

# $\Delta_R$ Ring Contributions to $^{31}\text{P}$ NMR Parameters of Transition-Metal-Phosphorus Chelate Complexes

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## 1. Introduction

One of the basic problems of the organotransition-metal chemist is the determination of the structure and stereochemistry of complex molecules. Organophosphines are building blocks which have wide use in the stabilization of a variety of such molecules, many of which catalyze processes which are now of great importance to the chemical industry. In recent years the widespread appearance of relatively cheap NMR



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equipment with Fourier transform capabilities has led to a great deal of  $^{31}\text{P}$  data aimed at exploring the potential of this technique for such structural and stereochemical elucidations. In the early '70s Shaw and co-workers<sup>1</sup> pointed out that there is a good linear correlation between the chemical shift of a tertiary phosphine,  $\delta F$ , and the change in the chemical shift upon coordination to a metal,  $\Delta$ . From the relationship  $\Delta = A\delta F + B$ , coordination shifts of phosphines can actually be predicted, for a given complex, once enough analogues are known for calculation of the constants  $A$  and  $B$ . This relationship faltered, however, upon examination of the  $^{31}\text{P}$  chemical shifts of a number of phosphorus chelate complexes. Yet the determination of the mode of bonding in potentially chelating ligands or ligands which are metalated is possible through knowledge of the empirical relationship of ring chelation to the  $\delta\text{P}$  values.

### 1.1. Previous Methods of Determining Chelation in Phosphine Complexes

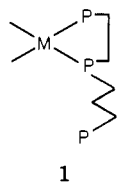
The three basic classes of potential phosphine chelate ligands are diphosphines, alkenylphosphines, and ligands with the potential to be cyclometalated. By far the largest number of problems have been encountered in the structural determination of cyclometalated complexes, while enough specific problems have arisen in both other categories to make it clear that one should have as many means of structural analysis available as possible.

Cyclometalation or orthometalation is used to describe complexes in which the ligand has undergone an

intramolecular metalation to form a chelate ring containing a metal-carbon  $\sigma$  bond. Such reactions have been identified for nitrogen, phosphine, and phosphite ligands. There are several relevant reviews on complexes of this type.<sup>2,3</sup> The identification of cyclo-metalated complexes was at first accomplished by infrared spectroscopy. The regions 700–800 and  $\sim 1100$   $\text{cm}^{-1}$  were studied when metalation occurred on a phenyl ring; however, these assignments are tenuous at best and cannot be looked at as positive confirmation of ring formation. For example, in a series of ortho-metalated  $\text{PPh}_3$  complexes of Ru the authors<sup>4</sup> noted that all the complexes reveal infrared absorptions in the region characteristic of ortho-disubstituted phenyl (1500–1600, 1400–1450, 1100, 730  $\text{cm}^{-1}$ ) of an ortho-metalated phosphine. They further report that many of the reported complexes have extra peaks in all of these regions, and assignments based on vibrations near 1100 and 730  $\text{cm}^{-1}$  are complicated by vibrations from monosubstituted phenyl rings. While examination of the IR spectra of “ $\text{Fe}[\text{P}(\text{O}^i\text{Ph})_3]_4$ ” and  $\text{Ni}[\text{P}(\text{O}^i\text{Ph})_3]_4$  revealed miniscule changes, other methods were necessary to identify orthometalation in the Fe compound.  $^1\text{H}$  NMR is also complicated by the presence of complex patterns when metalation has occurred either on a phenyl ring or an alkyl group in the presence of unmetalated ligands.<sup>4,5</sup>  $^{13}\text{C}$  NMR has also been examined,<sup>6</sup> but, on all but the simplest systems, this method is complicated by overlapping resonances and the inherent low intensity of the metalated carbon. Analyses of these spectra become research projects in their own right. The very fact that the structures of so many cyclo-metalated complexes have been solved by X-ray analysis is evidence of the need for alternate means of identification.

The structures of butenyl- and styrylphosphine complexes are usually resolved by a study of the  $^1\text{H}$  NMR of the olefinic protons and an IR study of the olefinic region.<sup>7-9</sup> Complications result with allylic phosphines which metalate,<sup>10</sup> and with a metal such as iridium, where  $\nu_{\text{C}=\text{C}}$  is usually obscured by phenyl resonances and/or which orthometalates butenylphosphines as well.<sup>11</sup>

Analysis of chelating phosphine complexes is usually accomplished by IR spectroscopy, if dealing with carbonyl complexes, or  $^{31}\text{P}$  spectroscopy where one observes a deshielding effect upon bonding and thus can easily tell whether a bisphosphine is functioning in a monodentate or bidentate fashion.<sup>12,13</sup> Problems can arise when polydentate ligands are examined which have the potential to form different size chelate rings, as in eptp (1).



## 1.2. Discovery of $\Delta_R$

During the early 70s researchers were beginning to examine the  $^{31}\text{P}$  spectra of such complexes in an attempt to use  $^{31}\text{P}$  NMR as a structural tool. The first observation of a chelating effect in  $^{31}\text{P}$  was by Merri-

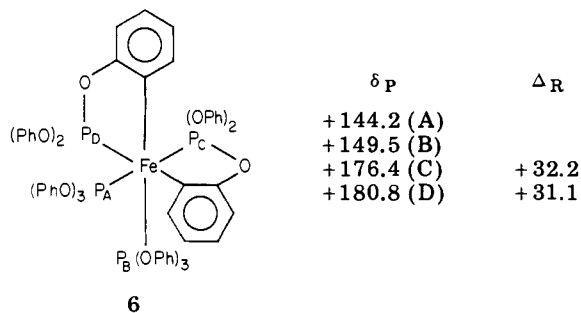
CHART I

	$\delta_P$	$\Delta F$	$\Delta$	$\Delta_R$
	-40.0	-22.6	-17.4	-51.9
	+54.5	-13.3	+67.7	+33.3
	+3.2	-17.3	-20.5	-14.0
	+6.4	-28.0	+34.4	

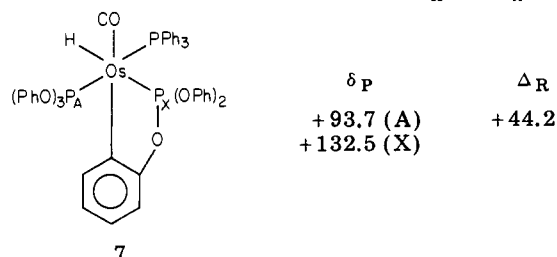
wether in 1961 during his examination of a series of nickel carbonyl-phosphine complexes.<sup>14</sup> This observation lay dormant until the mid 70s when several authors pointed out that chemical shift values ( $\delta_P$ ) are directly affected by the presence of phosphorus in chelate rings of diphosphines.<sup>15-17</sup> Also, we pointed out<sup>18</sup> that this “ring contribution” was a general phenomenon, observable in all known polyphosphines, alkenylphosphines, and orthometalated complexes, and caused chemical shifts to fall outside the range predicted for the  $\Delta = A\delta F + B$  relationship. In order to correlate such data a new parameter ( $\Delta_R$ , the “ring contribution” to a  $^{31}\text{P}$  chemical shift) was 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 atom in a chelate complex.

In the examples shown in Chart I, the ring contribution  $\Delta_R$  is calculated for 2, 3, and 4 based on the  $\Delta$  value of complex 5 (the closest available analogue). Obviously better comparisons would be made to complexes such as  $\text{Me}_2\text{Pt}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$ , and in all cases where possible such data should be used for comparison, but since data for these complexes do not exist, one can obtain a good approximation using data for a molecule such as 5. The error inherent in this method stems from the chemical shift differences of the free ligands. Thus  $\text{PPh}_2\text{Me}$  with  $\delta_F$  -28.0 is a better analogue to 2 than to 3. If data become available for  $\text{Me}_2\text{Pt}(\text{PPh}_2\text{Et})_2$  with  $\delta_F$  -13.5, obviously it should be used. The value of these  $\Delta_R$  comparisons is thus a qualitative one where one observes that vs. a nonchelated complex, 4-membered rings are shielded more than 6-membered rings and 5-membered rings are deshielded. The best calculations are made from the chemical shift data of molecules which allow internal comparisons such as 6 and 7.

In 6, phosphorus atom  $\text{P}_C$  is metalated and trans to a triphenyl phosphite ligand. This can be directly compared to the value of  $\delta_{\text{P}_A}$  which is a triphenyl phosphite ligand trans to a triphenyl phosphite ligand. Phosphorus atom  $\text{P}_D$  on the other hand is metalated but



trans to a  $\sigma$ -bound phenyl group which allows direct comparison to the value of  $\delta_{P_B}$  which is an unmetalated triphenyl phosphite ligand trans to a  $\sigma$ -bound phenyl group. Note the  $\Delta_R$  results are within 1 ppm of each other. If comparisons are made where the trans ligands are not the same, errors of 1–10 ppm and more are possible depending on the electronic differences (trans effects) of the ligands in question. This is exemplified in 7 where an internal comparison of  $\delta_{P_X}$  vs.  $\delta_{P_A}$  would



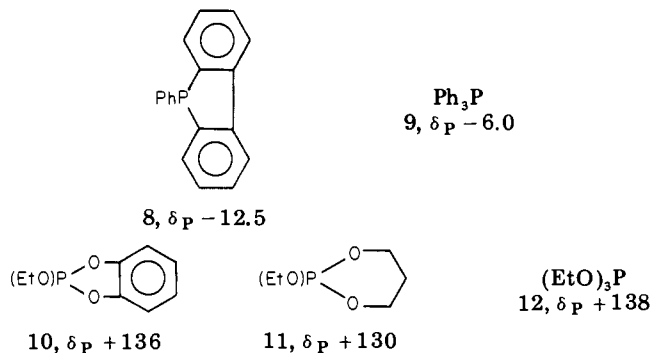
not take into account the chemical shift difference that would be caused by the different trans ligands, H and PPh<sub>3</sub>, and would result in a  $\Delta_R$  value of +38.8. A better comparison can be made to 102 which has a P(OPh)<sub>3</sub> trans to H and cis to PPh<sub>3</sub> with  $\delta_P$  of +88.3. This comparison results in a more accurate  $\Delta_R$  value of +44.2. Suffice it to say that whenever  $\Delta_R$  is reported, the molecule used for analogy should be clearly delineated.

The theoretical aspects of  $\Delta_R$  are not clear. <sup>31</sup>P chemical shifts are usually related to the C–P–C bond angle.<sup>13</sup> As the groups on phosphorus increase in steric size, the C–P–C angle opens and the phosphorus chemical shift moves to lower field. As we shall see later,<sup>47</sup> the only study that has compared analogous (Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>)PdCl<sub>2</sub> (*n* = 1–3) complexes in terms of  $\Delta_R$  and C–P–C angle find no correlation. From bond angle consideration, the ring strain expected and observed for a phosphorus contained in a 5-membered ring is small, but an unusually large deshielding is noted irrespective of the metal or other substituents in the ring.

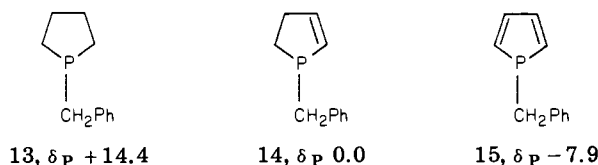
Although the theoretical aspects of the  $\Delta_R$  are not clear, the knowledge of its contribution to the  $\delta_P$  value is invaluable when one makes structural assignments in phosphine transition metal complexes.

### 1.3. Anomalous <sup>31</sup>P Chemical Shifts in Cyclic Organophosphorus Compounds

The first place to look in trying to understand the  $\Delta_R$  contribution is in the <sup>31</sup>P chemical shifts of cyclic organophosphorus complexes. The data that can be presented are inconclusive and in some ways contradictory. Very little  $\Delta_R$  is observed in the series 8, 9, or 10, 11, 12, although 8 and 10 are incorporated in 5-membered rings.<sup>19</sup>

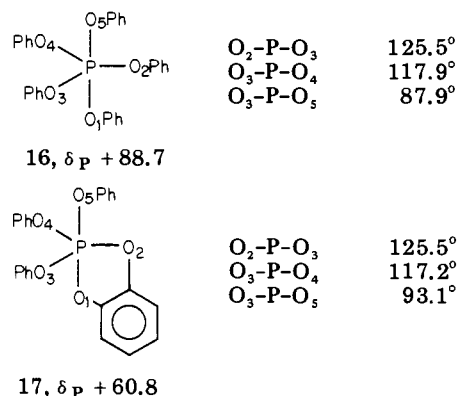


In contrast, deshielding due to phosphorus incorporation into 5-membered ring systems is observed when one compares 1-methylphosphole ( $\delta_P - 8.7$ ) to ethyldivinylphosphine ( $\delta_P - 20.8$ ).<sup>20</sup> Later<sup>21</sup> comparisons of 13–15 revealed that both the phosphole and the



phosphole analogues possess a considerably more deshielded phosphorus than does the saturated phosphine. No conclusions were drawn as to the reasons for these shifts; however, delocalization via  $p\pi-p\pi$  conjugation, bond angles, and conformational and steric differences were thought to play roles in the determination of  $\delta_P$ . Over a broader series of phosphole complexes a “ring contribution” to the chemical shift of +12 ppm is observed vs. acyclic analogues.<sup>21</sup>

Ramirez et al.<sup>22,23</sup> studied the <sup>31</sup>P spectra and determined the crystal structures for the pentaoxyphosphoranes 16 and 17. We can see that while the



bond angles are very similar, the chemical shift of the phosphorus in 17 is shielded by 27.9 ppm in this 5-coordinate phosphorus(V) compound.

It is thus clear that while anomalous chemical shift behavior has been observed in organophosphorus compounds, the trends are often in opposite directions and not well understood. Clearly the  $\Delta_R$  effect in organophosphine–transition-metal complexes is not simply a carryover from the cyclic organophosphorus complexes.

### 1.4. Scope, Definition of Terms, and List of Structural Abbreviations

The main purpose of this review is to point out the relationship of  $\Delta_R$  to the various aspects of <sup>31</sup>P NMR such as  $\delta_P$ ,  $J_{P-P}$ , and  $J_{M-P}$  and to probe the influence

## CHART II. Abbreviations Used

$\delta_P$	observed chemical shift of the phosphorus atom under study, in ppm relative to $H_3PO_4$ with deshielded values being given a + sign.
$\delta_F$	chemical shift of a free (noncoordinated) phosphine ligand.
$\Delta$	coordination chemical shift; the change between $\delta_F$ and the $\delta_P$ observed upon coordination of the phosphorus ligand to a metal ( $\Delta = \delta_P - \delta_F$ ).
$\Delta_R$	coordination shift of a chelated phosphine complex minus the coordination shift of an equivalent phosphorus in a nonchelated analogue.

Me	methyl	Ph	phenyl
Et	ethyl	Cy	cyclohexyl
<i>n</i> -Pr	<i>n</i> -propyl	CHT	cycloheptatriene
<i>i</i> -Pr	isopropyl	COD	cyclooctadiene
<i>n</i> -Bu	<i>n</i> -butyl	COT	cyclooctatetraene
<i>t</i> -Bu	<i>tert</i> -butyl	NBD	norbornadiene
diphosphines		alkenylphosphines	
dppm	$Ph_2PCH_2PPh_2$	mbp	$Ph_2P(CH_2)_2CH=CH_2$
dppe	$Ph_2P(CH_2)_2PPh_2$	dbp	$PhP((CH_2)_2CH=CH_2)_2$
dppp	$Ph_2P(CH_2)_3PPh_2$	tbp	$P(CH_2CH_2CH=CH_2)_3$
dppb	$Ph_2P(CH_2)_4PPh_2$	map	$Ph_2P(OCH_2CH=CH_2)$
polyphosphines			
etp	$PhP(CH_2CH_2PPh_2)_2$		
tripod	$MeC(CH_2PPh_2)_3$		
ttp	$(Ph_2PCH_2CH_2CH_2)_2PPh$		
eptp	$Ph_2PCH_2CH_2P(Ph)CH_2CH_2CH_2PPh_2$		
PP <sub>3</sub>	$P(CH_2CH_2PPh_2)_3$		
Me-etp	$MeP(CH_2CH_2PMe_2)_2$		

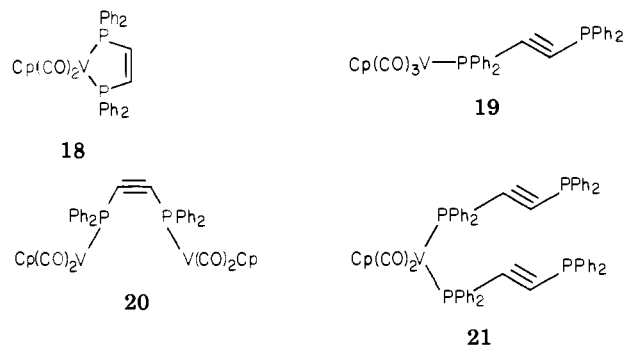
of factors such as metal radius, heteroatoms, and backbone unsaturation on the sign and size of  $\Delta_R$ . In addition it is hoped that sections such as those on phosphide complexes will spur research in this area so that a more basic understanding of the  $\Delta_R$  phenomenon will be possible.

This review covers all pertinent literature through 1979. The nomenclature within this review corresponds to that used by the authors of the various papers. Chemical shifts are given relative to 85%  $H_3PO_4$ . Since most of the literature citations occurred prior to the standardization of the  $\delta_P$  sign convention, corrections have been made so that all values deshielded relative to  $H_3PO_4$  are positive. The terms and structural abbreviations given in Chart II are used throughout this review.

## 2. Diphosphines

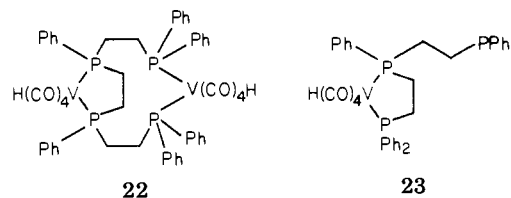
### 2.1. Group 5B: Vanadium

The reactions of  $CpV(CO)_4$  with *cis*- $Ph_2PCH=CHPPh_2$ , *trans*- $Ph_2PCH=CHPPh_2$ , and  $Ph_2PC\equiv CPh_2$  have been studied and complexes have been identified where the potentially bidentate ligands act in a bidentate, monodentate, and bridging fashion.<sup>24</sup> When compared to  $CpV(CO)_3PPh_2Et$ , the  $\delta_P$  value of +112 for  $CpV(CO)_2(dppe)$  reveals a  $\Delta_R$  of +22 indicative of chelation. The rest of the structural assignments, based on  $\Delta_R$  arguments, are much more tenuous.  $CpV(CO)_3(cis-Ph_2PCH=CHPPh_2)$ , which would be a 7-coordinate structure where the potentially bidentate phosphine coordinates in a monodentate fashion, reveals a  $\delta_P$  resonance at -25 vs. a free ligand value of -23.1. This is undoubtedly the  $\delta_P$  of the uncoordinated end inadvertently misassigned. Assignment of  $CpV(CO)_2(cis-Ph_2PCH=CHPPh_2)$  with a  $\delta_P$  resonance at +120 to structure 18 with a chelated diphosphine is consistent with the dppe value, while a structure as-



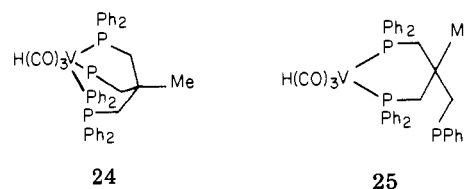
signed  $[CpV(CO)_2]_2(trans-Ph_2PCH=CHPPh_2)_2$  with a  $\delta_P$  shift of +120 is most likely a structure such as 18. Identical IR and C, H analysis is further substantiation of this new assignment. The reaction products isolated from reaction with  $Ph_2PC\equiv CPh_2$  are thought to be 19–21. Assignment of structure 19 based on  $\delta_P$  values of -35 and +69 ( $\delta_F$  -32.6) is consistent with free and coordinated phosphine. Assignment of structure 20 based on a  $\delta_P$  resonance at +73 is reasonable; however, the  $\delta_P$  resonance for “21” is reported at +91. This chemical shift movement 20 ppm to lower field is not consistent with the proposed assignment. Assignment of a chelated structure which would have  $\Delta_R$  of ~20 is also not possible since  $Ph_2PC\equiv CPh_2$  is a rigid ligand which is incapable of chelation.

Also examined was a series of complexes of the type  $HV(CO)_3L$  ( $L = ttp, tripod, PP_3$ ).<sup>25</sup> Again, some confusion exists over structural assignments based on what we now know about  $\delta_P$  and  $\Delta_R$  considerations. A complex formulated  $[H(CO)_4V]_2L$  with a  $\delta_P$  resonance at +68 (-73 °C) is assigned structure 22 although coor-



inated ligand  $[(Ph_2CH_2CH_2P(Ph)CH_2)_2]$  should show two distinct  $\delta_P$  resonances due to  $P(Ph)$  and  $P(Ph)_2$ . Exchange processes must be occurring among the phosphorus atoms in this molecule.

The  $\delta_P$  resonances at +87, +76, and -15.6 support the structural assignment of 23. The  $\delta_P$  resonances at -27 and +27 assigned to structure 24 are inconsistent with a 7-coordinate structure but rather consistent with one in which P is uncoordinated, such as 25.



### 2.2. Group 6B: Cr, Mo, W

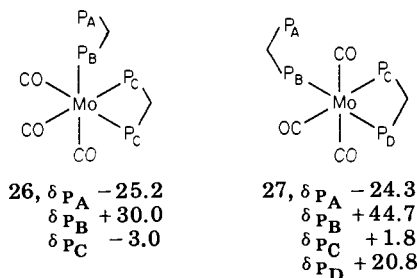
The data obtained by Grim et al.<sup>17</sup> for the chromium, molybdenum, and tungsten complexes of dppm, dppe, and dppp offer direct comparisons between phosphorus incorporated in 4-, 5-, and 6-membered rings (Table I). The data will be discussed later in terms of the effect of metal radius and chelate size on  $\Delta_R$ . However, without the knowledge of  $\Delta_R$ , one studying  $W(CO)_4$ -

TABLE I. <sup>31</sup>P Parameters for M(CO)<sub>4</sub>L Complexes<sup>17</sup>

M	L	δ <sub>P</sub> , ppm	Δ, ppm	Δ <sub>R</sub> , ppm	chelate ring size
	dppm	-23.6			
Cr		+25.4	+49.0	-12	4
Mo		0.0	+23.6	-19.3	4
W		-23.7	0	-25.4	4
	dppe	-12.5			
Cr		+79.4	+91.9	+31.0	5
Mo		+54.7	+67.2	+24.3	5
W		+40.1	+52.6	+27.3	5
	dppp	-17.3			
Cr		+41.4	+58.7	-2	6
Mo		+21.0	+38.3	-4.6	6
W		0.0	+17.3	-8.0	6

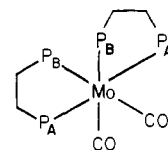
(dppm) would assume the observed δ<sub>P</sub> resonance represented free ligand and be hard pressed to explain why no Δ is observed. We now know that coordination deshields the δ<sub>P</sub> resonance, and the Δ<sub>R</sub> value for the 4 membered ring has a fortuitous shielding effect of the same magnitude. A series of unsymmetrical bidentate phosphines was also studied and the <sup>31</sup>P NMR spectrum used to determine monodentate coordination, bridging and/or chelation.<sup>26</sup> It can be seen in Table II that the chelated ligands reveal typical deshielding of 25–32 ppm vs. the monodentate and bridging structures.

The *fac* and *mer* isomers of Mo(CO)<sub>3</sub>(dppm) have been studied.<sup>27</sup> The *fac* isomer 26 shows three types of phosphorus in a 1:1:2 ratio.



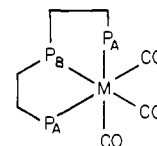
The chemical shift of P<sub>C</sub> reveals a Δ<sub>R</sub> contribution of -33 by internal comparison to the chemical shift of P<sub>B</sub>. The Δ<sub>R</sub> values of P<sub>C</sub> and P<sub>D</sub> in the *mer* complex, 27, are calculated to be -24 and -28 by comparison to P<sub>B</sub> (27) and P<sub>B</sub> (26), respectively. Thus the δ<sub>P</sub> resonance in chelated dppm is shielded ~30 ppm vs. monodentate dppm in these complexes. Complexes of the type Mo-(CHT)(CO)<sub>x</sub>L (x = 1, 2; L = dppm, dppe) have also been studied.<sup>28</sup> For L = dppm and dppe, Δ<sub>R</sub> values of -26.7 and +32.6 can be calculated. The effect of chelate ring size on the δ<sub>P</sub> resonance of M(CO)<sub>2</sub>Cl(C<sub>3</sub>H<sub>5</sub>)L (M = Mo, W; L = dppm, dppe) reveal a 50-ppm difference between the δ<sub>P</sub> values of phosphorus in the 4- and 5-membered rings.<sup>29</sup>

The <sup>31</sup>P NMR spectrum of complex 28<sup>16</sup> can be compared to that of Mo<sub>2</sub>(CO)<sub>6</sub>(dmpe)<sub>3</sub> which has δ<sub>P</sub> resonances at -2.5 and +24.4 for bridging and chelating



28, δ<sub>P<sub>A</sub></sub> +42.2  
δ<sub>P<sub>B</sub></sub> +23.6

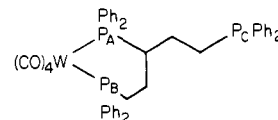
phosphorus atoms, respectively, resulting in a Δ<sub>R</sub> contribution of +26.1 to the value of δ<sub>P<sub>B</sub></sub>. King et al.<sup>30</sup> recognized the additive nature of Δ<sub>R</sub> in complexes of type 29 (M = Cr, Mo, W) where etp functions as a



29

tridentate ligand. Thus the δ<sub>P<sub>A</sub></sub> value where the phosphorus atoms are in a 5-membered ring is +78, whereas the δ<sub>P<sub>B</sub></sub> value where the phosphorus is in two 5-membered rings is +110.2, or 30 ppm further deshielded.

Reaction of W(CO)<sub>4</sub>(Ph<sub>2</sub>PCH=CH<sub>2</sub>)<sub>2</sub> with Ph<sub>2</sub>PH under free-radical conditions gives 30.<sup>31</sup> The resonance



30

at -20 ppm is assigned to P<sub>C</sub> since this is close to the free ligand value of PPh<sub>2</sub>Pr (-17.6) and the resonances at +4.0 ppm is assigned to P<sub>B</sub> because of its resemblance to the δ<sub>P</sub> value for W(CO)<sub>4</sub>(dppp).<sup>17</sup>

### 2.3. Group 7B: Mn, Re

The series M(CO)<sub>3</sub>BrL (Table III) reveals a δ<sub>P</sub>(dppm) - δ<sub>P</sub>(dppe) of 77 for Mn and 68 for Re.<sup>32</sup> Although no analogues are available for calculation of Δ<sub>R</sub> values, these data reveal the relative shielding and deshielding caused by the 4- and 5-membered rings. The same trends are observed in the cationic analogues M-(CO)<sub>3</sub>L(MeCN)<sup>+</sup> (M = Mn, Re; L = dppm, dppe).<sup>33</sup> When comparing CpMn(CO)L (L = dppm<sup>33</sup>, dppe,<sup>33</sup> dppp<sup>34</sup>), one can observe the Δ<sub>R</sub> effect in their δ<sub>P</sub> resonances at +58.4, +122.0, and +82.0 for the 4-, 5-, and 6-membered rings, respectively. Again no analogue such as CpMnCO(PPh<sub>2</sub>Et)<sub>2</sub> is available for comparison.

### 2.4. Group VIII

#### 2.4a. Fe, Ru, Os

Consider the series FeCp(CO)<sub>x</sub>L<sup>+</sup> (x = 1, 2; L = dppm, dppe).<sup>28</sup> Comparing δ<sub>P</sub> values of these complexes reveals a Δ<sub>R</sub> of -69 for the chelated dppm complex and +32.3 for the dppe complex.

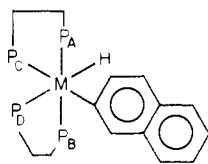
TABLE II. <sup>31</sup>P Shift Parameters of Group 6B Complexes of Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub><sup>26</sup>

complex	δ P(Ph) <sub>2</sub>	δ P(Me) <sub>2</sub>	Δ P(Ph) <sub>2</sub>	Δ P(Me) <sub>2</sub>	Δ <sub>R</sub> (P(Ph) <sub>2</sub> )	Δ <sub>R</sub> (P(Me) <sub>2</sub> )
L	-13.0	-31.4				
Cr(CO) <sub>4</sub> L	+80.0	+65.0	+93.0	+96.4		
Mo(CO) <sub>3</sub> L	+55.7	+39.0	+68.7	+70.4	+25.0	+27.7
W(CO) <sub>4</sub> L	+41.0	+22.6	+54.0	+54.0	+29.1	+32.0
[Mo(CO) <sub>5</sub> ] <sub>2</sub> L	+30.7	+11.3	+43.7	+42.7		
[W(CO) <sub>5</sub> ] <sub>2</sub> L	+11.9	-9.4	+24.9	+22.0		

TABLE III.  $^{31}\text{P}$  Shift Parameters for  $\text{MnBr}(\text{CO})_3\text{L}^{32}$ 

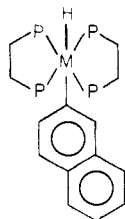
M	L	$\delta_{\text{P}}$	$\Delta$
Mn	dppm	+10.9	+33.6
	dppe	+67.6	+80.8
Re	dppm	-38.5	-15.8
	dppe	+30.0	+43.2

CHART III



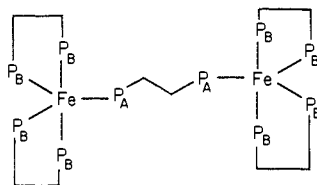
31

	$\delta_{\text{P}_A}$	$\delta_{\text{P}_B}$	$\delta_{\text{P}_C}$	$\delta_{\text{P}_D}$
Fe	73.3	70.5	59.8	53.6
Ru	45.4	40.1	33.3	27.4
Os	7.9	3.8	-5.0	-7.7



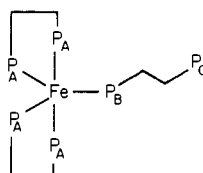
32,  $\delta_{\text{P}}(\text{Fe}) + 74$   
 $\delta_{\text{P}}(\text{Ru}) + 45.3$   
 $\delta_{\text{P}}(\text{Os}) + 9.3$

Tolman et al.<sup>35</sup> studied a series of complexes of the type (2-naphthyl)HM(dmpe)<sub>2</sub> (M = Fe, Ru, Os) which occur as cis (31) and trans (32) isomers as shown in Chart III. A shielding effect is observed as one descends the subgroup (see section 6.1). The complex Fe<sub>2</sub>(dmpe)<sub>5</sub>, 33, is another one of the existing examples



33

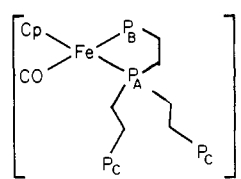
where both chelating and bridging ligand appear in the same complex; however,  $\Delta_{\text{R}}$  cannot be calculated since the AB<sub>4</sub>  $^{31}\text{P}$  spectrum indicates axial-equatorial exchange must be occurring. Fe(dmpe)<sub>3</sub> (34) is another



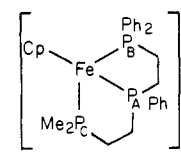
34,  $\delta_{\text{P}_A} + 60.4$   
 $\delta_{\text{P}_B} + 10.2$   
 $\delta_{\text{P}_C} - 49.8$

example where a difference can be seen between the chemical shifts of chelated and nonchelated bidentate phosphines. A  $\Delta_{\text{R}}$  value cannot be calculated since, once again, exchange is occurring.

In complex 35, the  $\delta_{\text{P}_A}$  resonance appears at +96.5, the  $\delta_{\text{P}_B}$  resonance at +93.6, and the  $\delta_{\text{P}_C}$  resonances at



35



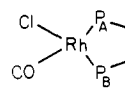
36

-12.5 and -13.3. Thus the bidentate nature of the potentially tetradentate ligand is substantiated.<sup>30</sup> In complex 36 the unsymmetrical etp ligand achieves tridentate coordination as revealed by a  $\delta_{\text{P}_A}$  value of +123.1. Comparison of the  $\delta_{\text{P}_A}$  value of 35 with the  $\delta_{\text{P}_A}$  value of 36 reveals the  $\delta_{\text{P}_A}$  resonance of 36 is 27 ppm further deshielded due, as shown later (section 2.4b), to its incorporation into two 5-membered rings.

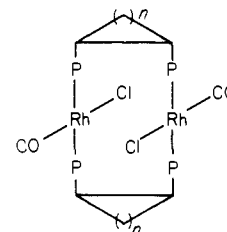
#### 2.4b. Co, Rh, Ir

Caulton et al.<sup>36</sup> studied a series of 4- and 5-coordinate rhodium and iridium complexes. Intramolecular rearrangement barriers were shown to decrease with decreasing ring size in the order dppp > dppe > dppm. This was assumed due to the fact that the smaller "bite" angle decreases the energy separation between the more stable trigonal bipyramid and less stable square-base pyramid structures. It should be noted that the  $\delta_{\text{P}}$  resonance of Rh(dppe)<sub>2</sub><sup>+</sup> is at lower field than the  $\delta_{\text{P}}$  resonance of Ir(dppe)<sub>2</sub><sup>+</sup>. In the series Ir(L)<sub>2</sub>CO<sup>+</sup> (L = dppp, dppe, dppm) both the axial and equatorial phosphorus atoms of the trigonal-bipyramidal dppe complex are ~45 ppm further downfield than the corresponding phosphorus atoms of the dppp complex. The dppm complex reveals a  $\delta_{\text{P}}$  resonance at -38 (-92 °C), indicating exchange must be occurring at this temperature. The authors noted "any attempt at extracting trends is doomed. . . since dppe moves downfield while dppp and dppm move upfield with respect to free ligand". These values in retrospect are normal when considering the  $\Delta_{\text{R}}$  effect.

From the reaction of Rh<sub>2</sub>Cl<sub>2</sub>(COD)<sub>2</sub> with dppm, dppe, dppp, and dppb,<sup>37</sup> it was learned that while dppe produces the monomeric complex 37, the rest produce binuclear bridged complexes such as 38.



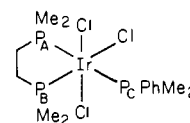
37



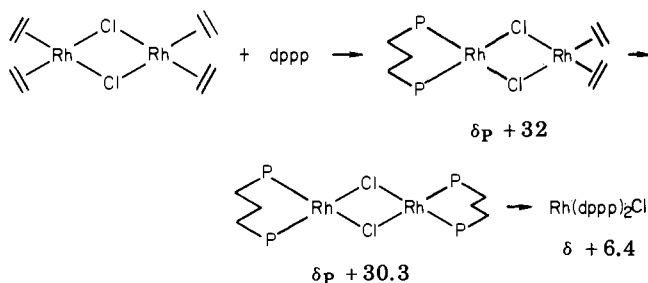
38, n = 1, 3, 4

The same trend is observed in the Ir complexes<sup>38</sup> which are assigned the structures [IrCO(dppe)<sub>2</sub>]<sup>+</sup>, [IrCl<sub>2</sub>(CO)<sub>2</sub>]<sup>-</sup>, [IrClCO(dppp)]<sub>2</sub>, and [IrClCO(dppb)]<sub>3</sub>. The dppe chelates while dppp and dppb bridge in dimeric and trimeric complexes.

In 39<sup>39</sup> comparison of the phosphorus (P<sub>A</sub>) involved in the 5-membered chelate ring can be made internally



39

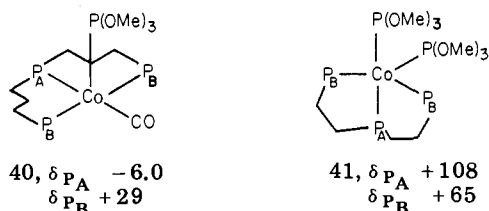


**Figure 1.**  $\delta_{31P}$  data for the intermediates in the reaction of  $Rh_2Cl_2(C_2H_4)_4$  with dppp.<sup>40</sup>

to the *trans*-PPhMe<sub>2</sub> ligand, resulting in a  $\Delta_R$  of +46.3. Once again, a *trans*-PEtMe<sub>2</sub> ligand would produce a more accurate  $\Delta_R$  value.

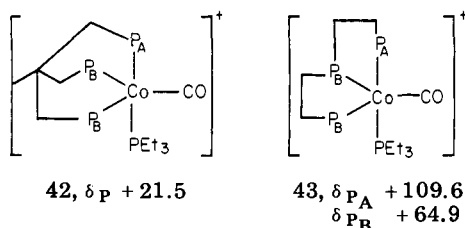
Baird et al.<sup>40</sup> have examined the species present during the reduction of olefins by Rh(I) complexes. The assignments of  $\delta_P$  resonances were made based on two criteria: "... (a) for a given tertiary phosphine in a series of rhodium complexes, <sup>31</sup>P resonances shift to lower field and values of  $J_{Rh-P}$  increase as the trans influence of the ligands trans to the phosphine decrease and (b) that ring strain contributions to the <sup>31</sup>P chemical shifts of chelating diphosphines vary in a characteristic, albeit as yet not understood, manner as the ring size varies". The addition of dppp to  $[RhCl(C_2H_4)_2]_2$  results in the observation of the intermediates in Figure 1. The  $\delta_P$  value of +30.3 for P trans to Cl as in a 6-membered ring (very little  $\Delta_R$  contribution) can be compared to the P trans to Cl in  $Rh(CO)Cl(dppe)$ .<sup>37</sup> dppp was chosen as a ligand in order to avoid  $\Delta_R$  contributions in any of the intermediates and allow correlations with data for monodentate phosphine systems to be made.

Meek et al.<sup>41</sup> have studied a series of tri- and tetradentate phosphorus complexes of Co. Crystal structure determinations<sup>42</sup> have shown that a change in the tridentate ligands from a six-membered chelate ttp (40)



to a five-membered chelate, etp (41), results in a change from a square-base-pyramid to trigonal-bipyramid structure.

In such complexes  $\Delta_R$  again has an additive effect, and thus the resonance due to the P<sub>A</sub> phosphorus is always found downfield for the 5-membered rings and further upfield for the 4- and 6-membered rings. Comparison of 42 with 43 reveals that all phosphorus

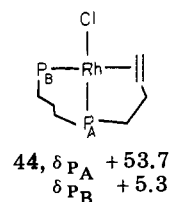


atoms in complex 42 exchange whereas those in 43 are not fluxional.

Again examination of 43 reveals that the <sup>31</sup>P resonance of  $\delta_{P_A}$ , which is involved in two five-membered

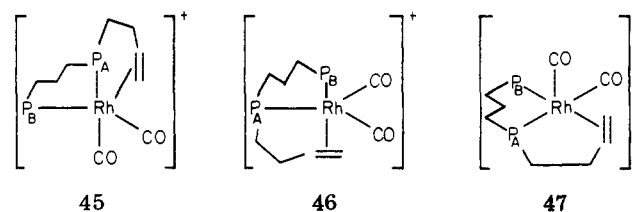
rings, is further downfield than  $\delta_{P_B}$ .

The potentially tridentate ligand  $Ph_2P(CH_2)_3P(Ph)(CH_2)_2CH=CH_2$  (ppol) reacts with  $[RhClCOD]_2$  to give  $RhClppol$  (44). The structure was confirmed by

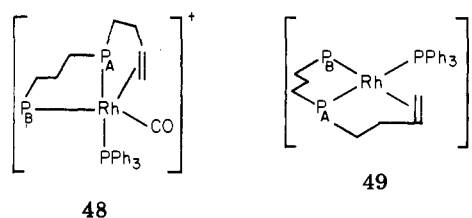


a crystal structure determination.<sup>43a</sup> This structure is very interesting since P<sub>B</sub> is incorporated into a 6-membered ring whereas P<sub>A</sub> is in both a 5- and 6-membered ring. The position of the  $\delta_{P_A}$  resonance appears to result from the average  $\Delta_R$  of a 5- and 6-membered ring when compared to the  $\delta_{P_A}$  value of 51. However, once again, trans effects here are not equal and better comparisons can be made when examining 50–52.

Reaction of 44 with CO results in a formulation which fits 45, 46, or 47 ( $\delta_{P_A} + 37.3$ ;  $\delta_{P_B} - 1.7$ ).

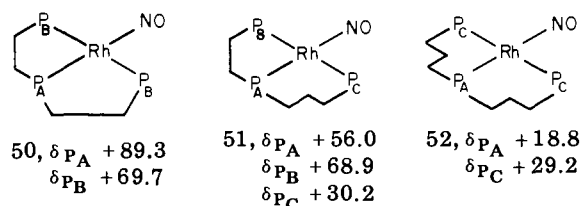


Reaction of 44 with PPh<sub>3</sub> and CO results in 48. Since



the outer lines of the AB spectrum are too weak to be observed, only a  $\delta_{P_A}$  value can be obtained. Reaction of 44 with PPh<sub>3</sub> results in 49 with  $\delta_P$  resonances at +29.1 and +7.3 due to P<sub>A</sub> and P<sub>B</sub>, respectively. These chemical shift differences are due both to  $\Delta_R$  differences between a 5- and 6-membered ring and a difference in trans ligand.

An exciting series of tridentate phosphine complexes is prepared by reaction of etp, eptp, or ttp with  $Rh-(PPh_3)_3NO$ ,<sup>44</sup> resulting in 50–52, respectively. This



series allows correlation of  $\Delta_R$  for phosphorus incorporated in both 5- and 6-membered rings. The  $\delta_{P_B}$  value of +69.7 for complex 50 is the expected value for phosphorus in a 5-membered chelate ring and is observed 40 ppm downfield from the  $\delta_{P_C}$  resonance for complex 51 which is in a 6-membered ring. When  $\delta_{P_A}$  values are compared between 50 and 52, a 70.3-ppm shift to lower field is observed between those phos-

TABLE IV. Relationship between Size of Ring and Size of  $\Delta_R$  As Observed in  $\text{RhNO}(\text{L})^{44}$ 

ring size	$\Delta_R^a$	no. of observations
5	+24.8	8
6	-10.7	7
7	0	1
two 5	+52.4	3
two 6	-5.8	2

<sup>a</sup> By comparison to  $\text{Rh}(\text{PPh}_3)_3\text{NO}$ ,  $\Delta$  57.4.

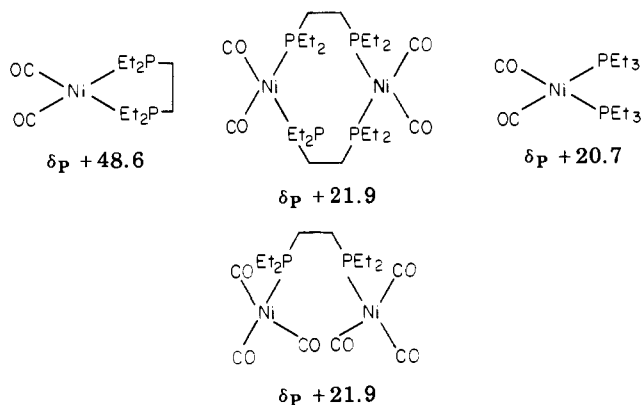


Figure 2.  $^{31}\text{P}$  data for Merriwether's Ni carbonyl-phosphine complexes.<sup>14</sup>

phorus nuclei involved in two 5- vs. two 6-membered rings. If the  $\delta_{\text{P}_A}$  resonance of **51** had an equal contribution from the 5- and 6-membered rings, it should appear midway between the  $\text{P}_A$  resonance of **50** and **52** at +59 ppm. Its appearance at +56 ppm is proof that an additive effect does indeed occur. Comparisons of all the compounds examined with  $\text{RhNO}(\text{PPh}_3)_3$  are summarized in Table IV. Note that the additive effect for 6-membered rings, derived from comparison of  $\text{P}_B$  to  $\text{P}_C$  in **52**, appears to give one-half the expected  $\Delta_R$  value, not two times the value.

#### 2.4c. Ni, Pd, Pt

By far the largest amount of work has been done in this subgroup. As previously mentioned, the first observation of an anomalous effect in the  $^{31}\text{P}$  of chelating diphosphines was by Merriwether, in 1961, while examining a series of nickel carbonyl-phosphine complexes.<sup>14</sup> He measured what we now refer to as  $\Delta$ , the difference in the chemical shift ( $\delta_{\text{P}}$ ) between free ligand and coordinated ligand in the series shown in Figure 2. He noted that the phosphines incorporated in the 5-membered chelate ring were found much further downfield and attributed this to the presence of phosphorus in a "planar 5-membered ring in which the C-P-C and Ni-P-C bond angles are distorted from the approximately tetrahedral angles in the unchelated complexes". He then postulated that "... it might be possible to use this unusually large resonance shift as a diagnostic test for the presence of phosphorus in a 4- or 5-membered ring". We now know that 4-membered rings induce a shielding effect. From this early data a normal  $\Delta_R$  of +28 for the phosphorus in the 5-membered ring can be calculated.

The  $^{31}\text{P}$  spectra of a series of Pt complexes of the type  $\text{PtMe}_2\text{L}$  have been recorded.<sup>45</sup> Table V reveals that standard  $\Delta_R$  values can be calculated from these data. The authors noted that deviations in  $\Delta$  in the chelating

TABLE V.  $^{31}\text{P}$  Data for the Series  $\text{Pt}(\text{Me})_2\text{L}^{45,47}$ 

L	$\delta_{\text{P}}$	$\delta_{\text{F}}$	$\Delta$	$\Delta_R$	size of chelate ring
dppm <sup>45</sup>	-40.4	-22.7	-17.7	-52.2	4
dppe <sup>45</sup>	+45.4	-13.2	+58.6	+24.1	5
dppp <sup>45</sup>	+3.2	-17.3	+20.5	-14.0	6
dppb <sup>47</sup>	+18.8	-15.0	+33.8	-0.7	7
<i>cis</i> - $\text{PtMe}_2(\text{PPh}_2\text{Me})_2$	+6.4	-28.1	+34.5		

TABLE VI.  $^{31}\text{P}$  Data for  $\text{MCl}_2\text{L}$  Complexes<sup>38</sup>

L	M	$\delta_{\text{P}}$	$\delta_{\text{F}}$	$\Delta$	$\Delta_R$
dppe	Pd	+68.3	-13.2	+81.5	+38.8
<i>cis</i> - $[\text{P}(\text{Ph}_2\text{Et})_3]_2$		+30.2	-12.5	+42.7	
dppp		+12.9	-17.3	+30.2	-14.8
<i>cis</i> - $[\text{P}(\text{Ph}_2\text{Pr})_3]_2$		+27.4	-17.6	+45.0	
dppb	Pt	+32.8	-15.0	+47.8	+3.8
<i>cis</i> - $[\text{P}(\text{Ph}_2\text{Bu})_3]_2$		+26.6	-17.1	+43.7	
dppm		-64.3	-22.7	-41.6	-68.5
<i>cis</i> - $[\text{P}(\text{Ph}_2\text{Me})_3]_2$		-1.2	-28.1	+26.9	
dppe		+45.3	-13.2	+58.5	+36.2
<i>cis</i> - $[\text{P}(\text{Ph}_2\text{Et})_3]_2$		+9.8	-12.5	+22.3	
dppp		-5.6	-17.3	+11.7	-12.8
<i>cis</i> - $[\text{P}(\text{Ph}_2\text{Pr})_3]_2$		+6.9	-17.6	+24.5	

TABLE VII. Important Bond Angles (Degrees) Obtained from the Crystallographic Data for the Series  $\text{PdCl}_2\text{L}^{47}$ 

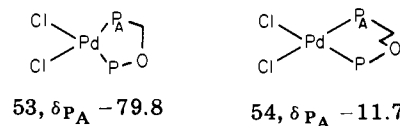
L	P-M-P	M-P-C(1)	P-C(1)-C(2)
dppm	73	94.7	93.0
dppe	85	108.5	107.9/108.2
dppp	90	115.9	112.9/118.1

series are presumably associated with the reduction of the P-Pt-P and P-C-P angles, but that "... it is remarkable that the sign of the strain effect should be opposite for dppe and dppm".

In the series  $\text{MCl}_2\text{L}^{38}$  similar results are observed (Table VI). Note that there is little difference in the  $\Delta_R$  values for the corresponding Pt and Pd complexes.

Comparison of  $\text{Ni}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2^{46}$  to  $\text{Ni}(\text{PMe})_4$  results in a  $\Delta_R$  of +26.4.

The  $\delta_{\text{P}}$  values for the chelating phosphinite complexes **53** and **54** can be compared to the theoretical values<sup>18</sup>



calculated for *cis*- $\text{PdCl}_2\text{L}_2$  and result in  $\Delta_R$  values of +52.1 and -12.3 for the 5- and 6-membered rings, respectively.

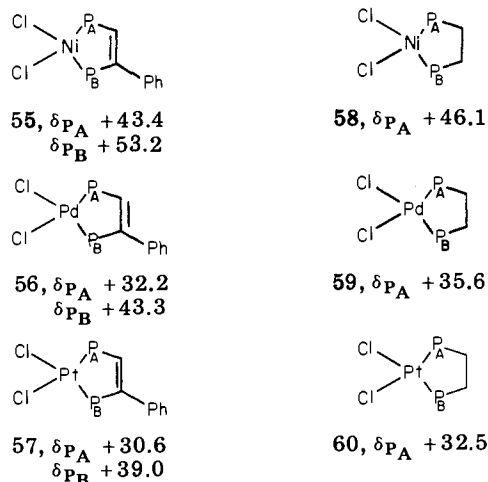
Vrieze et al.<sup>47</sup> have studied the  $^{31}\text{P}$ ,  $^{13}\text{C}$ , and  $^{195}\text{Pt}$  NMR spectra of the series  $\text{Pt}(\text{Me})_2[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]$  ( $n = 1-4$ ) in an attempt to correlate the NMR data of various nuclei with angle strain data determined by X-ray diffraction for an analogous Pd series. These data are the same as those in Table V with the addition of data for the analogous dppb complex which results in a  $\Delta_R$  of -0.7 for the 7-membered ring. Bond angles derived from crystallographic data are shown in Table VII for the analogous  $\text{PdCl}_2\text{L}$  series ( $\text{L} = \text{dppm}, \text{dppe}, \text{dppp}$ ). Comparison of these data reveals that in the 6-membered ring of  $\text{PdCl}_2(\text{dppp})$ , the angles are larger than normal but no irregularities were found for the  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR. On the other hand, the angles around phosphorus and carbon for  $\text{PdX}_2\text{dppe}$  are without



strain and yet show remarkable downfield shifts for the Pd<sup>38</sup> and Pt<sup>47</sup> complexes. The conclusion is that angle deformations are probably not responsible for the anomalous <sup>31</sup>P shift for 5-membered ring complexes.

Another study<sup>48</sup> is concerned with PtEt<sub>2</sub>L (L = dppe, dppp, dppb). The data are similar to that obtained for the PtMe<sub>2</sub>L complexes<sup>45,47</sup> with Δ<sub>R</sub> values of -24.8, +12.6, and -1.4 for phosphorus in the 4-, 5-, and 6-membered rings, respectively. Once again Δ<sub>R</sub> has been obtained by comparison to *cis*-Pt(Et)<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub>.

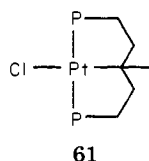
A series of phosphinoalkyne complexes *cis*-MCl<sub>2</sub>-(Ph<sub>2</sub>PC≡CR)<sub>2</sub> (M = Pd, Pt) undergo facile 1:1 reactions with secondary phosphines to give *cis*-MCl<sub>2</sub>-(Ph<sub>2</sub>CH=CR'PR<sub>2</sub>)<sub>2</sub>.<sup>49</sup> Some very interesting δ<sub>P</sub> and J<sub>P-P</sub> (to be discussed later) data can be extracted. In the series 55-60, one can see δ<sub>P</sub> values decrease within the



group (~10 ppm decrease from Ni to Pd and only 2-3 ppm decrease from Pd to Pt). Also note that PPh<sub>2</sub> in the saturated and unsaturated rings have nearly identical δ<sub>P</sub> values. This suggests that Δ<sub>R</sub> is unaffected by any of the steric and electronic differences involved in the formation of saturated rings as opposed to unsaturated rings and is in contrast to the findings for the organic molecules 13-15 discussed previously. Once again we observe that a phosphorus incorporated in an organic ring system and a phosphorus incorporated in an organometallic chelate system are not the same.

Shaw et al.<sup>50</sup> have studied the chemistry of a comprehensive series of large chelate ring metal complexes. One of these series is represented by PtCl<sub>2</sub>L [L = (t-Bu)<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>P(t-Bu)<sub>2</sub>, n = 9-12], where the δ<sub>P</sub> values of +28.2 to +31.8 are very close to the δ<sub>P</sub> value of +34.3 for *trans*-PtCl<sub>2</sub>P(*n*-Pr)<sub>2</sub>(t-Bu).<sup>18</sup> These δ<sub>P</sub> values point out that no metalation has occurred on the large ring backbone.

In a similar manner, two Pd complexes of the ligand (t-Bu)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH(Me)CH<sub>2</sub>CH<sub>2</sub>P(t-Bu)<sub>2</sub> were isolated,<sup>51</sup> namely *trans*-Pd<sub>2</sub>Cl<sub>4</sub>(L)<sub>2</sub> (δ<sub>P</sub> +39.0) and PtCIL (δ<sub>P</sub> +73.0). The latter downfield δ<sub>P</sub> resonance is consistent with structure 61 where the phosphorus atoms are in-

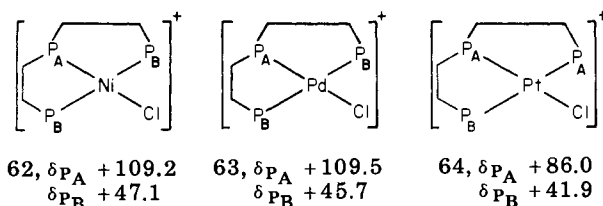


incorporated in 5-membered rings due to metalation of the tertiary carbon atom.

TABLE VIII. <sup>31</sup>P Data for PtMe<sub>2</sub>L (65)<sup>43</sup>

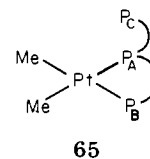
L	δ <sub>P<sub>A</sub></sub>	δ <sub>P<sub>B</sub></sub>	δ <sub>P<sub>C</sub></sub>
ttp	-3.7	+3.5	-18.9
etp	+49.4	+48.5	-15.2
PP <sub>3</sub>	+31.5	+32.4	-35.0
eptp	+44.0	+47.4	-18.9
tripod	+4.5		-28.8
ppol	-2.6	+3.4	

The series MCl(etp)<sup>+</sup> (M = Ni, Pd, Pt) has been examined.<sup>30</sup> In this series, 62-64, we see no change in the



δ<sub>P<sub>A</sub></sub> value for 62 and 63 whereas a decrease of 20 ppm is noted for 64. A steady, smaller decrease in δ<sub>P</sub> value is noted for P<sub>B</sub> as one descends the series.

The series Pt(Me)<sub>2</sub>L was further extended to potential tridentate ligands which adopt structures similar to 65.<sup>43b</sup> By the <sup>31</sup>P data in Table VIII we can distin-



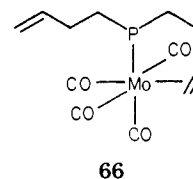
guish which P is bound in eptp and ppol. In the former we certainly have a 5-membered ring and in the latter we have a 6-membered ring and thus a free olefin.

### 3. Alkenylphosphine Complexes

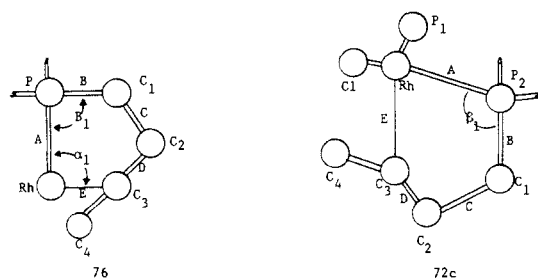
The majority of the <sup>31</sup>P data in this category exists in the areas of butenylphosphines, vinylphosphines, and styrylphosphines. Although reaction of the vinylphosphines results in complexes which are ortho-metalated, in this review they will be considered under this heading.

#### 3.1. Butenylphosphines

Reaction of Mo(CO)<sub>6</sub> with PhP(CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub> (dbp) produces 66 in which the potentially tridentate



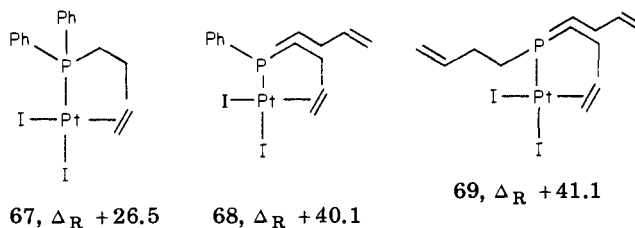
ligand achieves a bidentate coordination.<sup>7</sup> When this is compared to *cis*-Mo(CO)<sub>4</sub>[PPh(*n*-Bu)<sub>2</sub>]<sub>2</sub>, one obtains a Δ<sub>R</sub> of +28.6, indicating the presence of a 5-membered ring. Since common π bonding descriptions would describe this chelation as a "5<sup>1/2</sup>"-membered ring, this indicates that Δ<sub>R</sub> for π-bonded phosphine-olefin ligands will appear as though they are rounded off to the smaller ring size. This observation is pertinent to both the butenyl and styryl cases.



**Figure 3.** Bond lengths (Å) and angles (deg) for **72c**<sup>52a</sup> and **76**<sup>52b</sup>. **76:** A, 2.16; B, 1.82; C, 1.53; D, 1.50; E, 2.25;  $\beta_1$ , 108.2;  $\alpha_1$ , 83.3. **72c:** A, 2.37; E, 2.35;  $\beta_1$ , 106.3.

This is easily understood by examining the pertinent crystal structure parameters from butenylphosphine complexes such as **72c** and **76** (Figure 3). If one examines bond lengths A and E and envisions  $C_3$  being substituted by  $PR_2$ , then one sees that the conformation achieved by the butenylphosphines is in essence the same as that that would be achieved by a diphosphine ligand dppe.

A series of Pd(II) and Pt(II) complexes of the type  $MX_2L$  ( $L = mbp, dbp, tpb$ ) was prepared.<sup>8</sup> These complexes adopt a square-planar geometry in which only one of the olefins is bound to the metal in the solid state. <sup>1</sup>H NMR reveals exchange of the olefins on the NMR time scale. The  $\Delta_R$  values of the platinum complexes reveal  $\sim 14$  ppm greater deshielding for the potential tri- and tetradentate ligands. Since the <sup>1</sup>H NMR reveals average H-H and Pt-H coupling, one could naively expect the same  $\Delta_R$  for **67**–**69**. The reason the  $\Delta_R$  values for **68** and **69** are equal and 14 ppm larger



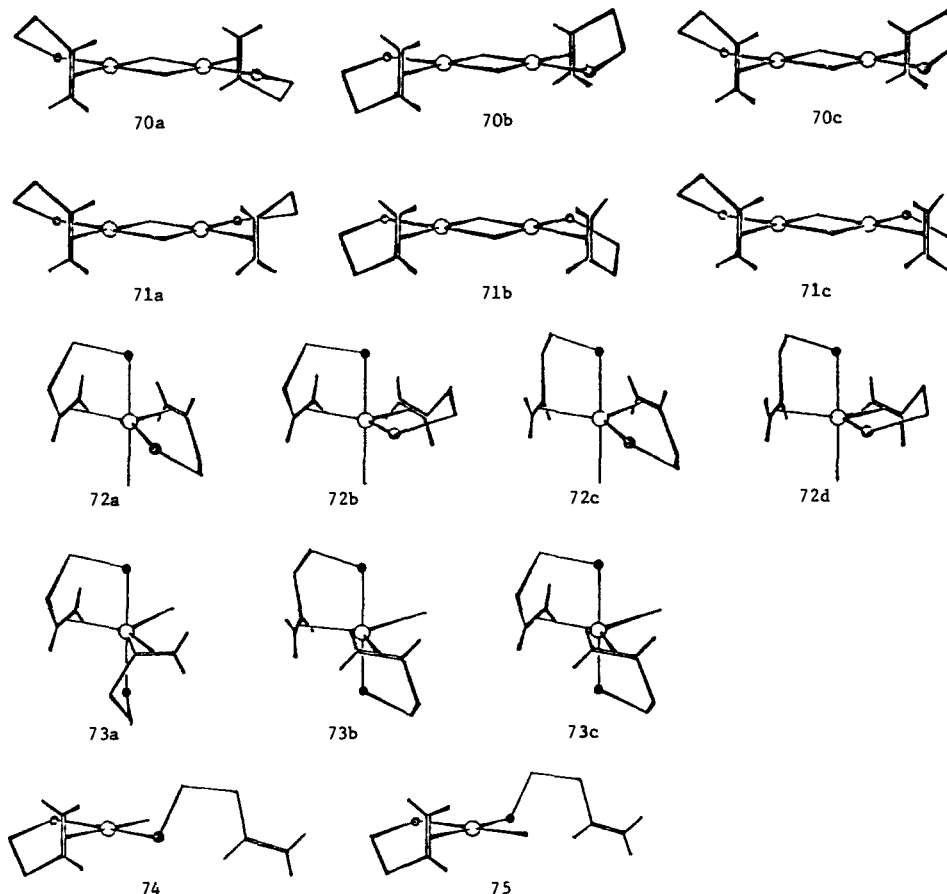
**67,**  $\Delta_R + 26.5$

**68,**  $\Delta_R + 40.1$

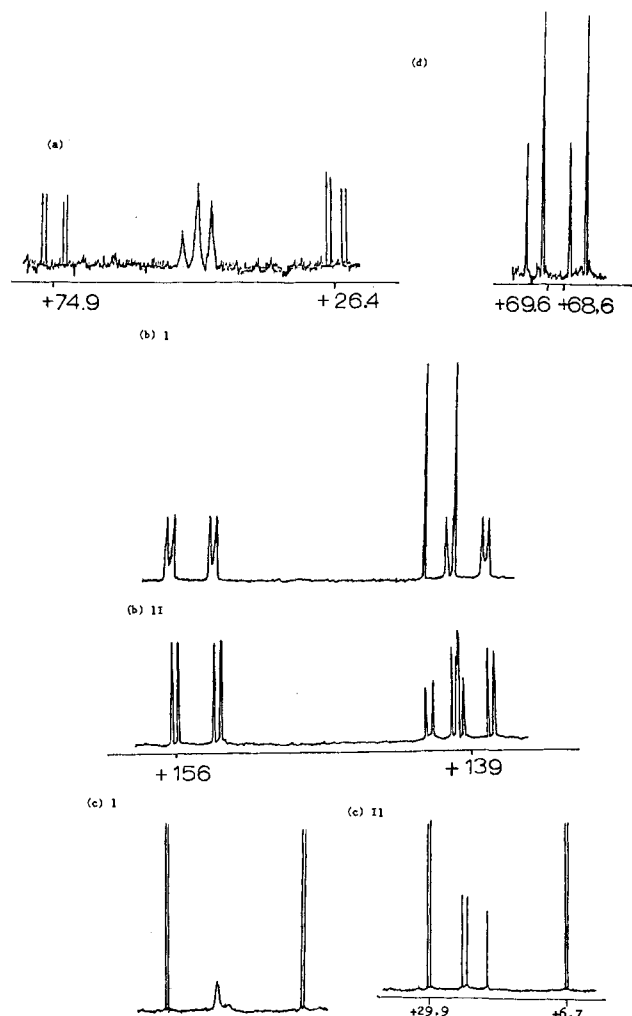
**69,**  $\Delta_R + 41.1$

than  $\Delta_R$  for **67** is at present unanswered. The same  $\Delta_R$  difference (15 ppm) is observed for the Pd analogues of **67** and **68**.<sup>8</sup>

The structures of the Rh and Ir complexes  $RhCl(mbp)_2$ ,  $RhCl(map)_2$ ,  $IrCl(mbp)_2$ , and  $Rh_2Cl_2(mbp)_2$  have been examined by infrared and <sup>31</sup>P spectroscopy<sup>9</sup> and the data used to assess the dynamic behavior of olefin bonding and the exchange of phosphine and olefin. Figure 4 reveals the possible structures for such complexes and Figure 5 their <sup>31</sup>P spectra. At 32 °C the <sup>31</sup>P spectrum of  $RhCl(mbp)_2$  exhibits a broad resonance at +50 ppm, indicating that the isomers of  $RhCl(mbp)_2$  that are present are exchanging both olefin and phosphorus (since Rh-P coupling is lost). At -75 °C (Figure 5a), the spectrum consists of two ABX patterns centered at +74.9 and +26.4 ppm, the outer lines of which are lost in the noise level. In addition there is a continuing broad multiplet at +50 ppm. The former resonances can be attributed to an isomer of **72**. Although four isomers are possible, isomer C was the one observed in a crystal structure determination.<sup>52</sup> The resonance centered at +26.4 ppm is assigned to an axial phosphorus and the resonance at +74.9 ppm to an equatorial phosphorus. The broad multiplet at +50 ppm may be

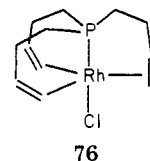


**Figure 4.** Possible structures of phosphine-olefin complexes.<sup>9</sup> Phenyls have been omitted for clarity. ● = phosphorus, ○ = Rh or Ir.



**Figure 5.** <sup>31</sup>P spectra of (a) RhCl(mbp)<sub>2</sub> at -75 °C, (b) RhCl(map)<sub>2</sub> at (I) 32 °C, (II) -75 °C, (c) IrCl(mbp)<sub>2</sub> at (I) 32 °C, (II) -75 °C, (d) Rh<sub>2</sub>Cl<sub>2</sub>(mbp)<sub>2</sub> at 32 °C.

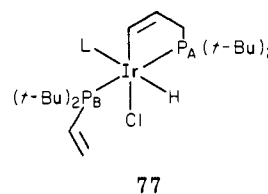
due to isomers of **73** still undergoing exchange at -75 °C. At 32 °C the <sup>31</sup>P spectrum of IrCl(mbp)<sub>2</sub> (Figure 5c) is consistent with the presence of an isomer of **72** with resonances centered at δ<sub>P(axial)</sub> -6.6 and δ<sub>P(equatorial)</sub> +29.5 with a *cis*-<sup>2</sup>J<sub>P-P</sub> of 11 Hz. The exchange processes causing the broad resonance centered at +22.2 ppm are frozen out at -75 °C, revealing resonances at +19.3, +23.9, and +22.0 ppm. The former is consistent with either isomer **73a** or **73b** where the phosphorus nuclei are equivalent. The resonances at +23.9 and +22.0 ppm are consistent with **72c** where the phosphorus nuclei are nonequivalent, resulting in an AB spectrum. The presence of isomers **74** and **75** was eliminated on the basis of Δ<sub>R</sub> arguments, since the δ<sub>P</sub> resonance of a chelated ligand should appear at ~25 ppm to lower field than that of an unchelated ligand. The <sup>31</sup>P spectrum of a solution of RhCl(map)<sub>2</sub> (Figure 5b) at 32 °C revealed an isomer of **72** whose structure was assigned in a similar manner. The <sup>31</sup>P spectrum of Rh<sub>2</sub>Cl<sub>2</sub>(mbp)<sub>2</sub> (Figure 5d) indicates the presence of two isomers. This can be explained in terms of the *cis* and *trans* isomers **70** and **71**. While one cannot say whether one or two isomers of **70** and **71** are being observed, it is clear that such structures are present from the Δ<sub>R</sub> of +30.4 ppm when compared to Rh<sub>2</sub>Cl<sub>2</sub>[P(tol)<sub>3</sub>]<sub>4</sub> which indicates chelating ligands are present. In a similar fashion, **76** shows a δ<sub>P</sub> of +134, and this large coordination chemical shift is due to tetradentate co-



ordination resulting in three times the “expected” Δ<sub>R</sub> of 21–30.<sup>9</sup>

### 3.2. Allylphosphines

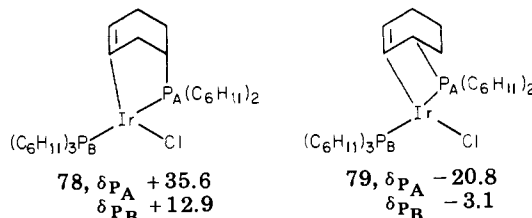
Vrieze et al.<sup>53</sup> studied the reaction of P(*t*-Bu)<sub>2</sub>allyl with [(COT)IrCl]<sub>2</sub> in α-picoline (L) which resulted in **77**. The <sup>31</sup>P spectra revealed an AB pattern with large



P–P coupling indicating the presence of two non-equivalent *trans* phosphorus atoms. At that time assignments were not made; however, we now know that the low-field resonance is due to P<sub>A</sub> and the high-field resonance to P<sub>B</sub>. This results in a Δ<sub>R</sub> of +40.9 ppm.

Reaction of Ir(acac)(C<sub>2</sub>H<sub>4</sub>) with P(*t*-Bu)<sub>2</sub>allyl in α-picoline (L) resulted in (acac)[(*t*-Bu)<sub>2</sub>PCH<sub>2</sub>CH=CH]Ir(H)(L). Although the stereochemistry is unknown,<sup>10</sup> the δ<sub>P</sub> value of +63.9 indicates metalation of the allyl group in a structure probably similar to **77**.

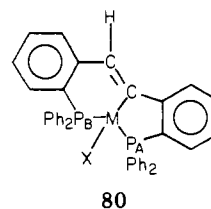
In a similar fashion, reaction of P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> with [(COT)IrCl]<sub>2</sub> yields **78** and **79** in which one cyclohexyl



group has been dehydrogenated to a cyclohexene group with the double bond occupying the fourth coordination site.<sup>54</sup> These complexes contain 5<sup>1/2</sup>- and 4<sup>1/2</sup>-membered rings, respectively, and the assignments are consistent with Δ<sub>R</sub> values of +22.7 and -17.7 ppm, respectively.

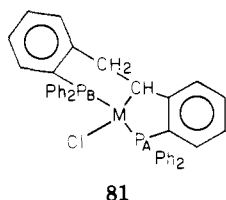
### 3.3. Styrylphosphines

The stilbene ligand *o*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH=CHC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> can lose a vinyl proton to give σ-vinyl chelates of type **80**.<sup>55</sup> P<sub>A</sub> is incorporated in a 5-membered ring while P<sub>B</sub> is in a 6-membered ring.

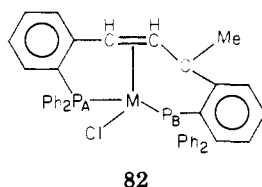


The bibenzyl analogue also forms chelating σ-benzyl complexes of the type **81**. Again both 5- and 6-membered rings are present. Structure **82** also reveals a

complex containing  $5^{1/2}$ - and  $6^{1/2}$ -membered rings,<sup>56</sup> and the resonances to lower field can be assigned to  $P_A$ .

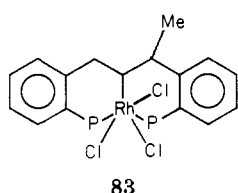


81

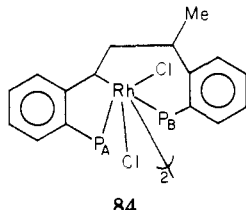


82

Reaction of 82 with HCl results in the isolation of 83 and 84. Assignment of the resonances can be made as



83



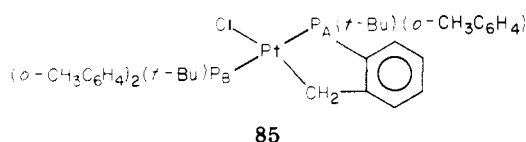
84

usual. The phosphorus atoms incorporated in the 5- and 7-membered rings in 84 should have  $\delta_P$  at a lower field than that found for the phosphorus atoms in the 6-membered rings in 83. The resonance at +45.9 is assigned to  $P_A$  and that at +31.4 to  $P_B$ .

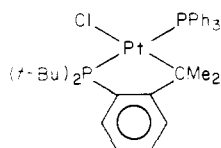
#### 4. Orthometalated Complexes

As indicated earlier,  $\Delta_R$  contributes to the elucidation of the structures of orthometalated complexes by allowing the accurate prediction of ring size from ligands that could potentially metalate in more than one position. The  $^{31}\text{P}$  NMR spectra are usually much easier to interpret than the  $^1\text{H}$  and  $^{13}\text{C}$  spectra. The following examples will expand upon these points.

One such example is in 85 where metalation of the tolyl group, as shown, results in a 5-membered ring



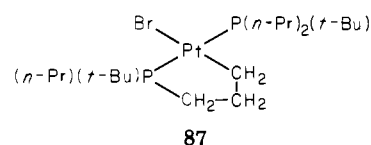
85



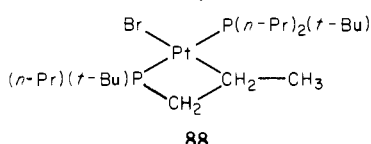
86

whereas metalation of the *tert*-butyl group would result in a 4-membered ring.<sup>57</sup> A  $\delta_{P_B}$  resonance at +31.1 and a  $\delta_{P_A}$  resonance at +52.0 result in a  $\Delta_R$  value of +20.9, and this is consistent with a 5-membered ring. A similar situation exists in compound 86,<sup>57</sup> where  $\Delta_R$  is +31.8 and the assignment of the structure containing a 5-membered ring is again confirmed. A more complex situation exists in identifying the presence of isomer 87 or 88.  $\delta_P$  resonances are observed at +67.4 and +25.9 ppm. Although the original assignment was made as structure 88,<sup>58</sup> reassignment based on  $\Delta_R$  of +41.5 was later made.<sup>18</sup> Metalation of  $\text{Me}_2\text{P}(\text{naphthyl})$  in the 4 position of the naphthyl group gives a 5-membered ring with a resultant  $\Delta_R$  of +30.8.<sup>59</sup>

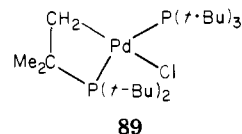
The Pd(II) hydride  $\text{PdHCl}[\text{P}(t\text{-Bu})_3]_2$  undergoes intramolecular metalation to produce 89.<sup>60</sup> The product



87



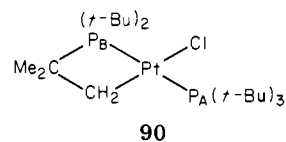
88



89

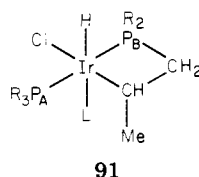
was identified by the loss of the hydride resonance and loss of Pd-H at 2190–2201  $\text{cm}^{-1}$ . Comparison of the  $\delta_P$  resonance of the unmetalated (+61.8 ppm) and metalated (-11.8 ppm) phosphine reveals a  $\Delta_R$  of -73.6, and this is consistent with the formation of a 4-membered ring.

In a similar fashion a  $\Delta_R$  of -79.6 can be calculated for 90.<sup>61</sup>

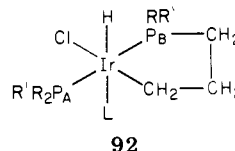


90

Reaction of  $[\text{CODIrCl}]_2$  with  $\text{P}(i\text{-Pr})_3$  or  $\text{P}(t\text{-Bu})_2(i\text{-Pr})$  in picoline (L) results in the isolation of 91 and 92, respectively.



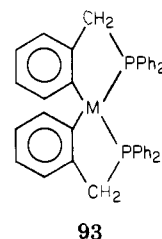
91



92

The assignments are consistent with  $\Delta_R$  values of -41.5 ppm for the 4-membered ring in 91 and +36.6 ppm for the 5-membered ring in 92.<sup>62</sup> In these cases  $\Delta_R$  is a very important analytical tool in determining whether the methylene or methyl has been abstracted.  $^1\text{H}$  NMR is complicated by the presence of resonances due to unmetalated ligand and these are less easily interpreted.

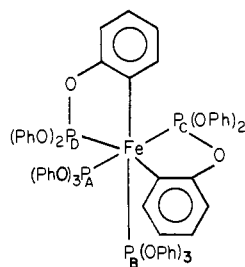
Issleib<sup>63</sup> prepared complexes of type 93. Comparison



93

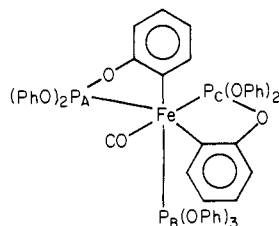
of  $\delta_P$  values to  $(\text{PPh}_2\text{bz})_2\text{MCl}_2$  gave the expected  $\Delta_R$  values of +20.6 (Pd) and +32.9 ppm (Pt) for the phosphorus atoms incorporated in 5-membered rings.

Tolman<sup>5</sup> found that reaction of  $\text{Fe}(\text{COD})_2$  with  $\text{P}(\text{O}^i\text{Pr})_3$  resulted in 94. The structural assignment was made based on the fact that metalated  $\text{P}(\text{O}^i\text{Pr})_3$  lies  $\sim 30$  ppm at lower fields than unmetalated ligands. By examination of the phosphorus chemical shifts, 94 obviously contains two metalated and two unmetalated



94,  $\delta_{P_A} + 144.2$   
 $\delta_{P_B} + 149.5$   
 $\delta_{P_C} + 176.4$   
 $\delta_{P_D} + 180.8$

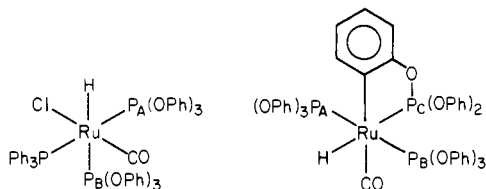
ligands. Reaction of 94 with CO gives 95. From  $\Delta_R$



95,  $\delta_{P_A} + 186.1$   
 $\delta_{P_B} + 151.3$   
 $\delta_{P_C} + 175.7$

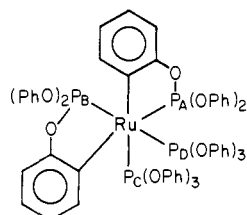
and the splitting pattern one would again surmise the presence of two metalated and one unmetalated ligands.

In a similar fashion structures can be assigned to 97 and 98<sup>64a</sup> by comparison to 96.



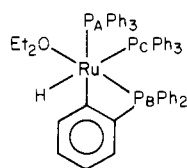
96,  $\delta_{P_A} + 129.0$   
 $\delta_{P_B} + 122.5$

97,  $\delta_{P_C} + 165.2$   
 $\delta_{P_B} + 137.5$



98,  $\delta_{P_A} + 155.8$   
 $\delta_{P_B} + 152.9$   
 $\delta_{P_C} + 127.8$   
 $\delta_{P_D} + 120.6$

The fact that orthometalated phosphines and phosphines trans to hydride ligands resonate at lower frequencies than other phosphines allowed the unequivocal assignment of the stereochemistry to 99 (P = PPh<sub>3</sub>).<sup>65</sup>

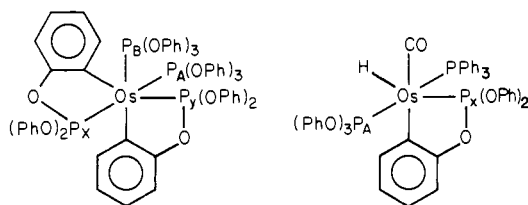


99

old assignment	new assignment
$\delta_{P_A} - 51.4$	$\delta_{P_A} + 20.0$
$\delta_{P_B} + 20.0$	$\delta_{P_B} - 51.4$
$\delta_{P_C} + 26.1$	$\delta_{P_C} + 26.1$

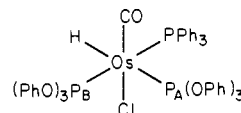
However, we now know that P<sub>B</sub> is incorporated into a 4-membered ring and should be assigned to the reso-

nance at -51 ppm. In the series 100-102,<sup>66</sup> metalation



100,  $\delta_{P_A} + 71.8$   
 $\delta_{P_B} + 84.8$   
 $\delta_{P_X} + 114.5$   
 $\delta_{P_Y} + 119.2$

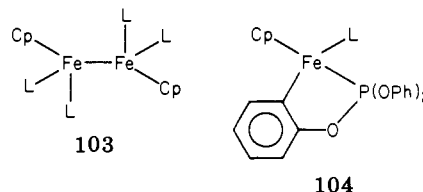
101,  $\delta_{P_A} + 93.7$   
 $\delta_{P_B} + 132.5$



102,  $\delta_{P_A} + 88.3$   
 $\delta_{P_B} + 88.2$

is indicated in 100 by  $\Delta_R$  of +42.7 and in 101 (by comparison to P<sub>A</sub> in 102) by a  $\Delta_R$  of +44.2. Again, the observed splitting pattern and knowledge of  $\Delta_R$  allow assignment of the stereochemistry of this molecule.

In a series of papers Stewart et al.<sup>67-69</sup> examined the use of <sup>31</sup>P to determine structures of triaryl phosphite complexes. Although CpFe(CO)<sub>2</sub>R + P(OPh)<sub>3</sub> in the early literature was said to give 103, the authors used  $\Delta_R$  arguments to show that the structure was more likely 104.

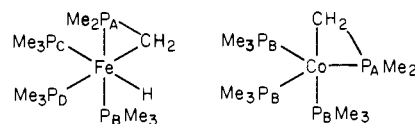


103

104

In a series of 5- and 6-coordinate P(OPh)<sub>3</sub> complexes of Fe, Mn, Ru, Os, Co, Pt, and Pd the authors point out  $\Delta_R$  values ranging from +23 to +42 ppm (see Table IX for complexes and  $\Delta_R$  values). A generalization made by these authors is that <sup>31</sup>P of unmetalated P(OPh)<sub>3</sub> lies in the range +71 to +94 ppm and is dependent on the trans ligand, whereas  $\delta_P$  for metalated P(OPh)<sub>3</sub> lies in the region +114 to +133.

Complex 105 has been studied by two groups,<sup>70,71</sup> and their data are very similar for the  $\delta_P$  of P<sub>A</sub> involved in the 3-membered ring. Note that P<sub>A</sub> is shielded vs.  $\delta_P$



105,  $\delta_{P_A} - 17.4$   
 $\delta_{P_B} + 24.1$   
 $\delta_{P_C} + 30.7$   
 $\delta_{P_D} + 38.1$

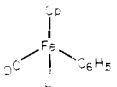
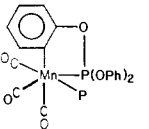
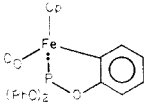
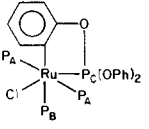
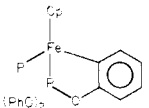
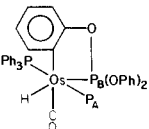
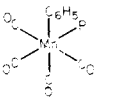
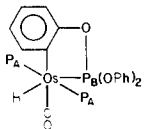
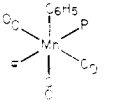
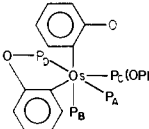
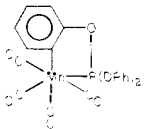
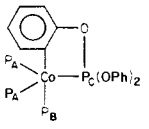
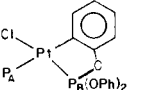
106,  $\delta_{P_A} - 30.0$   
 $\delta_{P_B} + 12.2$

for PMe<sub>3</sub> ligand. In a similar fashion,  $\delta_{P_A}$  of 106 is shielded vs.  $\delta_{P_B}$ .<sup>71</sup>

### 5. Phosphides

One of the newer areas in which <sup>31</sup>P data are being accumulated is that of phosphide complexes. It appears that these complexes also show  $\Delta_R$  effects which can be helpful in structural assignments, although not enough

TABLE IX.  $^{31}\text{P}$  Data for Triphenylphosphite Complexes<sup>68</sup>

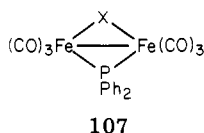
complex	$\delta^a$	$\delta^b$	$\Delta_R$	complex	$\delta^a$	$\delta^b$	$\Delta_R$
	+172.3				+157.1	+193.8	+36.7
		+203.4	+31.1		+114.0 (P <sub>A</sub> ) +121.0 (P <sub>B</sub> )	+152.0 (P <sub>C</sub> )	+38.0 +31.0
	+166.4	+200.0	+33.6		+93.7 (P <sub>A</sub> )	+132.5 (P <sub>B</sub> )	+38.8
	+159.8				+82.3 (P <sub>A</sub> )	+131.2 (P <sub>B</sub> )	+48.9
	+163.8				+71.8 (P <sub>A</sub> ) +84.8 (P <sub>B</sub> )	+114.5 (P <sub>C</sub> ) +119.2 (P <sub>D</sub> )	+42.7 +34.4
			+33.4		+122.0 (P <sub>A</sub> ) +144.0 (P <sub>B</sub> )	+160.0 (P <sub>C</sub> )	+38.0
					+112.8 (P <sub>A</sub> )	+100.5 (P <sub>B</sub> )	+22.9

<sup>a</sup> Unmetallated ligand, P = P(OPh)<sub>3</sub>. <sup>b</sup> Metallated ligand.

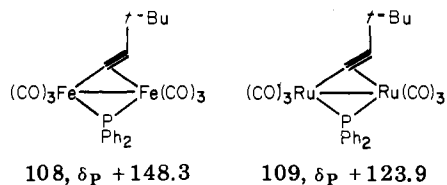
TABLE X. Comparison of Fe-Fe Bond Length and Fe-P-Fe Angle with  $\delta_P$  for a Variety of Iron Carbonyl Complexes

complex	Fe-Fe bond length, Å	Fe-P-Fe angle, deg	$\delta_{\text{P}(\text{C}_6\text{H}_5)_2}$
$\text{Fe}_2(\text{CO})_6[\text{Cl}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.5607 (5)	69.8 (0)	142.7
$\text{Fe}_2(\text{CO})_6[\text{CHC}\{\text{N}(\text{C}_2\text{H}_5)_2\}\{\text{C}_6\text{H}_5\}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.548 (1)	70.1 (0)	153.9
$\text{Fe}_2(\text{CO})_6[\text{CHC}\{\text{NHC}_6\text{H}_{11}\cdot\text{c}\}\{\text{C}_6\text{H}_5\}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.576 (1)	70.5 (0)	154.0
$\text{Fe}_2(\text{CO})_6[\text{C}\{\text{P}(\text{OC}_2\text{H}_5)_2\}\{\text{C}_6\text{H}_5\}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.671 (2)	74.0 (0)	194.5
$\text{Fe}_2(\text{CO})_6[\text{CC}\{\text{Ph}(\text{c}\cdot\text{C}_6\text{H}_{11})_2\}\{\text{C}_6\text{H}_5\}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.550 (2)	70.7 (1)	123.0
$\text{Fe}_2(\text{CO})_6[\text{C}_2\text{C}_6\text{H}_5][\text{P}(\text{C}_6\text{H}_5)_2]$	2.597 (2)	71.64 (7)	148.4
$\text{Fe}_2(\text{CO})_6[\text{C}\{\text{NHC}_6\text{H}_{11}\cdot\text{c}\}\text{CH}\{\text{C}_6\text{H}_5\}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.628 (1)	72.5 (0)	183.5
$\text{Fe}_2(\text{CO})_6[\text{C}\{\text{CN}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)\}\{\text{C}_6\text{H}_5\}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.644 (2)	73.4 (0)	190.3
$\text{Fe}_2\text{Ag}(\text{CO})_6[\text{CHC}\{\text{NHCH}_3\}\{\text{C}_6\text{H}_5\}][\text{P}(\text{C}_6\text{H}_5)_2]^+\text{ClO}_4^-$	2.682 (1)	74.1 (0)	173.4
$\text{Fe}_2(\text{CO})_6[\text{C}\{\text{CNC}(\text{CH}_3)_3\}\{\text{C}_6\text{H}_5\}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.671 (2)	74.1 (0)	194.2
$\text{Fe}_2(\text{CO})_6[\text{CCHC}\{\text{C}_6\text{H}_5\}\text{N}\{\text{C}_6\text{H}_5\}\text{HO}][\text{P}(\text{C}_6\text{H}_5)_2]$	2.60	71	179.0
$\text{Fe}_2(\text{CO})_6[\text{CH}_2\text{C}\{\text{C}_6\text{H}_5\}\text{NCH}_3][\text{P}(\text{C}_6\text{H}_5)_2]$	2.707 (1)	75.6 (0)	198.5
$\text{Fe}_2(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_2\text{C}_6\text{F}_8][\text{P}(\text{C}_6\text{H}_5)_2]$	2.791 (6)	~79	129.9
$\text{Fe}_2(\text{CO})_4[\text{CNC}(\text{CH}_3)_3]_2[\text{C}_2\text{C}(\text{CH}_3)_3][\text{P}(\text{C}_6\text{H}_5)_2]$	2.5946 (7)	71.5 (0)	145.3
$\text{Fe}_2(\text{CO})_6[\text{C}_2\text{C}(\text{CH}_3)_3][\text{P}(\text{C}_6\text{H}_5)_2]$	2.5959 (6)	71.7 (0)	148.3
$\text{Fe}_2(\text{CO})_6[\text{P}(\text{C}_6\text{H}_5)_2]_2$	2.623 (3)	72.0 (1)	142.8
$\text{Fe}_2(\text{CO})_5[\text{P}(\text{C}_6\text{H}_5)_3][\text{C}_2\text{C}_6\text{H}_5][\text{P}(\text{C}_6\text{H}_5)_2]$	2.648 (1)	73.1 (0)	153.0

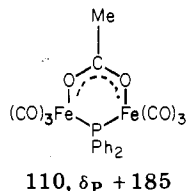
data have been accumulated to allow unequivocal structural assignments to be made solely on this basis. Compounds of structure 107 were prepared and their  $^{31}\text{P}$  spectra examined<sup>72,73</sup> (Table X).



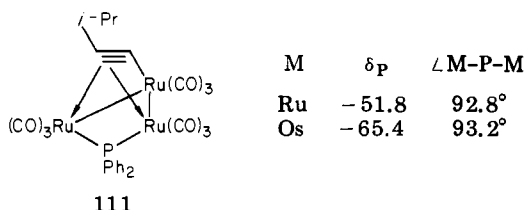
The values in Table X indicate that the phosphorus nuclei incorporated in the 3-membered rings are shifted far downfield with an apparent relation between the opening of the Fe-P-Fe angle and a deshielding of the phosphorus. This effect is also observed in structures 108 and 109 where crystal structures have shown the presence of Fe-Fe and the Ru-Ru bonds, respectively, and the phosphorus resonances lie at very low field.<sup>73</sup> Structure 110<sup>74</sup> also reveals a very low field  $\delta_P$  resonance



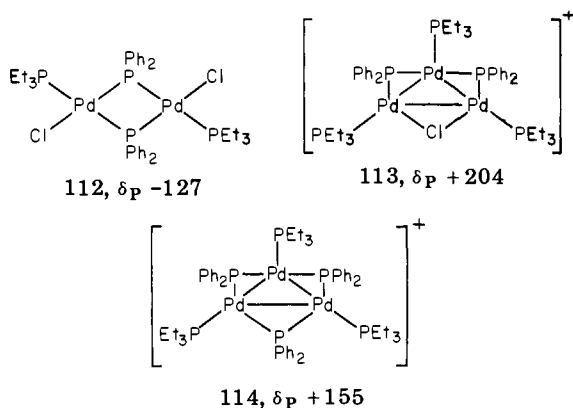
which can be explained on the basis of the Fe-Fe-P 3-membered ring.



For the  $\Delta_R$  effect to be valid for phosphides, one would expect phosphides bridging metals which are not involved in metal-metal bonds to be found upfield. Such is the case in structure 111<sup>73</sup> where the phosphorus atoms are involved in 4-membered rings.

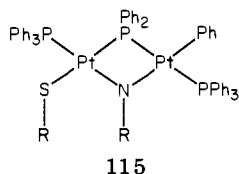


Recently<sup>75,76</sup> the phosphide palladium complexes 112-114 were prepared and their <sup>31</sup>P spectra examined.

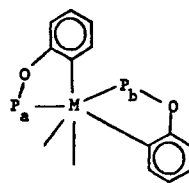


We again may compare phosphides definitely in 3-membered (113, 114) and 4-membered (112) rings. A chemical shift difference of ~300 ppm is observed between these examples, with the 3-membered ring being downfield. The authors note that such large chemical shift differences may some day allow determination of the presences of M-M bonds, and we fully concur!

Reaction of  $(PPh_3)_2Pt(C_2H_4)$  with 5,6-dimethyl-2,1,3-benzothiadiazole is said to give 115.<sup>77</sup> The <sup>31</sup>P



reveals a  $\delta_{P(Ph_2)}$  value of -68.6 for the 4-membered ring. Although there are no 3- or 5-membered analogues for comparison, note the relative shielded value is consistent with the 4-membered ring.



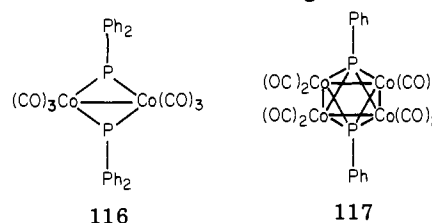
M	$\delta_{P_a}$ (ppm)	$\delta_{P_b}$ (ppm)
Fe	+180.8	+176.4
Ru	+155.6	+152.7
Os	+118.9	+113.4

Figure 6. Relationship between position in the periodic table and  $\delta_P$  shifts for an orthometalated Fe series.<sup>6</sup>

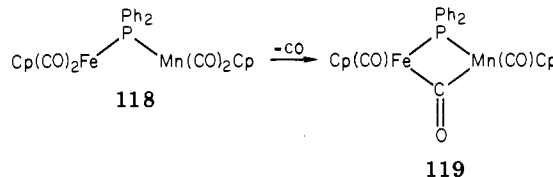
TABLE XI. Relationship between Metal Position in the Periodic Group and  $\delta_P$  for  $M(CO)_4L^{26}$

M	L	$\delta_{P(PPH_2)}$
Cr	$Ph_2PCH_2CH_2PPhMe$	+80
Mo		+55.7
W		+41.0
Cr	$Ph_2PCH_2PPhMe$	+125.8
Mo		+1.7
W		-23.4
Cr	$Ph_2P(CH_2)_3PPhMe$	+40.7
Mo		+20.1
W		-0.4

A  $\delta_P$  value of +62.3 for 116 can also be compared to a  $\delta_P$  of +134 for 117 which can be envisioned as being involved in four 3-membered rings.<sup>78</sup>



Crystallographic and <sup>31</sup>P data on a model series such as 118 and 119<sup>79</sup> would be useful since a downfield shift



of the phosphide resonance of 119 vs. 118 would indicate the presence of an M-M bond.

## 6. Effects

### 6.1. Of Position In the Periodic Group

It has been noted that for the same coordination number, molecular geometry, oxidation state, and phosphine, one generally observes a high-field shift of the <sup>31</sup>P resonance as one descends in a given group.<sup>13</sup> The same can be said for complexes which reveal a  $\Delta_R$  contribution. In the orthometalated series shown in Figure 6, we clearly see a decrease in  $\delta_P$  as one descends the Fe group.<sup>5</sup> As was previously mentioned (section 2.4a), this was also observed in 31.

Variation in  $\delta_P$  also follows this trend for the Ni series 55-60 as previously described.<sup>49</sup> In Table XI we again see  $\delta_P$  and therefore  $\Delta_R$  decreasing as we descend the Cr group. Finally, in the Mn series shown in Table III, we again see a decrease in  $\delta_P$  as we descend from Mn to Re.<sup>33</sup>

### 6.2. Of Heteroatoms

Since 1974 much work has been carried out in the area of incorporation of heteroatoms other than P and

TABLE XII.  $^{31}\text{P}$  Data for  $[\text{Ph}_2\text{P}(\text{x})\text{CH}_2\text{PPh}_2]\text{M}(\text{CO})_4$ <sup>81</sup>

X	M	$\delta_{\text{P}(\text{x})}$	$\delta_{\text{P}}$
Se		+30.7	-27.2
	Cr	+39.4	+69.1
	Mo	+38.3	+41.8
S	W	+41.8	+27.5
		+40.1	-28.0
	Cr	+57.5	+63.9
	Mo	+55.5	+37.9
	W	+59.6	+25.2

TABLE XIII.  $\Delta_{\text{R}}$  Values Obtained from 5-Membered Chelate Rings Containing Heteroatoms<sup>82</sup>

M	X-M'-CH <sub>2</sub> -X'	$\Delta_{\text{R}}$
Cr	N-Ge-C-P	+13.0
Mo		+10.0
W		+19.0
Cr	As-Si-C-P	+25.1
Mo		+18.2
W		+17.4
Cr	P-Ge-C-N	+19.8
Mo		+18.1
W		+30.1

TABLE XIV. Effect of R Group Cone Angle on the Coordination Chemical Shift ( $\Delta$ ) in  $\text{M}(\text{CO})_4\text{Ph}_2\text{PCH}_2\text{PR}_2$ <sup>83</sup>

R	cone angle, deg	$\Delta$		
		Cr	Mo	W
Me <sub>2</sub>	101	+57.5	+27.3	-1.4
Ph, Me	110	+52.9	+26.1	-0.5
Ph <sub>2</sub>	119	+49.0	+23.6	0.0
Ph, <i>i</i> -Pr	124	+48.3	+25.9	+2.0
<i>i</i> -Pr <sub>2</sub>	129	+48.1	+28.0	+5.4

C in the chelate structures. As mentioned previously,  $\Delta_{\text{R}}$  is now entrenched in the chemistry of ortho-metalated phosphite complexes<sup>67-69</sup> and chelating phosphite complexes.<sup>17</sup> In the series  $\text{M}(\text{CO})_4\text{L}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}; \text{L} = \text{Ph}_2\text{P}_A(\text{S})\text{CH}_2\text{P}_B\text{Me}_2$ )<sup>80</sup> where S is incorporated into the 5-membered rings, a normal  $\Delta_{\text{R}}$  is observed for  $\text{P}_A$  in the same ring. In the interesting series shown in Table XII, one observes the incorporation of S and Se into 5-membered chelates.<sup>81</sup> Note that  $\Delta_{\text{R}}$  is observed for the non-S-bonded P but not so easily in the P(S) phosphorus. This is due to the chemical shift initially reflecting phosphorus(V) and not phosphorus(III).

In the very unusual series shown in Table XIII, we see  $\Delta_{\text{R}}$  values of between 10 and 30 for the 5-membered chelates.<sup>82</sup>

### 6.3. Of R Group of Phosphorus

In the series shown in Table XIV, the effect of the R group in  $\text{Ph}_2\text{PCH}_2\text{PR}_2$  on  $\delta_{\text{P}}$  was examined in relation to the cone angle extended by the  $\text{PR}_2$  ligand.<sup>83</sup> It can be seen that R induces very little change in the  $\delta_{\text{P}}$  values. It is curious that as we increase the size of the R group, the Cr values decrease, the W values increase, and the Mo values go through a minimum.

### 6.4. Of Backbone Unsaturation

As discussed previously, Carty et al.<sup>49</sup> have shown that in the case of complexes of the type 120,  $\delta_{\text{P}}$  values

TABLE XV. Average  $J_{\text{P-P}}$  (Hz) Values for  $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PR}_2]\text{M}(\text{CO})_4$ <sup>84</sup>

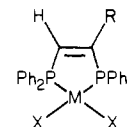
M	$n = 1$	$n = 2$	$n = 3$
	114	28	0
Cr	24	12	41
Mo	15	5	28
W	21	4	22

TABLE XVI. Average Observed  $^{\text{B}}J_{\text{P-P}}$  and  $^{\text{M}}J_{\text{P-P}}$  for  $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PRR}']\text{M}(\text{CO})_4$ <sup>84</sup>

M	$n$	$^{\text{B}}J_{\text{P-P}}$ , Hz	$^{\text{M}}J_{\text{P-P}}$ , Hz	$J_{\text{P-P}}$ (theor), <sup>a</sup> Hz	$J_{\text{P-P}}$ (obsd), Hz
Cr	1	12	41	53 or 29	23
	2	30	41	71 or 11	12
Mo	1	12	28	40 or 16	15
	2	30	28	58 or 2	5
W	1	12	22	34 or 10	21
	2	30	22	52 or 8	4

$$^a |J_{\text{P-P}}| = |^{\text{B}}J_{\text{P-P}} \pm ^{\text{M}}J_{\text{P-P}}|$$

vary only slightly from the corresponding values for a saturated backbone.



120

## 7. Ring Contributions Observed

### 7.1. In P-P Coupling

When the phosphorus atoms are chemically non-equivalent, phosphine ligands containing two or more phosphorus atoms give rise to  $^{31}\text{P}$  spectra in which the magnitude of  $J_{\text{P-P}}$  will strongly affect the spectral appearance. A good discussion of the parameters important in determining the magnitude and sign of this coupling has been presented.<sup>13</sup> For our discussion here, let us note that the  $^{31}\text{P}$  spectra of monodentate ligands reveal an algebraic increase in  $J_{\text{P-P}}$  of a transition metal bound phosphine as one descends a group. There are currently two schools of thought about the nature of P-P coupling in chelating phosphines.

Grim et al.<sup>84</sup> have suggested that the P-P coupling within a chelate ring can be divided into through-the-backbone and through-the-metal contributions  $J_{\text{P-P}} = ^{\text{B}}J_{\text{P-P}} + ^{\text{M}}J_{\text{P-P}}$  where  $^{\text{B}}J_{\text{P-P}}$  of the coordinated ligands is assumed equal to  $^{\text{B}}J_{\text{P-P}}$  in the free ligand. In a 5-membered ring these contributions are nearly equal but of opposite sign, which leads to a small  $J_{\text{P-P}}$ . In a 6-membered ring  $^{\text{B}}J_{\text{P-P}}$  is negligible, and thus the observed  $J_{\text{P-P}}$  is attributed solely to coupling through the metal. They note that the theory hinges on the Karplus-type angular dependence of the coupling constants in the flexible ring systems being minimal. By the Karplus theory, it is apparent that ring strain would have an effect on these values and, therefore, four-membered rings with greater strain would show the greatest deviation in this theory. When the same arguments are used, 5- and 6-membered rings for which crystal structures show very small angular strain values should fit this theory nicely. The results of a series of 29 complexes of the type  $\text{M}(\text{CO})_4(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PRR}')^{\text{84}}$  are given in Tables XV and XVI.

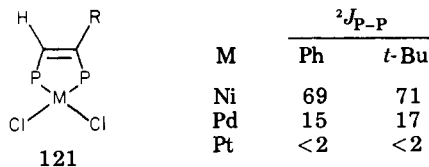


TABLE XVII.  $J_{P-P}$  Coupling for 122<sup>5</sup>

$J_{P-P}$ , Hz	Fe	Ru	Os
AB	87	53	38
AC	325	34	25
AD	74	52	35
BC	68	44	28
BD	75	685	651
CD	112	54	41

From Table XVI we observe that the best fits are achieved when a positive and negative component are used and that, in general, the fits for the 5-membered rings are better than the fits for the 4-membered rings, as one would expect.

In a series of phosphoalkene complexes of the type 121,<sup>49</sup>  $^2J_{P-P}$  shows no marked variation with R from Ph



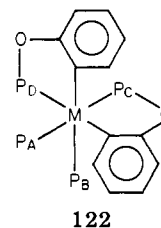
to *tert*-butyl. This is in sharp contrast to a value of 109 Hz for the free ligand. Carty et al. therefore favor an interpretation where it is unnecessary to invoke major contributions from backbone coupling to  $J_{P-P}$  (observed), but rather suggest that  $^M J_{P-P}$  is responsible for the observed decrease in the series Ni > Pd > Pt. They explain that since couplings are highly dependent on dihedral angles, distortions of the ligand skeleton on complexation greatly reduce the effectiveness of transmission through the olefinic linkage. Since the  $^3J_{P-P}$  values also closely resemble those for Cl<sub>2</sub>M-(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), they feel that the results further indicate that neither unsaturation in the backbone nor a change in the substituents on the backbone has much effect on  $J_{P-P}$  and, thus, the major source of P-P transmission must be  $^M J_{P-P}$ .

In a Rh series of polyphosphine complexes,<sup>44</sup> the phosphorus-phosphorus coupling values reveal a relationship between chelate size in 6-membered rings where  $^2J_{P-P} \sim 45-52$  Hz and 5-membered rings where  $^2J_{P-P} \sim 12-22$  Hz. Again, arguments about "through-the-metal" and "through-the-backbone" coupling are made. In the series of Pt-polyphosphine complexes studied by Meek,<sup>43</sup> one observes that when a ligand forms a 6-membered ring, the P-P coupling increases relative to the value of the free ligand (for Cyttp, 19.0 vs. 0.0 Hz), whereas for the phosphorus atoms involved in a 5-membered ring, P-P coupling decreases upon coordination (for etp, 0.8 vs. 29.0 Hz). Coupling between the dangling phosphorus atom and the coordinated central phosphorus atom of a polydentate ligand must be transmitted via the carbon backbone since both atoms are not contained in a chelate ring. For ttp which

contains a trimethylene backbone,  $^3J_{P-P} \sim 0$  in the free ligand and the PtMe<sub>2</sub>L complex.<sup>43</sup> However, in etp which has an ethylene backbone, one observes an increase of 29 to 37.5 Hz in going from the free ligand to the complex. This P-P coupling increase is attributed to an increased partial positive charge on the central P atom.<sup>43</sup> The Ni, Pd, and Pt complexes of Me<sub>2</sub>P-(CH<sub>2</sub>)<sub>2</sub>P(Me)(CH<sub>2</sub>)<sub>2</sub>PMe<sub>2</sub> reveal  $|J_{P-P}|$  of 50, 9, and <2 Hz, respectively.<sup>30</sup> Whereas the PtEtCl complexes of dppe, dppp, and dppb have  $J_{P-P}$  of <2, 20.6, and 13.2 Hz,<sup>48</sup> their PtMe<sub>2</sub>L analogues reveal corresponding values of 34, 0, and 0 Hz.<sup>47</sup>

In the HM(naphthyl)(dmpe)<sub>2</sub> series, the Fe, Ru, and Os complexes revealed  $J_{P-P}$  of 105, 281, and 265 Hz, respectively,<sup>35</sup> while in H<sub>2</sub>M(dmpe)<sub>2</sub>, going from M = Fe to M = Ru decreases  $J_{P-P}$  from 26.5 to 21 Hz.<sup>36</sup>

No fewer than six  $J_{P-P}$  couplings could be obtained from structure 122.<sup>5</sup> The data shown in Table XVII



do not reveal a clear trend. Whether  $J_{P-P}$  increases or decreases when going down a group depends on many factors, some of which are undoubtedly oxidation state of the metal, stereochemistry, nature of trans ligands, and coordination number. One must also remember that in most instances only  $|J_{P-P}|$  is evaluated, and an algebraic sign has not been determined.

## 7.2. In M-P Coupling

We earlier noted that there was no obvious relationship between chelation and phosphorus-metal coupling.<sup>18</sup> Since then further data have been compiled. In Table XVIII we see several series of W, Pt, and Rh complexes and the variation of  $J_{M-P}$  with the size of the chelate ring. Although the changes are sometimes small, it is clear that  $J_{M-P}$  increases in the order dppe > dppp > dppm for these bidentate phosphorus. The one example of a 7-membered ring reveals a  $J_{M-P}$  larger than that of dppe; other examples are needed to verify this trend. The comparison of these  $J_{M-P}$  values to unchelated ligands is more tenuous. In W(CO)<sub>4</sub>L-(Ph<sub>2</sub>Pbut)<sub>2</sub><sup>17</sup> the  $J_{M-P}$  value is identical with that of dppe; the same is found for PtCl<sub>2</sub>L,<sup>45,48</sup> while the  $J_{Pt-P}$  value for PtEt<sub>2</sub>(PPh<sub>2</sub>Me)<sub>2</sub> is closer to that of dppb than that of dppe. It should be noted that the larger trans effect of Me and Et relative to chloride is reflected in the smaller  $J_{Pt-P}$  observed in the PtMe<sub>2</sub>L and PtEt<sub>2</sub>L compounds.

TABLE XVIII. Relationship of  $J_{M-P}$  to Chelation by Diphosphines

L	W(CO) <sub>4</sub> L <sup>17,a</sup>	WCl(CO) <sub>2</sub> ·(C <sub>3</sub> H <sub>5</sub> )(L) <sup>29,a</sup>	PtCl <sub>2</sub> L <sup>45(48),a</sup>	PtMe <sub>2</sub> L <sup>45,a</sup>	PtEt <sub>2</sub> L <sup>48,a</sup>	[NBDRhL] <sup>† a</sup>	ring size
dppm	202	168	3078	1434			4
dppe	231	184	3618 (3609)	1794	1602	157	5
dppp	222		3420 (3408)	1776	1592	148	6
dppb					1677	152	7
(PPh <sub>2</sub> Me) <sub>2</sub>			3616 (3620)		1667		
(PPh <sub>2</sub> Bu) <sub>2</sub>	230						

<sup>a</sup> In hertz.

TABLE XIX. Relationship of  $J_{M-P}$  to Chelation by Polyphosphine Ligands<sup>43,44</sup>

	Rh-P <sub>1</sub> , Hz	Rh-P <sub>2</sub> , Hz	Rh-P <sub>3</sub> , Hz	size of ring	Pt-P <sub>1</sub> , Hz	Pt-P <sub>2</sub> , Hz	size of ring
etp	154	167		5, 5	1798	1900	5
ttp	154		164	6, 6	1807	1850	6
etp	156	166	169	5, 6	1824	1841	5

TABLE XX.  $J_{M-P}$  for a Series of Orthometalated Pt Complexes<sup>58,61</sup>

ligand	$^1J_{Pt-P}$ (unmetalated), Hz	$^1J_{Pt-P}$ (metalated), Hz	size of ring
P(OPh) <sub>3</sub> <sup>b</sup>	3229	6371	5
P(O- <i>o</i> -tolyl) <sub>3</sub> <sup>b</sup>	3201	6409	5
PPh( <i>t</i> -Bu) <sub>2</sub> <sup>a</sup>	2912	2222	4
P( <i>t</i> -Bu)( <i>n</i> -Pr) <sub>2</sub> <sup>a</sup>	3086	2984 <sup>c</sup>	5
P( <i>t</i> -Bu) <sub>3</sub> <sup>a</sup>	2680	2360	4

<sup>a</sup> Phosphorus cis. <sup>b</sup> Phosphorus trans. <sup>c</sup> The *n*-Pr chain is metalated.

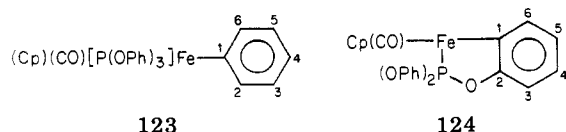
Table XIX reveals data for polydentate phosphines in a Rh<sup>44</sup> and a Pt<sup>43</sup> series. The same trends are *not* observed here. Values for the 5- and 6-membered ring systems etp, ttp, and etp reveal little change in the  $J_{Rh-P}$  values. In the Pt series  $J_{Pt-P_2(etp)}$ <sup>44</sup> is larger than  $J_{Pt-P_2(tp)}$ , but the reverse is true for  $J_{Pt-P_1}$ . One author<sup>44</sup> notes that in such complexes of polydentate phosphines  $J_{Rh-P}$  appears dependent on the number of chelate rings present, not on the size of the rings.  $J_{M-P}$  values for complexes containing nonchelated cis phosphines fall in the range 170–178 Hz while complexes containing one ring or two produce  $J_{Rh-P}$  values of 160–171 and 148–156 Hz, respectively, regardless of the size of the rings.

Table XX shows data for several orthometalated Pt complexes. Note that the  $J_{Pt-P}$  in a metalated ring is smaller than the unmetalated value irrespective of the size of the ring when the phosphorus atoms are trans. When the phosphorus are cis, the  $J_{Pt-P}$  values are higher due to trans effect differences in the cis complexes.

## 8. Comparison of <sup>31</sup>P NMR to NMR of Other Nuclei

### 8.1. <sup>13</sup>C

Stewart et al.<sup>67</sup> found that while the <sup>13</sup>C chemical shifts of the aromatic carbons in the unmetalated rings of 123 were not appreciably different from the corre-

TABLE XXI. <sup>13</sup>C Resonances for 123 and 124<sup>68</sup>

	$\delta^{13}C$ unmetalated				$\delta^{13}C$ phenyl (123) or metalated (124)			
	C <sub>1</sub> <sup>a</sup>	C <sub>2,6</sub>	C <sub>3,5</sub>	C <sub>4</sub>	C <sub>1</sub>	C <sub>2,6</sub>	C <sub>3,5</sub>	C <sub>4</sub>
P(OPh) <sub>3</sub>	+151.5	+120.6	+129.5	+124.1				
123	+151.7	+121.7	+129.4	+124.6	+150.0	+146.5	+126.4	+121.7
124	+151.4	+120.7	+129.3	+125.3	+141.6	+161.7 (C <sub>2</sub> ) +144.2 (C <sub>6</sub> )	+110.9 (C <sub>3</sub> ) +122.1 (C <sub>5</sub> )	+123.9

<sup>a</sup> Numbered as shown in 123 and 124.

sponding signals in free P(OPh)<sub>3</sub>, the <sup>13</sup>C shifts of the carbon atoms in the orthometalated ring of 125 varied over 50 ppm, as shown in Table XXI. Although the spectra are complex, one can analyze them. When comparing 123 and 124, note that the orthometalated phenyl signals are either shielded or deshielded depending on ring position. When one looks specifically at the C<sub>1</sub> and C<sub>2</sub> carbons of 124 which are incorporated in the 5-membered ring, the former is shielded 8.4 ppm while the latter is deshielded 15.2 ppm. If the resonances have been assigned correctly, no deshielding  $\Delta_R$  phenomenon is observed for these carbons incorporated into a 5-membered ring.

Hietkamp and Vrieze<sup>47</sup> have examined the <sup>13</sup>C spectra of a series of Me<sub>2</sub>PtL complexes as shown in Table XXII. The aromatic parts of the <sup>13</sup>C spectra are all very similar. However, the chemical shifts of the bridging carbon atoms are shielded for the 4-membered ring and deshielded for the 5-membered ring, resembling the  $\Delta_R$  trend in the <sup>31</sup>P shifts for the same compounds. The absolute values of these shifts are small and therefore could be attributed to other causes. More <sup>13</sup>C data are needed before anyone can clarify whether there is a  $\Delta_R$  effect in the <sup>13</sup>C spectra of molecules such as these.

### 8.2. <sup>195</sup>Pt

Vrieze<sup>47</sup> in the aforementioned series also examined the <sup>195</sup>Pt spectra of the PtMe<sub>2</sub>L complexes. The <sup>195</sup>Pt NMR shifts shown in Table XXII are all very similar except for PtMe<sub>2</sub>(dppm), for which a large deviation was found. This large shift difference for the 4-membered ring is purported to be due to ring strain.

### 8.3. <sup>51</sup>V

The <sup>51</sup>V spectra of *cis*-CpV(CO)<sub>2</sub>dpppe (−1110 ppm), Cp(CO)<sub>3</sub>(Ph<sub>2</sub>PC=CPPh<sub>2</sub>)V (−1139 ppm), and [CpV(CO)<sub>2</sub>]<sub>2</sub>(Ph<sub>2</sub>PC=CPPh<sub>2</sub>) (−1143 ppm) have been reported,<sup>24</sup> and one can see very little difference is observed between these chelating, nonchelating, and bridging ligands.

TABLE XXII. <sup>13</sup>C and <sup>195</sup>Pt Chemical Shifts for Chelating Phosphines and Their Me<sub>2</sub>PtL Complexes<sup>47</sup>

ligand	metal	δ <sup>13</sup> C <sub>CH<sub>2</sub>(1)<sup>a</sup></sub>	Δ <sub>CH<sub>2</sub>(1)</sub>	δ <sup>195</sup> Pt <sup>b</sup>
dppm	Pt	+28.0		
		+19.7	-8.3	-703.9
dppe	Pt	+23.7		
		+29.7	+6.0	+9.2
dppp	Pt	+29.6		
		+27.4	-2.2	-4.7
dppb	Pt	+27.7		
		+28.6	+0.9	+58.6

<sup>a</sup> Bridging CH<sub>2</sub> groups adjacent to phosphorus. <sup>b</sup> With respect to δ<sub>Pt</sub> for *cis*-(bz)<sub>2</sub>PtMe<sub>2</sub> = 0.

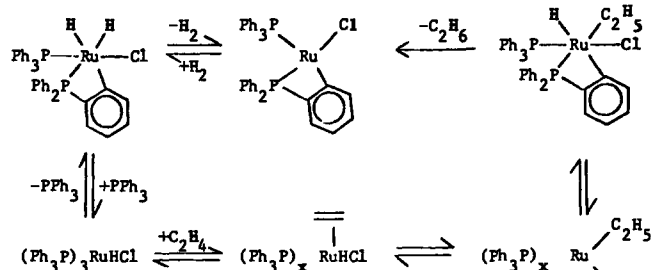


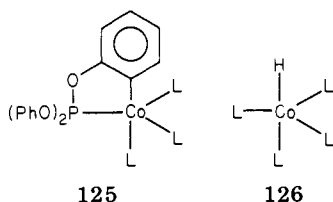
Figure 7. Proposed mechanism for ethylene hydrogenation by (Ph<sub>3</sub>P)<sub>3</sub>RuHCl.<sup>87</sup>

## 9. Relationships

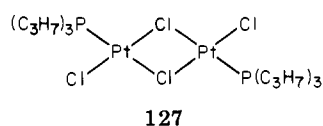
### 9.1. To Catalytic Reactions

A knowledge of Δ<sub>R</sub> will better allow interpretation of the <sup>31</sup>P spectra of intermediates in catalytic reactions which involve polyphosphines or orthometalation. <sup>31</sup>P NMR has been and should continue to be used in the analysis of such intermediates. In this section we will point out a few examples where such chelation has been identified in catalytic processes.

The greater activity of 125 vs. 126 in olefin hydrogenation has been attributed to the increased lability of L in the former [L = P(OPh)<sub>3</sub>].<sup>85</sup>



We have discussed earlier how many arylphosphine and aryl phosphite complexes undergo orthometalation. Such complexes are prone to undergo H-D exchange. Many of the complexes that catalyze such exchanges also are active for olefin hydrogenation.<sup>86</sup> It seems likely that the ligand hydrogens are somehow involved in the hydrogenation process. For example, the catalytic cycle shown in Figure 7 was proposed to explain the observed mechanism. The H is thought to be obtained by cyclometalation of a phenyl group with H<sub>2</sub> being necessary only to regenerate the (Ph<sub>3</sub>P)<sub>3</sub>RuHCl catalyst.<sup>87</sup> Again, in compound 127 deuteration occurs in the Me group



which corresponds to the presence of 5-membered ring intermediates.<sup>86</sup> In another study the deuteration of

Ph<sub>2</sub>P(OPh) by RhHCl(PPh<sub>3</sub>)<sub>3</sub> was shown to go 50 times as fast for the phenoxy group as for the phenyl group, consistent with 5-membered rings in the intermediates.<sup>86</sup>

Mason and Meek<sup>88</sup> have pointed out that polydentate ligands can provide (i) more control on the coordination number, stoichiometry, and stereochemistry of the complex, (ii) an increased basicity at the metal, and (iii) more detailed structural and bonding information in the form of M-P and P-P coupling. An example was given of RhCl(*ttp*) where the 90° P-Rh-P bond angle allows maximum overlap of the phosphorus and rhodium orbitals and contributes to its dissociative stability and basicity. Compared to RhCl(PPh<sub>3</sub>)<sub>3</sub>, chemical studies reveal that the Rh atom in RhCl(*ttp*) is quite nucleophilic and readily functions as a Lewis base, in which it mimicks IrCl(PPh<sub>3</sub>)<sub>3</sub> more closely than RhCl(PPh<sub>3</sub>)<sub>3</sub>.

Baird<sup>40</sup> has used chelating phosphines to examine the species present in solution in the olefin hydrogenation catalyst [NBDRh(diphosphine)]<sup>+</sup>. Knowing that a Δ<sub>R</sub> contribution would cause upfield and downfield shifts with dppm and dppe, respectively, they chose to examine the <sup>31</sup>P spectra of a dppp system to minimize Δ<sub>R</sub> contributions and more closely resemble the δ<sub>P</sub> values that would be obtained for monodentate tertiary phosphines. This study, as we pointed out earlier, provided insight into the intermediates present in such hydrogenation reactions. The observation of four or more species in solution revealed that kinetic data based on "catalyst concentration" in such systems should be avoided.

### 9.2. To Polymer-Anchored Reagents

There has been much recent interest in polymer-anchored catalytic reagents, many of which are anchored through phosphorus. In several instances compounds have been prepared which appear to be "chelated" (*cis* disubstituted). In such systems, one cannot envision 5-membered rings. Highly cross-linked resins could, however, conceivably mimic the rigid stereochemistry of a chelating diphosphine. Such systems could be studied by solid-state NMR.<sup>89</sup> As such data become more prevalent and the solid-state <sup>31</sup>P NMR of such complexes becomes commonplace, we will look with interest to see whether effects are noted as the degree of substitution of phosphorus on the polymer is varied and such "chelated" molecules are prepared and examined.

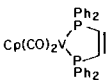
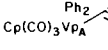
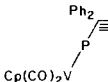
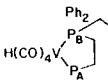
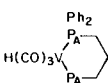
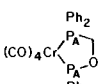
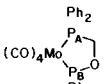
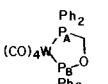
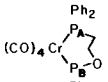
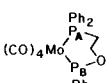
## 10. Conclusions

It appears that a ring contribution "Δ<sub>R</sub>" to the coordination chemical shift of phosphorus chelate complexes exists for a wide variety of transition-metal-phosphine complexes. Although the theoretical aspects of the ring contribution remain elusive, the awareness of its existence has proven useful in making structural assignments and should prove to continue to do so in the future. As exceptions to the Δ<sub>R</sub> rule are uncovered, it is likely that the theoretical reasons for Δ<sub>R</sub> will become more clear-cut.

## 11. Appendix

<sup>31</sup>P NMR data for diphosphine-, alkenylphosphine-, and orthometalated phosphine-transition-metal com-

TABLE XXIII.  $^{31}\text{P}$  NMR Data for Diphosphine, Alkenylphosphine and Orthometallated Phosphine Transition-Metal Complexes

ref	compd	complex	$\delta_{\text{P}}$	$\delta_{\text{F}}$	$\Delta$	$\Delta_{\text{R}}$	$ J_{\text{P-P}} $ , Hz	$J_{\text{M-P}}$ , Hz
24		<b>2.1 vanadium</b>						
	18		+120	-23.1	+143.1			$\delta^{51}\text{V} = -1143$
	19		( $\text{P}_{\text{A}}$ ) +69 ( $\text{P}_{\text{B}}$ ) -35	-32.6	+101.6			-1334
	20		+7.3	-32.6	+105.6			-1281
25	22	<b>H(CO)<math>_4</math>V(etp)</b>	+68 <sup>a</sup>					-1685
	23		( $\text{P}_{\text{A}}$ ) +87 ( $\text{P}_{\text{B}}$ ) +76 ( $\text{P}_{\text{C}}$ ) -15.6					
	25		( $\text{P}_{\text{A}}$ ) +27 ( $\text{P}_{\text{B}}$ ) -27					
17	Table I	<b>2.2 Cr, Mo, W</b>						
		Cr(CO) $_4$ (dppm)	+25.4	-23.6	+49.0	-12.0		
		Mo(CO) $_4$ (dppm)	0	-23.6	+23.6	-19.3		
		W(CO) $_4$ (dppm)	-23.6	-23.6	0	-25.4	202	
		Cr(CO) $_4$ (dppe)	+79.4	-12.5	+91.9	+31.0		
		Mo(CO) $_4$ (dppe)	+54.7	-12.5	+67.2	+24.3		
		W(CO) $_4$ (dppe)	+40.1	-12.5	+52.6	+27.3	231	
		Cr(CO) $_4$ (dppp)	+41.4	-17.3	+58.7	-2.0		
		Mo(CO) $_4$ (dppp)	+21.0	-17.3	+38.3	-4.6		
		W(CO) $_4$ (dppp)	0	-17.3	+17.3	-8.0	222	
			( $\text{P}_{\text{A}}$ ) +86.0 ( $\text{P}_{\text{B}}$ ) +196.7	-14.1	+100	+78.5	31	
			( $\text{P}_{\text{A}}$ ) +63.4 ( $\text{P}_{\text{B}}$ ) +174.4	-14.1	+77.5	+56.2	18.5	
17			( $\text{P}_{\text{A}}$ ) +49.5 ( $\text{P}_{\text{B}}$ ) +154.9	-14.1	+63.6	+36.7	11	234 260
			( $\text{P}_{\text{A}}$ ) +40.8 ( $\text{P}_{\text{B}}$ ) +161.4	-22.8	+63.6	+49.8	46.5	
			( $\text{P}_{\text{A}}$ ) +22.0 ( $\text{P}_{\text{B}}$ ) +141.6	-22.8	+44.8	+30.0	35	

26		(P <sub>A</sub> )	+ 2.2	- 22.8	+ 25.0	31	222
		(P <sub>B</sub> )	+ 116.2	- 111.6	+ 4.6		
		(P <sub>A</sub> )	+ 80.0	- 13.0	+ 93.0		
		(P <sub>B</sub> )	+ 65.0	- 31.4	+ 96.4		
26		(P <sub>A</sub> )	+ 55.7	- 13.0	+ 68.7		
		(P <sub>B</sub> )	+ 39.0	- 31.4	+ 70.4		
26		(P <sub>A</sub> )	+ 41.0	- 13.0	+ 54.0		
		(P <sub>B</sub> )	+ 22.6	- 31.4	+ 54.0		
26		(P <sub>A</sub> )	+ 77.4	- 12.8	+ 90.2		
		(P <sub>B</sub> )	+ 84.8	- 2.6	+ 87.4		
26		(P <sub>A</sub> )	+ 53.9	- 12.8	+ 66.7		
		(P <sub>B</sub> )	+ 63.6	- 2.6	+ 66.2		
27		(P <sub>A</sub> )	+ 38.9	- 12.8	+ 51.7		
		(P <sub>B</sub> )	+ 49.1	- 2.6	+ 51.7		
27		(P <sub>A</sub> )	- 25.2	- 22.7			<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub>
		(P <sub>B</sub> )	+ 30.0		+ 52.7		34.2
27		(P <sub>C</sub> )	- 3.0		+ 19.7	- 27	<sup>2</sup> J <sub>P<sub>B</sub>-P<sub>C</sub></sub>
		(P <sub>D</sub> )					24.4
27		(P <sub>A</sub> )	- 24.3	- 22.7			<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub>
		(P <sub>B</sub> )	+ 44.7		+ 67.4		64.4
		(P <sub>C</sub> )	+ 1.8		+ 24.5	- 24	<sup>2</sup> J <sub>P<sub>B</sub>-P<sub>D</sub></sub>
		(P <sub>D</sub> )	+ 20.8		+ 43.5	- 28	<sup>2</sup> J <sub>P<sub>C</sub>-P<sub>D</sub></sub>
28		(P <sub>A</sub> )	- 24.9	+ 21.4			<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub>
		(P <sub>B</sub> )	+ 33.6		+ 55.0		97.7
			+ 6.9	- 21.4	+ 28.3	- 26.7 <sup>b</sup>	
28			+ 68.3	- 12.9	+ 81.2	- 34.7 <sup>b</sup>	

TABLE XXIII (Continued)

ref	compd	complex	$\delta_P$	$\delta_F$	$\Delta$	$\Delta_R$	$ J_{P-P} $ , Hz	$J_{M-P}$ , Hz
29			-2.3	-22.7	+20.4			
			+49.7	-13.2	+52.9			
29			-19.5	-22.7	+3.2			168
			+35.1	-13.2	+48.3			184
16	28		(P <sub>A</sub> ) +42.2 (P <sub>B</sub> ) +23.6	-13.2	+55.4 +36.8		21.1 <sup>c</sup>	
			(P <sub>A</sub> ) +24.4 (P <sub>B</sub> ) -2.5	-13.2	+37.6 +10.7			
30	Table II		(P <sub>A</sub> ) +81.2 (P <sub>B</sub> ) +55.0	-13.5 -48.4	+94.7 +103.4		15	
30			(P <sub>A</sub> ) +57.1 (P <sub>B</sub> ) +26.3		+70.6 +74.7		7	
			(P <sub>A</sub> ) +42.2 (P <sub>B</sub> ) +7.9	+55.7 +56.3			<2	
		Cr(CO) <sub>3</sub> (etp)	(PPh) +110.2 (PPh <sub>2</sub> ) +77.9	-16.5 -12.9	+126.7 +90.8			12
	29	Mo(CO) <sub>3</sub> (etp)	(PPh) +82.4 (PPh <sub>2</sub> ) +55.3		+98.9 +68.2			~6
		W(CO) <sub>3</sub> (etp)	(PPh) +71.8 (PPh <sub>2</sub> ) +40.3		+88.3 +53.2			~6
31	30		(P <sub>A</sub> ) +17.7 (P <sub>B</sub> ) +4.0 (P <sub>C</sub> ) -20.0				<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 21.5 <sup>4</sup> J <sub>P<sub>B</sub>-P<sub>C</sub></sub> 3.6	J <sub>W-P<sub>1</sub></sub> 221.1 J <sub>W-P<sub>2</sub></sub> 226.5

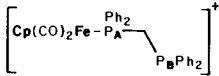
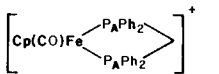
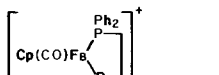
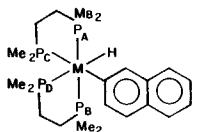
Table III	Complex	Chemical Shifts (ppm)			Coupling Constants (Hz)	
		$\delta_{PA}$	$\delta_{PB}$	$\delta_{PC}$		
32	2.3 Mn, Re					
	Mn(CO) <sub>3</sub> Br(dppm)	+10.9	-22.7	+33.6		
	Mn(CO) <sub>3</sub> Br(dppe)	+67.6	-13.2	+80.8		
	Re(CO) <sub>3</sub> Br(dppm)	-38.5		-15.8		
	Re(CO) <sub>3</sub> Br(dppe)	+30.0		+43.2		
	Mn(CO) <sub>3</sub> (dppm)(MeCN) <sup>+</sup>	+13.7		+36.4		
	Mn(CO) <sub>3</sub> (dppe)(MeCN) <sup>+</sup>	+73.5		+86.7		
	Re(CO) <sub>3</sub> (dppm)(MeCN) <sup>+</sup>	-35.0		-12.0		
	Re(CO) <sub>3</sub> (dppe)(MeCN) <sup>+</sup>	+38.0		+51.0		
	33	(MeCpMn(CO) <sub>2</sub> ) <sub>2</sub> (dppm)	+91.0		+113.7	
MeCpMn(CO)(dppm)		+58.4		+81.1		
[MeCpMn(CO) <sub>2</sub> ] <sub>2</sub> (dppe)		+91.0		+104.2		
(MeCp)Mn(CO) <sub>2</sub> (dppe)		+122.0		+135.2		
CpMn(CO)(dppe)		+117.3	-13.2	+130.5		
34	CpMn(CO)(dppp)	+82.0	-17.3	+99.3		
	CpMn(CO)(PPh <sub>3</sub> ) <sub>2</sub>	+92.0	-5.5	+97.5		
	2.4a Fe, Ru, Os					
28		$\delta_{PA}$ +33.6 $\delta_{PB}$ -24.9	-21.7	+82.0	90.0	
		$\delta_P$ -8.9	-12.9		-69.2	
		$\delta_P$ +92.3	-12.9		+32.3	
35	31		Fe			
			$\delta_{PA}$ +73.7 $\delta_{PB}$ +70.5 $\delta_{PC}$ +59.8 $\delta_{PD}$ +53.6			<sup>2</sup> J <sub>PA-PB</sub> 105 <sup>2</sup> J <sub>PA-PC</sub> 27 <sup>2</sup> J <sub>PA-PD</sub> 32 <sup>2</sup> J <sub>B-PC</sub> 28 <sup>2</sup> J <sub>B-PD</sub> 18 <sup>2</sup> J <sub>PC-PD</sub> 14
			Ru			
			$\delta_{PA}$ +45.5 $\delta_{PB}$ +40.1 $\delta_{PC}$ +33.3 $\delta_{PD}$ +27.4			<sup>2</sup> J <sub>PA-PB</sub> 281 <sup>2</sup> J <sub>PA-PC</sub> 13 <sup>2</sup> J <sub>PA-PD</sub> 25 <sup>2</sup> J <sub>B-PC</sub> 13 <sup>2</sup> J <sub>B-PD</sub> 13 <sup>2</sup> J <sub>PC-PD</sub> 13

TABLE XXIII (Continued)

ref	compd	complex	$\delta_P$	$\delta_F$	$\Delta$	$\Delta_R$	$ J_{P-P} $ , Hz	$J_{M-P}$ , Hz
			$\text{Os} \left\{ \begin{array}{l} \delta_{P_A} + 7.9 \\ \delta_{P_B} + 3.8 \\ \delta_{P_C} - 5.0 \\ \delta_{P_D} - 7.7 \end{array} \right.$				${}^2J_{P_A-P_B}$ 265 ${}^2J_{P_A-P_C}$ 5 ${}^2J_{P_A-P_D}$ 15 ${}^2J_{P_B-P_C}$ 10 ${}^2J_{P_B-P_D}$ 10 ${}^2J_{P_C-P_D}$ 10	
32			$\text{Fe} \delta_P + 74.2$ $\text{Ru} \delta_P + 45.3$ $\text{Os} \delta_P + 9.3$					
33			$\delta_{P_A}^d + 60.4$ $\delta_{P_B}^d + 7.2$					
			$\text{Fe} \delta_{P_A}^d + 76.0$ $\delta_{P_B}^d + 66.3$				26.5	
			$\delta_{P_A}^d + 49.6$ $\text{Ru} \delta_{P_B}^d + 39.7$				21	
34			$\delta_{P_A}^d + 60.4$ $\delta_{P_B}^d + 10.2$ $\delta_{P_C}^d - 49.8$				${}^2J_{P_A-P_B}$ 10 ${}^3J_{P_B-P_C}$ 20	
30	35		$\delta_{P_A} + 96.5$ $\delta_{P_B} + 93.6$ $\delta_{P_C} - 12.5, -13.3$	$-20.1$ $-48.9$	$+114.0$ $+106.7$			
	36		$\delta_{P_A} + 123.1$ $\delta_{P_B} + 68.7$	$-17.9$ $-49.0$	$+141.0$ $+117.7$		${}^2J_{P_A-P_B}$ 39 ${}^2J_{P_A-P_C}$ 29	



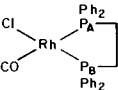
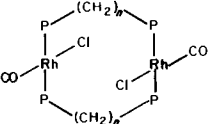
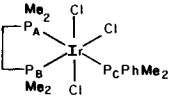
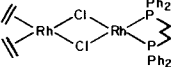
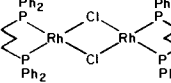
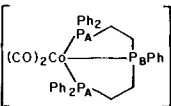
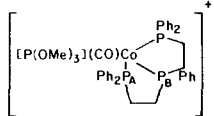
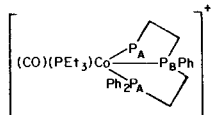
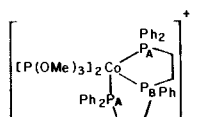
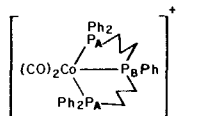
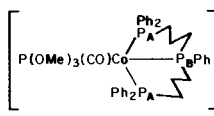
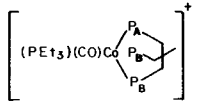
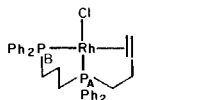
			$\delta_{PC}$ +104.3	-13.5	+117.8		$^2J_{PB-PC}$ 44	
36	2.4b	Co, Rh, Ir Rh(dppe) <sub>2</sub> <sup>+</sup> Ir(dppe) <sub>2</sub> <sup>+</sup> Ir(dppm) <sub>2</sub> CO <sup>+</sup> Ir(dppe) <sub>2</sub> CO <sup>+</sup>	+56.8 +50.2 -38.9 <sup>a</sup> P <sub>a</sub> <sup>i</sup> +28.7	-13.2 -13.2	+70.0 +63.4		$^2J_{Pa-Pe}$ 19.1	
		Ir(dppp) <sub>2</sub> CO <sup>+</sup>	P <sub>e</sub> +24.4 P <sub>a</sub> -16.9	-17.3	+37.6 +34.2		$^2J_{Pa-Pe}$ 37.1	
			P <sub>e</sub> -27.9		+45.2			
37	37		(P <sub>A</sub> ) +45.1 <sup>e</sup> (P <sub>B</sub> ) +66.7 <sup>e</sup>				$^2J_{PA-PB}$ 34.5	158.5 124.5
	38		n = 1 +96.8 <sup>e</sup> n = 2 +87.1 <sup>e</sup> n = 3 +89.1 <sup>e</sup>					125 121
38		IrCO(dppe) <sub>2</sub> <sup>+</sup> IrCO <sub>2</sub> Cl <sub>2</sub> <sup>-</sup> [IrCOCl(dppe)] <sub>2</sub> [IrCOCl(dppb)] <sub>3</sub>	+28.5 -4.6 +1.7	-13.2 -17.3 -15.0	+41.7 +12.7 +16.7			
39	39		(P <sub>A</sub> ) +4.2 (P <sub>B</sub> ) -42.1	-47.6	+51.8 +5.5	+46.3 (P <sub>A</sub> )		
40			+32	-17.0	+49.0			187
			+30.3	-17.0	+47.3			184
40		Rh(dppe) <sub>2</sub> Cl (NBD)RhL <sup>+</sup>	+6.4 <sup>f</sup> dppe +55.6 dppp +14.1 dppb +26.8 (-)-diop +16.2	-17.0	+23.4 -12.3 -17.0 -15.0 -24.0			132 157 148 152 153
41		PhP <sub>B</sub> (CH <sub>2</sub> CH <sub>2</sub> )P <sub>A</sub> Ph <sub>2</sub> ) <sub>2</sub> (etp)		(P <sub>A</sub> ) -12.9 (P <sub>B</sub> ) -16.5			$^2J_{PA-PB}$ 27	
			(P <sub>A</sub> ) +78.6 (P <sub>B</sub> ) +122.4				$^2J_{PA-PB}$ 48	

TABLE XXIII (Continued)

ref	compd	complex	$\delta_P$	$\delta_F$	$\Delta$	$\Delta_R$	$ J_{P-P} $ , Hz	$J_{M-P}$ , Hz
41			(P <sub>A</sub> ) + 68.2				<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 38	
			(P <sub>B</sub> ) + 113.3				<sup>2</sup> J <sub>P(OMe)<sub>3</sub>-P<sub>A</sub></sub> 88	
							<sup>2</sup> J <sub>P(OMe)<sub>3</sub>-P<sub>B</sub></sub> 211	
43			(P <sub>A</sub> ) + 64.9				<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 33	
			(P <sub>B</sub> ) + 109.6				<sup>2</sup> J <sub>PEt<sub>3</sub>-P<sub>A</sub></sub> 53	
							<sup>2</sup> J <sub>PEt<sub>3</sub>-P<sub>B</sub></sub> 104	
41	41		(P <sub>A</sub> ) + 65.6				<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 41.0	
			(P <sub>B</sub> ) + 108.0				<sup>2</sup> J <sub>P<sub>A</sub>-P(OMe)<sub>3</sub></sub> 93.5, 110.3	
							<sup>2</sup> J <sub>P<sub>B</sub>-P(OMe)<sub>3</sub></sub> 193.5, 105.5	
							<sup>2</sup> J <sub>P(OMe)<sub>3</sub>-P(OMe)<sub>3</sub></sub> 136.5	
		PhP <sub>B</sub> (CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P <sub>A</sub> Ph <sub>2</sub> ) <sub>2</sub> (ttp)		(P <sub>A</sub> ) - 17.0 (P <sub>B</sub> ) - 28.8				
			(P <sub>A</sub> ) + 37.0				<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 75	
			(P <sub>B</sub> ) - 7.3					
40			(P <sub>A</sub> ) + 29.0				<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 90	
			(P <sub>B</sub> ) - 6.0				<sup>2</sup> J <sub>P<sub>A</sub>-P(OMe)<sub>3</sub></sub> 18	
							<sup>2</sup> J <sub>P<sub>B</sub>-P(OMe)<sub>3</sub></sub> 49	
42			(P) + 21.5 <sup>a</sup>					
43a		Ph <sub>2</sub> P <sub>B</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> P <sub>A</sub> PhCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (ppol)		(P <sub>A</sub> ) - 27.1 (P <sub>B</sub> ) - 18.2				
44			(P <sub>A</sub> ) + 53.7		+ 80.8		<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 53	J <sub>Rh-P<sub>A</sub></sub> 156
			(P <sub>B</sub> ) + 5.3		+ 23.5			J <sub>Rh-P<sub>B</sub></sub> 153

45-47		(P <sub>A</sub> ) + 37.3		+ 64.4		<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 47	J <sub>Rh-P<sub>A</sub></sub> 88
		(P <sub>B</sub> ) - 1.7		+ 16.5			J <sub>Rh-P<sub>B</sub></sub> 115
48-49		(P <sub>A</sub> ) + 29.1		+ 56.2		<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 49	J <sub>Rh-P<sub>A</sub></sub> 122.5
		(P <sub>B</sub> ) + 7.3		+ 25.5			J <sub>Rh-P<sub>B</sub></sub> 146
44	50		(P <sub>A</sub> ) + 89.3		+ 105.9	<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 18	154
		(P <sub>B</sub> ) + 69.7		+ 82.5			167
		Ph <sub>2</sub> P <sub>B</sub> CH <sub>2</sub> CH <sub>2</sub> P <sub>A</sub> (CH <sub>2</sub> ) <sub>3</sub> P <sub>C</sub> Ph <sub>2</sub> (eptp)			(P <sub>A</sub> ) - 22.4 (P <sub>B</sub> ) - 13.2 (P <sub>C</sub> ) - 18.0		
	51		(P <sub>A</sub> ) + 56.0		+ 78.4	<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 12	156
			(P <sub>B</sub> ) + 68.9		+ 82.1	<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>C</sub></sub> 45	166
			(P <sub>C</sub> ) + 30.2		+ 48.3	<sup>2</sup> J <sub>P<sub>B</sub>-P<sub>C</sub></sub> 0	169
	52		(P <sub>A</sub> ) + 18.8	(P <sub>A</sub> ) - 28.8	+ 47.6	<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 48	154
			(P <sub>B</sub> ) + 29.2	(P <sub>B</sub> ) - 17.0	+ 46.2		164
			+ 48.8	- 5.8	+ 54.6		175
		<b>2.4c Ni, Pd, Pt</b>					
14	Fig. 2		+ 20.7				
			+ 48.6				
			+ 21.9				
			+ 21.9				
45	Table V	<i>cis</i> -PtMe <sub>2</sub> (PMePh <sub>2</sub> ) <sub>2</sub>	+ 6.4	- 28.1	+ 34.5		1851
		PtMe <sub>2</sub> (dppm)	- 40.4	- 22.7	- 17.7	- 52.2	1434
		PtMe <sub>2</sub> (dppe)	+ 45.4	- 13.2	+ 58.6	+ 24.1	1794
		PtMe <sub>2</sub> (dppp)	+ 3.2	- 17.3	+ 20.5	- 14.0	1790
47		PtMe <sub>2</sub> (dppb)	+ 18.8	- 15.0	+ 33.8	- 0.7	

TABLE XXIII (Continued)

ref	compd	complex	$\delta_P$	$\delta_F$	$\Delta$	$\Delta_R$	$ J_{P-P} $ , Hz	$J_{M-P}$ , Hz	
38	Table VI	<i>cis</i> -PdCl <sub>2</sub> [P(Ph <sub>2</sub> Et) <sub>3</sub> ] <sub>2</sub>	+30.2	-12.5	+42.7				
		PdCl <sub>2</sub> (dppe)	+68.3	-13.2	+81.5	+38.8			
		<i>cis</i> -PdCl <sub>2</sub> [P(Ph <sub>2</sub> Pr) <sub>3</sub> ] <sub>2</sub>	+27.4	-17.6	+45.0				
		PdCl <sub>2</sub> (dppp)	+12.9	-17.3	+30.2	-14.8			
		<i>cis</i> -PdCl <sub>2</sub> [P(Ph <sub>2</sub> but) <sub>3</sub> ] <sub>2</sub>	+26.6	-17.1	+43.7				
		PdCl <sub>2</sub> (dppb)	+32.8	-15.0	+47.8	+3.8			
		<i>cis</i> -PtCl <sub>2</sub> [P(Ph <sub>2</sub> Me) <sub>3</sub> ] <sub>2</sub>	-1.2	-28.1	+26.9				
		PtCl <sub>2</sub> (dppm)	-64.3	-22.7	-41.6	-68.5			
		<i>cis</i> -PtCl <sub>2</sub> [P(Ph <sub>2</sub> Et) <sub>3</sub> ] <sub>2</sub>	+9.8	-12.5	+22.3				
		PtCl <sub>2</sub> (dppe)	+45.3	-13.2	+58.5	+36.2			
		<i>cis</i> -PtCl <sub>2</sub> [P(Ph <sub>2</sub> Pr) <sub>3</sub> ] <sub>2</sub>	+6.9	-17.6	+24.5				
		PtCl <sub>2</sub> dppp	-5.6	-17.3	+11.7	-12.8			
46		Ni(PMe <sub>3</sub> ) <sub>4</sub>	+22.2	-63.3	+41.1				
		Ni(Me <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PMe <sub>2</sub> ) <sub>2</sub>	+18.1	-49.4	+67.5	-26.4			
18	53	<i>cis</i> -PdCl <sub>2</sub> (Ph <sub>2</sub> P <sub>A</sub> CH <sub>2</sub> OPPh <sub>2</sub> ) <sub>2</sub>	(P <sub>A</sub> ) +27.0	-14.1	+41.8				
		PdCl <sub>2</sub> (Ph <sub>2</sub> P <sub>A</sub> CH <sub>2</sub> OPPh <sub>2</sub> )	(P <sub>A</sub> ) +79.8	-14.1	+93.9	+52.1			
	54	<i>cis</i> -PdCl <sub>2</sub> (Ph <sub>2</sub> P <sub>A</sub> CH <sub>2</sub> CH <sub>2</sub> OPPh <sub>2</sub> ) <sub>2</sub>	(P <sub>A</sub> ) +24.0	-22.8	+46.8				
		PdCl <sub>2</sub> (Ph <sub>2</sub> P <sub>A</sub> CH <sub>2</sub> CH <sub>2</sub> OPPh <sub>2</sub> )	(P <sub>A</sub> ) +11.7	-22.8	+34.5	-12.3			
49		Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> Ph <sub>2</sub>		(P <sub>A</sub> ) -26.3			131		
		Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub>		(P <sub>B</sub> ) -18.0			146		
		Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub>		(P <sub>A</sub> ) -28.1					
		Ph <sub>2</sub> P <sub>A</sub> CH=C( <i>t</i> -Bu)P <sub>B</sub> Ph <sub>2</sub>		(P <sub>B</sub> ) -7.0					
		Ph <sub>2</sub> P <sub>A</sub> CH=C( <i>t</i> -Bu)P <sub>B</sub> Ph <sub>2</sub>		(P <sub>A</sub> ) -32.2				37	
		Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> EtPh		(P <sub>B</sub> ) -14.8					
		Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> EtPh		(P <sub>A</sub> ) -27.8					
		Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> EtPh		(P <sub>B</sub> ) -21.1					
		Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> (C <sub>2</sub> H <sub>4</sub> CN) <sub>2</sub>		(P <sub>A</sub> ) -23.0					
		Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> (C <sub>2</sub> H <sub>4</sub> CN) <sub>2</sub>		(P <sub>B</sub> ) -32.9					
		Cl <sub>2</sub> Ni(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>A</sub> ) +46.0	+74.1	+43.4		69		
		Cl <sub>2</sub> Ni(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>B</sub> ) +69.3	+76.3	+58.2				
		Cl <sub>2</sub> Ni(Ph <sub>2</sub> P <sub>A</sub> CH=C( <i>t</i> -Bu)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>A</sub> ) +43.8		+76.0	+44.0		71	
		Cl <sub>2</sub> Ni(Ph <sub>2</sub> P <sub>A</sub> CH=C( <i>t</i> -Bu)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>B</sub> ) +72.1		+86.9	+60.6			
		Cl <sub>2</sub> Ni(Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>A</sub> ) +48.0		+73.8	+43.9		66	
		Cl <sub>2</sub> Ni(Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>B</sub> ) +69.9		+95.7	+65.8			
		Cl <sub>2</sub> Pd(Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>A</sub> ) +56.6		+82.9	+36.5		21	
		Cl <sub>2</sub> Pd(Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>B</sub> ) +73.6		+91.6	+47.8			
56		Cl <sub>2</sub> Pd(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>A</sub> ) +51.1		+79.2	+32.2		15	
		Cl <sub>2</sub> Pd(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>B</sub> ) +75.6		+82.6	+42.3			
		Cl <sub>2</sub> Pd(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> PhEt)	(P <sub>A</sub> ) +51.4		+79.2	+32.3		17	
		Cl <sub>2</sub> Pd(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> PhEt)	(P <sub>B</sub> ) +80.4		+102.2	+57.4			
		Cl <sub>2</sub> Pd(Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> (C <sub>2</sub> H <sub>4</sub> CN) <sub>2</sub> )	(P <sub>A</sub> ) +54.6		+77.6	+32.3		20	
		Cl <sub>2</sub> Pd(Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> (C <sub>2</sub> H <sub>4</sub> CN) <sub>2</sub> )	(P <sub>B</sub> ) +77.1		+110.0	+61.5			
		Cl <sub>2</sub> Pt(Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>A</sub> ) +31.8		+58.1	+30.7		<2	
		Cl <sub>2</sub> Pt(Ph <sub>2</sub> P <sub>A</sub> CH=C(CF <sub>3</sub> )P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>B</sub> ) +48.3		+66.3	+41.6			
		Cl <sub>2</sub> Pt(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>A</sub> ) +30.5		+58.6	+30.6		<2	
57		Cl <sub>2</sub> Pt(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>B</sub> ) +53.1		+60.1	+39.0		3552	
		Cl <sub>2</sub> Pt(Ph <sub>2</sub> P <sub>A</sub> CH=C(Ph)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>A</sub> ) +25.9		+58.1	+28.8		3640	
		Cl <sub>2</sub> Pt(Ph <sub>2</sub> P <sub>A</sub> CH=C( <i>t</i> -Bu)P <sub>B</sub> Ph <sub>2</sub> )	(P <sub>B</sub> ) +53.2		+68.0	+44.2		<2	
50		M = Pt, n = 9	+31.0					2454	
			10	+31.8					2476
			12	+28.2					2444
		M = Pd, n = 10	+43.3						

18		<i>trans</i> -PtCl <sub>2</sub> [P( <i>n</i> -Pr) <sub>2</sub> ( <i>t</i> -Bu)] <sub>2</sub>		+ 34.3			
51	61			+ 73.0			3223
30			(P <sub>A</sub> )	+ 48.6	+ 97.0	76	
			(P <sub>B</sub> )	+ 58.4	+ 71.9		
			(P <sub>A</sub> )	+ 58.8	+ 107.2	10	
			(P <sub>B</sub> )	+ 64.5	+ 78.0		
30			(P <sub>A</sub> )	+ 30.8	+ 79.2	< 2	
			(P <sub>B</sub> )	+ 42.2	+ 55.7		
	62		(P <sub>A</sub> )	+ 109.2	+ 125.7	50	
			(P <sub>B</sub> )	+ 47.1	+ 70.0		
	63		(P <sub>A</sub> )	+ 109.5	+ 126.0	10	
			(P <sub>B</sub> )	+ 45.7	+ 68.6		
			(P <sub>A</sub> )	+ 86.0	+ 102.5	< 2	
			(P <sub>B</sub> )	+ 41.9	+ 54.8		
43b			(P <sub>A</sub> )	- 3.7	+ 24.5	<i>J</i> <sub>P<sub>A</sub>-P<sub>B</sub></sub>	<i>J</i> <sub>Pt-P<sub>A</sub></sub>
			(P <sub>B</sub> )	+ 3.5	+ 21.6	18.0	1807
			(P <sub>C</sub> )	- 18.9		<i>J</i> <sub>P<sub>A</sub>-P<sub>C</sub></sub>	<i>J</i> <sub>Pt-P<sub>B</sub></sub>
						0	1850
			(P <sub>A</sub> )	+ 49.4	+ 66.0	<i>J</i> <sub>P<sub>A</sub>-P<sub>B</sub></sub>	<i>J</i> <sub>Pt-P<sub>A</sub></sub>
			(P <sub>B</sub> )	+ 48.5	+ 61.3	0.8	1838
			(P <sub>C</sub> )	- 15.2		<i>J</i> <sub>P<sub>A</sub>-P<sub>C</sub></sub>	<i>J</i> <sub>Pt-P<sub>B</sub></sub>
						37.5	1853
			(P <sub>A</sub> )	+ 31.5	+ 49.0	<i>J</i> <sub>P<sub>A</sub>-P<sub>B</sub></sub>	<i>J</i> <sub>Pt-P<sub>A</sub></sub>
			(P <sub>B</sub> )	+ 32.4	+ 45.4	0	1773
			(P <sub>C</sub> )	- 35.0		<i>J</i> <sub>P<sub>A</sub>-P<sub>C</sub></sub>	<i>J</i> <sub>Pt-P<sub>B</sub></sub>
						32.8	1853

TABLE XXIII (Continued)

ref	compd	complex	$\delta_P$	$\delta_F$	$\Delta$	$\Delta_R$	$ J_{P-P} $ , Hz	$J_{M-P}$ , Hz
			(P <sub>A</sub> ) +44.0		+66.6		$J_{P_A-P_B}$ 3.7	$J_{Pt-P_A}$ 1824
			(P <sub>B</sub> ) +47.4		+60.0		$J_{P_A-P_C}$ 0	$J_{Pt-P_B}$ 1841
			(P <sub>C</sub> ) -18.9					
			(P <sub>A</sub> ) +4.5		+30.1		$J_{P_A-P_C}$ 2.4	1816
			(P <sub>C</sub> ) -28.8					
			(P <sub>A</sub> ) -2.6		+24.5		$J_{P_A-P_B}$ 18.0	$J_{Pt-P_A}$ 1789
			(P <sub>B</sub> ) +3.4		+21.6			$J_{Pt-P_B}$ 1827
7	66		+42.5		+67.9			
		<i>cis</i> -Mo(CO) <sub>4</sub> [PPh( <i>n</i> -Bu) <sub>2</sub> ] <sub>2</sub>		-26.2		+28.6 (avg)		
			+14.5		+40.7			
8	67		+34.1		+50.6	+26.6		3071
				-16.5				
			+37.8		+63.2	+40.1		3032
				-25.4				
			+42.1		+72.3	+41.1		2934
				-30.2				
		<i>cis</i> -Cl <sub>2</sub> Pt[PPh <sub>2</sub> ( <i>n</i> -Bu)] <sub>2</sub>	+7		+24.1			
8		<i>cis</i> -PtI <sub>2</sub> [P( <i>n</i> -Bu) <sub>3</sub> ] <sub>2</sub>	-1.1		+31.2			
		<i>cis</i> -PtI <sub>2</sub> [PPh( <i>n</i> -Bu) <sub>2</sub> ] <sub>2</sub>	-2.3		+23.1			
			+57.1		+73.6	+29.4		
				-16.5				
		<i>cis</i> -PdBr <sub>2</sub> [PPh <sub>2</sub> ( <i>n</i> -Bu)] <sub>2</sub>	+27.7		+44.2			
			+65.4		+90.8	+44.8		
				-25.4				

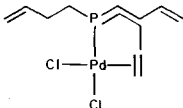
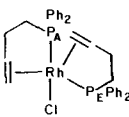
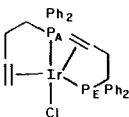
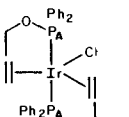
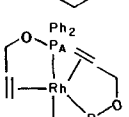
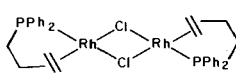
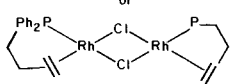
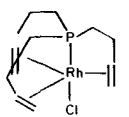
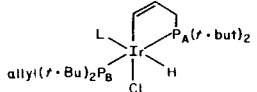
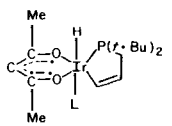
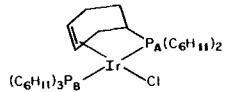
		$cis-PdCl_2[PPh(n-Bu)_2]_2$	+ 20.6		+ 46.0		
			+ 76.3	- 30.2	+ 106.5		
9	72		(P <sub>E</sub> ) + 74.9		+ 91.4		$J_{Rh-PE}$ 145
			(P <sub>A</sub> ) + 26.4	- 16.5	+ 42.9	+ 26.8	$J_{Rh-PA}$ 111
			(P <sub>E</sub> ) + 29.5		+ 46.0		
			(P <sub>A</sub> ) + 6.6	- 16.5	+ 23.1	+ 11.0	
	73		(P <sub>A</sub> ) + 19.3	- 16.5	+ 35.8		
			(P <sub>E</sub> ) + 156.2		+ 43.2		$J_{Rh-PE}$ 146
	72		(P <sub>A</sub> ) + 139.8	+ 113.0	+ 26.8	+ 21.0	$J_{Rh-PA}$ 116
	70-71		+ 68.6				188
		or					
			+ 69.6				189
	76		+ 134				
53	77		(P <sub>A</sub> ) + 57.7		+ 40.9	365	
			(P <sub>B</sub> ) + 16.8		+ 40.9		
10			+ 63.9				
54	78		(P <sub>A</sub> ) + 35.6		+ 22.7	356	
			(P <sub>B</sub> ) + 12.9				

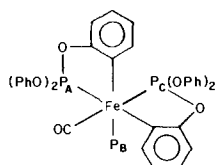
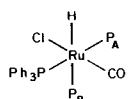
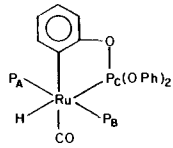
TABLE XXIII (Continued)

ref	compd	complex	$\delta_P$	$\delta_F$	$\Delta$	$\Delta_R$	$ J_{P-P} $ , Hz	$J_{M-P}$ , Hz
79			(P <sub>A</sub> ) -20.8 (P <sub>B</sub> ) -3.1			-17.7	427	
55	80		M Ni (P <sub>A</sub> ) +41.4 (P <sub>B</sub> ) +26.3 Pd (P <sub>A</sub> ) +44.9 (P <sub>B</sub> ) +23.4 Pt (P <sub>A</sub> ) +43.7 (P <sub>B</sub> ) +28.9	-13.7			326 435 425	
	81		Ni (P <sub>A</sub> ) +43.5 (P <sub>B</sub> ) +14.5 Pd (P <sub>A</sub> ) +37.3 (P <sub>B</sub> ) +13.9 Pt (P <sub>A</sub> ) +43.4 (P <sub>B</sub> ) +19.0	+15.8			410 421 425	
56	82		Rh (P <sub>A</sub> ) +39.1, +40.0 (P <sub>B</sub> ) +17.3, +15.5 Ir (P <sub>A</sub> ) +34.3, +35.2 (P <sub>B</sub> ) +9.5, +6.2				400 392	129 127
56	83		+18.2 +8.0				444	93 94
	84		+45.9 +34.1				26	147 145
57	85		(P <sub>A</sub> ) <sup>g</sup> +52.0 (P <sub>B</sub> ) +31.1	-37.99	+89.99 +69.09	+20.9	409	3262 2755
	86		(P <sub>A</sub> ) +71.3				391.4	
18		<i>trans</i> -PtCl <sub>2</sub> [PPh( <i>t</i> -Bu) <sub>2</sub> ] <sub>2</sub>	+41.2					
	87		(P <sub>A</sub> ) <sup>h</sup> +25.9 (P <sub>B</sub> ) +67.4	-8.74	+34.6 +76.1	+41.5	396.5	2984 3086
60	89		Cl (P <sub>A</sub> ) -11.8 (P <sub>B</sub> ) +61.8	-60.9		(P <sub>A</sub> ) -73.6		



61	90		CF <sub>3</sub> COO (P <sub>A</sub> ) (P <sub>B</sub> )	-13.8 +67.8		(P <sub>A</sub> ) -81.6		
			(P <sub>A</sub> ) (P <sub>B</sub> )	+66.8 -12.8	-60.9 +127.7 +48.1		383	2680 2360
60	89		(P <sub>A</sub> ) (P <sub>B</sub> )	+61.8 -11.8	-60.9 +122.7 +49.1	-73.6		
	89		L Et <sub>3</sub> P <sub>A</sub> (P <sub>A</sub> ) (P <sub>B</sub> ) P <sub>A</sub> Ph <sub>3</sub> (P <sub>A</sub> ) (P <sub>B</sub> ) Cy <sub>3</sub> P <sub>A</sub> (P <sub>A</sub> ) (P <sub>B</sub> ) Ph <sub>3</sub> As Py	+14.1 -14.1 +19.6 -19.2 +14.5 -25.3 -16.2 +13.1	-60.9 +46.8 +41.7 +35.6 +44.7 +47.8		441 422 409	
62	91		L Py (P <sub>A</sub> ) (P <sub>B</sub> ) CO (P <sub>A</sub> ) (P <sub>B</sub> ) P(OPh) <sub>3</sub> (P <sub>A</sub> ) (P <sub>B</sub> )	+10.5 -31.2 +18.3 -30.2 +6.3, +8.6 -41.1, -42.8		-41.6 -48.4 -47.5, -51.4	369.3 308.3 315.0, 315.7	
62	92		L Py (P <sub>A</sub> ) <sup>h</sup> (P <sub>B</sub> ) CO (P <sub>A</sub> ) (P <sub>B</sub> )	+76.2 +39.6 +67.8 +24.9		+36.6 +42.9	360 301	
	93		Pd R = Ph t-Bu Me Pt R = Ph t-Bu Me Pt R = Ph Me Pd R = Ph Me	+40.9 +77.3 +17.3 +42.8 +79.8 +17.3 +9.9 -8.4 +20.0 -2.7		+20.8 +32.9 +25.7		1856 1679 1791
		<i>cis</i> -(BzR <sub>2</sub> P) <sub>2</sub> MCl <sub>2</sub>	Pt R = Ph Me Pd R = Ph Me	+9.9 -8.4 +20.0 -2.7				3782 3600
5	94		M Fe { (P <sub>A</sub> ) <sup>j</sup> (P <sub>B</sub> ) <sup>j</sup> (P <sub>C</sub> ) (P <sub>D</sub> )	+144.2 +149.5 +176.4 +180.8				<sup>3</sup> J <sub>P<sub>A</sub>-P<sub>B</sub> 87 <sup>2</sup>J<sub>P<sub>A</sub>-P<sub>C</sub> 325 <sup>2</sup>J<sub>P<sub>A</sub>-P<sub>D</sub> 74 <sup>2</sup>J<sub>P<sub>B</sub>-P<sub>C</sub> 68</sub></sub></sub></sub>

TABLE XXIII (Continued)

ref	compd	complex	$\delta_P$	$\delta_F$	$\Delta$	$\Delta_R$	$ J_{P-P} $ , Hz	$J_{M-P}$ , Hz
							${}^2J_{PB-PD}$ 75	
							${}^2J_{PC-PD}$ 112	
			Ru	( $P_A$ ) +120.6			${}^2J_{PA-PB}$ 53.7	
				( $P_B$ ) +127.8			${}^2J_{PA-PC}$ 34.5	
				( $P_C$ ) +152.7			${}^2J_{PA-PD}$ 32	
				( $P_D$ ) +155.6			${}^2J_{PB-PC}$ 44.1	
							${}^2J_{PB-PD}$ 68.5	
							${}^2J_{PC-PD}$ 54.3	
			Os	( $P_A$ ) +74.9			${}^2J_{PA-PB}$ 38.3	
				( $P_B$ ) +85.9			${}^2J_{PA-PC}$ 25	
				( $P_C$ ) +113.4			${}^2J_{PA-PD}$ 35.3	
				( $P_D$ ) +118.9			${}^2J_{PB-PC}$ 27.9	
							${}^2J_{PB-PD}$ 65.1	
							${}^2J_{PC-PD}$ 41.2	
95			( $P_A$ ) +186.1				${}^2J_{PA-PB}$ 68	
			( $P_B$ ) <sup>j</sup> +151.3				${}^2J_{PA-PC}$ 110	
			( $P_C$ ) +175.7				${}^2J_{PB-PC}$ 85	
64	96		( $P_A$ ) <sup>j</sup> +129.0				${}^2J_{PA-PB}$ 36.8	
			( $P_B$ ) <sup>j</sup> +122.5					
	97		( $P_A$ ) <sup>j</sup> +141.5				${}^2J_{PA-PB}$ 390	
			( $P_B$ ) <sup>j</sup> +137.5				${}^2J_{PA-PC}$ 26	
			( $P_C$ ) +165.2				${}^2J_{PB-PC}$ 32	

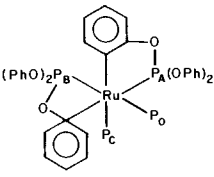
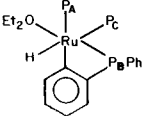
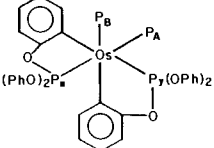
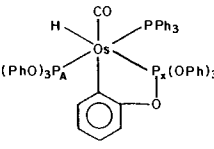
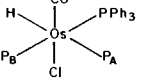
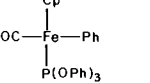
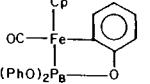
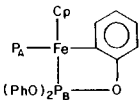
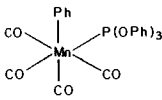
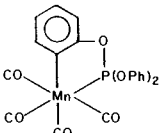
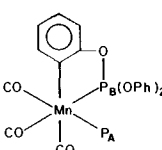
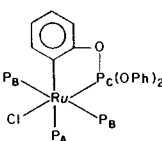
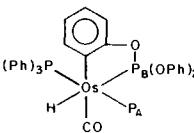
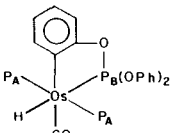
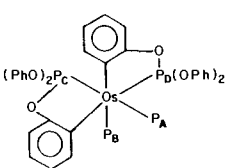
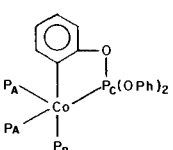
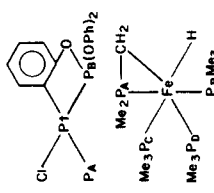
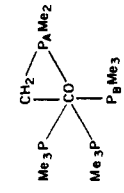
98		(P <sub>A</sub> ) + 155.8 (P <sub>B</sub> ) + 152.9 (P <sub>C</sub> ) <sup>j</sup> + 127.8 (P <sub>D</sub> ) <sup>j</sup> + 120.6	<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 53 <sup>2</sup> J <sub>P<sub>A</sub>-P<sub>C</sub></sub> 35 <sup>2</sup> J <sub>P<sub>A</sub>-P<sub>D</sub></sub> 52 <sup>2</sup> J <sub>P<sub>B</sub>-P<sub>C</sub></sub> 44 <sup>2</sup> J <sub>P<sub>B</sub>-P<sub>D</sub></sub> 685 <sup>2</sup> J <sub>P<sub>C</sub>-P<sub>D</sub></sub> 54	
65	99		(P <sub>A</sub> ) <sup>k</sup> + 20.0 (P <sub>B</sub> ) - 51.4 (P <sub>C</sub> ) <sup>k</sup> + 26.1	<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 23.7 <sup>2</sup> J <sub>P<sub>A</sub>-P<sub>C</sub></sub> 17.7 <sup>2</sup> J <sub>P<sub>B</sub>-P<sub>C</sub></sub> 17.7
66	100		(P <sub>A</sub> ) <sup>j</sup> + 71.8 (P <sub>B</sub> ) <sup>j</sup> + 84.8 (P <sub>X</sub> ) + 114.5 (P <sub>Y</sub> ) + 119.2	<sup>2</sup> J <sub>P<sub>A</sub>-P<sub>B</sub></sub> 41.2 <sup>2</sup> J <sub>P<sub>A</sub>-P<sub>X</sub></sub> 651.5 <sup>2</sup> J <sub>P<sub>A</sub>-P<sub>Y</sub></sub> 35.3 <sup>2</sup> J <sub>P<sub>B</sub>-P<sub>X</sub></sub> 27.9 <sup>2</sup> J <sub>P<sub>B</sub>-P<sub>Y</sub></sub> 25 <sup>2</sup> J <sub>P<sub>X</sub>-P<sub>Y</sub></sub> 38.3
66	101		(P <sub>A</sub> ) + 93.7 (P <sub>X</sub> ) + 132.5	17.9
	102		(P <sub>A</sub> ) <sup>j</sup> + 88.3 (P <sub>B</sub> ) <sup>j</sup> + 88.2	24.0
67-69			+ 172.3	
			+ 203.4	+ 31.1

TABLE XXIII (Continued)

ref	compd	complex	$\delta_P$	$\delta_F$	$\Delta$	$\Delta_R$	$ J_{P-P} $ , Hz	$J_{M-P}$ , Hz	
67-69			$(P_A)^j$ + 166.4 $(P_B)$ + 200.0			+ 33.6			
			+ 159.8						
			+ 193.2			+ 33.4			
			$(P_A)^j$ + 157.1 $(P_B)$ + 193.8			+ 36.7			
			$(P_A)^j$ + 114.0 $(P_B)^j$ + 121.0 $(P_C)$ + 152.0			+ 38.0			
			$(P_A)^j$ + 93.7 $(P_B)$ + 132.5			+ 38.8			
			$(P_A)^j$ + 82.3 $(P_B)$ + 131.2			+ 48.9			
			$(P_A)^j$ + 71.8 $(P_B)^j$ + 84.8 $(P_C)$ + 114.5 $(P_D)$ + 119.2			+ 42.7 + 34.4			
			$(P_A)^j$ + 122.0 $(P_B)^j$ + 144.0 $(P_C)$ + 160.0			+ 38.0			

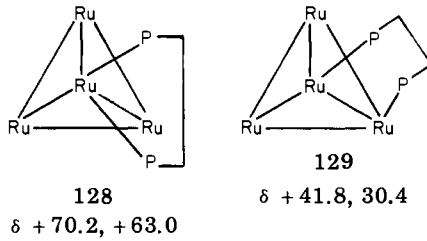
<p>70-71 105</p> 	<p>(P<sub>A</sub>)<sup>j</sup> + 112.8 (P<sub>B</sub>) + 100.5</p> <p>(P<sub>A</sub>) - 17.4 (P<sub>B</sub>) + 24.1 (P<sub>C</sub>) + 30.7 (P<sub>D</sub>) + 38.1</p> <p>(P<sub>A</sub>) + 12.2 (P<sub>B</sub>)<sup>a</sup> - 30.0</p>	<p>+ 22.9</p> <p><sup>2</sup>J<sub>P<sub>A</sub>-P<sub>B</sub> 34 <sup>2</sup>J<sub>P<sub>A</sub>-P<sub>C</sub> 40 <sup>2</sup>J<sub>P<sub>A</sub>-P<sub>D</sub> 40 <sup>2</sup>J<sub>P<sub>B</sub>-P<sub>C</sub> 28 <sup>2</sup>J<sub>P<sub>B</sub>-P<sub>D</sub> 28</sub></sub></sub></sub></sub></p>
<p>106</p> 		

<sup>a</sup> Fluxional. <sup>b</sup> By comparison to Δ<sub>P<sub>A</sub></sub> of CHT(CO)<sub>2</sub>Mo(dppm). <sup>c</sup> By comparison to P<sub>A</sub> of Mo<sub>2</sub>(CO)<sub>6</sub>(dimpe)<sub>3</sub>. <sup>d</sup> P<sub>x</sub> = dmpe (X = A, B, or C); values for δ<sub>P</sub> are exchange values. <sup>e</sup> Upfield from P<sub>4</sub>O<sub>6</sub>. <sup>f</sup> Possibly fluxional with TBP structure. <sup>g</sup> R = *t*-Bu, R' = *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>. <sup>h</sup> R = *t*-Bu, R' = *n*-Pr. <sup>i</sup> R = *t*-Bu, R' = *i*-Pr. <sup>j</sup> P = P(OPh)<sub>3</sub>. <sup>k</sup> P = PPh<sub>3</sub>. <sup>l</sup> a = axial; e = equatorial.

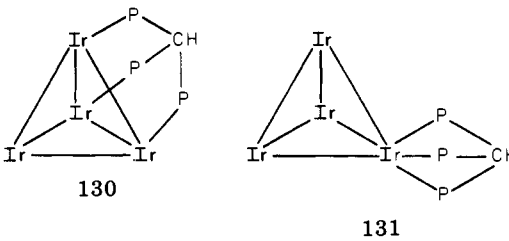
plexes are given in Table XXIII.

**Note Added in Proof**

Shapley et al.<sup>90</sup> were able to use Δ<sub>R</sub> arguments to determine the mode of bonding in diphosphine-substituted tetranuclear clusters. Specifically, when the δ<sub>P</sub> values of 128 and 129 are compared to the analogous

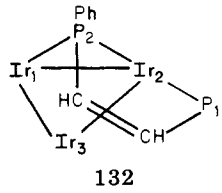


disubstituted PPh<sub>2</sub>Me complex (δ 19.6), one obtains Δ<sub>R</sub> values of +35.4 and 28.2 for 128 and +7.0 and -4.4 for 129 due to five-membered rings in the former and six-membered rings in the latter. In a similar fashion, recent reports of the reaction of HC(PPh<sub>2</sub>)<sub>3</sub> with Ir<sub>4</sub>(CO)<sub>12</sub> is reported to give 130.<sup>91</sup> We feel its δ<sub>P</sub> value



of -39.1 ppm indicates the presence of four-membered rings, and thus it is probably 131.

Gates and Davis<sup>92</sup> have recently solved the crystal structure of Ir<sub>3</sub>(CO)<sub>7</sub>(PhPCH=CHPPh<sub>2</sub>), 132, which



shows a phosphide bridge between Ir<sub>1</sub>-Ir<sub>2</sub> and a "phosphorus vinyl" unit bound to Ir<sub>2</sub>-Ir<sub>3</sub>. Although they did not assign the <sup>31</sup>P resonances at +99.4 and -22.9 ppm, it is clear from Δ<sub>R</sub> arguments that the former is due to the phosphide and the latter to the Ir<sub>3</sub>-Ir<sub>2</sub>-P<sub>1</sub>CH=CH unit. Omae has written a review<sup>93</sup> on intramolecular-coordination compounds containing phosphorus donor ligands which covers the literature through July 1979.

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