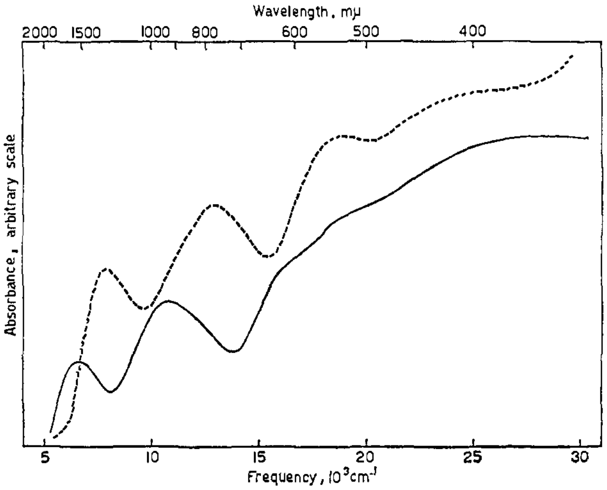

Figure 3. Reflectance spectra of $[Co(NP_3)I]I$ (——) and $[Co(NP_3)NCS]BPh_4$ (- - - - -).

of this NP_3 complex is a doublet can be ascribed to the high-field strength of the NCS group.

The complex $[Co(NP_3)I]I$ has a similar spectrum, with respect to the shape and frequencies of the bands, to that of the thiocyanate complex. The absorption maxima at 6500, 10,700, 16,000, and 20,000 cm^{-1} show the displacement, with respect to the thiocyanate, to be expected from the relative positions of iodide and thiocyanate in the spectrochemical series. Thus it may be concluded that this complex contains the low-spin pentacoordinate ion $[Co(NP_3)I]^+$. On the other hand, the cation $[Co(NP_3)I]^+$ in the compound $[Co(NP_3)I]BPh_4$ is high-spin five-coordinate. This leads to the conclusion that the set of donor atoms NP_3I represents the crossover point between ligands giving high-spin cobalt(II) complexes and those giving low-spin complexes. The difference in the environment caused by the difference in the counteranions is enough to change the spin multiplicity of the complexes.[25]

Acknowledgments. Thanks are expressed to Dr. J. Gelsomini for microanalyses and to Mr. P. Innocenti for technical assistance. The financial support of the Italian "Consiglio Nazionale delle Ricerche" is gratefully acknowledged.

[25] The spectrum of the complex $[Co(NP_3)I]I$ in nitroethane solution shows the coexistence of both high- and low-spin species. The relative proportion changes with temperature.

Reactions of Tetracyanoethylene with Hydridoplatinum(II) Complexes[1]

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Contribution from the Coates Chemical Laboratory, The Louisiana State University, Baton Rouge, Louisiana 70803. Received February 19, 1968

Abstract: Reactions of tetracyanoethylene (TCNE) with the complexes *trans*-$PtHX(PR_3)_2$ (R = Et, X = Cl, Br, I, NO_2, CN, NCO; R = Ph, X = Cl, Br, I, CN) have been studied under preparative and kinetic conditions. The square-planar complex $Pt(PR_3)_2TCNE$ is obtained in good yield for X = Cl and Br, but only in trace amounts, or not at all, for the other X groups, where the reactions are complicated because of formation of side products. Kinetic data are reported for reactions of the substrates where R = Et, X = Cl and R = Ph, X = Cl, Br, and are interpreted mechanistically in terms of the formation of a 1:1 adduct of TCNE and the platinum substrate *via* a fast preequilibrium step. The subsequent steps are believed to involve either (a) the reductive elimination of HX as the intermediate decomposes or (b) a hydrogen transfer to C_6N_4, followed by an acid-base equilibrium and an internal nucleophilic substitution reaction. For the reaction of *trans*-$PtHCN(PEt_3)_2$ with TCNE, a 1:1 adduct has been isolated and characterized as a hydridoolefinic complex, $PtHCN(PEt_3)_2TCNE$, which is believed to be the type of intermediate formed in homogeneous hydrogenation processes. The stereochemistry of the $PtHCN(PEt_3)_2TCNE$ has been deduced from a comparison of the infrared spectra of the hydrido complex and the analogous deuterated compound, in which a resonance interaction between the C≡N and Pt—H stretching vibrations has been observed.

The role of transitional metal complexes in homogeneous catalytic processes is currently a topic of great interest, from both a fundamental and practical point of view. One of the more prominent catalytic reactions is that whereby olefins may be hydrogenated in the presence of certain transitional metal substrates under very mild conditions. Successful attempts have been made by several workers[3-6] to understand the mechanisms of these reactions in which hydrido complexes are either starting materials or reactive intermediates. Pertinent to this general theme is an understanding of the fundamental principles involved in the reactions of olefins and metal hydrides, and at the present time these principles are by no means clarified.

One general feature which has emerged from studies

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[1] (a) Part IV of the series Metal Complexes of Cyanocarbons; (b) part III: W. H. Baddley, *J. Am. Chem. Soc.*, **90**, 3705 (1968).

[2] Postdoctoral Fellow, 1966–1967. We are grateful to the National Science Foundation for a Science Development Grant awarded to Louisiana State University, which made this tenure possible.

[3] J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965).

[4] B. R. James, *Coord. Chem. Rev.*, **1**, 505 (1966).

[5] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1966), and references cited therein.

[6] J. C. Bailar, Jr., and H. Itatani, *J. Am. Chem. Soc.*, **89**, 1592 (1967), and references cited therein.

of metal hydride–olefin reactions is that "insertion" of the olefin into the M–H bond occurs in many cases,[3,7] as in eq 1. Thus, ethylene[8] reacts with *trans*-PtHCl-

$$X{-}M{-}H + {>}C{=}C{<} \rightleftarrows X{-}M{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H \qquad (1)$$

$(PEt_3)_2$ in cyclohexane at 95° and 40 atm to give a 25% yield of the ethyl derivative $PtCl(C_2H_5)(PEt_3)_2$ in 18 hr, and the reaction is reversible. In contrast to this particular reaction, and ostensibly quite different from the general behavior, the highly activated olefin tetracyanoethylene was recently reported[9] to react with an equimolar amount of *trans*-$PtHCl(PEt_3)_2$ in benzene at room temperature immediately to give a quantitative yield of $Pt(PEt_3)_2TCNE$ with HCl being evolved in the reaction. The structure of the triphenylphosphine analog, $Pt(Ph_3P)_2TCNE$, is now known, and the molecule is essentially planar.[10]

In view of the unusual reaction of TCNE with *trans*-$PtHCl(PEt_3)_2$, and in hopes of contributing to a better understanding of the key interaction between metal hydrides and olefinic systems, we have carried out a detailed study of the reactions of tetracyanoethylene with the complexes *trans*-$PtHX(PR_3)_2$ (R = Et, X = Cl, Br, I, NO_2, CN, NCO; R = Ph, X = Cl, Br, I, CN) and report herein preparative and kinetic results.

Experimental Section

I. Materials. Tetracyanoethylene was purchased from Columbia Organic Chemicals Co., Inc. The dark, crude commercial material was purified by sublimation to give white crystals melting at 201–202°.

Reagent-grade benzene was dried over sodium wire and stored in tightly stoppered containers. All other chemicals used were reagent-grade materials.

The platinum-containing starting materials were obtained by literature methods or modifications of these. Thus, *trans*-PtHX-$(PEt_3)_2$ (X = Cl, Br, I, NO_2, CN, NCO) was prepared as described by Chatt and Shaw.[8] Preparation of the deuterated complex, *trans*-$PtDCl(PEt_3)_2$, has been mentioned in the literature,[8] but our attempts to so prepare the compound, which involved shaking of molten $PtHCl(PEt_3)_2$ with hot deuterium oxide in the presence of 10^{-3} *M* HCl, gave the deuterated complex in very low yield. A homogeneous reaction seemed more advisable, so a 1:2 mixture of D_2O and CH_3OD with a trace of hydrochloric acid was used as the deuterating medium. The acid concentration was quite critical. Deuteration did not occur in the absence of acid,[11] while moderately low concentrations were markedly effective in converting most of the substrate into *cis*-$PtCl_2(PEt_3)_2$. Accordingly, *trans*-PtHCl-$(PEt_3)_2$ (0.4 g) was dissolved in 50 ml of a 1:2 mixture of D_2O and CH_3OD containing 0.03 mmole of hydrochloric acid. The solution was refluxed for 1 hr, and then the solvent was removed under reduced pressure. The yellow residue was taken up with petroleum ether (bp 60–80°), and a negligible amount of insoluble *cis*-$PtCl_2$-$(PEt_3)_2$ was removed by filtration. From the solution, *trans*-deuteriochlorobis(triethylphosphine)platinum(II) was obtained in good yield as long white needles. The infrared spectrum of the product in Nujol mull showed a very weak band at 2231 cm^{-1} due to ν_{Pt-H} of unreacted hydrido complex and a strong band at 1598 cm^{-1}, which is ν_{Pt-D} of the deuterio complex.

The complex *trans*-deuteriocyanobis(triethylphosphine)platinum-(II), $PtDCN(PEt_3)_2$, was prepared by treating 0.1 g of *trans*-PtDCl-$(PEt_3)_2$ dissolved in 50 ml of a 2:1 mixture of CH_3OD and D_2O with 16 mg of KCN. After the mixture was stirred for 10 min at room temperature, the solvent was removed under reduced pressure and the wet residue was extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4, and, after evaporation of the solvent and recrystallization from petroleum ether (bp 40–60°), the complex was obtained as a white powder, mp 110°. The infrared spectrum of a Nujol mull of the complex includes bands at the following wave numbers:[12] 2140 (w), 2115 (vs), 2070 (vs), and 1507 (s). A small amount of the undeuterated complex was present as evidenced by the weak bands at 2140 and 2070 cm^{-1}. The possibility of the presence of other cyano complexes was ruled out because the ultraviolet spectra of the sample and *trans*-PtHCN-$(PEt_3)_2$ in dichloromethane were identical.

The triphenylphosphine complex, *trans*-$PtHCl(PPh_3)_2$, was prepared by a literature method,[13] and the corresponding bromo, iodo, and cyano complexes were obtained by metathesis in acetone.

II. Preparative Reactions of Tetracyanoethylene with Platinum Complexes. The complex *trans*-$PtHBr(PEt_3)_2$ (0.204 g, 0.4 mmole) was added at room temperature to a benzene solution (10 ml) of tetracyanoethylene (0.025 g, 0.2 mmole). The yellow color of the benzene solution disappeared immediately and a pale yellow precipitate began to form slowly. After 15 min the solid was collected on a filter, washed well with benzene and ether, and dried in air. Upon recrystallization from dichloromethane–methanol, 0.05 g of a white powder was obtained. *Anal.* Calcd for $C_{18}H_{30}N_4P_2Pt$: C, 38.64; H, 5.50. Found: C, 38.50; H, 5.30. The infrared spectrum of this compound was the same as that of $Pt(PEt_3)_2$-TCNE which was previously prepared from the reaction of *trans*-$PtHCl(PEt_3)_2$ and TCNE.

Reaction of *trans*-$PtHI(PEt_3)_2$ with TCNE gave a yellow solid which was unstable and changed color to pink in an hour or so. The pink solid was extracted with three portions of petroleum ether, leaving a pink residue. The pink residue is probably an impure sample of $Pt(PEt_3)_2TCNE$. *Anal.* Calcd for $C_{18}H_{30}N_4P_2Pt$: C, 38.64; H, 5.40; N, 10.01; P, 11.07. Found: C, 38.48; H, 5.16; N, 12.84; P, 9.23. The infrared spectrum of a Nujol mull includes a band at 2222 cm^{-1}. Evaporation of the petroleum ether extract gave a deep yellow, crystalline material which showed no absorptions in the C≡N stretching region of the spectrum. It melted at 134–136°. *Anal.* Found: C, 24.19; H, 4.53. The yellow material is probably an impure sample of *trans*-PtI_2-$(PEt_3)_2$, which melts at 136° and requires 21.0% C and 4.4% H. The ultraviolet spectrum of the yellow material exhibits an absorption maximum at the same position (355 mμ) as does an authentic sample of *trans*-$PtI_2(PEt_3)_2$.

A benzene solution (5 ml) of *trans*-$PtHCN(PEt_3)_2$ (0.46 g, 1 mmole) was added to a benzene solution (10 ml) of tetracyanoethylene (0.130 g, 1 mmole) at room temperature, and immediately a pale yellow precipitate appeared while at the same time the supernatant liquid became colorless. After a few minutes the solid was collected on a filter, washed with benzene and ether, and dried in air, whereupon 0.15 g of a pale yellow powder was obtained. This material changed color to orange over a period of a day or so. Elemental analysis suggests a 1:1 adduct, $PtHCN(PEt_3)_2TCNE$. *Anal.* Calcd for $C_{19}H_{31}N_5P_2Pt$: C, 38.91; H, 5.28, N, 11.94. Found: C, 38.24; H, 5.24; N, 11.93. Infrared data for freshly prepared samples are given in Table IV and corroborate the formulation. Tentative assignments of the bands (see Discussion and Table IV) were made by comparison with the spectrum of the material obtained by reacting TCNE with the deuterated compound *trans*-$PtDCN(PEt_3)_2$.

Reaction of *trans*-$PtH(NO_2)(PEt_3)_2$ and TCNE with conditions similar to those described above for *trans*-$PtHBr(PEt_3)_2$ gave a small yield (<10%) of $Pt(PEt_3)_2TCNE$. Likewise, when *trans*-PtH-$(NCO)(PEt_3)_2$ and TCNE were allowed to react at room temperature, a small yield of $Pt(PEt_3)_2TCNE$ was obtained.

Reaction of the triphenylphosphine complexes *trans*-PtHX-$(PPh_3)_2$ (X = Br, I, CN) with TCNE in benzene solution at room temperature gave a 50% yield of $Pt(Ph_3P)_2TCNE$ for X = Br, a small yield (<10%) of $Pt(Ph_3P)_2TCNE$ for X = CN, but no Pt-$(Ph_3P)_2TCNE$ for X = I.

III. Kinetic Studies. An attempt was made to measure the kinetics of the reaction given by eq 2 in benzene solution by monitoring changes in the infrared spectra of the reactants in the 2100–

$$trans\text{-}PtHCl(PEt_3)_2 + TCNE \longrightarrow Pt(PEt_3)_2TCNE + HCl \qquad (2)$$

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(7) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 115 (1965).

(8) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

(9) W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

(10) C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *J. Am. Chem. Soc.*, 90, 798 (1968).

(11) C. D. Falk and J. Halpern, *ibid.*, 87, 3523 (1965).

(12) Abbreviations used in this paper to describe infrared band intensities and widths are: s, strong; vs, very strong; m, medium; w, weak; vw, very weak; sp, sharp; and br, broad. All band positions are given in cm^{-1}.

(13) J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, 4, 1618 (1965).

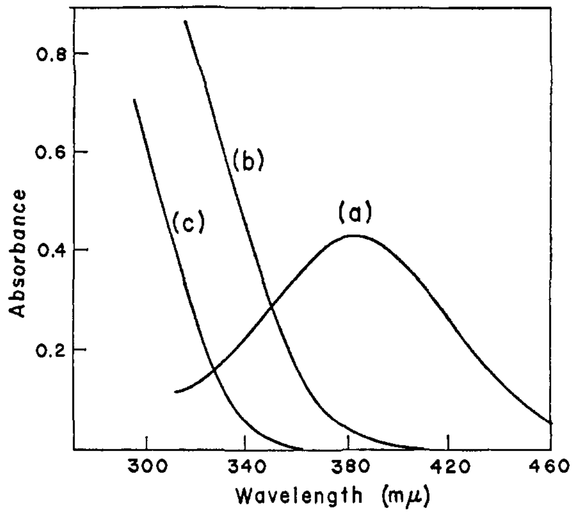

Figure 1. Spectral changes occurring during the reaction of tetracyanoethylene with *trans*-$PtHCl(PEt_3)_2$ in benzene at 30°. The reference cell contains a 10^{-3} *M* solution of *trans*-$PtHCl(PEt_3)_2$. (a) Spectrum of a 1.5×10^{-4} *M* solution of TCNE in benzene. (b) Spectrum of reaction mixture immediately after mixing a 10^{-3} *M* solution of *trans*-$PtHCl(PEt_3)_2$ with a 1.5×10^{-4} *M* solution of TCNE. (c) Spectrum of reaction mixture after completion of reaction. This spectrum is the same as that of a 1.5×10^{-4} *M* solution of $Pt(PEt_3)_2TCNE$ with a 10^{-3} *M* solution of *trans*-$PtHCl(PEt_3)_2$ in the reference cell.

2250-cm^{-1} region where Pt—H and C≡N stretching vibrations are observed. However, at the relatively high concentrations of reactants necessary to obtain appropriate absorptions, the reaction was complete before the first spectral measurement could be made. In addition, at such concentrations the sparingly soluble product separated as a precipitate.

To alleviate the difficulties described above, dilute solutions of the reactants were employed, and optical densities of the reaction mixture were measured in the near-ultraviolet region of the spectrum. The spectrum of a benzene solution of TCNE displays a strong absorption band at 384 mμ due to the C_6H_6·TCNE charge-transfer complex,[14] whereas both $PtHCl(PEt_3)_2$ and $Pt(PEt_3)_2$-TCNE absorb at lower wavelengths. Kinetic runs were carried out by mixing known volumes of freshly prepared benzene solutions of the reactants in a 1-cm quartz cell, the cell being positioned in the thermostated compartment of a Beckman DB spectrophotometer which was equipped with a Sargent recorder. The reactant solutions had been previously placed in a constant-temperature bath (30 ± 0.1°). Various hydrido complex/TCNE concentration ratios were used, and these ranged from 25:1 through 1:1 to 1:2. In studying the influence of reagent concentrations on rate in benzene, an excess of hydrido complex was used in most cases because the available range of concentrations of TCNE was limited by the strong absorptions of its solutions in benzene at wavelengths less than 460 mμ, and these strong absorptions would have obscured the optical path of the reference beam beyond instrument response had such solutions been used as blanks. The appropriate hydrido complex solutions were used in the reference cell. The spectral changes during the course of the reaction (Figure 1) indicated that reaction 2 was proceeding through two definite stages. With an excess of hydrido complex the first stage appeared to be over within the time of mixing of the reactants, as indicated by the immediate and complete disappearance of the charge-transfer band at 384 mμ due to the C_6H_6·TCNE complex. Within the same time a new absorption appeared at shorter wavelength which corresponded to a new species formed in the first stage. The intensity of the new absorption band was independent of the concentration of the hydrido complex in excess provided that the initial concentration of TCNE was the same in every run. These spectral observations suggested that, in solutions of TCNE and hydrido complex, an equilibrium existed between the reactants and a hitherto unspecified intermediate such that the intermediate was rapidly formed in the time of mixing, and that the equilibrium favored essentially complete formation of the intermediate. A similar type of behavior was observed when excess TCNE was used, if due allowance was made for the absorption of the unreacted TCNE. In the second, slower stage of the reaction, the disappearance of the intermediate, rather than the disappearance of TCNE, was being followed spectrally. The absorption band of the intermediate slowly decreased in intensity to give a final spectrum which was identical with that of $Pt(PEt_3)_2TCNE$. Measurements were usually made over three half-lines, and rate constants for the decomposition of the intermediate were obtained graphically from the slope of linear plots of $\log(A_t - A_\infty)$ *vs.* time.

Kinetic studies of reactions given by eq 3 were also made by a spectrophotometric method. For these triphenylphosphine derivatives, in contrast to the triethylphosphine complex, the form and

$$PtHX(PPh_3)_2 + TCNE \longrightarrow Pt(Ph_3P)_2TCNE + HX \qquad (3)$$

$$X = Cl, Br$$

intensity of initial spectra of reaction mixtures were dependent on the concentration of the hydrido complex in excess in such a manner as to indicate that only partial conversion to an intermediate had occurred. Hence, the observed spectra were a composite of the spectra of the C_6H_6·TCNE charge-transfer complex, the intermediate, and $Pt(Ph_3P)_2TCNE$. Experimental rate constants were obtained from linear plots of $\log(A_t - A_\infty)$ *vs.* time.

IV. Analyses and Instrumentation. Elemental analyses for carbon and hydrogen were carried out by Mr. R. Seab, Department of Chemistry, Louisiana State University. Analyses were also determined at Galbraith Laboratories, Inc., Knoxville, Tenn., and at the Istituto Di Chimica Generale, Universitá di Padova, Padua, Italy.

Infrared spectra in the NaCl region were recorded on a Beckman IR-7 spectrophotometer using Nujol and hexachlorobutadiene mulls.

Ultraviolet and visible spectra were obtained using Beckman DB or DK spectrophotometers.

Results

Reactions of tetracyanoethylene with *trans*-$PtHBr(PR_3)_2$ (R = Et, Ph) proceeded smoothly without detectable formation of side products and gave the same platinum-containing complex $Pt(PR_3)_2TCNE$ as was previously obtained[9] from the reactions of the analogous chloro complexes with tetracyanoethylene. For other X groups (X = I, CN, NO_2, NCO), however, the reactions were complicated by formation of side products, or the yield of $Pt(PR_3)_2TCNE$ was very low. When the triethylphosphine complex, $PtHCN(PEt_3)_2$, and TCNE were allowed to react in benzene, a pale yellow solid separated immediately. This product, which decomposes slowly to an unidentified orange solid, appeared to be a 1:1 adduct of $PtHCN(PEt_3)_2$ and TCNE on the basis of an elemental analysis and infrared data (*vide infra*).

A kinetic investigation of the reaction given by eq 2 was carried out in benzene at 30°. As noted in the Experimental Section, the reaction proceeded through two stages, and the first stage, which was complete during the time of mixing of the reagents, corresponded to the formation of an intermediate, which decomposed in the second stage and gave $Pt(PEt_3)_2TCNE$ as a product. The stoichiometric reaction given by eq 2 can be written as

$$PtHCl(PEt_3)_2 + TCNE \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{intermediate} \xrightarrow[\text{slow}]{k_1} Pt(PEt_3)_2TCNE + HCl \qquad (4)$$

First-order rate constants, k_1, for reactions of TCNE with $PtHCl(PEt_3)_2$ and $PtDCl(PEt_3)_2$ in benzene solution at 30° are given in Tables I and II, respectively. Attempts were made to follow the kinetics of reaction 2

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[14] R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

Table I. Rate Constants for the Reaction of *trans*-$PtHCl(PEt_3)_2$ with Tetracyanoethylene in Benzene at 30°

10^4(complex), *M*	10^4(TCNE), *M*	10^3k_1, sec^{-1}
1.5	2.5	1.05
5.0	1.5	1.05
10.0	1.5	1.13
50.0	2.0	1.10

Table II. Rate Constants for the Reaction of *trans*-$PtDCl(PEt_3)_2$ with Tetracyanoethylene in Benzene at 30°

10^4(complex), *M*	10^4(TCNE), *M*	10^3k_1, sec^{-1}
5.0	2.0	1.22
10.0	2.0	1.25
50.0	2.0	1.22

in dichloromethane and tetrahydrofuran. The reactions proceeded smoothly in these solvents but were too fast to measure by our techniques.

The reaction of TCNE with the triphenylphosphine complex, *trans*-$PtHCl(PPh_3)_2$, was considerably slower than with the triethylphosphine analog. Additionally, unlike the reaction of TCNE with $PtHCl(PEt_3)_2$, the shape and intensity of the initial spectra of reaction mixtures depended on the concentration of the hydrido complex (which was in excess) in such a manner as to suggest that only partial conversion to an intermediate species was occurring. Moreover, the experimentally observed first-order rate constants increased with increasing hydrido complex concentration and obey the rate law

$$k_{obsd} = k'[\text{hydrido complex}] \qquad (5)$$

Data are reported in Table III for reactions of *trans*-$PtHX(PPh_3)_2$ (X = Cl, Br) with TCNE in benzene and dichloromethane at 30°.

Table III. Rate Constants for the Reactions of *trans*-$PtHX(PPh_3)_2$ (X = Cl, Br) with Tetracyanoethylene in Benzene and/or Dichloromethane at 30°

Complex	10^3(complex), *M*	10^5k_{obsd}, sec^{-1}	k',[a] M^{-1} sec^{-1}
trans-$PtHCl(PPh_3)_2$[b]	2.0	1.17	0.00467
	6.0	2.78	
	10.0	4.50	
	20.0	9.68	
trans-$PtHCl(PPh_3)_2$[c]	4.0	400	1.07
	5.0	540	
	7.5	917	
	10.0	1040	
trans-$PtHBr(PPh_3)_2$[c]	4.0	9.17	0.0197
	10.0	19.2	
	15.0	30.0	
	20.0	40.8	

[a] The values of k' were obtained from the slope of a plot of k_{obsd} *vs.* complex concentration, and $k' = k_1K_{eq}$ where K_{eq} is the equilibrium constant for formation of the intermediate $PtHX(PPh_3)_2$-TCNE and k_1 is the rate constant for the decomposition of this intermediate into $Pt(PPh_3)_2TCNE$ and HX. [b] Benzene solution; the TCNE concentration is 2×10^{-4} *M*. [c] Dichloromethane solution; the TCNE concentration is 4×10^{-4} *M*.

Discussion

An interesting aspect of the chemistry of TCNE is that it is one of the strongest π acids known and forms numerous, highly colored complexes with aromatic substrates.[14] In view of the strong electrophilicity of TCNE, and since square-planar Pt(II) complexes may be considered as π bases on account of the presence of nonbonding electrons in the out-of-plane d orbitals, it is reasonable to suppose that the formation of intermediates in the reactions of TCNE with *trans*-$PtHX(PR_3)_2$ involves an electrophilic attack of TCNE at the platinum d orbitals. Hence, the immediate disappearance of the $C_6H_6 \cdot TCNE$ spectrum when $PtHX(PR_3)_2$ and TCNE are mixed is presumed to be due to a reaction of this sort, and it is supposed that a five- or six-coordinate (depending on one's viewpoint) intermediate species is formed, this intermediate being a 1:1 adduct of $PtHX(PR_3)_2$ and TCNE. The fact that the isoelectronic d^8 substrates $IrX(CO)(Ph_3P)_2$ (X = Cl, Br, I, NCO, NCS) react with TCNE immediately[1b] at room temperature to yield complexes of the type $IrX(CO)(Ph_3P)TCNE$ supports this view, as does the fact that a 1:1 adduct of TCNE and $PtHCN(PEt_3)_2$ has been isolated (*vide infra*).

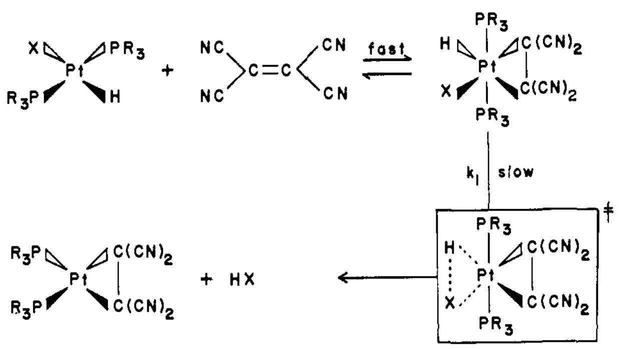

Figure 2. Reductive elimination mechanism for the reaction of *trans*-$PtHX(PR_3)_2$ with TCNE.

Two mechanistic paths for the reaction of *trans*-$PtHX(PR_3)_2$ with TCNE will be considered and it is suggested that in either mechanism an intermediate $PtHX(PR_3)_2TCNE$ is formed in a rapid preequilibrium step. In the first mechanism (Figure 2), this intermediate decays in a slow step *via* formation of a three-center transition state in which HX is eliminated to give the product $Pt(PR_3)_2TCNE$. The intermediate can reasonably be considered to be *formally* a Pt(IV) complex formed by oxidative addition of TCNE to *trans*-$PtHX(PR_3)_2$. The stereochemistry of the intermediate may be such that the H and X groups are *cis* or *trans*, depending on which of the two mutually *trans* ligands in *trans*-$PtHX(PR_3)_2$ depress out of the square plane as the electrophile approaches. As drawn arbitrarily in Figure 2, a *trans* configuration of phosphine ligands would place the H and X groups *cis* to one another, and elimination of HX might thus be favored energetically over a *cis* configuration of phosphine groups with H and X *trans* to each other.

The behavior of tetracyanoethylene toward hydridoplatinum(II) complexes as described herein is rather peculiar, since interaction of metal hydrides with olefins leads to, in many cases, a reversible addition of M-H across the olefin bond. There is a widespread belief in the applicability of insertion reactions, particularly in the area of catalytic hydrogenation and isomerization, and, in view of this wide spread acceptance, it is certainly pertinent to inquire as to whether this scheme,

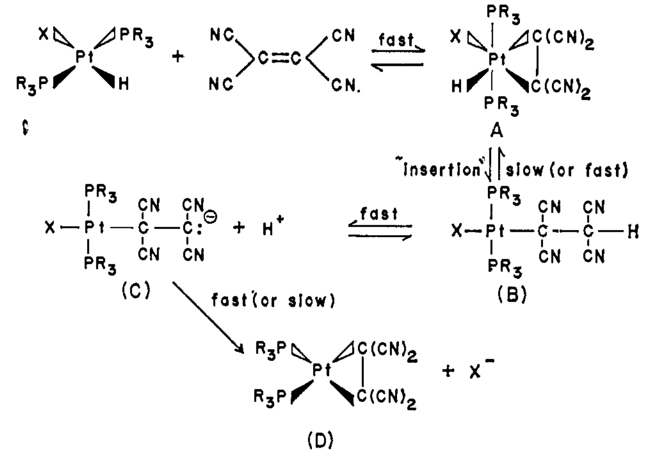

Figure 3. Hydride-transfer mechanism ("insertion") for the reaction of *trans*-$PtHX(PR_3)_2$ with TCNE.

with suitable modifications, is applicable to the reactions of tetracyanoethylene with platinum hydrides. Such a mechanism, which can be considered to be an alternative to that of Figure 2, is shown in Figure 3 and would involve, first of all, the formation of a 1:1 intermediate as was postulated in the previous mechanism. The next step, however, differs from that already described in that a C–H bond is formed instead of an H–X bond. Now, the tetracyanoethyl complex (B) so formed would be expected to be a moderately strong acid, since the acidic nature of protons attached to cyano carbons is well documented.[15] Thus, tetracyanoethane has a pK_A of 3.6[16] and complex B of Figure 3, which may be regarded as a derivative of tetracyanoethane, would be expected to have a comparable or even stronger acidity. The conjugate base C could then undergo an internal nucleophilic displacement of X by the carbanion. In this mechanism, it is reasonable to suppose that the equilibrium involving formation of A and the acid–base equilibrium ($B \rightleftarrows C$) would be fast, thus leaving either the hydride-transfer step ($A \rightleftarrows B$) or the internal nucleophilic substitution ($C \rightarrow D$) as the slow step.

Both proposed mechanisms are consistent with the kinetic data shown in Tables I–III, and these data may be summarized as follows: (a) rates are dependent on the nature of the phosphine ligands since the triethylphosphine complex reacts about 40 times faster than does the triphenylphosphine complex; (b) rates are faster in the more polar solvents dichloromethane and tetrahydrofuran than in benzene, the rate in dichloromethane being over 200 times faster than in benzene; (c) rate is dependent on the nature of X since the chloro complex reacts about 50 times faster than does the bromo complex; and (d) the kinetic isotope effect is small, the ratio k_H/k_D being 0.9. In terms of the proposed mechanisms, only the abnormally small isotope effect need be mentioned in detail. It is known[17,18] that the major portion of the kinetic isotope effect arises from contributions to the activation energy from changes in zero-point energy differences occurring when the activated complex is formed. Since the zero-point energy difference between Pt–H and Pt–D is *ca.* 0.9 kcal/mole, if only the stretching vibration is considered, complete loss of a Pt–H vibration in the transition state at 30° would result in a k_H/k_D value of *ca.* 4.5. The low value of 0.9 obtained experimentally indicates that complete rupture of the Pt–H bond does not play a significant role in formation of the activated complex. This in turn means that either (a) the Pt–H bond is broken in the first fast stage leading to the intermediate or (b) during the formation of the activated complex in the rate-determining step of the second stage the Pt–H bond is bent so that the hydrogen atom can attach itself to another part of the molecule, *i.e.*, a transition state is extant in which the loosening of the Pt–H bond occurs concurrently with the formation of a new Z–H bond, namely H–Cl if reductive elimination of HCl occurs or C–H if the hydride is transferred to the C_6N_4 moiety. If the first-mentioned interpretation (a) is correct, then a value of k_H/k_D equal to unity would be expected. The experimental value of 0.9 is not significantly different from unity. Nevertheless, in view of the fact that in the reaction of *trans*-$PtHCN(PEt_3)_2$ with TCNE a compound $PtHCN(PEt_3)_2TCNE$ was isolated in which infrared data shows unequivocally that the Pt–H bond has not been broken, the last-mentioned interpretation (b) is favored. Thus, loss of zero-point energy by bending and loosening of the Pt–H bond is more than compensated for by the energy gain through formation of the H–Cl or H–C bond since the zero-point energy of these, which is roughly the same, is greater than that of Pt–H by *ca.* 1 kcal/mole. A similar explanation has been offered to account for low values of k_H/k_D in many organic reactions[17,18] and is consistent with the formation of a three-center transition state involving concurrent breaking of the Pt–H bond and making of the H–X bond as shown in the reductive elimination scheme of Figure 2. For the insertion mechanism of Figure 3, a similar explanation is applicable if step $A \rightarrow B$ is rate determining. If only a primary isotope effect is considered, step $C \rightarrow D$ can be eliminated as rate determining because the ratio of acid ionization constants for B, $K_{B(H)}/K_{B(D)}$, would be expected to be greater than unity due to the fact that ionization constants of proton acids are usually larger than ionization constants of deuteron acids, and hence a kinetic isotope effect greater than unity would be predicted, which is inconsistent with the observed k_H/k_D value of 0.9. Nevertheless, if step $C \rightarrow D$ is rate determining, the low isotope effect can be rationalized on the basis of a secondary effect in step $A \rightarrow B$ which might counterbalance the expected large isotope effect of step $B \rightarrow C$. The experimental data which have been mentioned thus far are consistent with either of the mechanisms of Figure 2 or Figure 3.

Such labile intermediates as $PtHX(PR_3)_2TCNE$ (X = Cl, Br; R = Et, Ph) could not be isolated, even though intermediates, presumably of this type, are sufficiently stable to be present in spectrally detectable concentration during the course of the reactions. Since their decomposition requires rupture of a Pt–X bond in the mechanism of Figure 2, it might be expected that replacement of a halide ligand by a more strongly bound group would enhance the probability of isolating and characterizing the intermediate. To this end, the

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(15) W. J. Middleton, E. L. Little, D. D. Coffman, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2795 (1958).

(16) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *ibid.*, **80**, 2783 (1958).

(17) R. P. Bell, *Discussions Faraday Soc.*, **39**, 16 (1965).

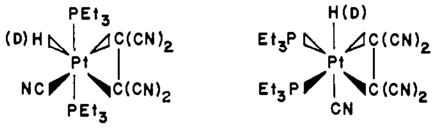
(18) F. H. Westheimer, *Chem. Rev.*, **61**, 625 (1961).

cyanide ligand might be suitable as a substituent, since cyano groups are much poorer leaving groups than halogens in Pt(II) substitution reactions. When equimolar amounts of TCNE and *trans*-$PtHCN(PEt_3)_2$ are allowed to react in benzene at room temperature, a pale yellow solid separates immediately. This material analyzes as a 1:1 adduct of $PtHCN(PEt_3)_2$ and TCNE, and infrared spectral data suggest that the yellow solid is a compound analogous to the intermediates that have been postulated above in the mechanistic schemes. The infrared band assignments (Table IV) have been made by comparison with the infrared spectrum displayed by the analogous deuterio complex. If the product is considered to have one of the structures shown in Figure 4, then the strong band at 2231 cm^{-1} in both the H and D derivatives can be assigned as the C≡N stretching frequency of the cyano groups in the TCNE moiety, which would be unaffected by deuteration. In complexes of the type $IrX(CO)Ph_3P)_2TCNE$ (X = Cl, Br, I, NCO, NCS), ν_{CN} values[1b] of the C_6N_4 moiety are observed at 2230–2235 cm^{-1}. The weak, broad band at 1560 cm^{-1} in $PtDCN(PEt_3)_2TCNE$, which is absent in the hydrido complex, is obviously due to the Pt–D stretching vibration and firmly establishes the presence of a Pt–H(D) bond in the products. The sharp, medium intensity absorption at 2155 cm^{-1} in $PtDCN(PEt_3)_2TCNE$ can be attributed to the stretching vibration of the C≡N group bound to platinum. The fact that a band is not present at 2155 cm^{-1} in $PtHCN(PEt_3)_2TCNE$ is important because it allows one to make a choice between the two stereochemical configurations of Figure 4. Recent investigations[19] of hydridocarbonyl complexes of Rh, Ir, Os, and Re have shown that when H and CO groups are *trans* to one another in the complexes, there is a resonance interaction or coupling of the metal–hydrogen and carbonyl stretching modes which is manifested by a shift of ν_{CO} in going from the hydrido to the deutero complex. Such a shift is not observed when the H and CO are *cis* to one another. To the best of our knowledge, such a resonance interaction has not previously been reported between M—H and C≡N stretching frequencies in hydridocyano complexes.[20] It is suggested that the reason for the absence of a band at 2155 cm^{-1} in $PtHCN(PEt_3)_2TCNE$ is due to such a resonance interaction, and, if this is the case, a *trans* configuration (structure B of Figure 4) of H and CN is extant in $PtHCN(PEt_3)_2TCNE$.[21] The ν_{CN} band in $PtHCN(PEt_3)_2TCNE$ could be either the one at 2198 cm^{-1} or the one at 2135 cm^{-1}, and the proper assignment[22] can be made on the basis of the noncrossing rule[23] for two energy levels with the same symmetry properties.

Table IV. Infrared Spectral Data for Hydridocyano Complexes[a]

	$PtHCN(PEt_3)_2$	$PtDCN(PEt_3)_2$	$PtHCN(PEt_3)_2TCNE$	$PtDCN(PEt_3)_2TCNE$
ν_{Pt-H}	2070 (w)	. . .	2198 (m)	. . . .
ν_{CN}	2140 (s)	2115 (vs)	2135 (w)[b]	2155 (m)[b]
			2231 (s)[c]	2231 (s)[c]
ν_{Pt-D}	. . .	1507 (s)	. . .	1560 (w)
ν'_{Pt-H}[d]	2095		2178	
ν'_{CN}[e]	2115		2155	

[a] Frequencies are in cm^{-1}. [b] C≡N stretch of cyanide bound to platinum. [c] C≡N stretch of cyanide in TCNE moiety. [d] The primed frequencies are unperturbed ones, *i.e.*, those calculated on the basis of a resonance interaction of ν_{Pt-H} and ν_{CN}. [e] The primed C≡N stretching frequencies are the unperturbed ones for the hydrido complexes and are the same as the observed C≡N stretching frequencies of the deuterated complexes where there is negligible interaction between Pt—D and C≡N modes.



Structure A(H) Structure B(H)
Structure A(D) Structure B(D)

Figure 4. Possible structures for the product of the reaction of TCNE with *trans*-$PtHCN(PEt_3)_2$ or the analogous deuterated complex.

The compound $PtHCN(PEt_3)_2TCNE$ is most interesting in that it contains both an olefin and a hydride bonded to the metal, and it therefore represents the sort of intermediate which is believed to be important in many catalytic reactions.[3–6, 24, 25] Few compounds

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(19) (a) L. Vaska, *J. Am. Chem. Soc.*, 88, 4100 (1966); (b) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *ibid.*, 89, 2851 (1967); (c) F. L. Eplattenier and F. Calderazzo, *Inorg. Chem.*, 6, 2092 (1967).

(20) Chatt and Shaw have previously reported[8] the preparation of *trans*-$PtHCN(PEt_3)_2$ and *trans*-$PtDCN(PEt_3)_2$ and observed bands in a Nujol mull spectrum of $PtHCN(PEt_2)_3$ at 2072 (m) and 2137 cm^{-1} (vs), which they assigned as ν_{Pt-H} and ν_{CN}, respectively. They also reported ν_{Pt-D} in $PtDCN(PEt_3)_2$ as occurring at 1504 (m), but did not report ν_{CN} for $PtDCN(PEt_3)_2$. In close agreement with their work, we find ν_{Pt-H} and ν_{CN} in $PtHCN(PEt_3)_2$ at 2070 and 2140, respectively. As mentioned in the Experimental Section, the product of the reaction of *trans*-$PtDCl(PEt_3)_2$ and KCN shows bands in a Nujol mull spectrum at 2140 (w), 2115 (vs), 2070 (vw), and 1507 (s). The strong band at 1507 cm^{-1} is assigned as ν_{Pt-D}, which is quite close to the value of 1504 cm^{-1} found by Chatt and Shaw. A small amount of undeuterated material was present in our product as shown by the weak band at 2070 cm^{-1}. The most interesting spectral feature is the weakness of the band at 2140 cm^{-1}, which is assumed to be due to ν_{CN} of the $PtHCN(PEt_3)_2$ impurity, and the strong, unprecedented band at 2115 cm^{-1}. We suggest that the band at 2115 cm^{-1} is attributable to ν_{CN} in *trans*-$PtDCN(PEt_3)_2$, and that the shift of ν_{CN} to 2140 cm^{-1} in $PtHCN(PEt_3)_2$ is a result of coupling of vibrational states of the Pt–H and C≡N in *trans*-$PtHCN(PEt_3)_2$.

(21) It is to be noted that it does not necessarily follow that there is a *trans* configuration of H and X in $PtHX(PR_3)_2TCNE$ (X = Cl, Br). A *cis* configuration of H and X was drawn *arbitrarily* in Figures 2 and 3.

(22) In $PtDCN(PEt_3)_2TCNE$ the C≡N stretching frequency for the cyanide bound to platinum differs by a large amount from the Pt–D stretching energy. The coupling of these vibrations will therefore be minimal, and the value of 2155 cm^{-1} can be considered as the frequency of the unperturbed, *i.e.*, in the absence of interaction, stretching frequency of a C≡N *trans* to D. Accordingly, if the band at 2198 cm^{-1} in $PtHCN(PEt_3)_2TCNE$ was assigned as ν_{CN}, the energy difference, 2198 − 2155 = 43 cm^{-1}, would represent the interaction energy between the vibrations ν_{Pt-H} and ν_{CN}. By use of this energy value, one can calculate the frequency of the unperturbed state ν'_{Pt-H} to be 2178 cm^{-1}, *i.e.*, 2135 + 43 = 2178 cm^{-1}. This value of 2178 cm^{-1} would then be higher than the unperturbed ν'_{CN} while the observed ν_{Pt-H} value of 2135 cm^{-1} would be lower than the observed ν_{CN} of 2198 cm^{-1}. This situation would be contrary to the noncrossing rule, which states that two energy levels with the same symmetry will repel each other, and the assignments of ν_{CN} and ν_{Pt-H} as 2198 and 2135 cm^{-1}, respectively, in $PtHCN(PEt_3)_2TCNE$ have to be discarded. On the other hand, if the band at 2135 cm^{-1} in $PtHCN(PEt_3)_2TCNE$ is assigned as ν_{CN}, the interaction energy is 2155 − 2135 = 20 cm^{-1}, and the unperturbed ν'_{Pt-H} is therefore 2178 cm^{-1}. In this case the noncrossing rule is obeyed since $\nu'_{Pt-H} > \nu'_{CN}$ and $\nu_{Pt-H} > \nu_{CN}$, and therefore the correct assignments are 2198 and 2135 cm^{-1} for ν_{Pt-H} and ν_{CN}, respectively. A diagram similar to that of Figure 3 in ref 19b is very useful in following this argument. It is worth noting that the choice of correct assignments cannot be made by exploiting another manifestation of the resonance interaction, namely an anomalous ν_{Pt-H}/ν_{Pt-D} ratio, since both possible assignments give rise to anomalous values.

(23) F. A. Cotton, "Chemical Applications of Group Theory," John Wiley and Sons, Inc., New York, N. Y., 1963, p 266.

(24) H. W. Sternberg and I. Wender, Special Publications No. 13, The Chemical Society, London, 1959, p 51.

(25) R. D. Cramer, *J. Am. Chem. Soc.*, 87, 4717 (1965).

of this type have been isolated and characterized. Robinson and Shaw[26] have prepared a stable hydridodiolefin complex of iridium [$\mathrm{IrHCl_2}$(cycloocta-1,5-diene)]$_2$, and very recently reaction intermediates in which a platinum atom is bonded simultaneously to hydride ion, an olefin, and trichlorostannate anion have been reported.[27] It is also worth mentioning that one of the products of the reaction of tetrafluoroethylene and *trans*-$\mathrm{PtHCl(PEt_3)_2}$, which was originally[28] formulated as a π-bonded tetrafluoroethylene complex, $\mathrm{PtHCl(PEt_3)_2}$ (π-$\mathrm{C_2F_4}$), has been shown[29] to be a carbonyl complex, *trans*-[$\mathrm{PtClCO)(PEt_3)_2]BF_4}$.

Concerning the mechanisms depicted in Figures 2 and 3, we favor the reductive elimination scheme of Figure 2. Either mechanism is compatible with the kinetic results relating to isotope effect, solvent effect, and relative reactivity of the chloro and bromo complexes. However, we believe that an argument can be made for the reductive elimination mechanism of Figure 2 on the basis of the fact that the compound isolated from the reaction of $\mathrm{PtHCN(PEt_3)_2}$ and TCNE was the hydridoolefinic complex, $\mathrm{PtHCN(PEt_3)_2TCNE}$, whereas, in the reaction of $\mathrm{PtHX(PEt_3)_2}$ (X = Cl, Br) with TCNE, an intermediate hydridoolefinic complex, $\mathrm{PtHX(PEt_3)_2TCNE}$, was not isolated. If the reaction path of Figure 3 was operative in reactions of $\mathrm{PtHX(PEt_3)_2}$ with TCNE, isolation of the σ-cyanoethyl complex B (or the conjugate base C) should instead be more likely if step C $\rightarrow$ D is rate determining. On the other hand, if step A $\rightarrow$ B is rate determining in the mechanism of Figure 3, there is no reason for believing that $\mathrm{PtHCN(PEt_3)_2TCNE}$ should be more stable than $\mathrm{PtHX(PEt_3)_2TCNE}$ (X = Cl, Br). To the contrary, it would seem that $\mathrm{PtHX(PEt_3)_2}$ (X = Cl, Br) would behave as stronger π bases toward the π acid TCNE than $\mathrm{PtHCN(PEt_3)_2}$ since the cyanide group is a much stronger π-acceptor ligand than is chloride or bromide.

In conclusion, we surmise that the contrasting behavior of ethylene and tetracyanoethylene toward hydridoplatinum(II) complexes as mentioned in the introductory section is primarily a manifestation of the greater strength of the platinum–TCNE bond relative to the platinum–ethylene bond.[30] Thus, when either TCNE or $\mathrm{C_2H_4}$ reacts with $\mathrm{PtHX(PR_3)_2}$, a 1:1 adduct, $\mathrm{PtHX(PR_3)_2}$(olefin), is formed initially as an intermediate, but for TCNE elimination of HX is more favorable energetically than "insertion" whereas the reverse is true for ethylene. The fact that we were able to isolate $\mathrm{PtHCN(PEt_3)_2TCNE}$, but not $\mathrm{PtHX(PEt_3)_2}$-TCNE (X = Cl, Br), is reasonable in terms of the greater strength of the Pt–CN bond as compared to the Pt–Cl and Pt–Br bonds.

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[26] S. D. Robinson and B. L. Shaw, *Tetrahedron Letters*, 1301 (1964).

[27] H. A. Tayim and J. C. Bailar, *J. Am. Chem. Soc.*, 89, 4330 (1967).

[28] H. C. Clark and W. S. Tsang, *Chem. Commun.*, 123 (1966); H. C. Clark and W. S. Tsang, *J. Am. Chem. Soc.*, 89, 529 (1967).

[29] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *ibid.*, 89, 3360 (1967).

[30] The complex $\mathrm{Pt(Ph_3P)_2}$(ethylene) decomposes at 122–125° (C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Letters*, 3, 31 (1967)), whereas the complex $\mathrm{Pt(Ph_3P)_2}$(tetracyanoethylene) decomposes at 268–270°.

Direct Characterization of the Mixed Complexes of Aluminum(III) with N,N-Dimethylformamide and 2,4-Pentanedione. Proton Magnetic Resonance Study of First-Coordination-Sphere Stoichiometry and Kinetics of Ligand Exchange

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Abstract: Proton magnetic resonance (pmr) spectra of N,N-dimethylformamide (DMF) solutions of $\mathrm{Al(DMF)_6(ClO_4)_3}$ and tris(2,4-pentanedionate)aluminum(III) ($\mathrm{Al(acac)_3}$) have been used to characterize directly the complexes $\mathrm{Al(acac)(DMF)_4{}^{2+}}$ and *cis*- and *trans*-$\mathrm{Al(acac)_2(DMF)_2{}^+}$. Thermodynamic parameters were obtained from the temperature dependence of the equilibria among these species and $\mathrm{Al(DMF)_6{}^{3+}}$ and $\mathrm{Al(acac)_3}$. Below 5° pmr signals of DMF in the first coordination sphere of complexes containing acac$^-$ can be distinguished, and, from a complete line-shape analysis of these signals, the rate of exchange of DMF from the acac complexes was estimated. Also below 5°, separate pmr signals are discernible for the *cis* and *trans* isomers of $\mathrm{Al(acac)_2(DMF)_2{}^+}$. The kinetic parameters obtained from the latter are consistent with a rate-determining step for *cis-trans* isomerization which proceeds by dissociation of DMF. Data from these studies are compared with those obtained for analogous Be(II) complexes.

Little is known about the solution chemistry of the colorless, diamagnetic, labile complexes of cations having d^0 and d^{10} electronic configurations, primarily because the properties of the cations preclude their study with the experimental techniques conventionally used in transition metal chemistry. Recently it has