Formation of Three-Coordinate Nickel(0) Complexes by Phosphorus Ligand Dissociation from NiL_4

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Abstract: Physical studies, including molecular weights, proton and ^{31}P nmr, and spectrophotometry, on a variety of NiL_4 complexes are reported. Values of K_d at 25° (benzene), ΔH_d, and ΔS_d for ligand dissociation have been determined: $NiL_4 \rightleftharpoons NiL_3 + L$ (K_d). Electronic factors have a strong influence on the rate constants k_d. Phosphines dissociate much more rapidly than do phosphites, as indicated by nmr line shape effects. Steric effects are largely responsible for the differences in equilibrium constants K_d. Electronically similar ligands P(O-*o*-tolyl)$_3$ and P(O-*p*-tolyl)$_3$ have values of K_d (benzene at 25°) of 0.04 and 6×10^{-10} *M*, differing by a factor of 0.7×10^8. Substituting –Cl for –H in the para position of P(O-*o*-tolyl)$_3$ reduces K_d by a factor of ~6. Smaller values of ΔH_d for more bulky ligands suggest a weaker metal–phosphorus bond.

Earlier[1] we reported the results of phosphorus ligand exchange studies indicated by eq 1. We were

$$NiL_4 + 4L' \rightleftharpoons NiL_{4-n}L'_n + nL \qquad (1)$$

surprised to find that the ability of the ligands to compete for coordination positions was largely determined by steric effects. Large ligands were displaced in preference to smaller ones. Steric effects were also shown to determine the extent to which CO could be displaced by L from $Ni(CO)_4$. A quantitative measure of ligand size was proposed for symmetrical PZ_3 ligands, the apex angle of a minimum cone, centered 2.28 Å away from P, which just touches the outermost atoms of the ligand at their van der Waals radii. Cone angles were measured using a simple jig and CPK atomic models.[2]

Since our paper appeared, it has become clear that a wide variety of phenomena are strongly dependent on phosphorus ligand steric effects. Some examples include the rates of decarbonylation of π-$C_5H_5Mo(CO)_2L(COMe)$ complexes,[3] rates of reduction of ethyl halides by $LCo(DH)_2$,[4] the reactivity of H_2ML_4 complexes,[5] the degree of dissociation in solution of $CuXL_3$[6] and CoX_2L_3[7] complexes, the degree of CO substitution by L from $M(CO)_6$[8] and $PzB(Pz)_3Mn(CO)_3$[9] complexes, reactivity in intramolecular cleavage of C–H bonds,[10] and even ^{31}P chemical shifts and ^{13}C–^{31}P coupling constants in phosphines.[11] Phosphorus ligand steric effects can have important consequences for product distributions and rates of homogeneous catalytic reactions. Examples include the Rh catalyzed hydroformylation of olefins[12a] and Ni catalyzed cyclodimerization of butadiene[12b] and dimerization of propylene.[12c]

We now wish to report studies in the ligand dissociation reaction (2) for a variety of phosphorus ligands, L. A combination of experimental techniques

$$NiL_4 \overset{K_d}{\rightleftharpoons} NiL_3 + L \qquad (2)$$

has been employed including molecular weight measurements, ^1H and ^{31}P nmr spectra, and spectrophotometry. Related studies have already been reported for the L = P(O-*o*-tolyl)$_3$[13] and PPh_3[14] systems. Preparations are described for the previously unreported complexes Ni[P(O-*p*-C_6H_4Cl)$_3$]$_4$, Ni[P(O-*p*-CH_3-*o*-tolyl)$_3$]$_3$, Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_3$, and Ni[P(OMe)Ph_2]$_4$. The rates and equilibria of ligand dissociation (eq 2) are discussed in terms of electronic and steric effects. Improved ligand cone angle measurements are described including definition of an effective cone angle for unsymmetrical phosphines $PX_1X_2X_3$ and for diphosphines.

Experimental Section

The nickel(0) compounds involved in this study are all sensitive to oxygen to some degree, so that their preparation and manipulation were generally carried out in an inert atmosphere of nitrogen. Special precautions[2] to avoid O_2 were necessary in order to get reliable results on dilute solutions for spectrophotometric studies. An argon atmosphere was used in some of the work with Ni[PEt_3]$_4$, since (N_2)Ni[PEt_3]$_3$ forms under nitrogen.[15] None of the other Ni(0) compounds appeared to react with N_2 under ambient conditions.

Molecular weights were determined cryoscopically using about 0.015 *M* solution of complex in N_2 blanketed benzene, employing a Hewlett-Packard quartz crystal thermometer.[16] Infrared spectra were recorded and calibrated as described earlier.[1] Melting points were determined under N_2 or in evacuated, sealed capillaries on a Mel-Temp apparatus and are uncorrected.

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Proton nmr spectra were recorded at 100 MHz on a Varian HA-100 spectrometer at ambient temperature (27°), using 5-mm o.d. tubes. The solvent contained 90% C_6D_6 and 10% tetramethylsilane (TMS). Chemical shifts (±0.02 ppm) are reported on the τ scale (TMS at 10.0) and coupling constants in Hz (±0.5).

^{31}P nmr spectra of toluene solutions were recorded at 36.43 MHz on a Bruker HFX-90 spectrometer, using 10-mm o.d. tubes. Each tube held a 5-mm o.d. concentric capillary containing $CBrF_2$-$CBrF_2$ for work at or below ambient temperature and C_6F_6 above. The spectrometer was locked on the ^{19}F signal of the reference capillary. In cases where the ^{31}P spectra showed extensive ligand dissociation or rapid exchange, spectra were investigated as a function of temperature over the range of −50 to +70°. Chemical shifts were measured with respect to external 85% H_3PO_4 with a precision of ±0.1 ppm.

In both proton and ^{31}P nmr studies spectra were recorded on solutions of ligand alone (0.4 *M*), complex alone (0.1 *M*), and on solutions of complex to which increasing concentrations of ligand were added.

Electronic spectra were recorded on a Cary 14 spectrophotometer, generally over the range 700–300 mμ in benzene solvent. Spectra of the alkyl phosphine complexes were also determined in *n*-heptane from 600 to 230 mμ. Equilibrium constants for ligand dissociation were determined spectrophotometrically using jacketed cells. The temperature in the cells was maintained by circulating water from a Forma constant-temperature bath and determined to ±0.5° with a 36-ga copper–constantan thermocouple in the center of the cell. Equilibrium constants for each complex were determined at at least three temperatures ranging from 10 to 70° in 15° intervals, generally with variable concentrations of added ligand.

The spectrum of each NiL_4 or NiL_3 complex was determined as follows. Beer's law was checked over a 100-fold range of metal concentration, running solutions in 0.1-, 1.0-, and 10.0-mm path length cells while keeping the product of concentration and path length constant. Substantial dissociation of some NiL_4 complexes to NiL_3 could be achieved by using dilute solutions and heating. Spectra were also determined in the presence of increasing concentrations of added ligand up to about 1.0 *M*. With this much added L, NiL_4 was the predominant nickel species in benzene solution in all cases except where L = PPh_3.[15] In other solvents, capable of coordination with Ni(0), NiL_4 might not predominate even with a large excess of added L. For example in acetonitrile $(CH_3CN)Ni[P(O\text{-}o\text{-tolyl})_3]_3$[17] is strongly preferred over $Ni[P(O\text{-}o\text{-tolyl})_3]_4$.

The electronic spectrum of $Ni[P(O\text{-}p\text{-Cl-}o\text{-tolyl})_3]_3$ was very similar to that of $Ni[P(O\text{-}o\text{-tolyl})_3]_3$,[13] showing an absorption maximum at 407 and shoulder at 450 mμ; however, extinction coefficients could not be accurately measured because our sample was a mixture of NiL_3 and NiL_4. Benzene solutions did not obey Beer's law, consistent with ligand dissociation at higher dilutions. Solutions of the complex were unstable, turning from red-orange to green-brown on standing for a few hours under N_2. The decomposition, which does not occur with $Ni[P(O\text{-}o\text{-tolyl})_3]_3$ or $Ni[P(O\text{-}p\text{-}CH_3\text{-}o\text{-tolyl})_3]_3$, is attributed to oxidative addition of the nickel by cleavage of ligand aryl–chloride bonds. Similar color changes were observed when chlorobenzene was added to a benzene solution of $Ni[P(O\text{-}o\text{-tolyl})_3]_3$.

In spite of these difficulties, however, it was possible to determine K_d. Solutions of $\sim 2 \times 10^{-4}$ *M* complex were freshly prepared with and without added ligand and spectra recorded as soon as possible, using a 10-mm thermostated cell. At this low concentration of complex dissociation to NiL_3 was essentially complete without added L; in solutions with added L the added ligand concentration was made much larger than that of the complex. Temperatures were kept below 40° in order to minimize thermal decomposition.

Thermal decomposition also precluded accurate measurements of K_d above 40° for $Ni[PMePh_2]_4$. The very small dissociation constants of $Ni[P(O\text{-}p\text{-tolyl})_3]_4$ and $Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_4$ made accurate determinations difficult below 40°. At higher temperature, especially at 70° solutions of these para substituted phenyl phosphite complexes became hazy. The resulting light scattering makes the thermodynamic data for these compounds less reliable than for the others.

Compounds. Tri(2,4-dimethylphenyl) phosphite, $P(O\text{-}p\text{-}CH_3\text{-}o\text{-tolyl})_3$, was prepared by the reaction of 300 g of 2,4-dimethylphenol with 66 ml of PCl_3 in the manner described by Walsh.[18] Distillation under high vacuum gave a colorless oil: 222 g (71%), bp ~190° (10 μ), $n^{26}D$ 1.5682.

Tri(4-chloro-2-methylphenyl) phosphite, $P(O\text{-}p\text{-Cl-}o\text{-tolyl})_3$, was prepared in an analogous manner from 300 g of 4-chloro-2-methylphenol and 66 ml of PCl_3. Distillation under high vacuum gave a colorless oil: 230 g (67%), bp about 215° (15 μ), $n^{26}D$ 1.5924.

Bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$ (dmpe), was prepared by the procedure of Parshall.[19] Other ligands were obtained commercially and used without further purification. Purities were checked by means of proton and ^{31}P nmr spectra.

Tetrakis(triisopropyl phosphite)nickel.[20] $Ni[P(O\text{-}i\text{-Pr})_3]_4$ was prepared by triethylaluminum reduction. To 5.2 g $[Ni(acac)_2]_3$ and 17 ml of triisopropyl phosphite in 200 ml of toluene at −25° was added 26 ml of 25% by weight $AlEt_3$ in hexane. The solution was stirred and allowed to warm to room temperature. Half of the solvent was removed under reduced pressure and 300 ml of cold isopropyl alcohol was slowly and carefully added. White crystals formed on cooling to −25°. The crystals were filtered, washed with acetonitrile, and dried *in vacuo* to gave the product: 6 g (30%), mp 183–189° dec.[20b]

Tetrakis(tri-*p*-chlorophenyl phosphite)nickel. $Ni[P(O\text{-}p\text{-}C_6H_4\text{-}Cl)_3]_4$ was prepared by the $AlEt_3$ reduction of nickel acetylacetonate. A solution of 2.6 g of $[Ni(acac)_2]_3$ and 16.6 g of *p*-chlorophenyl phosphite in 50 ml of toluene was cooled to −25°. Twelve milliliters of 25% by weight $AlEt_3$ in hexane was added with stirring. The solution was allowed to warm to room temperature. After 1 hr, 300 ml of methanol was slowly and carefully added, 1 ml at a time, causing vigorous gas evolution. Filtration and recrystallization from warm (50°) toluene and methanol gave the product as glistening white crystals, mp 167–173° dec.[20b]

Tris(tri-2,4-dimethylphenyl phosphite)nickel. The complex $Ni[P(O\text{-}p\text{-}CH_3\text{-}o\text{-tolyl})_3]_3$ was prepared by the sodium borohydride reduction of 8 g of $Ni(NO_3)_2 \cdot 6H_2O$ in the presence of 30 g of the phosphite ligand in 190 ml of acetonitrile. Twelve grams of $NaBH_4$ was slowly added to the stirred, water-cooled solution over a period of 3 hr. The mixture was filtered and the bulk of the filtrate decanted from a small amount of dense liquid, which was discarded. The filtrate was concentrated to a grease. The grease was treated with benzene and the solution was filtered. Removal of the solvent under vacuum gave a clear dark red grease. Addition of methanol and cooling, and filtration, gave an orange powder, 13.8 g. Crystallization of the crude material from hexane–ethanol gave the pure product as orange flakes (67%), dec 110–120°.[20b]

Tris(tri-4-chloro-2-methylphenyl phosphite)nickel. The complex $Ni[P(O\text{-}p\text{-Cl-}o\text{-tolyl})_3]_3$ was prepared by the reduction of 2.0 g of anhydrous $NiBr_2$ by 3 g of Zn dust in the presence of 5 g of the phosphite in 100 ml of a 1:1 mixture of ethanol and acetonitrile. After stirring for 3 hr at ambient temperature, the solvents were evaporated at reduced pressure. The residue was shaken with excess aqueous sodium bicarbonate and 150 ml of hexane. The organic phase was separated and dried with anhydrous $MgSO_4$. Removal of solvent under vacuum gave an orange foam: 2.1 g (16%), dec 60–70°.

The proton nmr spectrum (Table II) showed that the compound was not pure NiL_3. Resonances of NiL_4 and L accounted for about 15% of the total ligand and suggest a composition closer to $NiL_{3.5}$.

Tetrakis(methyl diphenylphosphinite)nickel. $Ni[P(OMe)Ph_2]_4$ was prepared by the reduction of nickel chloride by metallic zinc. An acetonitrile solution (100 ml) of 1.3 g of anhydrous $NiCl_2$ and 10 ml of $P(OMe)Ph_2$ was refluxed for 0.5 hr under N_2. After cooling to room temperature, 1.0 g of Zn dust was added and the solution was stirred overnight. The resulting precipitate was filtered off and dissolved in a minimum of hexane. Filtration, precipitation with methanol, and drying gave the product as yellow crystals: 6.2 g (65%), mp 185–187° dec.[20b]

Tetrakis(methyldiphenylphosphine)nickel.[21] $Ni[P(MePh_2]_4$ was prepared by Zn reduction in a similar fashion. The crude product was dissolved in a minimum of warm toluene (60°), filtered, and precipitated with methanol. Filtration and drying gave the pure product as red-orange crystals: 6.8 g (80%), mp 168–170° dec (lit.[21] mp 163–165°).[20b]

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Table I. Molecular Weights of Isolated Complexes[a]

Complex	Mol wt		%	Lit. value
	Calcd	Found	theory	
$Ni[P(OEt)_3]_4$	723	726	100	552,[b] 630[c]
$Ni[P(O\text{-}i\text{-}Pr)_3]_4$	891	839	94	714[d]
$Ni[P(O\text{-}p\text{-}CH_3\text{-}o\text{-tolyl})_3]_3$	1241	1267	102	
$Ni[P(O\text{-}p\text{-}Cl\text{-}o\text{-tolyl})_3]_3$	1426	1167	82[e]	
$Ni[P(O\text{-}p\text{-tolyl})_3]_4$	1467	1382	94	
$Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_4$	1713	1703	99	1264[f]
$Ni[P(OMe)Ph_2]_4$	923	842	91	
$Ni[PEt_3]_4$	521	299	56	
$Ni[PMePh_2]_4$	859	790	92	
$Ni[dmpe]_2$	359			366[g]
$Ni[PMe_3]_4$	363	339	93	

[a] Cryoscopic in benzene under N_2, as described in ref 16. [b] Cryoscopic in benzene, 0.0142 *m* solution, ref 25. [c] Osmometric, 0.02 *M* solution, ref 26. [d] Cryoscopic in benzene, ref 20a. [e] Nmr spectra showed that the sample contained ligand in excess of that required for NiL_3. [f] Osmometric, reported for a compound said to be $Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_3$ in ref 24. [g] Reference 22.

Bis[bis(dimethylphosphinoethane)]nickel.[22] $Ni[Me_2PCH_2CH_2PMe_2]_2$ was prepared by the reaction of bis(dimethylphosphinoethane) (dmpe) with bis(1,5-cyclooctadienenickel).[23] Crystallization from toluene–acetonitrile gave pale yellow crystals: 1.83 g (51%), mp 118–120° (lit.[22] 120°).[20b]

Tetrakis(triethyl phosphite)nickel, tetrakis(tri-*p*-tolyl phosphite)nickel, and tetrakis(trimethylphosphine)nickel were prepared as described earlier.[1] Tetrakis(triethylphosphine)nickel[21] was kindly provided by Dr. D. H. Gerlach as pale yellow crystals.

Results

Preparations and Molecular Weights. Preparation of some previously unreported Ni(0) complexes prepared for this study are given in the Experimental Section. We have also given a few improved preparations for known compounds. Levison and Robinson[24] reported the preparation of a white crystalline compound thought to be the tris complex $Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_3$ on the basis of its osmometric molecular weight. The only Ni(0) complex which we have been able to isolate with this ligand is the tetrakis complex. Since all our tris(aryl phosphite)nickel complexes are orange or red-orange, we conclude that Robinson's complex was probably also $Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_4$. Accurate molecular weights on these Ni(0) compounds cannot be obtained unless O_2 is rigorously excluded. The cryoscopic technique[16] which we have used has been far more successful than vapor pressure osmometry, which has given us consistently low molecular weights even after flushing the instrument overnight with N_2.

Molecular weights determined for the compounds of this study are given in Table I. Low molecular weights for $Ni[P(OEt)_3]_4$ were found earlier by Vinal and Reynolds[25] and by Meier, Basolo, and Pearson.[26] The former authors attributed the low value to ligand dissociation in solution.

Molecular weights on air sensitive compounds should be interpreted with caution in the absence of other confirmatory evidence for dissociation in solution. We tentatively ascribe little or no dissociation to complexes in Table I with measured molecular weights of 93–102% theoretical. $Ni[PEt_3]_4$ shows the most extensive dissociation of any complex in the series, due in part to formation of $(N_2)Ni[PEt_3]_3$.[15] The pure tris complex $Ni[P(O\text{-}p\text{-}CH_3\text{-}o\text{-tolyl})_3]_3$ shows no dissociation.

Proton Nmr Spectra. Proton nmr spectral data for solutions of the free ligands and isolated complexes are given in Table II. All of the compounds appeared to be pure, with the exception of $Ni[P(O\text{-}p\text{-}Cl\text{-}o\text{-tolyl})_3]_3$, which contained excess ligand corresponding to a composition of about $NiL_{3.5}$. Examination of the chemical shifts shows no clear correlation between coordination chemical shift and proton type. In the case of $L = P(O\text{-}p\text{-}CH_3\text{-}o\text{-tolyl})_3$, the lower field $-CH_3$ resonance is assigned to $o\text{-}CH_3$ in free L and to $p\text{-}CH_3$ in NiL_4, based on the behavior of the methyl resonances in the $L = P(O\text{-}o\text{-tolyl})_3$ and $L = P(O\text{-}p\text{-tolyl})_3$ systems.

Four types of behavior were observed when ligand was added to solutions of the nickel complexes. These are described as I to IV in Table II. Each type can be understood in terms of the degree of ligand dissociation of the NiL_4 complex and the rate of exchange of free and complexed ligand.

Type I. Little L Dissociation,[27] Slow Exchange. The solution of complex showed a single set of ligand resonances. Adding ligand simply added resonances of free ligand to the spectrum.

Type II. Extensive Dissociation, Slow Exchange. A solution of NiL_4 complex[28] showed three sets of ligand resonances, due to NiL_4, NiL_3, and L.

Type III. Little Dissociation, Fast Exchange. A solution of NiL_4 complex showed a single set of ligand resonances. Adding ligand gave a resonance in the position of free ligand but lacking the P–H coupling which had been present in the solution of ligand alone.

Type IV. Extensive Dissociation, Fast Exchange. A solution of NiL_4 complex showed a single set of ligand resonances. Adding L did not give resonances in the position of free L. The nmr behavior of phosphorus ligand complexes in this and earlier[13,14] studies is summarized in Figure 1.

It can be seen that the rates of ligand exchange are generally higher for phosphines and phosphinite than for phosphites. Slow exchange in the case of bis(dimethylphosphino)ethane is probably an effect of chelation.

Addition of $PMePh_2$ to a solution of the NiL_4 complex in a 2:1 ratio gave a new broad, featureless $-CH_3$ resonance at τ 8.5. Further $PMePh_2$ caused this resonance to sharpen and shift upfield toward the free ligand position at τ 8.65. The broad resonance is an average of NiL_3 and L in rapid exchange. The sharp $-CH_3$ resonance of $Ni[PMePh_2]_4$ remained at τ 8.33. Addition of PEt_3 to a solution of $Ni[PEt_3]_4$ in a 4:1 ratio gave no new resonances, but simply shifted the existing resonances ~0.05 ppm upfield and slightly modified their shape.[29]

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(27) Little L dissociation by the nmr criterion sets an upper limit of about 2.5×10^{-4} *M* on K_d, assuming that 5% dissociation of an NiL_4 complex would be detected. An absence of dissociation of $Ni[P(OEt)_3]_4$ by this proton nmr criterion was reported earlier by Meier, Basolo, and Pearson.[26]

(28) Solutions with the composition NiL_4 where L was an *o*-tolyl phosphite were prepared by adding ligand to solutions of NiL_3.

(29) The methylene quartet at τ 8.40 was unsymmetrical before addition of PEt_3; the higher field central line was most intense. After PEt_3 addition the lower field central line was most intense, and was exceptionally sharp. The center of the pattern was shifted upfield to τ 8.46.

Table II. Proton Nmr Spectral Data[a] for Phosphorus Ligands and Complexes

Compound	Behavior[b]	Aryl		Alkyl	
		H_o	H_m and H_p	$-CH_2-$ or $-CH-$	$-CH_3$
$P(OEt)_3$				6.21 dq(7.2)[c]	8.91 t(7.2)
$Ni[P(OEt)_3]_4$[d]	I			5.88 m[i]	8.76 t(7.0)
$P(O\text{-}i\text{-}Pr)_3$				5.60 d sept[e]	8.83 d(6.3)
$Ni[P(O\text{-}i\text{-}Pr)_3]_4$	I			5.13 br	8.66 d(6.0)
$P(O\text{-}p\text{-}CH_3\text{-}o\text{-}tolyl)_3$		2.63 d(8)	3.19, 3.25 d(8)		7.83, 7.97
$Ni[P(O\text{-}p\text{-}CH_3\text{-}o\text{-}tolyl)_3]_3$		2.53 d(8)	3.25		7.96
$Ni[P(O\text{-}p\text{-}CH_3\text{-}o\text{-}tolyl)_3]_4$[f]	II	2.30 d(8)	3.28, 3.40 d(8)		7.96, 8.02
$P(O\text{-}o\text{-}tolyl)_3$[g]		2.68 d(8)	3.07 m		7.89
$Ni[P(O\text{-}o\text{-}tolyl)_3]_3$[g]		2.48 d(8)	3.12 m		8.04
$Ni[P(O\text{-}o\text{-}tolyl)_3]_4$[g]	II	2.26 d(8)	3.24 m		8.04
$P(O\text{-}p\text{-}Cl\text{-}o\text{-}tolyl)_3$		3.08			8.14
$Ni[P(O\text{-}p\text{-}Cl\text{-}o\text{-}tolyl)_3]_3$[h]		2.73 d(9)	3.13, 3.17 d(9)		8.26
$Ni[P(O\text{-}p\text{-}Cl\text{-}o\text{-}tolyl)_3]_4$	II	2.75 d(9)	3.22, 3.31 d(9)		8.39
$P(O\text{-}p\text{-}tolyl)_3$		2.84 d(8.5)	3.14 d(8.5)		8.01
$Ni[P(O\text{-}p\text{-}tolyl)_3]_4$	I	2.82 d(8.5)	3.16 d(8.5)		7.97
$P(O\text{-}p\text{-}C_6H_4Cl)_3$		3.01 d(9)	3.22 d(9)		
$Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_4$	I	3.07 d(9)	3.28 d(9)		
$P(OMe)Ph_2$		2.40 m	2.85 m		6.62 d(14.0)
$Ni[P(OMe)Ph_2]_4$	III	2.63 m	2.94 m		6.94 m[i]
PEt_3				~8.76 m	
$Ni[PEt_3]_4$	IV			8.40 q(7.0)	8.94 t(7.0)
$PMePh_2$		2.60 m	2.86 m		8.65 d(4.0)
$Ni[PMePh_2]_4$	IV	2.76 m	2.98 m		8.33
dmpe				8.71 t(4.0)[i]	9.20 t(1.5)
$Ni[dmpe]_2$	I			8.60 m[i]	8.76
PMe_3					9.22 d(2.5)
$Ni[PMe_3]_4$	III				8.86

[a] Chemical shifts in C_6D_6 relative to TMS at τ 10.0. Coupling constants in parentheses in Hz. Abbreviations: dmpe, $Me_2PCH_2CH_2PMe_2$; d, doublet; t, triplet; q, quartet; sept, septet; br, broad; m, multiplet. [b] See discussion in text. [c] $J(CH_2-CH_3) = J(P-CH_2) = 7.2$ Hz. [d] Proton nmr data in $CDCl_3$ are given in ref 1. [e] $J(CH-CH_3) = 6.3$; $J(P-CH) = 9.0$ Hz. [f] Generated in solution by the addition of L to NiL_3. [g] Chemical shifts from ref 13. [h] The NiL_3 complex was impure and showed weak resonances due to NiL_4 and L whose area corresponded to 15% of the ligand in the sample. This corresponds to an empirical formula of about $NiL_{3.5}$. [i] Multiplet showed virtual coupling effects.

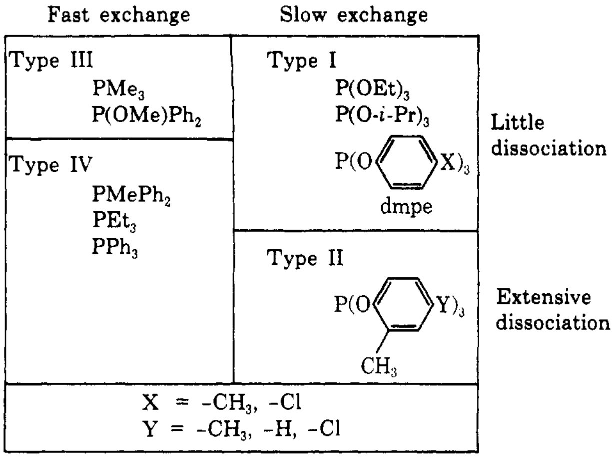

Figure 1. Nmr behavior of phosphorus ligand exchange on Ni(0).

^{31}P Nmr Spectra. Chemical shifts of free ligands and complexes at ambient temperature are shown in Table III. The entries are arranged in order of increasing chemical shift of free ligand. In the aryl phosphite series there is a good negative correlation between δ_L and the coordination chemical shift ($\delta_{NiL_4} - \delta_L$), with δ_L becoming less negative with substitution of more strongly electron withdrawing groups in the para position. More sterically bulky ligands appear to show a less negative coordination chemical shift. The large negative coordination chemical shift for dmpe is attributed to chelation.[30]

Table III. ^{31}P Nmr Chemical Shifts[a] for NiL_4, NiL_3, and L

	δ_{NiL_4}	δ_L	$\delta_{NiL_4} - \delta_L$
$P(OEt)_3$[b]	−158.4	−137.8	−20.6
$P(O\text{-}i\text{-}Pr)_3$	−154.1	−137.6	−16.5
$P(O\text{-}p\text{-}CH_3\text{-}o\text{-}tolyl)_3$	(−128.5)[c]	−130.5	(+2.0)[c]
	−128.8		+1.7
$P(O\text{-}o\text{-}tolyl)_3$[b]	(−128.3)[c]	−130.0	(+1.7)[c]
	129.0		+1.0
$P(O\text{-}p\text{-}Cl\text{-}o\text{-}tolyl)_3$	(−129.7)[c]	−128.9	(−0.8)[c]
	−130.4		−1.5
$P(O\text{-}p\text{-}tolyl)_3$[b]	−130.4	−127.7	−2.7
$P(O\text{-}p\text{-}C_6H_4Cl)_3$	−129.7	−125.8	−3.9
$P(OMe)Ph_2$	−126.2	−115.9	−6.3
PEt_3	−2.4[d]	+20.5	−22.9
$PMePh_2$	−2.9	+27.9	−30.8
dmpe	−18.0[e]	+49.3	−67.3
PMe_3[b]	+22.2	+63.3	−41.1

[a] Ppm (85% H_3PO_4) in toluene at +27°. [b] Data from ref 1. [c] Values in parentheses refer to NiL_3 complexes. The NiL_4 complexes were generated in solution by adding L. [d] Broad resonance ~100 Hz wide at 27°. [e] A value of −18.1 was reported in ref 1 for $Ni[dmpe]_2$ made in solution but not isolated.

The behavior of the ^{31}P spectra on adding ligand to a solution of the complex generally paralleled the proton nmr results. For example, addition of $P(O\text{-}p\text{-}C_6H_4Cl)_3$ to a solution of $Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_4$ gave a new sharp resonance in the position of free ligand.[31] Phosphorus–hydrogen coupling was generally not resolved so that behavior of types I and III could not be distinguished. Complexes of types II and IV were investigated as a function of temperature. Solu-

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

(31) ^{31}P nmr evidence against ligand dissociation was cited earlier[1] for $Ni[P(OEt)_3]_4$ and $Ni[P(O\text{-}p\text{-}tolyl)_3]_4$.

tions with *o*-tolyl phosphite ligands of composition NiL_4 showed three resonances at ambient temperature but only one, that of NiL_4, at low temperature.

The most unusual behavior was exhibited by $Ni[PMePh_2]_4$ and $Ni[PEt_3]_4$, which had shown extensive dissociation and rapid exchange (type IV behavior) in the proton spectra.

$Ni[PMePh_2]_4$ showed a single sharp (20-Hz wide at half height) resonance at −2.9 ppm at ambient temperature. Addition of 2 equiv of $PMePh_2$ gave an additional resonance at +27.9 ppm, the position of free ligand, but the ligand resonance was very broad (∼100 Hz). On cooling, the two resonances remained in place but the ligand peak sharpened. On heating the solution above 27°, the ligand peak broadened rapidly and could no longer be observed at +50°. The NiL_4 resonance also broadened with heating, reaching a width of 60 Hz at 70°. *The chemical shift and line shape of the NiL_4 resonance were the same in the presence of added $PMePh_2$ as in its absence.*

$Ni[PEt_3]_4$ under argon behaved similarly but at a lower temperature. Ligand exchange was already so rapid at 27° that the NiL_4 resonance had a width of 100 Hz and no new resonance was observed when PEt_3 was added to the solution. On cooling the solution to −15° with added ligand, sharp resonances due to NiL_4 and free L were observed at −2.9 and +20.5 ppm. At 0° the NiL_4 resonance was sharp and the free ligand resonance broad. The width of the free ligand resonance at 0° decreased as the concentration of free ligand increased. The chemical shift and line shape of the resonance due to complexed ligand were independent of free ligand concentration over the temperature range investigated of −50[32] to +50°.

The line shape effects in the nmr spectra of $Ni[PMePh_2]_4$ and $Ni[PEt_3]_4$ can be understood on the basis of partial ligand dissociation to NiL_3 and rapid ligand exchange.

$$NiL_4 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NiL_3 + L$$

The line shape of the NiL_4 resonance is independent of [L] because the life time of ligand in the complex depends only on k_2, $\tau_C = k_2^{-1}$. The line shape of the free L resonance depends on [L] by the relationship

$$\tau_L = \{k_{-2}[NiL_3]\}^{-1} = [L]\{k_2[NiL_4\}^{-1}$$

It should be emphasized that this line shape behavior is not consistent with ligand exchange by an associative mechanism involving an NiL_5 intermediate. Such a mechanism would require that the bound ligand resonance broaden as ligand was added.

Electronic Spectra and Equilibrium Constants. Electronic spectral data are given in Table IV for NiL_4 and NiL_3 complexes in this study along with some data from the literature. For a given ligand, electronic transitions occur at a higher frequency for NiL_4 than for NiL_3. More electron-withdrawing ligands tend to give higher frequency electronic transitions. These trends are clearly seen in Figure 2, where the frequency of the long wavelength absorption maximum is plotted against a measure of the ligand electron donor–acceptor character, $\nu_{CO}(A)$ of $Ni(CO)_3L$.[33] It is apparent that compounds containing phenyl groups attached to phosphorus do not lie on the solid lines correlating the other complexes. Orio, Chastain, and Gray[34] have given a qualitative molecular orbital diagram for tetrakis complexes of d^{10} metals and assigned the long wavelength absorption bands in $Ni[P(OEt)_3]_4$ and $Ni[P(OEt)_2Ph]_4$ to metal to ligand charge transfer transitions. The much higher energy of the $d \rightarrow \pi^*$ transitions in $Ni[P(OEt)_3]_4$ compared to $Ni[P(OEt)_2Ph]_4$ was attributed to electron repulsion of the ligand π^* orbitals by nonbonding electron pairs on oxygen. Our work suggests that this explanation is unlikely. In

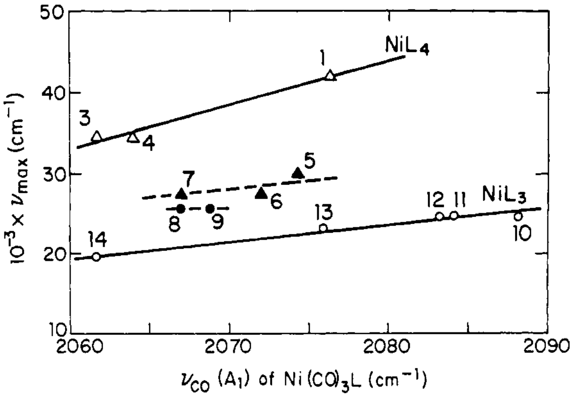

Figure 2. Frequency of longest wavelength electronic absorption maximum *vs.* A_1 stretching frequency of $Ni(CO)_3L$ from ref 33: Δ, NiL_4 without P–Ph; ▲, NiL_4 with P–Ph; ●, NiL_3 with P–Ph; ○, NiL_3 without P–Ph. The ligand numbers refer to Table IV.

Table IV. Electronic Spectral Data[a]

A. NiL_4 Complexes

Complex	λ_{max}	$10^4\epsilon_{max}$	Solvent
1. $Ni[P(OEt)_3]_4$[b]	238	2.5	M
2. $Ni[dmpe]_2$	288	2.4	H
3. $Ni[PEt_3]_4$	290	>1.7[c]	H
4. $Ni[PMe_3]_4$	292	2.3	H
5. $Ni[P(OEt)_2Ph]_4$[d]	333	1.75	C
6. $Ni[P(OMe)Ph_2]_4$	362	2.1	B
7. $Ni[PMePh_2]_4$	368	2.4[e]	B

B. NiL_3 Complexes

Complexes	λ_{max}	$10^3\epsilon_{max}$	λ_{sh}	10^3-ϵ_{sh}	Solvent
8. $Ni[PMePh_2]_3$	388	21			B
9. $Ni[PPh_3]_3$[j]	393	14	∼530	2.5	B
10. $Ni[P(O\text{-}p\text{-}Cl\text{-}o\text{-}tolyl)_3]_3$	407	*f*	450	*f*	B
11. $Ni[P(O\text{-}o\text{-}tolyl)_3]_3$	407	5.0[g]	450	3.7[g]	B
12. $Ni[P(O\text{-}p\text{-}CH_3\text{-}o\text{-}tolyl)_3]_3$	409	5.0	450	3.7	B
13. $Ni[P(O\text{-}i\text{-}Pr)_3]_3$	430	2.7[h]	460	2.3[h]	B
14. $Ni[PEt_3]_3$	502	∼2.6[h,i]			B

[a] Wavelengths in mμ (±2). λ_{sh} is the wavelength at the inflection. Extinction coefficients in cm^{-1} M^{-1} (±10%). Solvents are M, methanol; H, *n*-heptane; C, cyclohexane; B, benzene. [b] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 4217 (1970). [c] With 1 *M* PEt_3 added to suppress dissociation. Some $Ni[PEt_3]_3$ and $(N_2)Ni[PEt_3]_3$ are still present. [d] Reference 34. [e] With 2 *M* $PMePh_2$ added to suppress dissociation. [f] Accurate extinction coefficients could not be obtained because the sample was impure. [g] These extinction coefficients are slightly higher than those reported in ref 13 and are based on more accurate subsequent measurements. [h] Determined by heating a dilute solution of NiL_4 to complete dissociation. [i] Determined under argon. [j] Data from ref 14.

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(32) As the temperature was lowered below about −25°, the $Ni[PEt_3]_4$ signal became appreciably less intense due to crystallization of the complex from solution.

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

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

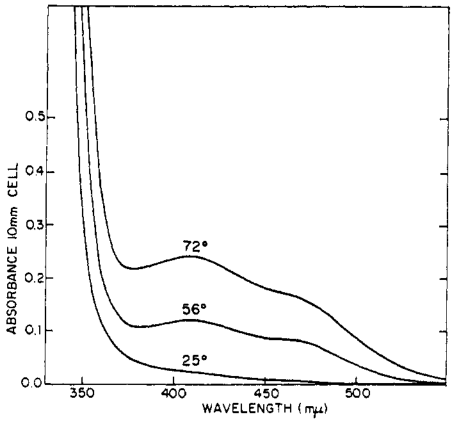

Figure 3. Optical spectra of 0.019 M Ni[P(O-p-tolyl)$_3$]$_4$ at various temperatures in benzene.

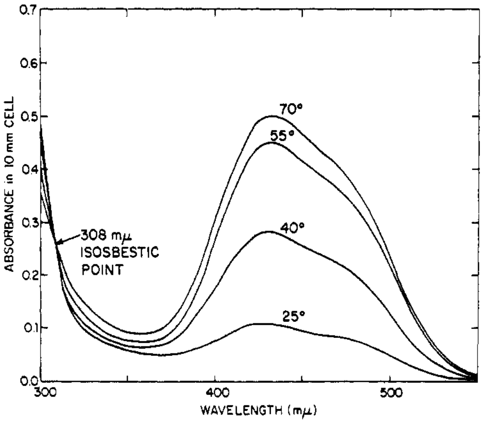

Figure 4. Optical spectra of 1.92×10^{-4} M Ni[P(O-i-Pr)$_3$]$_4$ at various temperatures in benzene.

particular the lowest energy band of Ni[PMe$_3$]$_4$ is *higher* in energy than that of Ni[P(OEt)$_2$Ph]$_4$. We suggest rather that the long wavelength absorptions of complexes with P–Ph groups involve substantial excitation of the benzene ring, causing both long wavelength shifts and exceptionally large extinction coefficients for the NiL$_3$ complexes.

The tetrakis(aryl phosphite) complexes Ni[P(O-p-tolyl)$_3$]$_4$ and Ni[P(O-p-C$_6$H$_4$Cl)$_3$]$_4$ are white crystalline solids and give colorless benzene solutions at 25°. On heating the solutions become yellow due to formation of small concentrations of the tris complexes NiL$_3$, identified by an absorption maximum at 407 and shoulder at 450 mμ as shown in Figure 3 for L = P(O-p-tolyl)$_3$. The extent of dissociation is very small even at 72°. Equilibrium constants were calculated assuming the same extinction coefficients as for Ni[P(O-o-tolyl)$_3$]$_3$.

The tetrakis(alkyl phosphite) complexes Ni[P(O-i-Pr)$_3$]$_4$ and Ni[P(OEt)$_3$]$_4$ are also white crystalline solids. Benzene solutions of the former are, however, yellow-orange in color and show an absorption maximum at 430 mμ and a shoulder at 460 mμ; the solutions do not obey Beer's law at 25° and the absorbance increases with increasing temperature as shown in Figure 4. Addition of small concentrations of P(O-i-Pr)$_3$ turn the solution colorless by suppressing the dissociation equilibrium. An isosbestic point at 308 mμ during the additions confirms the simple stoichiometry of the reaction.

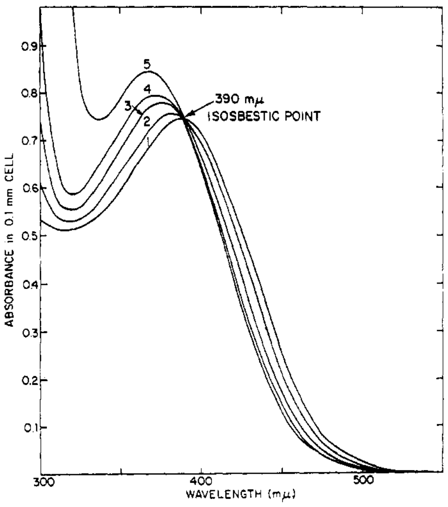

Figure 5. Optical spectra of 3.64×10^{-3} M Ni[PMePh$_2$]$_4$ in benzene at 25° with increasing concentrations of added PMePh$_2$: (1) none; (2) 0.02 M; (3) 0.05 M; (4) 0.10 M; (5) 2.0 M.

If one assumes the same extinction coefficients for Ni[P(OEt)$_3$]$_3$ as for Ni[P(O-i-Pr)$_3$]$_3$, K_d for Ni[P(OEt)$_3$]$_4$ must be smaller than 10^{-10} M at 70°.[35]

The phosphine complexes Ni[PMe$_3$]$_4$, Ni[dmpe]$_2$, and Ni[PEt$_3$]$_4$ are pale yellow crystalline solids of very similar appearance. While benzene solutions of the first two are pale yellow, that of the triethylphosphine complex is deep violet, about the color of aqueous permanganate.[15] The violet solution shows an absorption maximum at 502 mμ, attributed to Ni[PEt$_3$]$_3$. As expected, the violet solutions do not obey Beer's law and turn yellow at once on adding PEt$_3$.

Ni[PMe$_3$]$_4$ showed no evidence for ligand dissociation. A 10^{-2} M solution in a 10-mm cell showed an absorption tail dropping sharply from an absorbance of 2.0 at 324 mμ to less than 0.01 at 480 mμ. On heating the solution it became a deeper yellow[36] and the wavelength for an absorbance of 2.0 shifted to 333 mμ at 70°. There was still no appreciable absorbance above 500 mμ to indicate the formation of Ni[PMe$_3$]$_3$. The absorption tail regained its original appearance on cooling the solution back to 25°. The broadening of the electronic absorption band of Ni[PMe$_3$]$_4$ on heating is attributed to a vibronic effect.[37] Similar behavior was observed with Ni[dmpe]$_2$ and Ni[P(OEt)$_3$]$_4$.

The electronic spectral changes on ligand dissociation from complexes containing P–Ph groups are much less marked than those of the other compounds. Figure 5 shows the spectrum of Ni[PMePh$_2$]$_4$ alone and in the presence of increasing concentrations of added PMePh$_2$. Without added ligand, dissociation to NiL$_3$ and L is nearly complete. Association to NiL$_4$ is nearly complete in 2 M PMePh$_2$; the absorbance below 330 mμ is partly due to free PMePh$_2$. There is about half NiL$_3$ and half NiL$_4$ in 0.05 M PMePh$_2$, implying K_d = 0.05 M at 25°.[38]

Because of the rather small differences between the

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[35] A $K_d = 10^{-10}$ would give an absorbance of 0.01 at 430 mμ.

[36] H. F. Klein and H. Schmidbaur, *Angew. Chem.*, **82**, 885 (1970).

[37] Population of higher vibrational levels as the temperature is raised is expected to decrease the extinction coefficient at the band maximum and increase it in the wings of the band.

[38] About 94% NiL$_3$ is present in the absence of added ligand and 3% in 2 M PMePh$_2$, assuming K_d = 0.05 M for the 3.64×10^{-3} M solution.

Table V. Spectrophotometric Equilibrium Data in Benzene at 25°

$K_d = [NiL_3][L]/[NiL_4]$

L	$K_d{}^a$ (M)	Original θ^b (deg)	New θ^c (deg)
$Me_2PCH_2CH_2PMe_2$	$<10^{-10\ d}$		107
$P(OEt)_3$	$<10^{-10\ d}$	109 ± 2	109
PMe_3	$<10^{-9\ d}$	118 ± 4	118
$P(O\text{-}p\text{-}C_6H_4Cl)_3$	$\sim 2 \times 10^{-10}$	121 ± 10	128
$P(O\text{-}p\text{-tolyl})_3$	6×10^{-10}	121 ± 10	128
$P(O\text{-}i\text{-}Pr)_3$	2.7×10^{-5}	114 ± 2	130
$P(OMe)Ph_2$	$<4 \times 10^{-5}$		132
PEt_3	1.2×10^{-2}	132 ± 4	132
$P(O\text{-}p\text{-}Cl\text{-}o\text{-tolyl})_3$	0.7×10^{-2}	165 ± 10	141
$P(O\text{-}p\text{-}CH_3\text{-}o\text{-tolyl})_3$	3.1×10^{-2}	165 ± 10	141
$P(O\text{-}o\text{-tolyl})_3$	4.0×10^{-2}	165 ± 10	141
$PMePh_2$	5.0×10^{-2}		136
PPh_3	$>10^{e}$	145 ± 2	145

[a] Uncertainties are generally less than ±15% except for the para substituted phenyl phosphites where K_d was measured to within a factor of 3. [b] From ref 1. [c] Determined as described in text. Uncertainties generally ±2°. [d] No dissociation detected at 70°. [e] No association detected at 25° in 1.0 M PPh_3, ref 14.

spectra of $Ni[PMePh_2]_4$ and $Ni[PMePh_2]_3$ and the fact that each showed vibronic effects,[39] it was difficult to obtain accurate thermodynamic parameters.

A similar difficulty was encountered with $Ni[P(OMe)Ph_2]_4$. In this case, however, the complex was dissociated so little at 25° that addition of 1 M $P(OMe)Ph_2$ had no detectable effect on the spectrum of a 3.6×10^{-3} M solution. This implies that $K_d < 4 \times 10^{-5}$ M at 25°.[40] At higher temperatures the yellow solution became more deeply colored. Addition of 5×10^{-4} M ligand to a 10^{-2} M solution of complex at 70° had about half the effect of adding 1 M ligand. This indicates that K_d must have a value of the order of 5×10^{-4} M at 70°.

Ligand dissociation constants at 25° are given in Table V. Contrary to expectations based on the earlier literature,[26,34] but in agreement with those of ligand competition experiments,[1] K_d is strongly dependent on steric effects. In the para substituted o-tolyl phosphite series values of K_d of 0.007, 0.031, and 0.040 for p-Cl, $-CH_3$, and -H are the same within a factor of 6.

In striking contrast is the difference in dissociation constants of $P(O\text{-}p\text{-tolyl})_3$ and $P(O\text{-}o\text{-tolyl})_3$, which are electronically identical but differ in K_d by a factor of 0.7×10^8. The electronically similar PMe_3 and PEt_3 differ in K_d by a factor of at least 10^7. Successively replacing -Me by -Ph in PMe_nPh_{3-n} appears to increase K_d by a factor of $\sim 10^4$ for each replacement.

In several cases, equilibrium constants were measured as a function of temperature. Plots of log K_d against $1/T$ gave straight lines whose slopes and intercepts were used to determine ΔH_d and ΔS_d. These data appear in Table VI. It was assumed that the extinction coefficients were independent of temperature. In most cases vibronic corrections are expected to be small compared to the quoted uncertainties.

The greater ligand dissociation of bulky ligands is not an entropy effect. The thermodynamic data clearly show that the steric effects are felt primarily in the enthalpy of dissociation. Thus, values of ΔH_d for $P(O\text{-}p\text{-tolyl})_3$ and $P(O\text{-}o\text{-tolyl})_3$ differ by about 10 kcal/mol, while values of ΔS_d are practically the same within experimental error. The smaller energy requirement for breaking the Ni–P bond of a bulky ligand might be the result of a longer metal–phosphorus bond length in the tetrakis complex or relief of the strain energy which was required to compress the ligand cone sufficiently to coordinate four ligands.

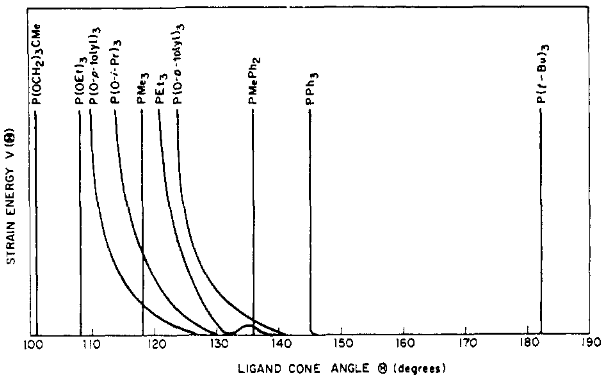

Figure 6. Strain energy in phosphorus ligand models as the ligand cone is compressed.

Table VI. Thermodynamic Parameters for Ligand Dissociation

L	ΔH_d, kcal/mol	ΔS_d, eu
$P(O\text{-}p\text{-tolyl})_3$	23 ± 3	35 ± 9
$P(O\text{-}p\text{-}C_6H_5Cl)_3$	21 ± 7	26 ± 20
$P(O\text{-}i\text{-}Pr)_3$	23.5 ± 1.5	58 ± 5
PEt_3	16 ± 2	45 ± 6
$P(O\text{-}p\text{-}Cl\text{-}o\text{-tolyl})_3$	12.5 ± 1	32 ± 3
$P(O\text{-}p\text{-}CH_3\text{-}o\text{-tolyl})_3$	12 ± 2	33 ± 6
$P(O\text{-}o\text{-tolyl})_3$	13 ± 1.5[a]	37 ± 4[a]

[a] Data from ref 13.

Ligand Cone Angles. Examination of Table V shows that our originally reported[1] ligand cone angles suggest that $P(O\text{-}i\text{-}Pr)_3$ (114°) should dissociate less than $P(O\text{-}p\text{-tolyl})_3$ (121°). $P(O\text{-}o\text{-tolyl})_3$ (165°) might be expected to dissociate more than PPh_3 (145°). These two expectations were not borne out by the measured values of K_d. We would like to suggest an improved method for determining these ligand cone angles and suggest how the concept can be extended to unsymmetrical phosphines like $P(OMe)Ph_2$ or to diphosphines like $Me_2PCH_2CH_2PMe_2$.

Some CPK phosphorus ligand models,[2] like $P(OCH_2)_3CMe$ or $P(t\text{-}Bu)_3$, are locked in position by geometrical constraints and possess no internal degrees of freedom which affect the cone angle. Some, like PPh_3, possess internal degrees of freedom but show a steep repulsive potential if one attempts to reduce the ligand cone beyond a certain point (145°). With other ligands, like $P(OPh)_3$, no abrupt barrier is encountered as the substituents are folded back to obtain the minimum cone. These features are shown schematically in Figure 6, where the strain energy in the models is shown as a function of cone angle. The value of 121 ± 10° for $P(OPh)_3$ reported earlier[1] was the result of several measurements with varying degrees of strain. The value of 114 ± 2° for $P(O\text{-}i\text{-}Pr)_3$ was for a highly strained limiting configuration. More careful inspection of the $P(O\text{-}i\text{-}Pr)_3$ model gives an

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(39) The extinction coefficient at the absorbtion maximum of NiL_3 or NiL_4 decreased about 3% for a 15° rise in temperature.

(40) Assuming that conversion of 10% of the Ni from NiL_3 to NiL_4 would be detectable.

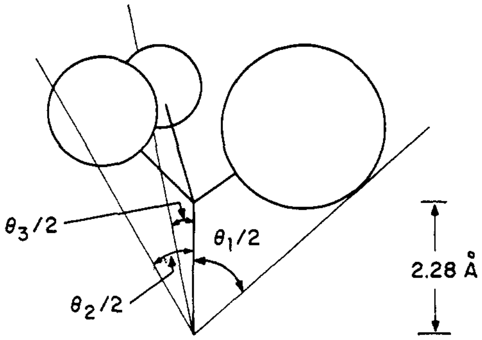

Figure 7. Method of measuring cone angles for unsymmetrical ligands.

essentially strain-free $\theta = 130°$.[41] A more complex potential is evident for PEt_3. The value of 165 ± 10° reported earlier for P(O-*o*-tolyl)$_3$ was based on a model with all three ortho methyl groups pointing toward P. Using the alternative model with methyl groups away from P gives a potential $V(\theta)$ as shown in Figure 6, with an essentially strain-free cone at $\theta = 141°$. By using angles based on essentially strain-free models, one does get the correct rank order of ligand dissociation constants: $P(OEt)_3 < PMe_3 <$ P(O-*p*-tolyl)$_3 <$ P(O-*i*-Pr)$_3 < PEt_3 <$ P(O-*o*-tolyl)$_3 < PPh_3$.

For unsymmetrical ligands $PX_1X_2X_3$ an effective ligand cone angle θ can be defined by reference to Figure 7. The *i*th substituent will have a half angle $\theta_i/2$ defined by the metal–phosphorus axis and an outermost van der Waals contact. An effective cone can be defined by the relation

$$\theta = 2/3 \sum_{i=1}^{3} \theta_i/2 \qquad (3)$$

and an essentially strain-free minimum cone found by minimizing θ using the various degrees of freedom available in the ligand. In practice one can often obtain a good approximation by taking the arithmetic mean of θ values appropriate for the symmetrical ligands. For example for $PMePh_2$ $\theta = {}^1/_3(118) + {}^2/_3(145) = 136°$. That $PMePh_2$ is really much smaller than PPh_3 is shown by its much smaller value of K_d.

In the case of chelating diphosphines, eq 3 can be used by letting $\theta_1/2$ be the angle between one P–M bond and the bisector of the PMP angle. A value of 84° may be taken as representative of PMP angles in five-membered chelate rings.[42] Thus for each end of dmpe one obtains $\theta = {}^2/_3(42 + 59 + 59) = 107°$.

The new values of θ shown in Table V can be seen to correlate well with the values of K_d. Even better agreement could be obtained by allowing a little strain, *i.e.*, letting θ for P(O-*o*-tolyl)$_3$ drop to 136°; however, such refinements do not now appear warranted on the basis of the limited data available.

While steric effects dominate equilibria involving association and exchange of phosphorus ligands on zerovalent nickel, it is to be expected that electronic effects will become much more important in other types of reactions, especially those involving a change in the formal oxidation state of the metal.

In subsequent papers we shall investigate the role of ligand steric and electronic effects on the formation constants of olefin complexes of zerovalent nickel.

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[41] In this context deformation of bond angles from 109.5° but not eclipsing of C–H bonds in adjacent carbons is considered in the strain in the model.

[42] P. Meakin, L. J. Guggenberger, F. N. Tebbe, and J. P. Jesson, *Inorg. Chem.*, in press.