TABLE II

Dye	Color	M.p., °C.	Theoretical, % C	H	N	Cu	Found, % C	H	N	Cu
I	Dark brown crystals	225–227			17.34	9.83			17.5	9.7
III	Brown microcrystalline powder	238–239	49.52	3.12	14.45		49.88	3.34	13.90	
IV	Brown crystalline powder	258–259	49.52	3.12	14.45		49.88	2.84	15.96	
VI	Brown crystalline powder	242–244			19.78	8.97			19.6	8.9

Calculations.—The molarity quotients were calculated by the method of Block and McIntyre.[5] At least 4 sets of $\bar{n}$ and $p\mathrm{Ch}^-$ values were used.

Discussion

The molarity quotients, Table I, show the same trend noted with other simple pyrazolone dyes. The strongest acid (the *meta*-nitro dye) forms quite stable 3:1, dye to metal, nickel(II), cobalt(II) and zinc derivatives. The other dyes form relatively weak 3:1 derivatives and their zinc 2:1 derivatives are poorly defined. Chloro and bromo substitution in both the *meta*- and the *para*-position have about the same inductive effect on the acidity of the dye molecule. Of course, with similar pQ_D values the molarity quotients for the metal derivatives of the chloro and the bromo dyes are about the same.

The decreasing order of acidity, Table I, of the *para*-substituted dyes as presented in a previous paper[4] is extended as follows: $NO_2 >> (Cl, Br) > I > OCH_3$[6] $> CH_3 > H$. With the exception of the methoxy derivative the order fairly well follows the electron attracting power of the substituent groups. It would seem that the inductive effect of the methoxy group is greater than the resonance effect. The pQ_{av} values of the metal derivatives increase in the same order; that is, the nitro dye forms the least stable 2:1 compounds. This stability order (exception methoxy dye) is in good agreement with that reported by Calvin and Bailes.[7] The more limited number of *meta*-substituted dyes and their metal derivatives follow the same order.

The *meta*-nitro dye is a slightly weaker acid than the *para*-nitro dye[4] and the tendency for 3:1 complex formation is decreased. The order of stability of the 3:1 derivatives appears to be the reverse of the 2:1 compounds. That is, the formation of the anion complex, $M(dye)_3^-$, occurs more readily with the stronger acids.

The *ortho* derivatives of this series of dyes (with the exception of *o*-OCH_3 and *o*-SCH_3)[6] are too insoluble to be studied at the concentrations used in this work, 1.00×10^{-2} *M* in azo compound. It is interesting to note that the only *ortho*-substituted dyes which were soluble enough to study were the two which contained relatively strong electron releasing groups.

Near the end of the potentiometric titrations the copper derivatives of four of the dyes precipitated as nicely crystalline compounds. They were suction filtered, washed with cold alcohol and dried in a vacuum desiccator (Table II).

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LANCASTER, PENNSYLVANIA

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[CONTRIBUTION FROM THE BASIC RESEARCH DEPARTMENT, STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION AMERICAN CYANAMID CO.]

Bonding in Ni(0) Complexes. I. Phosphine Exchange Kinetics and Infrared Spectra of Nickel–Carbonyl–Phosphine Complexes[1]

BY LEWIS S. MERIWETHER AND MARILYN L. FIENE

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The kinetics of the phosphine exchange reaction between nickel–dicarbonyl–diphosphine complexes and tertiary phosphines have been determined. The reaction is first order in complex and independent of the added phosphine. An SN1 dissociative mechanism is proposed. Nickel–tricarbonyl–monophosphines usually exchange a CO for phosphine initially. The effect of varying the structure of the phosphine ligand on the exchange rates and the the infrared carbonyl frequencies of the complexes has been determined. The nature of the bonding between nickel and the phosphine and carbonyl ligands is discussed.

Introduction

The mechanisms of ligand exchange in transition metal complexes only recently have been explored.[2] In general, exchange reactions may occur either by (1) unimolecular, dissociative, SN1-type processes or by (2) bimolecular, displacement, SN2-type processes. In their extensive studies of substitutions in octahedral Co(III) complexes, Ingold, Nyholm and co-workers[3] have presented stereochemical and kinetic evidence for both SN1 and SN2 mechanisms, the mode of exchange depending upon the nature of the ligands on the metal, the nucleophilicity of the attacking species, and the solvent. As a result of their investigation of the base hydrolysis of Co(III) complexes, Pearson and Basolo[4] have developed a dissociative SN1CB (substitution, nucleophilic, unimolecular, conju-

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(1) Presented at the Gordon Research Conference on Inorganic Chemistry, New Hampton, N. H., August 18–22, 1958.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

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gate base) mechanism in which the intermediate is pentacoördinated cobalt. The *trans*-effect[5] has long been used to predict the stereochemical course of substitution reactions on planar complexes of Pt(II). An S_N2 mechanism has been proposed for these reactions by Cardwell,[6] Chatt[7] and Orgel.[8] Recently, based on their kinetic studies of the reactions of Pt(II) complexes with various nucleophilic agents, Banerjea, Basolo and Pearson[9] have postulated a "dissociation" mechanism for substitution reactions of square-planar complexes which is consistent with the stereochemistry of these reactions, the *trans*-effect of the ligands and the observed kinetics.

However, no previous work has been reported on the mechanism of substitution reactions on tetrahedral metal complexes. It has been suggested[2] that these reactions may occur by S_N2-type displacement processes because of the large size of the central metal atom. The results of a kinetic study of the exchange reactions of some tetrahedral[10] nickel–carbonyl–phosphine complexes with various tertiary phosphines are reported in this paper. The rate of exchange of phosphine ligands in the complex with added free phosphine was determined spectrophotometrically by following the shifts in the metal carbonyl frequencies of the complexes in the infrared. The reaction kinetics are consistent with a dissociative S_N1 mechanism in which a tricoördinated nickel complex is the postulated intermediate. The effects of the nature of the bonding between nickel and the phosphine and carbonyl ligands on the rates of the exchange reactions and on the positions of the carbonyl stretching frequencies of the complexes have been determined.

Experimental

Materials.—Triphenylphosphine (Eastman White Label) was recrystallized from ethanol. Triethylphosphite (Eastman White Label), triphenylphosphite (Eastman practical), phosphorus trichloride (Baker & Adamson Reagent) and tributylphosphine (Westvaco) were purified before use by redistillation in an inert atmosphere. Eastman Spectro Grade cyclohexane and acetonitrile were used without further purification in all experiments.

Preparation of Complexes. Dicarbonylbis-(triphenylphosphine)-nickel, $Ni(CO)_2[P(C_6H_5)_3]_2$, was prepared by the method of Rose and Statham.[11] The complex was obtained as a pale yellow crystalline solid, m.p. 212° dec. (reported[11] m.p. 210–215° dec.). The infrared spectrum contained bands in the metal carbonyl region at 2000 and 1955 cm.$^{-1}$ (Nujol mineral oil mull).

Tricarbonyltriphenylphosphinenickel, $Ni(CO)_3P(C_6H_5)_3$.—This complex was prepared by the general method of Reppe and Sweckendiek.[12] Triphenylphosphine (6.5 g., 0.025 mole) in 65 ml. of absolute ethanol was brought to reflux and 3.25 ml. (0.025 mole) of nickel carbonyl in 35 ml. of absolute ethanol was added slowly. Carbon monoxide was evolved and crystals were deposited from the solution as refluxing was continued for 1 hr. The mixture was cooled and filtered and the complex was obtained as a pale, cream-colored crystalline solid, m.p. 126° (reported[12] m.p. 123°). The infrared spectrum contained bands in the metal carbonyl region at 2050 and 1990 cm.$^{-1}$ (Nujol mineral oil mull).

Dicarbonylbis-[tris-(2-cyanoethyl)-phosphine]-nickel, $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$.—Tris-(2-cyanoethyl)-phosphine was prepared by M. Rauhut of this Laboratory as described elsewhere.[13] The phosphine (11.6 g., 0.06 mole) in 100 ml. of methanol was brought to reflux and 3.9 ml. (0.03 mole) of nickel carbonyl in 50 ml. of methanol was slowly added. Carbon monoxide was evolved and crystals were deposited from the solution as refluxing was continued for 1 hr. The mixture was cooled and filtered and the complex was obtained as a white crystalline solid (12.5 g., 83%), m.p. 140° dec. The complex is very soluble in acetonitrile, slightly soluble in methanol and insoluble in ethanol, benzene and cyclohexane. The infrared spectrum contained bands in the metal carbonyl region at 2000 and 1938 cm.$^{-1}$ (Nujol mineral oil mull). *Anal.* Calcd. for $C_{20}H_{24}O_2N_6P_2Ni$: C, 47.93; H, 4.83; N, 16.77; P, 12.37; Ni, 11.7. Found: C, 48.03; H, 4.94; N, 16.31; P, 12.37; Ni, 11.3.

Dicarbonylbis-(tri-*n*-butylphosphine)-nickel, $Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$.—Tri-*n*-butylphosphine (14.2 g., 0.07 mole) in 100 ml. of ether was brought to reflux under nitrogen and 4.5 ml. (0.035 mole) of nickel carbonyl in 50 ml. of ether was added gradually. Refluxing was continued for 15 minutes after the carbonyl addition was complete. The ether was removed under vacuum at room temperature and the mixture finally was heated on the steam-bath under vacuum to remove any unreacted tributylphosphine. The complex, which could not be distilled, remained as an orange-colored viscous liquid. Infrared analysis of this material showed bands in the metal carbonyl region at 1995 and 1930 cm.$^{-1}$. *Anal.* Calcd. for $C_{26}H_{54}O_2P_2Ni$: C, 60.15; H, 10.41; P, 11.95. Found: C, 60.32; H, 10.41; P, 12.17.

Dicarbonylbis-(triphenylphosphite)-nickel, $Ni(CO)_2[P(OC_6H_5)_3]_2$, was prepared by the method of Reed.[14] The complex was obtained as a white crystalline solid from petroleum ether, m.p. 95° (reported[14] m.p. 95°). The infrared spectrum contained bands in the metal carbonyl region at 2040 and 1995 cm.$^{-1}$ (Nujol mineral oil mull). *Anal.* Calcd. for $C_{38}H_{30}O_8P_2Ni$: C, 62.07; H, 4.11; P, 8.43. Found: C, 61.56; H, 4.06; P, 8.18.

Dicarbonylbis-(triethylphosphite)-nickel, $Ni(CO)_2[P(OC_2H_5)_3]_2$.—Nickel carbonyl (1.29 ml., 0.01 mole) in 25 ml. of anhydrous ether was added dropwise to 3.32 g. (0.02 mole) of triethylphosphite in 10 ml. of anhydrous ether under nitrogen at 25°. When the carbonyl addition was complete, the solution was refluxed for one minute and the ether and unreacted starting materials were removed on a vacuum evaporator and finally with an oil pump at 60°. A pale yellow viscous liquid (1.8 g., 40%) was obtained which had infrared carbonyl bands at 1972 and 2036 cm.$^{-1}$. *Anal.* Calcd. for $C_{14}H_{30}O_8P_2Ni$: C, 37.67; H, 6.72; P, 13.90. Found: C, 36.98; H, 6.99; P, 14.38.

Tricarbonyltriethylphosphitenickel, $Ni(CO)_3[P(OC_2H_5)_3]$.—Triethylphosphite (1.66 g., 0.01 mole) was added dropwise to a solution of 6.5 ml. (0.05 mole) of nickel carbonyl in 25 ml. of anhydrous ether under nitrogen at 25°. After the phosphite addition was complete, the mixture was allowed to stand under nitrogen for 1 hr. The ether was removed on a rotating evaporator and the resulting oil was subjected to 0.1 mm. at 25° for several hours. The tricarbonyl complex was obtained as a colorless oil (2.35 g., 76%) which rapidly decomposed above room temperature to give a black deposit of nickel metal and which also rapidly developed a green gelatinous precipitate of bivalent nickel salts when exposed to the air. Infrared carbonyl bands were found at 2080 and 2000 cm.$^{-1}$. *Anal.* Calcd. for $C_9H_{15}O_6PNi$: C, 35.06; H, 4.87; P, 10.06. Found: C, 35.42; H, 5.50; P, 10.60.

Carbonyltris-(triethylphosphite)-nickel, $Ni(CO)[P(OC_2H_5)_3]_3$, was prepared by the method of Malatesta and Sacco.[15] The complex had one infrared carbonyl band at 1965 cm.$^{-1}$. *Anal.* Calcd. for $C_{19}H_{45}O_{10}P_3Ni$: C, 38.99; H, 7.69; P, 15.88. Found: C, 38.81; H, 7.70; P, 16.00.

Reaction of $Ni(CO)_4$ with Two Moles of PCl_3.—Nickel carbonyl (3.3 ml., 0.026 mole) in 25 ml. of anhydrous ether

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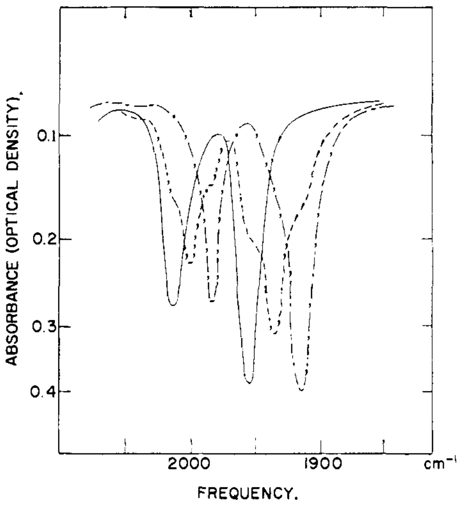


Fig. 1.—Infrared spectra of phosphine exchange reaction between $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$, 0.005 *M*, and $P(n\text{-}C_4H_9)_3$, 0.5 *M*, in acetonitrile at 25°: ———, $t = 0$; - - - -, $t = 20$ min.; — — —, $t = 2$ hr.

was added dropwise to a refluxing solution of 4.5 ml. (0.052 mole) of phosphorus trichloride in 75 ml. of anhydrous ether. The solution was refluxed for 30 min. after the carbonyl addition was complete. The yellow solution then was put on a rotating evaporator under vacuum to remove the ether and unreacted starting materials. An orange viscous liquid remained (4.5 g.) which rapidly turned black in the air and could not be purified further. The material could be stored reasonably well under nitrogen at −30°. The infrared spectrum contained bands in the metal carbonyl region at 2110, 2090, 2065 and 2050 cm.⁻¹. This indicates that the product was a mixture of $Ni(CO)_2(PCl_3)_2$ and $Ni(CO)_3PCl_3$. Bubbling CO gas into a cyclohexane solution of the product caused increases in the 2110 and 2050 cm.⁻¹ bands, which were reversible on switching to nitrogen sweeping. The addition of excess PCl_3 to a cyclohexane solution of the product resulted in decreases in the 2110 and 2050 cm.⁻¹ bands and increases in the 2090 and 2065 cm.⁻¹ bands. From these results it is reasonable to assume that the 2110 and 2050 cm.⁻¹ bands are due to $Ni(CO)_3PCl_3$ and that the 2090 and 2065 cm.⁻¹ bands are due to $Ni(CO)_2(PCl_3)_2$.

Spectrophotometric Method.—Each of the dicarbonyl and tricarbonyl complexes studied has two infrared carbonyl frequencies which vary with the nature of the phosphine ligands; these are listed in Table I. The reaction could be observed directly in solution by following the disappearance of one set of bands and the appearance of neighboring bands for the newly formed complexes resulting from the successive replacement of one or two phosphine ligands.

Table I

Infrared Carbonyl Frequencies for Some Nickel–Carbonyl–Phosphine Complexes in Solution

Complex	ν, cm.⁻¹ [a,b] Cyclohexane	Acetonitrile
$Ni(CO)_2(PCl_3)_2$	2090, 2065	
$Ni(CO)_2[P(OC_6H_5)_3]_2$	2050, 2000	
$Ni(CO)_2[P(OC_2H_5)_3]_2$	2034, 1975	
$Ni(CO)_2]P(CH_2CH_2CN)_3](PCl_3)$		2058, 2010
$Ni(CO)_2[P(CH_2CH_2CN)_3][P(OC_6H_5)_3]$		2035, 1980
$Ni(CO)_2[P(C_6H_5)_3][P(OC_6H_5)_3]$	2035, 1980	
$Ni(CO)_2[P(n\text{-}C_4H_9)_3][P(OC_6H_5)_3]$	2030, 1970	
$Ni(CO)_2[P(C_6H_5)_3]_2$	2010, 1955	2015, 1955
$Ni(CO)_2[P(C_6H_5)_3][P(n\text{-}C_4H_9)_3]$	2005, 1945	
$Ni(CO)_2[P(OC_2H_5)_3][P(n\text{-}C_4H_9)_3]$	2005, 1950	
$Ni(CO)_2[P(CH_2CH_2CN)_3]_2$		2015, 1955
$Ni(CO)_2[P(CH_2CH_2CN)_3][P(n\text{-}C_4H_9)_3]$		2000, 1935
$Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$	2000, 1935	1985, 1915
$Ni(CO)_3PCl_3$ [c]	2110, 2050	
$Ni(CO)_3[P(OC_2H_5)_3]$ [c]	2080, 2005	
$Ni(CO)_3[P(C_6H_5)_3]$ [c]	2070, 2000	2070, 2000
$Ni(CO)_3[P(n\text{-}C_4H_9)_3]$ [c]	2070, 2000	
$Ni(CO)[P(OC_2H_5)_3]_3$	1965	

[a] Frequency assignments are accurate to ±3–5 cm.⁻¹. [b] The higher frequency is probably the asymmetric stretching frequency; the lower, the symmetric stretching frequency. [c] Although there are three carbonyl groups in the complex, only two stretching frequencies are expected. Again, the upper frequency is probably the asymmetric stretch, but it is doubly degenerate.

A typical run at room temperature was begun by rapidly mixing a weighed portion of the complex, solvent and free phosphine compound in a volumetric flask. A small amount of the solution was quickly placed in a conventional 0.3 mm. infrared cell which was stoppered and placed in the infrared beam. A compensating cell of the same thickness containing only solvent was placed in the other beam of the instrument. The metal carbonyl region (2200–1900 cm.⁻¹) was then observed at timed intervals by continual retracing of the spectrum. Spectra were taken with a Perkin-Elmer Model 21 double-beam recording spectrophotometer with NaCl optics, programmed for maximum resolution (expanded scale and slow scanning) which was in a constant temperature room maintained at 25.0 ± 0.1°. Figure 1 shows the appearance of the infrared spectra in the metal carbonyl region as the phosphine ligands in $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$ are successively replaced by $P(n\text{-}C_4H_9)_3$. Optical densities were recorded at each of three carbonyl frequencies: (1) original complex, (2) intermediate complex containing one of the original phosphine ligands, and (3) final complex containing two new phosphine ligands. The optical densities at each wave length were corrected for background and the concentrations of the three complexes at various times were calculated from the linear relationship between optical density and concentration. The extinction coefficients of the original and final complexes, calculated from standard solutions of the pure materials, were found to be almost identical. Since the intermediate complex containing two different phosphine ligands could not be synthesized, its extinction coefficient was assumed to be identical with that of the original complex. In general, only the lower carbonyl frequencies were used in the calculations because of better separation of the bands. Data from a typical run are presented in Table II.

Table II

Data of Exchange Reaction between 0.005 *M* $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$ and 0.5 *M* $P(n\text{-}C_4H_9)_3$ in Acetonitrile at 25°

$p = P(CH_2CH_2CN)_3$; $p' = P(n\text{-}C_4H_9)_3$

Time, min.	D_{1955}, cor.	Concn. $Ni(CO)_2p_2$ (moles/l.)	D_{1935}, cor.	Concn. $Ni(CO)_2pp'$ (moles/l.)	D_{1915}, cor.	$Ni(CO)_2(p')_2$ (moles/l.)
0	0.300 (calcd.)	0.00500	...	.....	...	.....
3	.260	.00435	0.075	0.00121	...	.....
8	.190	.00316	.165	.00254	...	.....
12	.140	.00233	.205	.00331	...	.....
17	.095	.00159	.230	.00371	...	.....
25	.075	.00125	.230	.00371	...	.....
30	.045	.00075	.210	.00339	...	.....
35	.030	.00050	.200	.00323	0.170	0.00212
40	.015	.00025	.170	.00274	.200	.00250
45	...	.....	.165	.00254	.220	.00275
55	...	.....	.140	.00226	.250	.00312
70	...	.....	.105	.00170	.290	.00362
80	...	.....	.090	.00145	.305	.00381
100	...	.....	.060	.00097	.330	.00412

Conventional first-order plots of log c_0/c *vs.* time were made for disappearance of the original complex and disappearance of the intermediate complex after the original complex had essentially disappeared (see Fig. 2 for a typical plot). Using least-squares analysis to achieve best fit, the

TABLE III

RATES OF EXCHANGE REACTIONS OF SOME NICKEL–CARBONYL–PHOSPHINE COMPLEXES AT 25.0 ± 0.1°

Nickel complex	Concn. (moles/l.)	Added phosphine (PR'_3)	Concn. (moles/l.)	Solvent[a]	10^4k_1, sec.$^{-1}$	10^4k_2, sec.$^{-1}$
$\mathrm{Ni(CO)_2(PR_3)_2 + PR'_3 \xrightarrow{k_1} Ni(CO)_2(PR_3)(PR'_3) + PR_3}$						
$\mathrm{Ni(CO)_2(PR_3)(PR'_3) + PR'_3 \xrightarrow{k_2} Ni(CO)_2(PR'_3)_2 + PR_3}$						
$\mathrm{Ni(CO)_2(PCl_3)_2}$	0.0050[b]	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	0.50	C	>100	>100
$\mathrm{Ni(CO)_2[P(CH_2CH_2CN)_3]_2}$	.0090	$\mathrm{PCl_3}$	1.15	A	17.5	[c]
$\mathrm{Ni(CO)_2[P(CH_2CH_2CN)_3]_2}$	.0064	$\mathrm{P(OC_6H_5)_3}$	0.50	A	14.2	[d]
$\mathrm{Ni(CO)_2[P(CH_2CH_2CN)_3]_2}$	.0050	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	.50	A	11.6	2.88
$\mathrm{Ni(CO)_2[P(CH_2CH_2CN)_3]_2}$	.0010	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	.10	A	3.49	
$\mathrm{Ni(CO)_2[P(C_6H_5)_3]_2}$	.0053	$\mathrm{P(OC_6H_5)_3}$	.50	C	5.63	[d]
$\mathrm{Ni(CO)_2[P(C_6H_5)_3]_2}$	.0050	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	.50	C	5.34	4.04
$\mathrm{Ni(CO)_2[P(\textit{n}\text{-}C_4H_9)_3]_2}$	.0055	$\mathrm{P(CH_2CH_2CN)_3}$	.50	A	1.24	
$\mathrm{Ni(CO)_2[P(\textit{n}\text{-}C_4H_9)_3]_2}$	.0060	$\mathrm{P(C_6H_5)_3}$	.50	C	0.39	<0.01
$\mathrm{Ni(CO)_2[P(\textit{n}\text{-}C_4H_9)_3]_2}$	.0074	$\mathrm{P(OC_6H_5)_3}$	.50	C	0.32	[d]
$\mathrm{Ni(CO)_2[P(OC_2H_5)_3]_2}$	.0077	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	.50	C	<0.001	
$\mathrm{Ni(CO)_2[P(OC_6H_5)_3]_2}$	.0055	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	.50	C	<0.001	
$\mathrm{Ni(CO)_3(PR_3) + PR'_3 \xrightarrow{k_1} Ni(CO)_2(PR_3)(PR'_3) + CO}$						
$\mathrm{Ni(CO)_2(PR_3)(PR'_3) + PR'_3 \xrightarrow{k_2} Ni(CO)_2(PR'_3)_2 + PR_3}$						
$\mathrm{Ni(CO)_3[P(C_6H_5)_3]}$	0.0057	$\mathrm{P(CH_2CH_2CN)_3}$	0.49	A	13.7	
$\mathrm{Ni(CO)_3[P(C_6H_5)_3]}$	.0068	$\mathrm{P(C_6H_5)_3}$	.49	A	13.4	
$\mathrm{Ni(CO)_3[P(C_6H_5)_3]}$	.0070	$\mathrm{P(C_6H_5)_3}$	.50	C	5.66	
$\mathrm{Ni(CO)_3[P(C_6H_5)_3]}$	.0060	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	.50	C	8.23	4.57
$\mathrm{Ni(CO)_3[P(OC_2H_5)_3]}$	.0130	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	.50	C	2.76	
$\mathrm{Ni(CO)_3PR_3 + PR'_3 \xrightarrow{k_1} Ni(CO)_3PR'_3 + PR_3}$						
$\mathrm{Ni(CO)_3PR'_3 + PR'_3 \xrightarrow{k_2} Ni(CO)_2(PR'_3)_2 + CO}$						
$\mathrm{Ni(CO)_3PCl_3}$	0.0050[b]	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	0.50	C	>100	5.99
$\mathrm{Ni(CO)(PR_3)_3 + PR'_3 \xrightarrow{k_1} Ni(CO)(PR_3)_2(PR'_3) + PR_3}$						
$\mathrm{Ni(CO)[P(OC_2H_5)_3]_3}$	0.0095	$\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$	0.50	C	<0.001	

[a] A = acetonitrile, C = cyclohexane. [b] Concentration is based on the assumption that the sample used was a 50–50 mixture of dicarbonyl and tricarbonyl. [c] Decomposition of the mixed phosphine took place with loss of all CO. [d] The intermediate complex did not exchange.

rate constants for the two successive reactions were calculated from the first-order equation

$$k = \frac{2.303}{t} \log \left(\frac{c_0}{c}\right)$$

The rate constant (k_2) for the disappearance of the intermediate complex could only be determined when the ratio k_2/k_1 was small. In many cases the reaction either was not followed long enough or reached equilibrium too quickly to provide data for k_2. The rate constants for the exchange reactions studied at room temperature are presented in Table III. For most runs the average deviation of the calculated rate constants was ±2–6%. In the runs with half-lives greater than 200 minutes the average deviation was ±10–20%.

Temperature Dependence.—The reactions at elevated temperatures (Table IV) were carried out in an infrared cell especially designed for filling after the cell had reached temperature equilibrium. A conventional 2.5 mm. cell was modified by cementing two hypodermic needles into the liquid reservoir between the salt plates of the cell. The cell then was fitted into a small insulated box with the hypodermics protruding through the cover. The box was wound with resistance wire and covered with asbestos and had NaCl windows for the beam of radiation. A variac controlled the heater current and the temperature was measured by a thermometer mounted in a well in the body of the salt plates of the cell. After the cell had reached equilibrium at the desired reaction temperature, the reaction mixture, which had been mixed at reaction temperature, was quickly introduced into the cell through one of the hypodermic needles while suction was applied on the other. Temperature loss was negligible during the transfer. The

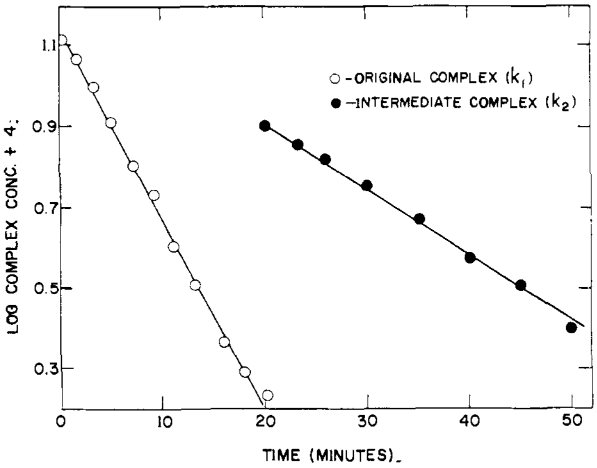


Fig. 2.—Phosphine exchange reaction between $\mathrm{Ni(CO)_2[P(CH_2CH_2CN)_3]_2}$ (0.0013 *M*) and $\mathrm{P(\textit{n}\text{-}C_4H_9)_3}$ (0.1 *M*) in acetonitrile at 36°.

metal carbonyl region then was retraced continually as described in the previous section.

TABLE IV

RATES OF EXCHANGE REACTIONS OF $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$ WITH $P(n\text{-}C_4H_9)_3$ IN ACETONITRILE AT DIFFERENT CONCENTRATIONS AND TEMPERATURES

Concn. complex (moles/l.)	Concn. P-$(n\text{-}C_4H_9)_3$ (moles/l.)	Temp., °C.	10^4k_1, sec.$^{-1}$	10^4k_2, sec.$^{-1}$
0.0050	0.50	25.0 ± 0.1	11.6	2.88
.0010	.10	25.0 ± .1	3.49	^{a}
.0010	.01	25.0 ± .1	3.89	^{a}
.0100	.10	25.0 ± .1	4.74	^{a}
.0010	.10	36.0 ± .5	17.9	6.4
.0010	.10	44.5 ± .5	49.8	21.5

^{a} Rate could not be measured since reaction came to equilibrium.

Results

Nickel–Dicarbonyl–Diphosphines.—The over-all process for the exchange reactions of nickel–dicarbonyl–diphosphine complexes with tertiary phosphine compounds is a two-step reversible reaction

$$Ni(CO)_2(PR_3)_2 + PR'_3 \underset{k_4}{\overset{k_1}{\rightleftharpoons}} Ni(CO)_2(PR_3)(PR'_3) + PR_3 \quad (1)$$

$$Ni(CO)_2(PR_3)(PR'_3) + PR'_3 \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Ni(CO)_2(PR'_3)_2 + PR_3 \quad (2)$$

These reactions are first order in the complex and zero order in the attacking phosphine, as shown by the nearly identical forward first-order rate constants for a tenfold variation in concentration of both the complex and added phosphine (see Table IV). At tri-*n*-butylphosphine concentrations greater than 0.1 *M* (3% free phosphine by volume) the first-order rate constant for the dissociation of the tris-(2-cyanoethyl)-phosphine complex in acetonitrile increases somewhat. A similar increase in the rate constant over the base rate in 0.1 *M* $P(n\text{-}C_4H_9)_3$ is also noted with 0.5 *M* $P(OC_6H_5)_3$ and 1.15 *M* PCl_3. However, the exchange rates of several complexes with 0.5 *M* phosphine are independent of the nature of the attacking phosphine, *e.g.*, the $P(n\text{-}C_4H_9)_3$ complex with $P(C_6H_5)_3$ (10^4k = 0.39 sec.$^{-1}$) and $P(OC_6H_5)_3$ (10^4k = 0.32 sec.$^{-1}$) and the $P(C_6H_5)_3$ complex with $P(OC_6H_5)_3$ (10^4k = 5.63 sec.$^{-1}$) and $P(n\text{-}C_4H_9)_3$ (10^4k = 5.32 sec.$^{-1}$), which would not be expected if a bimolecular mechanism were operating. These rate increases in systems containing 10–15% free phosphine by volume probably represent simple solvation effects of the phosphine on the complex rather than nucleophilic attack by the phosphine on the nickel. The low absorptivities of the complexes in the infrared and the need for working at large phosphine to complex ratios necessitated such high concentrations of free phosphine.

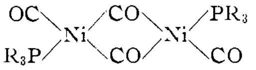
The mechanism of phosphine ligand exchange in the complex involves the unimolecular heterolytic dissociation of the original complex, which is the slow rate-determining step, into a tricoördinated nickel dicarbonyl–monophosphine

$$Ni(CO)_2(PR_3)_2 \rightleftharpoons Ni(CO)_2PR_3 + PR_3 \quad (3)$$

followed by a rapid combination with the replacing phosphine

$$Ni(CO)_2(PR_3) + PR'_3 \longrightarrow Ni(CO)_2(PR_3)(PR'_3) \quad (4)$$

No direct spectroscopic or other evidence for the presence of a tricoördinated nickel complex has been obtained; however, its equilibrium concentration may be extremely low. This is suggested since the infrared carbonyl bands do not shift appreciably and no new carbonyl bands indicative of a new complex species appear when the pure complexes are dissolved in inert solvents. The dissociated complex could also be in equilibrium with a dimeric form containing bridged carbonyls,[16] such as I, but no spectroscopic evidence for bridged carbonyl complexes in the system was obtained.


I

The rate of dissociation of these complexes is dependent upon the nature of the phosphine ligand. In the nickel–dicarbonyl–diphosphine complexes, the rate of dissociation of the first phosphine decreases in the order: $PCl_3 >> P(C_6H_5)_3 \sim P(CH_2CH_2CN)_3 > P(n\text{-}C_4H_9)_3 >> P(OC_2H_5)_3 \sim P(OC_6H_5)_3$. In many cases, dissociation of the mixed phosphine complex was too slow to be measured.

From the rate data at different temperatures (Table IV) the heat of activation for the exchange reaction of $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$ with $P(n\text{-}C_4H_9)_2$ is found to be 25.5 kcal./mole. The entropy of activation is calculated to be + 10.5 e.u.

Nickel–Tricarbonyl–Monophosphines.—The nickel–tricarbonyl–monophosphine complexes undergo ligand exchange with added phosphine either by (1) initial CO–phosphine exchange followed by phosphine–phosphine exchange or by (2) initial phosphine–phosphine exchange followed by CO–phosphine exchange. The tricarbonyl complexes of triphenylphosphine, tri-*n*-butylphosphine and triethylphosphite exchange with tri-*n*-butylphosphine according to mechanism 1 above (equations 5 and 6 where $PR_3 = P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$ or $P(OC_2H_5)_3$ and $PR'_3 = P(n\text{-}C_4H_9)_3$)

$$Ni(CO)_3 + PR'_3 \overset{k_1}{\rightleftharpoons} \underset{\text{II}}{Ni(CO)_2(PR_3)(PR'_3)} + CO \quad (5)$$

$$Ni(CO)_2(PR_3)(PR'_3) + PR'_3 \overset{k_2}{\rightleftharpoons} \underset{\text{III}}{Ni(CO)_2(PR'_3)_2} + PR_3 \quad (6)$$

In the reactions of $Ni(CO)_3P(C_6H_5)_3$ with $P(n\text{-}C_4H_9)_3$, the observed infrared carbonyl bands for the intermediate product II and the final product III are identical with those of $Ni(CO)_2[P(C_6H_5)_3][P(n\text{-}C_4H_9)_3]$ and $Ni(CO)_2[P(n\text{-}C_4H_9)_3]_2$, respectively. Further proof that the reaction follows equations 5 and 6 is shown by the nearly identical rate constants for the dissociation of the mixed phosphine complex II when it is formed from $Ni(CO)_2[P(C_6H_5)_3]_2$ and $P(n\text{-}C_4H_9)_3$ and when it

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(16) E. O. Fischer, *Angew. Chem.*, **69**, 715 (1957); E. O. Fischer and C. Palm, *Ber.*, **91**, 1725 (1958).

is formed from $\mathrm{Ni(CO)_3[P(C_6H_5)_3]}$ and $\mathrm{P(}n\mathrm{\text{-}C_4H_9)_3}$ (Table III).

As in the case of the nickel–dicarbonyl–diphosphine complexes, the initial step is probably a slow rate-determining dissociation of the original complex into a tricoördinated nickel species

$$\mathrm{Ni(CO)_3PR_3 \rightleftharpoons Ni(CO)_2PR_3 + CO} \qquad (7)$$

since the rate is independent of the nature of the attacking phosphine. In acetonitrile nearly identical rate constants are obtained for reaction of $\mathrm{Ni(CO)_3[P(C_6H_5)_3]}$ with $\mathrm{P(C_6H_5)_3}$ and with $\mathrm{P(CH_2CH_2CN)_3}$ (Table III).

The observed order of CO–phosphine exchange of these tricarbonyl complexes is $\mathrm{P(C_6H_5)_3}$ (10^4k = 8.23 sec.$^{-1}$) > $\mathrm{P(}n\mathrm{\text{-}C_4H_9)_3}$ (10^4k = 5.99 sec.$^{-1}$) > $\mathrm{P(OC_2H_5)_3}$ (10^4k = 2.76 sec.$^{-1}$). The similarity of these rate constants indicates that dissociation of CO from nickel–tricarbonyl–monophosphine complexes is only slightly dependent upon the nature of the phosphine ligand.

Tricarbonyltrichlorophosphinenickel exchanges with $\mathrm{P(}n\mathrm{\text{-}C_4H_9)_3}$ according to mechanism 2 above (equations 8 and 9 where $\mathrm{PR_3 = P(}n\mathrm{\text{-}C_4H_9)_3}$)

$$\mathrm{Ni(CO)_3PCl_3 + PR_3} \overset{k_1}{\rightleftharpoons} \underset{\mathrm{IV}}{\mathrm{Ni(CO)_3PR_3}} + \mathrm{PCl_3} \qquad (8)$$

$$\mathrm{Ni(CO)_3PR_3 + PR_3} \overset{k_2}{\rightleftharpoons} \mathrm{Ni(CO)_2(PR_3)_2 + CO} \qquad (9)$$

The rate of the first step was too fast to measure. The second step was the CO–phosphine exchange of $\mathrm{Ni(CO)_3[P(}n\mathrm{\text{-}C_4H_9)_3]}$ with $\mathrm{P(}n\mathrm{\text{-}C_4H_9)_3}$. Although $\mathrm{Ni(CO)_3[P(}n\mathrm{\text{-}C_4H_9)_3]}$ has not been prepared in a pure state, its identity with the intermediate complex IV has been established by the fact that it has infrared carbonyl bands at the same place (2070 and 2000 cm.$^{-1}$) as the compound produced by passing CO gas into a solution of $\mathrm{Ni(CO)_2[P(}n\mathrm{\text{-}C_4H_9)_3]_2}$ in cyclohexane.

We have demonstrated that a reversible equilibrium exists between nickel–tricarbonyl–monophosphine and nickel–dicarbonyl-diphosphine (*i.e.*, that equation 10 is reversible) for several different phosphines by the following experiment: carbon

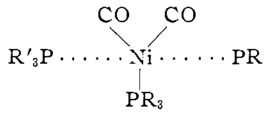
$$\mathrm{Ni(CO)_2(PR_3)_2 + CO \rightleftharpoons Ni(CO)_3PR_3 + PR_3} \qquad (10)$$

monoxide gas was bubbled through a solution of pure nickel–dicarbonyl–diphosphine in cyclohexane for a few minutes. Infrared analysis of this solution showed a large decrease in the bands due to dicarbonyl and a significant buildup of the bands due to tricarbonyl. The carbon monoxide stream was shut off and nitrogen was bubbled through the solution for several minutes to remove the dissolved carbon monoxide. The infrared spectrum of the solution at this point was identical with the original solution, *i.e.*, the dicarbonyl bands had increased to their original intensity and the tricarbonyl bands had disappeared. The relative concentrations of dicarbonyl and tricarbonyl species in the solution are a function of the concentration of free carbon monoxide in the system. Therefore, the primary dissociation of the dicarbonyl–diphosphine (equation 3) and the primary dissociation of the tricarbonyl–monophosphine with loss of CO (equation 7) are both reversible reactions.

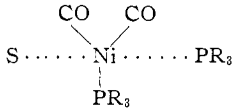
Solvent Effects.—The effect of solvent on the rate constant is shown in certain of the reactions of $\mathrm{Ni(CO)_3[P(C_6H_5)_3]}$ listed in Table III. The rate constant for the complex with $\mathrm{P(C_6H_5)_3}$ as the attacking reagent is nearly 2.5 times larger in a polar solvent, acetonitrile, than it is in a nonpolar solvent, cyclohexane. This rate enhancement may be due to complex formation between the nitrile group of acetonitrile and the nickel complex; however, the size of the rate increase suggests that this is simply a polar solvent effect. This solvent effect was taken into consideration in the order of initial dissociation of the diphosphine complexes reported below. These results indicate that the activated complex for dissociation is more polar than the original nickel complex, which is reasonable if the nickel–carbonyl–phosphine complexes are tetrahedral (see below) and therefore have a small dipole moment.

Discussion

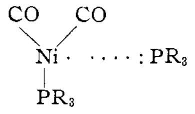
Nickel tetracarbonyl is tetrahedral[17] and the $\mathrm{Ni(PX_3)_4}$ (X = F, Cl, Br and NCO) compounds discovered by Wilkinson[18] are diamagnetic and presumably tetrahedral. The diamagnetic phosphine-sustituted nickel carbonyl complexes in all probability also have tetrahedral structure, possibly distorted by the difference in the steric requirements and the bonding of the phosphine and CO ligands. Since tetracoördinated Ni(0) has a filled 3d shell, the only type of bimolecular substitution on tetrahedral nickel theoretically possible would be through a partially bonded pentacoördinated "activated complex" analogous to that postulated for bimolecular substitutions on tetrahedral carbon



The kinetic results reported in this paper rule out such a structure for the activated complex. A solvent-assisted dissociation going through a structure such as



cannot be ruled out entirely but appears unlikely in view of the small solvent effect observed. Therefore, the unimolecular heterolytic dissociation of the complex through an activated state such as



to form a tricoördinated nickel species as an intermediate seems to be the most reasonable mechanism for the first step in these exchange reactions. The fourth coördination position of the nickel may be occupied subsequently by a solvent molecule;

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[17] L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, **3**, 828 (1935).

[18] J. W. Irvine and G. Wilkinson, *Science*, **113**, 742 (1951); G. Wilkinson, THIS JOURNAL, **73**, 5501 (1951); *Z. Naturforsch.*, **9b**, 446 (1954).

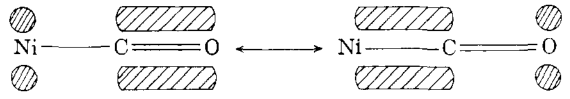
this is especially likely in polar complex-forming solvents such as acetonitrile.

Although a large number of complexes of phosphines with many of the transition metals have been prepared, the nature of the bonding in these complexes until recently has remained very obscure.[19,20] Almost the only work of a quantitative nature on transition metal complexes of phosphines has been done by Chatt and Wilkins,[21] but restricted to the planar complexes of Pt(II).

Trivalent phosphorus compounds can participate in both σ- and π-bonding in transition metal complexes because of the presence of an unshared electron pair in a 3s orbital for donation and of vacant 3d orbitals of energy low enough to accept electrons from the filled lower d orbitals of the metal by back-bonding. The σ-bonding ability or basicity of phosphines is found to be a function of the inductive effect of the substituents on the phosphorus.[22–24] In a comparison of basicities of phosphines toward protons by non-aqueous titration with perchloric acid in nitromethane, the order of decreasing basicity was found to be[25]: $P(n\text{-}C_4H_9)_3 > P(OC_2H_5)_3 \geqslant P(C_6H_5)_3 \geqslant P(CH_2CH_2CN)_3 \gg P(OC_6H_5)_3$. The basicity of PCl_3 probably is lower than that of $P(OC_6H_5)_3$. Therefore, the σ-bonding ability of phosphines is increased by electron-donating substituents and decreased by electron-withdrawing substituents.

The relative π-bonding ability of the phosphines has been established from the strength of their *trans*-effect in planar Pt(II) complexes.[19] The order of decreasing *trans*-effect, or π-bonding ability, $PF_3 > PCl_3 > P(OC_2H_5)_3 > P(alkyl)_3$, generally parallels the order of increasing σ-bonding ability. However, it is possible that these two types of bonds may additively enhance one another in transition metal complexes, conferring an unusually high stability on the phosphorus–metal bond.[7]

Carbon monoxide forms very weak σ-bonds with non-transition elements; hence the bonds between nickel and CO must have considerable π-character in order to form stable complexes.[10,19a] The frequency of the carbonyl absorption in nickel carbonyl complexes is primarily a function of the degree of π-bonding to give a structure such as Ni=C=O where a 3d electron pair of the nickel is donated to a 2p orbital of the carbon. The metal carbonyl bonding in these complexes may be represented by resonance between structures V and VI in which only those atomic and molecular orbitals in which bonding changes occur are shown in the usual MO representation[26] and the other bonds are represented by lines. Nickel carbonyl complexes absorb at frequencies (1850–2100 cm.$^{-1}$) intermediate between triply-bonded carbon monoxide (2143 cm.$^{-1}$)[27] and organic carbonyl groups $R_2C{=}O$ (about 1700 cm.$^{-1}$), in which a double bond exists between carbon and oxygen. It follows that the lower the carbonyl frequency in the complex, the less triple bonding exists between carbon and oxygen [structure V is less important], and the more double bonding exists between the metal and carbon [structure VI is more important].



V VI

The position of the infrared carbonyl bands of the nickel–dicarbonyl–diphosphine complexes is strongly influenced by the nature of the phosphine ligands. From the data in Table I, the phosphines can be arranged in the order of decreasing carbonyl stretching frequency: $PCl_3 > P(OC_6H_5)_3 > P(OC_2H_5)_3 > P(CH_2CH_2CN)_3 > P(C_6H_5)_3 > P(n\text{-}C_4H_9)_3$. The symmetric stretching frequency decreases from 2065 cm.$^{-1}$ for the PCl_3 complex to 1935 cm.$^{-1}$ for the $P(n\text{-}C_4H_9)_3$ complex. The frequencies for the mixed phosphine complexes fall between those for the two individual phosphines. The same trend can be seen in the tricarbonyl–monophosphine complexes, although here the effects are smaller. On closer inspection of the above series an interesting comparison can be made of the complexes of $P(OC_2H_5)_3$, $P(CH_2CH_2CN)_3$ and $P(C_6H_5)_3$. Although these three phosphines have about equal basicity, the carbonyl frequency of the complex of $P(OC_2H_5)_3$, the best π-bonding phosphine, is much higher than the others. Also, the k_b of $P(C_6H_5)_3$ is at least $1/10^{10}$ as large as $P(n\text{-}C_4H_9)_3$[25] and yet the carbonyl frequency of the complex decreases only 20 cm.$^{-1}$ in going from the former to the latter phosphine. Hence, we can conclude that the above order of decreasing carbonyl frequencies follows most closely the decreasing π-bonding character of the phosphorus.

These results can be interpreted readily by a consideration of the over-all bonding situation in these nickel complexes.[10] In a tetrahedral sp^3 complex only two of the five available d orbitals (d_{z^2} and $d_{x^2-y^2}$) can overlap strongly with d or p orbitals of the ligands to form double bonds.[28] Thus the maximum possible number of strong double (π) bonds in a tetrahedral complex is two. The nickel–dicarbonyl–diphosphine complexes can be pictured as consisting of resonance hybrids of structures VII and VIII, where the previous notation is used and the filled orbitals are shaded. The two available filled 3d orbitals of the nickel which can be used for π-bonding must be shared by the vacant 3d orbitals of the two phosphorus atoms and the 2p orbitals of the two carbon atoms by resonance among the various possible double-bonding structures. In the dicarbonyl–diphos-

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[19] (a) E. A. Magnusson, *Revs. Pure and Appl. Chem.* (*Australia*), **7**, 195 (1957); (b) J. Chatt and A. A. Williams, *J. Chem. Soc.*, 3061 (1951).

[20] R. C. Cass, G. E. Coates and R. Hayter, *ibid.*, 4007 (1955).

[21] J. Chatt and R. G. Wilkins, *ibid.*, 2532 (1951); 273, 4300 (1952); 70 (1953); 525 (1956).

[22] H. C. Brown, *ibid.*, 1248 (1956); H. C. Brown and R. R. Holmes, Abstracts of papers presented at the 129th Meeting of the American Chemical Society, held in Dallas, Texas, April, 1956, p. 28Q.

[23] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 24.

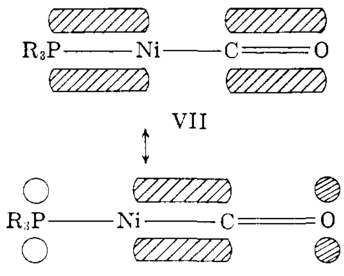
[24] K. Dimroth and A. Nurrenbach, *Angew. Chem.*, **70**, 26 (1958).

[25] C. A. Streuli, unpublished results.

[26] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949.

[27] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, "Diatomic Molecules" D. Van Nostrand Co., New York, N. Y., 1950, p. 123.

[28] G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).



VII

VIII

phine complexes containing weakly π-bonding phosphines (*e.g.*, $P(n\text{-}C_4H_9)_3$), the two π-bonds to the nickel are located more of the time in the carbonyl groups (structure VIII is more important); hence, the carbonyl frequencies are decreased. In those complexes containing strongly π-bonding phosphorus ligands (*e.g.*, PCl_3, $P(OR)_3$), the two carbonyl groups are forced to share the two strong π-bonds to nickel more of the time with the phosphorus ligands [structure VII is more important]; therefore, the double-bonding between nickel and carbon is reduced and the carbonyl frequencies are increased.

The effect of substituents on the phosphorus on the rate of dissociation of the phosphine ligand from nickel–dicarbonyl–diphosphine complexes seems to depend upon a number of factors. The observed order of decreasing relative dissociation rates of the various dicarbonyl–diphosphine complexes is ($P(n\text{-}C_4H_9)_3 = 1.0$): PCl_3 (> 300) $\gg$ $P(CH_2CH_2CN)_3$ (18.7) $\sim$ $P(C_6H_5)_3$(17.1) $>$ $P(n\text{-}C_4H_9)_3$ (1.0) $\gg$ $P(OC_2H_5)_3$ (< 0.003) $\sim$ $P(OC_6H_5)_3$ (< 0.003). This closely parallels the order of increasing basicity of the phosphines with the exception of the two phosphite complexes, which would be expected to fall between PCl_3 and $P(CH_2CH_2CN)_3$. The alkoxy and aryloxy substituents appear to greatly increase the strength of the Ni–P bond, possibly through the additive effect of the σ-bond with a strong π-bond. Indeed, this stabilizing effect is even transmitted to other Ni–P bonds, for the mixed phosphine complexes formed by exchange with $P(OC_6H_5)_3$, $Ni(CO)_2[P(OC_6H_5)_3](PR_3)$, do not exchange further with the phosphite except at elevated temperatures. Of course, π-bonding alone cannot account for the strength of the Ni–P bonds since the complex of PCl_3 exchanges at a very fast rate.

Bond rehybridization in the activated complex is another factor which may be of great importance in these systems. If the contribution of the bond dissociated form to the activated complex is predominant, bond reorganization energies will be large. Then the relative stability of the intermediate tricoördinated nickel complex which is formed will have a great influence on the dissociation rate. Instability of the dicarbonyl-monophosphite intermediate, $Ni(CO)_2P(OR)_3$, could account for the negligible exchange of $Ni(CO)_2[P(OR)_3]_2$ with phosphine and of $Ni(CO)_2[P(OR)_3](PR_3)$ with phosphite.

The results of the phosphine exchange reactions on tetrahedral nickel can best be interpreted by again referring to the limitation of two strong π-bonds in a tetrahedral complex.[28] This explains the low stability and rapid CO exchange[29] of $Ni(CO)_4$, which, in addition to having four weak σ-bonds, must share the two strong π-bonds among four CO ligands. This would also explain the difficulties frequently experienced in displacing more than two of the CO groups in $Ni(CO)_4$ with phosphines or other ligands. The relative stabilities of the series of nickel–carbonyl–phosphine complexes should reach a maximum in the dicarbonyl–diphosphines where the two strong π-bonds can be localized in the remaining two CO ligands and the two phosphine ligands are bound to the nickel by strong σ-bonds. This is also consistent with the fact that the only known tetrahedral complexes of Ni(0) with four phosphine ligands have been prepared from phosphines which form strong π-bonds, *e.g.*, PCl_3, PF_3 and $PCl_2(C_6H_5)$.[15,18]

On the basis of the above considerations, it is reasonable to expect primary dissociation of CO from nickel–tricarbonyl–monophosphine complexes and primary dissociation of phosphine from nickel–dicarbonyl-diphosphine complexes to give a common tricoördinated nickel species, $Ni(CO)_2PR_3$, with two strong π-bonds, one strong σ-bond, and one vacant $4s4p^3$ orbital on the nickel. The primary dissociation of PCl_3 from $Ni(CO)_3PCl_3$ probably is the result of the weaker σ-bond to this phosphine. The only nickel–monocarbonyl–triphosphine complex studied, $Ni(CO)[P(OC_2H_5)_3]_3$, did not exchange, apparently because of the unusual character of the nickel–phosphite bonds.

Our conclusion that π-bonding is relatively less important to the strength of the Ni–P bonds in nickel–carbonyl–phosphine complexes is contrary to the views of Nyholm and Short[10,30] but consistent with the observation of Woodward and Hall[31] that the force constant for the Ni–P bond in $Ni(PF_3)_4$ is in the range expected for single bonds and with the recent conclusions of Chatt and Hart[32] based on dipole moment studies of nickel–carbonyl–phosphine complexes. Fyfe[33] has also recently suggested that the strength of the bonds between the group V elements and transition metals is determined primarily by normal σ-donor bonding, and this leads him to predict a maximum of two strong π-bonds in the complexes of zero-valent nickel.

In conclusion, it appears that both the inductive (σ-bonding) and resonance (π-bonding) effects of the phosphine ligands influence the stability of the nickel–carbonyl–phosphine complexes, the σ-bonding properties governing the strength of the Ni–P bonds and the π-bonding properties affecting the strength of the Ni–C bonds. Our inability to fit $P(OC_2H_5)_3$ and $P(OC_6H_5)_3$ into this scheme underlines the fact that this is not a complete description of bonding in these complexes and suggests that other unknown factors may affect the bonding of phosphorus to metals generally. We are

[29] R. K. Sheline, R. W. Wolfgang and R. E. Johnson, Final Technical Report 2/1/55–6/30/57 Contract DA-01-009-ORD-461; D. F. Keeley and R. E. Johnson, Abstracts of papers presented at the 131st Meeting of the American Chemical Society, held in Miami, Florida, April, 1957, p. 4u.

[30] R. S. Nyholm and L. N. Short, *J. Chem. Soc.*, 2670 (1953).

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working currently to explore these factors further.

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STAMFORD, CONNECTICUT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Reactions of Nickel(II) with 2,3-Dimercapto-1-propanol[1]

BY D. L. LEUSSING

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A spectrophotometric investigation of the reactions in alkaline solutions of 2,3-dimercapto-1-propanol with nickel(II) ions has revealed the existence of two complexes, $Ni_2(DMP)_3OH^=$ and $Ni(DMP)_2^=$. The first of these complexes is brown and the second is green. The constants for the reactions $2Ni^{++} + OH^- + 3DMP^= \rightleftarrows Ni_2(DMP)_3OH^=$ and $Ni^{++} + 2DMP^= \rightleftarrows Ni(DMP)_2^=$ are calculated to be $4 \times 10^{+45}$ and $6 \times 10^{+22}$. The absorption spectra of the complexes have been determined and are discussed. The Ni–S bond appears to be predominantly σ.

The high stability of complexes of heavy metals with 2,3-dimercapto-1-propanol (British Anti Lewisite, BAL) has been recognized since its preparation. Little, however, is known quantitatively of the nature and stabilities of the complexes that are formed in solution. As one of a series of investigations into the nature of metal ion–mercaptide complexes a study was undertaken of the nickel(II)–2,3-dimercapto-1-propanol reactions. Hereafter, in this paper the latter will be referred to as DMP.

Zuman and Zumanova[2] have investigated by means of polarometric titrations the nature of the compounds formed by many heavy metal ions with DMP. They report that with nickel(II) an insoluble compound with a 1:1 ratio of metal to DMP is formed in slightly acid and alkaline solutions. They state also that in ammoniacal solutions a soluble complex is formed which is indicated to have a ratio of 1:1.5. Pribil and Roubal[3] report that nickel(II) reacts in alkaline solutions containing excess DMP to form an olive green complex.

The formation of the insoluble compound prevents the use of the conventional *p*H-titration method of determining stability constants. In the present work, the equilibria involving the soluble complexes which exist in alkaline solutions were investigated spectrophotometrically. It was found that the olive-green solutions are mixtures of two complexes, a brown one and a green one. Their absolute stabilities were obtained from the results of experiments in which DMP and ethylenediaminetetraacetate ions were allowed to compete for limited amounts of nickel ions.

In this connection, Pribil and Roubal[3] who have proposed the use of DMP in chelatometric titrations of mixtures of metal ions report that DMP does not replace EDTA bound to Ni(II), although the EDTA is replaced readily by DMP with the other divalent transition metal complexes. This seeming anomaly has been demonstrated in the present investigation to be due to the effect of rates of reaction. The soluble Ni(II)–DMP complexes were found to have very great stability, presumably, in line with those of the other transition metals.

Experimental

2,3-Dimercapto-1-propanol, J. T. Baker Chemical Company, was vacuum distilled. During the distillation dry, high purity nitrogen was bled into the system to prevent bumping. The fraction distilling at 74–76° (1 mm.) was collected and stored under nitrogen at −10°. Air-free aqueous solutions of DMP were prepared by weight from the redistilled reagent. Solutions which were 0.02 *M* or less in DMP were prepared by dissolution of the reagent in air-free water. Solutions which were 0.05 to 0.10 *M* were prepared by adding an equimolar amount of air-free sodium hydroxide solution to the weighed reagent and diluting with the necessary amount of de-aerated water.

Nickel nitrate solution, 0.516 *M*, was prepared from the reagent-grade material and standardized by the cyanide method.[4] Solutions for use in the experiments were prepared by dilution of this stock solution.

Disodium dihydrogenethylenediaminetetraacetate·$2H_2O$ solution, 0.1000 *M*, was prepared by weight from the Fisher reagent. Analysis[5] against a standard zinc solution showed this product to have a purity of 100 ± 0.5%.

Ammonia stock solutions were prepared from the redistilled reagent.

Redistilled water was used throughout.

Solutions of DMP, especially those which are alkaline, are extremely air-sensitive. For this reason rigorous precautions were taken to exclude air during the preparation and equilibration of all DMP solutions. The sealed bottle-syringe technique described previously[6] was employed in preparing solutions of the complexes.

Preliminary experiments revealed no essential differences in the equilibrium properties of Ni(II)–DMP mixtures in either sodium hydroxide solutions or ammonia buffers. Equilibrium was slow to be attained but appeared to be reached faster in the less alkaline solutions. For this reason most of the final measurements were made in ammoniacal buffers, 0.100 *M* in NH_4Cl and at *p*H 9.27, 9.88 or 10.14. The total nickel(II) concentration, Ni_t, was varied from 0.00052 to 0.00206 *M* and the total DMP concentration, DMP_t, was varied from 0.00050 to 0.0103 *M*. All solutions were equilibrated in a water-bath at 30.0 ± 0.5°. Twenty-

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