount of parent compound present in the sample). The very small frequency shift and negligible change in relative intensity of this band renders unlikely a single hydrogen bridge such as that found in $B_2H_7^-$ ($H_3B-H-BH_3^-$).[5] In the case of $(C_5H_5)_2WH_2 \cdot BF_3$ a broad absorption appears to underlie the bands in the 1100 to 1000 cm.$^{-1}$ region. This broad band is in the correct region for the asymmetric BF_3 stretching frequency of coordinated BF_3.[6] The symmetric BF_3 stretch, which is expected to be less intense, cannot be located with certainty, but, judging from band shapes, it may fall in the region of the 823 cm.$^{-1}$ absorption. Due to lack of a suitable solvent it was not possible to obtain n.m.r. spectra for the adduct.

In order to rule out the rather unlikely possibility of BF_3 interaction with C_5H_5 groups a comparable tensiometric titration was performed with ferrocene and BF_3, but a complex did not result.[7] As noted previously, boron trifluoride coordinated through a hydrogen bridge can also be discounted. The remaining alternative is a metal–boron bond analogous to $(C_5H_5)_2WH_3^+$. Like the protonated species the BF_3 adduct probably involves bonding with a lone pair in a hybrid orbital directed along the twofold axis of the parent molecule (Fig. 2).[3,8] The similar molecules $(C_5H_5)_2MoH_2$ and $(C_5H_5)ReH$ are also known to protonate with relative ease and may prove to have substantial affinities for Lewis acids.

(5) H. C. Brown, and P. A. Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958); D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963), and references therein.

(6) A. R. Katritzky, *J. Chem. Soc.*, 2049 (1959); G. L. Cole and H. W. Thompson, *Proc. Roy. Soc.* (London), **A210**, 217 (1951); G. M. Begun and A. A. Palko, *J. Chem. Phys.*, **38**, 2112 (1963).

(7) In this same connection, a referee has pointed out that F. A. Cotton and L. T. Reynolds [*J. Am. Chem. Soc.*, **80**, 269 (1958)] observed negligible absorption of BF_3 or BCl_3 by C_5H_5Tl.

(8) C. J. Ballhausen and J. P. Dahl, *Acta Chem. Scand.*, **15**, 1333 (1961).

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Configurations of the Complex Dithiocyanatobis-(triethylphosphine)cobalt(II)

Sir:

The correlation between physicochemical properties and structure of planar tetracoordinate cobalt(II) complexes is not well established. The complexes believed to be square-planar are generally of the spin-paired type.[1] A rigorously square-planar and spin-free cobaltous anionic complex has been described only very recently.[2]

The "pure" square-planar complexes of nickel(II) so far investigated are only of the spin-paired type and the paramagnetic complexes are either tetrahedral or octahedral. On the other hand, the existence in solution of the equilibrium *square-planar (diamagnetic)* ⇄ *tetrahedral (paramagnetic)* has clearly been established.[3]

We wish to report some results which seem to us to be both novel and important, because they suggest the existence of a similar equilibrium in the tetracoordinate cobalt(II) complex compound $[Co(PEt_3)_2(NCS)_2]$.

Anhydrous cobaltous thiocyanate in absolute ethanol reacted with $P(C_2H_5)_3$ to give a red crystalline product, which was washed with ice-cold ethanol and dried in an atmosphere of pure nitrogen, m.p. 72–74° dec. *Anal.* Calcd. for $Co(PEt_3)_2(NCS)_2$: C, 40.9; H, 7.35; N, 6.8; Co, 14.3. Found: C, 40.5; H, 7.4; N, 6.75; Co, 14.3.

The solid compound, stable at room temperature for months in the absence of oxygen, decomposes in a few seconds in contact with air. Preparation and measurements were carried out in an atmosphere of nitrogen to avoid oxidation.

The solid compound dissolves in alcohols giving solutions which initially are yellow-brown. Solutions in aprotic solvents (acetone, dimethylformamide, dichloromethane, and benzene) are deep blue or green. The spectrum in benzene or dichloromethane solution in the 500–1800-mμ region is extremely similar to the spectra of tetrahedral complexes such as $[Co(PCy_3)_2(NCS)_2]$ and $[Co(PPh_3)_2(CNS)_2]$.[4] In the 500–700-mμ region the solution spectra exhibit the characteristic multicomponent band associated with the $^4A_2 \leftarrow \ ^4T_1$ (P) transition in tetrahedral (or pseudo-tetrahedral) complexes.[4,5] The spectrum of the crystalline complex does not show absorption bands in this region. Thus, the electronic spectra indicate that the compound is not tetrahedral in the solid, whereas the tetrahedral species predominates in solution. We say predominates, because there are distinctive features in the 400–500-mμ region which strongly suggest the presence of nontetrahedral species in CH_2Cl_2 solution. In this region the extinction coefficient of the solution is greater than 150; whereas it is less than 30 for solutions of $[Co$ $PCy_3)_2(NCS)_2]$, $[Co(PEt_3)_2Cl_2]$, and $[Co(PEt_3)_2Br_2]$ at the same concentration. The occurrence of both tetrahedral and nontetrahedral species in CH_2Cl_2 solution is supported by magnetic and infrared measurements. The average magnetic moment at 25° of solid $[Co(PEt_3)_2(NCS)_2]$ corrected for diamagnetism is 2.3 B.M., in agreement with a low spin square-planar structure. An octahedral spin-paired coordination would require a noticeably smaller moment (1.7–2.0 B.M.).[1] The magnetic moment at 25° in CH_2Cl_2 (0.24 M solution) is 3.50 B.M. By analogy with the moments found for solid $[Co(PPh_3)_2(CNS)_2]$ and $[Co(PCy_3)_2(NCS)_2]$ (4.45 and 4.4 B.M., respectively) and for $[Co(PCy_3)_2(NCS)_2]$ in CH_2Cl_2 solution (4.35 B.M. in 0.27 M solution), it is reasonable to assume that the moment of the (not isolated) tetrahedral isomer of $[Co(PEt_3)_2(NCS)_2]$ is about 4.40 B.M. Hence, the moment 3.5 found in

(1) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

(2) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(3) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963); D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(4) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961); M. Nicolini, C. Pecile, and A. Turco, unpublished results.

(5) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

CH_2Cl_2 indicates that both high-spin and low-spin species are present in this solvent. Moreover, in view of the above it is tempting to postulate a planar structure for the low-spin compound.

The infrared spectrum of solid $[Co(PEt_3)_2(NCS)_2]$ in Nujol mull shows a strong band at 2090 cm.$^{-1}$ assigned to the CN stretching vibration of the SCN group and does not have absorption bands in the 2130–2160-cm.$^{-1}$ region. The possibility that the metal may effectively be six-coordinated through SCN groups seems in this case to be ruled out. It is worth noting that the CN stretching frequency of trans-$[Ni(PEt_3)_2(NCS)_2]$ has the same value of 2090 cm.$^{-1}$. The two strong bands observed at 830 and 795 cm.$^{-1}$ in the spectrum of $[Co(PEt_3)_2(NCS)_2]$ but absent in the spectra of $[Co(PEt_3)_2Cl_2]$ and $[Co(PEt_3)_2Br_2]$ are assigned to the CS (pseudo-symmetrical N–C–S) stretching vibration of the CNS group in isothiocyanates.[6] The doublet structure might arise either from a cis- or from a distorted trans-planar configuration. Similar conclusions apply to the infrared spectra in CH_2Cl_2 solution. In particular the spectra of 0.25 M solutions in this solvent exhibit bands having the integral intensity of coordinate isothiocyanate groups.

Conductivity measurements were made in CH_2Cl_2 at 25° at a concentration of 10^{-3} M. The small conductivity (<0.9 ohm^{-1} cm.$^{-2}$ mole^{-1}) indicates that the complex is a nonelectrolyte in CH_2Cl_2 and could arise from partial rearrangement in solution to the ionic form $[Co(PEt_3)_4][Co(NCS)_4]$ (Λ_M found for 1.8 × 10^{-3} M $N(C_2H_5)_4Br$, 13.2).

The X-ray powder pattern of $[Co(PEt_3)_2(NCS)_2]$, as it differs considerably from those obtained for the tetrahedral $[Zn(PEt_3)_2(NCS)_2]$ as well as for the planar trans-$[Ni(PEt_3)_2(NCS)_2]$ and cis-$[Pt(PEt_3)_2(NCS)_2]$, is not of great help in establishing the structure of the compound.

A reasonable conclusion which can be drawn from the combined analytical, conductance, spectral, and magnetic data is that $[Co(PEt_3)_2(NCS)_2]$ is an example of conformational isomerism between a low-spin (probably planar) and a high-spin (tetrahedral) form.

This problem is being further investigated and detailed reports will follow.

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(6) A. Turco and C. Pecile, Nature, **191**, 66 (1961).

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Competition Between Ionic and Free-Radical Reactions during Chlorination of Cyclohexene. Spontaneous Generation of Radicals

Sir:

Although considerable evidence suggests that chlorination of olefins in polar solvents involves electrophilic attack by chlorine,[1] the mechanism of chlorination in nonpolar solvents has not been as extensively studied. Such chlorinations produce both addition and substitution products.[2] Taft[3] has attempted to correlate the addition–substitution ratio with olefin structure on the basis of ionic intermediates; indeed, labeling experiments strongly suggest that chlorination of iso-

(1) P. B. D. de la Mare, Quart. Rev. (London), **3**, 126 (1949).

(2) See, for example, H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, Ind. Eng. Chem., **31**, 1239 (1939); D. V. Tishchenko, J. Gen. Chem. USSR, **8**, 1232 (1938).

(3) R. W. Taft, Jr., J. Am. Chem. Soc., **70**, 3364 (1948).

butylene proceeds by an ionic pathway.[4] However, several workers[5] have observed that chlorination of an olefin can induce chlorination of paraffinic solvents; these reactions appear to involve free-radical chain reactions. We wish to report some of our studies on chlorination of cyclohexene which shed light on this apparent anomaly.

Passage of chlorine diluted with nitrogen into cyclohexene in the *absence of light* at 25.0° produces in a rapid reaction[6] three major products: 1,2-dichlorocyclohexane (I),[7] 3-chlorocyclohexene (II), and 4-chlorocyclohexene (III)[8]; admixture with cyclohexane leads to considerable chlorocyclohexane (IV). Use of oxygen as a carrier gas eliminates III (and IV with cyclohexane present), whereas I and II are produced in a

I　　　　　　II　　　　　　III　　　　　　IV
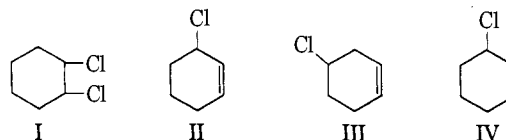
still rapid reaction[6]; use of polar solvents such as acetonitrile also eliminates III and IV. This behavior suggests the existence of both an ionic pathway producing I and II and a radical pathway producing I, II, and III.

Chlorination of cyclohexene diluted with 1,1,2-trichlorotrifluoroethane at low conversion (0.2–0.8 mmole of chlorine per 15 ml. of reaction mixture) gave the striking results plotted in Fig. 1; analysis was by temperature-programmed g.l.c. on a polypropylene glycol column. As dilution increased, chlorination under nitrogen in the absence of light gave constant ratios of III/II and I/II down to a mole fraction of olefin of ~0.40 followed by a sharp decrease of III/II toward zero at infinite dilution and a simultaneous less dramatic increase in I/II (curves 2 and 5). We therefore feel that at mole fractions >0.40 the reaction is almost exclusively radical, whereas at lower concentrations of olefin the ionic reaction becomes predominant. Consistent with this view is the fact that illumination (three 275-watt sunlamps at 6–9 in. through Pyrex) did not change the III/II and I/II ratios at high concentration (the expected result only if reaction were already entirely radical), but did practically eliminate the changes in III/II and I/II at low concentration (curves 3 and 4). If we assume that the radical process produces I, II, and III in the ratio 1.95:1.00:0.60 (the high concentration limit) and that the ionic process produces I and II in the same ratio under nitrogen as under oxygen at a given concentration of olefin (curve 1), the observed III/II ratios can be used to calculate the percentage of radical reaction (r) at each concentration and the corresponding value of I/II based on this r and the previous assumptions (Table I). The calculated results for I/II agree with the observed values within the apparent experimental error; to this extent the assumption that the radical yield ratio (1.95:1.00:0.60) is independent of dilution is confirmed.

Use of cyclohexane as diluent gave comparable results for cyclohexene-derived products and also allowed determination of the relative reactivities of a 4-cyclohexenyl hydrogen atom and a cyclohexyl hydro-

(4) W. Reeve, D. H. Chambers, and C. S. Prickett, ibid., **74**, 5369 (1952).

(5) (a) T. D. Stewart and D. M. Smith, ibid., **51**, 3082 (1929); (b) T. D. Stewart and M. H. Hanson, ibid., **53**, 1121 (1931); (c) T. D. Stewart and B. Weidenbaum, ibid., **57**, 2036 (1935); (d) T. D. Stewart and B. Weidenbaum, ibid., **58**, 98 (1936); (e) J. C. Kuriacose, Indian J. Appl. Chem., **22**, 181 (1959).

(6) No visual build-up of chlorine in solution.

(7) This product was $>99\%$ trans in reactions described herein as ionic, but up to 4% cis in those described as radical.

(8) Suggested as a product without isolation or positive identification by G. F. Bloomfield, J. Chem. Soc., 114 (1944).