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Formation of Olefin Complexes of Nickel(0). 5. Steric and Electronic Effects of Phosphorus Ligands[†]

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Spectrophotometric measurements by IR and vis/UV on solutions containing olefins, phosphorus ligands, and nickel(0) show that competition for coordination is strongly affected by both olefin structure and the steric and electronic properties of the phosphorus ligands L. The equilibrium constant K for the reaction $\mathrm{NiL_4}$ + olefin $\rightleftharpoons$ (olefin)$\mathrm{NiL_2}$ + 2L increases by about 10^{10} on going from cyclohexane to maleic anhydride and by about 10^8 on going from P(O-*p*-tolyl)$_3$ to P(O-*o*-tolyl)$_3$. Placing Cl in the para positions of the aryl phosphites decreases both K and its sensitivity to changes in olefin structure. Rates of ligand dissociation from Ni[P(O-*p*-tolyl)$_3$]$_4$ and Ni[P(O-*p*-$\mathrm{C_6H_4Cl}$)$_3$]$_4$ are reported as well as approximate Ni–olefin bond strengths.

Olefin complexes of transition metals are essential intermediates in a variety of catalytic processes.[1] A recent monograph summarizes the synthesis, structure, and bonding of nickel(0) olefin complexes.[2] Ittel and Ibers[3] discuss structure and bonding in transition-metal olefin complexes. In earlier papers[4] in this series, we described the preparation, properties, and solution behavior of nickel complexes containing P(O-*o*-tolyl)$_3$ and a wide variety of olefins.

In this paper, we are concerned with the rates and equilibria of formation of complexes of the type (olefin)$_n$NiL$_m$ in experiments that can be thought of as competitions between olefins and phosphorus ligands L for coordination to Ni(0). The primary focus is on variations in the steric and electronic properties[5] of L, but we have also looked at a range of olefins.

Prelinary experiments involved treatment of bis(acrylonitrile)nickel with various ligands, or reactions of NiL$_n$ complexes with acrylonitrile. Detailed studies were then carried out on the reactions of cyclohexene, 1-hexene, acrylonitrile (acn), and maleic anhydride (ma) with Ni[P(O-*p*-tolyl)$_3$]$_4$, Ni[P(O-*p*-$\mathrm{C_6H_4Cl}$)$_3$]$_4$, Ni[P(O-*o*-tolyl)$_3$]$_3$, and Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_3$. These phosphorus ligands were chosen to get a clean separation of steric and electronic effects. The effects of structural variations in the olefins themselves on the formation of (olefin)nickel(0) complexes containing P(O-*o*-tolyl)$_3$ have already been described,[4c] as have the isolation and properties of (acn)Ni[P(O-*o*-tolyl)$_3$]$_2$ and (ma)Ni[PO-*o*-tolyl)$_3$]$_2$.[4b]

Reactions of these NiL$_3$ or NiL$_4$ complexes with olefins in solution are described by eq 1–3. Studies of the ligand dissociation equilibrium (1) were reported earlier.[6] We have now studied the kinetics of reaction 4 [the sum of (1) and (2)] using Ni[P(O-*p*-tolyl)$_3$]$_4$ and Ni[P(O-*p*-$\mathrm{C_6H_4Cl}$)$_3$]$_4$ and maleic anhydride. Maleic anhydride was chosen for the kinetic studies because reaction 4 goes essentially to completion. Measurements of equilibrium constants over a range of temperatures enable us to compare the relative strengths of Ni–olefin and Ni–phosphorus bonds.

$$\mathrm{NiL_4} \overset{K_d}{\rightleftharpoons} \mathrm{NiL_3} + \mathrm{L} \tag{1}$$

$$\mathrm{NiL_3} + \text{olefin} \overset{K_1}{\rightleftharpoons} (\text{olefin})\mathrm{NiL_2} + \mathrm{L} \tag{2}$$

$$(\text{olefin})\mathrm{NiL_2} + \text{olefin} \overset{K_2}{\rightleftharpoons} (\text{olefin})_2\mathrm{NiL_2} \tag{3}$$

$$\mathrm{NiL_4} + \text{olefin} \overset{K}{\rightleftharpoons} (\text{olefin})\mathrm{NiL_2} + 2\mathrm{L} \tag{4}$$

Preparation and characterization of (ma)Ni[P(O-*p*-tolyl)$_3$]$_2$ is described as well as an improved synthesis of Ni[P(O-*o*-tolyl)$_3$]$_3$.[7]

Experimental Section

Proton NMR spectra were determined on Varian HA-100 or HA-220 spectrometers in 5-mm o.d. precision tubes. Benzene-d_6 and $\mathrm{CD_2Cl_2}$ were used as solvents, and internal tetramethylsilane was used as a chemical shift reference at δ 0. Chemical shifts were measured with a precision of ±0.05 ppm and coupling constants to ±0.5 Hz.

Infrared spectra were recorded on a Perkin-Elmer 221 spectrophotometer using $\mathrm{CH_2Cl_2}$ as solvent and 0.1-mm cells. In preliminary studies involving the reactions of various ligands with bis(acrylonitrile)nickel or of acrylonitrile with various NiL$_n$ complexes, the spectra were not calibrated and frequencies are given to the nearest 5 cm^{-1}. In subsequent studies, spectra were calibrated with CO gas (2143 cm^{-1}) or polystyrene (1605 cm^{-1}) to ±2 cm^{-1}. The Raman spectrum of 0.04 g of (acn)Ni[P(O-*o*-tolyl)$_3$]$_2$ in 0.8 g of $\mathrm{CH_2Cl_2}$ was determined on a Cary Model 81 laser instrument.

Electronic spectra in benzene were determined with a Cary 14 spectrophotometer over the region 600–270 nm. Beer's law for each of the isolated (olefin)NiL$_2$ complexes was checked over a 100-fold concentration range by comparing spectra of ca. 2×10^{-2}, 2×10^{-3}, and 2×10^{-4} M complex in cells of 0.1-, 1.0-, and 10-mm path length. Equilibrium constants as a function of temperature were determined by using thermostated 1.0- and 10-mm quartz cells from Opticell Co., Inc. The temperature in the cell was maintained by circulating water from a Forma constant temperature bath and checked to ±0.5 °C by a 36 gauge copper–constantan thermocouple in the center of the cell. Equilibrium constants were generally measured at 25, 40, 55, and 70 °C.

Kinetics of Reaction of Maleic Anhydride with Ni[P(O-*p*-tolyl)$_3$]$_4$ and Ni[P(O-*p*-$\mathrm{C_6H_4Cl}$)$_3$]$_4$. The reaction was followed spectrophotometrically at 345 nm, the wavelength where the spectrum of the product (ma)Ni[P(O-*p*-tolyl)$_3$]$_2$ shows an inflection. A 0.5-cm^3 solution of 1.0–0.008 M maleic anhydride was injected by syringe into a small serum-capped test tube containing 0.5 cm^3 of ca. 4×10^{-3} M NiL$_4$ under N$_2$. The tube was quickly

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[†] Contribution No. 3165.

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shaken and a portion of the solution loaded by syringe into a 1-mm jacketed cell at a reaction temperature of 25, 40, or 55 °C. The nitrogen atmosphere in the cell was maintained during loading by blowing N_2 through the side arm of a three-way stopcock attached to the neck of the cell.

Plots of log $[A_\infty(345) - A(345)]$ against time were linear over 3–4 half-lives, and the slopes were used to determine pseudo-first-order rate constants at each temperature. Spectra recorded during and after the kinetic runs confirmed that NiL_4 and (ma)NiL_2 were the only detectable species present. Activation parameters were determined from linear plots of log k against $1/T$.

Reactions of Various Phosphorus Ligands with Bis(acrylonitrile)nickel. Reactions were followed by running infrared spectra over the ν_{CN} region (2400–1800 cm^{-1}) following additions of neat phosphorus ligands to a suspension of 0.02 g of $Ni(acn)_2$ (0.125 mmol) in 0.5 cm^3 of CH_2Cl_2 in a serum capped tube. Bis(acrylonitrile)nickel was completely insoluble in CH_2Cl_2, and the supernatant solution showed no bands except those of solvent until phosphine was added to give L:Ni ratios of 0.5:1, 1:1, 2:1, 4:1, and 8:1. After the tube was shaken for about a minute, any remaining solid was allowed to settle and a 10–15-μL portion of solution taken for injection into an N_2-flushed microcell.

PBu_3 and $Ni(acn)_2$. Up to a 1:1 ratio of PBu_3:Ni, when all the $Ni(acn)_2$ dissolved, there was a weak band at 2205 cm^{-1} and a very weak one at 2225 cm^{-1}, assigned to ν_{CN} in $(acn)_2NiPBu_3$. With a ratio of 2:1 or higher PBu_3:Ni, these bands were replaced by stronger ones at 2170 and 2200 cm^{-1}, (intensity ratio 2.7:1), assigned to $(acn)_2Ni(PBu_3)_2$. There was no evidence for free acn ($\nu_{CN} \simeq$ 2225 cm^{-1}) even with a large excess of PBu_3.

$P(O$-*o*-$tolyl)_3$ and $Ni(acn)_2$. In a similar experiment, all of the solid did not dissolve until the ratio of L:Ni was ~2:1. Only two bands were observed in any of the spectra, one at 2195 cm^{-1} assigned to (acn)Ni[P(O-*o*-tolyl)$_3$]$_2$ and one at 2225 cm^{-1} due to free acn. The intensity ratio of these bands was a constant 2.1:1 during the additions.

$P(OPh)_3$ and $Ni(acn)_2$. In an experiment with a 4:1 ratio of L:Ni, a copious white precipitate of $Ni[P(OPh)_3]_4$ formed. The spectrum of the resulting solution showed a band of free acn at 2225 cm^{-1} and a very weak band at ~2195 cm^{-1} assigned to $(acn)Ni[P(OPh)_3]_2$.

$P(OMe)_3$ and $Ni(acn)_2$. In an experiment with added increments of ligand, most of the solid $Ni(acn)_2$ had dissolved when L:Ni reached 2:1. At that point bands at 2180, 2205, and 2225 cm^{-1} were observed in a 2.3:1:1 intensity ratio. The first two are tentatively assigned to $(acn)_2Ni[P(OMe)_3]_2$ and the last to free acn. When L:Ni reached 4:1, the only band in the spectrum was that of free acn.

Reactions of Acrylonitrile with Various NiL_n. Reactions were followed by infrared, similar to the experiments just described.

Acn and $Ni[PMe_3]_4$. Toluene was used as a solvent in this experiment because $Ni[PMe_3]_4$ is rapidly destroyed by CH_2Cl_2. Additions of acn to a 0.1 M solution of the complex gave bands at 2175 and 2210 cm^{-1} (intensity ratio 4:1) whose intensity reached a maximum value when the ratio of added acn:Ni was 2:1. These bands are assigned to $(acn)_2Ni[PMe_3]_2$. Further additions caused no change in the original bands and gave a new band of free acn at 2225 cm^{-1}.

Ni[P(O-*o*-tolyl)$_3$]$_3$ and acn. Additions of acn to a 0.125 M solution of the NiL_3 complex in CH_2Cl_2 gave a band of (acn)Ni[P(O-*o*-tolyl)$_3$]$_2$ at 2195 cm^{-1} whose intensity did not change appreciably after a 1:1 ratio of acn:Ni.

Compounds. Phosphorus ligands were obtained as described previously[8] and their purities checked by means of their proton and ^{31}P NMR spectra. Reagent grade cyclohexene and 1-hexene were used without further purification. Acrylonitrile was freshly distilled before use, and maleic anhydride was sublimed.

Complexes. The NiL_n complexes were prepared as described earlier,[7,8] except for the improved synthesis of Ni[P(O-*o*-tolyl)$_3$]$_3$ given below, which gave a nice crystalline product. In the case of L = P(O-*p*-Cl-*o*-tolyl)$_3$, the nickel complex was not pure but had a composition corresponding to about n = 3.5. Bis(maleic anhydride)nickel was prepared from $Ni(CO)_4$ by the literature procedure.[9]

Tris(tri-*o*-tolyl phosphite)nickel, Ni[P(O-*o*-tolyl)$_3$]$_3$, was prepared by the triethylaluminum reduction of bis(acetylacetonate)nickel in toluene. A mixture of 18.6 g of $[Ni(acac)_2]_3$ and 76.8 g of P(O-*o*-tolyl)$_3$ in 300 mL of toluene was cooled to 0 °C and 104 mL of 25% $AlEt_3$ in hexane added over 20 min. The solution was then heated to 65 °C for 1 h while maintaining a strong N_2 purge.

The volume of the reaction mixture was then reduced to 300 mL and the mixture added to 1000 mL of cold petroleum ether. After the solution was cooled to −25 °C, the red solids were removed by vacuum filtration and dissolved in a minimum amount of hot (75 °C) toluene. The product was precipitated with cold methanol (methanol–toluene, 5:1) and vacuum dried to give red orange crystals: 40 g (50%); UV (benzene)$_3$ λ_{max} 407 nm (ϵ 5.0 × 10^3), 450 (sh, 3.8 × 10^3) [lit.[7] ϵ 4.5 × 10^3, 3.5 × 10^3].

(Maleic anhydride)[bis(tri-*p*-tolyl phosphite)]nickel. (ma)Ni[P(O-*p*-tolyl)$_3$]$_2$ was prepared by the reaction of tetrakis(tri-*p*-tolyl phosphite)nickel with bis(maleic anhydride)nickel.[9] A mixture of 3.02 g of Ni[P(O-*p*-tolyl)$_3$]$_4$ and 0.55 g of $Ni(ma)_2$ in 10 cm^3 benzene was stirred and heated for 0.5 h at 60 °C. The solution was filtered and solvent removed under suction. Addition of 20 mL of petroleum ether to the resulting viscous brown oil gave a yellow powder, 0.82 g. The crude product was dissolved in 6 mL of benzene and the solution filtered. Methanol (25 cm^3) was added and the solution chilled and filtered. Washing with chilled CH_3OH and drying under vacuum gave yellow crystals: 0.65 g (18%); mp 119–121 °C dec; ^1H NMR (C_6D_6) δ 7.17 (d, 12, J = 8.5 Hz, *o*-C_6H_4), 6.83 (d, 12, J = 8.5 Hz, *m*-C_6H_4), 3.21 (s, 2, CH=CH), 2.00 (s, 18, CH_3). Anal. Calcd for $C_{46}H_{44}NiP_2O_9$: C, 64.1; H, 5.15; Ni, 6.8; P, 7.2. Found: C, 64.0; H, 5.30; Ni, 6.4; P, 7.0.

Results

Preliminary experiments in which phosphorus ligands were added to methylene chloride suspensions of bis(acrylonitrile) nickel indicated that both steric and electronic effects in the phosphorus ligands are important in determining the products. with excess L, three types of reactions, eq 5–7, were observed. The different course of

$$4P(OPh)_3 + Ni(acn)_2 \rightarrow 2acn + Ni[P(OPh)_3]_4 \quad (5)$$

$$2P(O\text{-}o\text{-}tolyl)_3 + Ni(acn)_2 \rightarrow acn + (acn)Ni[P(O\text{-}p\text{-}tolyl)_3]_2 \quad (6)$$

$$2PBu_3 + Ni(acn)_2 \rightarrow (acn)_2Ni(PBu_3)_2 \quad (7)$$

reactions 6 and 7) is largely an electronic effect, since the results of ligand competition experiments[8] suggest that P(O-*o*-tolyl)$_3$ and PBu_3 are sterically comparable. The more electron-donating phosphine is able to form a stable complex with two coordinated acrylonitriles. Trimethylphosphine is sterically similar to $P(OPh)_3$ yet $Ni[PMe_3]_4$ reacts smoothly with acrylonitrile to give $(acn)_2Ni[PMe_3]_2$. Trimethyl phosphite, a very small ligand of moderate electronegativity, completely displaces acn if the phosphite is present in excess. The observation of an intermediate of the type $(acn)_2NiL_2$ observed with trimethyl phosphite and $Ni(acn)_2$, but not with tri-*o*-tolyl phosphite, indicates that $(acn)_2Ni[P(OMe)_3]_2$ is more stable with respect to acn dissociation than is $(acn)_2$Ni[P(O-*o*-tolyl)$_3$]$_2$. The complex $(acn)_2NiPBu_3$ was our only example of (olefin)$_2$NiL stoichiometry but has a literature precedent in $(acn)_2NiPPh_3$.[10]

Because of possible ambiguities in separating steric and electronic effects in these systems, we went to the aryl phosphite ligand systems to be described next.

Spectroscopic Properties of the Olefin Complexes. Olefin complexes of the aryl phosphites were isolated with

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Table I. Infrared Stretching Frequencies[a] of $(\text{Olefin})_m\text{NiL}_n$ Complexes in CH_2Cl_2

compound	ma ν(CO)	acn ν(CN)
$(\text{olefin})_2\text{NiPBu}_3$		2205, 2225
$(\text{olefin})_2\text{Ni(PBu}_3)_2$		2170, 2200
$(\text{olefin})_2\text{Ni(PMe}_3)_2$		2175, 2210
$(\text{olefin})_2\text{Ni[P(OMe)}_3]_2$		2180, 2205
(olefin)Ni[P(O-*o*-tolyl)$_3$]$_2$	1733, 1805	2194
(olefin)Ni[P(O-*p*-tolyl)$_3$]$_2$	1733, 1803	~2195[b]
(olefin)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$[c]	1740, 1811	2198
(olefin)Ni[P(O-*p*-$C_6H_4Cl)_3]_2$	*d*	*d*
olefin	1777, 1845	2225

[a] In cm^{-1} [± 2 cm^{-1} except for the $(\text{olefin})_2\text{NiL}_n$ complexes which are ± 5 cm^{-1}]. [b] Observed as a weak shoulder on adding 10 M acn to 0.25 M Ni[P(O-*p*-tolyl)$_3$]$_4$. [c] Generated in solution by adding the olefins to Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_3$. [d] No bands except those of the starting materials were observed on adding excess olefin to Ni[P(O-*p*-$C_6H_4Cl)_3]_4$.

strongly electron-withdrawing olefins, maleic anhydride, and acrylonitrile. The isolated complexes have the composition (olefin)NiL$_2$ as shown by the relative integrated areas of olefinic and ligand protons in the proton NMR spectra. The vinylic protons of the two isolated maleic anhydride complexes were shifted upfield by about 2.6 ppm[11] from the free ma position at δ 5.70. Olefin bonding in (acn)Ni[P(O-*o*-tolyl)$_3$]$_2$ was confirmed earlier by a single-crystal X-ray structure.[12]

Infrared data for the $(\text{olefin})_m\text{NiL}_n$ complexes of acn and ma are shown in Table I. It can be seen that ν_{CO} of maleic anhydride and ν_{CN} of acrylonitrile show the typical[13] shifts to lower frequency on complexation. These bands are shifted less in complexes of P(O-*p*-Cl-*o*-tolyl)$_3$ than in those of P(O-*o*-tolyl)$_3$, consistent with reduced π donation from metal to olefin π^* orbitals in the chloro-substituted complexes. Frequencies of the tri-*p*-tolyl phosphite and tri-*o*-tolyl phosphite complexes are identical within the experimental uncertainty showing that ligand cone angle does not affect the electron density at nickel in the (olefin)NiL$_2$ complexes. Ni[P(O-*p*-$C_6H_4Cl)_3]_4$ did not give olefin complexes with either acn or ma in sufficiently high concentrations to identify by infrared spectroscopy. They could however be detected by vis/UV.

Isolated (olefin)NiL$_2$ complexes show no bands of free olefin in the infrared and obey Beer's law in their vis/UV spectra, indicating that dissociation via eq 8 does not occur to a detectable extent.

$$(\text{olefin})\text{NiL}_2 \rightleftharpoons \text{olefin} + \text{NiL}_2 \qquad (8)$$

The Raman spectrum of (acn)Ni[P(O-*o*-tolyl)$_3$]$_2$ shows a medium line at 2200 cm^{-1} assigned to ν_{CN} in the complex. The $\nu_{C=C}$ vibration is tentatively assigned to a weak line at 1485 cm^{-1} by analogy to the assignment of a weak line at 1487 to $\nu_{C=C}$ in (C_2H_4)Ni[P(O-*o*-tolyl)$_3$]$_2$.[4a]

Kinetics of Olefin Complex Formation. Color changes that occurred when olefins were added to the NiL$_3$ complexes Ni[P(O-*o*-tolyl)$_3$]$_3$ and Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_3$ and proton NMR spectra of the resulting solutions indicate that reaction 2 is extremely fast. Free and complexed olefin exchange rapidly on the NMR time scale, as do free L with ligand in NiL$_3$ and (olefin)NiL$_2$. NiL$_4$, which forms from NiL$_3$ and the ligand liberated in reaction 2, is not involved in the rapid exchange and gives a separate set of ligand resonances. Similar behavior was observed in the reaction of C_2H_4 with Ni[P(O-*o*-tolyl)$_3$]$_3$.[4a]

The tetrakis(aryl phosphite) complexes Ni[P(O-*p*-tolyl)$_3$]$_4$ and Ni[P(O-*p*-$C_6H_4Cl)_3]_4$ react much more slowly, requiring hours for complete reaction at 25 °C.[14a] Kinetic studies were carried out by using maleic anhydride because this olefin has a large enough equilibrium constant that reaction 4 goes essentially to completion. Rates were measured at 25, 40, and 55 °C, at maleic anhydride concentrations from 0.004 to 0.1 M.[14b] Most of the runs were carried out at 55 °C because of the inconveniently long times required at lower temperatures. The half-life for reaction of Ni[P(O-*p*-tolyl)$_3$]$_4$ at 25 °C is 1.0 h. The rate of formation of (ma)NiL$_2$ is independent of olefin concentration over the 25-fold range, indicating rate-determining ligand dissociation from NiL$_4$ in eq 1, followed by rapid reaction of olefin with NiL$_3$ in eq 2. Thus k_{obsd} is k_d, the forward rate constant in eq 1. Slow ligand dissociation from NiL$_4$, followed by a rapid olefin reaction, is also consistent with the proton NMR spectra. Thus a solution of 0.1 M Ni[P(O-*p*-tolyl)$_3$]$_4$ and 0.2 M ma showed a methyl ligand resonance at δ 2.02 due to ligand on NiL$_4$ and a stronger resonance at δ 1.97 which represents rapidly exchanging free L and ligand in (ma)NiL$_2$. The maleic anhydride protons appeared as a broad average signal at δ 5.1.

The activation parameters for ligand dissociation from Ni[P(O-*p*-tolyl)$_3$]$_4$ are $\Delta H_d^\ddagger = 29 \pm 1$ kcal/mol and $\Delta S_d^\ddagger = 21 \pm 3$ eu. These numbers can be compared with $\Delta H_d = 23 \pm 3$ kcal/mol and $\Delta S_d = 35 \pm 9$ eu for equilibrium 1 determined independently.[6] The similarity of $\Delta H_d^\ddagger$ and ΔH_d suggests that the activation energy for ligand recombination is small.

Rates of reaction of maleic anhydride with Ni[P(O-*p*-$C_6H_4Cl)_3]_4$ were measured at the same temperatures, varying [ma] from 0.004 to 0.5 M.[14b] Again k_{obsd} is essentially independent of [ma]. The slightly *higher* values of k_{obsd} obtained for the *lowest* maleic anhydride concentrations are a consequence of incomplete reaction and a contribution to k_{obsd} from the back-reaction. Incomplete reaction is clearly evident in the low values of $A_\infty(345)$ observed at the end of the runs and consistent with the equilibrium studies to be described. Ligand dissociation from Ni[P(O-*p*-$C_6H_4Cl)_3]_4$ is about half as fast as from Ni[P(O-*p*-tolyl)$_3$]$_4$, with $\Delta H_d^\ddagger = 28 \pm 2$ kcal/mol and $\Delta S_d^\ddagger = 16 \pm 6$ eu.

Electronic Spectra and Equilibrium Constants. Spectral data[14b] of olefin complexes of the type (olefin)NiL$_2$ show two bands in the 270–600 nm region, with the less intense one appearing as a shoulder at longer wavelength. Both bands shift to shorter wavelength as the electron-withdrawing ability of the olefin increases in the sequence cyclohexene < 1-hexene < C_2H_4 < acn < ma. A blue shift of the longest wavelength absorption maximum as the ligands become more electron withdrawing was also observed in the spectra of NiL$_3$ complexes,[6] suggesting that the visible bands have a high degree of ligand to metal charge-transfer character in both types of compounds.

The aryl phosphite ligands used in the present study give (olefin)NiL$_2$ complexes with similar electronic spectra. For acrylonitrile and maleic anhydride complexes with L = P(O-*o*-tolyl)$_3$ or P(O-*p*-tolyl)$_3$, the electronic spectra for a given olefin are identical within experimental error. A similar electronic environment at nickel is also suggested by the infrared data of Table I. The UV spectra of the

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(11) An upfield shift of 2.98 ppm (in acetone-d_6) has been reported for (ma)Fe(CO)$_4$ by: Weiss, E.; Stark, K.; Lancaster, J. E.; Murdoch, H. D. *Helv. Chim. Acta* **1963**, *46*, 288.

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Table II. Calculation of K for the Reaction Acrylonitrile + $NiL_4 \rightleftharpoons (acn)NiL_2 + 2L$[a]

soln no.	$[acn]_{total}$	$[acn]$[d]	$A(363)$	$10^3[(acn)NiL_2]$[b]	$10^3[NiL_4]$[c]	10^4K,[e] M
1	0.00	0.00	0.00	0.00	2.16	
2	0.01	0.0092	0.27	0.77	1.39	1.4
3	0.05	0.049	0.415	1.18	0.88	1.9
4	0.25	0.248	0.55	1.57	0.59	1.1
5	1.0	0.998	0.69	1.97	0.19	1.6
					av	1.5 ± 0.25

[a] 2.16×10^{-3} M $Ni[P(O\text{-}p\text{-tolyl})_3]_4$ in benzene at 40 °C; 1.0-mm Cell. [b] $[(acn)NiL_2] = A(363)/3.5 \times 10^3 \times 0.1$ M. [c] $[NiL_4] = 2.16 \times 10^{-3} - [(acn)NiL_2]$ M. [d] $[acn] = [acn]_{total} - [(acn)NiL_2]$ M. [e] $K = ([(acn)NiL_2][L]^2)/([acn][NiL_4]) = 4[(acn)NiL_2]^3/([acn][NiL_4])$ M.

p-chlorophenyl phosphite complexes show inflection points at slightly longer wavelengths (2–8 nm); however, the data are much less complete for those complexes. In the one case where reaction of $Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_4$ could be forced to completion, using maleic anhydride, the extinction coefficient at the inflection was identical with that determined for $(ma)Ni[P(O\text{-}o\text{-tolyl})_3]_2$ and $(ma)Ni[P(O\text{-}p\text{-tolyl})_3]_2$.

Benzene solutions of the isolated $(olefin)NiL_2$ complexes show Beer's law behavior over a concentration range of ca. 10^{-2}–10^{-4} M complex, indicating that no detectable dissociation by eq 8 occurs, even at high dilution.[15] Association of a second molecule of olefin to form bis(olefin) complexes did, however, occur at very high olefin concentrations. Spectra obtained with solutions of $Ni[P(O\text{-}o\text{-tolyl})_3]_3$ containing increasing concentrations of 1-hexene were published earlier.[16]

Reactions of acrylonitrile or maleic anhydride with the NiL_3 complexes to form $(olefin)NiL_2$ complexes occur with such large equilibrium constants that they could not be directly determined. Equilibrium constants could be determined indirectly in competition experiments involving added L or another olefin. In the case of L = $P(O\text{-}p\text{-Cl-}o\text{-tolyl})_3$ for example, the extent of reaction with acrylonitrile was determined in a solution containing ca. 2×10^{-3} M NiL_4 and 0.5 M added L.[17]

A similar attempt to determine an equilibrium constant with acrylonitrile in the L = $P(O\text{-}o\text{-tolyl})_3$ system with added 1.0 M L was frustrated by the appearance of an unexpected electronic band with a relatively sharp absorbance maximum at 367 nm. This band was not observed when acn was added to solutions of NiL_3 in the absence of high concentration of added ligand and is attributed to $(acn)Ni[P(O\text{-}o\text{-tolyl})_3]_3$ containing an N-bonded acrylonitrile.[4e] Evidence for this assertion is the presence of a similar electronic bond in solutions containing $Ni[P(O\text{-}o\text{-tolyl})_3]_3$, added ligand, and *cis*-2-cyano-2-butene. In that case, where olefin complex formation is suppressed by the two methyl substituents on the double bond, nitrile coordination has been established by ^{31}P NMR.[4e] Though $(RCN)Ni[P(O\text{-}o\text{-tolyl})_3]_3$ complexes of saturated nitriles show no electronic bonds at wavelengths as long as 367 nm, the benzonitrile complex does show an absorbance maximum at 396 nm, presumed to be a consequence of electron delocalization into the nitrile π system.[18]

Equilibrium constants for reaction 4, using $Ni[P(O\text{-}p\text{-tolyl})_3]_4$ or $Ni[P(O\text{-}p\text{-}C_6H_4Cl)_3]_4$, could be readily determined directly with acrylonitrile or in the presence of a small concentration of added liqand in the case of maleic anhydride. Figure 1 shows typical spectra with $Ni[P(O\text{-}p\text{-tolyl})_3]_4$ and increasing concentrations of acn at 40 °C. The calculation of K is shown in Table II. The extinction coefficient at 363 nm (3.5×10^3) was determined at higher temperatures where the reaction went to completion in 1 M acrylonitrile. The value of ϵ was identical with that measured for the isolated $(acn)Ni[P(O\text{-}o\text{-tolyl})_3]_2$ within experimental error. No evidence for the nitrile-bonded $(acn)Ni[P(O\text{-}p\text{-tolyl})_3]_3$ was observed in these experiments [no added $P(O\text{-}p\text{-tolyl})_3$].

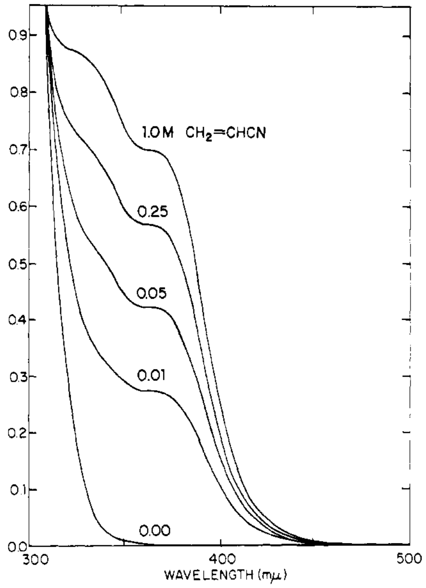

Figure 1. Optical spectra of benzene solutions at 40 °C containing 2.16×10^{-3} M $Ni[P(O\text{-}p\text{-tolyl})_3]_4$ and increasing concentrations of acrylonitrile.

The equilibrium constants at 25 °C and the thermodynamic parameters determined from their temperature dependence are given in Table III. They are divided into three groups depending on the reaction type. For ease of comparison, it is convenient to convert data of other reactions into those of Type 4. Since reaction 4 is the sum of reactions 1 and 2, $K = K_dK_1$ and $\Delta H° = \Delta H_d + \Delta H_1°$. Similarly K_1 (olefin$_2$) = $K'K_1$ (olefin$_1$). Figure 2 shows the result of plotting log K against ν_{sh} of the $(olefin)Ni[P(O\text{-}o\text{-tolyl})_3]_2$ complexes, which may be taken as a measure of the π-acceptor character of the particular olefin. Data for cyclohexene are not included because the reactions did not go far enough to completion in most cases to establish equilibrium constants or limiting electronic spectra.

Several features in Figure 2 may be noted. The equilibrium constants cover a very wide range—18 powers of 10. For a given ligand, K increases markedly as the olefin becomes more electron withdrawing. Electron-withdrawing p-chloro substituents in the phosphorus ligands reduce K *and reduce the sensitivity of K to electronic modifications of the olefin*, as evidenced by a reduced slope of the dashed lines. These electronic effects are those expected if the

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[15] Assuming that 10% dissociation would be detectable in 10^{-4} M solution, an upper limit of 10^{-6} M can be set on K_8.

[16] Figure 1 in ref 4c.

[17] Under these conditions 98.7% of the nickel was initially present as NiL_4. K_d at 25 °C is 6.7×10^{-3} M.

[18] Tolman, C. A. *Inorg. Chem.* 1971, *10*, 1540.

Table III. Equilibrium Constants at 25 °C and Thermodynamic Parameters[a] for Olefin Complex Formation in Benzene

A. $NiL_4 + \text{olefin} \overset{K}{\rightleftarrows} (\text{olefin})NiL_2 + 2L$

L	olefin	K(25 °C), M	ΔH, kcal/mol	ΔS, eu
$P(O\text{-}p\text{-tolyl})_3$	cyclohexene	10^{-13} [b]	34 ± 5	45 ± 15
	1-hexene	5.1×10^{-10}	23 ± 1	35 ± 3
	acn	4.5×10^{-5}	18.5 ± 1.5	42 ± 5
	ma	7.8×10^{-1}	12 ± 1.5	39 ± 5
$P(O\text{-}p\text{-}C_6H_4Cl)_3$	cyclohexene	$< 10^{-14}$ [b]		±
	1-hexene	8×10^{-12}	26 ± 2	36 ± 6
	acn	3.7×10^{-7}	18.5 ± 1.5	32 ± 5
	ma	8.3×10^{-4}	15 ± 1	36 ± 3

B. $NiL_3 + \text{olefin} \overset{K_1}{\rightleftarrows} (\text{olefin})NiL_2 + L$

L	olefin	K_1(25 °C)	ΔH_1, kcal/mol	ΔS, eu
$P(O\text{-}o\text{-tolyl})_3$	cyclohexene	3.5×10^{-4}	5 ± 1	1 ± 3
	1-hexene	5.6×10^{-1}	1 ± 1	2 ± 3
$P(O\text{-}p\text{-Cl-}o\text{-tolyl})_3$	cyclohexene	$< 3 \times 10^{-4}$ [b]		
	1-hexene[c]	2×10^{-1}		
	acn[d]	3.1×10^{3}		

C. $(\text{olefin}_1)NiL_2 + \text{olefin}_2 \overset{K'}{\rightleftarrows} (\text{olefin}_2)NiL_2 + \text{olefin}_1$

L	olefin$_1$	olefin$_2$	K'(25 °C)	$\Delta H'$, kcal/mol	$\Delta S'$, eu
$P(O\text{-}o\text{-tolyl})_3$	styrene[e]	acn	4.0×10^{3}		
	acn	ma	1.0×10^{4}	−6 ± 3	−2 ± 3
$P(O\text{-}p\text{-Cl-}o\text{-tolyl})_3$	acn[f]	ma	0.9×10^{3}		

[a] Results for L = $P(O\text{-}o\text{-tolyl})_3$ are from ref 4c and are given here for comparison. [b] Too small to be readily measured. [c] 0.05 M L added. [d] 0.5 M L added. [e] 1.0 M styrene added. [f] Increasing concentrations of acn were added to solutions containing ca. 2×10^{-3} M $(ma)NiL_2$. The ma complex was generated in solution by adding ma to the $NiL_{3.5}$ complex.

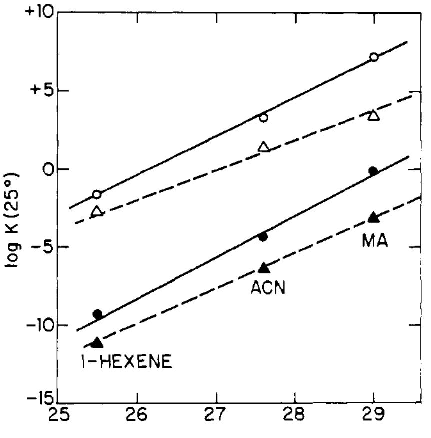

Figure 2. Plot of log K (equilibrium constant) at 25 °C in benzene for the reaction olefin + $NiL_4 \rightleftharpoons (\text{olefin})NiL_2 + 2L$ against ν_{sh} for the $(\text{olefin})Ni[P(O\text{-}o\text{-tolyl})_3]_2$ complexes: ○, L = $P(O\text{-}o\text{-tolyl})_3$; △, L = $P(O\text{-}p\text{-Cl-}o\text{-tolyl})_3$; ●, L = $P(O\text{-}p\text{-tolyl})_3$; ▲, L = $P(O\text{-}p\text{-}C_6H_4Cl)_3$.

strength of the Ni–olefin bond is primarily dependent on π back-bonding from filled metal d orbitals to empty olefinic π^* orbitals, which are lowered in energy in the sequence 1-hexene < acn < ma. The decreased slope with more electronegative ligands is related to our earlier[4c] observation that the sensitivity of olefin binding constants to the energy of the olefin π^* orbitals decreases in the sequence Ni(0) > Rh(I) > Ag(I)—the order of decreasing metal electron density (increasing ionization potential).

Phosphorus ligand steric effects also have a marked influence on the ability of a given olefin to compete with the phosphorus ligand. Values of K for the electronically similar $P(O\text{-}o\text{-tolyl})_3$ and $P(O\text{-}p\text{-tolyl})_3$ ligands for various olefins differ by a constant factor of $\sim 10^8$, giving parallel solid lines in Figure 2. This is just the factor by which K_d's for the two NiL_4 complexes differ.[7] Since $K = K_dK_1$, we therefore infer very similar values of K_1 for the two electronically similar ligands.

While we have not investigated formation of bis(olefin)nickel complexes in detail, it is clear from the work we have done that coordination of a second olefin by eq 3 in these aryl phosphite complexes is unimportant except at very high olefin concentrations. $(\text{Olefin})_2NiL_2$ complexes are *favored*, however, if L is a good electron donor such as PBu_3 or PMe_3. This is again consistent with the idea that back-donation from filled metal d orbitals to empty olefin π^* orbitals is the most important feature of metal–olefin bonding in these Ni(0) complexes. When very large ligands are used, complexes of the type $(\text{olefin})_2NiL$ are favored and the composition in the case of $(C_2H_4)_2NiPCy_3$ has been established by an X-ray crystal structure.[19]

Thermodynamic Data—Strengths of the Ni–Olefin Bonds. The thermodynamic parameters in Table III indicate that the changes in equilibrium constant for a given phosphorus ligand are primarily due to changes in ΔH as the olefin is varied. Entropy changes are essentially constant for a series of olefins. The large positive ΔS of ~ 40 eu associated with reaction 4 (Table III, Part A) arises from $\Delta S_d \approx 43$ eu in the first ligand dissociation step (1).[6] Thus ΔS_1 for reaction 2 is ~ 0. An olefin ligand is gained while a phosphorus ligand is lost.

Estimating Ni–olefin bond strengths from our data requires information about Ni–phosphorus bond strengths, since in most of the equilibria studied, one or more Ni–P bonds are broken. A calorimetric study[20] of the reactions of $Ni(COD)_2$ with various L showed that Ni–P bond strengths in unstrained Ni(0) complexes are about 37 kcal/mol, independent of the electron donor–acceptor

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(19) Kruger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1972**, *34*, 387.

(20) Tolman, C. A. Reutter, D. W.; Seidel, W. C. *J. Organomet. Chem.* **1976**, *117*, C30.

Table IV. Approximate Nickel–Olefin Bond Strengths (kcal/mol)

olefin	ligand P(O-*o*-tolyl)$_3$	 P(O-*p*-tolyl)$_3$	 P(O-*p*-C$_6$H$_4$Cl)$_3$
cyclohexene	32	26	*b*
1-hexene	36	37	34
acn	42[a]	42	42
ma	48	48	45

[a] Calculated assuming that $\Delta S_2 = 0$, using $\Delta H_2 = -RT \ln K_2$ with $K_2 = 4.0 \times 10^4$ from ref 4c. [b] Not determined.

character of L. The smaller values of 23 and 13 kcal/mol,[6] respectively, for ΔH_d for dissociation of the first ligands of Ni[P(O-*p*-tolyl)$_3$]$_4$ and Ni[P(O-*o*-tolyl)$_3$]$_4$ are a consequence of steric strain, which is greater for the more bulky ligand. If we break eq 4 into steps, with eq 9 and 10 being hypothetical,[21] we have

$$NiL_4 = NiL_3 + L \tag{1}$$

$$NiL_3 = NiL_2 + L \tag{9}$$

$$NiL_2 + \text{olefin} = (\text{olefin})NiL_2 \tag{10}$$

$$\text{Net} \quad NiL_4 + \text{olefin} = (\text{olefin})NiL_2 + 2L \tag{4}$$

The strength of the Ni–olefin bond given by $-\Delta H_{10}$ can then be determined from the data in Table III if we take ΔH_d = 23 kcal/mol for L = P(O-*p*-tolyl)$_3$ or P(O-*p*-C$_6$H$_4$Cl)$_3$[22] and ΔH_9 = 37 for all L. The results are given in Table IV.

It can be seen that the Ni–olefin bond strengths are equal within experimental error for L = P(O-*o*-tolyl)$_3$ and P(O-*p*-tolyl)$_3$ but are slightly less on average for the more electronegative P(O-*p*-C$_6$H$_4$Cl)$_3$. The values shown can be compared with the average Ni–olefin bond of 25 kcal/mol in Ni(COD)$_2$.[20] With ΔH_9 = 37 from the calorimetric work in place of the 30 assumed earlier,[4c] we estimate a Ni–ethylene bond strength of 40 kcal/mol in the tritolyl phosphite systems. The great strength of these Ni–olefin bonds explains why we do not observe the dissociation of (olefin)NiL$_2$ complexes in solution and why (C$_2$H$_4$)Ni[P(O-*o*-tolyl)$_3$]$_2$ can be recovered after pumping its solutions to dryness.[4a]

All known (C$_2$H$_4$)NiL$_2$ complexes of nickel have phosphorus ligands with cone angles of 130° or more. The reason why is now clear. Larger ligands cause sufficient strain energy[20] (>20 kcal/mol) in their NiL$_4$ complexes that ethylene can be effective in replacing two phosphorus ligands. With smaller ligands ethylene cannot compete, and NiL$_4$ complexes are preferentially formed.

Registry No. (acn)$_2$NiPBu$_3$, 86901-49-7; (acn)$_2$Ni(PBu$_3$)$_2$, 86901-50-0; (acn)$_2$Ni(PMe$_3$)$_2$, 86901-51-1; (acn)$_2$Ni[P(OMe)$_3$]$_2$, 86901-52-2; (acn)Ni[P(O-*o*-tolyl)$_3$]$_2$, 31666-48-5; (acn)Ni[P(O-*p*-tolyl)$_3$]$_2$, 86901-53-3; (acn)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$, 86901-54-4; (ma)Ni[P(O-*o*-tolyl)$_3$]$_2$, 41813-01-8; (ma)Ni[P(O-*p*-tolyl)$_3$]$_2$, 56558-10-2; (ma)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$, 86901-55-5; P(O-*p*-tolyl)$_3$, 620-42-8; P(O-*p*-C$_6$H$_4$Cl)$_3$, 5679-61-8; P(O-*o*-tolyl)$_3$, 2622-08-4; P(O-*p*-Cl-*o*-tolyl)$_3$, 86901-48-6; ma, 108-31-6; acn, 107-13-1; (acn)$_2$Ni, 12266-58-9; Ni[P(OPh)$_3$]$_4$, 14221-00-2; (acn)Ni[P(OPh)$_3$]$_2$, 86901-64-6; Ni[PMe$_3$]$_4$, 28069-69-4; Ni[P(O-*o*-tolyl)$_3$]$_3$, 28829-00-7; (cyclohexene)Ni[P(O-*p*-tolyl)$_3$]$_2$, 86901-56-6; (1-hexene)Ni[P(O-*p*-tolyl)$_3$]$_2$, 86901-57-7; (cyclohexene)Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_2$, 86901-58-8; (1-hexene)Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_2$, 86901-59-9; (acn)Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_2$, 86901-60-2; (ma)Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_2$, 86901-61-3; (cyclohexene)Ni[P(O-*o*-tolyl)$_3$]$_2$, 53323-39-0; (1-hexene)Ni[P(O-*o*-tolyl)$_3$]$_2$, 53323-45-8; (cyclohexene)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$, 86901-62-4; (1-hexene)Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_2$, 86901-63-5.

Supplementary Material Available: Tables of (1) steric and electronic parameters of the phosphorus ligands used, (2) kinetics of reaction of Ni[P(O-*p*-tolyl)$_3$]$_4$ and Ni[P(O-*p*-C$_6$H$_4$Cl)$_3$]$_4$ with maleic anhydride, and (3) electronic spectral data for the (olefin)NiL$_2$ complexes in benzene (5 pages). Ordering information is given an any current masthead page.

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[21] All of the compounds for which we have any evidence in solution obey the 16- and 18-electron rule: Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337. Ni(acn)$_2$ appears superficially to be a 14-electron complex. Its insolubility in CH$_2$Cl$_2$ in the absence of added phosphorus ligands suggests however that it is polymeric. Attempts to grow single crystals suitable for X-ray structure analysis were unsuccessful.

[22] Equal values of ΔH_d are not unreasonable since both Ni[P(O-*o*-tolyl)$_3$]$_4$ and Ni[P(O-*p*-Cl-*o*-tolyl)$_3$]$_4$ were found to have ΔH_d = 13 kcal/mol.

A Hydrido(μ-hydrido)methyldiplatinum(II) Complex. Reductive Elimination of Methane Induced by Reaction with an Alkyne

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Reaction of [Pt$_2$Cl$_2$(μ-CH$_2$)(μ-dppm)$_2$] with H[SbF$_6$] gives [Pt$_2$Cl(μ-Cl)Me(μ-dppm)$_2$][SbF$_6$] (II) and reduction of II with NaBH$_4$ gives [Pt$_2$H(μ-H)Me(μ-dppm)$_2$][SbF$_6$] (III), characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Complex III undergoes "A-frame inversion" on the NMR time scale, and it is proposed that a transition state with a linear MePtHPtH unit is involved; the activation energy at −60 °C is $\Delta G^{\ddagger}$ = 41 kJ mol^{-1}. Complex III reacts with CF$_3$C≡CCF$_3$ in MeCN solution to give 90% [Pt$_2$H(MeCN)(μ-CF$_3$C═CCF$_3$)(μ-dppm)$_2$][SbF$_6$] and methane and 10% [Pt$_2$Me(MeCN)(μ-CF$_3$C═CCF$_3$)(μ-dppm)$_2$][SbF$_6$] (VIII) and hydrogen. Pure VIII was prepared by the similar reaction of CF$_3$C≡CCF$_3$ with [Pt$_2$(μ-H)Me$_2$(μ-dppm)$_2$][SbF$_6$], with elimination of methane. The alkyne has ability to induce reductive elimination of methane from III or VIII, whereas phosphines induce loss of H$_2$ from III and react only slowly with VIII.

Introduction

There has been considerable interest in the chemistry of alkylhydridotransition-metal derivatives. Such complexes may be formed in the activation of alkanes by C–H oxidative addition,[1,2] and studies of the reductive elimination of alkanes, RH, from alkyl hydrido complexes [L$_n$MHR] may give insight into the mechanism and en-

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[1] Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3722.

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