resonance at 327.6 c.p.s. is assigned to the trifluoroacetylacetone methyl protons of this compound. By consideration of the other concentration extreme, the remaining resonances can be assigned. The six resonances are assigned as follows: the acetylacetone methyl protons of the compounds $Zr(acac)_4$, $Zr(acac)_3$-(tfac), $Zr(acac)_2(tfac)_2$, and $Zr(acac)(tfac)_3$ resonate at 320.0, 322.5, 325.2, and 327.6 c.p.s. respectively, and the trifluoroacetylacetone methyl protons of the compounds $Zr(acac)_3(tfac)$, $Zr(acac)_2(tfac)_2$, $Zr(acac)$-(tfac)_3, and $Zr(tfac)_4$ resonate at 325.2, 327.6, 329.8, and 332.1 c.p.s. This assignment is found to be consistent at all the concentrations studied. Additional evidence for this assignment is found in the small differences in the chemical shift of $Zr(acac)_4$ and $Zr(tfac)_4$ in the mixtures and in pure solutions. However, any argument based on values of the chemical shift is subject to question due to the large concentration dependence of the chemical shift for compounds in benzene solution.[4] The order of the resonances is intuitively satisfactory, since, if substitution of trifluoroacetylacetone for acetylacetone causes a shift in the resonance, one would expect a similar shift in the same direction with additional substitution. This is found to be true in all cases.

At $X = 0.70$, all five compounds are present in sufficient concentrations to allow calculation of the equilibrium constant. For the reaction $3Zr(acac)_4 + 3Zr(tfac)_4 \rightleftharpoons 2 Zr(acac)_3(tfac) + 2Zr(acac)_2(tfac)_2 + 2Zr(acac)(tfac)_3$, $K_{eq}$ is $1.0 \times 10^8$. The high value of $K_{eq}$ reflects the low concentrations of $Zr(acac)_4$ and $Zr(tfac)_4$ in the mixture. At $X = 0.70$, $Zr(acac)_4$ and $Zr(tfac)_4$ account for less than 3% of the species in solution.

Similar exchange has been observed for mixtures of $Hf(acac)_4$ and $Hf(tfac)_4$, $Hf(acac)_4$ and $Zr(tfac)_4$, $Zr(acac)_4$, and $Zr(dbm)_4$, and $Zr(tfac)_4$ and $Zr(dbm)_4$, where dbm represents dibenzoylmethane. These systems are presently being studied in more detail.

**Acknowledgment.**—This work was performed on apparatus purchased on an N.S.F. equipment grant.

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw–Hill Book Company, Inc., New York, N. Y., 1959, p. 424.

(5) N.S.F. Predoctoral Fellow, 1963–1964.

DEPARTMENT OF CHEMISTRY                A. C. ADAMS[5]
UNIVERSITY OF WISCONSIN                 E. M. LARSEN
MADISON 6, WISCONSIN

RECEIVED AUGUST 6, 1963

## Lewis Basicity of a Transition Metal. A Boron Trifluoride Adduct of Biscyclopentadienyltungsten Dihydride

*Sir:*

While transition metals in many complexes are potential Lewis bases (in the sense that they contain nonbonding electron pairs), only a few have appreciable proton affinities,[1] and basicity toward acids other than the proton has never been demonstrated. During studies on the Lewis basicity of certain metal coordinated ligands,[2] we have frequently inspected our data for the possibility of $BF_3$ coordination with electrons in the $d_{z^2}$-orbitals of square-planar Ni(II) and Pd(II) complexes (e.g., $Ni(CN)_4^{-2}$, $Pd(SCN)_4^{-2}$, and $Pd(bipy)$-$(NCS)_2$, bipy $= 2,2'$-bipyridine). We found no evidence for metal basicity in these cases; however,

(1) G. Wilkinson, "Advances in the Chemistry of Co-ordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 50; M. L. H. Green, Angew. Chem., 72, 719 (1960).

(2) D. F. Shriver, J. Am. Chem. Soc., 84, 4610 (1962); ibid., 85, 1405 (1963); A. Luntz and D. F. Shriver, unpublished observations.
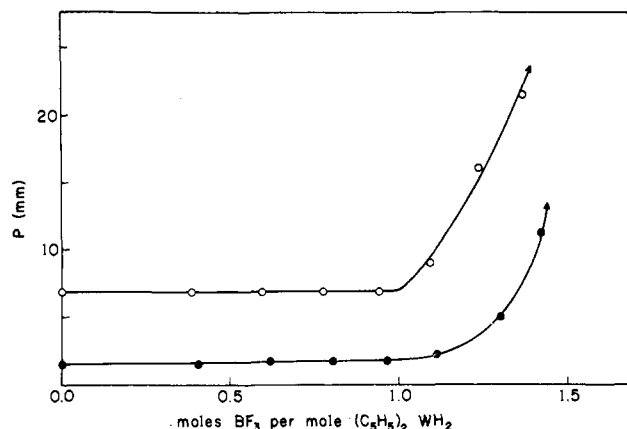


Fig. 1.—The pressure over a toluene solution of $(C_5H_5)_2WH_2$. The abscissa represents moles of boron trifluoride in the condensed phase(s) per mole of $(C_5H_5)_2WH_2$. Closed circles represent data collected at $-22.9°$ and open circles data obtained at $0°$.

recent experiments with $(C_5H_5)_2WH_2$ and $BF_3$ led to the formation of a $1:1$ addition compound which apparently contains a tungsten–boron bond.

The parent $(C_5H_5)_2WH_2$ was prepared by the procedure of Green, et al.[3] A melting range of 193 to 195° was observed rather than 163 to 165° as previously reported. This discrepancy is thought to be due to a misprint, since the color, chemical properties, and n.m.r. spectrum agreed with those of the original report and the infrared spectrum was also in substantial agreement. Additional support for the authenticity of this compound was gained from an X-ray powder pattern which was indexed using a slightly larger unit cell and the same space group $(C_c)$ as that reported for $(C_5H_5)_2MoH_2$.[4]
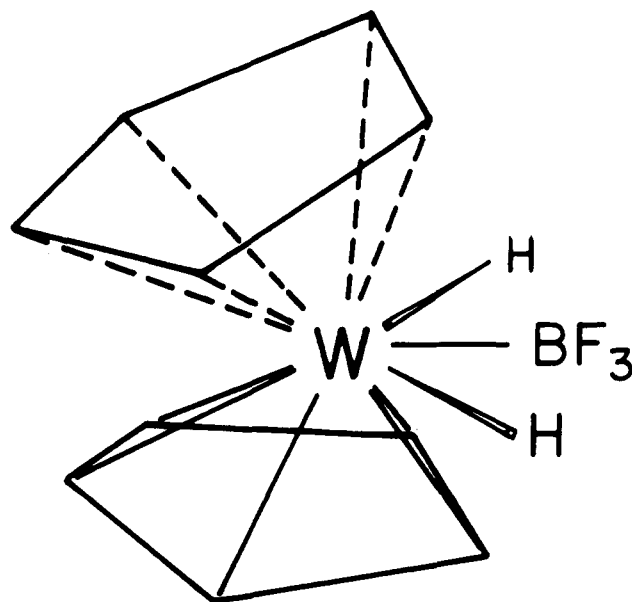


Fig. 2.—The probable molecular geometry of $(C_5H_5)_2WH_2 \cdot BF_3$.

Manipulation of $(C_5H_5)_2WH_2$ and its adduct was performed in either a vacuum line or a nitrogen-filled drybox. Direct interaction of the cyclopentadienyltungsten hydride with $BF_3$ led to absorption of 0.954 mole of boron trifluoride per mole of complex. Since this reaction was quite sluggish a tensiometric titration

(3) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, J. Chem. Soc., 4854 (1961).

(4) M. J. Bennett, M. Gerlach, J. A. McCleverty, and R. Mason, Proc. Chem. Soc., 357 (1962).

(Fig. 1) was performed, which confirmed the 1:1 stoichiometry. The compound may be conveniently prepared in benzene or toluene since biscyclopentadienyltungsten 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).

DEPARTMENT OF CHEMISTRY AND                    D. F. SHRIVER
MATERIALS RESEARCH CENTER
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

## 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)* $\rightleftarrows$ *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-m$\mu$ 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- m$\mu$ 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- m$\mu$ 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. Swaminatham, *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).