must occur in the formation of the activated complex. Our results for the *cis* isomer imply that the stretching of bonds to ligands *cis* to the bridging group is much less important. It would appear then that the chromium(III) complex undergoes tetragonal distortion in the formation of the activated complex, so that the activation process resembles in many respects Orgel's description[7] of the reaction of $Co(NH_3)_5Cl^{2+}$ with Cr^{2+}.

We have also measured the kinetics of the reactions of both isomers with Cr^{2+}, and we find that both reactions obey rate laws of the form

$$\text{rate} = k[Cr^{2+}][Cr(NH_3)_4(OH_2)Cl^{2+}] \qquad (2)$$

For the *cis* isomer $k = 0.098\ M^{-1}\ sec^{-1}$ at 25.0° and $E_a = 10.7$ kcal/mole; for the *trans* isomer $k = 0.89\ M^{-1}\ sec^{-1}$ at 25° and $E_a = 10.1$ kcal/mole. The difference in rates for the two isomers is much smaller than reported by Pennington and Haim[3] for the analogous ethylenediamine complexes. In the case of the ethylenediamine complexes, it may be necessary to change the conformation of the chelate rings in order to form the activated complex for the *cis* isomer, whereas the ligands of the ammine complexes may move independently of each other.

[7] L. E. Orgel, *Inst. Intern. Chim. Solvay, X^e Conseil Chim.*, 289 (1956).

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A Coordination Compound of Diethyldipyridylnickel with Acrylonitrile. A Polymerization Catalyst of Acrylonitrile

Sir:

Previously we reported the isolation of ethylnickel,[1,2] -iron,[1] and -cobalt[1b,2] complexes from mixed catalyst systems of metal acetylacetonates, diethylaluminum monoethoxide, and dipyridyl. These complexes catalyze the conversion of butadiene to oligomers on one hand and acrylonitrile to high polymers on the other.[1b,c] Polymerization of acrylonitrile takes place at room temperature with catalytic amounts of these complexes yielding white polyacrylonitrile with molecular weights of the order of 10^5. Although the infrared spectra of these polymers are similar to those obtained using a radical initiator, the mechanism of polymerization seems to be different from the ordinary radical-initiated polymerization. Styrene, methyl methacrylate, and vinyl chloride are not polymerized with these complexes; copolymerization of acrylonitrile with butadiene gave only a homopolymer of acrylonitrile. These facts suggest a specific interaction of acrylonitrile with the transition metal complexes. We could isolate an orange coordination compound of acrylonitrile with diethyldipyridylnickel (I) at low temperatures as an active species for acrylonitrile polymerization.

The adduct is extremely sensitive to air and stable only at low temperature. Over about −10° *in vacuo* it releases acrylonitrile, leaving the starting material I. The adduct was prepared and the amount of acrylonitrile contained determined as follows.

Acrylonitrile was distilled *in vacuo* into a flask containing dark green crystals of I (0.972 g, 3.56 mmoles) at −78°. The mixture was stirred for several hours until all the solid became orange. The excess acrylonitrile was removed by evaporation at 10^{-4} mm at −78° for 40 hr. The orange solid which remained was then warmed to room temperature *in vacuo*. The volatile matter was condensed with liquid nitrogen and shown to be acrylonitrile (0.180 g, 3.39 mmoles) by infrared and gas chromatography. The green residue (0.980 g, 101% of the original weight) was crystallized from acetone and proved to be the starting material I by infrared comparison and analytical data.

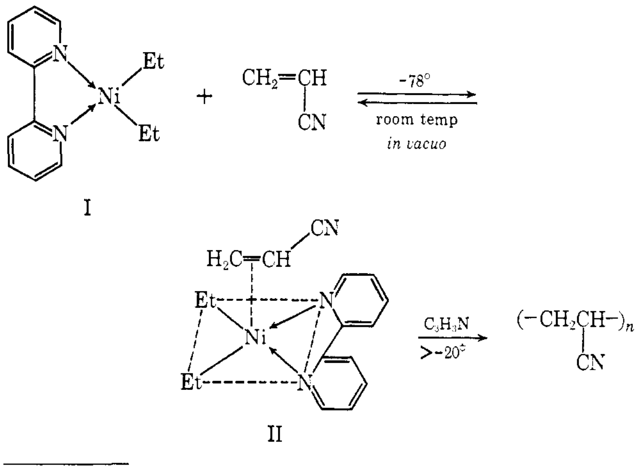
Anal. Calcd for $C_{14}H_{18}N_2Ni$: C, 61.61; H, 6.62; N, 10.25. Found: C, 61.8; H, 6.73; N, 10.3.

The orange 1:1 acrylonitrile adduct, II, dissociates in ether solution at −78° yielding a green solution of I. The adduct is an active catalyst for the polymerization of acrylonitrile, but not of styrene or butadiene.

Whereas I is thermally quite stable, interaction of acrylonitrile with I at room temperature causes immediate fission of the ethyl–nickel bonds, releasing a gas composed mainly of *n*-butane, with small amounts of ethane and ethylene. By reaction of I with acrylonitrile in ether at room temperature, relatively stable red crystals of composition $Ni(dipy)(CH_2{=}CHCN)_2$ were isolated.

Anal. Calcd for $C_{16}H_{14}N_4Ni$: C, 59.85; H, 4.40; N, 17.45. Found: C, 59.8; H, 4.51; N, 17.5.

The infrared spectrum of the red complex (KBr disk) showed a sharp $\nu_{C\equiv N}$ absorption band at 2169 cm^{-1} and the absence of absorption bands due to vinyl groups. This fact indicates that acrylonitrile may be coordinated with the nickel atom in the red complex through the vinyl groups as in the acrylonitrile–nickel complexes prepared by Schrauzer.[3] The mode of coordination of acrylonitrile with the nickel atom in the orange adduct II is not known, due to the instability of the complex. However it seems reasonable to assume that acrylonitrile is coordinated with the nickel



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[1] (a) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Am. Chem. Soc.*, **87**, 4652 (1965); (b) Preprint, International Symposium on Macromolecular Chemistry, Tokyo–Kyoto, 1966, I-102; (c) submitted for publication.

[2] T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Am. Chem. Soc.*, **88**, 5198 (1966); *J. Organometal. Chem.* (Amsterdam), **6**, 572 (1966).

[3] G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959); H. P. Fritz and G. N. Schrauzer, *Chem. Ber.*, **94**, 650 (1961). The $\nu_{C\equiv N}$ band at 2175 cm^{-1} of $Ni(CH_2{=}CHCN)_2(PPh_3)_2$ obtained by Schrauzer may be compared with that for our complex $Ni(dipy)(CH_2{=}CHCN)_2$.

atom in II through the vinyl group, and the interaction causes the "weakening" of the ethyl–nickel bonds. The weakening may lead to the fission of the ethyl–nickel bonds and the initiation of the polymerization by a coordinated mechanism. No reaction of I with acetonitrile was observed.

In explanation of the mechanism of polymerization with Ziegler-type catalysts, coordination of a monomer with an alkyl transition metal complex has often been postulated,[4] but the isolation of such a complex has not been reported to our knowledge.[5] Our orange complex II seems to provide the first example of the isolation of an alkyl transition metal complex which is coordinated with a monomer and is itself an active polymerization catalyst of the monomer.

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(4) For example, P. Cossee, *J. Catalysis*, 3, 80 (1964).

(5) R. Cramer obtained nmr evidence of such a complex in the dimerization of ethylene: *J. Am. Chem. Soc.*, 87, 4717 (1965).

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The Cleavage of $(CF_3P)_4$ by Primary and Secondary Phosphines and a Novel Insertion Reaction

Sir:

The chemical similarity of cyclopolyphosphines and cyclooctasulfur is exemplified by the interesting parallel between the reactions[1,2]

$$(C_6H_5)_3P + {}^1/_8S_8 = (C_6H_5)_3P\rightarrow S \qquad (1)$$

$$(CH_3)_3P + {}^1/_4(CF_3P)_4 = (CH_3)_3P\rightarrow PCF_3 \qquad (2)$$

The observation[3] that the S_8 ring is cleaved by primary phosphines suggested that cyclopolyphosphines might undergo a similar type of reaction. We now report that the reaction of CH_3PH_2 with $(CF_3P)_4$ (3 days at room temperature) proceeds virtually quantitatively according to the equation[4]

$${}^1/_4(CF_3P)_4 + CH_3PH_2 = CF_3PH_2 + {}^1/_5(CH_3P)_5 \qquad (3)$$

The extent of the above reaction appears to depend on the basicity of the phosphine. Thus, in a comparable reaction with $C_6H_5PH_2$ only 82.2% of the theoretical yield of CF_3PH_2 was realized, and excess PH_3 failed to react with $(CF_3P)_4$ after 31 days at room temperature. In the $C_6H_5PH_2$ experiment the nonvolatile residue was identified as $(C_6H_5P)_5$ on the basis of its proton nmr spectrum[5] (CS_2 solution).

The reaction of $(CF_3P)_4$ with $(CH_3)_2PH$ also proved interesting because one of the products resulted from insertion of a CF_3P group into a P–P bond. Fractionation of the volatiles resulting from the reaction of 0.5565 mmole of $(CF_3P)_4$ and 4.705 mmoles of $(CH_3)_2PH$ (1 day at room temperature) resulted in 1.586 mmoles of recovered $(CH_3)_2PH$, 1.706 mmoles of CF_3PH_2, 1.181 mmoles of $(CH_3)_4P_2$ (recognized by its vapor tension[6] and characteristic "deceptively simple" proton nmr spectrum[7]), and 38.0 mg of a substance with a vapor tension of 1 mm at 24°. Elemental analysis of this material suggested that it was the new triphosphine $CF_3P[P(CH_3)_2]_2$ (I). *Anal.* Calcd for $C_5H_{12}F_3P_3$: C, 27.02; H, 5.41. Found: C, 27.34; H, 5.51. The hypothesis that I arose from the reaction of $(CF_3P)_4$ with $(CH_3)_4P_2$ was confirmed by a separate experiment in which a mixture of 1.175 mmoles of $(CF_3P)_4$ and 4.863 mmoles of $(CH_3)_4P_2$ was allowed to stand 13 days at room temperature. Fractionation of the volatiles resulted in a 69.6% yield of I. *Anal.* Calcd for $C_5H_{12}F_3P_3$: C, 27.02; H, 5.41. Found: C, 27.19; H, 5.17. Strong support for the triphosphine formulation came from the ^{19}F nmr spectrum of I (neat liquid) which consisted of a pair of triplets assignable as J_{PCF} = 40.2 cps and J_{PPCF} = 6.4 cps.[8] The molecular weight determination of I was made difficult by absorption into vacuum greases and waxes. However, the value 219.0 (calculated 222.1) is probably reliable. The ultraviolet spectrum of I consisted of a broad maximum at 2400 A and a shallow minimum at 2275 A. Ultraviolet absorption in this range is characteristic of polyphosphines[9] and is presumably due to delocalization of lone-pair electrons across P–P bonds. The infrared spectrum of I also displayed the expected features: namely, C–H stretching at 2820, 2905, and 2965 cm^{-1}, C–F stretching at 1108 and 1133 cm^{-1} (with shoulders at 1112, 1150, and 1170 cm^{-1}), and CH_3 deformations at 1290 and 1435 cm^{-1}. A broad band at 701 cm^{-1} is probably due to P–CH_3 stretching. Vapor tension data for I in the range 24–68° determine the equation $\log p = 7.3510 - 2176/T$, giving an estimated boiling point of approximately 220° and a Trouton constant of 20.3 eu.

The CF_3P insertion reaction, which in some respects resembles a carbene insertion, might prove to be a source of other compounds with nonmetal–nonmetal bonds. This possibility is under investigation.

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(1) P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).

(2) A. B. Burg and W. Mahler, *ibid.*, **83**, 2388 (1961).

(3) L. Maier, *Helv. Chim. Acta*, **46**, 1812 (1963). For a review, see L. Maier, "Topics in Phosphorus Chemistry," Vol. 2, Interscience Publishers Inc., New York, N. Y., 1965, p 43.

(4) Identification of CF_3PH_2 was made on the basis of its vapor tension of 45 mm at −78.5° [W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958)] and proton nmr spectrum. The latter (neat liquid) consists of a pair of quartets centered at τ 6.48 with J_{PH} = 199.99 cps and J_{FCPH} = 11.90 cps (S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, to be published). The oily nonvolatile residue was identified as $(CH_3P)_5$ by its complex proton nmr spectrum (A. H. Cowley, unpublished observation). For neat samples the spectrum consists of 15 clearly resolved peaks in the τ 8.21–8.82 region. Some of the resolution is lost in $CDCl_3$ solution.

(5) W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963). These authors called this cyclopolyphosphine form A of $(C_6H_5P)_4$. However, since that time this compound has been shown to be $(C_6H_5P)_5$ in the solid state by J. J. Daly and L. Maier, *Nature*, **203**, 1167 (1964); and J. J. Daly, *J. Chem. Soc.*, 6147 (1964).

(6) A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961).

(7) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).

(8) These assignments compare with the values J_{PCF} = 64.1 cps and J_{PPCF} = 7.9 cps in the somewhat similar molecule $(CH_3)_2P–P(CF_3)_2$: S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, to be published.

(9) A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965), and references therein.