lency. Thus, the greater *g* anisotropy observed for the $Ni(Se_2C_2(CF_3)_2)_2^-$ complex is interpreted simply as a consequence of the larger spin–orbit coupling in the selenium donor atoms. As additional support for this idea, we note that the low symmetry of the bound ligand *requires* three different components of the *g* tensor, and the heavy donor atoms may give a substantial magnitude to the anisotropy even in the absence of a metal contribution. A large anisotropy in the *g* tensor has been found for several arsine radical cations,[16] and in sulfur containing radicals where *g* values as high as 2.056 have been observed.[17] We must conclude that the greater *g* anisotropy exhibited by $Ni(H_2gma)^-$ as compared to $Ni(gma)^-$ does not necessarily mean that the unpaired electron in the former complex has substantially more *metal* character.

We offer the following interpretation for the dissimilarity in the esr spectra of $Ni(H_2gma)^-$ and Ni(gma). From the fact that $Ni(gma)^-$ has an intact α-diimine linkage which is known to participate widely in electron transfer reactions of the same type as those found for the dithiolene ligands,[18,19] it follows that the α-diimine orbitals are probably of comparable energy to the metal d orbitals, and thus the precise composition and ordering of the molecular orbitals which contribute to the *g* values should be different for the two complexes in question. In addition, it is very possible that the unpaired electron in $Ni(gma)^-$ actually resides in an orbital primarily delocalized over the α-diimine linkage. If this is the case, there is no reason to expect the *g* values for the two complexes to be the same.[20] We propose that it is only when the α-diimine bridge is chemically transformed by hydrogenation that the unpaired electron is forced to spend a large fraction of its time associated with the sulfur donor atoms. This proposal is consistent with the fact that the *g* tensor anisotropies in $Ni(H_2gma)^-$ and $Ni(abt)_2^-$ are virtually the same, and both are significantly larger than that observed for $Ni(gma)^-$.

Acknowledgment. This research was supported by the National Science Foundation.

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Alkenylaryl Compounds of Nickel(II) and Palladium(II). Influence of the Transition Metal on Ligand Proton Chemical Shifts[1]

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Abstract: Compounds of the type *trans*-chloro(2-allylphenyl)bis(triethylphosphine)metal(II) (M = Ni, Pd) and *trans*-X(2-vinylphenyl)bis(triethylphosphine)metal(II) (M = Ni, X = Cl, Br, I, NO_2, CN, NCS, NCO; and M = Pd, X = Br) have been synthesized and characterized. The pmr spectra of the compounds reveal that protons on the hydrocarbon ligands which are in close proximity to the metal exhibit low field shifts relative to chemical shifts of the corresponding protons in the parent hydrocarbons. An explanation of this phenomenon in terms of the paramagnetic anisotropy of the transition metal ion is presented.

Association of the weak temperature-independent paramagnetism exhibited by a number of transition metal complexes with a second order Zeeman effect is well established. Van Vleck[3] proposed that transition metal ions possessing incompletely filled d levels, with all electrons paired in the ground state, may exhibit a weak paramagnetism in a magnetic field which derives from mixing of the ground state energy level with low-lying excited states.[4] The work of Van Vleck and coworkers served as a basis for the Ramsey theory which emphasizes the importance of a second order, paramagnetic contribution to the chemical shielding constant for a nucleus.[5] The importance of this contribution to the shielding constant of a transition metal ion is best documented for $^{59}Co(III)$ complexes.[6] Thus, Proctor and Yu[6a] first attributed the very large differences in the values of ^{59}Co chemical shielding constants for different cobalt complexes to temperature-inde-

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(1) (a) Some of these results have been reported in a preliminary communication: R. G. Miller, D. R. Fahey, and D. P. Kuhlman, *J. Amer. Chem. Soc.*, **90**, 6248 (1968); (b) taken in part from the Ph.D. thesis of D. R. Fahey, University of North Dakota, 1968.

(2) (a) NDEA Predoctoral Fellow, 1965–1968; (b) NDEA Predoctoral Fellow, 1965–1967.

(3) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.

(4) Attributed to the effect of matrix elements of the magnetic field operator between the ground state and excited states.

(5) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

(6) (a) W. G. Proctor and F. C. Yu, *ibid.*, **81**, 20 (1951); (b) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc.*, *A*, 148 (1967).

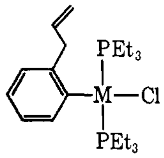
pendent paramagnetism. Griffith and Orgel, drawing from crystal field theory and the theory of Van Vleck for the contribution of second order paramagnetism to magnetic susceptibility, calculated the paramagnetic contribution to the shielding constants for ^{59}Co(III) nuclei.[7] Their views were confirmed by a satisfactory correlation of electronic absorption spectra with ^{59}Co(III) chemical shifts.[8]

Since the magnitude of the paramagnetic contribution to the magnetic susceptibility of a metal ion depends inversely upon the excitation energies between the ground state and low-lying excited states, one would expect this contribution to be of importance in complexes of many other transition metals. This was recognized by Wilkinson,[9] Nyholm and coworkers,[10] and Buckingham and Stephens,[11] the latter having proposed a theory to explain the very large proton chemical shifts in octahedral[11a] and planar[11b] transition metal hydride complexes.

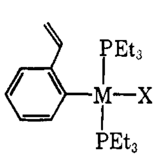
Exploitation of the anisotropy in the magnetic susceptibility of the metal ion in terms of its effect on chemical shifts of ligand protons provides a potentially powerful tool for determination of stereochemistry in transition metal complexes. We have recently synthesized some planar organonickel and -palladium compounds believed to possess features in common with participants in a number of olefin reactions accomplished by a nickel-based coordination catalyst.[12] Some properties of these compounds are described herein. The nmr spectra are of particular interest. They reveal that protons on the hydrocarbon ligands which experience environments in close proximity to the metal, in a region above the bonding plane, exhibit pronounced downfield shifts. We present in this paper the results of a study directed toward an explanation of this phenomenon.

Results and Discussion

Alkenylarylmetal Compounds. Reaction of 2-allylphenylmagnesium chloride with *trans*-dichlorobis(triethylphosphine)nickel(II) or with the palladium analog in tetrahydrofuran–ether has afforded *trans*-chloro(2-allylphenyl)bis(triethylphosphine)nickel(II), **1**, and the corresponding palladium compound, **2**. The styryl compounds, **3a** and **3b**, were readily prepared in the same manner by treatment of the appropriate *trans*-dihalobis(triethylphosphine)nickel(II) with the corresponding 2-vinylphenylmagnesium halide. The derivatives where X = CN, NCS, NCO, NO_2, and I were afforded by displacement reactions in which the appropriate metal salt was mixed with **3a** or **3b** in acetone. 2-Vinylphenylmagnesium bromide reacted with *trans*-dichlorobis(triethylphosphine)palladium(II) to give a mixture of *trans*-chloro(2-vinylphenyl)bis(triethylphosphine)palladium(II) and the bromo analog, **4**. Pure **4** could be obtained by treating the mixture, in acetone, with lithium bromide. The procedures used were essentially the same as those reported by Chatt and Shaw[13] and by Calvin and Coates[14] for the synthesis of other arylnickel and -palladium compounds.



1, M = Ni
2, M = Pd



3, M = Ni; a, X = Cl; b, X = Br;
c, X = I; d, X = NCS; e, X = CN;
f, X = NO_2; g, X = NCO;
4, M = Pd; X = Br

The alkenylarylnickel compounds are yellow to golden brown solids at room temperature, which can be handled in air but show signs of decomposition if their solutions are exposed to the atmosphere for a few hours. The colorless solid palladium compounds can be exposed to the atmosphere for longer periods of time without decomposition. The compounds have all electrons paired in the ground state, as indicated by the absence of any appreciable line broadening in the pmr spectra of freshly prepared deuteriobenzene or hexane solutions. Magnetic susceptibility measurements were not attempted due to the tendency of the organonickel compounds to decompose irreversibly on standing to give small amounts of paramagnetic products. Spectra of **1** and **3** exhibit some line broadening in deuteriochloroform and carbon disulfide due to the formation of paramagnetic material.

The compounds possess the *trans*-planar configuration. In palladium compounds **2** and **4** and in nickel compounds **3c** and **3e**, the phosphine methyl proton resonances consist of an apparent quintet similar to that found in *trans*-bis(triethylphosphine)platinum complexes.[15,16] The observed multiplicity has been attributed to coupling of the methyl protons with both phosphorus nuclei and with the $-CH_2-$ protons,[15–17] J_{P-H} being *ca.* 8 Hz. Only a part of the CH_3 quintet is discernible in the 60-MHz spectra of **3a**, **3b**, **3d**, **3f**, **3g**, and **1** due to overlap with the $-CH_2-$ proton resonance. The two multiplets were separated, however, in the 100-MHz spectrum of **3b**. *trans* configurations are also indicated by the relatively low dipole moments of 2.29 and 2.85 D determined for **1** and **3b**, respectively. These are well within the range of observed values for related compounds possessing the *trans* configuration.[13,18] The ^{31}P nmr spectra of **3b** and **4** were recorded and, in each case, only one multiplet resonance was observed, providing further support for the *trans* assignment in these compounds.[19] The chemical shifts relative to 85% H_3PO_4 were found to be -9.2 ppm ($CDCl_3$), -9.2 ppm (C_6H_6) for **3b** and -11.2 ppm ($CDCl_3$) for **4**. These may be compared to a value of -13.6 ppm (C_6H_6) reported for *trans*-[PtPhCl-

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[12] (a) R. G. Miller, *J. Amer. Chem. Soc.*, **89**, 2785 (1967); (b) R. G. Miller, T. J. Kealy, and A. L. Barney, *ibid.*, **89**, 3756 (1967); (c) R. G. Miller and P. A. Pinke, *ibid.*, **90**, 4500 (1968).

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[16] H. C. Clark and W. S. Tsang, *ibid.*, **89**, 533 (1967).

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[19] We are indebted to Dr. Martin Stiles and Mr. Frank Parker for the ^{1}H 100-MHz and ^{31}P spectra.

(PEt$_3$)$_2$].[20] Models of the compounds indicate that nonbonding interactions between the phosphine ligands and the alkenyl substituent should force the plane of the benzene ring perpendicular to the bonding plane of the transition metal system. These features are expected, based on evidence accumulated in studies of similar compounds possessing substituents at the 2 position in the aromatic ring.[13,14]

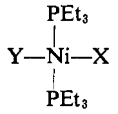
The infrared spectra (Nujol mull) of **1** and **2** exhibit characteristic peaks at 1637 cm^{-1} (vinyl C=C stretch), and at 993 cm^{-1}, 918 cm^{-1} (**1**), and 915 cm^{-1} (**2**) (vinyl C–H out-of-plane deformation vibrations). Peak positions in $CHCl_3$ solution spectra were essentially the same. These data, along with vinyl proton multiplets at τ 3.82, 4.60, 4.74, and 4.90 (C_6D_6) for **1** (3.90, 4.68, 4.79, 4.97 in **2**), indicate that no strong bonding interaction between the olefinic π system and the metal exists in the ground state. Significant changes in the chemical shifts of the vinyl protons from those of the free ligand and the shift to lower frequency of the C=C stretching vibration, characteristic of transition metal–olefin coordination,[21] are absent. The benzylic proton spectrum of each compound is a doublet resonance (due to spin coupling with the adjacent vinyl proton), each peak being further split by weaker long range coupling. The primary benzylic–vinyl proton coupling constants in allylbenzene, **1**, and **2** are all 6.7 ± 0.1 Hz. Formation of a chelate structure *via* intramolecular olefin-metal coordination should render the benzylic protons magnetically nonequivalent leading to a more complex spectrum.

Significant bonding between the vinyl group and the metal in **3** and **4** has been ruled out on similar grounds. The C=C stretching frequencies ranged from 1620 to 1628 cm^{-1}. Nmr spectra of styrene–platinum π complexes exhibit pronounced upfield shifts of the vinyl proton resonances,[21b] whereas *downfield* shifts are observed for the vinyl protons in **3**.

The NCS and NCO ligands in **3d** and **3g** are believed to be bound to nickel through nitrogen in benzene and heptane solution. These assignments are based upon the similar absorption frequencies in the visible electronic spectra (Table I), on the positions of these bands relative to those of the other styrylnickel compounds,[22] and on the nearly identical proton chemical shifts in the pmr spectra. The existence of only one isomer in deuteriobenzene solution was indicated by the presence of only one quartet resonance for each vinyl proton.

Electronic Absorption Spectra. The electronic spectra of compounds **1** and **3** exhibit a number of very intense absorptions in the ultraviolet region which are presumably charge transfer bands (see Experimental Section). In each case, an additional band, much weaker in intensity, is found in the 23,800-29,000-cm^{-1} region. This band is the lowest energy transition observed, no other bands being detected on into the near-infrared. Table I contains the measured frequencies and extinction coefficients of this lowest energy absorption in a number of planar nickel(II) complexes we have synthesized. The variation in the absorption frequency of this band with changes in ligand X in the styryl compounds is CN > NO$_2$ > NCS = NCO > Cl > Br > I, identical with the spectrochemical series.[22] This suggests that the absorption is a d → d band. No low intensity bands were detected in the electronic spectra of palladium compounds **2** and **4**. The spectra exhibited very intense bands in the ultraviolet region.

Table I. Lowest Energy Absorption in the Electronic Spectra of Organonickel Complexes[a]



$$Y\text{—}\underset{PEt_3}{\overset{PEt_3}{Ni}}\text{—}X$$

Y	X	ν, cm^{-1}	ϵ
Cl	Cl	21,100	400
2-Allylphenyl	Cl	24,800	430^b
Trichlorovinyl	Cl	24,500	502^b
o-α-Methylstyryl	Cl	24,600	473^b
o-Styryl	I	23,800	436^b
o-Styryl	Br	24,600	437^b
o-Styryl	Cl	25,200	430^b
o-Styryl	NCO	26,300	552^c
o-Styryl	NCS	26,300	791^c
o-Styryl	NO$_2$	27,900^d	590^c
o-Styryl	CN	28,900	862^c

^{a} Measured in *n*-heptane at *ca.* 22°. ^{b} Minor shoulder character. The total ϵ is reported. ^{c} Substantial shoulder character. The total ϵ is reported. ^{d} ν was the same in benzene solution.

The difficulties encountered in the interpretation of electronic spectra of planar d^8 complexes have recently been emphasized.[23–25] Uncertainty in the frequency assignments of d → d transitions, even in the simplest D_{4h} complexes, due to the paucity of reliable data and the obscurement of weak d → d bands by intense charge transfer bands makes rigorous assignments a formidable problem. Planar nickel compounds generally exhibit one to three bands associated with one or more of the following d → d transitions; $^1A_1 \rightarrow {}^1A_2$, $^1A_1 \rightarrow {}^1B_1$, $^1A_1 \rightarrow {}^1E$. In complexes possessing D_{4h} symmetry, these singlet → singlet transitions are forbidden as electric dipole transitions and the peaks are therefore of very low intensity with extinction coefficients generally $<10^2$.[26] The lowest energy absorption is the $^1A_{1g} \rightarrow {}^1A_{2g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$), which in many cases appears to be the only band observable due to overlap of the other two bands with intense charge transfer bands. In a recent analysis of the $Ni(CN)_4^{2-}$ spectrum, for instance, a shoulder near 30,500 cm^{-1} has been attributed to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition.[24] If the lowest energy band in the spectra of the organonickel compounds is that due to a transition with $^1A_1 \rightarrow {}^1A_2$ character, then it is reasonable to conclude that the corresponding $^1A_1 \rightarrow {}^1E$ and $^1A_1 \rightarrow {}^1B_1$ bands are at higher frequency and are masked by the charge transfer bands.

Hydrocarbon Ligand Proton Magnetic Resonance Spectra. The pmr spectra exhibit large downfield

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(20) F. H. Allen and A. Pidcock, *J. Chem. Soc., A*, 2700 (1968).

(21) (a) R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964), and references cited therein; (b) for a recent reference see T. Kinugasa, M. Nakamura, H. Yamada, and A. Saika, *Inorg. Chem.*, 7, 2649 (1968).

(22) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, pp 109, 121.

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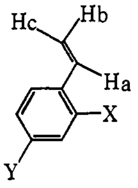
(24) W. R. Mason, III, and H. B. Gray, *ibid.*, **90**, 5721 (1968).

(25) A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *ibid.*, **90**, 5730 (1968).

(26) In compounds of low symmetry such as **1** and **3**, d → d singlet transitions are "less forbidden" in character. See L. E. Orgel, "An Introduction to Transition Metal Chemistry: Ligand Field Theory," Butler and Tanner, Ltd., London, 1960, pp 92–93. This could account for the relatively large extinction coefficients in Table I.

Table II. Vinyl Proton Chemical Shifts in Styrene Derivatives[a]



Substituent			Chemical shifts, τ			τ(styrene) − τ(deriv)		
X	Y	Solvent	H_a	H_b	H_c	Δa	Δb	Δc
H	H	$CDCl_3$	3.33	4.85	4.35			
H	H[b]	CCl_4	3.33	4.80	4.34			
H	H	C_6D_6	3.40	4.93	4.40			
NO_2	H[b]	CCl_4	2.81	4.55	4.32	0.52	0.25	0.02
H	NO_2[b]	CCl_4	3.22	4.54	4.13	0.11	0.26	0.21
$Ni(PEt_3)_2Cl$	H	$CDCl_3$	2.15	4.71	3.65	1.18	0.14	0.70
$Ni(PEt_3)_2NO_2$	H	C_6D_6	1.99	4.57	3.35	1.41	0.36	1.05
$Ni(PEt_3)_2Cl$	H	C_6D_6	1.99	4.70	3.55	1.41	0.23	0.85
$Ni(PEt_3)_2Br$	H	C_6D_6	2.02	4.70	3.65	1.38	0.23	0.75
$Ni(PEt_3)_2I$	H	C_6D_6	2.13	4.74	3.77	1.27	0.19	0.63
$Ni(PEt_3)_2NCO$	H	C_6D_6	2.22	4.70	3.45	1.18	0.23	0.95
$Ni(PEt_3)_2NCS$	H	C_6D_6	2.40	4.72	3.45	1.00	0.21	0.95
$Ni(PEt_3)_2CN$	H	C_6D_6	2.70	4.77	3.67	0.70	0.16	0.73
$Pd(PEt_3)_2Br$	H	C_6D_6	2.44	4.85	4.27	0.96	0.08	0.13
H	$Pd(PEt_3)_2Br$	C_6D_6	3.32	4.94	4.33	0.08	−0.01	0.07

[a] Chemical shifts of all styrylmetal compounds and the styrene standard were determined at ambient temperature (*ca.* 37°). The chemical shifts exhibited no temperature dependence between 37° and 69° and no concentration dependence in the detection range of the spectrometer. The C_6D_6 solution spectra were calibrated using the side-banding technique described in the Experimental Section, tetramethylsilane being employed as an internal standard. The precision in the τ values is greater than ±0.5 Hz. [b] The chemical shifts of styrene and the nitrostyrenes in carbon tetrachloride were reported by R. H. Wiley and T. H. Crawford. *J. Polym. Sci., Part A*, **3**, 82 (1965).

Table III. Benzylic Proton Chemical Shifts in 2-Allylphenyl and *o*-Methyl Derivatives[a]

Compound	Chemical shift, τ	Δ[b]	Solvent
Allylbenzene	6.79		C_6D_6
Allylbenzene	6.59		$CDCl_3$
trans-Cl(2-allylphenyl)$(PEt_3)_2$Ni	5.70	1.09	C_6D_6
trans-Cl(2-allylphenyl)$(PEt_3)_2$Ni	5.80	0.79	$CDCl_3$
trans-Cl(2-allylphenyl)$(PEt_3)_2$Pd	6.15	0.64	C_6D_6
trans-Cl(2-allylphenyl)$(PEt_3)_2$Pd	6.25	0.34	$CDCl_3$
Toluene	7.85		C_6D_6
Toluene	7.63		$CDCl_3$
trans-Br(*o*-tolyl)$(PEt_3)_2$Ni	7.18	0.45	$CDCl_3$
trans-(*o*-tolyl)$(C_2Cl_3)(PEt_3)_2$Ni	7.22, 7.30	0.41, 0.33	$CDCl_3$
trans-(*o*-tolyl)$(C_2Cl_3)(PEt_3)_2$Ni	7.14, 7.22	0.71, 0.63	C_6D_6
m-Xylene	7.66		$CDCl_3$
trans-Br(2,6-dimethylphenyl)$(PEt_3)_2$Ni	7.08	0.58	$CDCl_3$
Isopropylbenzene	7.27		C_6D_6
trans-Cl(2-isopropylphenyl)$(PEt_3)_2$Ni	5.56	1.71	C_6D_6

[a] The C_6D_6 solution spectra of allylbenzene, the 2-allylphenylmetal derivatives, cumene, and the 2-isopropylphenylnickel compound were calibrated using the side-banding technique described in the Experimental Section. Other chemical shifts were measured directly from the tetramethylsilane resonance which was employed as an internal standard. [b] τ(hydrocarbon) − τ(derivative), measured in the same solvent.

shifts of the resonances of two of the vinyl protons in compounds **3** and of the benzylic protons in **1** relative to the resonance positions of corresponding protons in the parent hydrocarbons. The low field shifts are not associated with a particular solvent, the same phenomena being observed in deuteriobenzene, hexane, tetrachloroethylene, and deuteriochloroform solutions. The vinyl proton spectra of compounds **3** are typical ABC spectra characteristic of the styrene moiety[27] except for the anomalous low field shifts of protons H_a and H_c. The resonance assignments for the vinyl protons are unambiguous, being based upon the larger *trans vs. cis* proton–proton spin coupling constants. The values were 17.5–17.8 Hz for J_{ac}, 10.8–11.0 Hz for J_{ab}, and ~1.2 Hz for J_{bc}. These may be compared to +17.5, +10.9, and +1.1 Hz reported for styrene.[27] The proton spectrum of the allyl group in **1** is very similar to that of allylbenzene with the exception of the low field resonance of the benzylic protons. The downfield shifts of the same protons in the palladium compounds **2** and **4** are not as pronounced, H_c in **4** showing little change from H_c in styrene. Tables II and III contain chemical shift data for these compounds alongside those available for other pertinent compounds. Spectra of the alkenylaryl ligand protons in **3b** and **1** are presented in Figures 1 and 2.

Discussion of the Proton Magnetic Resonance Spectra. The antishielding of ligand protons could derive from any one or a combination of principal sources: (a) the local diamagnetic contribution to the proton shielding constant, (b) the contribution from the field associated with the ring current of the aromatic system, (c)

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(27) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

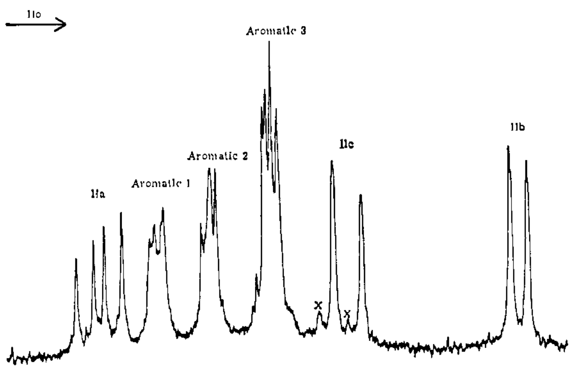
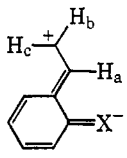


Figure 1. The 100-MHz pmr spectrum of the styryl ligand in **3b** recorded at ambient temperature in C_6D_6 solution. X denotes impurity.

the contribution from the magnetic field associated with a neighboring atom.

a. Electrical Influence of the Nickel Substituent. The importance of source a would depend upon the ability of the nickel substituent to reduce electron density around the protons in question. The vinyl protons in the styryl derivatives seem to serve as a suitable probe in the investigation of the nature and magnitude of this capability. If conjugative withdrawal of electrons were mainly responsible for the antishielding in compounds **3**, H_b and H_c should *both* be shifted further downfield than is H_a as in *p*-nitrostyrene due to the importance of contributions to the resonance hybrid such as **5**. Large downfield shifts are observed only for H_a and H_c in **3**.[28] Compound **6** was synthesized for comparison with the 2-vinylphenyl isomer. The chemical shifts of vinyl protons in styrene are almost insensitive to the presence of a bromobis(triethylphosphine)palladium substituent in the *para* position (Table II). A 4-vinylphenylnickel derivative could not be isolated in a pure state.[30] The pmr spectrum (C_6D_6) of a mixture of compounds derived from reaction of *trans*-dichlorobis(triethylphosphine)nickel(II) with 4-vinylphenylmagnesium bromide exhibited resonances near τ 3.3, 4.9, and 4.3, assigned to H_a, H_b, and H_c, respectively.



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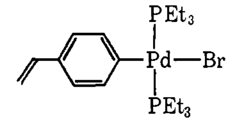

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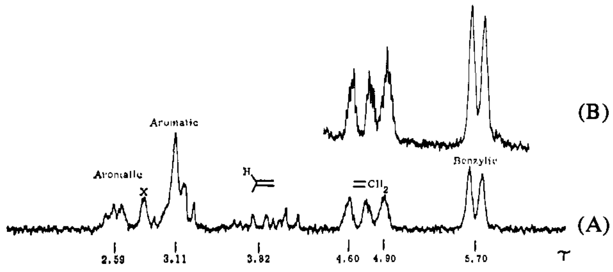

Figure 2. (A) The 60-MHz pmr spectrum of the 2-allylphenyl ligand in **1** recorded at ambient temperature in C_6D_6 solution. X denotes proton impurity in C_6D_6. (B) A portion of the spectrum of **1** in C_6H_6 illustrating the best resolution obtained with this compound.

Parshall[15] has determined the ^{19}F shielding parameters for a series of *m*- and *p*-fluorophenylplatinum(II) complexes possessing the same auxiliary ligands as the compounds listed in Tables II and III. His results indicate that the $-Pt(PEt_3)_2X$ substituent when bound to fluorobenzene is an electron donor by both resonance and inductive mechanisms. One would predict that the direction of the effects due to analogous palladium and nickel substituents would be the same. Neither the *meta* nor the *para* ^{19}F shielding parameter sequence for a variety of *trans* ligands (X) resembles the sequence of H_a and H_c chemical shifts in compounds **3**.

The aromatic proton spectra in **1**, **2**, **3**, and **4** consist of complex multiplets which have not been analyzed. However, the absence of any pronounced downfield shifts relative to chemical shifts of aromatic protons in the parent hydrocarbons (Table IV) also precludes electron withdrawal by the transition metal substituent as being a major factor. In fact, part of the aromatic proton absorption is upfield. The downfield shifts of H_a and H_c in **3** and of the benzylic protons in **1** are much more pronounced than the shift of the lowest field aromatic proton resonance from that in the parent compounds. Vinyl proton H_a in **3a** appears *downfield* from the aromatic proton resonances, shifted *ca.* 1.4 ppm from the resonance of the corresponding proton in styrene. The shift for H_c is 0.85 ppm, whereas the

Table IV. Proton Magnetic Resonance Positions of the Aromatic and Triethylphosphine Proton Multiplets in **3** and **4**[a]

Ligand X	Aromatic multiplets, τ[b] 1	 2	 3	Et3P multiplets, τ[c,e] CH2	 CH3
3 NO2	2.60	2.81	3.16	8.93	9.06
Cl	2.43	2.74	3.14	8.88	9.00
Br	2.42	2.77	3.15	8.67	9.01
I	2.51	2.78	3.13	8.58	9.05
NCO	2.61	2.81	3.14	8.94	9.08
NCS	2.68	*d*	3.15	8.94	9.08
CN	2.69	2.79	3.10	8.67	9.06
4 Br	2.63	3.06		8.45	9.07

[a] Measured in C_6D_6 solution at ambient temperature. τ values are for the estimated center of each multiplet. [b] Determined by the side-banding technique described in the Experimental Section. [c] Measured directly from the tetramethylsilane signal, present as an internal standard. [d] Multiplet 2 obscured by proton impurity in C_6D_6. The aromatic proton values may be compared to τ 2.85 determined for styrene in C_6D_6. [e] The reported values for triethylphosphine are τ 9.04 (CH_3) and 8.8 (CH_2): J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

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(28) 2-Nitrostyrene is not used for comparison here because the nitro and vinyl substituents cannot simultaneously be coplanar with the aromatic ring, resulting in steric inhibition to resonance.[29]

(29) R. H. Wiley and T. H. Crawford, *J. Polym. Sci., Part A*, **3**, 82 (1965).

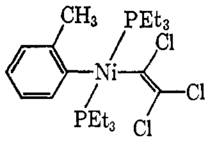
(30) As expected,[13] the product did not exhibit the stability of the *ortho*-substituted compounds. The structure assignment is based upon the mode of preparation and on infrared and nmr spectra. The material appeared to be a mixture of the chloro and bromo analogs and was stable in solution under nitrogen for sufficient time to obtain the spectra. The complete characterization of the more stable **6** provided spectra for comparison and therefore aided in the identification.

analogous shift for the benzylic protons in **1** relative to allylbenzene is 1.09 ppm. Although the antishielding of the corresponding protons in the palladium analogs is much less pronounced, the positions of the lowest field aromatic proton multiplets are very similar to those in the nickel compounds. The transmission of any electrical effect, the magnitude of which depends largely on the distance of the affected proton from the metal, should result in a much greater antishielding of the aromatic proton *ortho* to the metal if the same affect is responsible for the anomalous shifts of the alkenyl substituent protons.

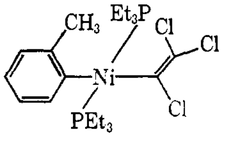
b. **Influence of the Aromatic Ring Current.** The resonances of protons H_a and H_c in styrene are found at an abnormally low field for alkene protons. This has been attributed by Banwell and Sheppard to the effect of the magnetic field associated with the aromatic ring current.[27] Their calculations indicate that protons a, b, and c are at distances 3.5, 4.9, and 3.8 Å from the center of the ring when the molecule is planar. Using these values, they have calculated the ring current contributions to the chemical shifts to be *ca.* -0.7, -0.02, and -0.5 ppm for H_a, H_b, and H_c, respectively.[27,31] These values represent the maximum ring current contributions in the undistorted molecule. The low-field shifts of ligand protons in **1** and **3** could be attributed, in part, to the aromatic ring current. This would be plausible if the magnitude of the ring current in the nickel compounds were greater than in the hydrocarbons, or if the conformations in which the affected protons are closest to the periphery of the ring were more highly populated in the nickel compounds. The former condition is clearly not satisfied. This would demand that resonances of some or all of the aromatic protons be shifted further downfield than are those of the alkenyl ligand protons. It is conceivable that the vinyl group in **3** and the propenyl moiety in **1** are restricted to conformations which place H_a and H_c in **3** and the benzylic protons in **1** in the deshielding region of the aromatic ring. These appear to be the preferred conformations, providing the least contact with the phosphine ligands. The fact remains that the two equivalent planar conformations must already be highly populated in the parent styrene molecule at room temperature.[27,32] Also, examination of the magnitude of the chemical shifts of the low field benzylic and vinyl protons in **1** and **3** from allylic or vinyl proton resonances in compounds where no ring current effect exists indicates that some other factor is largely responsible.

The methyl proton resonances for the tolyl derivatives in Table III exhibit the same anomalous low field shifts. Free rotation of the *o*-methyl groups in these organonickel compounds is clearly not restricted. Therefore, any added influence of the aromatic ring current on proton chemical shifts over that found in the free hydrocarbons should be small. With the exception of the trichlorovinylnickel compound, the *o*-methyl proton spectra consist of a single sharp peak at ambient temperature. The multiplicity and chemical shift of this resonance in *trans*-bromo(*o*-tolyl)bis(triethylphosphine)nickel(II) remained the same on cooling its solution to $-80°$. Also, the CH_3 C–H stretching frequency was found to be identical with that in toluene at 2870 cm^{-1}. The chemical shifts, measured in benzene solution, of the tolyl methyl protons in some compounds of the type *trans*-X(*o*-tolyl)bis(dimethylphenylphosphine)nickel(II) were reported by Moss and Shaw.[33] All of the resonances are downfield from that of toluene which we have measured to be τ 7.85 in benzene solution.

The *o*-CH_3 proton resonance in *trans*-*o*-tolyl(trichlorovinyl)bis(triethylphosphine)nickel(II), **7**, appears as two peaks at τ 7.22 and 7.30, 4:3 ratio, in $CDCl_3$ solution. The nonequivalence of the methyl protons in this instance appears to result from the existence of two conformers, **7i** and **7ii**, in solution. Molecular models suggest that rotation of both the *o*-tolyl and trichlorovinyl ligands about the C–Ni bonds should be severely restricted. Elevation of the temperature of a chlorobenzene solution of the compound to the decomposition temperature of the complex did not cause the peaks to coalesce. Evidence for this explanation would be available on examination of the pmr spectrum of *trans*-2,6-dimethylphenyl(trichlorovinyl)bis(triethylphosphine)nickel(*II*). Attempts to synthesize the compound have been unsuccessful.



7i



7ii

c. **Influence of the Metal Ion Magnetic Field.** We believe the paramagnetic anisotropy of the nickel ion to be the major cause of the antishielding. To examine the effect of the induced field associated with the metal ion on ligand proton chemical shifts, we draw on the predictions of Buckingham and Stephens, who have explained the high field proton shifts in planar platinum hydride complexes in terms of the paramagnetic anisotropy of the metal.[11b] Implicit in their theory is the prediction that protons above the metal and the bonding plane should experience downfield shifts.

As stated in the introduction, the paramagnetic contribution to the magnetic susceptibility of the metal ion derives from a mixing of the electronic ground state with low-lying excited states. Thus, in a magnetic field, the molecule exists in a new ground state which possesses some of the character of low-lying excited states. The orbital angular momentum and, therefore, the magnetic moment of the new state will have excited state character. The electronic spectra of the organonickel compounds exhibit absorptions of low enough energy to be responsible for an induced paramagnetism in a magnetic field.[8,10,11]

The antishielding of ligand protons in the organonickel compounds can be interpreted as being a consequence of two major contributing factors. First, the fixed geometry of these complexes dictates that the average magnetic environment of the benzylic protons in **1**, of H_a (and probably of H_c) in **3**, and of the *o*-CH_3 protons in the tolyl derivatives must include regions in

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(31) (a) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); (b) J. S. Waugh and R. W. Fessenden, *J. Amer. Chem. Soc.*, **79**, 846 (1957); 80, 6697 (1958); (c) D. G. Farnum and C. F. Wilcox, *ibid.*, **89**, 5379 (1967).

(32) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 510 (1965).

(33) J. R. Moss and B. L. Shaw, *J. Chem. Soc., A*, 1793 (1966).

close proximity to the metal near an apical site in the complexes. Association of the antishielding with nickel-proton proximity is emphasized by the relatively large Δ value for the benzylic proton in *trans*-chloro-(2-isopropylphenyl)bis(triethylphosphine)nickel(II) (Table III). The clearly preferred orientation of the isopropyl group places the affected proton above the metal. Second, the paramagnetic contribution to the susceptibility of the nickel ion perpendicular to the bonding plane should be greater than that in the plane. The sign and magnitude of the paramagnetic contribution of the nickel field to the screening tensor of a ligand proton will depend upon the relative magnitudes of the three principal susceptibilities of the nickel ion, $\chi_{Ni}{}^{i}$, in directions which make angles θ_i with the nickel-proton line, if the primary field, H_o, is in the ith direction.[34] These orientations are described in Figure 3. The phosphine ligands are omitted for clarity. Orientation a places the direction of the applied field perpendicular to the bonding plane whereas, in b and c, the direction of the field is coincident with the plane. To take a specific example, the mean paramagnetic contribution to the proton screening constant for the conformational extreme in which H_a in **3a** is in closest proximity to the metal will be given by eq **1** where R is the proton–nickel internuclear distance, i = a, b, c, and χ is positive.[34] Based on examination of molecular models the θ's for H_a in **3a** are estimated to be 24, 90, and 66° for orientations a, b, and c, respectively. Equation 1 then reduces to (1a). This indicates that in orientation a, the proton experiences a stronger field from the nickel atom than in b or c, and is in a deshielding region. The proton is shielded in orientations b and c. The relative magnitudes of the paramagnetic

$$\Delta\sigma = (1/3)R^{-3}\sum\chi_{Ni}{}^{i}(1 - 3\cos^2\theta_i) \qquad (1)$$

$$\Delta\sigma = (1/3)R^{-3}(-1.5\chi_a + 1.0\chi_b + 0.5\chi_c) \qquad (1a)$$

contributions to the susceptibility parallel and perpendicular to the bonding plane are approximated by taking a D_{4h} planar complex as a model. This model differs from the low symmetry organonickel complexes in that the ^1E level is degenerate and only $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1E_g$ mixing contributes to the induced paramagnetic susceptibility. The same approximation has been used in the theoretical treatment of shielding effects in planar platinum hydride complexes.[11b] The contributions are given in eq 2 and 3, where C_M is the metal d orbital coefficient in the equation for the MO, N is Avogadro's number, and β is the Bohr magneton.[23] Using the symbolism of Ballhausen,[35] $\chi_\parallel$ is the susceptibility when the principal symmetry axis (z axis in this case) is coincident with the applied field, $\chi_\perp$ being the susceptibility when this axis is perpendicular. The antishielding of a proton above the bonding plane in the organonickel compounds thus arises from the large contribution to the proton shielding constant afforded by principal orientation a in Figure 3, *i.e.*, χ_a is greater than χ_b or χ_c, and the large coefficient of χ_a in eq 1a reflects the stronger secondary field experienced by the proton in this orientation. A low-field shift for the proton at the 6 position in the aromatic ring is also predicted, although its magnitude should be smaller than that observed for alkenyl substituent protons because the former is further from an apical site. It is noteworthy that if free rotation about the phenyl carbon–metal bond were operative, the coefficients of χ_a and χ_b would each be zero, and the remaining contribution would shield the protons in question.

$$\chi_\perp = \frac{(C_M)^2 4N\beta^2}{\Delta E(^1A_{1g} \rightarrow {}^1E_g)} \qquad (2)$$

$$\chi_\parallel = \frac{(C_M)^2 16N\beta^2}{\Delta E(^1A_{1g} \rightarrow {}^1A_{2g})} \qquad (3)$$

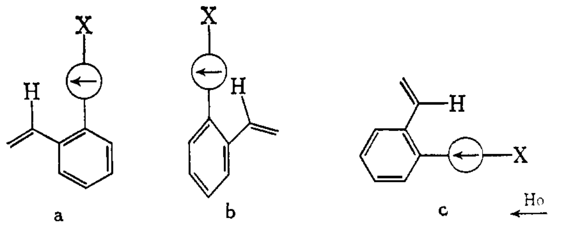

Figure 3. The three principal orientations of a *trans*-X(2-vinylphenyl)bis(triethylphosphine)nickel(II) compound in a magnetic field.

This explanation of the antishielding of ligand protons is supported by the observations of Busch and coworkers in a study of nickel(II) complexes possessing ligands of an entirely different nature. The low-field shift of the axial geminal methyl proton resonance in hexamethyl-1,4,8,11-tetraazacyclotetradecadienenickel(II) isomers aided in the structure assignments for these compounds.[36] The axial methyl protons are restricted to a region above the bonding plane and these workers suggested that the low-field shifts were interpretable in terms of the paramagnetic anisotropy of the metal ion. The dissimilarity in the electronic requirements of the ligands in the arylnickel compounds and Schiff base–amine complexes supports our contention that the low-field shifts are not caused by reduction of electron density around the proton. This difference also suggests that the magnetic anisotropy is not associated with a particular ligand or ligand–metal bond.

The pronounced low-field shifts of H_a and H_c in **3** indicate that *both* protons experience magnetic environments which include regions near an apical site in the complexes. Support for this view is found in the pmr spectrum of *trans*-chloro(*o*-α-methylstyryl)bis(triethylphosphine)nickel(II), **8**. The resonance for H_c (C_6D_6) appears at τ 1.37, 3.31 ppm downfield from that of the corresponding proton in α-methylstyrene! The allylic CH_3 and H_b resonances are found at τ 7.66 and 4.50, compared to values of 8.02 and 5.01 in the parent hydrocarbon. The resonance assignments for H_b and H_c are based upon the reported larger α-CH_3-*cis*-vinyl proton spin–spin coupling constant *vs.* the corresponding *trans* coupling in α-methylstyrene and its derivatives.[37] The low-field vinyl proton multiplet in Figure 4 is therefore assigned to H_c. We interpret these data as indicating that rotation of the propenyl group in **8** is restricted due to the presence of the α-CH_3 group, placing H_c near an apical site. The chemical

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[34] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 178.

[35] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 30.

[36] L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, 90, 6938 (1968).

[37] D. R. Davis and J. D. Roberts, *ibid.*, **84**, 2252 (1962).

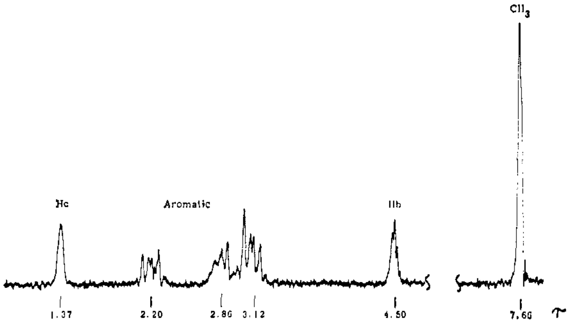
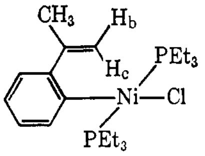


Figure 4. The 60-MHz spectrum of the α-methylstyryl ligand in **8** recorded at ambient temperature in C_6D_6 solution.

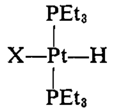
shifts of the H_c and α-CH_3 resonances exhibited a temperature dependence between 37 and 100°, H_c shifting 13 Hz to high field and the α-CH_3 resonance shifting 3 Hz to low field with increase in temperature. The change was reversible and reproducible. The complex, in C_6D_6 solution (sealed tube), decomposed above 100° producing paramagnetic material which caused severe line broadening.



8

The less pronounced antishielding of ligand protons in the palladium compounds probably results, in large part, from the larger ΔE's (d → d). Molecular models suggest that increasing the size of the metal should favor the conformation that places H_a in **4** above the metal and the bonding plane. This may account for the small Δ observed for H_c (Table II).

The effect of the variation of ligand X on the chemical shifts of the M–*H* proton,[38,39] the ^{31}P nucleus,[40] and the ^{195}Pt nucleus[40] in complexes **9** has been studied. The paramagnetic anisotropy of platinum apparently has little influence on the ^{31}P chemical shifts.[40] This would



$$\begin{array}{c} PEt_3 \\ | \\ X{-}Pt{-}H \\ | \\ PEt_3 \end{array}$$

9

also appear to be the case in the organonickel complexes. It has been predicted that variation in τ for the proton bound to platinum in **9** should be strongly dependent upon the M-H internuclear distance.[11b] A linear correlation of the proton chemical shift with the Pt-H stretching frequency, where ligands X are variously substituted benzoates, supports this prediction.[39] However, when the nature of X is varied greatly (as is X in compounds **3**, Table II) the cause of the variation in σ_p with X is more complex.[39] We feel that it is significant that the variation in τ for H_c in **3** with ligand X, I > CN > Br > Cl > NCS = NCO > NO_2, is almost identical with the inverse variation of the Pt-H proton chemical shift in compounds **9**.[38b] With the exception of NCO and NCS, the variation of τ for H_a in **3** follows the same inverse trend. This would seem to indicate that the same factors which cause the variation in the high-field shifts in **9** determine the magnitudes of the low-field shifts in **3**.

The importance of the second-order paramagnetic contribution to the magnetic susceptibility of the metal ion in the organonickel compounds could be related to their low symmetry for the same reasons that the importance of this contribution increases relative to that of the diamagnetic term with decrease in symmetry in octahedral Co(III) complexes.[41] Thus, paramagnetic anisotropic shielding of ligand protons in planar transition metal complexes of low symmetry may be a general phenomenon.

Experimental Section

All reactions were conducted under a nitrogen atmosphere in dry deoxygenated solvents. Melting points are uncorrected. Elemental analyses and molecular weight determinations were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. The C_6D_6 solution spectra were calibrated through introduction by the audiooscillator of TMS "side-band" peaks within 20 Hz of the low field resonances in the recorded spectra.[42] Proton ratios as determined from integrated peak areas were, in all cases, consistent with the proposed structures. The ^{31}P nmr spectra were recorded at 40.4 MHz on a Varian HA-100 instrument and were calibrated by introduction of a peak 1968 Hz to low field of the sample resonance. P_4O_6 was used as an external standard.[43] The chemical shifts from 85% H_3PO_4 reported in the text were then determined from the accurately known shift of P_4O_6 from H_3PO_4.[43] The ultraviolet-visible and infrared spectra were recorded on Cary 14 and Beckman IR 12 spectrophotometers, respectively. Ultraviolet spectra were measured in *n*-heptane solution.

Dipole moments were determined in benzene solution using the method reported by Chatt and Shaw.[18] Five concentrations were used in the determination of each value. The atom polarization was estimated to be 15% of the electron polarization. Dielectric constants were measured with the DM01 dipolemeter manufactured by Wissenschaftlichen-Technische, Werkstatten.

Materials. Tetrahydrofuran was purified by distillation from lithium aluminum hydride and was stored over molecular sieves. Diethyl ether was purified by distillation from phosphorus pentoxide. Hydrocarbon solvents were dried over silica gel. Aluminum oxide used for chromatography was Baker "Analytical Reagent for Chromatography," pH 3.8.

1-Allyl-2-chlorobenzene was prepared from allyl chloride and 2-chlorophenylmagnesium iodide according to the procedure of Nyholm, *et al.*[44] 2-Bromostyrene and 4-bromostyrene were purchased from K and K Laboratories, Inc. and were distilled immediately prior to use. *trans*-Dichlorobis(triethylphosphine)nickel(II) and the bromo analog were prepared by the procedure of Jensen and Nygaard.[45] *trans*-Dichlorobis(triethylphosphine)palladium(II) was prepared from potassium tetrachloropalladate and triethylphosphine according to the method of Mann and Purdie.[46] Triethylphosphine was purchased from Orgmet, Inc., and was used without further purification. Magnesium turnings were ground in a mortar to expose fresh surface prior to use.

Preparation of Alkenylaryl Metal Compounds. ***trans*-Chloro(2-allylphenyl)bis(triethylphosphine)nickel(II), 1.** Magnesium turnings, 0.486 g (20 mg-atoms), were treated with 30 ml of tetrahydrofuran. After 2 drops of methyl iodide were added, the

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[38] (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962); (b) J. Powell and B. L. Shaw, *ibid.*, 3879 (1965).

[39] P. W. Atkins, J. C. Green, and M. L. H. Green, *ibid.*, *A*, 2275 (1968).

[40] R. R. Dean and J. C. Green, *ibid.*, 3047 (1968).

[41] C. J. Ballhausen and R. W. Asmussen, *Acta Chem. Scand.*, 11, 479 (1957).

[42] G. V. D. Tiers, *J. Phys. Chem.*, 62, 1151 (1958).

[43] A. C. Chapman, J. Homer, D. J. Mowthorpe, and R. J. Jones, *Chem. Commun.*, 121 (1965).

[44] L. V. Interrante, M. A. Bennett, and R. S. Nyholm, *Inorg. Chem.*, 5, 2212 (1966).

[45] K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, 3, 474 (1949).

[46] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

mixture was warmed to light reflux and a solution of 3.05 g (20 mmol) of 1-allyl-2-chlorobenzene in 20 ml of tetrahydrofuran was added slowly. The resulting mixture was refluxed gently until essentially all of the magnesium had disappeared, *ca.* 24 hr. (Glpc analysis of the hydrocarbon product from hydrolysis of the Grignard reagent indicated the presence of only one monomeric component with a retention time identical with that of allylbenzene.) The solution of the Grignard reagent was then filtered and added dropwise to a stirred solution of 3.65 g (10 mmol) of *trans*-dichlorobis(triethylphosphine)nickel(II) in 50 ml of ether, cooled to −10°. The addition was terminated when the red reaction mixture turned amber in color, after which the mixture was stirred for *ca.* 5 min. The solvent was then removed *in vacuo* and the residue was extracted with four 50-ml portions of pentane, the extracts were filtered in a fritted disk funnel, and the pentane was removed *in vacuo* from the filtrate. Recrystallization of the partly crystalline residue from a small volume of cold methanol afforded 3.85 g (86%) of golden brown crystals of **1**, mp 63–65°. Alternatively, the residue could be dissolved in pentane and chromatographed on acid-washed alumina under nitrogen, eluting with ether–pentane mixtures, affording comparable yields of **1** after recrystallization.

Anal. Calcd for $C_{21}H_{39}ClNiP_2$: C, 56.32; H, 8.78; Cl, 7.92; Ni, 13.12; P, 13.84; mol wt, 448. Found: C, 56.27; H, 8.77; Cl, 7.99; Ni, 13.07; P, 13.81; mol wt (cryoscopic in benzene), 451.

trans-**Chloro(2-allylphenyl)bis(triethylphosphine)palladium(II), 2.** The Grignard reagent of 1-allyl-2-chlorobenzene (13 mmol) in tetrahydrofuran, prepared in the above manner, was added dropwise to a solution of 4.13 g (10 mmol) of *trans*-dichlorobis(triethylphosphine)palladium(II) in 50 ml of ether, cooled to 0°. After addition was complete, the reaction mixture was stirred for 5 min, during which the mixture turned black. The solvent was then rapidly removed *in vacuo*, and the residue was extracted with four 50-ml portions of pentane containing a small amount of benzene. The combined extracts were filtered and concentrated after which the solution was placed on a column of acid-washed alumina. Fractions eluted with 40:60 benzene:ether were recrystallized from cold hexane affording 2.38 g (48%) of colorless crystals of **2**, mp 92–93°.

An excess of Grignard reagent was used in the synthesis of all of the organopalladium compounds to ensure complete reaction. It was found that unreacted $(Et_3P)_2PdCl_2$ was extremely difficult to separate from the organopalladium products.

Anal. Calcd for $C_{21}H_{39}ClPdP_2$: C, 50.92; H, 7.94; mol wt, 495. Found: C, 50.95; H, 7.81; mol wt (cryoscopic in benzene), 501. λ_{max} 295 mμ (sh) (ϵ 4700), 255 (15,000), 230 (sh) (21,800), 208 (45,800).

trans-**Chloro(2-vinylphenyl)bis(triethylphosphine)nickel(II), 3a.** The Grignard reagent of 2-chlorostyrene was prepared in the same manner as was 2-allylphenylmagnesium chloride. Its reaction with *trans*-dichlorobis(triethylphosphine)nickel(II) was conducted using the same procedure as for the preparation of **1** with the exception that both the Grignard reagent and the nickel precursor, 2.20 g (5.90 mmol), were in tetrahydrofuran solution. The resulting residue, after removal of the reaction solvent, was extracted with 100 ml of hexane, the extract was filtered, and the volume of the filtrate was concentrated *in vacuo* to 25 ml. This solution was then placed on a 35 × 3.0 cm column of acid-washed alumina prepared in deoxygenated hexane. Elution of the product under nitrogen with a 1:4 ether:hexane mixture afforded a 31.5% yield of **3a** which was recrystallized from hexane to give yellow-brown crystals, mp 91–92°.

Anal. Calcd for $C_{20}H_{37}ClNiP_2$: C, 55.40; H, 8.60; Cl, 8.18; P, 14.28. Found: C, 55.30; H, 8.49; Cl, 8.16; P, 14.09. λ_{max} 315 mμ (sh) (ϵ 3300), 295 (8200), 256 (20,300), 230 (36,300).

trans-**Bromo(2-vinylphenyl)bis(triethylphosphine)nickel(II), 3b.** The procedure was the same as for **3a** except that 2-vinylphenylmagnesium bromide was added to *trans*-dibromobis(triethylphosphine)nickel(II), 8.7 g (19 mmol). The residue, after removal of the reaction solvent, was extracted with pentane. The combined extracts were filtered, and the pentane was removed *in vacuo* from the filtrate. The solid residue afforded by this procedure was then recrystallized directly from cold methanol affording a 63% yield of **3b**, yellow-brown crystals, mp 106.5–108°.

Anal. Calcd for $C_{20}H_{37}BrNiP_2$: C, 50.25; H, 7.80; Br, 16.71; Ni, 12.28; P, 12.96; mol wt, 478. Found: C, 52.84; H, 7.94; Br, 16.75; Ni, 12.58; P, 12.84; mol wt (cryoscopic in $CHCl_3$), 449. Note: An interference in the carbon analysis occurred with this compound. The sum of the elemental analyses was 102.95%, the excess over 100% being close to the discrepancy between the calculated and found values for carbon. λ_{max} 302m μ (ϵ 9000), 259 (sh) (22,600), 237 (41,500), 214 (35,300).

Treatment of *trans*-dichlorobis(triethylphosphine)nickel(II) with 2-vinylphenylmagnesium bromide using the procedure described above afforded a mixture of **3a** and **3b** as determined by nmr analysis. Treatment of the mixture, in refluxing acetone, with a 2 molar excess of lithium bromide for 10 min afforded pure **3b** after removal of the acetone *in vacuo*, extraction of the residue with hexane, removal of the hexane from the extract, and recrystallization of the residue.

Reaction of *trans*-Dichlorobis(triethylphosphine)nickel(II) with 4-Vinylphenylmagnesium Bromide. Formation of the Grignard reagent derived from 4-bromostyrene was initiated using the procedure of Pearson, *et al.*[47] Magnesium turnings, 0.71 g (29 mg-atoms), were treated with 10 ml of tetrahydrofuran. The stirred mixture was then warmed to a gentle reflux and a solution of 3.11 g (17 mmol) of 4-bromostyrene and 2.27 g (12 mmol) of 1,2-dibromoethane in 70 ml of tetrahydrofuran was added dropwise. After the addition was complete, the reaction mixture was stirred at reflux temperature for *ca.* 24 hr. A portion of the resulting solution, at room temperature, was then added slowly to a stirred solution of 3.29 g (9.0 mmol) of *trans*-dichlorobis(triethylphosphine)nickel(II) in 60 ml of tetrahydrofuran, cooled to 0°, until the solution turned amber in color. The mixture was then stirred for 5 min, after which the solvent was removed *in vacuo*. The resulting residue was then extracted with five 50-ml portions of pentane. The combined extracts were filtered, and the pentane was removed from the filtrate *in vacuo*. This procedure afforded 1.90 g of air-sensitive yellow crystals. Recrystallization from methanol under a nitrogen atmosphere gave yellow crystals, dec 96–99°. The material was too sensitive to submit for analysis. The infrared spectrum (Nujol mull) exhibited peaks at 1624, 991, and 905 cm^{-1}.

Overlapping multiplets (C_6D_6) centered near τ 8.8 and 9.0 are assigned to the Et_3P protons, and an apparent quartet at *ca.* τ 2.78 attributed to the aromatic proton resonances.

trans-**Bromo(4-vinylphenyl)bis(triethylphosphine)palladium(II), 6.** The Grignard reagent prepared from 1.08 g (44.4 mg-atoms) of magnesium and 8.14 g (44.4 mmol) of 4-bromostyrene in 190 ml of tetrahydrofuran was added slowly to a solution of 5.5 g (13.3 mmol) of *trans*-dichlorobis(triethylphosphine)palladium(II) in ether, cooled to *ca.* 0°. The reaction solvent was then removed *in vacuo* and the residue was triturated with three 50-ml portions of hexane, followed by three 50-ml portions of benzene. The extracts were combined and concentrated, and the resulting solution was placed on an acid-washed alumina column prepared in pentane. Elution with ether–pentane mixtures of increasing polarity afforded a colorless solid which was recrystallized from hexane, affording 6.09 g of nearly colorless crystals which appeared to be a mixture of **6** and the chloro analog. The material could be converted almost quantitatively to **6** using the following procedure. The mixture was treated with an excess of lithium bromide in acetone solution and the resulting solution was refluxed for 3 hr, whereupon the acetone was removed under vacuum. The residue was then treated with water to dissolve the lithium salts. The resulting mixture was filtered, and the solid residue in the funnel was recrystallized from ethanol affording light yellow crystals of **6**, mp 145.0–146.5°.

Anal. Calcd for $C_{20}H_{37}BrPdP_2$: C, 45.68; H, 7.09. Found: C, 45.76; H, 7.06. The aromatic pmr spectrum (C_6D_6) consisted of an apparent A_2B_2 quartet centered at τ 2.69. The Et_3P proton resonance consisted of two multiplets centered at τ 8.43 and 9.07, the latter being a quintet.

trans-**Bromo(2-vinylphenyl)bis(triethylphosphine)palladium(II), 4.** *trans*-Dichlorobis(triethylphosphine)palladium(II), 4.41 g (10.0 mmol), was treated with 2-vinylphenylmagnesium bromide according to the procedure described for the preparation of **6**. Chromatography of the crude product on acid-washed alumina as described above afforded 3.07 g of colorless crystals which were treated with lithium bromide as in the preparation of **6**. Recrystallization of the product from ethanol afforded **4**, which exhibited anomalous melting behavior, melting in two regions, 109–110° and 127–128°.

Anal. Calcd for $C_{20}H_{37}BrPdP_2$: C, 45.68; H, 7.09; Br, 15.20. Found: C, 45.76; H, 7.06; Br, 15.11.

Displacement Reactions of Organonickel Compounds. In each case, **3a** or **3b**, in acetone solution, was treated with an excess of the appropriate alkali metal salt for *only* 10–15 min. Longer reaction times led to mixtures of products which could not be resolved. A short reaction time is mandatory in order to obtain the compounds described in the text.

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***trans*-Isothiocyanato(2-vinylphenyl)bis(triethylphosphine)nickel(II), 3d.** Compound **3a**, 0.226 g (0.522 mmol), and potassium thiocyanate, 0.079 g (0.811 mmol), were dissolved in 20 ml of acetone and the mixture was warmed to reflux for 10 min. The mixture was then cooled to room temperature and the solvent was removed *in vacuo*. The resulting solid was triturated with 25–50 ml of 10% benzene in hexane, the extract was filtered, and the solvent was removed from the filtrate. Recrystallization of the filtrate residue from hexane afforded 0.143 g, 60%, of orange-yellow crystals of **3d**, mp 156–157°.

Anal. Calcd for $C_{21}H_{37}NiNP_2S$: C, 55.28; H, 8.17; mol wt, 456. Found: C, 55.15; H, 8.08; mol wt (vapor pressure osmometry, benzene), 455. λ_{max} 298 mμ (ε 18,000), 260 (sh) (19,050), 219 (60,700). The infrared spectrum (Nujol mull) exhibited peaks at 2110 (s) and 832 cm^{-1} (m) and at 2092 (vs) and 835 cm^{-1} (m) in benzene solution assigned to the C–N and C–S stretching frequencies, respectively. These values indicate that the ligand is present as an isothiocyanate (Ni—N═C═S).[15,48]

***trans*-Iodo(2-vinylphenyl)bis(triethylphosphine)nickel(II), 3c.** Using the same procedure as for **3d**, 0.260 g (0.535 mmol) of **3b** was treated with 0.101 g (9.60 mmol) of potassium iodide affording 0.190 g, 65%, of **3c** (brown prisms), mp 134–135°.

Anal. Calcd for $C_{20}H_{37}INiP_2$: C, 45.76; H, 7.10; I, 24.17. Found: C, 45.98; H, 7.27; I, 24.34. λ_{max} 311 mμ (sh) (ε 5600), 259 (24,000), 238 (24,000), 220 (34,300).

***trans*-Cyano(2-vinylphenyl)bis(triethylphosphine)nickel(II), 3e,** From 0.353 g (0.73 mmol) of **3b** and 0.042 g (0.84 mmol) of sodium cyanide in 20 ml of acetone and 1 ml of water, stirred for 10 min at room temperature, was obtained 0.223 g of yellow needles of **3e**, 72%, mp 119–120°.

Anal. Calcd for $C_{21}H_{37}NiNP_2$: C, 59.46; H, 8.79. Found: C, 59.31; H, 8.72. λ_{max} 300 mμ (ε 5000), 265 (9750), 227.5 (sh) (19,300), 217.5 (33,600). The infrared spectrum (Nujol mull) contained a peak at 2095 cm^{-1} (s) (sharp), C≡N stretch.

***trans*-Nitro(2-vinylphenyl)bis(triethylphosphine)nickel(II), 3f.** From **3b**, 0.323 g (0.68 mmol) and sodium nitrite, 0.074 g (1.08 mmol), dissolved in 19 ml of acetone and 1 ml of water and warmed to reflux temperature for 10 min, was obtained 0.201 g of orange-yellow crystals of **3f**, 66.5%, mp 103.5–105°.

Anal. Calcd for $C_{20}H_{37}NiNO_2P_2$: C, 54.08; H, 8.40. Found: C, 53.99; H, 8.34. λ_{max} 282 mμ (ε 7300), 243 (sh) (29,000), 218 (37,600). The infrared spectrum contained peaks at 1342 cm^{-1} (m), 1325 cm^{-1} (m), and 809 cm^{-1} (w) (sharp) (Nujol mull); and at 1350, 1327, and 810 cm^{-1} (benzene solution).

***trans*-Isocyanato(2-vinylphenyl)bis(triethylphosphine)nickel(II), 3g.** From 0.247 g (0.517 mmol) of **3b** and 0.069 g (0.847 mmol) of potassium cyanate in 18 ml of acetone and 2 ml of water, warmed to reflux temperature for 15 min, was obtained 0.077 g, 35%, of orange-yellow prisms, mp 180–181°.

Anal. Calcd for $C_{21}H_{37}NiNOP_2$: C, 57.30; H, 8.47. Found: C, 57.40; H, 8.43. λ_{max} 310.5 mμ (sh) (ε 2700), 290 (7000), 259 (18,500), 224 (29,000). The infrared spectrum showed peaks at 2230 (vs) and 1322 cm^{-1} (m) (Nujol mull) and at 2225 (vs) and 1329 cm^{-1} (ms) in benzene solution, C–N and C–O stretching frequencies consistent with the isocyanato structure.[15,49]

2-Chlorostyrene. The procedure used was essentially the same as that reported by Overberger and Saunders.[50] From 29.40 g (0.188 mol) of 2-chlorophenylmethylcarbinol added dropwise to 9 g of fused and powdered potassium hydrogensulfate at 210° and 3 mm pressure was obtained a mixture of the carbinol and product. Fractional distillation afforded 13.61 g, 52%, of 2-chlorostyrene, bp 46–47° (2.5 mm) [lit.[51] bp 186.4° (760 mm)]. The structure was verified by infrared and nmr spectra.

2-Chloro-α-methylstyrene. The compound was prepared from 2-chlorophenyldimethylcarbinol using the same procedure as above.[50] The structure of the product, bp 51–52° (3.25 mm) [lit.[52] bp 75° (14 mm)], was verified by infrared and nmr spectra.

***trans*-Chloro(*o*-α-methylstyryl)bis(triethylphosphine)nickel(II), 8.** The compound was prepared from the Grignard reagent derived from 2-chloro-α-methylstyrene and *trans*-dichlorobis(triethylphosphine)nickel(II), 3.65 g (10.0 mmol), using the same procedure as for the synthesis of **3a**. Recrystallization from hexane of the material obtained from the hexane trituration step afforded 3.52 g (78%) of crude **8**. A portion of this, 1.35 g, was then dissolved in hexane and chromatographed on a 32 × 3 cm column of acid-washed alumina prepared in hexane. Elution with 1:9 ether–hexane afforded material which on recrystallization from hexane gave 0.733 g of golden brown crystals of **8**, mp 78–79°.

Anal. Calcd for $C_{22}H_{39}ClNiP_2$: C, 56.35; H, 8.78. Found: C, 56.50; H, 8.75. λ_{max} 292 mμ (ε 8420), 250 (sh) (17,000), 229 (38,400). The infrared spectrum exhibited peaks at 1618 (m) and 876 cm^{-1} (s) and the pmr spectrum (C_6D_6) contained aromatic proton multiplets centered near τ 2.20, 2.86, and 3.12 and two Et_3P proton multiplets near τ 8.64 and 9.04.

***trans*-Chloro(trichlorovinyl)bis(triethylphosphine)nickel(II).**[53] *bis*-(Pentanedionato)nickel(II), 10.88 g (0.0423 mol), was suspended in a mixture of 100 ml of tetrachloroethylene and 100 ml of toluene. Triethylphosphine, 10.00 g (0.0846 mol), was added and the resulting mixture was cooled to −25°. To the cold, stirred mixture was added 24.20 ml of 2.72 *M* triethylaluminum in toluene (10.30 g, 0.090 mol) *via* hypodermic syringe at such a rate to keep the temperature of the reaction mixture below −10°. The resulting mixture was then allowed to warm slowly to room temperature, after which the mixture was stirred at 43° for 1.25 hr until the dark red mixture was homogeneous. The mixture was then cooled to room temperature, 10 ml of 2-propanol was added, and the solvent and volatiles were removed *in vacuo* affording a solid red-yellow residue. The residue was then triturated with pentane and the pentane-soluble material was chromatographed on a 45 × 3 cm column of acid-washed alumina, prepared in pentane. The product was eluted with 1:3 ether–pentane. Recrystallization from pentane afforded 13.0 g, 66.7%, of golden brown crystals, mp 91–92°. The material was found to be identical with *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II), formed in the thermolysis of **1** in tetrachloroethylene.[1]

***trans*-Bromo(*o*-tolyl)bis(triethylphosphine)nickel(II).** From the Grignard reagent of 2-bromotoluene (10 mmol) and 2.35 g (6.42 mmol) of *trans*-dichlorobis(triethylphosphine)nickel(II), using the procedure for the preparation of **3b**, were obtained 2.64 g, 81%, of orange-brown crystals, mp 104–105° (lit.[13] mp 102–103°) after recrystallization from methanol.

***trans*-Bromo(2,6-dimethylphenyl)bis(triethylphosphine)nickel(II).** A solution of 2,6-dimethylphenyllithium, prepared from 0.10 g (14 mg-atoms) of lithium shavings and 1.08 g (5.8 mmol) of 2,6-dimethyl-1-bromobenzene in 40 ml of ether, was added dropwise to a stirred solution of 1.10 g (3.0 mmol) of *trans*-dichlorobis(triethylphosphine)nickel(II) in 30 ml of ether at 25°. Two minutes after the addition was complete, the ether was removed *in vacuo*. The residue was triturated with two 30-ml portions of hexane, the extracts were filtered, and the hexane was removed from the filtrate. Recrystallization of the filtrate residue from methanol afforded 1.07 g, 73%, of orange-brown crystals, mp 112°.

Anal. Calcd for $C_{20}H_{39}BrNiP_2$: C, 50.04; H, 8.19. Found: C, 50.07; H, 8.29.

***trans*-*o*-Tolyl(trichlorovinyl)bis(triethylphosphine)nickel(II).** A solution of 2-lithiotoluene was prepared by stirring 0.20 g (29 mg-atoms) of lithium shavings and 2.0 g (12 mmol) of 2-bromotoluene in 100 ml of ether. The resulting solution (20 ml) was added dropwise to a stirred solution of 1.09 g (2.37 mmol) of *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II) in 20 ml of ether at room temperature. Five minutes after the addition was complete, the ether was removed *in vacuo*, the residue was triturated with 30 ml of hexane, and the extract was chromatographed on acid-washed alumina. Elution with 1% ether in hexane afforded 0.41 g, 34%, of pale yellow crystals, dec pt 155°. Elution with 1:1 ether–hexane afforded 0.33 g, 30%, of recovered *trans*-chloro(trichlorovinyl)bis(triethylphosphine)nickel(II).

Anal. Calcd for $C_{21}H_{37}Cl_3NiP_2$: C, 48.83; H, 7.22. Found: C, 48.93; H, 7.18. The dipole moment was determined to be 1.49 D.

2-Chloroisopropylbenzene. The title compound was prepared by hydrogenation of 2-chloro-α-methylstyrene, 4.53 g (30 mmol), in 20 ml of hexane, using palladium on charcoal, 0.20 g, as a catalyst. Upon removal of solvent, 4.55 g (98%) of 2-chloroisopropylbenzene,

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(53) We are indebted to Mr. David Kuhlman for conducting this experiment.

bp 63–64° (8 mm) [lit., bp[54] 191 °(760 mm)] was obtained. The pmr spectrum verified the structure.

trans-**Chloro(2-isopropylphenyl)bis(triethylphosphine)nickel(II).** The compound was prepared from the Grignard reagent of 2-chloroisopropylbenzene (17 mmol) and 3.65 g (10 mmol) of *trans*-dichlorobis(triethylphosphine)nickel(II) in tetrahydrofuran, using the same procedure as for the synthesis of **3a**. Recrystallization from hexane of the material obtained in the hexane trituration step afforded 3.20 g (70%) of crude product. A portion of this, 0.76 g, was chromatographed on acid-washed alumina under nitrogen. Recrystallization from hexane of material afforded by elution with 1:4 ether–hexane gave 0.65 g of golden brown crystals, mp 121–122°.

Anal. Calcd for $C_{21}H_{41}ClNiP_2$: C, 56.09; H, 9.19. Found: C, 56.05; H, 9.13. The pmr spectrum (C_6D_6) exhibited aromatic proton multiplets at τ 2.62 and 3.13, a single doublet at τ 8.64 attributed to the isopropyl substituent CH_3 protons, and two Et_3P proton multiplets near τ 8.77 and 8.99. The "benzylic" proton resonance (Table III) consisted of a septet with line separations identical with those in isopropylbenzene.

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A Structural Study of Titanium Tetraethoxide in Solution

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Abstract: A special light-scattering photometer equipped with a He–Ne CW laser source has been used for the precise measurement of the anisotropic Rayleigh scattering needed to calculate the optical anisotropy of titanium tetraethoxide in cyclohexane and carbon tetrachloride solutions. Turbidity measurements have confirmed the existence of a trimer unit in solution. The anisotropy values of likely titanium ethoxide structures have been calculated using a Δ-function model to obtain bond polarizabilities. Comparison of calculated and experimentally determined anisotropy values has indicated that the structure in solution consists of three polyhedra sharing edges, with the central titanium atom being six-coordinate with respect to the oxygens and the two terminal titanium atoms being five-coordinate. Raman, ir, and nmr data also support this structural assignment.

Although a large number of transition metal alkoxides are known[1] and have been used for a variety of purposes for decades, only in the rather recent past have attempts been made to study the structures of the polymeric species which are soluble in the common organic solvents. One of the few X-ray crystal studies of such compounds has been performed by Ibers,[2] who determined that titanium tetraethoxide in the solid state exists as a tetramer represented by $Ti–O_6$ octahedra sharing edges. A similar structure has been assigned to the solid methoxide[3] derivative.

A large number of benzene-soluble alkoxides have been studied in solution cryoscopically and ebulliometrically by Bradley and others. Bradley[4] has proposed a structural theory which relates the coordination number, stereochemistry, and the minimum degree of polymerization of polymeric alkoxides. Specifically it has been asserted that metal alkoxides adopt the smallest possible structural unit consistent with all of the metal atoms attaining a higher coordination number. Choice of structure is limited also by the condition that the coordination number of oxygen not exceed four.

For example, Bradley and Westlake[5] have predicted that a trimer should predominate in solutions of titanium tetraethoxide since such a structure will allow all titanium atoms in the molecule to be six-coordinate. The structure proposed can best be described as a linear molecule with three TiO_6 octahedra sharing faces. Yet, it is apparent that a tetramer exists in the solid state, not a trimer.

All structural assignments for titanium tetraethoxide in solution have been based heavily upon cryoscopic and ebulliometric measurements. Unfortunately, agreement upon molecular weight values from study to study has not been good. For instance, it has been reported that the molecular weight in benzene varies with time[6] and that after several hours the substance behaves as a monomer. Other workers have claimed that extensive depolymerization[7,8] occurs in dilute benzene solutions. More recently, Bradley claimed that the degree of aggregation is precisely three and is concentration-independent.[9] Early structural studies were not especially successful. Dipole moments[10–12] reported for titanium alkoxides ranged in value between 1.0 and 2.0 D. Interpretation of these data in terms of structure has been

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