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Phosphorus-31 Nuclear Magnetic Resonance as a Method of Predicting Ligand Basicity and Rates of Homogeneous Catalysis

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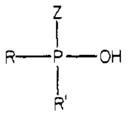
Variations in CPC bond angles caused by bulky substituents on phosphines change the shielding on the phosphorus nucleus and can often mask correlations between chemical reactivity and ^{31}P NMR chemical shifts. With use of the chemical shift of the tetrahedral oxide of the parent compound the steric effects are minimized, thus allowing the chemical shift to provide successful correlations with the reactivity of the parent compound. Group contribution effects of the substituents attached to phosphorus suggest a new linear free energy relationship, and the direct relationship between reactivity and chemical shift of the phosphine oxide can aid in the choice of ligands for homogeneous catalysis. The correlations of the chemical shift of the phosphine oxides with ligand basicity and infrared and NMR data of metal-phosphine complexes indicate the influence of both σ and π bonding between the metal and the phosphine ligands.

Introduction

Although success has been attained in predicting the chemical reactivity of phosphines by group contribution effects, this method has previously been unsuccessful in providing ^{31}P NMR chemical shift correlations. Henderson and Streuli[1] measured the basicities of a variety of primary, secondary, and tertiary phosphines and correlated the pK_a of the phosphines using the Taft equation[2] based on the sum of the group contributions of the alkyl and aryl substituents ($\sum\sigma^*$). They found that this linear free energy relation gave three parallel lines for the three types of phosphines with a fourth point for PH_3. Kabachnik and Balueva[3] recorrelated the pK_a data with a σ derived for phosphorus using acidity measurements[4] of phosphorus acids of the type



$$R{-}\overset{Z}{\underset{R'}{P}}{-}OH$$

Where R, R′ = alkyl, aryl, alkO, or H, Z is S or O. The correlation of Henderson and Streuli's data with Kabachnick's σ is linear with the primary, secondary, and tertiary phosphines all falling in the same line, showing that the basicity of phosphines is mainly determined by group contribution inductive effects. Only minor deviations are caused by steric hindrance.

Grim and McFarlane[5] later noted that group contribution effects of alkyl and aryl substituents also determine ^{31}P NMR chemical shifts of secondary and tertiary phosphines, but they found no correlation of chemical shift with the Taft σ^* parameter or with the meta and para Hammett parameters. The absence of a correlation between the basicity and chemical shift group contribution studies shows that the inductive effect which governs basicity is not the major factor influencing the chemical shift of phosphines.

Three factors, two electronic and one steric, contribute to the observed ^{31}P NMR chemical shifts of phosphorus compounds: the distribution of electron density in the σ bonds between phosphorus and its substituents, the extent to which phosphorus participates in π bonding, and the variations in the CPC bond angles.[6] Small changes in CPC bond angles which lead to dramatic differences in the shielding of the phosphorus atom are easily effected by the substituents in phosphines because of the lability of the phosphorus lone pair of electrons. Lone-pair hybridization allows the molecule to take on configurations ranging from p^3 to sp^3; in the sp^3 configuration the lone pair acts as an abortive bond. Limiting the flexibility of the molecule by bonding the lone pair of electrons suppresses sterically induced changes in the shielding and minimizes its effect on chemical shift. This allows the electronic effects to dominate, and useful correlations between chemical shift and other electronic effects may be observed.

From the standpoint of available data, the most convenient class of phosphines in which the lone pair is well localized are the phosphine oxides. Phosphine oxides also restrict hybridization of the lone pair more effectively than sulfides or selenides because of the high electronegativity and double bonding of the oxygen. As a result, a smaller amount of deformation of the molecule takes place as the R substituents are varied. Quantum mechanical calculations[6] also show that the chemical shift of the tetrahedral structure of OPR_3 is especially insensitive to bond angle variations and changes in π-bond distributions.

A compilation of ^{31}NMR chemical shifts of phosphine oxides obtained from the literature is presented in Table I. The numbers preceding the compounds are used for ligand identification in all subsequent figures. Chemical shifts in ppm are referenced to 85% H_3PO_4 with positive values being downfield.

NMR Correlations of the Basicity and Reactivity of Phosphines

The pK_a's of alkyl- and arylphosphines, PR_3, reported by Henderson and Streuli[1] can be correlated with the chemical shift of the corresponding oxides, OPR_3. Figure 1 shows that basicity of the phosphines is directly related to the chemical shift and, like Kabachnik and Balueva's correlation, it consolidates the three classes of phosphines. It is apparent that, when bond angle variations are minimized, the chemical shift becomes a fair measure of electronic effects transmitted through the phosphorus atom. Deviations from the correlation are in the same direction as observed by Henderson and Streuli, who concluded that this is probably due to the steric effect of solvation of the product phosphonium ion. The success of this correlation prompted further attempts to relate the reactivity of phosphines to the electronic component of the phosphorus chemical shift.

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Table I. ^{31}P NMR Chemical Shifts of Phosphine Oxides[a]

no.	compd PR_3	δ of the oxide	ref
1	PMe_3	−48	34
2	PEt_3	−48	33, 12
3	$P(i\text{-}Pr)_3$	−55	35
4	PBu_3	−43	12
5	$P(t\text{-}Bu)_3$	−41	33
6	$P(c\text{-}C_5)_3$	−68	35
7	PCy_3	−50	33
8	PPh_3	−27	35
9	$P(octyl)_3$	−47	35
10	$PPhMe_2$	−33	38
11	PPh_2Me	−29	38
12	$PPhEt_2$	−42	33
13	PPh_2Et	−33	38
14	$PHCy_2$	−46	33
15	PH_2Cy	−22	33
16	$PHBu_2$	−29	33
17	$PH(octyl)_2$	−28	33
18	$PH_2(octyl)$	−10	33
19	$PHPh_2$	−26	36
20	$P(CH_2CH_2CN)_3$	−37	33
21	$PPh_2(t\text{-}Bu)$	−39	38
22	PI_3	+273	37
23	PBr_3	+103	33
24	PCl_3	−2	33
25	PF_3	+36	12, 33
26	PPh_2Cl	−43	33
27	$PPhCl_2$	−35	33
28	$P(m\text{-}C_6H_4F)_3$	−21	39
29	$P(p\text{-}C_6H_4Cl)_3$	−21	39
30	$P(OMe)_3$	−2	34, 12
31	$P(OEt)_3$	+1	15, 12
32	$P(O\text{-}i\text{-}Pr)_3$	+6	35
33	$P(OBu)_3$	−1	35
34	$P(O\text{-}t\text{-}Bu)_3$	+14	15, 12
35	$P(O\text{-}n\text{-}C_5)_3$	+4	35
36	$P(OPh)_3$	+18	35, 12
37	$P(O\text{-}p\text{-}tol)_3$	+16	33
38	$PPh(OMe)_2$	−19	34
39	$PPh_2(OMe)$	−21	34
40	$P(OCH_2)_3CCH_3$	−8	40
41	$PPh_2(i\text{-}Pr)$	−36	38
42	$PPh(Bu)_2$	−45	35
43	$P(NMe_2)_3$	−23	12, 35
44	$PPh_2(OEt)$	−31	34
45	$P(p\text{-}C_6H_4F)_3$	−21	39
46	diphos	−36	34
47	$P(O\text{-}o\text{-}tol)_3$	+17	33
48	$P(OCH_2CCl_3)_3$	+9	33
49	$PPh(OEt)_2$	−17	33
50	$PPh(OPh)_2$	−12	33
51	$P(p\text{-}tol)_3$	−33	*b*
52	PBz_3	−34	41

[a] Key to abbreviations: Ph, phenyl; Cy, cyclohexyl; tol, tolyl; diphos, 1,2-bis(diphenylphosphino)ethane. [b] Estimated from carbonyl stretching frequency of $Ni(CO)_3P(p\text{-}tol)_3$ with use of Figure 3.

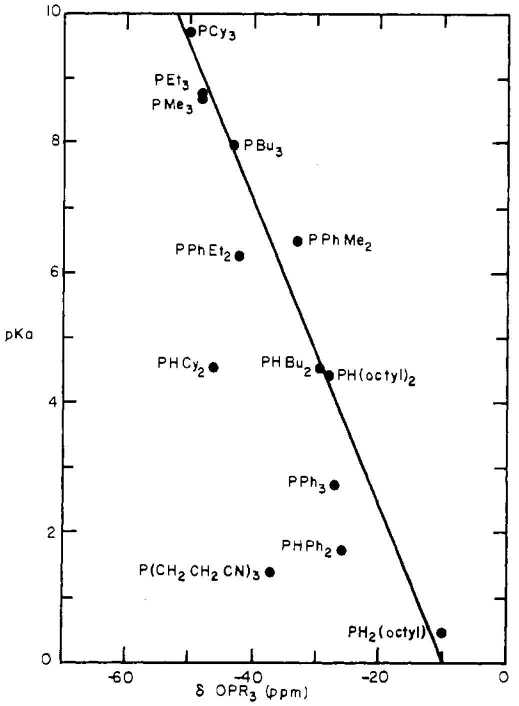

Figure 1. Relationship between phosphine basicity and the ^{31}P NMR chemical shift of the corresponding oxide (correlation coefficient = 0.71).

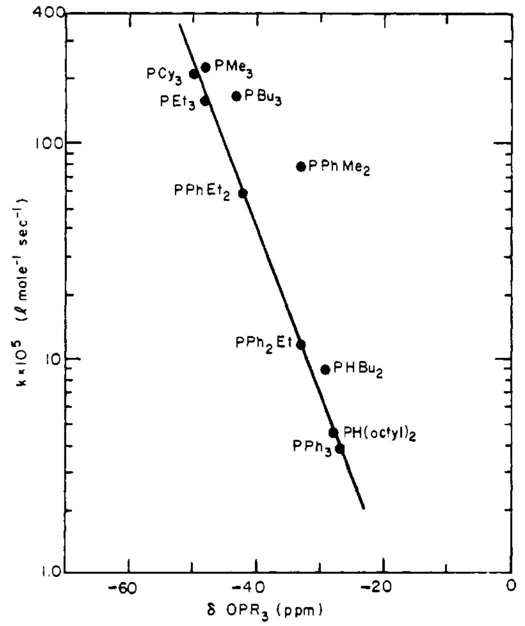

Figure 2. Linear free energy relationship for the reaction of secondary and tertiary phosphines with ethyl iodide in acetone at 35 °C (correlation coefficient = 0.85).

The effect of structure on the reactivity of phosphines was described by Henderson and Buckler.[7] The nucleophilicity of phosphines in S_N2 attack on alkyl halides in the reaction

$$R_1R_2R_3P + C_2H_5I \xrightarrow{k} R_1R_2R_3C_2H_5P^+ + I^-$$

gave a linear free energy relationship with the Taft σ^* parameter that was adequate for the tertiary phosphines. Inclusion of primary and secondary phosphines gave appreciable scatter since their basicities were not well described by σ^*, probably because σ^* was derived for carbon, not for phosphorus. Figure 2 demonstrates a linear free energy relationship between the nucleophilicity of the phosphine and the chemical shift of the corresponding oxide. The fit of Henderson and Buckler's data is greatly improved. Chemical shift data were not available for all the compounds; nonetheless, all types of phosphines are represented. The fit of the data reinforces the hypothesis that once the effects of substituent bulk are minimized, inductive effects can be predicted by chemical shift. The major advantage of using chemical shift over σ is the availability and ease of compiling chemical shift data.

Infrared Frequency Correlations for Metal Carbonyls

The correlations of infrared stretching frequencies in metal carbonyl complexes containing phosphorus ligands with ligand basicity and Hammett parameters have been cited as evidence for inductive effects and π bonding.[8-11] The correlations are

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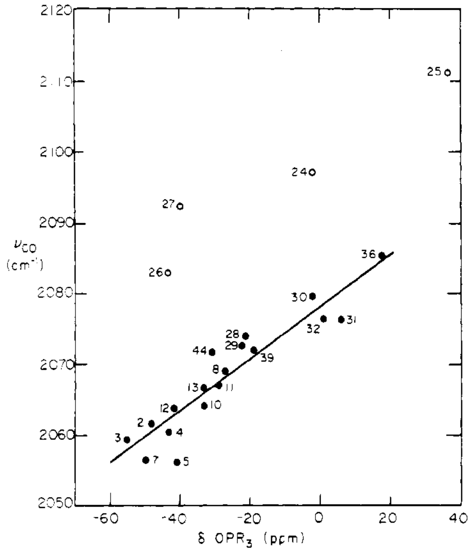

Figure 3. Carbonyl stretching frequency of $Ni(CO)_3PR_3$ correlated with ^{31}P NMR chemical shift of OPR_3 (correlation coefficient = 0.82, without phosphines containing halogens, shown as open circles).

linear for aryl- and alkylphosphines and aryl and alkyl phosphites but fail to encompass the halogen-substituted compounds, notably PF_3 and PCl_3.[8,12] The deviation of the halogen phosphines has been attributed to π bonding between the metal and phosphorus induced by the highly electronegative halogens. The concept of the σ phosphorus–metal bond predominating in alkyl- and arylphosphine–metal complexes is reinforced when ^{31}P NMR data are viewed in conjunction with infrared measurements of metal carbonyl complexes containing phosphine ligands.

Tolman reported the measurement of the A_1 carbonyl stretching frequency for tetrahedral $Ni(CO)_3L$.[8] Data for 70 monodentate phosphorus ligands, L, could be correlated by assigning each substituent a contribution effect χ_i such that, for any $Ni(CO)_3PR_1R_2R_3$, the stretching frequency ν_{CO} in cm^{-1} is

$$\nu_{CO} = 2056.1 + \sum_{i=1}^{3} \chi_i$$

The value of the equation lies in its ability to predict the stretching frequency where direct data are not available. Comparison of χ_i with Kabachnik's σ gives a nonlinear relation, indicating that electronic effects are indeed transmitted through the phosphorus–metal–carbon σ bonds, but the nonlinearity suggests that other factors, perhaps reduced σ donation or enhanced π-acceptor behavior, are present in the complexes. The substituent contribution parameter χ_i is also useful in showing that inductive effects determine ν_{CO}.

Tolman found no success in correlating the infrared frequencies with the ^{31}P NMR chemical shifts of the ligands[13] due, in retrospect, to the ease of rehybridization of the phosphine. In Figure 3, Tolman's frequencies are correlated with the ^{31}P NMR chemical shifts of the oxides of the substituting ligands. For the alkyl- and arylphosphines and alkyl and aryl phosphites the carbonyl stretching frequency can be predicted by the expression

$$\nu_{CO} = 2078 + 0.36\delta_{OPR_3}$$

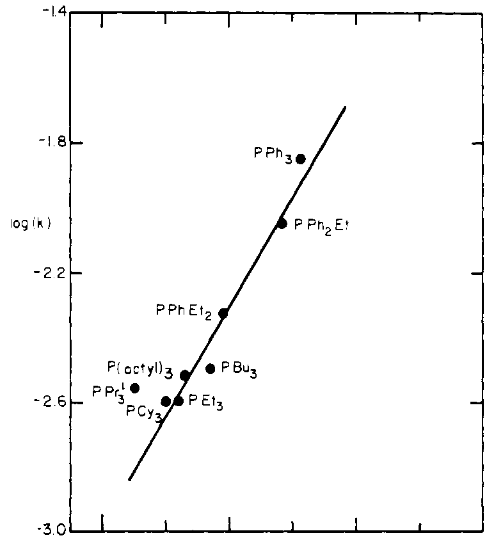

Figure 4. Rate of hydroformylation of 1-hexene in benzene with $HCo(CO)_4PR_3$ at 160 °C and 1000 psi H_2/CO (1.2:1) (correlation coefficient = 0.89).

Slight deviations from the line are noted for the bulkier ligands having a cone angle above 145°.[14] As in correlations with Hammett parameters, major deviations from the correlation with ν_{CO}, depicted in Figure 3, are apparent for phosphines containing halogen substituents (shown as open circles). Carbonyl stretching frequency data are not available for PI_3- and PBr_3-substituted $Ni(CO)_4$, but examination of the chemical shifts of the oxides (273 and 103 ppm) suggests that they will also have large deviations from the correlation.

Effects of Ligands on Metal Complex Activity

A large portion of phosphorus chemistry involves the use of phosphorus ligands with metal complexes for synthesis of homogeneous catalysts. The effect of the ligands on catalytic activity is not well understood although for some reactions such as hydroformylation it has been shown to depend directly on basicity.[14,15] The relationship between ligand basicity and chemical shift, δ_{OPR_3}, prompted correlations of catalytic activity of metal–phosphine complexes such as shown in Figure 4. As expected, Figure 4 shows that rate of hydroformylation of 1-hexene with $HCo(CO)_4PR_3$ depends directly on the chemical shift of the ligand oxide.

An important step in homogeneous hydrogenation of metal complexes is oxidative addition of hydrogen to a square-planar complex to form a *cis*-dihydrogen octahedral complex. This is exemplified by

$$trans\text{-}Ir^{I}X(CO)L_2 + H_2 \rightleftharpoons Ir^{III}H_2X(CO)L_2$$

where X = halogen and L = tertiary phosphorus ligand. Both the forward and reverse rates depend on the ligands X and L. Data taken by Mays, Simpson, and Stefanini[16] on the reverse of a similar reaction, the reductive elimination of hydrogen from $IrH_2(CO)_2L_2$ by trimethyl phosphite, are shown in Figure 5. The basicity dependent rate data can be correlated by Kabachnik's σ, but a better fit is obtained if the chemical shift of the ligand oxide is used. Whether the correlation retains a simple linear dependence when extended to phosphites cannot be determined without more data.

The forward rate of oxidative addition measured by Strohmeier and Onada[17] has a more complicated ligand de-

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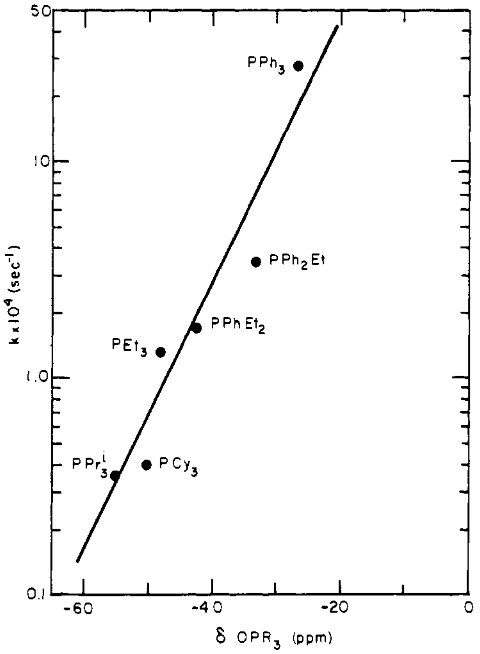

Figure 5. Rate of reductive elimination of hydrogen by $P(OMe)_3$ from $[Ir(CO)_2L_2H_2]^+$ at 25 °C in $CHCl_3$ (correlation coefficient = 0.91).

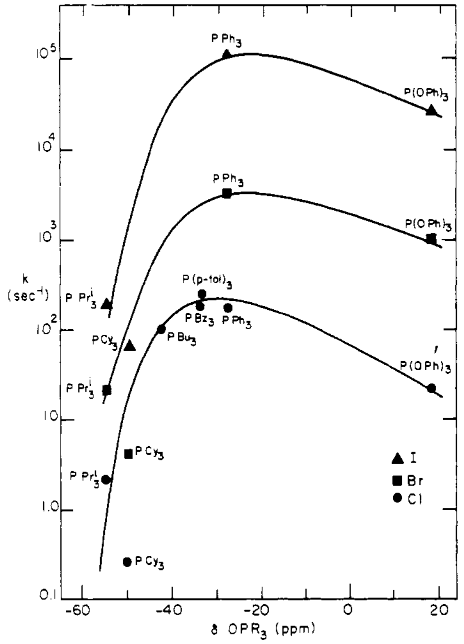

Figure 6. Ligand influence on rate of oxidative addition of hydrogen to $IrX(CO)L_2$ to form $IrH_2X(CO)L_2$ at 30 °C in toluene (X = I, Cl, or Br).

pendence. Figure 6 shows that the three curves, one for each halogen in $IrX(CO)L_2$, go through a maximum. Incidently, as with $Ni(CO)_3L$, the infrared CO stretching frequency of $IrX(CO)L_2$ is linearly related to δ_{OPR_3}.

Behavior similar to that of iridium was observed[18] in this laboratory for anthracene hydrogenation with $[Mn(CO)_4L]_2$ (Figure 7). The kinetics of this system indicated that two manganese complexes, $HMn(CO)_4L$ and a hydrogen-deficient anthracene–manganese carbonyl complex, compete for the available hydrogen via oxidative addition to form intermediates. The rate-determining steps of the hydrogen–manganese carbonyl–anthracene intermediate formation combining with a trihydride of manganese carbonyl govern the reaction, giving a second-order rate dependence on manganese concentration. An extensive number of ligands were studied, and only two, PPh_3 and PPh_2Cl, failed to fall on the curve. The unusual behavior of the rate of hydrogenation for both the iridium and manganese complexes on ligand substitution are not predicted by Hammett parameters or Kabachnik's σ.

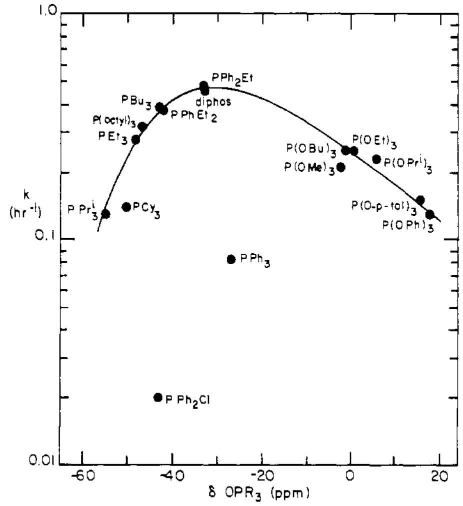

Figure 7. Rate of anthracene hydrogenation by $Mn_2(CO)_8(PR_3)_2$ in decane at 200 °C with 41.3 bar H_2/CO (1:1).

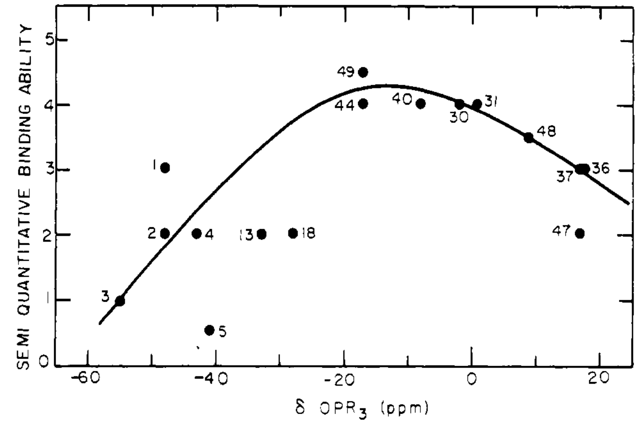

Figure 8. Steric and electronic effects in $Ni(PR_3)_4$.

The relationship between chemical shift and basicity (and in effect Kabachnik's σ) suggests that a correlation of reaction rate with chemical shift is a linear free energy relationship. If this is so, the nonlinear nature of rate with chemical shift implies a change in the mechanism such as caused by solvent effects.[19] More likely, hydrogenation of anthracene by $[Mn(CO)_4L]_2$ exhibits a maximum because of the necessity of two intermediates of manganese, one a hydride the other an aryl complex, each being stabilized to a different extent by the ligands. A more tempting explanation is that steric effects are limiting the reaction rates, since PCy_3 and $P(i\text{-}Pr)_3$ are bulky ligands. This does not fully explain the downturn behavior, however, because in both systems the reaction rate decreases at PBu_3, but the cone angle of PBu_3 (132°) is less than that of $P(p\text{-tol})_3$ (145°), PBz_3 (165°), or PPh_2Et (140°).

A substitution reaction, relevant to determining the importance of steric influence on metal complexes, was conducted by Tolman.[13] One phosphorus ligand, L′, was used to displace another on NiL_4 to form NiL_3L', and an empirical ordering scheme, termed the semiquantitative binding ability, was de-

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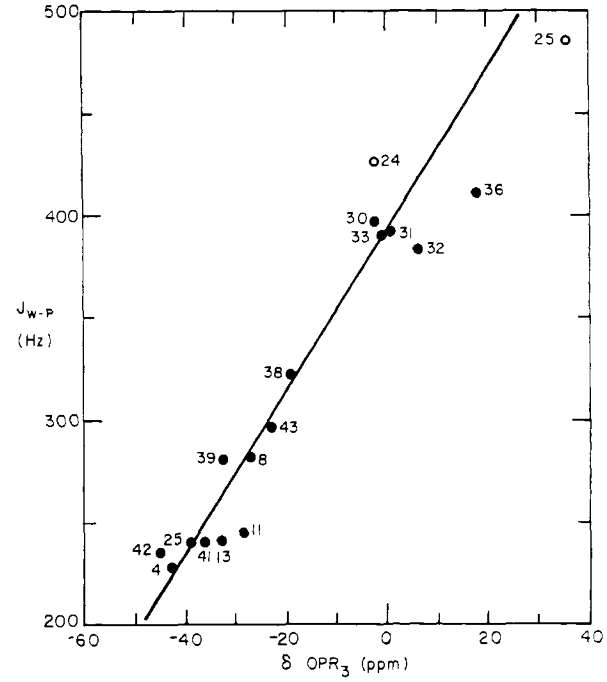

Figure 9. Relationship between tungsten–phosphorus coupling constant and chemical shift of OPR_3 in $W(CO)_5PR_3$ (correlation coefficient = 0.91 not including trihalides, shown as open circles).

termined. Thus, if 4 mol of PMe_3 could displace PBu_3 from 1 mol of $Ni(PBu_3)_4$ to form predominantly $Ni(PBu_3)(PMe_3)_3$, then it was assigned a higher value of binding ability than PBu_3. The data did not correlate with the carbonyl stretching frequency of the related $Ni(CO)_3L$ compounds, and it was judged that steric effects dominate electronic effects for NiL_4 ligand exchange. Figure 8 is a correlation of Tolman's empirical semiquantitative binding ability observed as a function of δ_{OPR_3}. The interesting aspect of Figure 8 is that the maximum does not occur at the alkyl phosphites which have the smallest cone angle (i.e., $P(OMe)_3$ (**30**) (107°) or $P(OEt)_3$ (**31**) (109°) but at $PPh(OEt)_2$ (**49**) or $PPh_2(OEt)$ (**44**) which have cone angles of 116 and 133°, respectively.[14] This is the same behavior that is observed in Figures 6 and 7, in that the downturn at about −30 ppm is caused by electronic effects; and steric hindrance becomes rate limiting only for very bulky ligands. It is surprising that for oxidative addition a ligand as bulky as PBz_3 has no deleterious effect on rate.

Relationship of Spin–Spin Coupling in Metal Complexes to Chemical Shift

Phosphorus-31 NMR studies of compounds containing other magnetically active nuclei yield information due to mutual interaction in the form of spin–spin coupling constants. This can be especially fruitful for metal–phosphorus ligand complexes where the metal is also active, e.g., such as Rh, W, Pt, etc. Grim et al.[20] found a rather unsatisfactory correlation between the carbonyl stretching frequency of $W(CO)_5L$ and the tungsten–phosphorus coupling constant J_{W-P}. Two crossing lines were drawn through the data, one for phosphines and the other for phosphites. The fit of the data is better if the stretching frequency is graphed as a function of chemical shift of the corresponding phosphoryl as was done for substituted nickel carbonyls. More importantly, it can be seen from Figure 9 that the chemical shift δ_{OPR_3} is directly related to the coupling constant. More recent data has been included.[21-23] Minor

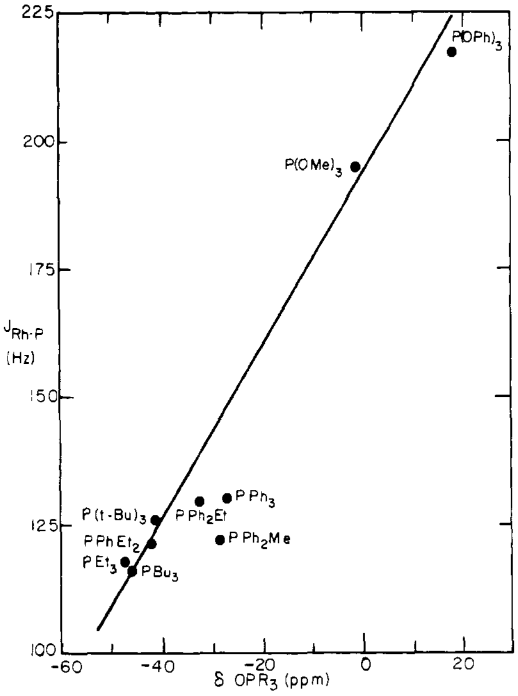

Figure 10. Relationship between rhodium–phosphorus coupling constant and chemical shift of OPR_3 for *trans*-$RhCl(CO)(PR_3)_2$ (correlation coefficient = 0.92).

deviations are noted for the trihalide phosphines PCl_3 and PF_3, shown as open circles in Figure 9. PBr_3 and PI_3 (J_{W-P} = 398, 334 Hz; δ_{OPR_3} = 103, 273) deviate widely from the correlation and have not been included in the plot. The same relationships apply to rhodium–phosphorus ligand–metal complexes such as *trans*-$RhCl(CO)(PR_3)_2$,[24,25] shown in Figure 10. Data for the trihalide phosphine ligands were not available in the literature.

Coupling constants have been related to Hammett parameters[26,27] as have chemical shifts for closely related compounds,[28,29] so the relationship between J and δ_{OPR_3} is not coincidental. Since p, d, f, ... atomic orbitals have zero density at the nucleus, the interaction between magnetically active nuclei is transmitted mainly by the s-orbital components of the metal–phosphorus bond. Increasing s-orbital hybridization to form stronger σ bonds can be expected to be paralleled by a larger J. The direct relationship between J and chemical shift of OPR_3 reflects the similarity between σ components of the O═P bond and the W—P bond as seen by NMR. For this reason the fit of the coupling constant data with δ of OPR_3 for the non-π-bonding alkylphosphines is better than with trihalogen phosphines which have been shown to π bond.[12,30]

A direct relationship between Tolman's infrared frequencies[8] and ^{13}C NMR chemical shifts of $Ni(CO)_3PR_3$ complexes was found by Bodner,[27] and a group contribution equation was formulated to predict ^{13}C NMR shifts. Bodner concluded that ^{13}C shift is a measure of the ratio of electron donor to the acceptor character of PR_3. The ^{13}C chemical shifts are correlated with ^{31}P chemical shifts of OPR_3 in Figure 11. The

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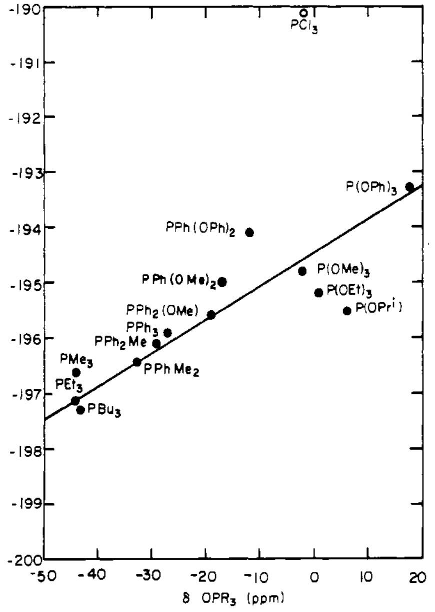

Figure 11. Relationship between ^{13}C NMR shift and ^{31}P NMR shift of OPR_3 in $Ni(CO)_3(PR_3)$ (correlation coefficient = 0.75).

major deviation is again from a halogen species, PCl_3—which was in line in the ν_{CO} vs. ^{13}C chemical shift correlation. The different behavior of PCl_3 in the two systems is a result of the inability of ^{13}C NMR to differentiate between σ and π effects in the metal-phosphorus bond because they have been transmitted through the metal.

Although coupling constants are directly related to δ_{OPR_3}, ^{31}P NMR shifts of metal complexes such as $Ni(CO)_3PR_3$[31] and $M(CO)_5PR_3$ (M = Mo, W, Cr^{32}) are only roughly correlated by δ_{OPR_3} and have been customarily described by the difference in the chemical shift between the complexed and uncomplexed ligand.

In summary, the ^{31}P chemical shift of phosphoryls, OPR_3, is a good measure of the basicity of the parent phosphines PR_3 because the sterically induced component of the chemical shift is minimized by localization of the phosphine lone-pair electrons in the O-P bond, allowing the electronegativy of the substituents, R, attached to the phosphorus to determine the chemical shift. Correlations of reaction rate constants with OPR_3 chemical shift may, like linear free energy relationships, have the potential to predict homogeneous catalysis reactivity.

Experimental Section

$Mn_2(CO)_{10}$, was purchased from Alfa Inorganics, Inc., and used without further purification. Phosphines and phosphites used to prepare $[Mn(CO)_4L]_2$ were obtained from Aldrich Chemical Co., with the exception of tri-*p*-tolyl phosphite, diethylphenylphosphine, and triisopropylphosphine which were purchased from Pfalz and Bauer, Inc.

The solvent was technical grade 95+% normal decane, purchased from Phillips Petroleum. Anthracene (95%) was obtained from Eastman Chemicals and 9,10-dimethylanthracene (95+%) from Aldrich. The nitrogen and hydrogen (99.999%) were supplied by Lawrence Berkeley Laboratories and contained less than 1.5 ppm water or oxygen. The hydrogen was passed through a Matheson catalytic deoxygenator before use. Carbon monoxide was obtained as "Matheson purity" 99.999% min.

The reactions were conducted in a 600-mL autoclave purchased from Parr Instruments, Co. The autoclave internals consisted of a stirrer, cooling loop, thermocouple well, sample tube, and glass liner. The bomb was fitted for gas inlet and sampling and liquid injection and sampling. Reactor temperature was automatically controlled by alternately energizing a heating mantle or a solenoid valve which admits cooling water to the cooling loop. Reaction temperature varied ±1 °C during a run. Pressure was indicated by a gauge reading either 0-1000 psi or 0-2000 psi, calibrated to ±10 psi.

In the typical procedure, 10 mmol of anthracene and 1 mmol of metal carbonyl were weighed out and placed in the glass liner. A total of 100 mL of decane was added, and 1 mmol of substituting ligand was either weighed in or added by pipette. The glass liner was placed in the reactor and sealed. The appropriate support lines were connected, and a vacuum line was attached to the gas outlet.

The reactor was purged by alternately drawing a vacuum and pressurizing to 21 bar with either hydrogen, carbon monoxide, or a 1:1 mixture of the two. The reactor was then pressurized to the initial condition, and heating was started; the reaction was conducted for the heat-up time plus 1 h. During the run, liquid samples were taken for later analysis by gas chromatography using a Varian aerograph, Model A-90-P, with a $^1/_8 \times 10$ ft column containing 4% Dexsil 300 GC on Chromasorb, HP (100-120 mesh), operated isothermally at 200 °C. Injector, detector, and collector temperatures were 280, 295, and 290 °C, respectively. These conditions can sharply separate decane, dihydroanthracene, and anthracene, eluting in that order. Anthracene is not completely soluble in decane at these levels at room temperature. Dihydroanthracene was referenced to the solvent, decane, which was used as an internal standard for concentration calculations. Since only one hydrogenated product (9,10-dihydroanthracene) is produced, the amount of anthracene can be calculated by difference.

For a study of the influence of ligand type on the rate of reaction, dimanganese decacarbonyl was substituted in situ by the addition of phosphines and phosphites. A 1:1 ratio of metal atom to phosphorus was maintained.

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Registry No. $Mn_2(CO)_8(PEt_3)_2$, 15529-60-9; $Mn_2(CO)_8(P(i\text{-}Pr)_3)_2$, 75847-41-5; $Mn_2(CO)_8(PBu_3)_2$, 15609-33-3; $Mn_2(CO)_8(PCy_3)_2$, 15662-81-4; $Mn_2(CO)_8(PPh_3)_2$, 10170-70-4; $Mn_2(CO)_8(P(octyl)_3)_2$, 75847-42-6; $Mn_2(CO)_8(PPhEt_2)_2$, 15444-75-4; $Mn_2(CO)_8(PPh_2Et)_2$, 15444-76-5; $Mn_2(CO)_8(PPh_2Cl)_2$, 75847-43-7; $Mn_2(CO)_8(P(OMe)_3)_2$, 15529-61-0; $Mn_2(CO)_8(POEt)_3)_2$, 15488-14-9; $Mn_2(CO)_8(P(O\text{-}i\text{-}Pr)_3)_2$, 75862-69-0; $Mn_2(CO)_8(P(OBu)_3)_2$, 75847-44-8; $Mn_2(CO)_8(P(OPh)_3)_2$, 15529-62-1; $Mn_2(CO)_8(P(O\text{-}p\text{-}tol)_3)_2$, 75847-45-9; $Mn_2(CO)_8$(diphos), 75847-46-0; anthracene, 120-12-7.

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