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Ethylene[bis(tri-*o*-tolyl phosphite)]nickel(0)

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The preparation and properties of ethylene[bis(tri-*o*-tolyl phosphite)]nickel(0) are described. The ethylene appears in the proton nmr spectrum at τ 8.06, 3.3 ppm to high field of free C_2H_4. The $\nu(C{=}C)$ of ethylene in the complex was observed in the Raman spectrum at 1487 cm^{-1}, 136 cm^{-1}, lower than that of free C_2H_4. Spectrophotometric measurements show that addition of tri-*o*-tolyl phosphite to a solution of the ethylene complex rapidly converts it to tris- and tetrakis(tri-*o*-tolyl phosphite)nickel complexes. The equilibrium constant K_1, to give the tris-phosphite complex *via* the reaction $(C_2H_4)NiL_2 + L \overset{K_1}{\rightleftharpoons} NiL_3 + C_2H_4$, has a value of $6.8 \pm 0.5 \times 10^{-3}$ in benzene at 28°.

Introduction

Earlier studies[1] on phosphorus ligand exchange on zerovalent nickel showed that most nickel(0)–phosphorus complexes are four-coordinate and do not detectably dissociate in solution. Complexes with very bulky ligands can, however, dissociate appreciably. The preparation and properties of the three-coordinate tris(tri-*o*-tolyl phosphite)nickel were recently reported.[2] In that paper, spectroscopic evidence was presented against dissociation of the tris complex to bis(tri-*o*-tolyl phosphite)nickel. McCall and Coover[3] have recently claimed the preparation in solution of bis(tri-*o*-tolyl phosphite)nickel by the triethylaluminum reduction of nickel acetylacetonate in the presence of *excess* ligand, a result which was clearly inconsistent with our physical measurements on the tris-phosphite complex. We have carried out the synthesis in a fashion similar to theirs and have prepared a yellow crystalline solid which is unequivocally shown to be an olefin complex of Ni(0), ethylene[bis(tri-*o*-tolyl phosphite)]nickel, first reported by Wilke.[4] Spectroscopic studies have shown that the complex is stable to dissociation but very labile in exchange of both ethylene and phosphite ligands. The equilibrium constants for conversion to the tris- and tetrakis-phosphite complexes in the presence of added phosphite ligand have been determined.

Experimental Section

Because the complex is sensitive to oxygen, it was synthesized in a nitrogen atmosphere using deoxygenated solvents. Special precautions to exclude oxygen in the spectrophotometric experiments were described earlier.[2]

Ethylene[bis(tri-*o*-tolyl phosphite)]nickel, $(C_2H_4)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2$, was prepared by the reduction of 4.6 g of nickel acetylacetonate (18 mmol) in the presence of 12.8 g of tri-*o*-tolyl phosphite[5] (36 mmol) in 200 ml of toluene at −50°. The solution was saturated with ethylene[6] and 5.4 ml of triethylaluminum (40 mmol) rapidly added with stirring. The reaction mixture was allowed to warm to 30° and 100 ml of toluene was removed under reduced pressure. To the remaining solution was gradually added 300 ml of methanol saturated with ethylene. The solution was cooled and the yellow crystals were separated by vacuum filtration. Recrystallization from benzene–methanol gave 11.3 g of product (80% yield), dec pt 118–120°. *Anal.* Calcd for $C_{44}H_{46}NiO_6P_2$: C, 66.8; H, 5.8; Ni, 7.4; P, 7.8. Found: C, 66.6; H, 5.7; Ni, 7.3; P, 7.8.

The complex is readily soluble in benzene or toluene but is rapidly decomposed by halogenated solvents.

The cryoscopic molecular weight in benzene was 745 (calcd 791).

The infrared spectrum of the complex (Nujol) in the region of 4000–600 cm^{-1} was the same as that of the ligand. The Raman spectrum of a concentrated yellow solution in benzene was obtained on a Cary 81 laser Raman with 6328-Å excitation. A weak line at 1487 cm^{-1}, not present in the spectrum of the ligand, was assigned to $\nu(C{=}C)$ of ethylene in the complex.

Proton and phosphorus nmr spectra were determined at ambient temperature (29 ± 1°) using a Varian HA-100 spectrometer at 100 and 40.5 Mc, respectively. Proton spectra were run in 90% C_6D_6–10% tetramethylsilane. Phosphorus-31 spectra were run in toluene, using side bands from P_4O_6 in a concentric capillary to measure chemical shifts. Reported shifts with respect to 85% H_3PO_4 were determined by subtracting 112.5 ppm from the measured shifts. Nmr spectra are depicted in the text.

Optical spectra of benzene solutions were recorded on a Cary 14 spectrophotometer against benzene reference in matched cells. Beer's law was confirmed for solutions of $(C_2H_4)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2$ over a 100-fold concentration range by running spectra at concentrations of 1.98×10^{-2}, 1.98×10^{-3}, and 1.98×10^{-4} M in cells of 0.1–10 mm so that the production of concentration and path length was held constant. The spectrum of the yellow complex (benzene) showed an absorption maximum at 350 mμ (ϵ 4.5×10^3 cm^{-1} M^{-1}) and a shoulder with an inflection at 383 mμ (3.6×10^3) (Figure 3). Equilibrium constants for displacement of ethylene by phosphite ligand were determined by running spectra after additions of neat $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ to a 0.1-mm cell containing 1 ml of 1.98×10^{-2} M $(C_2H_4)NiL_2$. The temperature of the Cary 14 sample compartment during these measurements was 28°.

The stability of the complex to dissociation of ethylene was shown by an experiment in which 0.04 g $(C_2H_4)NiL_2$ in 0.5 ml of toluene was subjected to vacuum for 1.5 hr, during which the solution was evaporated to dryness. The yellow solid, dissolved in C_6D_6, exhibited a proton nmr spectrum identical with that of the starting complex, showing that no C_2H_4 had been removed by this treatment.

Results and Discussion

The proton nmr spectrum of ethylene[bis(tri-*o*-tolyl phosphite)]nickel (abbreviated hereafter $(C_2H_4)NiL_2$) is shown in Figure 1a. Four resonances can be seen

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[1] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

[2] L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, **9**, 2350 (1970).

[3] M. A. McCall and H. W. Coover, British Patent 1,146,074 (1969).

[4] G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **2**, 105 (1963).

[5] E. N. Walsh, *J. Amer. Chem. Soc.*, **81**, 3023 (1959).

[6] The same product can be obtained without adding ethylene to the system, but in much lower yield. The ethylene, in that case, is a product of the decomposition of triethylaluminum.[7]

[7] G. Wilke and G. Herrmann, *Angew. Chem., Int. Ed. Engl.*, **1**, 549 (1962).

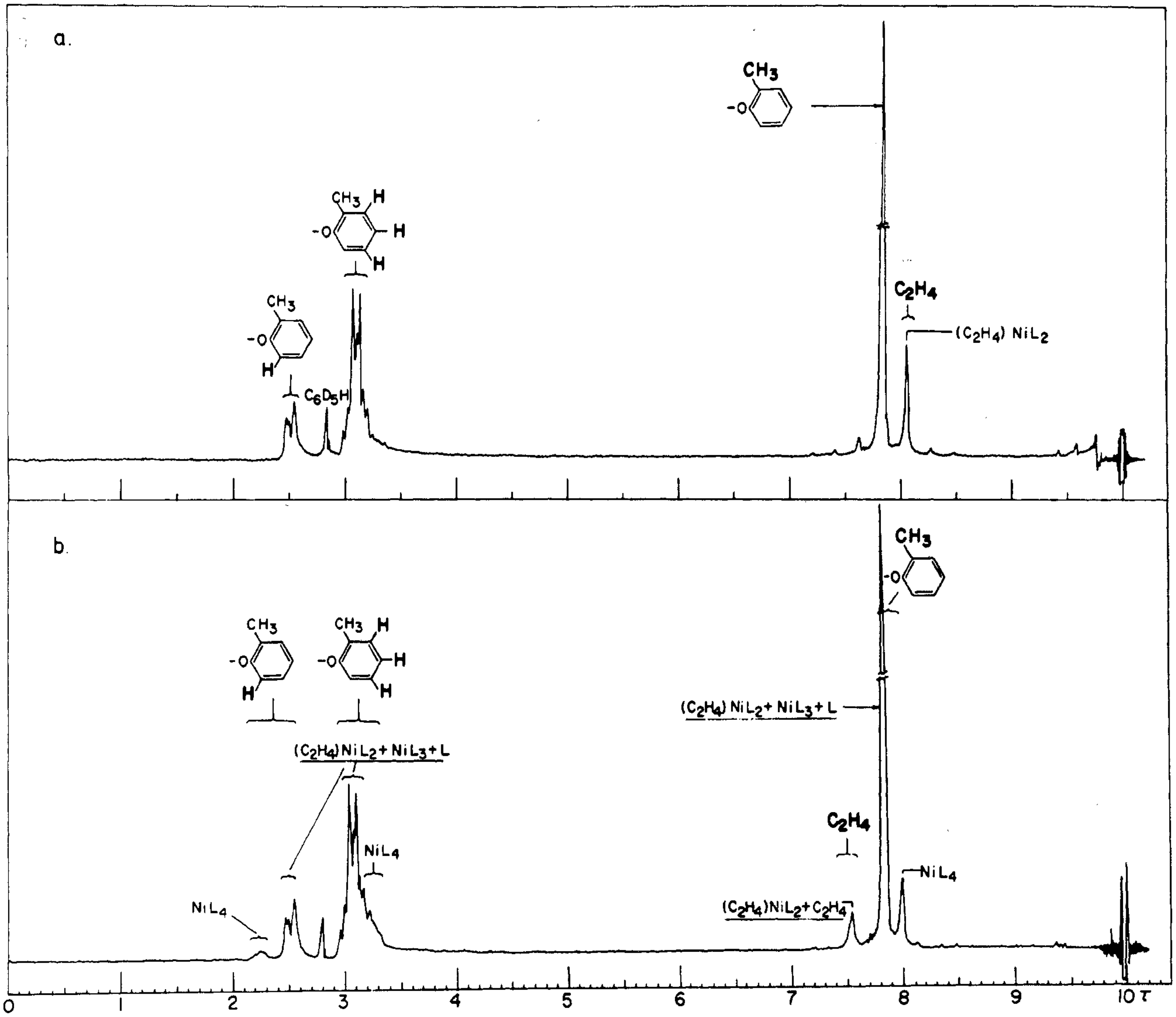

Figure 1.—The 100-Mc proton nmr spectrum of (a) 0.1 mmol of $(C_2H_4)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2$ in 0.4 ml of C_6D_6 solution and (b) the same solution with 0.1 mmol of $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ added. Each resonance indicated by an underlined sum of species is an average caused by rapid exchange.

whose integrated intensities are in the ratio 6:18:18:4. They are assigned to the *o*-H, unresolved *meta* and *para* protons, and *o*-CH_3 of the phosphite ligand, and to complexed C_2H_4, respectively. The assignment of the high-field peak was confirmed by the addition of either C_2H_4 or acrylonitrile to the solution. The addition of C_2H_4 caused the peak at τ 8.06 to move downfield, grow in intensity, and broaden, indicating a rapid exchange of free and complexed ethylene,[8] while acrylonitrile caused the bound C_2H_4 peak at τ 8.06 to be replaced by a new resonance at τ 4.76, the chemical shift of free ethylene.[9-11]

Addition of neat tri-*o*-tolyl phosphite (L) to a solution of $(C_2H_4)NiL_2$ gave proton nmr resonances for two types of phosphite ligands and for one type of ethylene, the latter shifted to low field from the starting position of τ 8.06. A spectrum obtained after addition of 0.1 mmol of L to 0.1 mmol of $(C_2H_4)NiL_2$ in 0.4 ml of solution is shown in Figure 1b. Resonances denoted by an underlined sum of species are due to an average of those species in rapid exchange. Further additions of ligand caused an increase in intensity of resonances assigned to NiL_4 and a further downfield shift of the average ethylene resonance. Proton chemical shifts for these solutions are listed in Table I.

The ^{31}P nmr spectra for a similar experiment in toluene are shown in Figure 2. The ethylene complex alone shows a single sharp resonance at −139.7 ppm (H_3PO_4), which was unaffected by the addition of excess ethylene. When a small amount of ligand was added, the sharp resonance disappeared and was replaced by a broad resonance to higher field. Further additions of ligand caused the broad resonance to move upfield

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[8] A kinetic study of the ethylene exchange based on line shape analysis is currently under way. For equal concentrations of free and bound C_2H_4 the average lifetime in the complex is less than 10^{-4} sec at 28°.

[9] Acrylonitrile forms a stronger complex and quantitatively displaces ethylene. Exchange of bound and free acrylonitrile is also rapid on an nmr time scale. $(CH_2{=}CHCN)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2$ has been reported by Kutepow, *et al.*[10]

[10] (a) W. Reppe, N. von Kutepow, and A. Magin, *Angew. Chem., Int. Ed. Engl.*, **8**, 727 (1969); (b) N. von Kutepow, H. Seibt, and F. Meier, U. S. Patent 3,346,608 (1967).

[11] Assignment of this resonance to C_2H_4 was confirmed by infrared identification of ethylene in the gas phase over a solution of $(C_2H_4)NiL_2$ to which acrylonitrile or oxygen had been added.

TABLE I

PROTON NMR SPECTRA OF L = TRI-*o*-TOLYL PHOSPHITE AND SOME OF ITS Ni(0) COMPLEXES IN C_6D_6 (τ(TMS))

Species	*o*-H	*m*- and *p*-H	*o*-CH_3	C_2H_4
NiL_4[a]	2.26	3.24	8.04	. . .
NiL_3[a]	2.48	3.12	8.04	. . .
$(C_2H_4)NiL_2$	2.56	3.11	7.86	8.06
$(C_2H_3CN)NiL_2$[b]	2.62	3.08	7.90	4.76[b]
L[a]	2.68	3.07	7.89	. . .

[a] Data reproduced from ref 2. [b] Generated in solution by the addition of acrylonitrile to $(C_2H_4)NiL_2$.

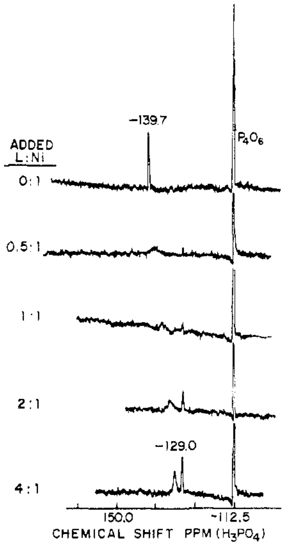

Figure 2.—The 40.5-Mc ^{31}P nmr spectra after additions of $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ to 0.25 *M* $(C_2H_4)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2$ in toluene.

and increase in intensity; at the same time, a sharp peak which did not move grew at −129.0 ppm. Earlier studies[1] showed that −129.0 ppm was the chemical shift of NiL_4 [$L = P(O\text{-}o\text{-}C_6H_4CH_3)_3$].

The nmr spectra are consistent with two equilibria in the system, the first being fast on an nmr time scale and the second slow.[12]

$$L + (C_2H_4)NiL_2 \overset{K_1}{\rightleftharpoons} NiL_3 + C_2H_4 \quad (1)$$

$$L + NiL_3 \overset{K_2}{\rightleftharpoons} NiL_4 \quad (2)$$

The rapidity of the first reaction gives one average ligand spectrum for L, $(C_2H_4)NiL_2$, and NiL_3 in the proton and phosphorus nmr spectra[13] and one average ethylene resonance for C_2H_4 and $(C_2H_4)NiL_2$ in the proton spectrum. The slowness of reaction 2 isolated NiL_4 from the rapid-exchange system. It is interesting to note that in the absence of ethylene, a solution containing L, NiL_3, and NiL_4 showed three separate resonances in the nmr.[2] The addition of even a small amount of C_2H_4, however, averaged the resonances of L and NiL_3, *via* eq 1.

Identical ^1H and ^{31}P spectra could be obtained by the addition of 1 mol of L to a solution of $(C_2H_4)NiL_2$ as by addition of 1 mol of C_2H_4 to a solution of NiL_3, a further confirmation of the composition of the complexes and the nature of the reactions.

The interpretation was confirmed and values for K_1 and K_2 were determined in spectrophotometric experiments in which neat L was added to a deep yellow benzene solution of $(C_2H_4)NiL_2$. The color changed rapidly as ligand was mixed in, successive additions causing the solution to become orange and finally light yellow. A series of selected spectra are shown in Figure 3. The increasing and subsequent decreasing absorption in the 425–525-mμ region gave the transitory orange color. This is the region where NiL_3 absorbs most strongly[14] relative to $(C_2H_4)NiL_2$. As L is added, NiL_3 forms *via* eq 1 and then diasppears as the nickel is forced over to NiL_4 by excess L *via* (2).

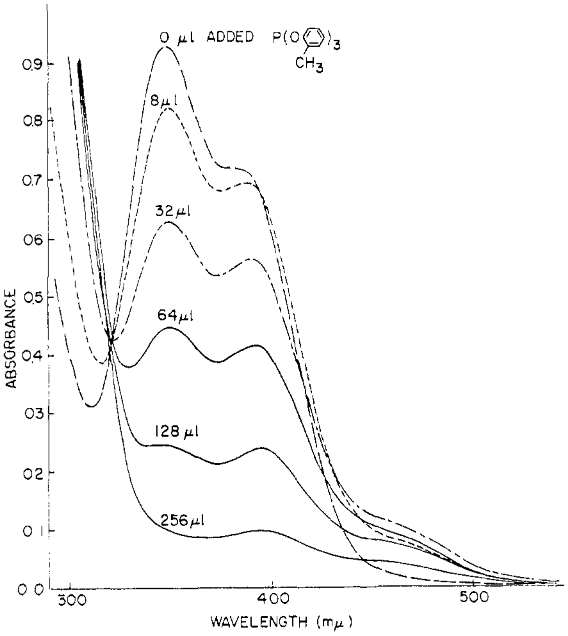

Figure 3.—Optical spectra of 1 ml of 1.98 × 10^{-2} *M* $(C_2H_4)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2$ in benzene with additions of neat $P(O\text{-}o\text{-}C_6H_4CH_3)_3$. The temperature was 28° and the cell length 0.1 mm. A 0.1-mm cell of benzene was used in the reference beam.

Absorbance data at three wavelengths were used to calculate the concentrations of all species in solution as shown in Table II. The wavelength where NiL_3 and NiL_4 have equal extinction coefficients[2] (0.75 × 10^3 cm^{-1} M^{-1}) is 328 mμ so that the absorbance at 328 mμ, *A*(328), was used to determine the conversion of $(C_2H_4)NiL_2$ to NiL_3 and NiL_4. At 386 mμ $(C_2H_4)NiL_2$ and NiL_3 have the same extinction coefficient (3.64 × 10^3), so that *A*(386) was used to determine the conversion of $(C_2H_4)NiL_2$ and NiL_3 to NiL_4. *A*(460) was used to determine [NiL_3] since it is the main absorbing species at this wavelength (ϵ 3.15 × 10^3).[15]

The resulting equilibrium constants (Table II) show good precision over a wide range of concentrations of the reacting species. The value of $K_1' = 0.012 \pm$

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(12) A value of 15 ± 2 M^{-1} for K_2 at 28° was determined earlier.[2]

(13) The average ligand resonance is broad in the ^{31}P spectrum but not in the ^1H spectrum. This is because the chemical shift differences between species are small in the proton spectrum compared to the exchange frequencies. This condition is not met in the ^{31}P spectrum, where the chemical shift differences are much larger.

(14) The optical spectrum of NiL_3 was given in ref 2.

(15) The extinction coefficient at 460 mμ was determined from the spectrum of NiL_3 reported earlier.[2] A small correction was made for absorption of $(C_2H_4)NiL_2$ at 460 mμ (ϵ 0.08 × 10^3).

TABLE II

ADDITION OF TRI-*o*-TOLYL PHOSPHITE TO 1.0 ML OF 1.98×10^{-2} *M* $(C_2H_4)NiL_2$ IN BENZENE AT 28° (0.1-MM CELL)

Added L,[a] μl	10^2[L],[b] *M*	*A*(328)[c]	$10^2[(C_2H_4)NiL_2]$,[d] *M*	*A*(460)[c]	$10^2[NiL_3]$,[e] *M*	$10^2 \times [C_2H_4]_{total}$,[f] *M*	*A*(380)[c]	$10^2[NiL_4]$,[g] *M*	K_1'[h]	K_2,[i] M^{-1}
0	0	0.575	1.98	0.106	0.00	0.00	0.715	0.00	...	...
2	0.52	0.555	1.89	0.052	0.12	0.09	0.715	0.00	0.0111	...
4	1.08	0.545	1.84	0.064	0.16	0.15	0.71	0.014	0.0121	8
8	2.18	0.53	1.77	0.080	0.21	0.20	0.69	0.07	0.0109	15
16	4.37	0.495	1.60	0.093	0.26	0.35	0.645	0.19	0.0130	17
32	8.57	0.455	1.42	0.107	0.31	0.50	0.555	0.44	0.0127	17
64	17.2	0.385	1.09	0.091	0.26	0.77	0.405	0.85	0.0107	19
128	33.3	0.29	0.65	0.070	0.21	1.11	0.225	1.36	0.0108	19
256	63.9	0.19	0.186	0.040	0.12	1.40	0.09	1.74	0.0141	23
∞		0.15	0.00	0.00	0.00	1.98	0.00	1.98	...	...
									0.012 ± 0.001	17 ± 3

[a] The molar volume of L is 314 ml/mol. [b] $[L] = \{(\mu l \text{ of } L/314) - (1 + v)[NiL_3] - 2(1 + v)[NiL_4]\}/(1 + v)\ M$. [c] Absorbances at wavelengths indicated. [d] $[(C_2H_4)NiL_2] = [(A(328) - 0.15)/0.425](1.98 \times 10^{-2})\ M$. [e] $[NiL_3] = (A(460) - A'(460))/31\ M$, where $A'(460) = (0.016/1.98 \times 10^{-2})[(C_2H_4)NiL_2]$. [f] $[C_2H_4]_{total} = \{1.98 \times 10^{-2} - (1 + v)[(C_2H_4)NiL_2]\}/(1 + v)\ M$. [g] $[NiL_4] = [(0.715 - A(386))/0.715](1.98 \times 10^{-2})\ M$. [h] $K_1' = [NiL_3][C_2H_4]_{total}/[L][(C_2H_4)NiL_2]$. [i] $K_2 = [NiL_4]/[L][NiL_3]\ M^{-1}$.

0.001 was calculated with the assumption that all the ethylene liberated from $(C_2H_4)NiL_2$ was present in solution as free C_2H_4. Because of the further equilibration of ethylene between liquid and vapor phases, the true equilibrium constant K_1 is smaller by the fraction of C_2H_4 remaining in solution: $K_1 = K_1'[C_2H_4]/[C_2H_4]_{total}$. Assuming that the fraction was 0.57,[16] a value of $K_1 = 6.8 \pm 0.5 \times 10^{-3}$ was calculated. This small value of K_1 indicates that C_2H_4 is preferred to L in bonding to NiL_2 by a factor of about 150.

The value of $K_2 = 17 \pm 3\ M^{-1}$ is in excellent agreement with the value of $15 \pm 2\ M^{-1}$ reported earlier.[2]

The solutions did not contain a detectable concentration of two-coordinate species such as NiL_2. Absence of dissociation is best shown by the adherence of the $(C_2H_4)NiL_2$ solutions to Beer's law.[17] Lack of dissociation of ethylene is also shown by the quantitative recovery of the complex after a toluene solution was exposed to vacuum for a long period.

Both three- and four-coordinate phosphite complexes were present in solutions of $(C_2H_4)NiL_2$ to which L has been added. We also considered the possibility of four-coordinate complexes containing ethylene, such as $(C_2H_4)_2NiL_2$[18] or $(C_2H_4)NiL_3$.[19] The fact that the ^{31}P spectrum of $(C_2H_4)NiL_2$ was unaffected by the addition of C_2H_4 is strong evidence against the formation of $(C_2H_4)_2NiL_2$ at these concentrations and temperatures. The complex $(C_2H_4)NiL_3$ is regarded as unlikely in view of the constancy of the calculated equilibrium constants in Table II.

That the system is completely described by the species in eq 1 and 2 was further shown by fitting the electronic spectra shown in Figure 2. Electronic spectra from 300 to 600 mμ were represented for each of the chromophores, NiL_3, $(C_2H_4)NiL_2$, and NiL_4, by a sum of gaussian terms. Composite spectra were calculated on a computer using the individual spectra and the concentrations of chormophores from Table II and plotted with a Calcomp plotter. The agreement between calculated and observed spectra was excellent.

Our data do not permit a detailed description of the structure of $(C_2H_4)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2$,[20] but it is probably quite similar to that reported[21] for $(C_2H_4)Ni[P(C_6H_5)_3]_2$, in which the olefin C to Ni distances are equal and the ethylene is nearly in the PNiP plane. The shift to high field (3.3 ppm) of the olefin protons in the nmr and the decrease in the carbon–carbon double bond stretching frequency are both consistent with a π-bonded olefin structure. Our observed $\Delta\nu(C{=}C)$ of 136 cm^{-1} [22] can be compared with the values in the range of 78–133 cm^{-1} reported for a series of ethylene complexes of Pt(II).[23]

The importance of metal to olefin π-electron donation in the olefin complexes is indicated by the quantitative displacement of ethylene by acrylonitrile. In this case, the strength of the metal–olefin bond was greatly enhanced by the replacement of one H of C_2H_4 by the more electronegative CN. The greater stability of the acrylonitrile complex is clearly an electronic effect since ethylene, the smaller olefin of the two, should be sterically preferred.

Acknowledgments.—The authors are indebted to Dr. P. Meakin for assistance in reproducing the electronic spectra by computer and in determining the lifetime for ethylene exchange.

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(16) The fraction of C_2H_4 in solution was determined from the fact that the liquid volume in the cell was 1.0 ml and the vapor volume 2.5 $cm.^3$ The solubility of ethylene in benzene at 28° was taken to be 3.3 cm^3 per cm^3: A. Seidell, "Solubilities of Organic Compounds," Vol. II, 3rd ed, Van Nostrand, New York, N. Y., p 96.

(17) Assuming that a 10% dissociation either of C_2H_4 to give NiL_2 or of L to give $(C_2H_4)NiL$ would have been detectable in the 1.98×10^{-4} *M* solution, an npper limit of about 2×10^{-6} *M* can be set on such dissociation constants.

(18) A related complex, $(CH_2{=}CHCN)_2Ni(P(C_6H_5)_3)_2$, was reported by G. N. Schrauzer, *J. Amer. Chem. Soc.*, **82**, 1008 (1960).

(19) $(C_2F_4)Ni(P(C_6H_5)_3)_3$ was reported by G. W. Parshall and F. N. Jones, *ibid.*, **87**, 5356 (1965).

(20) An X-ray study of the crystal structure of the related $(C_2H_3CN)Ni[P(O\text{-}o\text{-}C_6H_4CH_3)_3]_2$ is currently under way in these laboratories.

(21) (a) C. D. Cook, C. H. Koö, S. C. Nyberg, and M. T. Shiomi, *Chem. Commun.*, 426 (1967); (b) W. Dreissig and H. Dietrich, *Acta Crystallogr., Sect. B*, **24**, 108 (1968).

(22) The $\nu(C{=}C)$ of free C_2H_4 in the gas phase was taken as 1623 cm^{-1} from D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **13**, 69 (1958).

(23) Infrared data for a series of *trans*-dichloroethylene(4-substituted pyridine N-oxide)platinum(II) complexes were reported by S. I. Shupack and M. Orchin, *J. Amer. Chem. Soc.*, **85**, 902 (1963).