

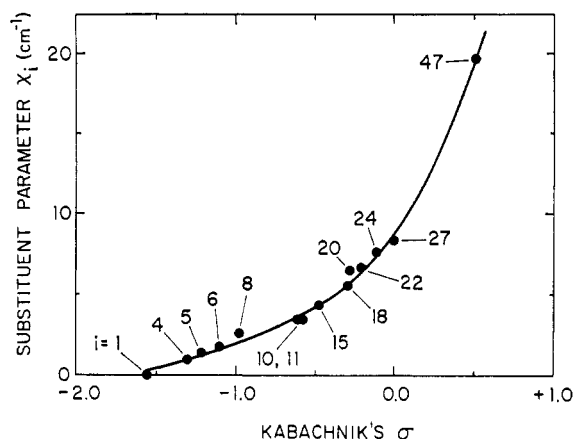
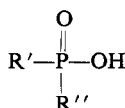


Figure 2. Correlation of substituent parameter χ_i with Kabachnik's σ from ref 24. The substituent indices refer to Table II.

been proposed by Kabachnik, based on acid ionization constants in water of phosphorus acids of the type²⁴



He subsequently found an excellent correlation (correlation coefficient $r = 0.95$) between these parameters and the phosphonium ion $\text{p}K_a$'s of HPR_3^+ reported by Henderson and Streuli,²³ with the points for PR_2H and PRH_2 phosphines falling on the same line.²⁵ The ex-

(24) M. I. Kabachnik, *Dokl. Akad. Nauk. SSSR*, **110**, 393 (1956); *Proc. Acad. Sci. USSR, Chem. Sect.*, **110**, 577 (1956).

cellent correlation between our substituent parameters based on CO stretching frequencies and Kabachnik's σ values²⁴ is shown in Figure 2. We have found a similar correlation between χ_i and the phosphonium $\text{p}K_a$'s. It is clear that in the reaction of H^+ with PR_3 to form a phosphonium ion, it is the σ donor ability of the phosphorus which determines the equilibrium constant, since π bonding cannot be involved between H and P.

While it is clear that more electron-withdrawing substituents give higher CO stretching frequencies, there does not appear to be sufficient evidence at this time to say to what extent the reduced electron density on nickel is to be attributed to a reduced σ donation or an enhanced π -acceptor behavior of phosphorus in the complexes.

It might be expected that double bond character in the Ni-P bonds might reflect itself in greater strength of the bonds and in more stability of the complexes. The effect of electronic changes in phosphorus ligands on the stability of their Ni(0) complexes will be considered in the following paper.²⁶

Acknowledgments. I am indebted to several persons in these laboratories for the donation of ligand samples: C. W. Alegranti, R. D. Cramer, W. D. Drinkard, L. W. Gosser, W. H. Knoth, P. J. Krusic, J. J. Mrowca, M. T. Musser, G. S. Reddy, R. A. Schunn, W. A. Sheppard, A. C. L. Su, and O. F. Vogl. I also wish to thank R. D. Coulson for bringing the work of Kabachnik to my attention.

(25) M. I. Kabachnik and G. A. Balueva, *Izv. Akad. Nauk SSSR*, 536 (1962); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 495 (1962).

(26) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

Phosphorus Ligand Exchange Equilibria on Zerovalent Nickel. A Dominant Role for Steric Effects

Chadwick A. Tolman

Contribution No. 1604 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received August 29, 1969

Abstract: Ligand exchange on Ni(0) was carried out using 24 phosphorus ligands L and 12 NiL_4 complexes. The new complexes $\text{Ni}[\text{P}(\text{CH}_3)_3]_4$, $\text{Ni}[\text{P}(\text{OCH}_2\text{CCl}_3)_3]_4$, and $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$ are disclosed. ^{31}P nmr data on the starting ligands and complexes and on a number of mixed complexes of the type $\text{NiL}_{4-n}\text{L}'_n$ are reported. From the product distributions after toluene solutions of NiL_4 and $4\text{L}'$ were equilibrated, the ligands can be ranked in a series according to the stability of the complexes. A quantitative measure of steric effects in phosphorus-transition metal complexes is proposed, based on measurements on atomic models. It is shown that steric effects are much more important than electronic effects in determining the exchange equilibria among phosphorus ligands on Ni(0), as well as in determining the degree of substitution of CO from $\text{Ni}(\text{CO})_4$ by these ligands. Implications of these results for other transition metal complexes are discussed. Spectroscopic evidence indicates that $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ and $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$, the complexes with the largest ligands, are extensively dissociated in solution; the other complexes are not.

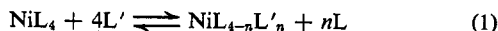
Since the discovery of $\text{Ni}[\text{PCl}_3]_4$ ¹ and $\text{Ni}[\text{PF}_3]_4$ ² in 1951, a variety of zerovalent nickel complexes with phosphorus ligands have been described in the litera-

(1) J. W. Irvine, Jr., and G. Wilkinson, *Science*, **113**, 742 (1951).

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

ture. Little appears to be known, however, about the relative stabilities of the complexes or about the factors which are important in determining the stability. We wish to report the results of a series of experiments which indicate the relative importance of electronic and

steric factors. Ligand-competition experiments were carried out in which a toluene solution of a NiL_4 complex, usually 0.2 M, was treated with a competing ligand L' , usually 0.8 M, so that the total concentration of each ligand was the same. The exchange indicated by eq 1 was allowed to proceed to equilibrium by allowing



the solutions to stand at room temperature for 1 week, or by heating in some cases at a temperature of 100° for various periods of time. Equilibration of the solutions was established in several cases by running the reactions in reverse, by treating NiL'_4 with 4L .

From the relative intensities of free and bound ligand resonances in the ^{31}P nmr spectra of the equilibrated solutions, the extent of exchange was determined and each ligand assigned a position in a relative stability series. The order of ligands in the series was not correlated with the electronic properties of the phosphorus ligands. Atomic models were used to define a quantitative steric effect parameter which did correlate well with the stability data. Displacement of CO from $\text{Ni}(\text{CO})_4$ by various phosphorus ligands confirmed the expectation that the degree of replacement would decrease as the size of the ligand increased.

Finally, spectrophotometric experiments show that $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$ and $\text{Ni}[\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3]_4$ are not dissociated to any detectable extent even in highly dilute solution. Complexes $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ and $\text{Ni}[\text{P}(\text{O}-\text{C}_6\text{H}_4\text{CH}_3)_3]_4$ with much bulkier ligands are extensively dissociated in solution.

Experimental Section

^{31}P nmr spectra were recorded at ambient temperature using a Varian HA-100 spectrometer at 40.5 Mc. Chemical shifts were measured by the side-band technique with P_4O_6 in a concentric capillary. Chemical shifts were reproducible to ± 0.3 ppm and coupling constants to ± 5 cps. Solutions for nmr were prepared and stored in a N_2 atmosphere in a drybox using deoxygenated reagent grade solvents, usually toluene.

Infrared spectra were recorded on a Perkin-Elmer 221 using 0.1-mm NaCl cells made by Barnes Engineering, Inc. Spectra were calibrated using 0.2 atm of CO gas in a 10-cm cell.³ Reported frequencies were generally reproducible to ± 2 cm^{-1} . Reactions involving substitution of carbonyls of $\text{Ni}(\text{CO})_4$ by various ligands were carried out under N_2 in 20-cm (5-mm o.d.) nmr tubes. To each tube were added 0.2 mmol of phosphorus ligand and 0.5 ml of 0.05 M $\text{Ni}(\text{CO})_4$ in toluene. The tubes were allowed to stand for 1 day at room temperature before infrared spectra were run. The tubes were then chilled in liquid N_2 , evacuated, and sealed. After being heated for 64 hr at 100° to ensure completion of the reaction, the tubes were opened under N_2 and a second series of ir spectra recorded.

Resealing several of the tubes as before and heating further at 100° for 74 hr did not alter the degree of substitution, indicating that equilibrium had been reached at 100° during the first 64-hr heating period.

Ultraviolet spectra were recorded on a Cary 14 using quartz cells from Optical Cell Co., Inc. Deoxygenated anhydrous reagent CH_3OH was used as a solvent. Beer's law was confirmed for $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$, $\epsilon_{\text{max}}(\text{CH}_3\text{OH})$ 238 $\text{m}\mu$ (ϵ 2.6×10^4), and $\text{Ni}[\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3]_4$, $\epsilon_{\text{max}}(\text{CH}_3\text{OH})$ 237 (2.8×10^4), at concentrations of 3.03×10^{-3} , 3.03×10^{-4} , and 3.03×10^{-5} M in cells of from 0.1 to 10 mm, so that the product of concentration and path length was held constant. Spectra of 5.0×10^{-3} M $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$ in an 0.1-mm cell with added concentrations of 0.5, 1.0, 2.0, and 4.0 M $\text{P}(\text{OC}_2\text{H}_5)_3$, run against corresponding concentrations of ligand in the reference cell, were identical with the spectrum with no added ligand.

(3) "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," as reprinted in *Pure Appl. Chem.*, 1 (4), 581 (1961).

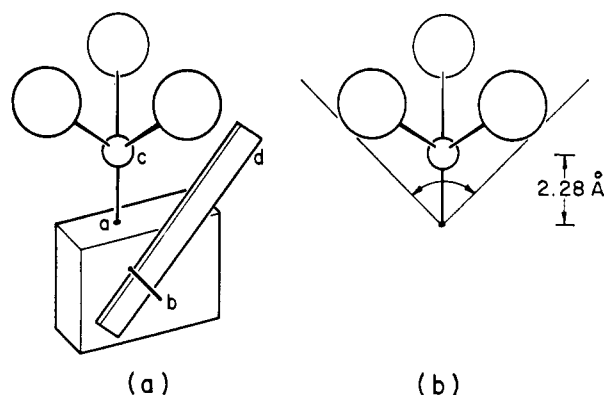


Figure 1. (a) Ligand angle measuring device, (b) the ligand cone.

Although $\text{Ni}[\text{P}(\text{OCH}_2\text{CCl}_3)_3]_4$ was only slightly soluble in CH_3OH , a saturated solution in a 1-mm cell showed a maximum at 238 $\text{m}\mu$ with an absorbance of 0.29.

Proton nmr spectra were recorded on Varian A-60 and HA-100 spectrometers using internal tetramethylsilane as reference.

Melting points were determined in evacuated, sealed capillaries on a Mel-Temp apparatus and are uncorrected.

CPK atomic models from the Ealing Corp., Cambridge, Mass., were used to make models of various phosphorus ligands, with a scale of 1.25 cm/Å. An angle measuring device was constructed consisting of a block of wood with a hole "a" in the top and a pivot pin "b" on the side, as shown in Figure 1. Into the hole went a supporting pin joined by means of an Ealing connector to one face of a tetrahedral P atom, "c." The ligand could be freely rotated about the supporting pin. The lower tip of the supporting pin and the lower edge of the pivot pin were located 2.85 cm (2.28 Å) from the center of the P atom. The distance was chosen to represent the distance between centers of P and Ni.⁴

A straightedge, "d", held to the side of the block and touching the pivot pin was used to determine the maximum clearance angle for rotation of the ligand. Clearance angles on both right and left sides were determined and measured with a protractor. The sum of these angles was taken to be the apex angle of the subtending cone illustrated in Figure 1. In cases where a ligand model had some flexibility, an effort was made to fold back the substituents on P so as to minimize the subtending cone while maintaining threefold symmetry. With rigid ligands such as PH_3 , $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, or $\text{P}(\text{C}_6\text{H}_5)_3$, the reproducibility was $\pm 2^\circ$. In other cases, especially where the introduction of angle strain could lead to smaller cone angles, the uncertainty was as large as $\pm 10^\circ$.

Complexes

Warning. Trimethylphosphine is highly toxic and volatile, and ignites spontaneously on exposure to air. The complex $\text{Ni}[\text{P}(\text{CH}_3)_3]_4$ flashes and crackles in air and might present an explosion hazard in large quantities.

Tetrakis(trimethylphosphine)nickel. The complex $\text{Ni}[\text{P}(\text{CH}_3)_3]_4$ was prepared by the reaction of $\text{P}(\text{CH}_3)_3$ with bis(1,5-cyclooctadiene)nickel,⁵ which was provided by Dr. F. M. Armbricht, Jr. To a stirred slurry of 2.7 g (10 mmol) of bis(1,5-cyclooctadiene)nickel in 20 ml of anhydrous ether at -50° was added 3.6 g (42 mmol) of PMe_3 in 5 ml of ether. The slurry was allowed to warm slowly with stirring, then heated at reflux for 0.5 hr. The dark brown solution was cooled to 0° , filtered, and evaporated under vacuum. To the residual 3.0 g of brown oil was added 5 ml of acetonitrile. Cooling, filtering, and washing with chilled acetonitrile and methanol gave the light yellow crystalline product: 2.2 g (62%), decomposition above 160° , pmr (C_6D_6) τ 8.83 (m, $-\text{CH}_3$).

(4) The nickel-phosphorus bond length used of 2.28 Å is probably overestimated. There appear to be no Ni-P bond distances available for tetrahedral Ni(0) complexes; however, a value of 2.22 Å has been reported in $[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$ by W. A. Spofford, III, P. D. Carfagna, and E. L. Amma, *Inorg. Chem.*, 6, 1553 (1967), while a value of 2.19 Å has been reported for $(\text{C}_6\text{H}_5)_4\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ by C. D. Cook, C. H. Koo, S. C. Nyburg, and M. T. Shioml, *Chem. Commun.*, 426 (1967).

(5) B. Bogdanovic, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, 699, 1 (1966).

Anal. Calcd for $C_{12}H_{38}NiP_4$: C, 39.7; H, 10.0; Ni, 16.2; P, 34.2. Found: C, 37.3; H, 9.3; Ni, 16.3; P, 33.4.

The complex is soluble in ether or hydrocarbons, slightly soluble in methanol or acetonitrile, and insoluble in water; it reacts rapidly with CCl_4 or $CHCl_3$ and somewhat more slowly with CH_2Cl_2 . Though rapidly destroyed by air, the complex is stable indefinitely under nitrogen at room temperature.

Tetrakis(tri-2,2,2-trichloroethyl phosphite)nickel. The complex $Ni[P(OCH_2CCl_3)_4]$ was prepared by the addition of 7.0 g (14.7 mmol) of $P(OCH_2CCl_3)_3$ in 15 ml of ether to a stirred slurry of 0.56 g (3.4 mmol) of bis(acrylonitrile)nickel in 10 ml of anhydrous ether. Stirring for 1 hr gave a cream colored precipitate. The solvent was evaporated under vacuum. The crude product was dissolved in 15 ml of CH_2Cl_2 . Addition of 50 ml of methanol gave a white precipitate. Cooling, filtering, and washing with chilled methanol gave the product as a white powder: 6.2 g (93%), dec 200–203°, pmr ($CDCl_3$) τ 5.16 ($-OCH_2CCl_3$).

Anal. Calcd for $C_{24}H_{54}Cl_{18}NiP_4O_{12}$: C, 14.7; H, 1.2; Cl, 64.9; Ni, 3.0; P, 6.3. Found: C, 15.2; H, 1.3; Cl, 63.3; Ni, 2.4; P, 6.6.

The complex was soluble in CH_2Cl_2 , acetone, and benzene, and insoluble in methanol, acetonitrile, and water. The complex is very stable toward oxidation; there were no signs of decomposition after a week at room temperature in air.

Tetrakis(triethyl phosphite)nickel.⁶ The white crystalline complex $Ni[P(OC_2H_5)_4]$ was prepared from $NiCl_2 \cdot 6H_2O$ and $P(OC_2H_5)_3$ in the presence of diethylamine: decomposition⁷ above 200° [lit.⁶ mp 108°]; pmr ($CDCl_3$) τ 6.13 (m, 2, $-OCH_2CH_3$), 8.86 (t, 3, $J = 7$ cps, $-OCH_2CH_3$).

Anal. Calcd for $C_{24}H_{60}NiP_4O_{12}$: C, 39.8; H, 8.4; Ni, 8.1; P, 17.1. Found: C, 40.0; H, 8.4; Ni, 8.1; P, 17.0.

Tetrakis(trimethyl phosphite)nickel.⁸ The complex $Ni[P(OCH_3)_4]$ was prepared by the reaction of bis(acrylonitrile)nickel with $P(OCH_3)_3$ by the method of Kutepow, *et al.*⁹ To a stirred slurry of 3.6 g (22 mmol) of bis(acrylonitrile)nickel in 30 ml of anhydrous ether was added 12 ml of $P(OCH_3)_3$ (100 mmol) in 20 ml of ether. The clear gray solution was evaporated under vacuum. The residual 12.8 g of crude gray solid was dissolved in 10 ml of methanol. Chilling in Dry Ice, filtering, and washing with 5 ml of chilled methanol gave a white crystalline product: 9.95 g (82%), decomposition above 215°, pmr ($CDCl_3$) τ 6.56 (m, $-OCH_3$).

Anal. Calcd for $C_{12}H_{18}NiP_4O_{12}$: C, 26.0; H, 6.5; Ni, 10.6; P, 22.4. Found: C, 25.8; H, 6.5; Ni, 10.7; P, 23.1.

Tetrakis(tri-2-chloroethyl phosphite)nickel.¹⁰ The compound $Ni[P(OCH_2CH_2Cl)_4]$ was prepared by a modification of the method of Vinal and Reynolds.⁶ A slurry of 2.4 g of crushed $NiCl_2 \cdot 6H_2O$ (10 mmol) in 30 ml of acetonitrile was brought to a boil and allowed to cool. To this was added 10 ml (50 mmol) of $P(OCH_2CH_2Cl)_3$ and the deep purple solution filtered. Addition of 2 ml (20 mmol) of diethylamine gave a light yellow solution. Addition of 15 ml of water gave two phases. The heavier organic phase was separated, dried with anhydrous Na_2SO_4 , and evaporated under vacuum.

The 11.0 g of residual pale yellow oil was dissolved in 3 ml of CH_2Cl_2 . Addition of 15 ml of methanol gave a white precipitate. Cooling, filtering, and washing with chilled methanol gave a white crystalline solid: 3.2 g (28%), dec¹¹ 196–198° (lit.^{10a} mp 138–140°); pmr ($CDCl_3$) τ 5.76 (m, 2, $-OCH_2CH_2Cl$), 6.30 (t, 2, $J = 6$ cps, $-OCH_2CH_2Cl$).

Anal. Calcd for $C_{24}H_{48}Cl_{12}NiP_4O_{12}$: C, 25.4; H, 4.3; Cl, 37.5; Ni, 5.2; P, 10.9. Found: C, 25.6; H, 4.3; Cl, 35.7; Ni, 5.4; P, 11.1.

Tetrakis(triphenyl phosphite)nickel, $Ni[P(OC_6H_5)_4]$, was donated by Dr. W. C. Drinkard, and **tetrakis(tri-*p*-tolyl phosphite)nickel**, $Ni[P(O-*p*-C_6H_4CH_3)_4]$, and **tetrakis(tri-*p*-methoxyphenyl phosphite)nickel**, $Ni[P(O-*p*-C_6H_4OCH_3)_4]$, by Dr. R. G. Downing. They can all be prepared from nickelocene and the ligand as described by Olechowski, *et al.*^{10a} **Tetrakis(diethyl phenylphospho-**

nite)nickel, $Ni[P(C_6H_5)(OC_2H_5)_3]_4$, and **tetrakis(4-methyl-2,6,7-tri-oxa-1-phosphabicyclo[2.2.2]octane)nickel**, $Ni[P(OCH_2)_3CCH_3]_4$, were furnished by Dr. J. J. Mrowca. Both were prepared from nickelocene by the method of Olechowski, *et al.*^{10a} **Tetrakis(triphenyl phosphine)nickel**, $Ni[P(C_6H_5)_3]_4$, was furnished by Dr. R. A. Schunn. It was prepared by the reduction of bis(acetylacetonato)nickel with triethylaluminum as described by Wilke, *et al.*⁵ **Tetrakis(tri-*o*-tolyl phosphite)nickel**, $Ni[P(O-*o*-C_6H_4CH_3)_4]$, was furnished by Dr. L. W. Gosser.¹²

Ligands

$P(OCH_2CCl_3)_4$ was prepared by the reaction of PCl_3 with $HOCH_2CCl_3$ in the presence of pyridine.¹³ The $P(CH_3)_3$ was prepared by the thermal decomposition of the silver iodide complex¹⁴ provided by Dr. F. N. Tebbe. The ligands $P(C_6H_5)(OC_2H_5)_3$ ¹⁵ and $P(OCH_2)_3CCH_3$ ¹⁶ were provided by Dr. J. J. Mrowca, who prepared them by literature methods. The $(CH_3)_2PCH_2CH_2P(CH_3)_2$ ¹⁷ was furnished by Dr. R. A. Schunn and the $P(CH_3)_3CF_3$ ¹⁸ by Dr. W. Mahler. $P(t-C_4H_9)_3$ was prepared by Dr. O. F. Vogl, who will report on its preparation and properties in a separate publication. The $P(O-*p*-C_6H_4OCH_3)_3$, $P(O-*p*-C_6H_4CH_3)_3$, and $P(O-*o*-C_6H_4CH_3)_3$ were prepared by Drs. R. G. Downing, R. J. Kassal, and L. W. Gosser by reaction of the substituted phenols with PCl_3 .¹⁵ $P(C_6F_5)_3$ ¹⁹ was supplied by Drs. A. C. L. Su and R. A. Schunn.

$P(OCH_2CH_2Cl)_3$ was kindly provided by Mobile Chemical, Industrial Chemicals Division, as a research sample. Other phosphorus ligands were obtained from commercial sources and were used without further purification.

Results and Discussion

Ligand Exchange Experiments

The ³¹P chemical shifts of the complexes and free ligands measured in this study are shown in Table I. The spectra of the NiL_4 complexes $Ni[P(CH_3)_4]$, $Ni[P(C_6H_5)(OC_2H_5)_3]_4$, $Ni[P(OC_2H_5)_4]$, $Ni[P(OCH_3)_4]$, $Ni[P(OCH_2CH_2Cl)_4]$, $Ni[P(O-*p*-C_6H_4OCH_3)_4]$, $Ni[P(O-*p*-C_6H_4CH_3)_4]$, $Ni[P(OC_6H_5)_4]$, and $Ni[P(OCH_2CCl_3)_4]$ all consisted of a single resonance, lying from 1 to 41 ppm downfield from the position expected for free ligand. Adding free ligand of the same type as in the complex gave a second resonance at the chemical shift of ligand alone in solution. These observations show that these complexes are not detectably dissociated in solution at complex concentrations of 0.2 *M* and that exchange of free and complexed ligand is slow on the nmr time scale.²⁰

Spectrophotometric experiments in methanol with $Ni[P(OC_2H_5)_4]$ and $Ni[P(OCH_2CH_2Cl)_4]$ showed that Beer's law was obeyed at concentrations of from 3×10^{-2} to 3×10^{-5} *M* complex. Thus little if any ligand dissociation occurred.²¹ Spectrophotometric evidence

(12) Preparation, physical properties, and some reactions of tetrakis(tri-*o*-tolyl phosphite)nickel and of tris(tri-*o*-tolyl phosphite)nickel will be described in a later publication.

(13) W. Gerrard, W. J. Green, and R. J. Phillips, *J. Chem. Soc.*, 1148 (1954).

(14) F. G. Mann, A. F. Wells, and D. Purdie, *ibid.*, 1828 (1937).

(15) Prepared by the reactions of $P(C_6H_5)_3-nCl_n$ by the general method given by G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p 184.

(16) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, 1, 392 (1962).

(17) G. W. Parshall, *J. Inorg. Nucl. Chem.*, 14, 291 (1960).

(18) R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3631 (1956).

(19) L. A. Wall, R. E. Donadio, and W. J. Pummer, *J. Amer. Chem. Soc.*, 82, 4846 (1960).

(20) An upper limit of about 5×10^{-4} *M* can be placed on a ligand dissociation equilibrium constant



for these complexes based on the ³¹P data, assuming that 5% dissociation would have been detected.

(21) For these complexes an upper limit of about 3×10^{-7} *M* can be estimated for *K* assuming that a 10% dissociation in the most dilute solution would have been detectable. This result for $Ni[P(OC_2H_5)_4]$ is

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

(7) The compound darkened without melting. The much lower reported melting point was presumably determined in air, where oxidation occurred at the temperature reported.

(8) H. Bigorgne, *Bull. Soc. Chim. Fr.*, 1986 (1960).

(9) N. von Kutepow, H. Seibt, and F. Meier, U. S. Patent 3,346,608 (1967).

(10) (a) J. R. Olechowski, C. G. McAlister, and R. F. Clark, *Inorg. Chem.*, 4, 246 (1965); (b) R. F. Clark, U. S. Patent 3,152,158 (1964).

(11) Presumably the literature melting point is lower because it was determined in air, where oxidation of the complex occurred.

Table I. ^{31}P Chemical Shifts of NiL_4 Complexes and Free Ligands^a

Ligand	σ_{NiL_4}	δ_{L}	$\delta_{\text{NiL}_4} - \delta_{\text{L}}$	Lit.	
				δ_{NiL_4}	δ_{L}
1. $\text{P}(i\text{-C}_4\text{H}_9)_3$		-61.1			
2. $\text{P}(i\text{-C}_2\text{H}_5)_3$		-19.3			
3. $\text{P}(\text{C}_6\text{H}_5)_3$		+33.3			+32.6 ^h
4. $\text{P}(\text{C}_2\text{H}_5)_3$		+21.0			+20.4 ⁱ
5. $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$	-18.1 ^b	+49.4	-67.5		
6. $\text{P}(\text{CH}_3)_3$	+22.2	+63.3	-41.1		+62 ^j
7. $\text{P}(o\text{-C}_6\text{H}_4\text{CH}_3)_3$		+30.2			
8. $\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)$		+13.1			+12.0 ^h
9. $\text{P}(\text{C}_6\text{H}_5)_3$	<i>c</i>	+5.8			+5.9 ⁱ
10. $\text{P}(\text{C}_6\text{H}_5)_2(\text{OC}_2\text{H}_5)$		-110.5			-109.5 ^k
11. $\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2$	-162.1	-153.5	-8.6		-158.5 ^l
12. $\text{P}(\text{OC}_2\text{H}_5)_3$	-158.4	-137.8	-20.6	-160 ^h	-140 ^h
13. $\text{P}(\text{OCH}_3)_3$	-163.3	-140.4	-22.9	-163 ^m	-141 ⁿ
14. $\text{P}(\text{CH}_3)_2\text{CF}_3$		+26.9 ^d			
15. $\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3$	-156.7	-138.2	-18.5		-138.7 ⁱ
16. $\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	-131.6	-128.2	-3.4		
17. $\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{CH}_3)_3$	-130.4	-127.7	-2.7		-127.6 ⁱ
18. $\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3$	(-128.3) ^e	-130.0	(+1.7) ^e		
	-129.0		+1.0		
19. $\text{P}(\text{OC}_6\text{H}_5)_3$	-128.8 ^f	-127.3	-1.5		-126.8 ⁱ
20. $\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$		-92.5		-128 ^m	-94.0 ^o
21. $\text{P}(\text{OCH}_2)_3\text{CCH}_3$	<i>s</i>	-90.9			-91.5 ^p
22. $\text{P}(\text{C}_6\text{F}_5)_3$		+75.1 ^q			+75.5 ^r
23. $\text{P}(\text{OCH}_2\text{CCl}_3)_3$	-150.2	-136.9	-13.3		
24. $\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{CN})_3$		-125.0 ^o			

^a Ppm (85% H_3PO_4) in toluene. Values obtained by subtracting 112.5 ppm from measured ppm (P_4O_6). ^b Complex not isolated but made in solution by treating $\text{Ni}[\text{P}(\text{CH}_3)_3]_4$ with $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$. ^c No ^{31}P resonance observed in saturated solution at ambient temperature. ^d $J_{\text{PF}} = 65$ cps. ^e Values refer to the tris complex $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_3$. ^f At 100° owing to low solubility at ambient temperature. ^g Benzotrinitrile solvent. ^h Reference 27. ⁱ N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Amer. Chem. Soc.*, **78**, 3557 (1956). ^j W. A. Henderson Jr., and S. A. Buckler, *ibid.*, **82**, 5794 (1960). ^k F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron*, **22**, 567 (1966). ^l R. B. Clappitt, unpublished results, as given in ref 25. ^m K. J. Coskran, R. D. Bertrand, and J. G. Verkade, *J. Amer. Chem. Soc.*, **89**, 4535 (1967). ⁿ J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *ibid.*, **78**, 5715 (1956). ^o G. H. Birum, unpublished results, as given in ref 25. ^p J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962). ^q $J_{\text{PF}} = 36$ cps. ^r O. Glemser, M. Fild, and I. Hollenberg, *Z. Naturforsch.*, **B**, **22**, 253 (1967). ^s No ^{31}P resonance observed due to poor solubility of complex.

that $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2]_4$ is not dissociated in solution has been given by Gray.²² These arguments assume that the NiL_4 and NiL_3 species would have different electronic spectra, a reasonable expectation in view of the fact that $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$, which does, in fact, dissociate extensively in solution, is white, while the tris complex and its solutions are red-orange.¹²

The two complexes which gave evidence of extensive dissociation were $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ and $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$. A saturated solution (about 0.1 *M*) of the former in toluene exhibited no detectable ^{31}P resonance at ambient temperature. Excess $\text{P}(\text{C}_6\text{H}_5)_3$ was added to a concentration of about 0.4 *M* but still no resonance could be found. The most likely explanation appears to be extensive dissociation of $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ in solution²³ accompanied by an exchange rate of free and complexed ligand which gives a very broad average resonance at room temperature.

The highly unusual complex $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$ is white as a solid but gives a red-orange toluene solution showing three resonances corresponding to free L, NiL_4 , and NiL_3 , going to higher field. The assignment was confirmed by adding additional ligand to the solution; the resonance assigned to free L increased in intensity while that assigned to NiL_3 diminished. The red-orange color also faded. The results are consistent

with the equilibrium



with $K \sim 0.06$ *M* at ambient temperature.

The ligands in Table I are arranged in order of increasing electron-accepting character, based on the carbonyl stretching frequencies of $\text{Ni}(\text{CO})_3\text{L}$ complexes.²⁴ It can readily be seen that there is no general correlation between the ^{31}P chemical shift of the free ligand with its electron donor or acceptor character.²⁵ The same holds true for the coordination chemical shift, $\delta_{\text{NiL}_4} - \delta_{\text{L}}$. Complexes of tri-*o*-tolyl phosphite are among the few reported cases of a *positive* coordination chemical shift for a phosphorus-transition metal complex.²⁶

Spectra of equilibrated solutions in the competition experiments generally contained new resonances in addition to those of the starting materials. Where detectable exchange occurred the spectra were generally of two types: (1) those in which resonances of at least some of the mixed $\text{Ni}(0)$ species $\text{NiL}_{4-n}\text{L}'_n$, $n = 0-4$, were resolved (Table II), in addition to those of free ligands L and L', and (2) those in which only broad unresolved "bound ligand" resonances were observed in

(24) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2953 (1970).

(25) A lack of dependence of ^{31}P chemical shift on the electronic nature of substituents on phosphorus was also noted by J. R. Van Wazer and J. H. Letcher in "Topics in Phosphorus Chemistry," Vol. 5, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Division of John Wiley and Sons, New York, N. Y., 1967, pp 176-179.

(26) The occurrence of a ^{31}P resonance of a complex at higher field than free ligand has also been observed in the case of $\text{Ni}(\text{PCl}_3)_4$ by Meriwether and Leto.²⁷

(27) L. S. Meriwether and J. R. Leto, *J. Amer. Chem. Soc.*, **83**, 3192 (1961).

inconsistent with the extensive dissociation proposed by Vinal and Reynolds⁶ based on molecular weight data.

(22) A. Orio, B. B. Chastain, and H. B. Gray, *Inorg. Chim. Acta*, **3**, 8 (1969).

(23) Extensive dissociation has been suggested on the basis of molecular weight data by P. Heimbach, *Angew. Chem.*, **76**, 586 (1964).

Table II. ^{31}P Chemical Shifts of Mixed Complexes $\text{NiL}_n\text{-}_4\text{L}'_n$ in Toluene^a

Ligand L	Ligand L'	Resonances due to L				Resonances due to L'			
		NiL_4	$\text{NiL}_3\text{L}'$	$\text{NiL}_2\text{L}'_2$	NiLL'_3	$\text{NiL}_3\text{L}'$	$\text{NiL}_2\text{L}'_2$	NiLL'_3	NiL'_4
$\text{P}(\text{C}_6\text{H}_5)_3(\text{OC}_2\text{H}_5)_2$	$\text{P}(\text{OCH}_2)_3\text{CCl}_3$	-162.1	-167.7 d (25) ^b	-176.1	-185.6		[-125.9] ^c	[-125.9]	
$\text{P}(\text{OCH}_3)_3$	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	-163.3	-165.5 d (22)	-168.9 t (25)			[-125.9]	[-125.9]	
$\text{P}(\text{OCH}_3)_3$	$(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$	-163.3		-165.9			-14.2		-18.1
$\text{P}(\text{OC}_2\text{H}_5)_3$	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	-158.4	-161.5 d (28)	-165.0			[-124.8]	[-124.8]	
$\text{P}(\text{OC}_2\text{H}_5)_3$	$\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	-158.4	-156.7 d (30)			-135.9			-131.6
$\text{P}(\text{OC}_2\text{H}_5)_3$	$\text{P}(\text{C}_6\text{H}_5)_2(\text{OC}_2\text{H}_5)$	-158.4	-155.1 d (19)			-128.9			
$\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3$	$\text{P}(\text{OCH}_2)_3\text{CCH}_3$	-156.7	-161.1 d (18)	-165.4			[-126.1]	[-126.1]	
$\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	$\text{P}(\text{OCH}_2\text{CCl}_3)_3$	-131.6		-131.5			-151.8 t (31)		-150.2
$\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	$(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$	-131.6		-140.2 t (29)			-11.7		-18.1
$\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	$\text{P}(\text{CH}_3)_3$	-131.6	-133.2	-135.6 t (25)			+19.6 t (25)		+22.2
$\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	$\text{P}(\text{C}_6\text{H}_5)_3$	-131.6	-130.4 d (10)			-4.6			
$\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	$\text{P}(\text{C}_6\text{H}_5)_3$	-131.6	-128.9 d (20)			-33.2			
$\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$	$\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3$		-128.9 d (29)						
$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{OCH}_2)_3$	+22.2		+20.8	+18.7			-165.4	-163.3
$\text{P}(\text{CH}_3)_3$	$(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$	+22.2		+17.9 t (32)			-11.9		-18.1
$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{OC}_6\text{H}_5)_3$	+22.2		+21.9			-133.5 t (24)		-128.8
$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{C}_6\text{H}_5)_2(\text{OC}_2\text{H}_5)$						-125.9 t (26)	-124.1	
$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3$	+22.2	+22.0 d (44)			-130.5 q (44)			-129.0
$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{C}_6\text{H}_5)_3$	+22.2	+25.6 d (26)			-35.4			
$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)$	+22.2	+25.7 d (28)			-28.1			
$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{C}_2\text{H}_5)_3$	+22.2	+25.6 d (23)			-17.1			
$\text{P}(\text{CH}_3)_3$	$\text{P}(\text{C}_4\text{H}_9)_3$	+22.2	+25.5 d (25)			-12.3 q (25)			
$\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3$	$\text{P}(\text{C}_4\text{H}_9)_3$	-129.0		-126.6 t (32)			+0.2 t (32)		
$\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3$	$\text{P}(\text{C}_2\text{H}_5)_3$	-129.0		-126.8 t (34)			-6.7		
$\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3$	$\text{P}(i\text{-C}_3\text{H}_7)_3$	-129.0	-125.1						

^a Ppm (85% H_3PO_4). Values obtained by subtracting 112.5 ppm from measured ppm (P_4O_{10}). ^b Numbers in parentheses are coupling constants J_{PP} in cps. Abbreviations are d, doublet; t, triplet; q, quartet. ^c Numbers in square brackets are assigned to unresolved overlapping resonances.

addition to resolved and relatively sharp resonances of the free ligands. In only two cases, both involving $\text{P}(\text{C}_6\text{H}_5)_3$ as one of the ligands, was there a rapid exchange process giving only two resonances in the spectra.²⁸ The observation of separate sharp resonances for both bound and free ligand in the majority of competition experiments indicates that the ligand exchange processes were slow on the nmr time scale.

No systematic effort was made to study the kinetics of the ligand exchange processes; however, some qualitative observations can be made, based upon color changes in some of the competition experiments and ^{31}P spectra run before equilibrium in others. The complexes differed greatly in the rates with which the original ligands were replaced. The complexes $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_4$ and $\text{Ni}[\text{P}(\text{C}_6\text{H}_5)_3]_4$ appeared to react as soon as another ligand was mixed in. Reaction of $\text{Ni}[\text{P}(\text{CH}_3)_3]_4$ took only a few minutes, while $\text{Ni}[\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3]_4$ required several minutes. The phosphite complexes $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$ and $\text{Ni}[\text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3]_4$ took several hours.²⁹ The least labile appeared to be $\text{Ni}[\text{P}(\text{OCH}_2\text{CCl}_3)_3]_4$. In the experiment

(28) See Table III, footnotes d and e.

(29) This result is in accord with quantitative rate measurements on the reaction of $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$ with $\text{C}_6\text{H}_{11}\text{NC}$ in hexane,³⁰ where a rate constant of $1.2 \times 10^{-6} \text{ sec}^{-1}$ at 35.3° was reported. They also found that $\text{Ni}[\text{P}(\text{OC}_6\text{H}_5)_3]_4$ reacted more rapidly than did $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$.

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

with added $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ there was no detectable exchange in the ^{31}P spectrum after 10 days at room temperature. Equilibrium was only achieved after hours of heating at 100° . Generally those ligands seemed to be most rapidly displaced which gave the least stable complexes, as judged from the equilibrated ligand exchange solutions.

Chemical shifts and P-P coupling constants observed for $\text{NiL}_4\text{-}_n\text{L}'_n$ complexes are listed in Table II. The assignments were made on the basis of chemical shifts, relative intensities, phosphorus spin-spin coupling, and in some cases the order in which resonances appeared in time, assuming stepwise replacement of ligand L by ligand L'.

The observation of a simple doublet resonance for L in $\text{NiL}_3\text{L}'$ complexes and of a triplet for L in $\text{NiL}_2\text{L}'_2$ (corresponding to quartet and triplet resonances for L' in the two types of complex) is consistent with the expected tetrahedral coordination in these complexes, but inconsistent with square-planar coordination. The coupling constants J_{PP} are all in the range of 10–45 cps.³¹ No simple correlation is apparent between the changes in chemical shifts of L in $\text{NiL}_4\text{-}_n\text{L}'_n$ as n increases and the nature of L', contrary to the expectation based on

(31) Coupling constants $J_{\text{PP}} = 21$ and 49 cps have been reported for the octahedral complexes *cis*- and *trans*- $\text{Mo}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_4\text{H}_9)_2$ by S. O. Grim, D. A. Wheatland, and P. R. McAlister, *ibid.*, **7**, 161 (1968).

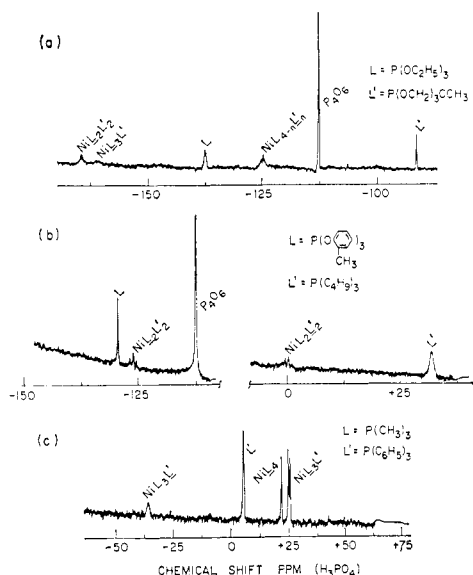


Figure 2. Sample ^{31}P nmr spectra at 40.5 Mc. The starting complex was NiL_4 , the attacking ligand L' . The ligand in the complex giving rise to the resonance is underlined.

the work of Meriwether and Leto.²⁷ Table II does show that the chemical shift of bound L changes regularly as n is increased.

Some interesting observations can be made concerning the product distributions in some of the spectra. If two ligands are bound equally well, one might expect a statistical mixture of the various $\text{Ni}(0)$ species, with the concentrations of NiL_4 , $\text{NiL}_3\text{L}'$, $\text{NiL}_2\text{L}'_2$, NiLL'_3 , and NiL'_4 being in the ratio of 1:4:6:4:1. The intensities of the resonances due to L, weighted according to the number of L's in the complex, would be in the ratio 1:3:3:1:0, with the intensity of free L equal to the total bound L. This case is shown in Figure 2a. In this spectrum the $\text{L} = \text{P}(\text{OC}_2\text{H}_5)_3$ resonances of $\text{NiL}_3\text{L}'$ and $\text{NiL}_2\text{L}'_2$ are observed; the wings of the 1:3:3:1 quartet are too weak to be easily seen. All the resonances of bound $\text{L}' = \text{P}(\text{OCH}_2)_3\text{CCH}_3$ occur at -126 ppm and are not resolved.

Figure 2b, however, shows a different type of behavior. The concentrations of free $\text{L} = \text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3$ and $\text{L}' = \text{P}(\text{C}_4\text{H}_9)_3$ are the same, so that the ligands are equally bound. However, there is only one type of bound ligand resonance for each ligand, a triplet due to $\text{NiL}_2\text{L}'_2$. This same type of behavior was found when L' was $\text{P}(\text{C}_2\text{H}_5)_3$ and again when one ligand was $\text{P}(\text{CH}_3)_3$ and the other $\text{P}(\text{OC}_6\text{H}_5)_3$ or $\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$. This special stability of the $\text{NiL}_2\text{L}'_2$ complex occurred with ligands of comparable binding ability but differing markedly in their electronic character, when one ligand was a good electron acceptor and the other a good electron donor, and must be ascribed to an electronic effect.

Figure 2c shows the more usual type of spectrum, where one ligand, in this case $\text{P}(\text{CH}_3)_3$, is much more strongly bound than the other, $\text{P}(\text{C}_6\text{H}_5)_3$.

A list of the ligand competition experiments and their results is shown in Table III. The relative intensities of the ^{31}P resonances of the free ligands and mixed complexes were used to assess the relative binding ability of the two competing ligands. The starting complexes are listed in order of descending stability. For each starting

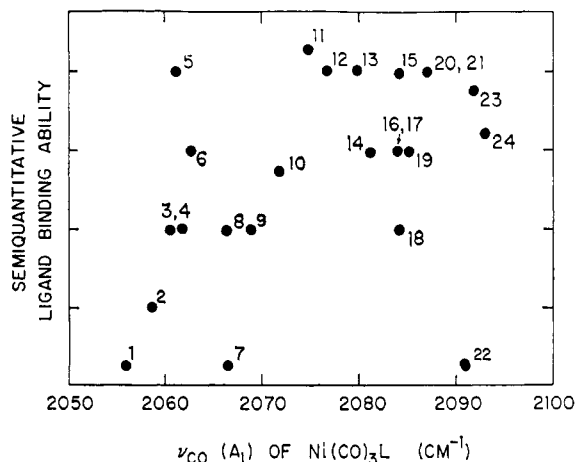


Figure 3. Plot of semiquantitative stability of $\text{Ni}(0)$ complexes of various ligands against ν_{CO} (A_1) of $\text{Ni}(\text{CO})_3\text{L}$ from ref 24. The ligand numbers refer to Table I. A difference between ligands of one unit on the vertical scale means that the upper ligand L is much more strongly bound than the lower ligand L' , such that the major $\text{Ni}(0)$ species at equilibrium are NiL_4 and $\text{NiL}_3\text{L}'$. The bottom three points correspond to no detected complexing.

complex the attacking ligands are listed in order of decreasing ability to replace the starting ligand. Competitions where $\text{NiL}_2\text{L}'_2$ was the only $\text{Ni}(0)$ product detected are indicated by an asterisk.

From these data it is possible to rank the 24 ligands tested into a stability series as follows: $\text{P}(\text{C}_6\text{H}_5)_3(\text{OC}_2\text{H}_5)_2 \gtrsim \text{P}(\text{OCH}_2)_3\text{CCH}_3 = \text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5 = (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2 = \text{P}(\text{OCH}_3)_3 = \text{P}(\text{OC}_2\text{H}_5)_3 = \text{P}(\text{OCH}_2\text{CH}_2\text{Cl})_3 \gtrsim \text{P}(\text{OCH}_2\text{CCl}_3)_3 \gg \text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{CN})_3 \gtrsim \text{P}(\text{OC}_6\text{H}_5)_3 = \text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{CH}_3)_3 = \text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3 = \text{P}(\text{CH}_3)_3 = \text{P}(\text{CH}_3)_2\text{CF}_3 \gtrsim \text{P}(\text{C}_6\text{H}_5)_2(\text{OC}_2\text{H}_5) \gg \text{P}(\text{C}_2\text{H}_5)_3 = \text{P}(\text{C}_4\text{H}_9)_3 \sim \text{P}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5) \sim \text{P}(\text{C}_6\text{H}_5)_3 \sim \text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3 \gg \text{P}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{O}-\text{C}_6\text{H}_4\text{CH}_3)_3, \text{P}(\text{C}_6\text{F}_5)_3$.

The results in Table III can be put on a semiquantitative basis as shown in Figure 3, where the most strongly bound ligands are represented by the highest points. A difference between ligands of one unit on the vertical scale signifies that the upper ligand L is much more strongly bound than the lower ligand L' , such that the major $\text{Ni}(0)$ species at equilibrium are NiL_4 and $\text{NiL}_3\text{L}'$ ($\text{L} \gg \text{L}'$ in the terminology of Table III). The horizontal scale is a measure of the electron withdrawing ability of the ligand, the symmetric carbonyl stretching frequency of $\text{Ni}(\text{CO})_3\text{L}$.²⁴

The most stable NiL_4 complexes might have been expected from ligands which are strongly electron withdrawing, so-called strong " π acceptors," according to the commonly held notion that such ligands would have a greater double bond character between Ni and P. The double bond character is thought to arise from donation of electrons from the transition metal to the vacant d orbitals of phosphorus. The lack of correlation between complex stability and the electronic nature of the ligands is clearly shown in Figure 3. Thus, there is a large electronic difference between $\text{P}(\text{OC}_2\text{H}_5)_3$ and $\text{P}(\text{OCH}_2)_3\text{CCH}_3$, (points 12 and 21 in Figure 3) yet the stabilities are nearly the same. Though $\text{P}(\text{O}-p\text{-C}_6\text{H}_4\text{OCH}_3)_3$ (point 16) is a stronger π acceptor than $\text{P}(\text{OC}_2\text{H}_5)_3$, the alkyl ligand gives a more stable complex, the complexes in the equilibrium mixture consisting predominantly of $\text{Ni}[\text{P}(\text{OC}_2\text{H}_5)_3]_4$, with a lesser amount

Table III. Results of Ligand Competition Experiments

Starting complex, NiL ₄	Attacking ligand, L'	Ligand stability result ^a
Ni[P(C ₆ H ₅)(OC ₂ H ₅) ₂] ₄	P(OC ₂ H ₅) ₃ CC ₂ H ₅	L > L'
	P(OC ₂ H ₅) ₃	L > L'
	P(C ₆ H ₅) ₃	L >>> L'
Ni[P(OCH ₂) ₃ CCH ₃] ₄	P(OCH ₂ CH ₂ Cl) ₃	L = L' ^b
	P(OCH ₂ CCl ₃) ₃	L > L'
	P(OCH ₂) ₃ CCH ₃	L = L'
Ni[P(OCH ₃) ₃] ₄	(CH ₃) ₂ PCH ₂ CH ₂ P(CH ₃) ₂	L = L'*
	P(CH ₃) ₃	L >> L'
	P(C ₆ H ₅) ₃	L >> L'
Ni[P(OC ₂ H ₅) ₃] ₄	P(C ₆ H ₅)(OC ₂ H ₅) ₂	L < L'
	P(OCH ₂) ₃ CCH ₃	L = L'
	P(C ₆ H ₅) ₂ (OC ₂ H ₅)	L >> L'
Ni[P(OCH ₂ CH ₂ Cl) ₃] ₄	P(O- <i>p</i> -C ₆ H ₄ OCH ₃) ₃	L >> L'
	P(<i>i</i> -C ₃ H ₇) ₃	L >>> L'
	P(OCH ₂) ₃ CCH ₃	L = L'
Ni[P(OCH ₂ CCl ₃) ₃] ₄	P(OCH ₂) ₃ CCH ₃	L < L'
	P(OC ₂ H ₅) ₃	L <<< L'
	P(OCH ₂ CCl ₃) ₃	L < L'
Ni[P(O- <i>p</i> -C ₆ H ₄ OCH ₃) ₃] ₄	P(O- <i>p</i> -C ₆ H ₄ CN) ₃	L < L'
	P(OC ₂ H ₅) ₃	L = L'
	P(O- <i>p</i> -C ₆ H ₄ CH ₃) ₃	L = L'
Ni[P(CH ₃) ₃] ₄	P(C ₆ H ₅) ₂ (OC ₂ H ₅)	L ~ L'
	(CH ₃) ₂ PCH ₂ CH ₂ P(CH ₃) ₂	L = L'*
	P(CH ₃) ₃	L = L'*
Ni[P(C ₆ H ₅) ₃] ₄	P(C ₆ H ₅) ₃	L >> L'
	P(C ₆ H ₅) ₃	L >> L'
	P(O- <i>o</i> -C ₆ H ₄ CH ₃) ₃	L >> L'
Ni[P(CH ₃) ₃] ₄	P(OCH ₂) ₃	L << L'
	(CH ₃) ₂ PCH ₂ CH ₂ P(CH ₃) ₂	L << L'
	P(CH ₃) ₂ CF ₃	L = L'
Ni[P(C ₆ H ₅) ₃] ₄	P(OC ₂ H ₅) ₃	L = L'*
	P(C ₆ H ₅) ₂ (OC ₂ H ₅)	L > L'
	P(O- <i>o</i> -C ₆ H ₄ CH ₃) ₃	L >> L'
Ni[P(C ₆ H ₅) ₃] ₄	P(C ₆ H ₅) ₃	L >> L'
	P(C ₆ H ₅) ₂ (C ₂ H ₅)	L >> L'
	P(C ₂ H ₅) ₃	L >> L'
Ni[P(C ₆ H ₅) ₃] ₄	P(C ₄ H ₉) ₃	L >> L'
	P(<i>i</i> -C ₃ H ₇) ₃	L >>> L'
	P(<i>t</i> -C ₄ H ₉) ₃	L >>> L'
Ni[P(C ₆ H ₅) ₃] ₄	P(<i>o</i> -C ₆ H ₄ CH ₃) ₃	L >>> L'
	P(C ₆ F ₅) ₃	L >>> L'
	P(C ₆ H ₅)(OC ₂ H ₅) ₂	L <<< L'
Ni[P(O- <i>o</i> -C ₆ H ₄ CH ₃) ₃] ₄	P(C ₆ H ₅) ₂ (OC ₂ H ₅)	L << L' ^d
	P(O- <i>p</i> -C ₆ H ₄ CH ₃) ₃	L << L'
	P(CH ₃) ₃	L < L'
Ni[P(C ₆ H ₅) ₃] ₄	P(C ₂ H ₅) ₃	L = L'*
	P(C ₄ H ₉) ₃	L = L'*
	P(C ₆ H ₅) ₃	L ~ L' ^e
Ni[P(C ₆ H ₅) ₃] ₄	P(<i>i</i> -C ₃ H ₇)	L >> L'
	P(C ₆ F ₅) ₃	L >>> L'

^a The meaning of the results is as follows: L >>> L', only Ni(0) species was NiL₄, starting complex; L >> L', major Ni(0) species NiL₄ and NiL₃L'; L > L', major Ni(0) species NiL₃L' and NiL₂L'₂; L > L', as above with only a slight difference in stability; L = L', major Ni(0) species NiL₂L'₂ with same concentrations of free L and L'. An added asterisk means that NiL₂L'₂ was the only Ni(0) species detected. The remaining symbols have similar meaning with L <<< L' corresponding to complete exchange. ^b Methylene chloride solvent. ^c Benzonitrile solvent. ^d Observation of only two weak resonances in the spectrum at -122.4 and at ~+8 ppm (very broad) suggests a rapid exchange process with most of the initial ligand displaced. ^e Only two weak resonances at -127.5 and -32.0 ppm suggest a rapid exchange process with about the same amount of bound ligand of each type.

of Ni[P(OC₂H₅)₃]₃[P(O-*p*-C₆H₄OCH₃)₃]₁ and no higher complexes of aryl phosphite detected.

The near equality in the stabilities of the sterically comparable *para*-substituted phenyl phosphites indicates that the effect in the series of electronic differences, if any, is small. On the other hand, the *ortho* and *para* isomers of tritolyl phosphite, while electronically indis-

tinguishable, differ greatly in the stability of the complexes with Ni(0). Treatment of the tetrakis(tri-*o*-tolyl phosphite)nickel complex with *p*-tolyl phosphite ligand leads to nearly total replacement by the less sterically demanding *para* isomer.

Perhaps the most remarkable results are those involving P(CH₃)₃ and P(C₆F₅)₃ (points 6 and 22 in Figure 3). The former, a good electron donor, gave a remarkably stable Ni(0) complex while the latter, one of the best electron acceptors, failed to bond to Ni(0) in competition with P(CH₃)₃, or even P(O-*o*-C₆H₄CH₃)₃.

The failure of the notion of metal-phosphorus double bond character to explain the results of the competition experiments was indeed startling. It became clear, however, while looking at atomic models of these ligands that it was the smaller ones that came out best in the competitions. What was needed was a quantitative measure of steric effects in the complexes.

Measurement of Steric Effects

The measurement of ligand cone angles from atomic models as described in the Experimental Section was an attempt to obtain such a quantitative measure. The idea was that each ligand in a complex will subtend some solid angle as viewed from the center of the metal atom. Rather than the solid angle itself, the measure chosen was the apex angle of a cone, centered on the metal, just large enough to enclose the van der Waals radii of the outermost atoms of the ligand.

Ligands with some flexibility were folded back into as small a cone as possible, while threefold symmetry was maintained for a PZ₃ ligand.³² This was achieved for P(C₆H₅)₃, for example, by feathering the phenyl rings like the blades of a fan, through an angle of about 45°. The results of cone angle measurements of this sort are included in Table IV, where the ligands are divided according to type. Notice that the angles shown cover a very large range, over 100°. Several common ligands have surprisingly large cone angles, for example P(C₆H₅)₃ with 145° and P(C₆H₁₁)₃ with 179°.

To the extent that the ligands approach cylindrical symmetry about the M-P bond, coordination of six, four, three, or two such ligands should not be possible for cone angles larger than 90, 109.5, 120, or 180°, respectively. Because real ligands have less than cylindrical symmetry, somewhat larger ligands can be accommodated by "meshing" one ligand with another.

A rather good correlation between semiquantitative ligand binding ability, from the ligand competition experiments, and the ligand cone angles for the ligands of the type PZ₃ can be seen in Figure 4. The ligands giving complexes of highest and equal stability are the alkyl phosphites, which have cone angles of 109.5° or less; points for these lie along the horizontal line at the upper left in Figure 4. Once the tetrahedral angle is exceeded, larger ligands give increasingly less stable complexes as the size of the ligand is increased. The much greater stability of complexes of P(CH₃)₃ compared to those of P(C₂H₅)₃ and P(C₄H₉)₃ can be seen to be a result of the smaller size of trimethylphosphine, the electronic differences being rather small.³³ It must be

(32) Only ligand models with three identical substituents were used for the cone angle measurements. The minimum cone angle is difficult to define when the substituents are not the same. It is quite reasonable, however, that a ligand PX₂Y would occupy a solid angle intermediate between those of PX₃ and PY₃.

Table IV. Ranking of Various Phosphorus Ligands PZ_3 ^b According to Size

PX_3	$P(OR)_3$ ⁱ	$P(OAr)_3$ ⁱ	PR_3	PAR_3	Minimum cone angle, ^a deg
PH_3 ^b					87 ± 2
PF_3 ^b	$P(OCH_2)_3CCH_3$ ^{b,c}				101 ± 2
	$P(OCH)_3(CH_2)_3$ ^{b,c}				104 ± 2
	$P(OCH_3)_3$				106 ± 2
	$P(OC_2H_5)_3$				107 ± 2
	$P(OCH_2CH_2Cl)_3$				109 ± 2
	$P(O-i-C_3H_7)_3$				110 ± 2
			$P(CH_3)_3$ ^{b,d}		114 ± 2
		$P(OC_6H_5)_3$			118 ± 4
PCl_3 ^b					121 ± 10 ^f
PBr_3 ^b	$P(OCH_2CCl_3)_3$				125 ± 2
			$P(C_2H_5)_3$		131 ± 2
			$P(C_4H_9)_3$		131 ± 10 ^f
			$P(CF_3)_3$ ^b		132 ± 4
				$P(C_6H_5)_3$	130 ± 4
			$P(i-C_3H_7)_3$		137 ± 2
		$P(O-o-C_6H_4CH_3)_3$ ^e			145 ± 2
			$P(C_6H_{11})_3$ ^d		160 ± 10 ^f
			$P(t-C_4H_9)_3$		165 ± 10 ^f
				$P(C_6F_5)_3$	179 ± 10 ^f
				$P(o-C_6H_4CH_3)_3$ ^e	182 ± 2
					184 ± 2
					194 ± 6

^a Defined as the apex angle of a minimum cone, centered 2.28 Å away from the center of the P atom, which just touches the outermost extremities of a ligand folded back while maintaining C_3 symmetry. ^b C_{3v} symmetry. ^c Long Ealing connectors (+0.08 Å) used for C–O bonds. ^d Chair form of cyclohexyl. ^e *ortho* methyl groups facing toward Ni atom. ^f Large uncertainties arise in cases where the cone angle can be further reduced by introducing strain in the ligand, as evidenced by nonparallel faces between the atoms or nonstaggered conformations about C–C bonds. ^g The much smaller cone angle of $P(CH_3)_3$ as compared to $P(C_2H_5)_3$ or $P(C_4H_9)_3$ is a result of the fact that $P(CH_3)_3$ can assume C_{3v} symmetry whereas the higher homologs cannot because of the β carbons. Alkyl chains longer than ethyl can, however, be kept within a cone of $\sim 130^\circ$. The greater stability of the $P(CH_3)_3$ complexes and near equivalence of $P(C_2H_5)_3$ and $P(C_4H_9)_3$ can be seen in the ligand stability series. ^h See ref 32. ⁱ R represents alkyl and Ar aryl.

concluded that the property of the ligands which primarily determines the stability of the $Ni(0)$ complexes is their size rather than their electronic character.

Substitution Reactions on $Ni(CO)_4$

To test this conclusion, a different sort of experiment was done in which toluene solutions of $Ni(CO)_4$ were treated with an eightfold excess of phosphorus ligand; substitution of CO by ligand was followed by means of the carbonyl stretching vibrations in the infrared spectrum. The solutions were equilibrated by heating in sealed tubes for 64 hr at 100° . Further heating at 100° for an additional 74 hr did not significantly change the spectra. The frequencies and intensities of the carbonyl stretching bands in the spectra of the equilibrated solutions are shown in Table V. The 14 ligands tested are ranked in order of decreasing degree of substitution of CO by ligand.³⁴ The degree of substitution can be estimated semiquantitatively from the relative intensities and the assumption that the extinction coefficients of the bands are all of the same order of magnitude. For example, in the case of $P(C_6H_{11})_3$ the A_1 band of $Ni(CO)_3L$ and the B_1 band of $Ni(CO)_2L_2$ are of about the same intensity, so that the degree of substitution is estimated at 1.5. The estimates are probably reliable to ± 0.2 .

The estimated degrees of substitution for these ligands and their cone angles are shown in Table VI. Except for the last two entries, especially that of PCl_3 , the results are entirely in accord with the notion that the degree of substitution of CO from $Ni(CO)_4$ by a phos-

phorus ligand is determined in most cases by the size of the ligand rather than by its electronic character. Ligands which compete effectively with CO for $Ni(0)$ are the same ones which do well against other phosphorus ligands in the ^{31}P experiments.

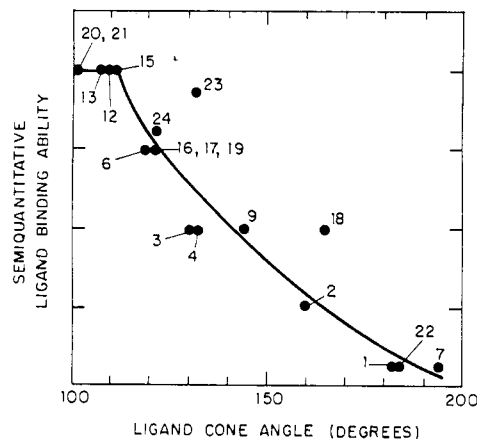


Figure 4. Plot of semiquantitative stability of $Ni(0)$ complexes of various PZ_3 ligands against the ligand cone angle from Table IV. The vertical scale is the same as in Figure 3. The bottom three points correspond to no detected complexing.

The one ligand which is clearly poorer at replacing CO than would be expected solely on the basis of size is PCl_3 ; electronic factors must dominate in this case. Unfortunately, ligand competition experiments involving PCl_3 and $Ni[P(OC_2H_5)_3]_4$ or $Ni[P(CH_3)_3]_4$ led to side reactions so that the relative bonding ability of PCl_3 vs. the other ligands could not be determined.

(33) The smaller measured cone angle of 118° for $P(CH_3)_3$ compared to about 130° for $P(C_2H_5)_3$ and $P(C_4H_9)_3$ is a consequence of being able to rotate the methyl groups to give $P(CH_3)_3$ C_{3v} symmetry.

(34) The assignments can be made easily, based on the data in ref 8.

Table V. Reaction of Various Ligands with Ni(CO)₄. Infrared Carbonyl Stretching Frequencies in Toluene^a

Ligand	Ni(CO) ₄ T	Ni(CO) ₃ L		Ni(CO) ₂ L ₂		Ni(CO)L ₃ A ₁
		A ₁	E	A ₁	B ₁	
P(OCH ₂) ₃ CCH ₃						1985 m
P(OCH ₃) ₃						1952 vs, b
(CH ₃) ₂ PCH ₂ CH ₂ P(CH ₃) ₂				1993 vw?	(1910) ^d	1910 vs
P(OC ₆ H ₅) ₃				2043 m, sp	(1996)	1996 s
P(CH ₃) ₃				1990 vs	1926 vs, b	1900 s
P(C ₄ H ₉) ₃				1987 vs	1922 vs	1896 m
P(C ₆ H ₅) ₃				2000 vs, sp	1941 vs, b	
P(O- <i>o</i> -C ₆ H ₄ CH ₃) ₃				2045 vs, sp	1988 vs	
P(<i>i</i> -C ₃ H ₇) ₃		2063 m, sp	(1984)	1984 vs, b	1922 vs, b	
P(C ₆ H ₁₁) ₃		2060 s, sp	(1980)	1980 vs	1912 s, b	
P(<i>t</i> -C ₄ H ₉) ₃ ^b		2059 vs, sp	1976 vs, b			
P(<i>o</i> -C ₆ H ₄ CH ₃) ₃ ^b	2041 m, b	2067 s, sp	1990 vs, b			
PCl ₃ ^{b,c}	2044 vs, b	2102 s, sp	(2044)	2081 m, sp		
P(C ₆ F ₅) ₃ ^{b,c}	2042 vs, b	2089 m, sp	(2042)			

^a After 64 hr at 100°, 0.05 M Ni(CO)₄ + 0.4 M ligand, 0.1-mm cell. ^b Black metallic nickel precipitated during the heating. This can be explained by the presence of Ni(CO)₄ in equilibrium with Ni(CO)₃L. Nickel tetracarbonyl itself decomposes in toluene solution on heating and on standing. In the case of the P(*o*-C₆H₄CH₃)₃ solution, with an intermediate rate of decomposition, the infrared bands due to both Ni(CO)₄ and Ni(CO)₃P(*o*-C₆H₄CH₃)₃ diminished with time, showing that equilibrium was maintained as the concentration of the Ni(CO)₄ was reduced by decomposition. ^c Data are for spectrum after 6 hr at 25°. After 64 hr at 100° the sample had completely decomposed and no carbonyl bands were observed. ^d Numbers in parentheses are assigned to unresolved, overlapping bands. Abbreviations used are: vs, very strong; s, strong; m, medium; vw, very weak; sp, sharp; b, broad.

Table VI. Degree of Substitution of CO from Ni(CO)₄ by Various Ligands Based on Ir Intensities

Ligand	Estimated ^a degree of substitution	Ligand cone angle, deg
P(OCH ₂) ₃ CCH ₃	3.7	101 ± 2
P(OCH ₃) ₃	3.0	107 ± 2
(CH ₃) ₂ PCH ₂ CH ₂ P(CH ₃) ₂	2.9	^b
P(OC ₆ H ₅) ₃	2.7	121 ± 10
P(CH ₃) ₃	2.4	118 ± 4
P(C ₄ H ₉) ₃	2.2	130 ± 4
P(C ₆ H ₅) ₃	2.0	145 ± 2
P(O- <i>o</i> -C ₆ H ₄ CH ₃) ₃	2.0	165 ± 10
P(<i>i</i> -C ₃ H ₇) ₃	1.7	160 ± 10
P(C ₆ H ₁₁) ₃	1.5	179 ± 10
P(<i>t</i> -C ₄ H ₉) ₃	1.0	182 ± 2
P(<i>o</i> -C ₆ H ₄ CH ₃) ₃	0.8	194 ± 6
PCl ₃	0.4	125 ± 2
P(C ₆ F ₅) ₃	0.3	184 ± 2

^a The method of estimation is described in the text. ^b Undefined for chelating ligand.

Others have reported the replacement of two CO's from Ni(CO)₄ by phosphines^{35,36} and of three³⁷ or even four^{8,38} by phosphites. Several authors have given arguments based solely on electronic effects to explain the failure of phosphines to replace more than two CO's.^{8,39-41} Verkade suggested that small size might be one factor in the ease of formation of NiL₄ complex from Ni(CO)₄ using the bicyclic P(OCH₂)₃CCH₃.³⁸

Electronic and Chelation Effects

The stability of Ni(0) complexes has usually been explained on the basis of electronic rather than steric effects. Indeed, not all our experimental results can be

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accounted for on the basis of ligand size alone. The reaction of PCl₃ with Ni(CO)₄ has been mentioned. In the ligand competition experiments there were cases where ligands of comparable size but very different electronic character gave NiL₂L'₂ as the sole Ni(0) species. Another observation concerns the ranking of P(C₄H₉)₃, P(C₆H₅)₃, and P(O-*o*-C₆H₄CH₃)₃ in the ligand stability series. It will be noted in Table III that the order in L' was P(C₄H₉)₃ > P(C₆H₅)₃ > P(O-*o*-C₆H₄CH₃)₃ when these ligands were competing against L = P(O-*p*-C₆H₄-OCH₃)₃. In all three cases the major Ni(0) species were NiL₄ and NiL₃L'; however, the distribution depended on the ligand, with the concentrations varying from (NiL₄) << (NiL₃L') to (NiL₄) ~ (NiL₃L') to (NiL₄) > (NiL₃L') for the three ligands, respectively. On the other hand, when these ligands were competing against L = P(CH₃)₃, the order was reversed, with P(C₄H₉)₃ < P(C₆H₅)₃ < P(O-*o*-C₆H₄CH₃)₃, the concentrations being (NiL₄) > (NiL₃L'), (NiL₄) ~ (NiL₃L'), and (NiL₄) << (NiL₃L'), respectively. This inversion depends on the electronic character of the ligand L. When L was P(O-*p*-C₆H₄OCH₃)₃, a good electron acceptor, the preferred ligand of the three was P(C₄H₉)₃, the best donor. When L was P(CH₃)₃, a good electron donor, the preferred competing ligand was P(O-*o*-C₆H₄CH₃)₃, the best acceptor of the three.

The effect of chelation can also be mentioned. The chelating ligand bis(dimethylphosphino)ethane (dmpe) was ranked at the top of the stability series together with the alkyl phosphites because the treatment of Ni[P(OCH₃)₃]₄ with the chelate gave Ni(dmpe)[P(OCH₃)₃]₂ as the only Ni(0) product (Table III). Reaction with Ni[P(CH₃)₃]₄ gave Ni(dmpe)[P(CH₃)₃]₂ as well as a new resonance at -18.1 ppm, assigned to Ni-(dmpe)₂. The presence of only a very weak resonance at the chemical shift of free dmpe and the absence of unassigned resonances in the spectrum indicate that all bound dmpe was held as a bidentate ligand. A combination of chelating and electronic effects seems to have been operating in the experiment when Ni[P(O-*p*-C₆H₄OCH₃)₃] was treated with dmpe; the only Ni(0) complex appeared to be Ni(dmpe)[P(O-*p*-C₆H₄OCH₃)₃]₂ with no evidence for Ni(dmpe)₂. Thus the

mixed complex with dmpe was favored when L was P(O-*p*-C₆H₄OCH₃)₃ more than when L was P(CH₃)₃.

The chelate performed about as well as P(OMe)₃ in reacting with Ni(CO)₄ (Table VI).

Implications of the Results for Other Complexes

It is difficult to say to what degree the rank ordering of ligands in terms of the stability of Ni(0) complexes may apply with other transition metals and oxidation states. To the extent that ligand size is important, the ordering might be quite general. It should be understood that the ligand cone angles shown in Table IV were based upon a model which assumed tetrahedral bonding for phosphorus and a metal-phosphorus bond length of 2.28 Å. Both bond angles and lengths might be different for different transition metals, and might depend on the oxidation state of the metal and on the nature of the other ligands. Nevertheless, it appears unlikely that these factors could significantly affect the rank ordering of ligands according to size.

A few examples from the literature illustrate the breadth of the implications of these results. It has been reported that P(C₆F₅)₃ is irreversibly displaced by P(C₆H₅)₃ or P(OC₆H₅)₃ from the Rh(I) complex {[P(C₆F₅)₃]₂RhCl}₂.⁴² The stability order found for ligands in the complexes L₂PdX₂ and L₂PtX₂ is reported⁴³ to be in the order P(OC₆H₅)₃ > P(C₆H₅)₃ > P(C₆H₅)₂(C₆F₅) > P(C₆H₅)(C₆F₅)₂ > P(C₆F₅)₃, also the order of increasing size. There is a report that Ni(CO)₂[P(CF₃)₃]₂, prepared from Ni(CO)₄ and P(CF₃)₃, fails to react with excess P(CF₃)₃, even at 100°. ⁴⁴ This result might have been predicted from the data in Tables IV and VI, since P(CF₃)₃ is intermediate in size between P(C₄H₉)₃ and P(C₆H₅)₃.

The reaction of Ni[PF₃]₄ with P(C₆H₅)₃ does not go beyond Ni[PF₃]₂[P(C₆H₅)₃]₂, a result that has been explained as an electronic effect.⁴⁵ However, in view of the similarity of PF₃ and CO in their electronic character and small size, the reaction of various ligands with Ni[PF₃]₄ should give results similar to those in Table VI.

Steric requirements probably also explain the observation that the direct reaction of chromium, molybdenum, or tungsten hexacarbonyls with phosphorus ligands gives disubstituted products with P(C₂H₅)₃ or P(C₆H₅)₃, trisubstituted with P(OC₆H₅)₃, and tetrasubstituted with P(OCH₃)₃.⁴⁶ They may also explain why *trans*-Mo(CO)₄[P(C₂H₅)₃]₂ is more stable than *cis*-Mo(CO)₄[P(C₂H₅)₃]₂.⁴⁶ The steric requirements in these group VI complexes are probably more severe than in the Ni(0) complexes, in spite of the slightly longer

metal-phosphorus bonds, because six groups need to be accommodated instead of four. It is not surprising that no zerovalent ML₆ complexes except M[PF₃]₆⁴⁵ have been reported, though it might be possible to make the octahedral complexes using the smallest ligands such as P(OCH₂)₃CCH₃, P(OCH)₃(CH₂)₃, or P(OCH₃)₃.

Mechanism of Exchange and the Nature of the Ni-P Bond

Ligand exchange in the reactions of NiL₄ with L' and of Ni(CO)₄ with L is probably a first-order dissociative process involving three-coordinate intermediates. This mechanism has been established for the reaction of Ni[P(OC₂H₅)₃]₄ with C₆H₁₁NC³⁰ and of Ni[P(O-*p*-C₆H₄OCH₃)₃]₄ with a variety of two-electron donors,⁴⁷ for reactions of Ni(CO)₄ with CO or P(C₆H₅)₃,⁴⁸ and for reactions of Ni(CO)₃P(C₆H₅)₃ with P(C₆H₅)₃ to give Ni(CO)₂[P(C₆H₅)₃]₂ and of various L' with Ni(CO)₂L₂ to give Ni(CO)₂LL'.⁴⁰ An S_N1 process is highly likely since a five-coordinate intermediate would require nickel to exceed the 18-electron inert gas configuration and would be quite impossible with many of the ligands because of their large size.

The nature of the nickel-phosphorus bond has been the subject of controversy for several years.⁴⁹ The basic issue is the extent to which the bond should be described as a simple single bond, formed by σ donation of two electrons by phosphorus, or as a double bond, the additional bond order arising from back-donation of electrons from nickel into the empty d orbitals of phosphorus. It has been commonly held that ligands having a higher π-acceptor strength (giving higher carbonyl frequencies in substituted carbonyls) form a bond with a greater double bond character. Meier, Basolo, and Pearson have recently used this argument to explain the greater dissociation in solution of Ni[P(C₆H₅)₃]₄ compared to Ni[P(OC₂H₅)₃]₄.³⁰ Our experiments have shown that electronic effects play only a secondary role compared to steric effects in determining the stability of the Ni(0) complexes studied. It can be concluded that double bonding between nickel and phosphorus, if it does occur in these complexes, is much less important in determining the relative stability of the complexes than the dominant steric effects.

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