Tris(hexafluoroacetylacetonato)cobalt(III).—Initially 1.1 g (26 mmol) of powdered sodium fluoride, which had been dried at 110° for 3 hr followed by cooling under vacuum, was dissolved in 18.0 g (86.5 mmol) of hexafluoroacetylacetone which had been dehydrated as described above. One gram (8.7 mmol) of CoF_3 was added to the solution and after approximately 1 min of gentle swirling the solution turned dark green. The solution was kept at room temperature for 12 hr. All transfers and weighings were performed in a dry nitrogen glove bag and the reaction vessels were removed only when stoppered. The excess ligand was vacuum distilled from the solid at 25°. The dark green complex sublimed directly from the reaction vessel into an air-cooled glass column upon being heated to 45–50° in an oil bath; yield 2.6 g, 44%; mp 98–99° (lit. mp 93–94°,[8] 94–95°[9]). *Anal.* Calcd for $C_{15}H_3O_6CoF_{18}$: C, 26.47; H, 0.44; mol wt, 680. Found: C, 26.75; H, 0.60; mol wt, 775.[33]

Infrared Spectra.—All infrared spectra were obtained on a Beckman Model IR-10 infrared spectrophotometer. Potassium bromide disks of the solids were used for recording spectra while the spectra of the ligands were recorded neat between sodium chloride plates.

Visible–Ultraviolet Spectra.—The visible and ultraviolet spectra of all of the complexes were obtained with a Coleman Model EPS-3T Hitachi ratio recording spectrophotometer using methanolic solutions wherever possible in 1-cm cells. The spectra of $Co(hfa)_3$ were obtained in tetrahydrofuran and methylene chloride which had been dried over and distilled from CaH_2.

Proton Magnetic Resonance Spectra.—Proton magnetic resonance spectra were obtained with a Varian A-60 high-resolution spectrometer at 60 Mc using tetramethylsilane as an internal standard. The bis(acetylacetonato)(ethylenediamine)cobalt(III) perchlorate spectrum was also recorded by Varian Associates on a Varian HA-100 high-resolution spectrometer at 100 Mc in D_2O using tetramethylsilane as an external standard.

Molecular Weights.—Molecular weights of neutral complexes were obtained with a Mechrolab vapor-phase osmometer (Model 301A) with a 25° probe using reagent grade benzene solutions. The instrument was calibrated using benzene solutions of benzil.

Chromatographic Substrates.—For the column chromatography separation Silica Gel Woelm (M. Woelm, Eschwege, Germany) was used after presoaking in hexane. The thin layer chromatographic plates were prepared from aqueous suspensions of Silica Gel D-5 (Camag, Muttenz, Switzerland), dried at room temperature for 2–3 hr, and then dried at 100° for 4 hr.

Acknowledgments.—The authors wish to acknowledge the support of the National Science Foundation. We also wish to thank Mr. Charles Meade for his expedience and thoroughness, Dr. D. W. Moore of China Lake, Calif., for the ^{19}F spectrum of $Co(hfa)_3$, Mr. Norman S. Bhacca of Varian Associates for checking the $Co(acac)_2en^+$ pmr spectra in D_2O at both 60 and 100 Mc, and Dr. Robert Fay for stimulating discussion and a relevant preprint.

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(33) The molecular weight was obtained in benzene in which the solubility of $Co(hfa)_3$ is low. The measurements were actually made at concentrations well below the accepted limits of the instrument.

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Rates of Substitution Reactions of Tetrakis(triethyl phosphite)metal(0) Compounds of the Nickel Triad

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The rate of ligand substitution between tetrakis(triethyl phosphite)nickel(0) and cyclohexyl isocyanide has been studied in *n*-hexane and benzene solutions by infrared spectroscopy. The reaction is first order in complex concentration and independent of the isocyanide concentration. The activation parameters are $\Delta H^{\ddagger} = 32$ kcal/mol and $\Delta S^{\ddagger} = +19$ eu in *n*-hexane solution and $\Delta H^{\ddagger} = 27$ kcal/mol and $\Delta S^{\ddagger} = +2$ eu in benzene. Tetrakis(triethyl phosphite)palladium(0) and tetrakis(triethyl phosphite)platinum(0) were prepared and the rates of ligand exchange between these complexes and free triethyl phosphite were studied in toluene solution by proton magnetic resonance. For both complexes the exchange reaction is first order in complex concentration and independent of the concentration of free phosphite. The activation parameters [$\Delta H^{\ddagger} = 22$ kcal/mol and $\Delta S^{\ddagger} = +30$ eu for the exchange reaction between $Pd[P(OC_2H_5)_3]_4$ and $P(OC_2H_5)_3$; $\Delta H^{\ddagger} = 26$ kcal/mol and $\Delta S^{\ddagger} = +24$ eu for the reaction between $Pt[P(OC_2H_5)_3]_4$ and $P(OC_2H_5)_3$] are compatible with a dissociative (SN1) mechanism. These results show that the activation energies for M–P bond rupture in the compounds $M[P(OC_2H_5)_3]_4$ vary in the order Ni > Pd < Pt.

Introduction

Complexes of zerovalent nickel, palladium, and platinum with phosphites or phosphines as ligands have been known for several years.[1] However, there is as yet no quantitative information on the M–P bond strengths in these systems. The experiments reported in this paper were carried out with the objective of studying the kinetics of ligand exchange or ligand substitution reactions for the nickel triad series of $M[P(OC_2H_5)_3]_4$ and to obtain data on the M–P bond dissociation energy.

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(1) L. Malatesta, R. Ugo, and S. Cenini, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 318.

Experimental Section

Materials.—*n*-Hexane, benzene, and toluene (all Baker Analyzed reagents) were refluxed over and distilled from potassium under a nitrogen atmosphere and stored under argon or nitrogen. Cyclohexane (Eastman Spectro Grade) was used without further purification. Triethyl phosphite (Eastman) was distilled under vacuum prior to use.

Cyclohexyl isocyanide was prepared from cyclohexylamine, chloroform, and potassium hydroxide according to Malatesta.[2] Potassium tetrachloropalladate(II) was prepared by dissolving stoichiometric amounts of KCl and $PdCl_2$ (Engelhard Industries, Inc.) in water and subsequent precipitation of K_2PdCl_4 with acetone. K_2PtCl_4 was prepared from elemental platinum by standard literature techniques.[3]

Tetrakis(triethyl phosphite)nickel(0).—$Ni[P(OC_2H_5)_3]_4$ was prepared according to the method of Vinal and Reynolds.[4] Diethylamine was slowly added with stirring to an ice-cooled solution of 5 g of $NiCl_2 \cdot 6H_2O$ and 18 ml of triethyl phosphite in 100 ml of methanol, until the red color of the solution faded to pink. The white crystals were collected on a filter, washed with cold methanol, and dried under vacuum. *Anal.* Calcd for $C_{24}H_{60}O_{12}P_4Ni$: C, 39.83; H, 8.30. Found: C, 39.92; H, 8.36.

Tetrakis(triethyl phosphite)palladium(0).—A saturated aqueous solution of K_2PdCl_4 (330 mg, 1 mmol) at room temperature was added to a solution containing triethyl phosphite (840 mg, 5 mmol) in 3 ml of methanol. The resulting yellow solution was cooled in an ice–water bath and 150 mg of diethylamine (2 mmol) was slowly added with stirring. The white precipitate was filtered, washed with an ice-cooled 50% methanol–water mixture, and immediately dried under vacuum (mp 65 °dec). *Anal.* Calcd for $C_{24}H_{60}O_{12}P_4Pd$: C, 37.35; H, 7.87. Found: C, 37.39; H, 7.84. $Pd[P(OC_2H_5)_3]_4$ is insoluble in water, somewhat soluble in methanol, and very soluble in hydrocarbons.

Tetrakis(triethyl phosphite)platinum(0).—The method used for the preparation of $Pt[P(OC_2H_5)_3]_4$ is analogous to the procedure described for the preparation of $Pt[P(OC_6H_5)_3]_4$.[5] A saturated aqueous solution of K_2PtCl_4 (1.24 g, 3 mmol) at room temperature was slowly added with vigorous stirring to a warm (60°) solution of triethyl phosphite (2.5 g, 15 mmol) in ethanol containing potassium hydroxide (350 mg, 6 mmol). Within a few minutes colorless crystals separated. The precipitate was filtered, washed with a 50% ethanol–water mixture, and dried under vacuum (mp 114°). *Anal.* Calcd for $C_{24}H_{60}O_{12}P_4Pt$: C, 33.53; H, 7.03. Found: C, 33.24; H, 7.06. $Pt[P(OC_2H_5)_3]_4$ is insoluble in water, slightly soluble in methanol, and very soluble in hydrocarbons.

Kinetic Measurements. ^{1}H Nmr Spectra.—The spectra were obtained in toluene solutions under an argon atmosphere using a Varian A-60 spectrometer equipped with a variable-temperature probe. Temperature readings were obtained from the peak separations of methanol or ethylene glycol. Saturation effects were avoided by using a low-radiofrequency power.

Infrared Spectra.—The spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. The runs were conducted as follows. The reaction flask connected to an argon- or nitrogen-filled balloon and equipped with a side arm for the introduction of a syringe was flushed with inert gas and placed in a constant-temperature bath. A measured volume of a prethermostated solution containing a known concentration of $Ni[P(OC_2H_5)_3]_4$ was introduced into the reaction flask. At zero time a measured volume of prethermostated cyclohexyl isocyanide solution of known concentration was injected into the flask. At timed intervals small samples were withdrawn into the syringe and transferred into a 1-mm NaCl cell. A compensating cell containing only the solvent was placed in the other beam of the instrument. The spectrum of the sample was recorded in the C–N stretching region (2200–1900 cm^{-1}).

Molecular Weights.—Measurements were performed by Miss H. E. Beck on cyclohexane solutions at 37° with a Mechrolab Model 302 osmometer.

Analyses.—Carbon and hydrogen determinations were carried out in these laboratories by Miss H. E. Beck on an F & M Carbon Hydrogen Nitrogen Analyzer, Model 185.

Results

Ligand Exchange in the System $Pt[P(OC_2H_5)_3]_4$–$P(OC_2H_5)_3$.—The ^{1}H nmr spectrum of triethyl phosphite shows the same pattern as the triethyl phosphate spectrum.[6] The methyl resonance of $Pt[P(OC_2H_5)_3]_4$ consists of the same well-resolved triplet (J = 7 cps) as the methyl resonance of free triethyl phosphite but is shifted 7 cps (at 60 Mcps) downfield with respect to the latter (Figure 1). In the spectrum of a solution containing $Pt[P(OC_2H_5)_3]_4$ at a concentration of 2.5×10^{-2} M no free triethyl phosphite is detected. Therefore the complex does not dissociate extensively. The spectrum of solutions containing the complex and free triethyl phosphite consists of the superposition of the spectra of the two components. At temperatures over 50° the lines broaden, they coalesce at 70°, and at still higher temperatures the methyl triplet appears at the average position (Figure 2). In the temperature range below coalescence the line widths of lines a and b are related to the average lifetime τ_c of a phosphite molecule in the complex and the average lifetime τ_f of a ligand molecule in the free state: $W_a = W^0{}_a + (\pi\tau_c)^{-1}$ and $W_b = W^0{}_b + (\pi\tau_f)^{-1}$, where W is the observed line width at half-height and W^0 is the line width in absence of exchange, both measured in cps. In order to determine the rate law for the exchange reaction, the spectra of the following solutions (C, concentration of complex; L, concentration of free phosphite) were recorded at 61°: $C = 9 \times 10^{-2}\,M$, $L = 3.6 \times 10^{-1}\,M$; $C = 9 \times 10^{-2}\,M$, $L = 1.8 \times 10^{-1}\,M$; $C = 9 \times 10^{-2}\,M$, $L = 9 \times 10^{-2}\,M$; $C = 4.5 \times 10^{-2}\,M$, $L = 9 \times 10^{-2}\,M$; $C = 4.5 \times 10^{-2}\,M$, $L = 3.6 \times 10^{-1}\,M$. The width of line a (due to the complex) was the same for all solutions within experimental uncertainty, *i.e.*, independent of the complex concentration as well as of the concentration of free ligand, and the width of line b (due to free phosphite) is determined by the ratio of complex concentration and free ligand concentration according to[7]

$$\frac{1}{\tau_c} = k \text{ and } \frac{1}{\tau_f} = k\frac{4[Pt(P(OC_2H_5)_3)_4]}{[P(OC_2H_5)_3]}$$

Therefore the reaction is first order in platinum complex and zero order in free triethyl phosphite.

In the temperature range above coalescence the line widths were evaluated by using[8]

$$(\pi\partial\nu\tau)^{-1} = \{(W^0/\partial\nu) + (W/\partial\nu)\,[1 + 2(W/\partial\nu)^2 - (W^0/\partial\nu)^4]^1/_2\}[(W/\partial\nu)^2 - (W^0/\partial\nu)^2]^{-1}$$

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(2) L. Malatesta, *Gazz. Chim. Ital.*, **77**, 237 (1949).

(3) W. E. Cooley and D. H. Busch, *Inorg. Syn.*, **5**, 208 (1957).

(4) R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, **3**, 1062 (1964).

(5) L. Malatesta and C. Cariello, *J. Chem. Soc.*, 2323 (1958).

(6) "NMR Spectra Catalog," Vol. 2, Varian Associates, 1963, Spectrum No. 482.

(7) D. R. Eaton and S. R. Stuart, *J. Am. Chem. Soc.*, **90**, 4170 (1968).

(8) A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *ibid.*, **88**, 3185 (1966).

Here $\delta\nu$ is the chemical shift in the absence of exchange. For a discussion of the accuracy of the above formula see 8.

Spectra recorded near the coalescence temperature were not evaluated because overlap of the lines did not allow the measurement of line widths. Activation parameters were calculated from data collected below and above coalescence separately (Table I).

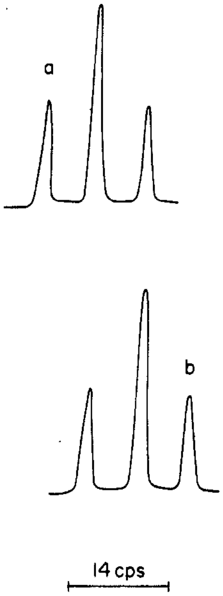

Figure 1.—Top: methyl resonance of $Pt[P(OC_2H_5)_3]_4$ recorded on a 9×10^{-2} *M* solution. Bottom: methyl resonance of $P(OC_2H_5)_3$ recorded on a 3.6×10^{-1} *M* solution. The letters a and b refer to the text.

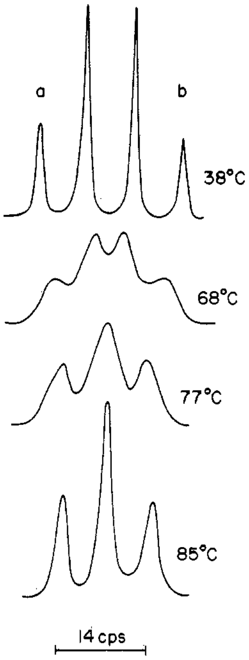

Figure 2.—Spectra of a solution containing $Pt[PO(C_2H_5)_3]_4$ in a concentration of 9×10^{-2} *M* and free $PO(C_2H_5)_3$ in a concentration of 3.6×10^{-1} *M* recorded at different temperatures.

TABLE I

RATES OF $P(OC_2H_5)_3$ EXCHANGE WITH $Pt[P(OC_2H_5)_3]_4$ IN TOLUENE FOR 0.090 *M* $Pt[P(OC_2H_5)_3]_4$ AND 0.360 *M* $P(OC_2H_5)_3$

Below coalescence temp		Above coalescence temp	
Temp, °C	k, sec^{-1}	Temp, °C	k, sec^{-1}
51.0	1.3	76.5	35
54.0	1.6	79.0	45
56.0	2.0	81.0	53
61.0	3.5	82.0	
64.5	5.3	84.8	90
68.3[a]	10.6	$\Delta H^\ddagger = 27.5 \pm 1.6$ kcal/mol[b]	
$\Delta H^\ddagger = 26.2 \pm 1.5$ kcal/mol[b]		$\Delta S^\ddagger = +26.8 \pm 4.4$ eu[b]	
$\Delta S^\ddagger = +22.3 \pm 4.6$ eu[b]			

[a] Rate determined from the width of line b for a solution 0.045 *M* in $Pt[P(OC_2H_5)_3]_4$ and 0.360 *M* in $P(OC_2H_5)_3$. [b] The deviations given equal one standard deviation.

At temperatures below 50°, where the lines are not broadened, and at 90°, where exchange is very fast, the line width of the CH_3 peak of toluene was found to be the same as the width of the lines constituting the triplets. Therefore, the CH_3 peak of toluene was also recorded on each spectrum and its line width at half-height was equal to W^0 for each measurement.

Ligand Exchange between $Pd[P(OC_2H_5)_3]_4$ and $P(OC_2H_5)_3$.—The same experimental and evaluation procedures were used for the study of the $Pd[P(OC_2H_5)_3]_4$–$P(OC_2H_5)_3$ system. The methyl triplet of $Pd[P(OC_2H_5)_3]_4$ is shifted 9 cps downfield with respect to the methyl triplet of the free phosphite. At −40° the spectra of solutions containing only $Pd[P(OC_2H_5)_3]_4$ show no lines attributable to free phosphite. Mixtures of the complex and the free ligand show the expected number of lines (Figure 3). At −20° the lines are broadened and coalesce at −8°. Above −5° the methyl triplet appears at the average position. The spectra of the following solutions (*C*, complex concentration; *L*, free ligand concentration) were recorded at −12°: $C = 5.5 \times 10^{-2}$ *M*, $L = 4 \times 10^{-1}$ *M*; $C = 9.7 \times 10^{-2}$ *M*, $L = 3.3 \times 10^{-1}$ *M*; $C = 5.7 \times 10^{-2}$ *M*, $L = 6.7 \times 10^{-2}$ *M*. The exchange reaction is first order in palladium complex and the rate does not depend on the free phosphite concentration.

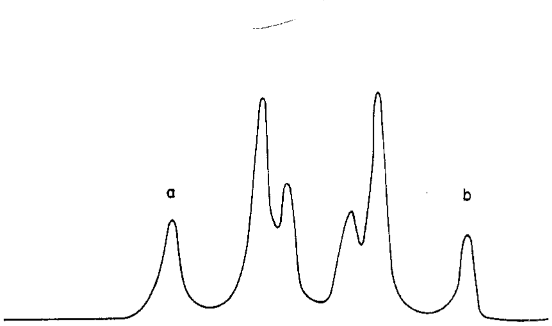

Figure 3.—Spectrum of a solution containing $Pd[P(OC_2H_5)_3]_4$ in a concentration of 9.7×10^{-2} *M* and $P(OC_2H_5)_3$ in a concentration of 3.3×10^{-1} *M* recorded at −42°.

TABLE II

RATES OF $P(OC_2H_5)_3$ EXCHANGE WITH $Pd[P(OC_2H_5)_3]_4$ IN TOLUENE FOR 0.097 M $Pd[P(OC_2H_5)_3]_4$ AND 0.330 M $P(OC_2H_5)_3$

Below coalescence temp		Above coalescence temp	
Temp, °C	k, sec^{-1}	Temp, °C	k, sec^{-1}
−17.4	2.3	−4.5	36
−16.2	3.8	−2.5	51
−13.7	4.7	+0.4	62
−12.3	6.1	+3.3	86
−10.5	8.5	+8.1	260
$\Delta H^{\ddagger} = 22.4 \pm 2.2$ kcal/mol[a]		$\Delta H^{\ddagger} = 22.0 \pm 2.3$k cal/mol[a]	
$\Delta S^{\ddagger} = +31.2 \pm 8.4$ eu[a]		$\Delta S^{\ddagger} = +30.4 \pm 8.6$ eu[a]	

[a] The deviations given equal one standard deviation.

There is satisfactory agreement between the activation parameters calculated from the data below and above the coalescence temperature (Table II). The Arrhenius plots for the temperature dependence of the rates of exchange of the palladium and platinum compounds are shown in Figure 4.

The System $Ni[P(OC_2H_5)_3]_4$–$P(OC_2H_5)_3$.—The methyl triplet of $Ni[P(OC_2H_5)_3]_4$ is shifted 7 cps (at 60 Mcps) downfield with respect to the methyl resonance of free $P(OC_2H_5)_3$. Spectra of solutions containing the nickel complex and free phosphite show no line broadening up to 90°.

Molecular weight determinations by the freezing point depression method in benzene solutions reported by Vinal and Reynolds[4] indicate that the complex $Ni[P(OC_2H_5)_3]_4$ does dissociate to some extent. Jensen, *et al.*,[9] obtained molecular weights by the same method, which do not suggest that dissociation occurs. Our osmometric molecular weight determinations in cyclohexane give essentially the same molecular weights as those obtained by Vinal and Reynolds (apparent molecular weight in a 5×10^{-2} M solution, 640; in a 2×10^{-2} M solution, 630; calcd, 723). The nmr spectrum of $Ni[P(OC_2H_5)_3]_4$ and its reaction with cyclohexyl isocyanide, however, do not indicate that the compound is dissociated in solution. Of course, a few per cent of dissociation would not be detectable by the nmr technique.

Ligand Substitution between $Ni[P(OC_2H_5)_3]_4$ and Cyclohexyl Isocyanide.—The rate of ligand substitution between $Ni[P(OC_2H_5)_3]_4$ and cyclohexyl isocyanide was measured in *n*-hexane and benzene solutions by following the decay of the band c (Figure 5) at 2140 cm^{-1} (NC stretch in free isocyanide). The decay of the band c was accompanied by the growth of two new bands—d at 2070 cm^{-1} and e at 2050 cm^{-1}. The ratio of the absorbancies of the new bands d and e remains constant during a run, indicating that the new bands are due to the same product. Figure 5 shows a sequence of spectra recorded during a kinetic run. The observed spectral changes are explained by

$$Ni[P(OC_2H_5)_3]_4 + C_6H_{11}NC \xrightarrow[k^1]{slow} Ni[P(OC_2H_5)_3]_3(C_6H_{11}NC) \quad (1)$$

$$Ni[P(OC_2H_5)_3]_3C_6H_{11}NC + C_6H_{11}NC \xrightarrow{fast} Ni[P(OC_2H_5)_3]_2(C_6H_{11}NC)_2 \quad (2)$$

with the monosubstituted product reaching rapidly a low, steady-state concentration.[10] The increase of the free triethyl phosphite concentration was not followed. Our experiments confirm the observation of Jensen, *et al.*,[9] that the spectra of $Ni[P(OC_2H_5)_3]_4$ and $P(OC_2H_5)_3$ are almost identical in the NaCl range. The initial concentration A_0 of the nickel complex was 4 to 15 times larger than the initial isocyanide concentration B_0. Data were collected from the beginning of the reaction only until 50–75% of the isocyanide was consumed, in order to exclude erroneous absorbance readings resulting from overlap of the isocyanide band and the bands of the product. The reactions went to completion; *i.e.*, the band of the free isocyanide disappeared entirely. Plots of the absorbance of the band c *vs.* time yield straight lines (Figure 6) (pseudo-zero-order reaction) with the slope proportional to the concentration A_0 of $Ni[P(OC_2H_5)_3]_4$. Changes of the initial concentration of cyclohexyl isocyanide have no effect on the observed rate. The decrease of the concentration of free isocyanide is thus described by $B = B_0 - 2kA_0t$, where k is the first-order rate constant for reaction 1. The factor 2 is required by the fast

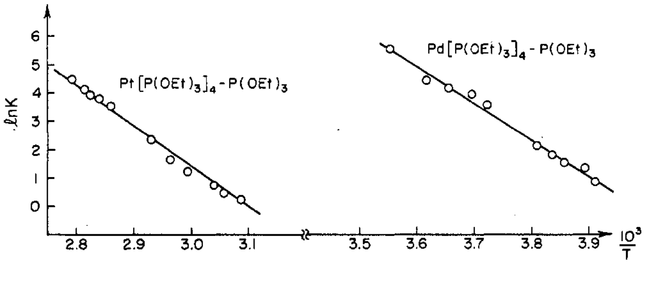

Figure 4.—Arrhenius plots for ligand exchange in the systems $Pd[P(OC_2H_5)_3]_4$–$P(OC_2H_5)_3$ and $Pt[P(OC_2H_5)_3]_4$–$P(OC_2H_5)_3$.

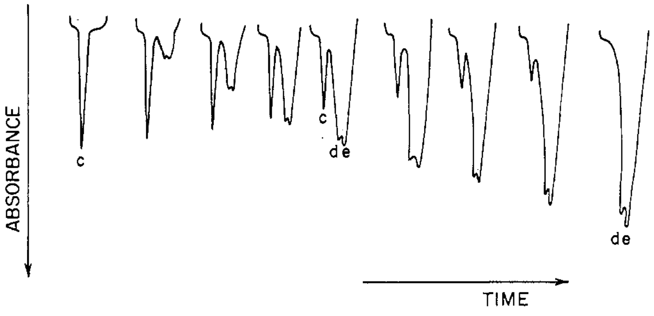

Figure 5.—Ligand substitution between $Ni[P(OC_2H_5)_3]_4$ and $C_6H_{11}NC$ in benzene solution. Sequence of spectra recorded during a typical kinetic run. Band c at 2140 cm^{-1} is that of free $C_6H_{11}NC$ and the bands d and e at 2070 and 2050 cm^{-1} are of the reaction product $Ni[P(OC_2H_5)_3]_2(C_6H_{11}NC)_2$.

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(9) K. A. Jensen, B. Nygaard, G. Elisson, and P. H. Nielsen, *Acta Chem. Scand.*, **19**, 768 (1965).

(10) See A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, pp 166–168.

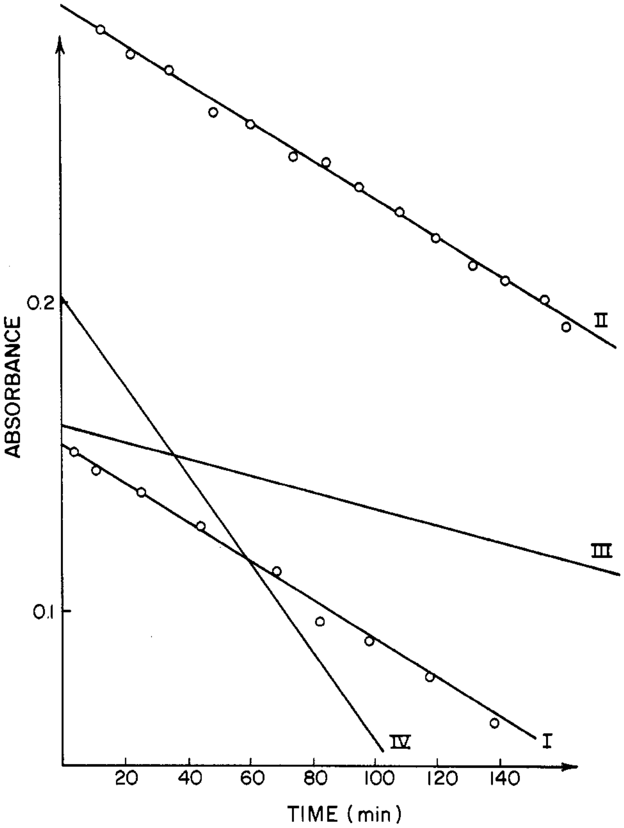

Figure 6.—Zero-order kinetic plots obtained in hexane at 40.8° on the following solutions: $Ni[P(OC_2H_5)_3]_4$: (I) 4.82×10^{-2} *M;* (II) 4.66×10^{-2} *M;* (III) 2.25×10^{-2} *M;* (IV) 9.52×10^{-2} *M.* $C_6H_{11}NC$: (I) 4.98×10^{-3} *M;* (II) 9.84×10^{-3} *M;* (III) 5.56×10^{-3} *M;* (IV) 6.46×10^{-3} *M.*

reaction (2), consuming a second molecule of isocyanide. The results are compiled in Table III.

TABLE III

RATES OF REACTION OF $Ni[P(OC_2H_5)_3]_4$ WITH $C_6H_{11}NC$ IN HEXANE AND IN BENZENE

$[Ni[P(OC_2H_5)_3]_4]$, *M*	$[C_6H_{11}NC]$, *M*	Temp, °C	10^6k, sec^{-1}
	n-Hexane		
0.0554	0.00412	35.3	1.19
0.0482	0.00498	40.8	3.60
0.0466	0.00984	40.8	3.76
0.0225	0.00556	40.8	3.77
0.0952	0.00646	40.8	3.52
0.0451	0.00681	46.0	8.90
0.0451	0.00681	46.0	8.15
0.0287	0.00700	50.4	15.4
0.0287	0.00700	50.4	16.0
$\Delta H^{\ddagger} = 32.1 \pm 1.0$ kcal/mol, $\Delta S^{\ddagger} = +18.8 \pm 3.0$ eu			
	Benzene		
0.0492	0.00673	35.9	4.90
0.0470	0.00672	40.8	9.68
0.0488	0.00740	46.0	19.5
0.0474	0.00690	40.8	6.35[a]
0.0581	0.00658	40.8	3.88[b]
$\Delta H^{\ddagger} = 26.2 \pm 1.0$ kcal/mol, $\Delta S^{\ddagger} = +1.8 \pm 3.0$ eu			

[a] $[P(OC_2H_5)_3] = 0.0204$ *M.* [b] $[P(OC_2H_5)_3] = 0.0430$ *M.*

Competition experiments were also carried out in which triethyl phosphite was added to the usual reaction mixture. Kinetic experiments on benzene solutions containing $Ni[P(OC_2H_5)_3]_4$, cyclohexyl isocyanide, and free triethyl phosphite again yield, under the conditions of the measurements, zero-order plots. The observed rate constants are lower (see *a* and *b* of Table III). The free phosphite thus competes with the isocyanide for the activated complex. However, the reactions at these conditions also went to completion; *i.e.*, the band due to free cyclohexyl isocyanide disappeared entirely.

Other Tetrakis(phosphite)nickel(0) Systems.—The triphenyl phosphite compound $Ni[P(OC_6H_5)_3]_4$ was prepared from π-cyclopentadienylnickel (Alfa Inorganics, Inc.) and triphenyl phosphite (Eastman) as previously described.[11] It was established qualitatively by ir spectroscopy on benzene solutions at room temperature that $Ni[P(OC_6H_5)_3]_4$ reacts with isocyanide as well as with carbon monoxide much faster than does $Ni[P(OC_2H_5)_3]_4$. However, owing to the low solubility of the triphenyl phosphite compound (2×10^{-3} *M* in benzene and toluene, even less in saturated hydrocarbons), no kinetic study was made.

Tetrakis(trimethyl phosphite)nickel(0) was prepared from nickel(II) chloride hexahydrate and trimethyl phosphite (Eastman, distilled under nitrogen prior to use) by the same method as the triethyl phosphite complex.[4] The substitution experiment was carried out in complete analogy to the experiments described previously with the triethyl phosphite complex. The initial concentration of $Ni[P(OCH_3)_3]_4$ was about 10 times as large as the initial concentration of cyclohexyl isocyanide. The decay of the band at 2140 cm^{-1} (due to the free isocyanide) was accompanied by the growth of two new bands at 2075 and 2060 cm^{-1}. The absorbance ratio of the two new bands remained constant during the kinetic run. The reaction went to completion; *i.e.*, the band at 2140 cm^{-1} disappeared completely. A plot of the absorbance of the free isocyanide band *vs.* time gives a straight line in accord with a pseudo-zero-order reaction. A rate constant $k = 2.96 \times 10^{-6}$ sec^{-1} at 40.2° was obtained for this reaction. Thus $Ni[P(OCH_3)_3]_4$ reacts about three times slower than $Ni[P(OC_2H_5)_3]_4$ at 40°.

The caged phosphite esters

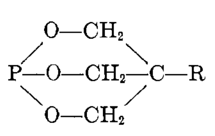

exhibit lower steric hindrance and stronger σ- and π-bonding abilities than the trialkyl phosphites.[12] The caged phosphites with R = CH_3 and R = *n*-propyl were prepared from trimethyl phosphite (Eastman) and trimethylolethane (Aldrich Chemical Co., Inc.) and

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[11] J. R. Olechowski, C. G. McAlister, and R. F. Clark, *Inorg. Chem.*, **4**, 246 (1965).

[12] J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *ibid.*, **4**, 228 (1965).

from trimethyl phosphite and trimethylolbutane (obtained as a gift from the Trojan Powder Co.), respectively. The tetrakis(phosphite)nickel(0) compound with the ligand in which R = CH_3 is insoluble in hydrocarbons. The caged phosphite with R = *n*-propyl gives a nickel compound which is soluble in benzene and toluene.

Toluene solutions containing cyclohexyl isocyanide and the complex were kept at 60° for 4 hr. The ir spectra did not change during this time. After bubbling carbon monoxide through a toluene solution of the complex for 4 hr at 60°, the ir spectrum showed no carbonyl band.

Discussion

The results of this investigation show (1) that substitution reactions of $M[P(OC_2H_5)_3]_4$, where M = Ni, Pd, or Pt, proceed by an SN1 dissociation mechanism, (2) that the relative rates of reaction follow the order Ni < Pd > Pt, and (3) that the compounds are not appreciably dissociated in solution.

That these reactions take place by a dissociation process is in accord with previous observations made on other zerovalent nickel triad systems. For example, the exchange and substitution reactions of $Ni(CO)_4$ take place by a first-order process involving the active intermediate $Ni(CO)_3$.[13] Similarly, the solid $Pt[P(C_6H_5)]_4$ dissolves to give solutions containing largely the tris species $Pt[P(C_6H_5)]_3$.[1,14]

The point of primary interest is that the results obtained provide a quantitative measure of the relative M–P bond strengths in these zerovalent nickel triad systems of $M[P(OC_2H_5)_3]_4$. The enthalpies of activation for M–P bond rupture in aromatic solvents vary in the order Ni (26) > Pd (22) < Pt (27), where the numbers in parentheses are values of $\Delta H^{\ddagger}$ in kcal/mol for the dissociation reaction

$$M[P(OC_2H_5)_3]_4 \rightarrow M[P(OC_2H_5)_3]_3 + P(OC_2H_5)_3 \quad (3)$$

Of course the enthalpies of activation are not equal to the bond dissociation energies unless the activation energy for the reverse reaction of eq 3 is zero. In fact it is likely that these recombination reactions have a modest activation energy.[13,14]

This order of substitution reactivity for the zerovalent nickel triad systems does not correlate with that for the divalent nickel triad complexes. For the latter, the M–L bond strengths and rates of substitution of low-spin d^8 complexes of the type $M^{II}L_4$ decrease in the order Ni > Pd >> Pt.[15] The M–L bonding is probably largely σ bonding in these divalent metal complexes, because the positive oxidation state of the metal lessens its capacity so back-donate electron density in the form of π bonding. Since for this triad Pt(II) is the most electronegative, it is expected to form the strongest σ bonds, which agrees with the experimental observations.

The bond strength of Ni(II) and Pd(II) toward various ligands is probably of similar magnitude, though there is little evidence on bond strengths in the gas phase where solvation effects are not predominant. The hydration energies are nearly equal for the two gaseous ions.[15] Gas-phase data on the halides show that nickel forms somewhat stronger bonds than palladium does,[16] though the data are not every reliable.

An explanation using σ bonding alone cannot account for the observations made on the relative stabilities and reactivities of the compounds $M[P(OC_2H_5)_3]_4$. However, in these systems the metal is in a zerovalent state and it will tend to donate electron density toward the ligand in the form of π bonding. This means that both σ and π bonding will contribute to the M–L bond strength. We have already mentioned that σ bonding increases in the triad with increasing atomic number of the metal. There is also good reason to believe that Ni(0) has the greatest tendency to π bond.

The most striking chemical evidence that, for this triad of metals, Ni(0) has the greatest tendency to π bond is that it forms the stable compound $Ni(CO)_4$. It has not been possible to prepare the corresponding tetracarbonyls of Pd(0) and Pt(0). Since π bonding is believed to make a significant contribution to the M–C bond strength in metal carbonyls, it follows that the maximum π-bonding ability is exhibited by Ni(0). Nyholm[17] pointed out that on the basis of the ionization potential 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 (5.81) >> Pt (8.20) ≥ Pd (8.33). The numbers in parentheses are the ionization potential values in electron volts.

Considering that both σ and π bonding contribute to the M–P bond strength in the compounds $M[P(OC_2H_5)_3]_4$, it is possible to give a qualitative explanation for the relative stabilities of Ni > Pd < Pt. The stability of the Ni compound is due primarily to π bonding and that of Pt to σ bonding. Since Pd has a small tendency to π bond and an intermediate tendency to σ bond, it forms the least stable compound. That both σ bonding and π bonding make a contribution to the total bond strength in $Ni[P(OR)_3]_4$ is supported by the fact that the enthalpies of activation for the dissociation of $Ni[P(OC_2H_5)_3]_4$ and of $Ni(CO)_4$ in hexane solution are 32 and 24 kcal/mol, respectively.[13] If π bonding alone were important, then the carbonyl would be expected to have the larger value, since CO is a better π bonder than is $P(OC_2H_5)_3$.[18]

The order of reactivity found for the nickel triad compounds $M[P(OC_2H_5)_3]_4$ is not unique among low-valent metal compounds of this type. For example, the same behavior is found in the chromium triad where the rates of substitution of $M(CO)_6$ vary in the order Cr < Mo > W.[19] Similarly, the rates of reaction of

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[13] J. P. Day, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **90**, 6927 (1968).

[14] J. P. Birk, J. Halpern, and A. L. Pickard, *ibid.*, **90**, 4491 (1968).

[15] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1967, p. 81 and Chapter 5.

[16] R. C. Feber, Los Alamos Report LA-3164, 1965.

[17] R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961).

[18] W. D. Horrocks and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

[19] R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

$C_5H_5M(CO)_2$ for the cobalt triad of compounds vary in the order Co < Rh > Ir.[20] An explanation for this behavior has been given[21] in terms of the low electronegativity of the metal of the first transition series as one factor and a good matching of the orbital energies of the third transition series metal and of CO as the second factor.

The relative order of stabilities found for the tetrakis(ligand)metal(0) compounds of $P(OC_2H_5)_3$ is apparently the same as that for the PF_3 ligand. Thus for $M(PF_3)_4$, the decomposition temperatures reported[22] for the three metals are: Ni, $>155°$; Pd, $> -20°$; Pt, $>90°$. The ligand PF_3 is a weaker base than $P(OC_2H_5)_3$ but a better π bonder, being comparable to CO. The relatively more basic and weaker π-bonding ligand $P(C_6H_5)_3$ seems to exhibit a different behavior. The compounds $M[P(C_6H_5)_3]_4$ appear to increase in stability[1] in the order Ni < Pd < Pt. This presumably reflects the greater importance of σ bonding in these systems containing a more basic ligand.

One other important difference between the compounds $M[P(OC_2H_5)_3]_4$ and $M[P(C_6H_5)_3]_4$ is that the phosphites are largely present as the tetracoordinated species in solution, whereas the phosphines are largely present in the form of $M[P(C_6H_5)_3]_3$.[1,14] This seems to be due to the relatively good σ- and poor π-bonding properties of $P(C_6H_5)_3$ which result in an accumulation of negative charge on the metal. Apparently, three phosphines make the metal sufficiently negative that it is only weakly bound to the fourth phosphine. Since phosphite ligands are relatively poorer σ-electron donors and better π-electron acceptors than are phosphines, it follows that there is less negative charge on the metal and a greater tendency toward tetracoordination in the phosphite systems.

Extensive studies have only been made with $P(OC_2H_5)_3$, but some observations have also been made on other phosphites. Qualitatively it can be said that the rates of substitution reactions of $Ni[P(OR)_3]_4$ for different phosphites vary in the order $P(OC_6H_5)_3 > P(OC_2H_5)_3 \geq P(OCH_3)_3 >> P(OCH_2)_3CC_3H_7$. The rapid rate of reaction of the $P(OC_6H_5)_3$ compound is probably due to a steric acceleration of the dissociation process. The small steric requirements of the caged phosphite $P(OCH_2)_2CC_3H_7$ and its strong bonding capacity[12] are in accord with its forming the least reactive nickel(0) compound.

It should also be noted that the rate of reaction of $Ni[P(OC_2H_5)_3]_4$ (eq 1) is slower than that of $Ni[P(OC_2H_5)_3]_3(CNC_6H_{11})$ (eq 2). Furthermore, none of this monosubstituted species is detected even in a reaction mixture containing an excess of the unsubstituted nickel compound. At equilibrium no free isocyanide can be detected by means of ir analysis and it is entirely present in the reaction products as $Ni[P(OC_2H_5)_3]_2(CNC_6H_{11})_2$. This behavior is somewhat similar to that of $Ni(CO)_4$ which readily reacts with σ-bonding phosphines to form $Ni(CO)_2(PR_3)_2$.

The rate of reaction of $Ni[P(OC_2H_5)_3]_4$ with $C_6H_{11}NC$ decreases in the presence of added $P(OC_2H_5)_3$ (Table III, *a* and *b*). This is expected for a dissociation mechanism, where both reagents compete for the tricoordinated active intermediate

$$\begin{tikzcd} Ni[P(OC_2H_5)_3]_4 \arrow[r, shift left, "k"] & Ni[P(OC_2H_5)_3]_3 \arrow[l, shift left, "k_p"] \arrow[d, "C_6H_{11}NC"', "k_c"] & + \ P(OC_2H_5)_3 \\ & Ni[P(OC_2H_5)_3]_3C_6H_{11}NC & \end{tikzcd} \qquad (4)$$

From the rate of formation of the isocyanide product and the concentrations of the competing reagents, it is possible to estimate the ratio of rate constants k_p/k_c. This can be done by means of the equation

$$\frac{k_c[C_6H_{11}NC]}{k_p[P(OC_2H_5)_3] + k_c[C_6H_{11}NC]} = f \qquad (5)$$

where f is the fraction of the intermediate that reacts to form the isocyanide product. The results obtained show that $k_p/k_c = 0.2$ or that $C_6H_{11}NC$ is about five times more reactive than $P(OC_2H_5)_3$ toward $Ni[P(OC_2H_5)_3]_3$. It should be noted that $P(C_6H_5)_3$ is about five times more effective a reagent than is CO toward the active intermediate $Ni(CO)_3$.[13]

Finally it should also be mentioned that the rate of dissociation of $Ni[P(OC_2H_5)_3]_4$ is faster, and its activation energy less, in benzene than in hexane solution. This suggests that the aromatic solvent has a greater stabilizing influence on the tricoordinated intermediate than does the aliphatic solvent. The same solvent effect has been observed for the reactions of $Ni(CO)_4$.[23]

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[20] H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Scc.*, **88**, 1657 (1966).

[21] N. A. Beach and H. B. Gray, *ibid.*, **90**, 5713 (1968); D. R. Lloyd and E. W. Schlag, *ibid.*, in press.

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[23] R. J. Angelici and B. E. Leach, Jr., *J. Organometal. Chem.*, **11**, 203 (1968).