exact comparison is not available, it is evident[13,14] that the activation energy for the insertion reaction is several kcal./mole less than that for a corresponding carbonyl displacement reaction of $Mn(CO)_5Br$.

By contrast the second step, that of the formation of the chelate

$$CH_3COMn(CO)_4(diphos) \longrightarrow CH_3COMn(CO)_3(diphos) + CO$$

is very similar to the corresponding step for $Mn(CO)_5Br$ and will probably have a similar activation energy. This, therefore, gives an added measure of stability to the monodentate phosphine complex $CH_3COMn(CO)_4$(diphos).

The isolation of bridge complexes from the reactions of metal carbonyl compounds with the diphosphine is a consequence of the stability of the monodentate diphosphine complexes. The slow rate at which these intermediates are converted to chelate complexes allows them to react preferentially with more metal carbonyl complex (if present) to form the bridge complexes. Thus, the criteria for the formation of a good yield of bridge complex are: (a) a monodentate diphosphine complex which is formed from starting material at a rate considerably faster than that at which it is converted to the corresponding chelate complex; (b) an excess of metal carbonyl complex over diphosphine.

The isolation of an unsymmetrical bridge complex, $Fe(NO)_2(CO)(diphos)Co(NO)(CO)_2$, believed to be the first compound of this type to be prepared with the diphosphine, is a natural extension of the isolation of symmetrical bridge complexes.

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[13] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964).

[14] R. J. Angelici and F. Basolo, *ibid.*, **84**, 2495 (1962).

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Metal Complexes of Cyanocarbons. I. Preparation of Some Platinum Compounds of Tetracyanoethylene

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Reactions of tetracyanoethylene with various platinum complexes have been investigated, and the first examples of this cyanocarbon covalently bonded to a transitional metal ion have been synthesized. These compounds, which are formulated as $Pt(PR_3)_2(C_6N_4)$ where R is C_2H_5 and C_6H_5, were prepared by two methods, the first being the replacement of phenylacetylene from complexes of the type $Pt(PR_3)_2(C_6H_5C{\equiv}CH)$, and the second being the reaction of tetracyanoethylene with some platinum hydrides.

Introduction

Metal complexes containing hydrocarbons bonded to a transitional metal ion have been the subject of much study. Replacement of the hydrogen atoms by fluorine in such compounds has resulted in fluorocarbon derivatives of metal ions, which in many cases are uniquely different from the parent hydrocarbon complexes.[3] One might suppose that cyanocarbons, analogous to hydrocarbons and fluorocarbons, would give rise to interesting metal complexes. Such a hypothesis can now be subjected to scrutiny, because several years ago a series of cyanocarbons was synthesized.[4] We have commenced an investigation of the reactions of such substances with transitional metal compounds and have chosen tetracyanoethylene, C_6N_4, for our initial work. The organic chemistry of this particular cyanocarbon has been extensively studied.[5]

Reactions of tetracyanoethylene with metal complexes have received cursory attention. It was noted that $Ni(CO)_4$ is decarbonylated and oxidized by this cyanocarbon.[6] Another worker[7] found that $Ni(CO)_4$ and C_6N_4 reacted violently. Oxidation of the nickel atom occurred and probably the tetracyanoethylene anion radical was formed as an intermediate, which under the conditions employed led to polymeric materials with nonstoichiometric nickel content. Reaction of copper(I) halides with C_6N_4 did not yield complexes but resulted in oxidation of the copper.[8] The solid-state reaction of ferrocene and tetracyanoethylene was reported to give a salt, ferricinium tetracyanoethylenide.[9] Recent work, however, indicates that the com-

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[3] P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

[4] For a review of cyanocarbon chemistry, see T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73**, 520 (1961).

[5] T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Englehardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

[6] O. W. Webster, W. Mahler, and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960).

[7] G. N. Schrauzer, *Chem. Ind.* (London), 1270 (1961).

[8] G. N. Schrauzer and S. Eichler, *Chem. Ber.*, **95**, 260 (1962).

[9] O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

pound is really a charge-transfer complex.[10] The product of the reaction between tetracyanoethylene and dibenzenechromium[11] has been formulated as the tetracyanoethylenide salt of dibenzenechromium(I). Thus, there has not been a report in the literature of covalent bond formation between tetracyanoethylene and a transitional metal ion.

Experimental Section

Materials.—Tetracyanoethylene was kindly supplied by E. I. du Pont de Nemours and Co., Inc. It was freshly sublimed for the experiments. Because of the tendency of C_6N_4 to react with a number of substances, including water and moist air, to release HCN, all work was done in a well-ventilated hood.

Benzene was purified by repeated shaking with sulfuric acid, followed by distillation and storage over sodium wire.

The platinum(0) complex, $Pt[(C_6H_5)_3P]_4$ was synthesized according to the literature method,[12] as were $Pt[P(C_6H_5)_3]_2(C_6H_5C{\equiv}CH)$,[13] *trans*-$Pt[P(C_6H_5)_3]_2HCl$,[14] and *trans*-$Pt[P(C_2H_5)_3]_2HCl$.[14]

Reactions of Tetracyanoethylene with Some Platinum Complexes. (**A**).—To 0.8 g. of $Pt[P(C_6H_5)_3]_2(C_6H_5C{\equiv}CH)$ (1 mmole) suspended in 5 ml. of benzene was added slowly a solution of C_6N_4 (0.25 g., 2 mmoles) in 10 ml. of benzene. The resulting light orange solution was diluted with 50 ml. of absolute ethanol and in 5 min. small crystals had begun to form. These were collected on a filter, washed with ethanol and ether, and then air dried. The yield of pale yellow solid was 0.1 g. Analysis for all elements present and a molecular weight determination suggest the formulation to be $Pt[P(C_6H_5)_3]_2C_6N_4$.

Anal. Calcd. for $PtC_{42}H_{30}N_4P_2$: C, 59.50; H, 3.57; N, 6.61; Pt, 23.01; P, 7.31; mol. wt., 847. Found: C, 58.86; H, 3.73; N, 6.69; Pt, 22.65; P, 7.3; mol. wt. (by osmometer in $CHCl_3$), 887. The infrared spectrum, omitting absorptions due to phenyl groups, shows bands at the following wave numbers: 2220 (s), 1175 (s), 1160 (m), and 845 (m). Recrystallization of the pale yellow solid from methylene chloride-ethanol gave pure white crystals, the infrared spectrum of which was identical with that of the unrecrystallized substance.

Anal. Found: C, 59.32; H, 3.53; N, 6.50.

(**B**).—A solution of tetracyanoethylene (0.25 g., 2 mmoles) in 20 ml. of benzene was added slowly to a stirred solution of *trans*-$Pt[P(C_6H_5)_3]_2HCl$ (0.8 g., 1 mmole) in 20 ml. of benzene. The solution first attained a light orange color and after about 5 min. a solid began to form. Moist pH indicator paper held near the outlet of the reaction vessel showed that an acidic vapor was being evolved. The tetracyanoethylene solution was added over a period of 15 min., at which time the pale yellow solid which had formed was collected on a filter. After being washed well with benzene, ethanol, and ether, the substance was air-dried, yielding 0.75 g. The infrared spectrum of the solid shows two strong bands in the C≡N stretching region at 2230 and 2280 cm.$^{-1}$. The solid was added to 50 ml. of boiling benzene and slowly dissolved to give a yellow-orange solution. Apparently HCl was evolved during this dissolution. A rod moistened with NH_3 fumed when held near the solution and pH indicator paper also gave an acidic reaction. The volume of the solution was reduced to half by heating and the color changed to a pale yellow. The solution was filtered, cooled, and diluted with ethanol. After being kept in the refrigerator for 7 days the white crystals which had formed were collected on a filter and washed with ethanol and ether. The yield was 0.5 g. The infrared spectrum is different from that of the unrecrystallized material, but identical with that of $Pt[P(C_6H_5)_3]_2(C_6N_4)$ prepared from $Pt[P(C_6H_5)_3]_2(C_6H_5C{\equiv}CH)$ as described above.

Anal. Calcd. for $PtC_{42}H_{30}N_4P_2$: C, 59.50; H, 3.57; N, 6.61. Found: C, 59.37; H, 3.61; N, 6.48.

(**C**).—The complex *trans*-$Pt[P(C_2H_5)_3]_2HCl$ (0.47 g., 1 mmole) was dissolved in 2 ml. of benzene and 0.12 g. of tetracyanoethylene (1 mmole) was added. Bubbles formed in the mixture and a pungent gas was evolved. This gas was passed into an aqueous solution of $AgNO_3$, and a white solid formed. This white solid was collected and its infrared spectrum showed no absorption in the C≡N stretching region. The bubbling of the gas subsided in *ca.* 10 min., and the solid which had formed was collected on a filter. After washing the solid well with benzene and petroleum ether, a recrystallization from methylene chloride–ethanol was carried out, yielding 0.25 g. of shiny white needles.

Anal. Calcd. for $PtC_{18}H_{30}N_4P_2$: C, 38.64; H, 5.40; N, 10.01; Pt, 34.87; Pt, 34.87; P, 11.07. Found: C, 38.51; H, 5.34; N, 10.01; Pt, 35.24; P, 10.90 (by difference). This analysis suggests the formulation to be Pt $[P(C_2H_5)_3]_2[C_6H_4)$.[15] The infrared spectrum, disregarding alkyl absorptions, shows bands at the following wave numbers: 2245 (sh), 2220 (vs), 2165 (sh), 2140 (sh), 1220 (m), 1185 (s).

(**D**).—Tetracyanoethylene (0.36 g., 3 mmoles) was added to a suspension of 1.2 g. (1 mole) of $Pt[P(C_6H_5)_3]_4$ in 10 ml. of benzene and a deep red solution was formed immediately. Ethanol was added (20 ml.) and after 12 hr. the solid which had formed was collected on a filter. This appeared to be a mixture of bronze crystals and a pale yellow powder, predominantly the latter. Methylene chloride dissolved the bronze crystals but an insufficient quantity was obtained for characterization. Recrystallization of the pale yellow solid from benzene–ethanol gave 0.3 g. of pure white crystals. The infrared spectrum of this substance shows a strong, very sharp band at 2135 cm.$^{-1}$. This absorption is *ca.* 100 cm.$^{-1}$ lower than the C≡N stretch in tetracyanoethylene and, in fact, is in the range of 2040–2170 cm.$^{-1}$, which is diagnostic of cyanide ion being bonded directly on a metal.[16] Analytical data fit the formulation $Pt[P(C_6H_5)_3]_2(CN)_2$.

Anal. Calcd. for $PtC_{38}H_{30}N_2P_2$: C, 59.14; H, 3.92; N, 3.63; Pt, 25.28. Found: C, 59.46; H, 4.30; N, 3.86; Pt, 25.47.

Analyses.—Carbon, hydrogen, and nitrogen elemental analyses were carried out by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max Planck Institut für Kohlenforschung, Mulheim (Ruhr), Germany. Platinum was determined by a spectrophotometric method,[17] as was phosphorus. The method used for phosphorus was a modification of the literature method for arsenic.[18]

Spectra.—Infrared spectra in the NaCl region were measured on a Perkin-Elmer 237 Grating infrared spectrophotometer using Nujol and hexachlorobutadiene mulls.

Discussion

The compounds $Pt[P(C_6H_5)_3]_2(C_6N_4)$ and $Pt[P(C_2H_5)_3]_2[C_6N_4)$ may be regarded in a formal sense as either (a) three-coordinate complexes of Pt(0) in which tetracyanoethylene is bonded to the metal in the conventional manner of olefin–metal complexes[19] or (b) four-coordinate planar complexes of Pt(II) in which the tetracyanoethylene is a dicarbanion functioning as a bidentate ligand with two σ bonds to the metal. Bonding through the nitrogen atom as in alkylnitrile complexes of metal ions is ruled out from considerations of the infrared spectral data. In the C≡N stretching

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[10] N. Rosenblum, R. W. Fish, and C. Bennett, *J. Am. Chem. Soc.*, **86**, 5166 (1964).

[11] J. W. Fitch and J. J. Lagowski, *Inorg. Chem.* **4**, 864 (1965).

[12] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

[13] J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

[14] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

[15] Dr. G. W. Parshall informs us that he has prepared independently $Pt[C_2H_5)_3P]_2(C_6N_4)$ by the method described here.

[16] K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 166.

[17] E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York, N. Y., 3rd Ed., 1950, p. 726.

[18] H. J. Magnuson and E. B. Watson, *Ind. Eng. Chem., Anal. Ed.*, **16**, 339 (1944).

[19] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

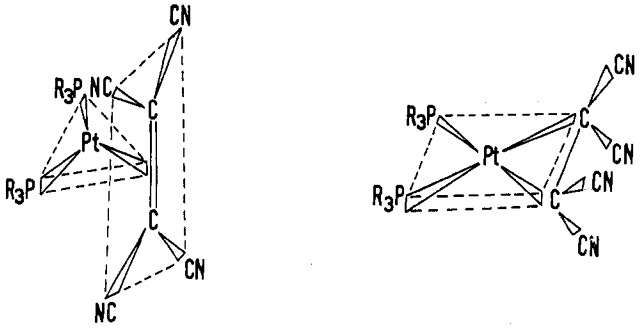

Figure 1.—Possible structure for $Pt(PR_3)_2(C_6N_4)$.

region, tetracyanoethylene exhibits two strong bands at 2214 and 2262 cm.$^{-1}$ with shoulders at 2202 and 2229 cm.$^{-1}$.[20] Both $Pt[P(C_6H_5)_3]_2(C_6N_4)$ and $Pt[P(C_2H_5)_3]_2(C_6N_4)$ show a single, strong absorption at 2220 cm.$^{-1}$. Since coordination of alkylnitriles through the nitrogen atoms usually results in an increase in the infrared-active C≡N stretching frequency,[21] it is assumed that such coordination is not in effect in these complexes of tetracyanoethylene. For comparison, the C≡N stretch in CH_3CN occurs at 2250 cm.$^{-1}$,[22] but shifts to 2320 cm.$^{-1}$ when coordinated to platinum in the complex $Pt(CH_3CN)_2Cl_2$.[23]

A detailed discussion of the electronic structures of the tetracyanoethylene complexes will be deferred until an X-ray study of $Pt[P(C_2H_5)_3]_2(C_6N_4)$, which is now in progress, is completed. The chemical evidence at hand, however, seems to indicate that the complexes should be regarded as derivatives of Pt(II) rather than Pt(0) because tetracyanoethylene oxidized the *bona-fide* Pt(0) complex $Pt(P(C_6H_5)_3)_4$ under very mild conditions to the divalent state.

The two methods of preparation of $Pt[P(C_6H_5)_3]_2(C_6N_4)$ illustrate the unorthodox reactivity of tetracyanoethylene toward platinum complexes. Chatt and co-workers[13] prepared a series of complexes of the type $Pt[P(C_6H_5)_3]_2(ac)$ where ac represents various acetylenes. It was observed that one acetylene would displace another in solution at room temperature,

$$\mathrm{Pt[P(C_6H_5)_3]_2ac + ac' \rightleftarrows Pt[P(C_6H_5)_3]_2ac' + ac} \qquad (1)$$

and that the stability of complexes decreased as the acetylene was changed in the order $C_6H_5C{\equiv}CC_6H_5 > C_6H_5C{\equiv}CH > \text{alk—}C{\equiv}C\text{—alk} > HC{\equiv}CH$. An analogous series of complexes of the type $Pt[(C_6H_5)_3P]_2$(olefin) were prepared,[24] but these were much less stable than the acetylene complexes. Even gaseous acetylene itself displaced the olefin from the most stable olefin complex. In contrast to this, we now find that an olefin, tetracyanoethylene, displaces phenylacetylene from $Pt[P(C_6H_5)_3]_2(C_6H_5C{\equiv}CH)$ quite easily. Thus, tetracyanoethylene is the first olefin known that will displace an acetylene from complexes of the type $Pt[P(C_6H_5)_3]_2ac$.

The behavior of tetracyanoethylene toward *trans*-$Pt[P(C_6H_5)_3]_2HCl$ and *trans*-$Pt[P(C_2H_5)_3]_2HCl$ is quite different from that of other olefins toward metal hydrides. For example, ethylene was found to react with *trans*-$Pt[P(C_2H_5)_3]_2HCl$ at 95° and 40 atm. over a period of 18 hr. to give a 25% yield of the alkyl complex, $Pt[P(C_2H_5)_3]_2(CH_2CH_3)Cl$.[14] This is to be contrasted with the reaction of tetracyanoethylene with the same hydride, in which equimolar amounts of the reactants yield $Pt[P(C_2H_5)_3]_2(C_6N_4)$ almost quantitatively at room temperature in a matter of minutes.

The kinetic and mechanistic aspects of this rather unusual reaction are presently under investigation.[25]

[20] D. A. Long and W. O. George, *Spectrochim. Acta*, **19**, 1717 (1963).

[21] H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958).

[22] P. Venkateswarlu, *J. Chem. Phys.*, **19**, 293 (1951).

[23] R. D. Gilliard and G. Wilkinson, *J. Chem. Soc.*, 2835 (1964).

[24] J. Chatt, B. L. Shaw, and A. A. Williams, *ibid.*, 3269 (1962).

[25] W. H. Baddley, to be published.

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A Crystal Field Model for High-Spin Five-Coordinated Nickel(II) Complexes

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The splitting of the terms of the free nickel(II) ion in fields of five point dipoles arranged in trigonal-bipyramidal and square-pyramidal configurations is calculated. The weak-field scheme with interaction of configurations has been used. Only for large field strengths or extensive nephelauxetic effects, the five-coordinated nickel(II) complexes are expected to be diamagnetic. The spectra of two high-spin nickel(II) complexes of approximate trigonal-bipyramidal and square-pyramidal stereochemistries are compared with the predicted transitions. The agreement is found to be satisfactory. The crystal field stabilization energies of both configurations are discussed.

Introduction

During the past years five-coordinated nickel(II) complexes have been shown to be more common than previously believed. The first examples reported have been low-spin complexes[1,2]. Recently, however, the first cases of high-spin nickel(II) complexes have been

[1] G. A. Barclay and R. S. Nyholm, *Chem. Ind.* (London), 378 (1953); C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960); G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 170 (1961); R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963); G. S. Benner, W. E. Hartfield, and D. W. Meek, *ibid.*, **4**, 1544 (1965).

[2] G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).