out to be a most unusual compound. It is considered a metal hydride that functions as an acid catalyst; its reactions are influenced by the coordination state of the cobalt; it forms π (η^2), π-allyl (η^3), and σ (η^1) complexes; the σ complexes undergo migratory insertion, oxidative addition, and reductive elimination reactions as well as skeletal rearrangements; it is a potent isomerization catalyst, and its reactions with olefins can lead to aldehydes, alcohols, and/or hydrocarbons. The partitioning among these products can be influenced by temperature, pressure, and ligand structure. It can show both normal and inverse isotope effects and can be a remarkably effective hydrogenation agent. Its reactions encompass the whole gamut of the known reactions of organometal catalysts entitling it to be called the quintessential catalyst.

Determination of Structural and Dynamic Aspects of Organometallic and Coordination Chemistry by Phosphorus-31 NMR Spectroscopy

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In recent years, transition-metal complexes of tertiary phosphine ligands have been used in many important and diverse chemical reactions such as (i) homogeneous hydroformylation,[1] oxidation,[2] hydrogenation,[3] and hydrosilylation of olefins;[4] (ii) oxidative addition to the metal center;[5] (iii) stabilization of small elemental fragments (e.g., S_2,[6] Se_2,[7] P_3,[8,9] and As_3[9]); and (iv) asymmetric synthesis via optically active metal phosphine catalysts.[10] It is expected that the use of polyphosphine ligands will become increasingly important in such future studies, since the special properties of phosphine ligands can be accentuated by a chelating polyphosphine;[11] also, the steric and electronic properties of the ligands can be altered relatively easily by changing the organic substituents on phosphorus.

Research efforts in our laboratories have been concentrated on the synthesis of chelating polydentate ligands and on the electronic, catalytic, and structural properties of the resulting complexes of transition metals.[11] Compared to a monodentate phosphine, a polyphosphine ligand can provide simultaneously (i) more control on the coordination number, stoichiometry, and stereochemistry of the resulting complex; (ii) an increased basicity (or nucleophilicity) at the metal; (iii) slower intra- and intermolecular exchange processes; and (iv) detailed structural and bonding information in the form of metal–phosphorus and phosphorus–phosphorus coupling constants. For example, polydentate ligands may be used to change the magnetic states and coordination geometries of complexes by judiciously selecting parameters such as (i) sets of donor atoms, (ii) "chelate bite angle", and (iii) sterically demanding substituent groups.[12] Flexible polyphosphine ligands (e.g., 1–5), which contain either ethylene or trimethylene linkages, have been used to form complexes with different coordination numbers (four, five, and six) and different structures (distorted tetrahedral, planar, square pyramidal, trigonal bipyramidal, and octahedral).[13-15] A properly designed polyphosphine ligand can define the relative positions

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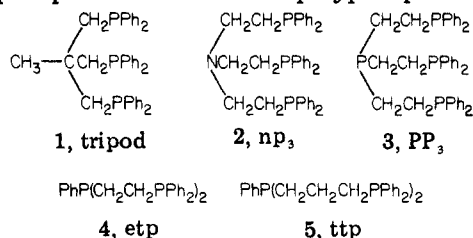(14) (a) Sacconi, L. *Coord. Chem. Rev.* 1972, *8*, 351; (b) *J. Chem. Soc. A* 1970, 248. (c) Morassi, R.; Bertini, I.; Sacconi, L. *Coord. Chem. Rev.* 1973, *11*, 343.
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of the phosphorus atoms while allowing the remaining ligands to be varied; thus, the nature of the variable ligands can be monitored by ^{31}P NMR spectroscopy by observing the chemical shifts and coupling constants of the phosphorus atoms in the polyphosphine ligand.

CH₂PPh₂
/
CH₃—CCH₂PPh₂
\
CH₂PPh₂

1, tripod

CH₂CH₂PPh₂
/
NCH₂CH₂PPh₂
\
CH₂CH₂PPh₂

2, np₃

CH₂CH₂PPh₂
/
PCH₂CH₂PPh₂
\
CH₂CH₂PPh₂

3, PP₃

PhP(CH₂CH₂PPh₂)₂

4, etp

PhP(CH₂CH₂CH₂PPh₂)₂

5, ttp

Until recently, relatively few groups have routinely utilized ^{31}P NMR spectroscopy as an analytical method in the study of metal–phosphine complexes. Now the commercial availability of FT NMR spectrometers should rapidly increase the number of applications of ^{31}P NMR to organometallic and biochemical compounds, which often are either too insoluble or "phosphorus-deficient" for conventional CW instruments. The increased signal-to-noise ratio available with FT is particuarly useful for measurements of phosphorus-31 coupling to the elements of low natural abundance with spin $^1/_2$ nuclei, which are often encountered in coordination and organometallic chemistry (i.e., ^{199}Hg, ^{183}W, ^{195}Pt, $^{107,109}Ag$, $^{111,113}Cd$, $^{117,119}Sn$, etc.). Low-intensity, spectral transitions in a complex second-order spectrum are sometimes necessary for interpretation of the spectrum, but often such data cannot be obtained without FT instrumentation.[16]

Subtle metal–ligand and metal–substrate interactions are critical for understanding catalytic mechanisms involving organometallic and coordination compounds. Phosphorus-31 chemical shifts and coupling constants are uniquely sensitive to these interactions, since a phosphorus atom is bonded directly to the metal center in most cases. Consequently, phosphorus-31 NMR is becoming a particularly valuable analytical tool for the study of stereochemistry and bonding in phosphine complexes.

This Account will attempt to demonstrate the practical applications of ^{31}P NMR spectroscopy to several different aspects of organometallic and coordination chemistry. We will also emphasize recent studies with polydentate ligands that demonstrate the unusual properties of these ligands and the role of ^{31}P NMR spectroscopy as an analytical tool in such studies. For more comprehensive discussions of ^{31}P NMR spectroscopy, particularly concerning the theoretical principles,[17] organic applications,[18] biochemical studies,[19] and metal–phosphine complexes,[20] the reader is directed to the cited review articles.

General Features of Phosphorus-31 NMR

The phosphorus-31 nucleus is ideally suited as a probe of bonding in metal–phosphine complexes, having

100% natural abundance, a nuclear spin of one-half ($I = {}^1/_2$), and a relative sensitivity of 6.6% that of the proton (at constant field).[21] These properties make it one of the few nuclei that can be observed on conventional CW instruments, albeit with some difficulty for dilute to moderately concentrated solutions. By comparison, the ^{13}C nucleus has a sensitivity of 1.6% that of the proton and a natural abundance of 1.1%, making it 340 times less receptive than ^{31}P. As with ^{13}C NMR spectroscopy, the development of signal-averaging and Fourier-transform (FT) technology now makes ^{31}P spectra routinely practical for studies on slightly to moderately soluble coordination and organometallic compounds containing phosphorus. In fact, the wide range of phosphorus chemical shifts (>600 ppm) generally makes ^{31}P NMR more useful than proton NMR for characterization of reaction mixtures and products, particularly if the phosphorus ligands are PPh_3 or contain PPh_2 groups, wherein proton NMR spectra are complicated and, consequently, not very useful for stereochemical studies.

The large variation of phosphorus chemical shifts has been successfully correlated with the electronegativity of the substituents on phosphorus,[22] the angles between them,[23] and the oxidation state of phosphorus.[24] When a phosphorus ligand is coordinated to a metal, the phosphorus chemical shift changes in a fairly predictable manner.[20,25] In addition, the number and size of the chelate rings involving the phosphorus atom have a pronounced effect on its ^{31}P chemical shift (vide infra). Other factors such as the coordination number[26] and oxidation state of the metal,[27] the presence of metal–metal bonds,[28] the influence of trans ligands,[29,30] and the position of the phosphorus ligand within the coordination sphere[31] also influence ^{31}P chemical shifts.

Phosphorus-31 coupling has been reported for over 25 nuclei that have nonzero spins ($I \neq 0$), and it is a sensitive indicator of the bonding between the atoms involved.[21] The coupling of two covalently bound atoms, A and B, is believed to be dominated by the Fermi contact term

$$^1J_{AB} \alpha \gamma_A \gamma_B \alpha_A{}^2 \alpha_B{}^2 |\Psi_{A(ns)}(0)|^2 |\Psi_{B(ns)}(0)|^2 ({}^3\Delta E)^{-1} \quad (1)$$

γ_A = magnetogyric ratio for A; γ_B that of B; $\alpha_A{}^2$ = s character of the A hybrid orbital in the A–B bond; $\alpha_B{}^2$ that of the B orbital; $|\Psi_{A(ns)}(0)|^2$ = the magnitude of the ns wavefunction of A evaluated at nucleus A; and $^3\Delta E$ = the singlet–triplet mean excitation energy. Arguments based on this equation are commonly invoked to interpret the observed trends in the element–phosphorus coupling.[32,33]

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The magnitudes of metal–phosphorus coupling can be quite large. For example, with metals such as platinum and mercury $^1J_{M-P}$ values are in the range 1500–12000 Hz,[17,34] whereas the values for rhodium are usually <200 Hz. For rhodium–, tungsten–, and platinum–phosphine complexes, the $^1J_{M-P}$ values are positive;[20] however, $^{117}Sn-^{31}P$ and $^{119}Sn-^{31}P$ couplings are negative, with the values sometimes exceeding 1000 Hz.[20,35] Generally, coupling between phosphorus and the numerous ligand hydrogen atoms gives rise to featureless, broad ^{31}P resonances that obscure the desired M–P and P–P magnetic couplings; thus, ^{31}P spectra of metal–phosphine complexes are usually obtained with broad-band proton decoupling, which produce ^{31}P spectra with sharp peaks for the different phosphorus resonances. When the need arises, selective decoupling of hydrogen, fluorine, and other nuclei can provide additional simplification of the ^{31}P spectra.

Homonuclear $^{31}P-^{31}P$ couplings are also useful probes of structure and bonding. In some cases P–P coupling has been observed between phosphorus atoms separated by as many as nine bonds,[36] although generally phosphorus atoms couple only weakly if they are separated by four or more bonds. In metal–phosphine complexes, the magnitudes of $^2J_{P-P}$, involving coupling through the metal center, are sensitive to the stereochemical location of the two phosphorus atoms, oxidation state of the metal, and overall structure of the complex.[37] Examples will be presented below to illustrate how judicious use of arguments based on chemical shifts and coupling constants, augmented by a minimal amount of other chemical and spectroscopic data, often permit accurate structural assignments to be made.

Determination of Symmetry and Structure

A common problem in organometallic and transition-metal chemistry is the determination of the stereochemistry around the metal. The trans-influence difference between various ligands is generally useful for assigning the stereochemistry of four-, five-, and six-coordinate complexes, as both the metal–phosphorus coupling constant and the ^{31}P chemical shift are affected by the trans ligand.[38,39]

For an illustration of the usefulness of the effect of different trans ligands on the magnitudes of the downfield shifts of the phosphorus resonances, consider the two compounds that result by allowing $RuCl_3 \cdot 3H_2O$, CO, and $PhP(CH_2CH_2CH_2PPh_2)_2$ (ttp) to react under different conditions. A white or a yellow compound can be isolated; both compounds have elemental analyses and infrared and NMR spectra consistent with the formula $RuCl_2(CO)(ttp)$.[40] Since the triphosphine

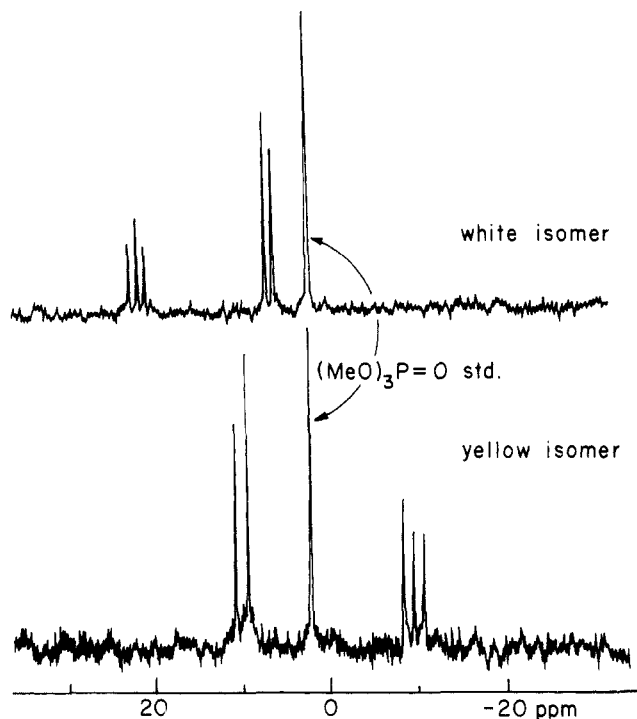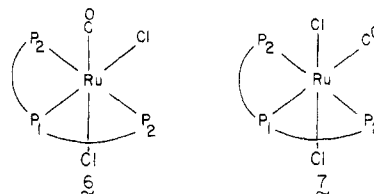(33) Kroshefsky, R. D.; Verkade, J. G.; Pipal, J. R. *Phosphorus Sulfur* **1979**, *6*, 377–389.
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Figure 1. Phosphorus-31 NMR spectra of *cis*-RuCl$_2$(ttp)CO (white isomer) and *trans*-RuCl$_2$(ttp)CO (yellow isomer) in THF.

ligand ttp usually occupies a meridian of the coordination geometry around a heavy metal, the two isomers are probably 6 and 7, where the CO is cis and trans, to P$_1$, respectively. The CO infrared stretching frequen-

cies at 1970 (white isomer) and 1980 cm^{-1} (yellow isomer) do not, by themselves, permit discrimination between the two structural possibilities. However, the ^{31}P NMR spectra do provide a structural assignment since the P$_1$ resonance of the yellow compound is located ∼30 ppm to higher field than for the white isomer (Figure 1). The yellow isomer is assigned structure 7, in which the strong trans-influence ligand CO is opposite P$_1$, whereas the white compound, 6, has the weaker trans-influence ligand, chloride, opposite P$_1$.

Particularly in planar and octahedral complexes, considerable ^{31}P data are available to suggest that the ligand opposite the phosphorus atom strongly affects its ^{31}P chemical shift.[29,41] In general, strong-field ligands cause the ^{31}P resonance to occur at higher chemical shifts, compared to a similar complex with a halide trans to the phosphine. The relative trans-influence sequence Cl < P < C < H seems to hold for a wide variety of metals.

The ^{31}P NMR resonance of a phosphorus ligand commonly shifts downfield when the ligand is bonded to a metal atom relative to its position in the free ligand; this shift is treated quantitatively by the coordination chemical shift, Δ, defined as $\delta P_{coordinated} - \delta P_{free\ ligand}$.[42,43]

(41) Blum, P. R., Ph.D. Dissertation, The Ohio State University, Columbus, OH, Dec 1977.

The magnitude of Δ has been a useful diagnostic tool for determining the presence of linkage isomers with polydentate phosphine ligands. For example, Grim et al.[44] determined which end of an unsymmetrical diphosphine ligand was coordinated in $W(CO)_5(P\sim P')$ complexes $(P\sim P' = Ph_2PCH_2CH_2P(Ph)R, R = CH_3, C_2H_5, i\text{-}C_3H_7)$ by comparing the magnitudes of Δ. Analogously, Verkade's caged phosphine–phosphite $P(OCH_2)_3P$ may bond at either (or both) end(s).[37]

Incorporation of phosphorus atoms into a chelate ring makes an additional contribution to the chemical shift, designated Δ_R.[45] This phenomenon is defined as the difference between the coordination chemical shift, Δ, of a cis-substituted bisphosphine complex and the observed Δ value for an equivalent phosphorus in a chelate complex. An empirical correlation has been noted by several authors, but Garrou has accented the effect, which causes a deshielding of the phosphorus resonance by $\sim$21–33 ppm for chelating phosphorus atoms in five-membered rings, whereas these resonances are shifted to higher field by amounts varying from 2 to 25 ppm for four-, six-, and seven-membered chelate rings in complexes of a large number of metals and geometries. As a result of the coordination chemical shift in rings, phosphorus-31 NMR has become the preferred analytical method for determining when "ortho-metalation" has occurred with a phosphorus ligand.[46,47]

Additional studies have shown that the deshielding effect associated with five-membered rings can be significantly larger than 30 ppm. For example, if a phosphorus atom is the bridgehead of two or three five-membered rings as in 8 and 9, respectively, the
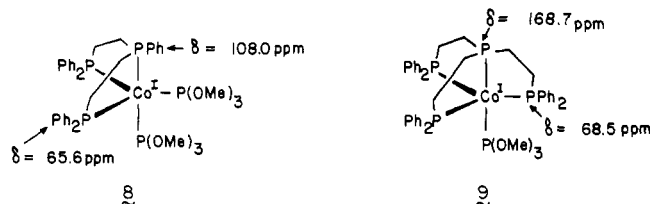
large downfield shift is nearly additive for each additional chelate ring.[48]

We recently studied a series of Rh(–I)–nitrosyl compounds of formula $RhL_n(PPh_3)_{3-n}(NO)$ (L_n = a polyphosphine ligand containing n phosphorus atoms), in which the chelate ring size was varied systematically with five-, six-, and seven-membered rings while pseudotetrahedral geometry around the metal[49] was being maintained. Average values of Δ_R were 24.8 ($\pm$1.0), –10.7 ($\pm$1.6), and $\sim$0.0 ppm for five-, six-, and seven-

Figure 2. A schematic drawing showing the range of $^2J_{P-P}$ values (Hz) in $[Co(triphos)(L)(CO)]X$ complexes ($L = PEt_3$, PPh_2Me, PPh_2H, CO) of trigonal-bipyramidal and square-pyramidal geometries; a = axial, e = equatorial.

membered rings, respectively. Incorporation of a bridgehead phosphorus atom into a second ring resulted in an additive effect in the case of five-membered rings [i.e., for Rh(etp)NO, $\Delta_R = 52.4$, $\Delta_R(calcd) = 49.6$ ppm], but not for six-membered rings. Surprisingly, Δ_R was unaffected by changing the substituents (e.g., CH_3, Ph, and $c\text{-}C_6H_{11}$ groups) on phosphorus in either five- or six-membered chelate rings.

Five-coordinate transition-metal complexes present a problem (and consequently an opportunity to use ^{31}P advantageously) that is not encountered with four- and six-coordination. That is, which of the two nearly equivalent energy geometries (square pyramidal and trigonal bipyramidal) is the ground-state structure?[50] Often, X-ray crystallography is the only definitive way of determining the structure of a five-coordinate complex, although a series of $^{31}P\{^1H\}$ studies by the Du Pont group on ML_5–trialkyl phosphite complexes of Fe(0), Ru(0), Os(0), Co(I), Rh(I), Ir(I), Ni(II), Pd(II), and Pt(II) showed the low-temperature structures of these molecules to be trigonal bipyramidal and not square pyramidal.[51]

A series of five-coordinate Co(I)-triphosphine complexes were studied by Meek and DuBois to determine if an empirical relationship existed between the structures and the $^2J_{P-P}$ values for phosphorus ligands at different sites of a trigonal bipyramid and a square pyramid.[48a] The range of phosphorus–phosphorus coupling constants, based on the ^{31}P NMR spectra of 19 $[Co(triphos)(L)(L')]^+X^-$ complexes $[(L = CO; L' = CO, PEt_3, PPh_2Me, PPh_2H, or P(OMe)_3]$ and two X-ray crystal structure determinations, are summarized schematically in Figure 2. Although there is some overlap, the ranges are sufficiently different to permit differentiation between the two structural types.

The cobalt(I)–triphosphine study highlights three distinct advantages of studying polyphosphine complexes as compared to ML_5^{n+} complexes: (i) the lower symmetry of these complexes permits more coupling data, and concomitantly more structural information, to be obtained from each spectrum; (ii) the slower rate (or absence) of intramolecular exchange allows many more of the compounds to be studied at room temperature; and (iii) both square-pyramidal and trigonal-bipyramidal complexes were obtained, whereas all of the ML_5 complexes were trigonal bipyramidal at the low-temperature limit.

Ligand Effects Determined by ^{31}P NMR

One of the uses of ^{31}P NMR spectroscopy has been to establish correlations between features of M–P bonds

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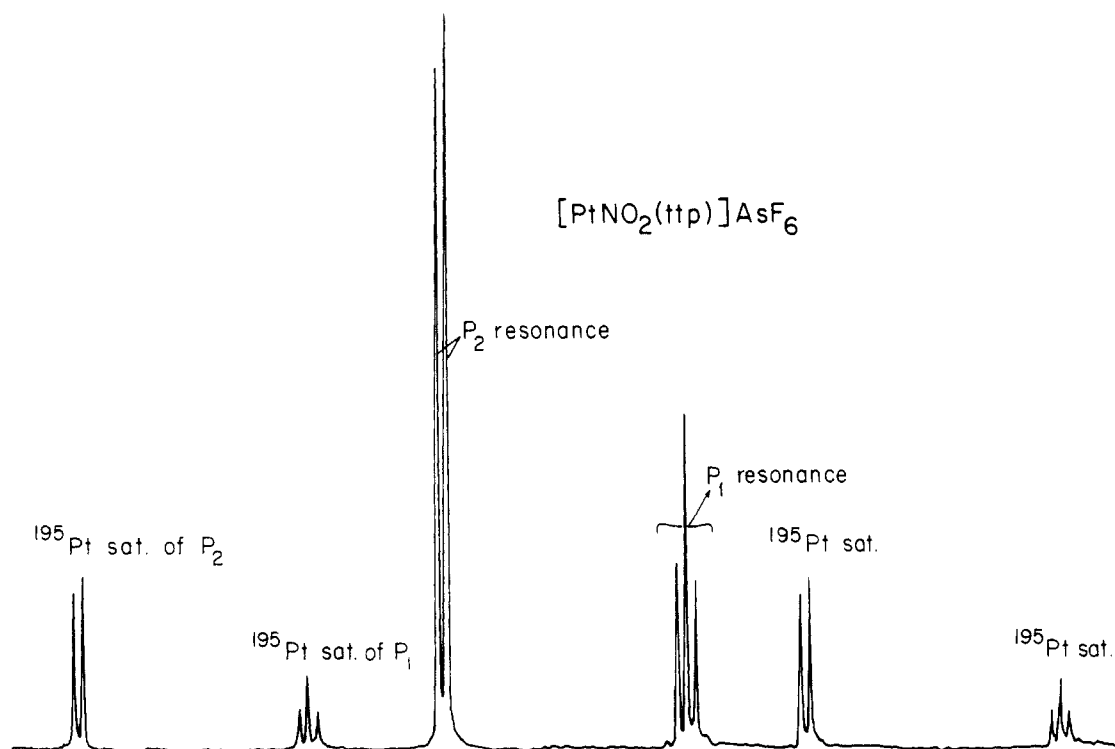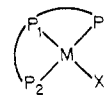
Figure 3. $^{31}P\{^1H\}$ NMR spectrum of [Pt(NO$_2$)(ttp)]AsF$_6$ in CH$_2$Cl$_2$.

and the ^{31}P NMR parameters. Such correlations may naturally result from the relationship that is assumed to exist between the one-bond coupling constants and the s character of the orbitals used for the bond (eq 1). For example, a correlation between the Pt–P bond lengths and the ^{195}Pt–^{31}P coupling constants has been demonstrated for a series of Pt(II) and Pt(0) complexes.[11b,24,52,53] Thus, shorter Pt–P distances (as determined via X-ray studies) are associated with larger values of $^1J_{Pt-P}$. To a first approximation, the $^1J_{M-P}$ values for a series of closely related compounds probably reflect variations in the nature of the M–P σ bonds; however, one must be cautious to consider other factors (e.g., steric effects or strong M–L π bonding) when making such comparisons.[54]

Trans Influence. A trans or cis influence is defined as the extent to which a ligand L weakens the bond trans or cis to itself in the ground state of a metal complex.[55,56] Although the cis and trans influence can be measured directly via bond lengths, most of the investigations reported in the literature have used indirect methods (e.g., vibrational spectra and NMR spectra) as measurements.[56] The number of applications of ^{31}P NMR in this area is surprisingly small, although the initial correlations of Pt–P bond distances with Pt–P coupling constants look promising. Where there is no satisfactory correlation, the failure usually can be attributed to the steric and electronic effects of the cis ligands.

Since the overall bonding factors in a metal complex depend on the nature of the ligands and the metal coordination geometry, it is imperative that all of the factors be fixed, except for the one variable ligand, if one is to determine the cis or trans influence of a ligand. The chelating triphosphine PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$ (ttp) appears to be an ideal ligand for X-ray crystallography and ^{31}P NMR studies on planar metal complexes, since it fixes three of the four coordination positions into a relatively constant environment, and the $|\Psi_{P(0)}|$ and α_P^2 terms must be constant to a first approximation. Physical measurements on its planar complexes give simultaneously both the cis and trans influences of the fourth ligand; in addition, the conformational flexibility of the trimethylene chain permits the P–M–P angles within each chelate ring to be very near the ideal angle of 90°,[11b,57] rather than constrained to ~83 ± 1° for chelating diphosphine ligands containing an ethylene chain, e.g., Ph$_2$PCH$_2$CH$_2$PPh$_2$. Also, the 1:2 ratio of phosphorus environments in PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$ makes assignment of the different ^{31}P resonances unambiguous; thus, changes in the chemical shifts and coupling constants of P$_1$ in planar complexes of the type

readily indicate the effect of the trans ligand X. The spectrum of [Pt(NO$_2$)ttp]AsF$_6$ (Figure 3) clearly shows the wealth of ^{31}P data that can be obtained when the metal has a magnetic nucleus (e.g., ^{103}Rh or ^{195}Pt).[58]

(52) Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133.

(53) Hitchcock, P. B.; Jacobson, B.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 2043.

(54) Hitchcock, P. B.; Jacobson, B.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1977**, 2038.

(55) (a) Pidcock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707. (b) Venanzi, L. M. *Chem. Br.* **1968**, *4*, 162.

(56) A good review of the earlier trans-influence studies is: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(57) (a) Christoph, G. G.; Blum, P.; Liu, W. C.; Elia, A.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 894. (b) Blum, P. R.; Meek, D. W. *Inorg. Chim. Acta* **1977**, *24*, L75.

(58) (a) Tau, K. D., Ph.D. Dissertation, The Ohio State University, Columbus, OH, March 1978. (b) Tau, K. D.; Meek, D. W. *Inorg. Chem.* **1979**, *18*, 3574.

Table I
Selected Metal-Phosphorus Coupling Constants
for $Pt(CH_3)(X)(dppe)^{n+}$ and $M(X)(ttp)^{n+}$ Complexes

X	$Pt(CH_3)(X)(dppe)^{n+}$, $n = 0$ or 1, $^1J_{Pt-P_1}$,[a,b] Hz	$Pt(X)(ttp)^{n+}$, $n = 1$ or 2, $^1J_{Pt-P_1}$,[a] Hz	$Rh(X)(ttp)^{n+}$, $n = 0$ or 1, $^1J_{Rh-P_1}$,[a] Hz
Cl	4224	3109	162
NCS	3719	3049	149
py	3738		140
NO₂	3345	2453	
CN	2870		123
P(OMe)₃		1980	112
PEt₃		1895	113
H		1690	
CO	3212		113
CH₃	1794	1624	113

[a] P_1 is the phosphorus atom trans to ligand X.   [b] Data from reference 59.

Some ³¹P NMR spectral data for [Pt(ttp)X]⁺ (X = anionic ligand) and [Pt(ttp)Y]²⁺ complexes (Y = neutral ligand) are listed in Table I. The values of $^1J_{Pt-P_1}$ in the complexes decrease in the order Cl⁻ > NCS⁻ > NO₂⁻ > P(OMe)₃ > PEt₃ > CH₂CN⁻ > H⁻ > CH₃⁻.[58] In general, this order is in agreement with several series of trans-influence ligands that have been obtained by other methods.[56] The trend given by the σ-donor ligands can be interpreted most readily in terms of the covalency of Pt–X and the resultant effect on the trans Pt–P bond.[58,59] One would expect the stronger σ-donor ligands to compete with the trans phosphorus atom for s character, thereby producing a smaller value of $^1J_{Pt-P_1}$ for the phosphorus trans to X, as observed experimentally.

Extensive series of RhX(ttp) and RhX(ttp)·SO₂ complexes have been examined by ³¹P NMR,[41,57] and Tables I and II contain data for selected examples. As in the platinum complexes, the relative chemical shifts of P_1 and P_2 as well as the Rh–P_1 and Rh–P_2 coupling constants are sensitive indicators of the bonding properties of the ligand trans to P_1 (note that the magnitudes of the Rh–P coupling constants are about one-tenth that of the corresponding Pt–P coupling constants, a reflection of the difference in the magnetogyric ratio of the two metals). A correlation between Rh–P bond distances and $^1J_{Rh-P}$ values, similar to that observed in the platinum complexes, can be seen from the data in Table II. The trans-influence series derived from the planar RhX(ttp) complexes is CH₃ ~ CO ~ PEt₃ ~ P(OMe)₃ > CN > py > NCS > Cl. Note that there is general agreement between the two series derived from the Pt(II)- and Rh(I)-ttp complexes.

The exceptions between the Pt(II) to Rh(I) orders may result from different degrees of M–L π bonding;[60] also, the smaller Rh(I) atom becomes sterically congested more readily in the presence of bulky X groups, i.e., PEt₃. The stronger π-bonding ligands apparently differ somewhat in their relative trans influence, depending on the metal under consideration.

Oxidation State of the Metal. Assuming that M–P coupling constants vary smoothly through a series of similar complexes, ³¹P NMR may be used to probe the subtle balance of charge that exists between a metal and various coordinated ligands. For example, in a series

of square-pyramidal RhCl(Cyttp)·A complexes (e.g., 10),
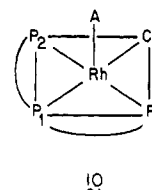
the electron density on the metal atom changes to accomodate the relative σ-donor/π-acceptor properties of the apical ligand A. Metal–phosphorus coupling constants decrease as the net oxidation state of the metal increases.[27,41] Table III summarizes the ³¹P NMR data of the RhCl(Cyttp)·A compounds for A = S₂, O₂, NO⁺, N=NPh⁺, CO, and SO₂. (Also, two six-coordinate, Rh(III) compounds have been included.) When the formal oxidation state of the rhodium atom is clearly +I, $^1J_{Rh-P}$ is significantly larger than when the oxidation state of the metal is +III [e.g., $^1J_{Rh-P_1}$ = 174 Hz in RhCl(Cyttp) vs. 106 Hz in RhCl₃(Cyttp)]. The decreasing Rh–P coupling constants in the five-coordinate adducts have been interpreted in terms of a gradual increase in the formal oxidation state of rhodium along the series A = CO, SO₂, NO⁺, N₂Ph⁺, O₂, S₂.[40] In this series, however, a complicating factor in correlating the J_{Rh-P} values directly to Rh–P bond properties is due to the different coordination numbers in the Rh(I) and Rh(III) complexes; hence, the α_{Rh}^2 term varies.

Dynamic Processes. Stereochemical nonrigidity is characteristic of a large number of organometallic compounds, and NMR spectroscopy has been used extensively to investigate the temperature-dependent behavior of these systems. Cotton's pioneering work (principally ¹H NMR) on metal–annulene and metal-carbonyl complexes demonstrates the power of NMR spectroscopy to establish mechanisms and rates of molecular rearrangements.[61] Meakin and Jesson pioneered the use of variable-temperature ³¹P NMR for dynamic processes and showed that many of the ML₅ⁿ⁺ (L = phosphine or phosphite ligands) complexes underwent intramolecular exchange via the Berry mechanism.[51]

To date, most of the dynamic systems studied by ³¹P NMR have involved complexes of monophosphine ligands; however, recently a number of studies using polydentate ligands have also been reported. Polyphosphine ligands provide advantages over monodentate ligands with comparable donor groups by reducing the rates of intramolecular exchange and by limiting the number of chemically reasonable pathways for the rearrangments. These advantages were demonstrated elegantly by Wreford et al.[62] in studying the mechanism of intramolecular exchange in seven-coordinate complexes of the type XM(CO)₂(diphos)₂ⁿ⁺.

We have taken a somewhat different approach in studying dynamic systems. Rather than investigating

(59) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.
(60) (a) Shustorovich, E. M.; Porai-Koshits, M. A.; Buslaev, Y. A. *Coord. Chem. Rev.* **1975**, *17*, 1. (b) Gofman, M. M.; Nefedov, V. I. *Inorg. Chim. Acta* **1978**, *28*, 1.

(61) Cotton, F. A. "Stereochemical Nonrigidity in Organometallic Compounds", p 377, and Adams, R. D.; Cotton, F. A. "Stereochemical Nonrigidity in Metal Carbonyl Complexes", p 489, in "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M.; Cotton, F. A., Eds.; Academic Press: New York, 1975.
(62) (a) Brown, L. D.; Datta, S.; Kouba, J. K.; Smith, L. K.; Wreford, S. S. *Inorg. Chem.* **1978**, *17*, 729. (b) Albright, J. O.; Brown, L. D.; Datta, S.; Kouba, J. K.; Wreford, S. S.; Foxman, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 5518. (c) Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134. (d) Domaille, P. J.; Wreford, S. S. *Inorg. Chem.* **1980**, *19*, 2188. (e) Meakin, P.; Guggenberger, L. J.; Tebbe, F. N. Jesson, J. P. *Inorg. Chem.* **1974**, *13*, 1025.

Table II
Selected Rhodium–Phosphorus Coupling Constants and Bond Distances for RhX(ttp)·SO$_2$ Complexes[41]

| complex	$^1J_{Rh-P_1}$[a]	$^1J_{Rh-P_2}$[a]	Rh–P$_1$, Å	Rh–P$_2$, Å
RhCl(ttp)	162.5 Hz	128.7 Hz	2.201 (2)	2.228 (1)[b]
RhCl(ttp)·SO$_2$	147.5	113.8	2.24 (2)	2.35 (2)[c,d]
RhN$_3$(ttp)·SO$_2$	138.7	116.7		
RhCN(ttp)·SO$_2$	113.8	117.2		
[Rh(ttp)(CO)(SO$_2$)]AsF$_6$	113.6	113.6	2.346 (6)	2.363 (6)[c,d]

[a] P$_1$ is the central phosphorus atom and P$_2$ represents the two terminal phosphorus atoms of the tridentate ligand PhP(CH$_2$CH$_2$CH$_2$PPh$_2$)$_2$. [b] Reference 11b. [c] The distance given is the average of two very similar Rh–P distances. [d] Eller, P. G.; Ryan, R. R. *Inorg. Chem.* 1980, 142.

Table III
Phosphorus-31 NMR Data for RhCl(Cyttp)·X Compounds

complex	δP_1[a,b]	δP_2[a,b]	$^2J_{P-P}$[c]	$^1J_{Rh-P_1}$[c]	$^1J_{Rh-P_2}$[c]
RhClL[d]	20.6	9.2	−49	174	126
RhClL·SO$_2$	18.8	3.2	−36	156	107
RhClL·NO$^+$	15.9	8.3	−28	147	99
RhClL·N$_3$Ph$^+$	19.7	6.7	−30	142	98
RhClL·O$_2$	21.4	2.3	−33	139	90
RhClL·S$_2$	10.1	−1.4	−32	134	84
RhClL·SO$_4$[e]	14.8	6.7	−27	123	79
RhCl$_3$L[e]	5.3	−2.9	−28	106	78

[a] Chemical shifts are in ppm relative to 85% H$_3$PO$_4$; positive shifts are downfield. [b] The P$_1$ is the central phosphorus atom and P$_2$ are the two terminal phosphorus atoms in the tridentate ligand. [c] Coupling constants in hertz; relative signs obtained by computer simulation. [d] L = PhP(CH$_2$CH$_2$CH$_2$PCy$_2$)$_2$. [e] Six-coordinate compound.

intramolecular rearrangments of complexes that maintain a constant coordination number, we have studied several complexes of Pt(II)[63] and Rh(–I)[49] in which the objective was to increase the coordination number by employing a ligand that contained more phosphine groups than are normally present in a corresponding complex of monophosphines. For example, by using Pt–CH$_3$ compounds and the strong chelating tendency of tri- and tetraphosphine ligands, we have synthesized a series of Pt(II) complexes of formulae Pt(CH$_3$)$_2$(polyphosphine).[49a] The polyphosphine ligands ttp, etp, Cyttp, tripod, and PP$_3$ readily displace COD (COD = 1,5-cyclooctadiene) from Pt(CH$_3$)$_2$(COD); the resultant Pt(CH$_3$)$_2$ (polyphosphine) complexes of ttp, etp, and PP$_3$ are fluxional at modest temperatures, whereas the Cyttp and tripod ligands give complexes that do not exchange the bonded and nonbonded phosphine groups up to 100 °C.[63] The variable-temperature ^{31}P NMR spectra of Pt(CH$_3$)$_2$(ttp) for the temperature range 0–100 °C are presented in Figure 4. The low-temperature ^{31}P{^{1}H} spectrum (0 °C) consists of an AB pattern and the two corresponding satellites that result from coupling to ^{195}Pt (33.8% abundant, $I = {}^1/_2$). Thus, two phosphorus atoms are bonded to the metal, and the singlet is due to the uncoordinated terminal phosphorus atom, as in 11. As the temperature increases, the
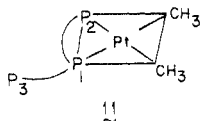
resonances due to the two terminal phosphorus atoms (P$_2$ and P$_3$) broaden, and the Pt–P coupling is lost for

(63) (a) Tau, K. D.; Meek, D. W. *J. Organomet. Chem.* 1977, *139*, C83. (b) Tau, K. D.; Uriarte, R. J.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* 1979, *101*, 6614.

Scheme I
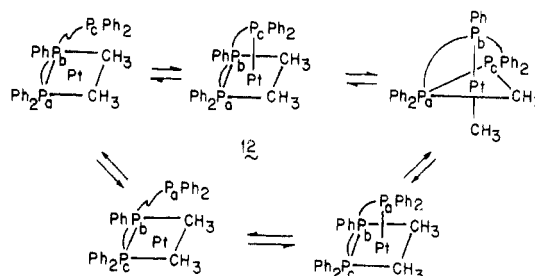
those signals, whereas the central phosphorus atom always remains coupled to the ^{195}Pt nucleus; its spectrum changes into a triplet at high temperatures. The phosphorus–phosphorus coupling at the high temperature (9 Hz at 100 °C) is the average of the two couplings in the frozen structure (0 and 18 Hz at 0 °C) and indicates rapid exchange on the NMR time scale. A computer simulation of this exchange (included in Figure 4) gives $\Delta H_{298}^{\ddagger} = 6.53$ kcal/mol, $\Delta G^{\ddagger} = 7.1$, and $\Delta S^{\ddagger} = -30.4$ eu.[63] The large negative entropies of activation for the Pt(CH$_3$)$_2$(polyphos) complexes (polyphos = ttp, etp, PP$_3$) indicate that the exchange occurs via an associative process involving five-coordinate intermediates (e.g., Scheme I). Additional evidence for an associative process is provided by the closely related complex Pt(CH$_3$)$_2$(Cyttp), which does not undergo exchange even at 100 °C. The ttp and Cyttp ligands differ only in the substituents on the terminal phosphorus atoms; however, the increased steric requirements of the cyclohexyl substituents on the terminal phosphorus atoms of Cyttp presumably inhibits formation of the crowded five-coordinate intermediate in which the dicyclohexylphosphino groups would be only 90° apart (e.g., 12 in Scheme I).[63]

Prospectus

As illustrated in this Account, phosphorus-31 NMR is rapidly becoming the analytical method of choice for rapid characterization of organometallic and coordination compounds that contain phosphorus ligands. The recent examples cited below demonstrate that future ^{31}P studies can be expected to provide definitive identification of "intermediates" in reaction mechanisms and in catalytic systems, since ^{31}P NMR spectra supply direct characterization of the phosphorus-containing species in solution. For example, Hughes and Unruh[64] used a combination of ^{31}P{^{1}H} NMR and reactor testing studies to identify the composition and structure of the catalyst, HRh(CO)(P~P)(P), under hydroformylation conditions (793 kPa, 1:1 H$_2$/CO, 110 °C) for 1-hexene

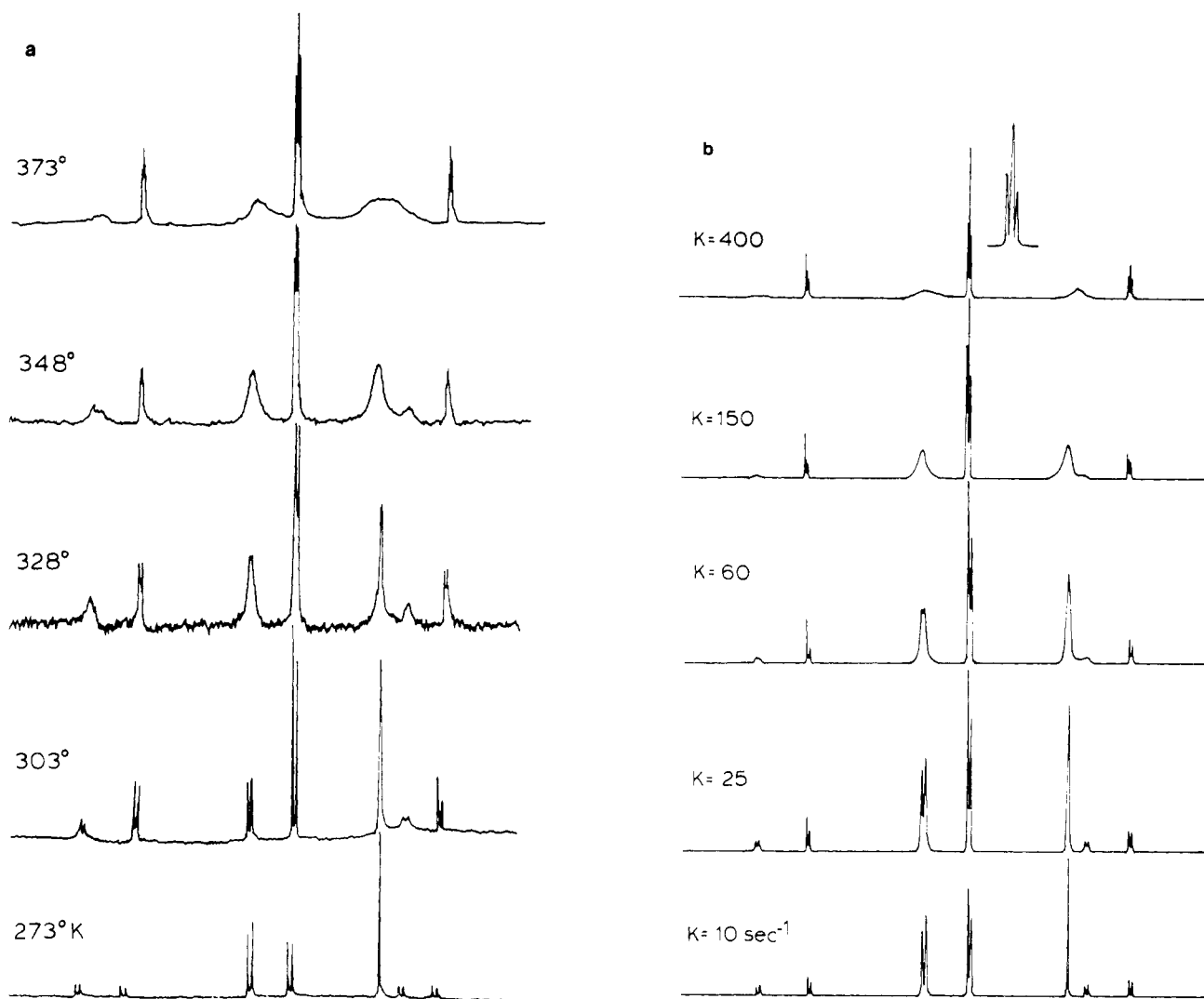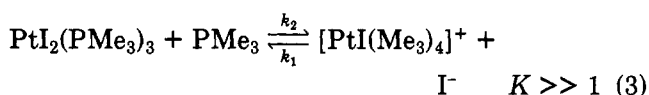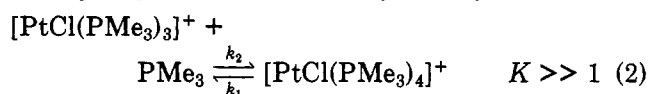(64) Hughes, O. R.; Unruh, J. D. *Ann. N.Y. Acad. Sci.* 1981, in press.

Figure 4. Variable-temperature $^{31}P\{^{1}H\}$ NMR spectrum of $Pt(CH_3)_2(ttp)$; $ttp = PhP(CH_2CH_2CH_2PPh_2)_2$: (a) the experimental spectrum at the indicated temperatures in toluene; (b) the computer-simulated spectrum for the indicated exchange rates for P_2 and P_3. from ref 63b).

hydroformylation to heptanal. With certain diphosphines they showed that three phosphino groups (rather than two as generally thought) are coordinated to rhodium at the instant straight-chain selectivity is determined.[64]

A ^{31}P NMR study of the phosphine-catalyzed cis–trans isomerization of four-coordinate platinum(II) complexes gave direct characterization of the intermediates in solution and showed that the cis–trans isomerization of PtX_2L_2 catalyzed by L proceeds by rapid displacement of X^- by L followed by a slow displacement of L by X^- and *not by pseudorotation of a five-coordinate intermediate.* The fastest process observed for both triphosphine complexes $[PtCl(PMe_3)_3]^+$ and $PtI_2(PMe_3)_3$ is the *intermolecular* phosphine exchange through equilibria 2 and 3, respectively.[65]

$$[PtCl(PMe_3)_3]^+ +$$

$$PMe_3 \overset{k_2}{\underset{k_1}{\rightleftharpoons}} [PtCl(PMe_3)_4]^+ \quad K \gg 1 \quad (2)$$

$$PtI_2(PMe_3)_3 + PMe_3 \overset{k_2}{\underset{k_1}{\rightleftharpoons}} [PtI(Me_3)_4]^+ +$$

$$I^- \quad K \gg 1 \quad (3)$$

(65) Favez, R.; Roulet, R.; Pinkerton, A. A.; Schwarzenbach, D. *Inorg. Chem.* **1980**, *19*, 1356.

Phosphorus-31 NMR may prove to be extremely useful for determining whether metal–metal bonds are present in phosphide-bridged metal complexes. For example, Kreter found that a large downfield shift of the phosphorus resonance occurs when an organophosphide group bridges two metals that contain a metal–metal bond.[66] This large downfield shift is not limited to bimetallic complexes of Ir and Rh, as it has been observed also in the $Rh_4(\mu\text{-}PPh_2)_5(CO)_5^-$ cluster[67] and in other complexes that contain a bridging phosphide group and a metal–metal bond.[28,68]

Finally, the very difficult problem of determining the stereochemistry of a catalyst bound to a polymer support has been at least partially overcome by the use of ^{31}P NMR.[69] Titration of poly[4-(diphenylphosphino)styrene] with $[RhCl(olefin)_2]_2$ was followed by ^{31}P NMR, and comparison of the spectra with those

(66) Kreter, P. E., Jr.; Meek, D. W. paper presented at the 11th Central Ohio Regional Meeting of the American Chemical Society, Columbus, OH, May 1979; see Abstracts INOR 4, p 64. Kreter, P. E., Jr.; Meek, D. W., unpublished data, 1980.

(67) Kreter, P. E., Jr.; Meek, D. W.; Christoph, G. G. *J. Organometal. Chem.* **1980**, *188*, C27.

(68) Examples are given in Table V of the paper: Peterson, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186.

(69) Naaktgeboren, A. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc.* **1980**, *102*, 3350.

of monomeric complexes established the coordination geometry of the major species as either
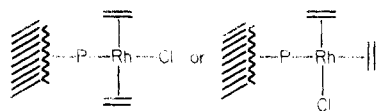
depending on the olefin employed and the Rh/P ratio. The novel observation of a dependence of $^1J_{Rh-P}$ on the Rh/P ratio could provide an additional parameter by which to characterize the metal environment in these polymer-anchored systems.