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The Kinetics and Mechanism of Substitution Reactions of the Tetrakis(trifluorophosphine) Complexes of Nickel(0) and Platinum(0)

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The rates of ligand substitution reactions of tetrakis(trifluorophosphine)nickel(0) with cyclohexyl isocyanide in *n*-heptane and toluene and of tetrakis(trifluorophosphine)platinum(0) with cyclohexyl isocyanide in *n*-hexane and toluene have been studied by ir spectrophotometry. The reactions are first order in complex concentration and independent of the ligand concentration. Activation parameters for the reaction of the nickel complex are $\Delta H^* = 29$ kcal/mol and $\Delta S^* = 14$ eu in *n*-heptane and $\Delta H^* = 28$ kcal/mol and $\Delta S^* = 11$ eu in toluene. For the platinum complex, in *n*-hexane $\Delta H^* = 24$ kcal/mol and $\Delta S^* = 18$ eu, and in toluene, $\Delta H^* = 23$ kcal/mol and $\Delta S^* = 12$ eu. These results are compatible with a dissociative (SN1) mechanism. Evidence is presented that the activation energies for metal-P bond rupture vary in the order Ni > Pd < Pt. The nature of the metal-PF_3 bond is discussed and compared with the metal-CO and metal-$P(OC_2H_5)_3$ bonds.

Introduction

The possibility that phosphorus trifluoride might form a compound analogous to nickel carbonyl was suggested by Chatt[1] in 1950 and confirmed by the isolation of $Ni(PF_3)_4$ by Wilkinson.[2] Since then Kruck and his school[3] and Clark and his coworkers[4] have prepared a large number of PF_3 compounds analogous to the metal carbonyls. It has been claimed by a number of workers on the basis of qualitative evidence that carbon monoxide and phosphorus trifluoride are very similar in coordinating ability toward transition metals.[3-6]

As part of a continuing study of the kinetics and mechanisms of reactions of zerovalent compounds of metals of the nickel triad[7-10] and of metal-phosphorus bond strengths,[10] we have examined the rates of nucleophilic substitution reactions of $Ni(PF_3)_4$ and $Pt(PF_3)_4$, reaction 1.

$$M(PF_3)_4 + L \longrightarrow M(PF_3)_3L + PF_3 \qquad (1)$$

Experimental Section

Materials.—*n*-Hexane, *n*-heptane, and toluene (Baker Analyzed reagents) were refluxed over and distilled from sodium wire under a nitrogen atmosphere immediately prior to use.

Cyclohexyl isocyanide was prepared by the carbylamine reaction from cyclohexylamine, chloroform, and potassium hydroxide according to the method of Malatesta.[11] Because of the "penetrating and disgusting"[11] odor of this compound, all reactions were carried out in closed systems and transfers were made by syringes fitted with Teflon stopcocks.

The toxicities of $Ni(PF_3)_4$ and $Pt(PF_3)_4$ are not known but are generally assumed to be similar to that of nickel carbonyl.[8] Kruck[3] reported the vapors have musty, stifling odors which cause difficulty in breathing. Hence all experiments were carried out in closed systems and all residues and reaction products were destroyed by treatment with concentrated solutions of NaOH. The $Ni(PF_3)_4$ was obtained from Ozark-Mahoning Co. (Tulsa, Okla.) and distilled twice under high vacuum (*ca.* 10^{-4} mm) from one trap at −30° to another at −196° and stored under vacuum at −10°. The purity of the compound was checked by an examination of its ir spectrum in the ν(PF) region, where only bands at 898 (vs) and 860 cm^{-1} (vs) were observed, characteristic of $Ni(PF_3)_4$.[12]

The compound $Pt(PF_3)_4$ was prepared according to the method of Kruck and Baur.[13] The starting materials, $PtCl_4$ (6.0 g), prepared by the action of a stream of chlorine on a solution of H_2PtCl_6 at 115°,[14] and activated copper powder (15 g), prepared by passing a stream of hydrogen over copper oxide wire at 350°, were mixed together in a mortar and pestle and transferred to a Monel Metal autoclave of capacity 95 ml (Hoke Inc., Cresskill, N. J.). The autoclave was attached to a vacuum line and evacuated, and *ca.* 20 ml of PF_3 (K & K Laboratories, Plainview, N. Y.) prepurified by two trap-to-trap distillations was condensed into the autoclave. This quantity of PF_3 was sufficient to produce a pressure of about 60 atm at ambient temperature. This small bomb was placed in a large rocking autoclave and heated to 105° for 45 hr. After cooling, the bomb was attached to a vacuum line and cooled to −80°, and unreacted PF_3 was distilled into a trap at −190° and thence back into the PF_3 cylinder. This procedure was repeated twice and then the autoclave was allowed to warm to room temperature and the volatile $Pt(PF_3)_4$ was distilled into a −190° trap. Two trap-to-trap distillations were performed to purify the product. The yield was 7.95 g (81.6%). A boiling point measurement of 85.5° at 730 cm (Kruck[13] reported 86° (730 cm)) and bands in the ir spectrum at 906 (vs) and 872 cm^{-1} (vs) (*cf.* Kruck,[13] 905, 867 cm^{-1}) confirmed the purity of the product.

Both $Ni(PF_3)_4$ and $Pt(PF_3)_4$ were stored in the dark at −10°. Over a period of a few months some decomposition was evident and the decomposition products appeared to be particularly corrosive to the thermocouple vacuum gauge. Solutions of $Ni(PF_3)_4$ and $Pt(PF_3)_4$ in the various solvents were prepared at weekly intervals in volumetric flasks fitted with stopcocks and rubber septum caps and stored in the dark at −10°, and over this period they appeared to be quite stable.

Kinetic Measurements.—The apparatus used for carrying out kinetic measurements of solution reactions in a temperature-variable cell with the exclusion of all gas phase has been previously described.[8] Infrared measurements were carried out with a Perkin-Elmer 337 spectrophotometer coupled to an ex-

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[1] J. Chatt, *Nature (London)*, **165**, 637 (1950).

[2] G. Wilkinson, *J. Amer. Chem. Soc.*, **73**, 5501 (1951).

[3] T. Kruck, *Angew. Chem., Int. Ed. Engl.*, **6**, 53 (1967).

[4] C. A. Udovich, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969), and references therein.

[5] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

[6] C. G. Barlow, J. F. Nixon, and M. Webster, *ibid., A*, 2216 (1968).

[7] J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **90**, 1925 (1968).

[8] J. P. Day, F. Basolo, and R. G. Pearson, *ibid.*, **90**, 6927 (1968).

[9] J. P. Day, R. G. Pearson, and F. Basolo, *ibid.*, **90**, 6933 (1968).

[10] M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **8**, 795 (1969).

[11] L. Malatesta, *Gazz. Chim. Ital.*, **77**, 238 (1947).

[12] T. Kruck and K. Baur, *Z. Anorg. Allg. Chem.*, **364**, 192 (1969).

[13] T. Kruck and K. Baur, *Angew. Chem., Int. Ed. Engl.*, **4**, 521 (1965).

[14] R. N. Keller, *Inorg. Syn.*, **2**, 253 (1960).

ternal potentiometric recorder. The temperature of the cell was measured by an iron–constantan thermocouple inserted into one of the sodium chloride windows and attached to a direct-reading temperature potentiometer (Leeds and Northrup, Philadelphia, Pa.).

In the case of substitution reactions of $Ni(PF_3)_4$, at suitable temperatures to observe the reactions (40–50°), concentrations of $C_6H_{11}NC$ of the order of 10^{-2} *M* resulted in considerable polymerization of the isocyanide leading to the deposition of a pale yellow solid which interfered with the observations of spectral changes. Hence these reactions were carried out with the $Ni(PF_3)_4$ substrate in excess concentration, and the decrease of the band at 2138 cm^{-1} (ν(CN) absorption of the free ligand) was measured to determine the rate of the substitution reaction. Prior experiments had shown that under these conditions the monosubstituted compound was the major product and little replacement of a second PF_3 group occurred until the majority of substrate had been converted to the monosubstituted compound. A_∞ was taken to be the base line absorbance, as it was shown independently that the reactions went to completion.

For $Pt(PF_3)_4$, substitution reactions proceeded at a suitable rate for observation at temperatures of about 0°, and at these temperatures, polymerization of the isocyanide occurred only to a minor extent. Hence for the study of $Pt(PF_3)_4$ the ligand was in excess concentration and the reaction was followed by measuring the increase of the band at 2152 cm^{-1} (ν(CN) of coordinated $C_6H_{11}NC$). As the solution of $Pt(PF_3)_4$ and $C_6H_{11}NC$ was warmed from −196° and transferred to the reaction cell, the experimental zero time could not be determined with accuracy. However the rate plot was linear for a sufficient period of time to allow extrapolation of the rate curve to zero time. The substitution of a second PF_3 group occurred more rapidly than for $Ni(PF_3)_4$, but the rate of increase of the band at 2152 cm^{-1} was constant over a sufficient period to allow accurate rate data to be obtained. The rate constants are considered to be accurate within the limits ±5%.

Rate constants and activation parameters were calculated using simple least-squares techniques on the Northwestern University CDC 6400 computer.

Tris(trifluorophosphine)(cyclohexyl isocyanide)nickel(0).—A sample of $Ni(PF_3)_4$ was purified by trap-to-trap distillation under high vacuum, and then 1.64 g (4 mmol) was condensed into a Schlenk tube. The tube was filled with argon, $C_6H_{11}NC$ (0.33 g, 3 mmol) in 15 ml of *n*-hexane was added *via* a syringe, and the solution was heated with stirring to 45° until samples of the solution showed no trace of the ν(CN) of free $C_6H_{11}NC$ in their infrared spectrum (*ca.* 5 hr). During this time a bulky yellow solid precipitated. The solution was cooled to 0° and unreacted $Ni(PF_3)_4$ was removed by distillation under vacuum. At room temperature the hexane was removed by distillation and the yellow residue was extracted with ether under an argon atmosphere. The yellow residue showed an ir absorption at 1650 cm^{-1}, identifying it as the linear polymer $(C_6H_{11}NC)_n$.[15] Addition of hexane to the ether solution resulted only in an oil, so the ether was removed, and the residue was dissolved in a large volume of hexane, filtered, and evaporated to dryness at 0°. Repeated treatment by this method led to the isolation of a pale yellow powder which was dried under vacuum. The yield was 0.52 g (31.7% based on $Ni(PF_3)_4$). *Anal.* Calcd for $C_7H_{11}NF_9P_3Ni$: C, 19.47; H, 2.57; N, 3.24; Ni, 13.59. Found: C, 19.64; H, 2.70; N, 3.28; Ni, 13.41. The ν(CN) band was observed at 2169 cm^{-1} and ν(PF) absorptions were at 860 (vs), 827 (vs), and 807 cm^{-1} (vs).

Tris(trifluorophosphine)(cyclohexyl isocyanide)platinum(0).—A sample of $Pt(PF_3)_4$ was purified by trap-to-trap distillation and then 1.1 g (2 mmol) was condensed into a Schlenk tube. The tube was filled with argon and cyclohexyl isocyanide (0.16 g, 1.5 mmol) in 10 ml of *n*-hexane added *via* a syringe, and the solution was stirred at room temperature. A pale yellow precipitate rapidly formed and after 30 min there was no evidence in the ir spectrum of the presence of free ligand. The solution was cooled to 10° and the unreacted $Pt(PF_3)_4$ and subsequently the solvent were removed by distillation under vacuum. The residue was extracted with ether, leaving a small amount of a pale yellow residue identified as $(C_6H_{11}NC)_n$ by its ir absorption at 1645 cm^{-1}.[15] The ether solution was filtered and a layer of pentane was added. On standing at 0°, a microcrystalline off-white solid deposited. The yield was 0.41 g (36.1% based on $Pt(PF_3)_4$). *Anal.* Calcd for $C_7H_{11}NF_9P_3Pt$: C, 14.80; H, 1.95; N, 2.47; Pt, 34.34. Found: C, 14.93; H, 2.02; N, 2.51; Pt, 33.92. The ν(CN) band was observed at 2152 cm^{-1} and the ν(PF) absorptions were at 878 (vs), 838 (vs), and 815 cm^{-1} (vs).

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed in these laboratories by Miss H. E. Beck on an F & M carbon–hydrogen–nitrogen analyzer, Model 185. Nickel analyses were carried out gravimetrically by dimethylglyoxime precipitation. Platinum was determined by combustion of the compound to 700°.

Results

Ligand Substitution between $Ni(PF_3)_4$ and $C_6H_{11}NC$.—The rate of ligand substitution between $Ni(PF_3)_4$ and cyclohexyl isocyanide was measured in *n*-heptane and toluene solutions by following the decay of the band at 2138 cm^{-1} due to the NC stretch of the free isocyanide. The decay of this band was accompanied by the growth of a band at 2169 cm^{-1}, which was assigned to the ν(NC) of coordinated $C_6H_{11}NC$ in $Ni(PF_3)_3(C_6H_{11}NC)$. The assignment was confirmed by the isolation of this compound. Data were collected from the beginning of the reaction until *ca.* 75% of the isocyanide had been consumed, in order to avoid erroneous absorbance measurements due to formation of small amounts of the disubstituted compound. Rate constants were calculated from the slopes of the linear plots of log ($A - A_\infty$) *vs.* time and are collected in Tables I and II. It can be seen that changes in the initial concentration of cyclohexyl isocyanide have no effect on the reaction rate. Rate constants for reaction in toluene are about twice those for reaction in the aliphatic solvent.

TABLE I

RATES OF REACTION OF $Ni(PF_3)_4$ WITH $C_6H_{11}NC$ IN *n*-HEPTANE[a]

$10^2[Ni(PF_3)_4]$, *M*	$10^3[C_6H_{11}NC]$, *M*	Temp, °C	10^5k, sec^{-1}
5.49	21.3	54.70	9.18
5.49	7.73	54.70	9.30
5.49	3.33	52.30	6.58
6.57	13.8	52.20	5.88
6.57	7.73	50.50	5.18
6.57	7.73	50.50	5.30
5.29	21.3	50.50	5.41
5.29	3.33	47.20	3.16
5.07	21.3	47.20	3.22
5.07	4.62	45.45	2.28
5.07	13.8	45.45	2.29
4.89	4.62	40.20	1.23
4.89	13.8	40.20	1.05

[a] $\Delta H^* = 29.1 \pm 1.0$ kcal/mol; $\Delta S^* = 13.8 \pm 2.0$ eu.

Attempts were made to study the substitution reaction of $Ni(PF_3)_4$ with phenyl isocyanide, but the latter was polymerized at such a rate that measurements of a substitution reaction were not possible. The reaction with carbon monoxide was also examined. After the

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[15] Y. Yamamoto, T. Takizawa, and N. Hagihara, *Nippon Kagaku Zasshi*, **87**, 1355 (1966).

TABLE II

RATES OF REACTIONS OF $Ni(PF_3)_4$ WITH $C_6H_{11}NC$ IN TOLUENE[a]

$10^2[Ni(PF_3)_4]$, *M*	$10^2[C_6H_{11}NC]$, *M*	Temp, °C	10^5k, sec^{-1}
5.32	4.25	54.70	17.3
5.32	17.3	52.50	12.8
4.76	8.28	47.20	6.09
4.76	17.3	47.20	6.16
4.51	4.25	45.45	4.82
4.51	17.3	45.45	4.74
9.41	8.28	39.80	2.07
9.41	17.3	37.50	1.48

[a] $\Delta H^* = 28.4 \pm 1.1$ kcal/mol; $\Delta S^* = 10.7 \pm 1.9$ eu.

substitution of the first PF_3 group with CO, a second group was also rapidly replaced, but the relative rates of these two reactions were such that no steady-state conditions were achieved and hence no simple study of the kinetics of these reactions could be made.

Ligand Substitution between $Pt(PF_3)_4$ and $C_6H_{11}NC$.—The rate of ligand substitution between $Pt(PF_3)_4$ and cyclohexyl isocyanide was measured in *n*-hexane and toluene solutions by following the growth of the band at 2152 cm^{-1}. This band was assigned to the NC stretching vibration of $Pt(PF_3)_3(CNC_6H_{11})$ and the isolation of this compound confirmed this assignment. Data were collected until the band at 2152 cm^{-1} reached its maximum absorbance and this value was taken as A_∞. Subsequently this band decreased as the second substitution took place. Plots of log $(A - A_\infty)$ *vs.* time were linear over 80% of this time and rate constants could be calculated from this linear section of the plot. The results for these substitution reactions in *n*-hexane and toluene are collected in Tables III and IV, respectively. The data show that the reactions follow a first-order law with respect to the complex irrespective of the concentration of the isocyanide ligand. As for $Ni(PF_3)_4$, reactions in the aromatic solvent have rate constants approximately double those in aliphatic solvents.

TABLE III

RATES OF REACTION OF $Pt(PF_3)_4$ WITH $C_6H_{11}NC$ IN *n*-HEXANE[a]

$10^2[Pt(PF_3)_4]$, *M*	$10[C_6H_{11}NC]$, *M*	Temp, °C	10^3k, sec^{-1}
2.21	1.96	−2.30	0.89
2.21	0.328	−1.40	1.03
1.67	0.741	0.80	1.47
1.67	1.96	0.80	1.53
1.67	1.08	2.00	1.91
1.67	2.45	2.00	1.80
2.73	0.328	2.00	1.86
2.56	1.08	3.20	2.23
2.56	0.328	3.40	2.16
2.73	0.741	6.55	3.79
2.56	2.45	6.55	3.84
2.73	1.08	6.65	4.02
2.21	0.741	10.60	7.47
2.21	1.08	10.70	7.19
1.74	0.328	13.30	11.0
1.74	2.45	13.30	11.0

[a] $\Delta H^* = 24.4 \pm 0.6$ kcal/mol; $\Delta S^* = 17.6 \pm 2.2$ eu.

The reaction of $Pt(PF_3)_4$ with carbon monoxide at 0° was also examined, but no band characteristic of coordinated CO could be detected. If substitution did take place, then the product was so unstable that the coordinated carbon monoxide was immediately released.[3]

TABLE IV

RATES OF REACTION OF $Pt(PF_3)_4$ WITH $C_6H_{11}NC$ IN TOLUENE[a]

$10^2[Pt(PF_3)_4]$, *M*	$10[C_6H_{11}NC]$, *M*	Temp, °C	10^3k, sec^{-1}
4.97	0.512	0.80	3.28
4.97	1.13	0.80	3.40
4.38	7.24	0.80	3.52
4.38	0.512	5.40	6.75
4.38	2.62	5.40	6.97
5.04	0.512	9.20	11.6
5.04	1.13	9.20	12.4
4.73	1.13	13.50	21.0
4.73	2.62	13.50	22.1
4.73	7.24	13.50	23.4

[a] $H^* = 22.5 \pm 0.9$ kcal/mol; $\Delta S^* = 12.3 \pm 1.4$ eu.

As $Pd(PF_3)_4$ decomposes above −20°,[12] it was not possible to complete the study of the tetrakis(trifluorophosphine)metal(0) complexes of the nickel triad.

Discussion

On the basis of the observed first-order rate laws for the substitution reactions of $Ni(PF_3)_4$ and $Pt(PF_3)_4$, the most plausible mechanism for reaction 1 consists of a rate-determining dissociation of a PF_3 group (eq 2), followed by rapid addition of the isocyanide ligand (eq 3). The values of the activation parameters also suggest a dissociative activation step. The enthalpies of activation of the substitution reactions of $Ni(PF_3)_4$ (29 kcal/mol) and $Pt(PF_3)_4$ (24 kcal/mol) would appear to be *reasonable* values for the rupture of an Ni–P and a Pt–P bond, respectively. The positive entropies of activation are also consistent with this SN1 process.

$$M(PF_3)_4 \xrightarrow{k_{sub}} M(PF_3)_3 + PF_3 \quad \text{(slow)} \tag{2}$$

$$M(PF_3)_3 + L \longrightarrow M(PF_3)_3L \quad \text{(fast)} \tag{3}$$

A number of studies of substitution reactions of complexes of the zerovalent metals of the nickel triad have shown these reactions to occur by a dissociation process. The exchange and substitution reactions of $Ni(CO)_4$ have been shown to take place by a first-order process involving the active intermediate $Ni(CO)_3$.[8] Similarly, the exchange reactions of $Pt[P(OC_2H_5)_3]_4$ and $Pd[P(OC_2H_5)_3]_4$ and the substitution reactions of $Ni[P(OC_2H_5)_3]_4$ have been shown to occur *via* a dissociative mechanism.[10] The solid $Pt[P(C_6H_5)_3]_4$ dissolves to give solutions containing largely the tris species $Pt[P(C_6H_5)_3]_3$.[16] The observation that these tetrahedral compounds react by an SN1 rather than an SN2 process has been explained[17] in terms of the repulsive interaction which the filled d orbitals may offer to any attacking nucleophilic reagent.

Comparison of the rate constants of Table I with Table II shows that the rate of dissociation of $Ni(PF_3)_4$ is faster, and its activation energy is slightly less in toluene than in heptane solution. A similar effect is in

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[16] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

[17] F. Basolo and A. Wojcicki, *ibid.*, **83**, 520 (1961).

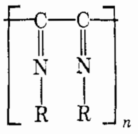
evidence for the rate constants of the substitution reactions of $Pt(PF_3)_4$. This solvent effect has been noticed for the reactions of $Ni(CO)_4$[8,18] and of $Ni[P(OC_2H_5)_3]_4$.[10] It is suggested that the aromatic solvent has a greater stabilizing influence on the tricoordinate intermediates than an aliphatic solvent.

The enthalpies of activation obtained in this study provide a quantitative measure of the relative metal–phosphorus bond strengths in $Ni(PF_3)_4$ and $Pt(PF_3)_4$. The decomposition temperatures of the $M(PF_3)_4$ compounds of the nickel triad have been reported[3] as follows: Ni, >155°; Pd, >−20°; Pt, >90°. Concluding from these data that the Pd–P bond is weaker than Ni–P and Pt–P, a similar ordering is obtained for the enthalpies of activation for metal–phosphorus bond rupture: Ni > Pd < Pt. The enthalpies of activation are not directly comparable to bond energies, but it is probable that the relative order of bond strengths is valid.

This ordering is the same as that obtained in the $M[P(OC_2H_5)_3]_4$ series,[10] except that in the case of the $M(PF_3)_4$ system, the metal–phosphorus bond strength in the nickel compound is considerably greater than that of the platinum compound. This trend of stability, in which the compound of the 4d transition metal is less stable and more reactive than the analogous compounds of the third-row and fifth-row metals, is not uncommon in the low-valent complexes of the transition metals.[19,20]

An explanation for this behavior rests on the contribution of both σ and π bonding to the metal–ligand bond strength in complexes of low-valent metals. Electronegativity is considered to increase down a triad of transition metals, so the strongest σ bonds are expected to be formed by a 5d metal. On the other hand, π bonding is thought to be greatest for the first-row transition metals and decrease down the triad. Evidence for this is supplied by the stability of $Ni(CO)_4$ and the inability to prepare the corresponding tetracarbonyls of Pd(0) and Pt(0). Nyholm[21] has argued that on the basis of the ionization potentials of the metal atoms in the spin-paired states ($d^{10} \rightarrow d^9$) the abilities to form dπ bonds decreased in the order Ni ≫ Pt ≥ Pd. Thus considering both σ and π bonding, the stability of $Ni(PF_3)_4$ is due primarily to π bonding and that of $Pt(PF_3)_4$ to σ bonding. The instability of the $Pd(PF_3)_4$ can be attributed to the small tendency of Pd to π bond and its intermediate tendency to σ bond. The fact that for the $M(PF_3)_4$ series the Ni–P bond strength is greater than the Pt–P bond whereas for the $M[P(OC_2H_5)_3]_4$ compounds the values are similar indicates that for the compounds of PF_3, π bonding is more important than σ bonding. This is in agreement with PF_3 being a better π-acceptor ligand than $P(OC_2H_5)_3$.[22]

Isocyanide Polymerization.—It is well known that alkyl and aryl isocyanides polymerize on heating to produce poly Schiff bases (I).[23] In the presence of $Pt(PF_3)_4$ and particularly $Ni(PF_3)_4$, the rate of this polymerization reaction was sharply increased. The polymerization of isocyanides has been shown to be catalyzed by metal carbonyl and organometallic compounds,[15] and apparently trifluorophosphine complexes can also cause coordination polymerization of isocyanides.



I

Infrared Spectral Studies.—Malatesta and Bonati[23] have stated that coordination of an isocyanide to a transition metal in a low oxidation state causes a lowering of the frequency of the CN stretching vibration. This is consistent with significant electron flow from the metal d orbitals into the π* orbitals of the ligand, analogous to the situation in other π-bonding ligands. However this study reveals that in $Ni(PF_3)_3(CNC_6H_{11})$ the ν(CN) vibration is raised from 2138 to 2169 cm^{-1}, and in $Pt(PF_3)_3(CNC_6H_{11})$ the ν(CN) occurs at 2152 cm^{-1}.

This increase in the CN stretching frequency indicates that there is no significant electron transfer into the π* orbitals of the ligand. In these compounds isocyanide ligands act simply as σ donors. The π-acceptor ability of CO and PF_3 is so much greater than that of the isocyanides that the metal–isocyanide bond has essentially no double-bond character. Monosubstitution of $Ni(PF_3)_4$ and $Pt(PF_3)_4$ with a ligand that is a much poorer π-acceptor than PF_3 should lead to an increase in the double-bond character of the remaining metal–phosphorus bonds. This is indeed the case as shown by the shift to lower energy of the ν(PF) vibration of $Ni(PF_3)_3(NCC_6H_{11})$ compared with $Ni(PF_3)_4$ ($\Delta\nu = 44\ cm^{-1}$) and of $Pt(PF_3)_3(NCC_6H_{11})$ compared with $Pt(PF_3)_4$ ($\Delta\nu = 28\ cm^{-1}$); this lowering of ν(PF) is indicative of a decrease in the electron density of the P–F π orbital.[24-26]

The increase in the metal–phosphorus bond strength on substitution of one PF_3 group with $C_6H_{11}NC$ also provides an explanation for the observation that substitution of a second PF_3 group occurs much more slowly than replacement of the first group by isocyanide in $M(PF_3)_4$ compounds. This is in contrast to the reaction of $Ni[P(OC_2H_5)_3]_4$ with $C_6H_{11}NC$, in which the monosubstituted compound could not be detected and only $Ni[P(OC_2H_5)_3]_2(CNC_6H_{11})_2$ was isolated.[10] The phosphites are known to be poorer π acceptors than PF_3[22] and this is confirmed by the large shift to lower frequencies of the CN stretching vibration of $Ni[P(OC_2H_5)_3]_2(CNC_6H_{11})_2$ compared with the free ligand.[10]

The Nature of the Metal–Phosphorus Trifluoride

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Bond.—Since the first phosphorus trifluoride complex was prepared,[5] it has generally been assumed that CO and PF_3 have much in common as ligands, since the bonding possibilities of the two are similar, and a number of studies have confirmed this viewpoint.[27–29]

The data obtained in this study of the substitution reactions of $Ni(PF_3)_4$ and $Pt(PF_3)_4$ provide new insight into the nature of the metal–PF_3 bond and its supposed similarity to metal–CO bonds. The activation parameters for substitution reactions of CO–, PF_3–, and $P(OC_2H_5)_3$–metal complexes of the nickel triad are collected in Table V. The first obvious conclusion to be drawn from these data is that in activation enthalpies, and hence presumably in bond strengths, the PF_3 complexes are more similar to the $P(OC_2H_5)_3$ complexes than to the CO complexes. It is suggested that the better π-acceptor ability of PF_3 makes up for its poorer σ-donor strength, when compared with $P(OC_2H_5)_3$, resulting in similar metal–phosphorus bond strengths.

Table V

Rate Constants and Activation Parameters for Substitution Reactions of ML_4 Complexes in Toluene

	L		
	CO[a]	PF_3[b]	$P(OC_2H_5)_3$[c]
		M = Ni	
$k(25°)$, sec^{-1}	2.03×10^{-2}	2.06×10^{-6}	9.94×10^{-7}
ΔH^*, kcal/mol	22.3 ± 0.2	28.4 ± 1.1	26.2 ± 1.0
ΔS^*, eu	8.4 ± 1	10.7 ± 1.9	1.8 ± 3.0
		M = Pd	
$k(25°)$, sec^{-1}	...	...	2.07×10^{3}
ΔH^*, kcal/mol	...	...	22.0 ± 2.3
ΔS^*, eu	...	...	30.4 ± 8.6
		M = Pt	
$k(25°)$, sec^{-1}	...	1.05×10^{-1}	2.60×10^{-2}
ΔH^*, kcal/mol	...	22.5 ± 0.9	27.5 ± 1.6
ΔS^*, eu	...	12.3 ± 1.4	26.8 ± 4.4

[a] Reference 8. [b] This work. [c] Reference 10.

Comparison of the enthalpies of activation for metal–ligand bond rupture in $Ni(PF_3)_4$ and $Ni(CO)_4$ indicates that the metal–PF_3 bond is considerably stronger than the metal–CO bond. Of course the enthalpies of activation are not equal to the bond dissociation energies unless the activation energies for the reverse reaction of eq 2 are zero. However in comparison of $Ni(CO)_4$ and $Ni(PF_3)_4$, it is considered unlikely that the activation energies of recombination of $Ni(CO)_3$ with CO and $Ni(PF_3)_3$ with PF_3 have very different values, and hence the activation enthalpies should provide a reasonably good measure of the relative metal–ligand bond strengths.

It must also be noted that in these dissociative reactions the CO and PF_3 are leaving different residues; *i.e.*, CO dissociates leaving $Ni(CO)_3$ and PF_3 dissociates leaving $Ni(PF_3)_3$. It would clearly be desirable to have data in which CO and PF_3 leave from a common residue. In any case it appears that the assumption that carbon monoxide and phosphorus trifluoride have very similar bonding properties should be viewed with considerable caution.

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Catalatic Activity of Metal Chelates and Mixed-Ligand Complexes in the Neutral pH Region. III. Copper Chelates with Bidentate and Tetradentate Amines

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The catalytic decomposition of hydrogen peroxide, *i.e.*, catalatic reaction, in phosphate buffer by Cu(II) chelates of ethylenediamine (en), 1,3-diaminopropane (DAP), and triethylenetetramine (TETA) has been investigated from the initial rates of O_2 evolution using a differential manometric technique. The rates of O_2 evolution are first order with respect to the 1:1 metal–ligand chelates of copper with the diamines and HOO^-. The chelates of DAP or histamine which form six-membered rings with Cu(II) appear more active than the five-membered chelate ring of Cu(II)–en. The four-coordinated Cu(II)–TETA complex possesses little catalatic activity. For the reaction of hydrogen peroxide with Cu(II) complexes to proceed, the data suggest that (1) the copper complex must have a suitable redox potential to facilitate electron transfer from the peroxide anion to the central metal ion and (2) the complex must possess two adjacent free sites to facilitate the reaction of the intermediate $L–Cu–OOH^+$ with a second peroxide anion.

Introduction

In previous communications[1–3] on the kinetics of decomposition of hydrogen peroxide by copper complexes and chelates, we observed that the reaction appeared to involve a Cu(II)–Cu(I) couple. Factors controlling the oxidation–reduction potential of copper complexes, therefore, should also control the catalatic (*i.e.*, catalase-like) activity of these complexes.

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