plete conversion to ethylene complex at 0.17 or 0.34 atm of C_2H_4. Dimer cleavage was first order in C_2H_4 pressure and first order in dimer with $k_4 = 45 \pm 4$ min^{-1} atm^{-1}. At steady-state conditions under 0.64 atm of H_2, spectra showed that a substantial fraction of the Rh remained as ethylene complex. There was a small but measurable rate of pressure drop due to ethylene hydrogenation.

Addition of increasing pressure of C_2H_4 to toluene solutions of 10^{-3} *M* RhCl[P(*p*-tolyl)$_3$]$_3$ and 0.01 *M* P(*p*-tolyl)$_3$ gave rapid equilibration[49] with ~80% conversion of $RhClL_3$ to ethylene complex with 0.34 atm of C_2H_4. Steady-state conditions were rapidly achieved after H_2 addition. Spectra showed a predominance of H_2RhClL_3 but some $(C_2H_4)RhClL_2$ was still present. The rate of ethylene hydrogenation was less when most of the Rh was initially present as monomer than when dimer was used.

The much slower hydrogenation of ethylene compared to cyclohexene (*cf.* expt no. 2 Table VIII and expt no. 3 Table VII) indicates that the "hydride route" involving reaction of H_2 (with dimer in this case) prior to olefin coordination must be much faster than the "unsaturate route" involving oxidative addition of H_2 to a preformed (olefin)$RhClL_2$ complex, in agreement with Wilkinson's original postulate.[2]

While we do not claim to have a complete mechanism for homogeneous hydrogenation by Wilkinson's catalyst, we hope that our studies have brought that goal closer, particularly with regard to characterizing the species present in solution under hydrogenation conditions. Our work emphasizes the value of breaking complex reaction sequences into simpler steps and of monitoring steady-state concentrations of species during homogeneous catalytic reactions.

Acknowledgments. We are indebted to Professor Jack Halpern of the University of Chicago for communication of results[8,44] prior to publication and for helpful discussions on the mechanism of H_2 reaction with solutions of $RhClL_3$. Special thanks are due to Mr. Martin A. Cushing for preparing many of the complexes, to Mr. John R. Kraus for assistance in constructing the gas reaction cells, and to Messrs. D. Wesley Reutter and George Watunya for technical assistance.

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[49] The half-life on adding the first 0.02 atm of C_2H_4 was ~0.6 min.

Olefin Complexes of Nickel(0). II. Preparation and Properties of (Olefin)bis(tri-*o*-tolyl phosphite)nickel Complexes

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Abstract: The preparation and properties of (olefin)NiL_2 complexes [L = P(O-*o*-tolyl)$_3$] are described where the olefin is maleic anhydride, acrylonitrile, styrene, propylene, 1,5-cyclooctadiene, and tetrafluoroethylene. In the case of tetrafluoroethylene, the complex $(C_2F_4)NiL_2$ was identified in solution but the compound actually isolated was cyclo-(C_4F_8)Ni[P(O-*o*-tolyl)$_3$]$_2$. Formation of $(C_2F_4)NiL_2$ from NiL_3 occurs *via* an associative reaction with $k_2 = 0.25 \pm 0.025$ sec^{-1} M^{-1} in benzene at 25°. $\Delta H^{\ddagger} = 6.5 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -40 \pm 3$ eu. Proton nmr, vibrational, and structural data on these and other transition metal olefin complexes are correlated with the ionization potential of the metal and the degree of metal to olefin π^* back bonding.

Olefin complexes of the transition metals are essential intermediates in a variety of homogeneous catalytic processes and have been studied with increasing interest in recent years. Several review articles have appeared,[1,2] but there is a shortage of quantitative data.[3]

Our work was initiated to understand the factors which determine the kinetics and thermodynamics of formation of olefin complexes of zerovalent nickel. Equilibrium studies have since been reported for a series of olefin(dipyridyl)nickel complexes.[4] The kinetics and equilibria of reactions of methyl methacrylate and styrene with Ni[P(OC$_6$H$_5$)$_3$]$_4$ have been investigated.[5] We have reported the results of studies on ethylene–(triarylphosphine)[6a] and ethylene–(triethylphosphine)[6b] complexes of zerovalent Ni, Pd, and Pt.

In part I[7a] we described the preparation and properties of (C_2H_4)Ni[P(O-*o*-tolyl)$_3$]$_2$. We now report the results of studies on the preparation and characterization in solution of related (olefin)Ni[P(O-*o*-tolyl)$_3$]$_2$ complexes where olefin[7b] is maleic anhydride, acrylonitrile, styrene, propylene, 1,5-cyclooctadiene, and tetrafluoroethylene. Part III[8] will describe spectro-

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[7] (a) W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, **9**, 2354 (1970). (b) Abbreviations for olefins in this paper are: MA, maleic anhydride; ACN, acrylonitrile; S, styrene; and COD, 1,5-cyclooctadiene.

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photometric determination of formation constants for these and a wide variety of other olefins in reactions 1 and 2 where L = P(O-*o*-tolyl)$_3$.

$$\text{olefin} + \text{NiL}_3 \xrightleftharpoons{K_1} (\text{olefin})\text{NiL}_2 + \text{L} \quad (1)$$

$$\text{olefin} + (\text{olefin})\text{NiL}_2 \xrightleftharpoons{K_2} (\text{olefin})_2\text{NiL}_2 \quad (2)$$

Experimental Section

Because the compounds involved in this study are sensitive to oxygen, syntheses were carried out and solutions handled under nitrogen. Melting points were determined in sealed evacuated capillary tubes and are uncorrected.

Infrared spectra in CH_2Cl_2 were determined with a Perkin-Elmer 221 spectrometer using 0.1-mm NaCl cells. Spectra were calibrated with CO gas (2143 cm^{-1}) and reported frequencies are accurate to +3 cm^{-1}.

Proton nmr spectra were determined at ambient temperature (29 ± 1°) at 100 MHz in 90% C_6D_6–10% tetramethylsilane using a Varian HA-100 spectrometer and at 220 MHz in C_6D_6 or CD_2Cl_2 using a Varian HR-220.

Fluorine-19 spectra were measured at ambient temperature on a Varian A56–60 at 56.4 MHz. C_6D_6 was used as a solvent and external $CFCl_3$ as a chemical shift reference. Phosphorus-31 spectra at 36.43 MHz were determined on a Bruker HFX-90 spectrometer using toluene or CH_2Cl_2 solutions in 10-mm spinning tubes. A concentric capillary of Freon 114B2 ($CBrF_2CBrF_2$) was used for a ^{19}F lock and chemical shift reference. Chemical shifts are reported with respect to 85% H_3PO_4 with an accuracy of ±0.3 ppm.

Optical spectra of benzene solutions were recorded in the range 600–290 mμ with a Cary 14 spectrophotometer. Special precautions were required to avoid oxygen in these dilute solutions.[6a] Thermostating was provided by a Forma constant temperature bath, with water circulating through the walls of the spectrometer cell compartment. Temperatures in the center of the cell were measured with a 36 gauge copper constantan thermocouple to ±0.5°. Beer's law for the olefin complexes was checked over a 100-fold concentration range, by running spectra of $\sim 2 \times 10^{-2}$, 2×10^{-3}, and 2×10^{-4} *M* complex in serum capped cells of 0.1-, 1.0-, and 10-mm path length.

(Maleic anhydride)[bis(tri-*o*-tolyl phosphite)]nickel. (MA)Ni-[P(O-*o*-tolyl)$_3$]$_2$ was prepared by the reaction of maleic anhydride with (C_2H_4)Ni[P(O-*o*-tolyl)$_3$]$_2$.[7] To a solution of 8.0 g of the ethylene complex in 10 ml of benzene was added 1.0 g of maleic anhydride. The benzene was removed under vacuum and the resulting solid crystallized from benzene–methanol to give the product as yellow orange crystals: 8.1 g (93%); uv (C_6H_6) max 295 mμ (ϵ 13.1 × 10^3), sh 345 (4.8 × 10^3); ir (CH_2Cl_2) 1805, 1733 cm^{-1} (C=O). *Anal.* Calcd for $C_{46}H_{44}NiO_9P_2$: C, 64.1; H, 5.2; Ni, 6.8; P, 7.2. Found: C, 63.9; H, 5.3; Ni, 6.9; P, 8.0.

Acrylonitrile[bis(tri-*o*-tolyl phosphite)]nickel.[9] (ACN)Ni[P(O-*o*-tolyl)$_3$]$_2$ was prepared by the reaction of the phosphite with bis-(acrylonitrile)nickel.[10] To 0.50 g of Ni(ACN)$_2$ (3 mmol) were added 3.17 g of P(O-*o*-tolyl)$_3$ (9 mmol) and 10 ml of ACN. On stirring, a light yellow solid precipitated. Chilling, filtering, and washing with chilled CH_3OH gave a light yellow powder: 2.34 g (76%); dec 153–155°; uv (C_6H_6) max 296 mμ (ϵ 4.8 × 10^3), max 326 (4.6 × 10^3), sh 362 (3.7 × 10^3); ir (CH_2Cl_2) 2194 cm^{-1} (C≡N). *Anal.* Calcd for $C_{45}H_{45}NNiO_6P_2$: C, 66.2; H, 5.6; N, 1.7; Ni, 7.2; P, 7.6. Found: C, 66.1; H, 5.5; N, 1.1; Ni, 7.1; P, 7.6.

Styrene[bis(tri-*o*-tolyl phosphite)]nickel. (S)Ni[P(O-*o*-tolyl)$_3$]$_2$ was prepared from (C_2H_4)Ni[P(O-*o*-tolyl)$_3$]$_2$. The ethylene complex (4 g) was dissolved in 4 ml of styrene. Ethylene and excess styrene were removed under vacuum. The remaining oil was dissolved in 40 ml of pentane and 30 ml of CH_3OH was added with sitrring. Stirring was continued for several hours until crystals formed. Filtration and drying gave the product as bright yellow crystals: 3.1 g (70%); dec 90–92°; uv (C_6H_6) max 312 mμ (ϵ 10.5 × 10^3), sh 390 (3.9 × 10^3). *Anal.* Calcd for $C_{50}H_{50}NiO_6P_2$: C, 69.1; H, 5.8; Ni, 6.8; P, 7.2. Found: C, 67.2; H, 5.6; Ni, 6.9; P, 7.1.

Propylene[bis(tri-*o*-tolyl phosphite)]nickel. Propylene was bubbled through 1.30 g of (C_2H_4)Ni[P(O-*o*-tolyl)$_3$]$_2$ in 10 ml of benzene for 2 hr. The solution was filtered and the solvent partially removed under suction, and 17 ml of CH_3OH was added with chilling. Filtering and washing with chilled CH_3OH gave the product as yellow crystals: 1.34 g (100%); dec 100–104°.

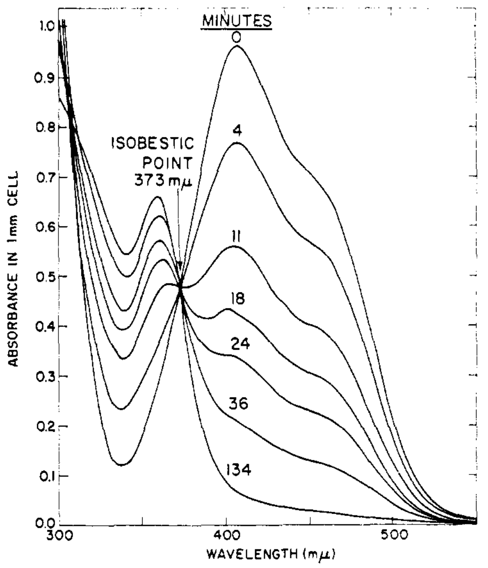

Figure 1. Spectra obtained at various times after injecting 0.2 cc of C_2F_4 gas into 2 cc of 1.89×10^{-3} *M* Ni[P(O-*o*-tolyl)$_3$]$_3$ in benzene at 25°.

The complex decomposed slowly on standing under nitrogen and more rapidly in solution. It was not analyzed but characterized by its proton nmr spectrum (Table III).

1,5-Cyclooctadiene[bis(tri-*o*-tolyl phosphite)]nickel. (COD)Ni[P-(O-*o*-tolyl)$_3$]$_2$ was prepared by the reaction of 1,5-cyclooctadiene with the ethylene complex. (C_2H_4)Ni[P(O-*o*-tolyl)$_3$]$_2$ (3 g) was dissolved in 5.0 ml of 1,5-cyclooctadiene. The ethylene and excess 1,5-cyclooctadiene were pumped off under full vacuum (1.0 mm) for 4 hr. The complex remained behind. As first prepared, the sample was a viscous pale yellow oil. On standing for several weeks it solidified to a light yellow solid, dec 104–108°. *Anal.* Calcd for $C_{50}H_{54}NiO_6P_2$: C, 68.9; H, 6.2; Ni, 6.7; P, 7.1. Found C, 68.1; H, 6.0; Ni, 7.0; P, 7.4.

Octafluoronickelacyclopentane Bis(tri-*o*-tolyl phosphite). A benzene solution (50 ml) of tris(tri-*o*-tolyl phosphite)nickel(0) (5.0 g) was allowed to react with an excess of C_2F_4 overnight. The light yellow solution was then vacuum evaporated to a heavy oil. This oil was scrubbed with two 5-ml portions of methanol to give the crystalline complex 0.9 g (25%). The complex is soluble in methanol: uv (C_6H_6) max 315 mμ (ϵ 2.7 × 10^3), broad max 373 (0.53 × 10^3). *Anal.* Calcd for $C_{46}H_{42}F_8NiO_6P_2$: F, 15.8; Ni, 6.1; P, 6.5. Found: F, 13.1; Ni, 5.6; P, 6.5.

Kinetics of the Reaction of C_2F_4 with Ni[P(O-*o*-tolyl)$_3$]$_3$. The kinetics of the reaction of tetrafluoroethylene with Ni[P(O-*o*-tolyl)$_3$]$_3$[11] in benzene was studied spectrophotometrically by following the loss of absorbance at 407 mμ after injecting C_2F_4 gas into the 1.0-mm serum capped cell. The cell had been allowed to stand in the thermostated Cary 14 sample compartment for at least 15 min prior to the run in order to reach the reaction temperature (15, 25, or 35°). After injection of the gas, the cell was briskly shaken for ~10 sec to ensure equilibration of C_2F_4 between the liquid and vapor phases.

In several of the slower runs at low C_2F_4 concentration, repeated sweeps of the spectrum showed a well-defined isosbestic point at 373 mμ (Figure 1), indicating that NiL$_3$ and (C_2F_4)NiL$_2$ were the only chromophoric species detected. Plots of log [$A_0(407) - A_s(407)$] against time were linear over 4-5 half-lives. Values of k_{obsd} are given in Table I. The apparent second-order rate constant k_2' was not corrected for the fraction of C_2F_4 in solution. This correction was applied in Table II using Cramer's data[12] for the solubility of C_2F_4 in toluene at 0 and 25°, assuming the same solubilities in benzene as in toluene and log (solubility) = constant/*T*.

Results

Complexes of (olefin)NiL$_2$ where L is P(O-*o*-tolyl)$_3$

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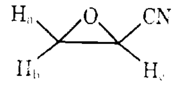
[12] R. Cramer, *J. Amer. Chem. Soc.*, **89**, 4621 (1967).

Table I. Kinetics of the Reaction of C_2F_4 with $\sim 2 \times 10^{-3}$ *M* Ni[P(O-*o*-tolyl)$_3$]$_3$ in Benzene[a]

Temp, °C	cc of C_2F_4	$10^2[C_2F_4]_{total}$[b]	$10^3 k_{obsd}$, sec^{-1}	k_2',[c] sec^{-1} M^{-1}
35	1	2.05	4.54	0.222
	1	2.05	4.61	0.225
	0.5	1.025	2.75	0.268
				0.24 ± 0.02
25	2	4.1	5.84	0.142
	2	4.1	5.58	0.136
	1	2.05	3.30	0.161
	1	2.05	3.42	0.167
	0.5	1.025	1.73	0.169
	0.2	0.41	0.816	0.199
				0.162 ± 0.016
15	2	4.1	4.80	0.117
	2	4.1	4.53	0.110
	1	2.05	2.53	0.123
	1	2.05	2.53	0.123
	0.5	1.025	1.24	0.121
				0.119 ± 0.004

[a] 407 mμ, 1-mm cell. [b] $[C_2F_4]_{total}$ = cc of $C_2F_4 \times 2.05 \times 10^{-2}$ assuming an ideal gas with 41 μmol/cc at 25° and 1 atm. [c] $k_2' = k_{obsd}/[C_2F_4]_{total}$.



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Compound	τ_a	τ_b	τ_c	J_{ac}	J_{bc}	J_{ab}
$CH_2{=}CHCN$	4.71	5.08	5.36	17	12	2
(ACN)NiL_2	8.72	8.83	8.31	13	10	3
1	6.90	7.11	6.52	2.6	4.1	5.5

mean coordination chemical shift Δτ is +3.6 ppm, indicating carbon–carbon double bond coordination. Coordination to the nitrile nitrogen is expected to give only very small changes in chemical shifts and coupling constants for the acrylonitrile protons.[14] Olefinic coordination in the crystal is indicated by an X-ray study[15] and in solution by ^{31}P nmr, infrared, and electronic spectra. This is the first case where a complete proton nmr assignment has been made for an olefin-bonded acrylonitrile complex.[16]

The vinylic protons of (styrene)Ni[P(O-*o*-tolyl)$_3$]$_2$ show a mean Δτ of +1.5 ppm. The proton at τ 3.60 is at low field for an olefin complex; H_c of free styrene is at 3.39.

Because of decomposition in solution, a well-resolved spectrum was not obtained for $(C_3H_6)NiL_2$. The only resonance assignable to the propylene was a broad unresolved multiplet at τ 8.8. Integration indicated a 1:2 ratio of C_3H_6–L if all six propylene protons were in this band. Addition of excess acrylonitrile eliminated the multiplet and gave sharp resonances characteristic of free propylene; there was no evidence for free ethylene in the spectrum.

Table II. Data for Calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the Reaction of C_2F_4 with Ni[P(O-*o*-tolyl)$_3$]$_3$

Temp, °C	$1/T$, $°K^{-1}$	k_2', sec^{-1} M^{-1}	Sol of C_2F_4,[a] cc/cc	f[b]	k_2,[c] sec^{-1} M^{-1}
35	3.25×10^{-3}	0.24 ± 0.02	1.27	0.620	0.39 ± 0.03
25	3.36×10^{-3}	0.162 ± 0.016	1.43	0.648	0.25 ± 0.025
15	3.47×10^{-3}	0.119 ± 0.004	1.63	0.677	0.176 ± 0.006

[a] Taken from a plot of log (solubility) *vs.* $1/T$ with solubility data in toluene from ref 12. [b] $f = 2 \times sol/(2 \times sol + 1.56)$ represents the initial fraction of C_2F_4 in solution. [c] $k_2 = k_2'/f$.

can be conveniently prepared in most cases by displacement of C_2H_4 from the ethylene complex. The acrylonitrile complex can also be prepared from bis(acrylonitrile)nickel. With the exception of the propylene complex, the compounds are stable in an inert atmosphere. The attempted isolation of $(C_2F_4)NiL_2$ yielded a complex containing two C_2F_4 units and a nickel atom in a five-membered ring.

Proton nmr data for the complexes are given in Table III. The olefin complexes have the correct ratios of integrated areas of olefin relative to phosphite ligand protons for the composition (olefin)NiL_2. This is the best way to establish the stoichiometry of these compounds since the elemental analyses for C, H, Ni, and P are insensitive to the number of olefins present.

The maleic anhydride (MA) complex shows the vinylic protons shifted upfield by +2.5 ppm from free MA at 4.50 in C_6D_6. This was the only compound with resolved P–H coupling. The triplet pattern (J_{PH} = 3 Hz) is consistent with coupling of the protons to two equivalent phosphorus nuclei.

We assigned the olefinic protons of (ACN)Ni[P(O-*o*-tolyl)$_3$]$_2$, in CH_2Cl_2 solution, at 220 MHz. For comparison, data are also given for free ACN (in C_6D_6) and for glycidonitrile[13] (**1**), a model for a three-membered ring. The coupling constants in the nickel complex are more similar to those in free ACN. The

In the chelated COD complex the vinylic protons shift only +0.6 ppm from the free COD value of τ 4.50. The methylene protons shift *downfield* on coordination from 7.80 to 7.60.

The compound isolated in low yield from the reaction of tetrafluoroethylene and Ni[P(O-*o*-tolyl)$_3$]$_3$ has a proton nmr spectrum showing coordinated tri-*o*-tolyl phosphite. The ^{19}F spectrum shows two resonances in a 1:1 intensity ratio. The lower one at 97.4 ppm ($CFCl_3$), split into a triplet by coupling with two phosphorus nuclei (J_{PF} = 40 ± 1 Hz), is assigned to the α-fluorines and the upper one at 137.6 to the β-fluorines of **2**. Similar chemical shifts and coupling constants

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(15) L. J. Guggenberger, *Inorg. Chem.*, **12**, 499 (1973).

(16) Incomplete proton nmr data have been reported previously for the olefin complexes (ACN)$_3$W(CO)$_3$,[14] (ACN)Fe(CO)$_4$,[17] (ACN)-(π-C_5H_5)Mn(CO)$_2$,[18] and (ACN)Pt[(C_6H_5)$_3$]$_2$.[19]

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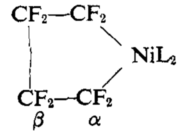
(19) S. Cenini, R. Ugo, F. Bonati, and G. L. Monica, *J. Chem. Soc. A*, 409 (1971).

Table III. 100-MHz Proton Nmr Data[a] on Isolated (Olefin)NiL_2 Complexes[i] with L = P(O-*o*-tolyl)$_3$

	o-H[b]	*m*- and *p*-H[c]	-CH_3	Olefin
L[f]	2.68	3.07	7.89	
(MA)NiL_2	2.63	3.11	7.89	7.08 t, $J_{PH} = 3$
(ACN)NiL_2	2.56	3.13	7.83	~8.7[c]
(C_2H_4)NiL_2[g]	2.56	3.11	7.86	8.06 s
(S)NiL_2[e]	2.59	3.08	7.88	3.60, 5.92,[d] 7.5
(C_3H_6)NiL_2	2.55	3.10	7.82	~8.8[c]
(COD)NiL_2	2.50	3.14	7.89	5.10 d ($J = 11$), 7.60
(C_4F_8)NiL_2	2.42	3.15	7.94	+97.4 t ($J_{PF} = 40$), +137.6 s[h]
NiL_3[f]	2.48	3.12	8.04	
NiL_4[f]	2.26	3.24	8.04	

[a] Chemical shifts in C_6D_6 with respect to internal TMS at τ 10. [b] Appeared as a doublet with $J(o\text{-}m) \sim 8$ Hz. [c] Appeared as a complex unresolved multiplet at 100 MHz. [d] Triplet of triplets with $J = 11$ and 3 Hz. [e] The styrene aromatic resonances were obscured by L. [f] Data from ref 11. [g] Data from ref 7a. [h] ^{19}F nmr data at 56.4 MHz with respect to external $CFCl_3$. [i] Abbreviations: MA, maleic anhydride; ACN, acrylonitrile; S, styrene; COD, 1,5-cyclooctadiene; s, singlet; d, doublet; t, triplet.



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have been reported for analogous nickel complexes with other ligands L.[20]

The ^{31}P nmr spectrum of (ACN)NiL_2 in CH_2Cl_2 showed a single resonance at −139.4 ppm, similar to −139.7 observed for (C_2H_4)NiL_2 in toluene,[7a] and suggesting a similar mode of binding. The resonance of (COD)NiL_2 in toluene at −140.1 ppm indicates that the ^{31}P chemical shift in these olefin complexes is not very sensitive to structural modifications in the olefin.

Infrared spectra of the (olefin)NiL_2 complexes were generally similar to that of free P(O-*o*-tolyl)$_3$. The maleic anhydride and acrylonitrile complexes showed strong bands due to ν_{CO} and ν_{CN} which were considerably reduced in frequency (40 and 44 cm^{-1} for the two ν_{CO} bands of MA and 33 cm^{-1} for the ν_{CO} of ACN) from the values in the free olefins. The absence of bands due to free MA or ACN in CH_2Cl_2 solutions of the complexes indicates that olefin dissociation as shown in eq 3 does not occur to a detectable extent.

$$\text{(olefin)NiL}_2 \overset{K_3}{\rightleftharpoons} \text{olefin} + \text{NiL}_2 \qquad (3)$$

The 1,5-cyclooctadiene complex was shown to contain chelating COD by its infrared spectrum. Free COD in CH_2Cl_2 shows a sharp band at 1655 cm^{-1} (ϵ 27 cm^{-1} M^{-1}) assigned to $\nu_{C=C}$. A solution of 0.7 *M* (COD)NiL_2 showed only a trace of a band at 1655 cm^{-1}. It is concluded that COD is principally bonded as a chelate, since a complex with one free double bond should have given an easily detected band at ~1655 cm^{-1}.

The monodentate olefin complexes of the type (olefin)NiL_2 generally show two electronic transitions in the region of 290–600 mμ, a weaker longer wavelength band appearing as a shoulder and a stronger, shorter wavelength band appearing as an absorption maximum (Figure 2). The wavelength of the lowest energy electronic transition becomes shorter as the electron-withdrawing character of the olefin increases in the series S < C_2H_4 < ACN < MA. Increasing electron withdrawal from nickel in the series is indicated by increasing Ni 2p$^{3/2}$ binding energies in the ESCA spectra.[21]

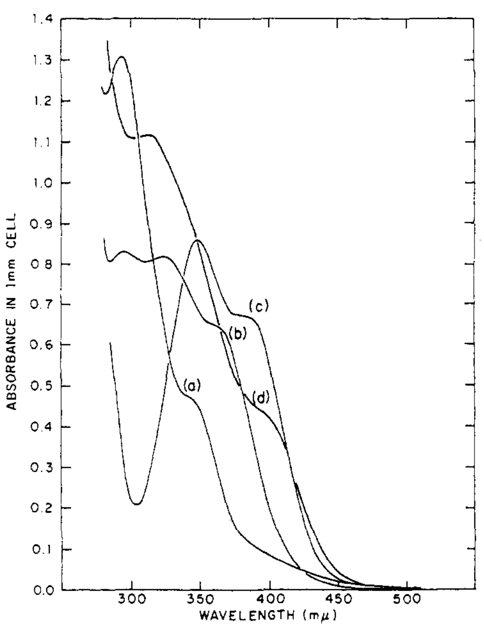

Figure 2. Electronic spectra of (olefin)Ni[P(O-*o*-tolyl)$_3$]$_2$ complexes in benzene: (a) 1.01 × 10^{-3} *M* (MA)NiL_2; (b) 1.77 × 10^{-3} *M* (ACN)NiL_2; (c) 1.98 × 10^{-3} *M* (C_2H_4)NiL_2, from ref 7a; (d) 1.21 × 10^{-3} *M* (styrene)NiL_2.

The monodentate olefin complexes all obey Beer's law, good evidence for an absence of dissociation of either olefin by eq 3 or phosphite by eq 4. Upper limits of 2 × 10^{-6} *M* can be placed on K_3 and K_4 assuming that 10% dissociation in 2 × 10^{-4} *M* solutions would have been detectable. The bidentate (COD)NiL_2 complex showed only a featureless tailing absorption above 300 mμ at concentrations above 10^{-2} *M*. The compound did not obey Beer's law, however, and a 2 × 10^{-4} *M* solution showed shoulders with inflections at 340 and 390 mμ. The two new electronic bands are assigned to a three-coordinate complex (COD)NiL containing chelating COD, formed by dissociation of one L in dilute solution.[22]

$$\text{(olefin)NiL}_2 \overset{K_4}{\rightleftharpoons} \text{(olefin)NiL}_2 + \text{L} \qquad (4)$$

The electronic spectrum of the initial product formed in the reaction of C_2F_4 with NiL_3 (Figure 1) shows two electronic bands at ~300 and 359 mμ as expected for (C_2F_4)NiL_2. These solutions appear to be stable for a few hours at 25° but on prolonged standing in the presence of excess C_2F_4 the spectra go over to that found for the isolated (C_4F_8)NiL_2, with loss of the prominent 359-mμ band. Tetrafluoroethylene can be easily recovered by pumping from solutions of (C_2F_4)NiL_2 freshly prepared from NiL_3 but cannot be so removed from (C_4F_8)NiL_2.

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(20) C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 1647 (1970).

(21) C. A. Tolman, W. M. Riggs, W. J. Linn, C. M. King, and R. C. Wendt, *Inorg. Chem.*, **12**, 2770 (1973).

(22) A compound of the type (olefin)$_2$NiL has a precedent in (C_2H_4)$_2$NiP(C_6H_{11})$_3$, whose X-ray structure has been reported by C. Kruger and Y.-H. Tsay, *J. Organometal. Chem.*, **34**, 387 (1972).

Additional evidence for a simple monoolefin complex of C_2F_4 in freshly prepared solutions is the ^{19}F spectrum of a solution of C_2F_4 and NiL_3 in a 2:1 ratio. After allowing 15–20 min for the initial reaction to go to completion, the spectrum shows two single resonances of approximately equal intensity, one at +127.6 ppm assigned to $(C_2F_4)NiL_2$[23] and one at +132.1 ppm, the position of free C_2F_4.

The ligand exchange behavior of the olefin complexes was investigated in the proton nmr spectra by adding olefin and P(O-*o*-tolyl)$_3$ to solutions of (olefin)NiL_2 and by adding olefin to solutions of NiL_3. Addition of the olefins to the (olefin)NiL_2 complexes gave separate resonances due to free and complexed olefin for MA, styrene, and COD. With ACN, the original olefin resonances disappeared and were replaced by a broad average resonance intermediate in chemical shift between free and coordinated ACN. A similar rapid exchange was found in the case of ethylene.[7]

Spectra obtained after addition of P(O-*o*-tolyl)$_3$ to solutions of the (olefin)NiL_2 complexes indicate that rapid phosphite exchange is a general feature of these solutions.[7] One exception was the (COD)NiL_2 complex, where slow exchange and displacement of COD occurred; adding L gave separate resonances of (COD)NiL_2, L, NiL_3, and NiL_4.

Addition of L to a solution containing (S)NiL_2 and free S accelerated the rate of olefin exchange enough to wash out the H–H coupling of the free styrene. This suggests the exchange mechanism in eq 5, involving an

$$\text{(olefin)NiL}_2 + \text{L} \rightleftarrows \text{(olefin)NiL}_3 \rightleftarrows \text{olefin} + \text{NiL}_3 \qquad (5)$$

(S)NiL_3 intermediate. An (olefin)NiL_3 complex where the olefin is C_2F_4 and L_3 is the tridentate ligand, 1,1,1-tris(diphenylphosphinomethyl)ethane, has been isolated and its structure determined by X-ray diffraction.[24]

Proton nmr spectra obtained on adding increasing amounts of olefins (MA, ACN, S, C_3H_6, and COD) to solutions of 0.15 *M* NiL_3 in C_6H_5 were generally similar to those obtained on adding C_2H_4 to NiL_3.[7] With less than stoichiometric amounts of added olefin weak resonances of NiL_4 appeared. NiL_4 was produced from NiL_3 and the free L displaced by olefin in reaction 1. As the olefin concentration increased, the amount of NiL_4 increased to some maximum value and then decreased as most of the nickel was converted to (olefin)NiL_2. The maximum concentraton of NiL_4, about 25% of the nickel present in the ~0.15 *M* C_6D_6 solutions, was achieved when half of the nickel was converted to olefin complex.

The reactions of MA, ACN, S, and C_3H_6 NiL_3 appeared to be instantaneous on mixing, judging by the rapid color change from red-orange to yellow. Extremely rapid reactions are also indicated by the proton nmr spectra. The reaction of tetrafluoroethylene was, however, abnormally slow and could be followed by conventional means. The rate data in Table I show that the reaction of C_2F_4 with NiL_3 obeys the rate law

$$\text{rate} = k_2[C_2F_4][NiL_3]$$

This behavior is consistent with an associative process involving a $(C_2F_4)NiL_3$ intermediate, the reverse of reaction 5. A plot of log k_2 against $1/T$ gives $\Delta H^{\ddagger} = 6.5 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -40 \pm 3$ eu. The large negative entropy of activation is responsible for the slow rate of the reaction.

Discussion

Preparation and Solution Behavior The isolable mixed complexes of tri-*o*-tolyl phosphite and monoenes on nickel(0) have the composition (olefin)NiL_2. In the triphenyl phosphine–nickel(0) system both $(ACN)_2Ni[P(C_6H_5)_3]_2$[25] and $(ACN)_2NiP(C_6H_5)_3$[10] have been isolated. In the dipyridyl–nickel(0) system $(MA)_2Ni$(dipy) and (ACN)Ni(dipy) are reported.[4a] With L = *t*-BuNC the complexes (MA)NiL_2, $(MA)_2NiL_2$, and (MA)NiL_3 have been prepared.[26] The enhanced stability of (olefin)$_2NiL_2$ complexes in these other systems is presumably due to the better electron donor character of these ligands compared to P(O-*o*-tolyl)$_3$. A high electron density on nickel is required if two strongly π-accepting olefins are to be accommodated. In our system, an isolable bis(olefin) complex is obtained by using 1,5-cyclooctadiene as a chelating ligand. Unisolable (monoene)$_2$Ni[P(O-*o*-tolyl)$_3$]$_2$ do form in solution with small formation constants K_2, as shown spectrophotometrically.[8]

The isolation of (C_4F_8)Ni[P(O-*o*-tolyl)$_3$]$_2$ from the reaction of C_2F_4 and NiL_3 is not surprising. Many other nickel(0) compounds give these five-membered rings.[20] Our spectrophotometric studies show that $(C_2F_4)NiL_2$ has a moderate lifetime at 25°. Reaction of a second C_2F_4 to form the octafluoronickelacyclopentane presumably occurs by coupling of the olefins in an (olefin)$_2NiL_2$ complex.

The solution behavior of our (monoene)NiL_2 complexes indicates that they are extremely stable to dissociation. The ethylene complex can be recovered quantitatively after exposure of its solutions to vacuum for long periods.[7a] Yamamoto, *et al.*,[4b] attributed color changes (red or red-brown to green) to formation of (THF)Ni(dipy) when $(MA)_2$Ni(dipy) or $(ACN)_2$Ni(dipy) was dissolved in tetrahydrofuran (THF). Based on our results, this interpretation is unlikely since THF seems likely to be a poor ligand for Ni(0) compounds. The color change they observed is probably due to dissociation of one olefin from (olefin)$_2$Ni(dipy) to give (olefin)Ni(dipy), the reverse of eq 2.

Bamford and Hughes[5] found that $Ni[P(OC_6H_5)_3]_4$ reacts slowly with methyl methacrylate and styrene by a dissociative mechanism with $\Delta H_d^{\ddagger} \sim 27$ kcal/mol but thought that the products of the reactions were (olefin)NiL_3 complexes. Their published electronic spectra are, however, those of (olefin)NiL_2 complexes.[27] We have also found a slow reaction by a dissociative mechanism ($\Delta H_d^{\ddagger} = 29 \pm 1$ kcal/mol, $\Delta S_d^{\ddagger} = 21 \pm 3$ eu)[28] of Ni[P(O-*p*-tolyl)$_3$]$_4$ with maleic anhydride, producing (MA)Ni[P(O-*p*-tolyl)$_3$]$_2$.

The much more rapid reaction of MA with Ni[P(O-*o*-tolyl)$_3$]$_3$ can be understood in terms of the 16 and

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[23] A resonance at +130.0 ppm was reported for $(C_2F_4)Ni[P(C_6H_5)_3]_2$ by A. Greco, M. Green, S. K. Skakshooki, and F. G. A. Stone, *Chem. Commun.*, 1374 (1970).

[24] J. Browning and B. R. Penfold, *Chem. Commun.*, 198 (1973).

[25] G. N. Schrauzer, *J. Amer. Chem. Soc.*, **82**, 1008 (1960).

[26] S. Otsuka, T. Yoshida, and Y. Tatsuno, *J. Amer. Chem. Soc.*, **93**, 6462 (1971).

[27] Compare Figure 1 in ref 5b with the spectrum of (styrene)Ni[P(O-*o*-tolyl)$_3$]$_2$ in our Figure 2. Our work[28] indicates that electronic spectra of (olefin)NiL_2 are insensitive to substitution on the aryl phosphite.

[28] C. A. Tolman, W. C. Seidel, and L. W. Gosser, unpublished results.

18 electron rule.[29] The 16-electron NiL_3 complex has available an associative path with a low activation energy. The 18-electron NiL_4 complex must first lose a phosphite ligand before an olefin can coordinate. The rule also explains the much faster phosphite exchange of the 16-electron (monoene)NiL_2 complexes compared to that of the 18-electron (COD)NiL_2.

An associative mechanism in the reaction of tetrafluoroethylene with NiL_3 is established by our kinetic studies. Much slower reaction of C_2F_4 than of other olefins has also been observed in the associative reactions of C_2F_4 with acacRh$(C_2H_4)_2$[12] (acac = acetylacetonate) and IrCl(CO)[P$(C_6H_5)_3]_2$.[30a] We attribute the slow rates of C_2F_4 to the inaccessability of the high olefin π^* orbital[8] and the bending back of the fluorines required to give a stable metal–C_2F_4 bond. An X-ray structure[30b] of $(\pi\text{-}C_5H_5)Rh(C_2H_4)(C_2F_4)$ shows that the fluorines are bent away from the metal to a marked degree, even more than the CN groups of TCNE complexes.

Structure and Bonding. In the familiar Dewar[31]–Chatt–Duncanson[32] picture, the bonding in transition metal–olefin complexes consists of σ donation of electrons to the metal from filled olefin π orbitals and π acceptance of electrons from the metal into empty olefin π^* orbitals. The relative importance of these two features of the bonding varies widely, depending on the olefin, the metal and its oxidation state, and the other ligands present. The (olefin)Ni[P(O-*o*-tolyl)$_3]_2$ complexes are important in understanding the nature of metal–olefin bonding because they make extensive use of olefin π^* orbitals and because we have such a complete knowledge on their spectral properties, structures, and stabilities.

Quinn and Tsai[1] have pointed out a general correlation between the chemical shift τ of olefinic protons in the nmr spectra and infrared frequencies $\nu_{C=C}$ for a wide variety of transition metal ethylene complexes. Larger values of τ and smaller values of $\nu_{C=C}$ indicate greater donation of electrons from metal d to olefin π^* orbitals. The values of τ 8.1 and $\nu_{C=C}$ 1487 cm^{-1} for (C_2H_4)Ni [P(O-*o*-tolyl)$_3]_2$[7a] are among the highest chemical shifts and lowest stretching frequencies reported for transition metal ethylene complexes. Population of olefin π^* orbitals reduces the C=C bond order and lengthens the carbon–carbon bond. The bond length[15] of 1.46 Å in (C_2H_4)Ni[P(O-*o*-tolyl)$_3]_2$ is the longest found so far for an ethylene complex and is close to the 1.472-Å C–C bond in ethylene oxide.[33] Comparative spectral and structural data for a variety of olefin complexes are given in Table IV, along with data on the olefin epoxides and free olefins. Ni(0) heads the list of transition metal complexes for which data were available. The $(C_2H_4)NiL_2$ complex is similar in several respects to ethylene oxide. As the ability of the metals to π back bond decreases in the series Ni(0) > Fe(0) ~ Pt(0) > Rh(I) > Pt(II) > Ag$^+$, values of τ, $\nu_{C=C}$, and $d_{C=C}$ tend to approach those characteristic of free ethylene. A decreasing ability of the metal to π back bond correlates with increasing ionization potential for the isolated atom or ion.[34]

Table IV. Nmr, Ir,[a] and Structural Data on Olefin Epoxides and Transition Metal Complexes

Compound	τ	$\nu_{C=C}$,[b] cm^{-1}	$d_{C=C}$,[c] Å	Ground state IP of atomic M^{n+}, eV[d]
Ethylene oxide	7.2[e]	1487[f]	1.472[g]	13.6
(C_2H_4)Ni[P(O-*o*-tolyl)$_3]_2$	8.1[h]	1487[h]	1.46 (2)[i]	7.6
$(C_2H_4)Fe(CO)_4$	7.5[j]	1510[k]	1.46 (6)[j]	7.9
$(C_2H_4)Pt[P(C_6H_5)_3]_2$	7.4[l]		1.43[l]	9.0
$(C_2H_4)_2$Rh(acac)	6.9	1524	1.41 (3)[m]	18.1
$(C_2H_4)PtCl_3^-$	5.3	1526	1.35 (1)[n]	18.6[p]
$(C_2H_4)Ag^+$	4.3	1583		21.5
C_2H_4	4.7	1623	1.337 (3)[o]	

Compound	mean τ	ν_{CN}, cm^{-1}	$d_{C=C}$, Å
Glycidonitrile	6.8[q]	2255[q]	
(ACN)Ni[P(O-*o*-tolyl)$_3]_2$	8.7[r]	2194[r]	1.46 (2)[i]
(ACN)Pt[P$(C_6H_5)_3]_2$	7.9[s]	2195[s]	
(ACN)Fe$(CO)_4$	7.9[t]	2210[t]	1.40 (2)[u]
ACN	5.05[r]	2227[r]	1.339[v]

Compound	τ	$\nu_{C=O}$, cm^{-1}
(MA)Ni[P(O-*o*-tolyl)$_3]_2$	7.9[r]	1805, 1733[r]
(MA)Pt[P$(C_6H_5)_3]_2$	6.7[s]	1800, 1725[s]
(MA)Fe$(CO)_4$	5.6[w]	1824, 1746[w]
MA	4.5[r]	1845, 1777[r]

[a] Nmr and ir data are taken from Table VII of ref 1 unless noted otherwise. [b] Near the top of the table ν_2 is predominantly CH_2 scissoring. See discussion in text. [c] Number in parentheses indicates uncertainty in last digit. [d] Ionization potentials frcm C. E. Moore, "Atomic Energy Levels," National Bureau of Standards, Circular No. 467, Vol. I, 1949; Vol. II, 1952; Vol. III, 1958. [e] L. H. Meyer, A. Saika, and W. S. Gutowski, *J. Amer. Chem. Soc.*, **75**, 4567 (1953); **76**, 4242 (1954). [f] Band in Raman spectrum of liquid assigned to CH_2 scissors ν_2: G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N. Y., 1956, p 341. [g] Reference 33. [h] Reference 7a. [i] Reference 15. [j] M. I. Davis and C. S. Speed, *J. Organometal. Chem.*, **21**, 401 (1970). [k] D. C. Andrews and G. Davidson, *ibid.*, **35**, 161 (1972). [l] P. T. Cheng, C. D. Cook, S. C. Nyburg, and K. Y. Wan, *Inorg. Chem.*, **10**, 2210 (1971). [m] J. A. Evans and D. R. Russell, *Chem. Commun.*, 197 (1971). [n] W. C. Hamilton, K. A. Klanderman, and R. Spratley, *Acta Crystallogr., Part A*, **25**, 8172 (1969). [o] H. C. Allen and E. K. Plyler, *J. Amer. Chem. Soc.*, **80**, 2673 (1958). [p] This value is for Pt$^+$ = Pt^{2+} + e$^-$. The desired IP of Pt^{2+} was not available. [q] Reference 13. [r] This work. [s] Reference 19. [t] Reference 17. [u] A. R. Luxmoore and M. T. Truter, *Acta Crystallogr.*, **15**, 1117 (1962). [v] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959). [w] Reference 40.

The frequencies given for $\nu_{C=C}$ in Table IV were assigned to this vibration in the references quoted except for ethylene oxide. Detailed vibrational studies of Zeise's salt by Nakamoto[36] and Hiraishi[37] show that the band near 1500 cm^{-1} is due to a normal mode of vibration containing a significant mixture of CH_2 scissoring deformation. Hiraishi has observed a strong polarized Raman line at 1243 cm^{-1} which he believes contains more C–C stretch than does the one at 1526

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[29] C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

[30] (a) M. F. Werneke, Ph.D. Thesis, Clarkson College of Technology, 1971; (b) L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, **94**, 3779 (1972).

[31] M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

[32] J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

[33] G. L. Cunningham, A. W. Boyd, R. J. Myers, W. G. Gwinn, and W. I. LeVan, *J. Chem. Phys.*, **19**, 676 (1951).

[34] The ionization potential of the metal and its ability to back bond are of course modified by its ligands. For example, ionization potentials of Fe(CO)$_4$L complexes vary from 8.14 eV with L = CO to 7.29 with L = P(n-C_4H_9)$_3$.[35]

[35] G. Distefano, G. Innorta, S. Pignataro, and A. Foffani, *J. Organometal. Chem.*, **14**, 165 (1968).

[36] M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, **90**, 918 (1968).

[37] J. Hiraishi, *Spectrochim. Acta, Part A*, **25**, 749 (1969).

cm^{-1}. This has caused some confusion about the meaning of the frequency near 1500 cm^{-1}.

The $\sim$1500-cm^{-1} band is not a pure C–C stretch in any of these compounds; there is significant coupling between the C–C stretch and the symmetric scissoring vibration even in ethylene.[38] In the local C_{2v} symmetry of an M-ethylene complex there will be five normal modes of A_1 symmetry (ν_1, ν_2, ν_3, ν_4, ν_5) which are mixtures of symmetric C–H stretch, C–C stretch, CH_2 scissors, CH_2 wag, and M–C stretch. The column labeled $\nu_{C=C}$ in Table IV should really be labeled ν_2. As the extent of metal π back donation increases, ν_2 falls in frequency from 1623 in free C_2H_4 to 1487 cm^{-1} in C_2H_4O and goes from a mixture containing mostly C–C stretch to one with mostly CH_2 scissoring. Its infrared frequency is still useful in assessing the nature of the metal olefin bond. Examination of our Raman spectrum[7a] of $(C_2H_4)Ni[P(O\text{-}o\text{-tolyl})_3]_2$ shows a strong line at 1245 cm^{-1}, which may correspond to Hiraishi's 1243-cm^{-1} line in Zeise's salt. The similarity of these frequencies suggests that ν_3 may be insensitive to the nature of the metal–olefin bond and therefore less useful than ν_2.

Based on the ethylene complexes alone, one might conclude that an olefin epoxide is a fair model for (olefin)NiL_2 complexes. Other data suggest that this "metallocyclopropane" model is misleading in several respects. Table IV shows that the frequency ν_{CN} in olefin-bonded acrylonitrile complexes is *lower* than in free ACN and decreases as back donation from the metal increases.[39] Glycidonitrile, the epoxide model of an acrylonitrile complex, has a C–N stretching frequency *higher* than that of free ACN. While the mean τ of the complex (8.7) is closer to that of the epoxide (6.8) than to the free olefin (5.05), the values of J_{HH} in $(ACN)Ni[P(O\text{-}o\text{-tolyl})_3]_2$ are much more similar to those of free ACN than to those of glycidonitrile. Small changes in J_{HH} on coordination have also been found for iron tetracarbonyl complexes of acrylic acid, methyl acrylate, and acrylamide.[40] The frequencies of the olefin ν_{CO} bands in these complexes are uniformly lower than in the free olefins ($\Delta\nu$ = 15–30 cm^{-1}). Frequencies of carbonyl groups adjacent to epoxide rings are higher than in the alkenes or even the saturated alkanes.[41]

Another difficulty with the metallocyclopropane model is the ambiguity of oxidation states arising from the convention of regarding σ-bonded alkyl groups as carbanions in assigning formal oxidation states. By this convention, $(C_2H_4)Ni[P(O\text{-}o\text{-tolyl})_3]_2$ should be regarded as a Ni(II) complex. The ESCA results[21] show that the electron density on nickel in $(C_2H_4)NiL_2$ is similar to that in NiL_3 so that the nickel should be regarded as Ni(0) if an oxidation state is to be assigned. The bonds are sufficiently covalent in character that little net transfer of electron density from metal to ethylene occurs. In the Dewar–Chatt–Duncanson description, electron withdrawal into the olefin π^* orbital is partially compensated by electron donation by the olefin π orbital, with the result that ethylene has an electronegativity in the complex comparable to that of an aryl phosphite.

Replacing the hydrogens of ethylene by substituents which lower the energy of the π^* orbital greatly enhances the stability of the olefin complexes, as we shall see in the following paper.[8]

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[38] H. W. Thompson and J. W. Linnett, *J. Chem. Soc.*, 1376 (1937).

[39] Cenini, *et al.*,[19] have also suggested that reduction of ν_{CN} or ν_{CO} of olefins with conjugated cyanide or carbonyl groups provides a measure of metal–olefin π bonding.

[40] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

[41] L. A. Yanovaskaya, B. I. Kozyrkin, G. A. Kogan, and V. F. Kucherov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **11**, 2319 (1967).

Olefin Complexes of Nickel(0). III. Formation Constants of (Olefin)bis(tri-*o*-tolyl phosphite)nickel Complexes

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Abstract: The reactions of 38 olefins with $Ni[P(O\text{-}o\text{-tolyl})_3]_3$ have been investigated and equilibrium constants determined spectrophotometrically in benzene. Values of K_1 at 25° vary from $\sim 10^{-4}$ to 4×10^8, depending on olefin structure (eq 1). Electron-withdrawing substituents on acyclic olefins give more stable olefin complexes, with resonance effects more important than inductive effects. Fluorine, alkoxy, and acetoxy substituents destabilize the complexes. Log K_1 correlates well with σ_p^+ with $\rho = +5.5$. For cyclic olefins K_1 is enhanced by ring strain and to a much greater extent than in Ag^+ complexes. Temperature studies in a few cases show that K_1 is determined by ΔH_1, with $\Delta S_1 \sim 0$. Assuming a nickel–phosphorus bond strength of 30 kcal/mol, nickel–olefin bond strengths can be estimated to lie in the range of about 25 kcal/mol for *trans*-di(*tert*-butyl)ethylene to 42 kcal/mol for maleic anhydride. The results are discussed in terms of energy level separations of highest occupied and lowest unoccupied molecular orbitals of $Ni[P(O\text{-}o\text{-tolyl})_3]_3$ and the free olefins and compared with data on other metals.

Nickel occupies an important position among the transition metals by virtue of the large variety of homogeneous catalytic reactions involving acetylenes and olefins in which it is involved. Polymerization and cyclization of acetylenes,[1] cyclization of butadiene,[2] formation of 1,4-hexadiene from butadiene

[1] W. Reppe and W. K. Schwenkendiek, *Justus Liebigs Ann. Chem.*, **560**, 104 (1948).