Scheme II

$$\begin{array}{ll}
\text{L} = \text{acac} & \text{L} = \text{SacSac} \\
\text{CoL}_3 + \text{e}^- \xrightarrow{k_sE^1{}_{1/2}} \text{CoL}_3{}^- & \text{CoL}_3 + \text{e}^- \xrightarrow{E^1{}_{1/2}} \text{CoL}_3{}^- \\
\text{CoL}_3{}^- \rightleftharpoons \text{CoL}_2 + \text{L}^- & \text{CoL}_3{}^- \rightleftharpoons \text{CoL}_2 + \text{L}^- \\
\text{CoL}_2 + \text{e}^- \xrightarrow{E^2{}_{1/2}} \text{CoL}_2{}^- & \text{CoL}_2 + \text{e}^- \xrightleftharpoons{E^2{}_{1/2}} \text{CoL}_2{}^- \\
\text{CoL}_2 \rightarrow \text{products} & \\
E^2{}_{1/2} < E^1{}_{1/2} & E^2{}_{1/2} \geqslant E^1{}_{1/2}
\end{array}$$

of a complete thermodynamic and kinetic description of the redox and associated reactions, meaningful comparisons of observed $E_{1/2}$ values cannot be made.

## Summary and Conclusions

The substitution of oxygen for sulfur produces a negative shift in the reduction potential, $E_{1/2}{}^{\text{r}}$, which is consistent with corresponding trends observed for other metals and ligand atoms.[40,41] A consequence of the more negative $E_{1/2}{}^{\text{r}}$ values of the oxygen chelates is that the products of these reductions are thermodynamically more reactive than those of their sulfur analogs and are therefore more likely to undergo follow-up chemical reactions. Despite the marked differences in $E_{1/2}{}^{\text{r}}$ values, the overall mechanisms of the electrode processes appear to differ little for corresponding oxygen and sulfur chelates. Thus, under favorable conditions, the oxygen chelates are capable of supporting electron-transfer series similar to those of their sulfur analogs.

A further consequence of the change of donor atom is an increase in the rate of the heterogeneous charge transfer such that $k_s(\text{S}) > k_s(\text{O})$. Additionally, the rate constant is larger at a mercury than at a platinum working electrode, i.e., $k_s(\text{Hg}) > k_s(\text{Pt})$. Although the rate constants are not corrected for double-layer effects, these trends seem to be general[34] and not influenced by the magnitude of the potential difference $E_{1/2}(\text{S}) - E_{1/2}(\text{O})$ or by the value of the absolute potential, implying that the observed trends are real.

The $k_s$ dependence upon the donor atom and electrode material is consistent with the electron-transfer step occurring via a bridging mechanism involving the electrode and the donor atom, the inequality $k_s(\text{S}) > k_s(\text{O})$ reflecting the thiophilic natures of mercury and platinum. That the $E_{1/2}$ values of the sulfur chelates are independent of the electrode surface is a consequence of the large $k_s$ values. Even though $k_s(\text{S})$ may depend on the electrode material, the electron transfer is sufficiently fast for $E_{1/2}$ to remain unaltered.

**Registry No.** $\text{Cr(acac)}_3$, 13681-82-8; $\text{Mn(acac)}_3$, 14284-89-0; $\text{Fe(acac)}_3$, 14024-18-1; $\text{Co(acac)}_3$, 13681-88-4; $\text{Cr(SacSac)}_3$, 39838-20-5; $\text{Co(SacSac)}_3$, 26304-94-9.

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Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

# Ring Contributions to the Phosphorus-31 Chemical Shifts of Transition Metal–Phosphorus Chelate Complexes

Philip E. Garrou

*Received August 20, 1974* AIC40588X

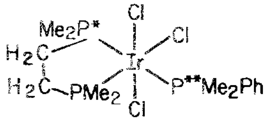
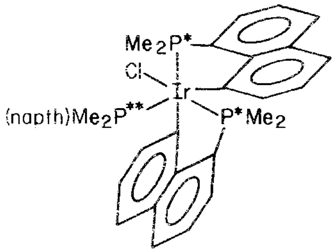
Recent studies have reported a good linear correlation between the chemical shift of a tertiary phosphine, $\delta_{\text{f}}$, and the change in chemical shift upon coordination to a metal, $\Delta$.[1-3] The coordination shift of a tertiary phosphine can therefore be predicted from the equation $\Delta = A\delta_{\text{f}} + B$ when enough examples are known to calculate values for $A$ and $B$. This relationship is valid for a variety of transition metal–tertiary phosphine complexes.[1]

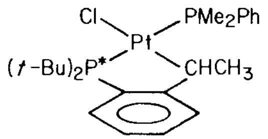
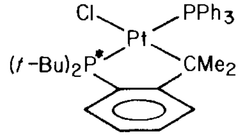
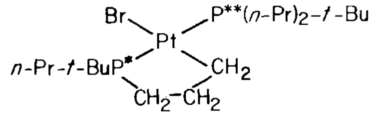
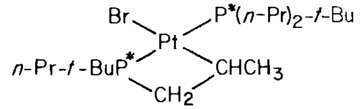
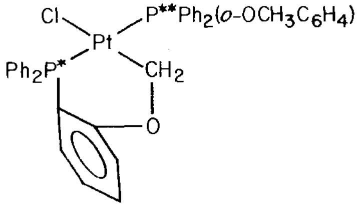
The $^{31}$P chemical shifts of a number of phosphorus chelate complexes have been reported recently which cannot be predicted from the $\Delta = A\delta_{\text{f}} + B$ relationship.[4-7] This was first explained on the basis of ring strain; however, examination of four-, five-, and six-membered rings revealed a substantially larger degree of deshielding for the five-membered analogs.[6]

We wish herein to compile and compare $^{31}$P chemical shift data for three types of phosphorus chelate complexes that exhibit such unusual deshielding effects. Knowledge of the presence and magnitude of such effects can prove to be a valuable aid in making structural assignments.

Discussion of these data is aided by the definition of a new

**Table I.** $^{31}P$ Data for Transition Metal-Phosphorus Chelate Complexes

| | | No. | $\delta_f{}^a$ | $\delta_c{}^a$ | $\Delta^b$ | $\Delta_R{}^c$ | Chelate ring size | $J_{M-P}$, Hz |
|---|---|---|---|---|---|---|---|---|
| Cr(0) | Diphosphines | | | | | | | |
| | $Cr(CO)_4(Ph_2PCH_2PPh_2)$ | I | $+23.6^{6}$ | $-25.4^{6}$ | −49.0 | +12 | 4 | |
| | $Cr(CO)_4(Ph_2PCH_2CH_2PPh_2)$ | II | $+12.5^{6}$ | $-79.4^{6}$ | −91.9 | −31 | 5 | |
| | $Cr(CO)_4(Ph_2PCH_2CH_2CH_2PPh_2)$ | III | $+17.3^{6}$ | $-41.4^{6}$ | −58.7 | +2 | 6 | |
| | *cis*-$Cr(CO)_4(Ph_2P\text{-}n\text{-}Bu)_2{}^d$ | IV | $+17.1^{3}$ | Ca. −44 | Ca. −61 | | | |
| Mo(0) | Diphosphines | | | | | | | |
| | $Mo(CO)_4(Ph_2PCH_2PPh_2)$ | V | $+23.6^{6}$ | $0.0^{6}$ | −23.6 | +19.3 | 4 | |
| | $Mo(CO)_4(Ph_2PCH_2CH_2PPh_2)$ | VI | $+12.5^{6}$ | $-54.7^{6}$ | −67.2 | −24.3 | 5 | |
| | $Mo(CO)_4(Ph_2PCH_2CH_2CH_2PPh_2)$ | VII | $+17.3^{6}$ | $-21.0^{6}$ | −38.3 | +4.6 | 6 | |
| | *cis*-$Mo(CO)_4(PPh_2\text{-}n\text{-}Bu)_2$ | VIII | $+17.1^{3}$ | $-25.8^{8}$ | −42.9 | | | |
| | Alkenylphosphines | | | | | | | |
| | $Mo(CO)_4(PPh(CH_2CH_2CH{=}CH_2)_2)$ | IX | $+26.2^{10}$ | $-42.5, -44.3^{10,e}$ | −67.9, −69.0 | −28.6 | 5.5 | |
| | *cis*-$Mo(CO)_4(PPh(n\text{-}Bu)_2)_2$ | X | $+26.2^{8}$ | $-14.5^{8}$ | −40.7 | | | |
| W(0) | Diphosphines | | | | | | | |
| | $W(CO)_4(Ph_2PCH_2PPh_2)$ | XI | $+23.6^{6}$ | $+23.6^{6}$ | 0 | +25.3 | 4 | 202 |
| | $W(CO)_4(Ph_2PCH_2CH_2PPh_2)$ | XII | $+12.5^{6}$ | $-40.1^{6}$ | −52.6 | −27.3 | 5 | 231 |
| | $W(CO)_4(Ph_2PCH_2CH_2CH_2PPh_2)$ | XIII | $+17.3^{6}$ | $0.0^{6}$ | −17.3 | +8.0 | 6 | 222 |
| | *cis*-$W(CO)_4(PPh_2\text{-}n\text{-}Bu)_2$ | XIV | $+17.1^{3}$ | $-8.2^{8}$ | −25.3 | | | 230 |
| Ru(II) | Alkenylphosphines | | | | | | | |
| | $RuCl_2[PPh_2(o\text{-}CH_2{=}CHC_6H_4)]_2{}^f$ | XV | $+6.8^{16}$ | $-47.2^{12}$ | −5 | −25.6 | 5.5 | |
| | $RuCl_2(CO)_2(PPh_2Et)_2{}^g$ | XVI | $+12.5^{18}$ | $-15.9^{17}$ | −27.9 | | | |
| Rh(I) | Alkenylphosphines | | | | | | | |
| | $[RhCl(PPh_2(CH_2CH_2CH{=}CH_2))]_2{}^h$ | XVII | $+17.1^{10}$ | $-69.6^{13}$ | −86.7 | −30.4 | 5.5 | 188 |
| | $[RhCl(P(p\text{-}CH_3C_6H_4)_3)]_2{}^i$ | XVIII | $+6.8^{16}$ | $-49.5^{16}$ | −56.3 | | | 196 |
| Ir(III) | Diphosphines | | | | | | | |
| |  | XIX | $+47.6^{1}$ | $-4.2\ (*)^{27}$<br>$+42.1\ (**)^{27}$ | −51.8<br>−5.5 | $-46.3^{j}$ | 5 | |
| | Internally metalated phosphines | | | | | | | |
| |  | XX | $+47.6^{1}$ | $+15.1\ (*)^{22}$<br>$+14.5\ (*)^{22}$<br>$+45.6\ (**)^{22}$ | −32.5<br>−33.1<br>−1.95 | −30.8<br>−30.2 | 5 | |
| Ni(0) | Diphosphines | | | | | | | |
| | $Ni[Me_2PCH_2CH_2PMe_2]_2$ | XXI | $+49.4^{9}$ | $-18.1^{9}$ | −67.5 | −26.4 | 5 | |
| | $Ni[PMe_3]_4$ | | $+63.3^{9}$ | $+22.2^{9}$ | −41.1 | | | |
| Pd(II) | Diphosphines | | | | | | | |
| | $PdCl_2(Ph_2P{*}CH_2OPPh_2)$ | XXII | $+14.1^{6}$ | $-79.8^{6}$ | −93.9 | −52.1 | 5 | |
| | *cis*-$PdCl_2(Ph_2P{*}CH_2OPPh_2)_2$ | XXIV | $+14.1^{6}$ | $-27.0^{2}$ | −41.8 | | | |
| | $PdCl_2(Ph_2P{*}CH_2OPPh_2)$ | XXV | $+22.8^{6}$ | $-11.7^{6}$ | −34.5 | +12.3 | 6 | |
| | $PdCl_2(Ph_2P{*}CH_2CH_2OPPh_2)_2$ | XXVI | $+22.8^{6}$ | $-24.0^{2}$ | −46.8 | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Alkenylphosphines | | | | | | | |
| | $PdCl_2(Ph_2PCH_2CH_2CH{=}CH_2)$ | XXVII | $+17.1^{11}$ | $-57.1^{11}$ | $-74.2$ | $-30.5$ | 5.5 | |
| | *cis*-$PdCl_2(Ph_2PCH_2CH_2CH{=}CH_2)_2$ | XXVIII | $+17.1^{11}$ | $-26.6^{11}$ | $-43.7$ | | | |
| | Internally metalated phosphines | | | | | | | |
| | $PdCl(PPh_3)[(o\text{-}CH_2C_6H_4P\text{-}t\text{-}Bu(o\text{-}CH_3C_6H_4)]^{k}$ | XXIX | $-15.9^{1}$ | $-58.8^{19}$ | $-42.9$ | $-20.8$ | 5 | |
| | *trans*-$PdCl_2[P\text{-}t\text{-}Bu(p\text{-}CH_3C_6H_4)_2]_2$ | XXX | $-15.9^{1}$ | $-38.0^{1}$ | $-22.1$ | | | |
| Pt(II) | Alkenylphosphines | | | | | | | |
| | $PtI_2(Ph_2PCH_2CH_2CH{=}CH_2)$ | XXXI | $+17.1^{11}$ | $-34.1^{1}$ | $-51.2$ | $-27.1$ | 5.5 | 3071 |
| | *cis*-$PtCl_2(Ph_2P\text{-}n\text{-}Bu)_2$ | XXXII | $+17.1^{11}$ | $-7.0^{18}$ | $-24.1$ | | | 3641 |
| | Internally metalated phosphines | | | | | | | |
| | $PtCl[P^{**}(t\text{-}Bu)_2Ph][o\text{-}C_6H_4P^{*}(t\text{-}Bu)_2]^{l}$ | XXXIII | $+37.99^{1}$ | $+31.7\ (^{*})^{21}$<br>$-48.6\ (^{**})^{21}$ | $+69.7$<br>$-10.61$ | $+80.3^{m}$ | 4 | 2222<br>2912 |
| | $PtCl[P^{**}\text{-}t\text{-}Bu(o\text{-}CH_3C_6H_4)_2][o\text{-}CH_2C_6H_4P^{*}\text{-}t\text{-}Bu(o\text{-}CH_3C_6H_4)]$ | XXXIV | $+37.99^{1}$ | $-52.0\ (^{*})^{20}$<br>$-31.1\ (^{**})^{20}$ | | $-20.9$ | 5 | 3262<br>2755 |
| |  | XXXV | $+37.99^{1,n}$ | $-73.0\ (^{*})^{24}$ | $-35.0$ | $-31.8$ | 5 | 3279 |
| | *trans*-$PtCl_2[P(t\text{-}Bu)_2Ph]_2$ | XXXVI | $+37.99^{1}$ | $-41.2^{2}$ | $-3.2$ | | | |
| |  | XXXVII | $+37.99^{1}$ | $-71.3\ (^{*})^{24}$ | $-33.3$ | $-30.1$ | 5 | |
| |  | XXXVIIIa | $+8.74^{1}$<br>$+8.74^{1}$ | $-67.4\ (^{*})^{21,o}$<br>$-25.9\ (^{**})^{21}$ | $-76.1$<br>$-34.6$ | $-41.5$ | 5 | 3086<br>2984 |
| |  | XXXVIIIb | | | | | | |
| | *trans*-$PtCl_2[P(n\text{-}Pr)_2\text{-}t\text{-}Bu]_2$ | XXXIX | $+8.74^{1}$ | $-34.3^{2}$ | $-43.1$ | | | |
| |  | XL | $+6.8^{16}$<br>$+6.8^{16}$ | $-8.3\ (^{*})^{23,p}$<br>$-25.1\ (^{**})^{23,p}$ | $-15.1$<br>$-31.9$ | $+16.8$ | 6 | 3178<br>3177 |

[a] In ppm downfield from 85% $H_3PO_4$. [b] $\Delta = \delta_f - \delta_c$; $\delta_f$ = chemical shift of free ligand and $\delta_c$ = chemical shift of coordinated ligand. [c] $\Delta_R = \Delta(\text{obsd}) - \Delta(\text{coordinated for nonchelate})$. [d] Estimated by comparison to analogous molybdenum and tungsten complexes (see discussion). [e] Two isomers observed (see ref 10). [f] Cl and olefin cis; P trans; $\delta_f$ given for $P(p\text{-}CH_3C_6H_4)_3$. [g] Cl and CO cis; P trans. [h] Cl bridged; P trans across dimer. [i] Cl bridged. [j] Data obtained by $^1H\{^{31}P\}$ INDOR methods. [k] Trans P; $\delta_f$ given for $P(p\text{-}CH_3C_6H_4)_2\text{-}t\text{-}Bu$. [l] Trans P. [m] For $PtCl_2[PPh(t\text{-}Bu)_2]_2$ $\Delta_R(\text{calcd}) = +79.2$ ppm. [n] $\delta_f$ given for $PPh(t\text{-}Bu)_2$. [o] New corrected assignment for isomer a. [p] $\delta_f$ given for $P(p\text{-}CH_3C_6H_4)_3$.

term, the "ring contribution", which will be assumed in some way responsible for the unusual chemical shifts. The ring contribution to the coordination chemical shift, $\Delta_R$, may be defined as the difference between the coordination chemical shift, $\Delta$, of a cis-disubstituted phosphine complex and the observed coordination chemical shift of an equivalent phosphorus in a chelate complex. The $\Delta$ value of the cis-disubstituted phosphine complex can be either observed experimentally or calculated, when possible, from the $\Delta = A\delta_f + B$ relationship.

Examination of the literature reveals three types of phosphorus chelate complexes for which $^{31}P$ data are available: diphosphines, alkenylphosphines, and internally metalated phosphines. Table I lists the chelate complexes to be discussed and the cis-disubstituted phosphine complexes used for comparison.

## Diphosphines

The data obtained for the chromium, molybdenum, and tungsten complexes of $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$, and $Ph_2PCH_2CH_2CH_2PPh_2$ (I–III, V–VII, and XI–XIII) offer direct comparisons between phosphorus incorporated in four-, five-, and six membered rings.[6] Since phosphorus chemical shift, $\delta_c$, values for *cis*-$M(CO)_4L_2$ where M = Cr, Mo, or W and L = $PPh_2Me$, $PPh_2Et$, or $PPh_2$-*n*-Pr are not available, $\Delta_R$ values must be obtained by comparison with *cis*-$M(CO)_4(PPh_2$-*n*-$Bu)_2$. Data for such complexes have been reported for molybdenum and tungsten but not for chromium.[8] Comparison of *cis*-$M(CO)_4L_2$ complexes where L = PPh(*n*-$Bu)_2$ and $PPh_2$-*n*-Bu reveals $\delta_c$ values of −14.5 and −25.8 and of +4.0 and −8.2 ppm for molybdenum and tungsten, respectively. The observation of a ~12-ppm lower $\delta_c$ value for the PPh(*n*-$Bu)_2$ cases can be applied to chromium. One would predict a $\delta_c$ value of ~−44 ppm for *cis*-$Cr(CO)_4(PPh_2$-*n*-$Bu)_2$ when comparing the literature value[8] for the analogous PPh(*n*-$Bu)_2$ complex. $\delta_c$ values for *cis*-$M(CO)_4L_2$ complexes cannot be obtained from the $\Delta = A\delta_f + B$ relationship because sufficient data for the calculation of the $A$ and $B$ constants are not available.

The $\Delta$ values for the chelating phosphinite–palladium(II) complexes (XXII and XXV) can be compared with theoretically obtained values for *cis*-$PdCl_2L_2$ where L = $Ph_2P^*CH_2OPPh_2$ ($\delta_f$ = 14.1,[6] $A$ = −0.32, $B$ = −38.1[1]) and $PPh_2^*CH_2CH_2OPPh_2$ ($\delta_f$ = 22.8,[6] $A$ = −0.32, $B$ = −38.1[1]) resulting in $\Delta_R$ values of −52.1 and +12.3 for the five- and six-membered rings, respectively. In the iridium(III) complex XIX comparison of the phosphorus involved in the five-membered chelate ring can be made internally to the *trans*-$PPhMe_2$ ligand, resulting in a $\Delta_R$ value of −46.3 ppm.

Comparison of XXI to $Ni(PMe_3)_4$ results in a $\Delta_R$ value of −26.4 ppm. Comparison would better be made to $Ni(PMe_2Et)_2$ but these data are not available.

## Alkenylphosphines

Recent studies on molybdenum(0),[10] palladium(II),[11] platinum(II),[11] ruthenium(II),[12] and rhodium(I)[13] chelating alkenylphosphine complexes have included $^{31}P$ data. In order to obtain $\Delta_R$ values one must compare the phosphorus $\Delta$ value in these complexes to cis-disubstituted phosphine complexes in which olefin has been replaced by a phosphorus. This is permitted since it is well documented that cis ligands exhibit little influence on phosphorus chemical shifts.[14,15] The recent data[17] comparing the complexes *trans*-$RhCOCl(P(p\text{-}CH_3C_6H_4)_3)_2$ and *trans*-$Rh(C_2H_4)Cl(P(p\text{-}CH_3C_6H_4)_3)_2$ ($\delta_c$ = −27.3 and −33.3 ppm, respectively), where CO has been replaced by ethylene, are a further substantiation of this premise.

Complexes XXVII, XXXI, and IX can be compared to $PdCl_2(PPh_2CH_2CH_2CH{=}CH_2)$,[18] $PtCl_2(PPh_2$-*n*-$Bu)_2$,[18] and *cis*-$Mo(CO)_4(PPh(n\text{-}Bu)_2)_2$,[8] giving $\Delta_R$ values of −30.5, −27.1, and −28.6 ppm, respectively, for the 5.5-membered rings. The ruthenium(II) complex XV can be compared to $RuCl_2(CO)_2(PPh_2Et)_2$[17] resulting in a $\Delta_R$ value of −25.6 ppm. The rhodium(I) dimer XVII can be compared to $Rh_2Cl_2[P(p\text{-}CH_3C_6H_4)_3]_4$,[16] resulting in a $\Delta_R$ value of −30.4 ppm. A more appropriate comparison would be to $Rh_2Cl_2[PPh_2$-*n*-$Bu]_4$ but such data are not available. To date no data are available on 4.5- or 6.5-membered ring alkenylphosphine chelate complexes.

## Internally Metalated Phosphines

A large number of internally metalated complexes have been prepared for which $^{31}P$ NMR data are available. However, there has been no discussion concerning the deshielding observed upon chelation. Complex XXIX[19] reveals a $\Delta_R$ value of −20.8 ppm when compared to trans-$PdCl_2(P(p\text{-}CH_3C_6H_4)_2\text{-}t\text{-}Bu)_2$.[1] Complex XXXIV[20] can be compared internally to the unmetalated trans ligand resulting in a $\Delta_R$ of −20.9 ppm. Complexes XXXIII,[21] XX,[22] and XL[23] also allow internal comparisons to unmetalated ligands resulting in $\Delta_R$ values of +80.3, −30.8, and +16.8 ppm for the four-, five-, and six-membered rings, respectively. Data for complexes XXXV[24] and XXXVII[24] can be compared to the theoretical value of −41.2 ppm for *trans*-$PtCl_2[PPh(t\text{-}Bu)_2]_2$ ($\delta_f$ = −38.0,[1] $A$ = −0.48, $B$ = −21.4[1]) resulting in $\Delta_R$ values of −31.8 and −30.1, respectively.

The $^1H$ NMR spectrum of XXXVIII[21] reveals a complex pattern including signals due to metalated and unmetalated *n*-propyl groups. Two $^{31}P$ resonances are observed at −67.4 and −25.9 ppm and were assigned to unmetalated and metalated phosphines, respectively. A choice between four- or five-membered chelate structures (XXXVIIIa or XXXVIIIb) was not made at the time. A calculated $\delta_c$ value of −34.3 ppm can be obtained for *trans*-$PtCl_2[P\text{-}t\text{-}Bu(n\text{-}Pr)_2]_2$ ($\delta_f$ = +8.7,[1] $A$ = −0.48, $B$ = −21.4[1]). This value is expected to shift to slightly higher field (ca. 5 ppm) when the trans chlorides are changed to alkyl and bromide as evidenced by comparison between trans-$Pd(PEt_3)_2Cl_2$ and *trans*-$Pd(PEt_3)_2MeBr$ ($\delta_c$ = −17.8 and −13.9, respectively[25]). This suggests that the original assignments were in error and the resonance at −25.9 ppm is due to unmetalated ligand and the resonance at −67.4 ppm to metalated ligand. Furthermore, the resulting $\Delta_R$ value of −41.5 ppm, obtained by internal comparison, is consistent only with the five-membered ring structure XXXVIIIa.

## Size of the Metal

It has been noted that deviations from monodentate coordination shifts appear to increase in the order Cr < Mo < W, which is the order of increasing metal radius.[6] Clearly the $\Delta_R$ values of the four- and six-membered rings increase in this order (see Table I); however this trend is not observed for the five-membered analogs. Comparison can also be made between the palladium(II)– and platinum(II)–alkenylphosphine complexes XIX and XXXI where $\Delta_R$ shows a slight decrease and the internally metalated complexes XXIX and XXXIV where the $\Delta_R$ values are equal. Clearly more examples are needed before a relationship between metal radius and $\Delta_R$ can be deduced.

## Metal–Phosphorus Coupling

Also of interest is the effect of chelation on metal–phosphorus couplings. The tungsten–phosphorus couplings in XI, XII, and XIII show little deviation from the value of 230 Hz observed for XIV. Comparisons between the alkenylphosphine complexes reveals a substantially smaller coupling for the platinum(II) complex XXXI while the rhodium(I) complex XVII reveals only an 8 Hz smaller value for the chelate. Examination of internally metalated complexes reveals a smaller coupling for the four-membered ring in XXXIII, slightly larger couplings for the five-membered rings in XXXIV and XXXVIII, and no difference for the six-membered ring in XL. No obvious relationships between chelation and phosphorus–metal coupling can be deduced from these data.

## Additional Heteroatoms

Thus far only ring systems in which phosphorus is bound to a transition metal and carbon have been considered. Examples are known of phosphite and phosphinite ligands which are capable of chelation.[6,26] Comparisons between such complexes, in which phosphorus is bonded to a metal, a carbon, and an oxygen, seem inappropriate at the time due both to the lack of $^{31}$P data available for such complexes and to the fact that the $\Delta = A\delta_f + B$ relationship has not been shown to be valid for disubstituted metal–tertiary phosphite complexes.

## Conclusions

It appears that a ring contribution to the coordination chemical shift of phosphorus chelate complexes exists for a wide variety of transition metals. A deshielding contribution ranging from −21 to −33 ppm is observed for 15 complexes containing five-membered rings; three examples show larger deshielding and fall outside this range. Four- and six-membered rings exhibit shielding in the ranges +12 to +25 (three examples) and +2 to +17 ppm (four examples), respectively. No well-defined relationships are apparent concerning the effect of metal radius on the ring contribution or the effect of the ring contribution on metal–phosphorus coupling. Although the theoretical aspects of $\Delta_R$ are not clear-cut, awareness of its existence may prove to be useful in making $^{31}$P structural assignments in the future.

**Registry No.** P, 7723-14-0; XXXVIIIa, 36426-97-8.

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