Δ_R Ring Contributions to ^{31}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 equipment with Fourier transform capabilities has led to a great deal of ^{31}P data aimed at exploring the potential of this technique for such structural and stereochemical elucidations. In the early '70s Shaw and co-workers[1] pointed out that there is a good linear correlation between the chemical shift of a tertiary phosphine, δF, and the change in the chemical shift upon coordination to a metal, Δ. 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}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 δP values.

P. E. Garrou was born in New York City in 1949 and received his Ph.D. at Indiana University in 1974. During postdoctoral work with Dick Heck in Delaware, he studied the mechanism of CO insertion into organo-Ni, -Pd, and -Pt complexes and discovered and proposed the general utility of Δ_R for ^{31}P spectroscopy. He then joined Dow Chemical's New England Laboratory where he is presently leading the catalysis group. His research interests include homogeneous catalysis, supported organometallics, and synthesis gas chemistry.

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

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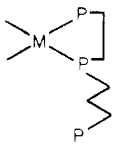
intramolecular metalation to form a chelate ring containing a metal–carbon σ bond. Such reactions have been identified for nitrogen, phosphine, and phosphite ligands. There are several relevant reviews on complexes of this type.[2,3] The identification of cyclometalated complexes was at first accomplished by infrared spectroscopy. The regions 700–800 and ~1100 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 orthometalated PPh_3 complexes of Ru the authors[4] noted that all the complexes reveal infrared absorptions in the region characteristic of ortho-disubstituted phenyl (1500–1600, 1400–1450, 1100, 730 cm^{-1}) of an orthometalated 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 cm^{-1} are complicated by vibrations from monosubstituted phenyl rings. While examination of the IR spectra of "$Fe[P(OPh)_3]_4$" and $Ni[P(OPh)_3]_4$ revealed miniscule changes, other methods were necessary to identify orthometalation in the Fe compound. ^{1}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.[4,5] ^{13}C NMR has also been examined,[6] 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 cyclometalated 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}H NMR of the olefinic protons and an IR study of the olefinic region.[7–9] Complications result with allylic phosphines which metalate,[10] and with a metal such as iridium, where $\nu_{C=C}$ is usually obscured by phenyl resonances and/or which orthometalates butenylphosphines as well.[11]

Analysis of chelating phosphine complexes is usually accomplished by IR spectroscopy, if dealing with carbonyl complexes, or ^{31}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.[12,13] Problems can arise when polydentate ligands are examined which have the potential to form different size chelate rings, as in eptp (1).



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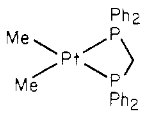
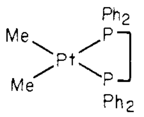
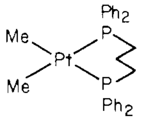
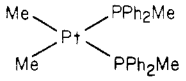
1.2. Discovery of Δ_R

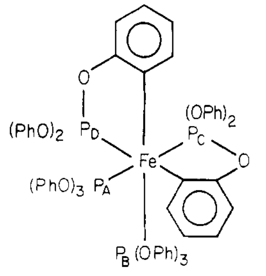
During the early 70s researchers were beginning to examine the ^{31}P spectra of such complexes in an attempt to use ^{31}P NMR as a structural tool. The first observation of a chelating effect in ^{31}P was by Merriwether in 1961 during his examination of a series of nickel carbonyl–phosphine complexes.[14] This observation lay dormant until the mid 70s when several authors pointed out that chemical shift values (δ_P) are directly affected by the presence of phosphorus in chelate rings of diphosphines.[15–17] Also, we pointed out[18] 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 (Δ_R, the "ring contribution" to a ^{31}P chemical shift) was defined as the difference between the coordination chemical shift, Δ, of a cis-disubstituted phosphine complex and the observed coordination chemical shift of an equivalent phosphorus atom in a chelate complex.

CHART I

	δ_P	ΔF	Δ	Δ_R
 Me, Me, Pt, Ph2, P, P, Ph2 2	−40.0	−22.6	−17.4	−51.9
 Me, Me, Pt, Ph2, P, P, Ph2 3	+54.5	−13.3	+67.7	+33.3
 Me, Me, Pt, Ph2, P, P, Ph2 4	+3.2	−17.3	−20.5	−14.0
 Me, Me, Pt, PPh2Me, PPh2Me 5	+6.4	−28.0	+34.4	

In the examples shown in Chart I, the ring contribution Δ_R is calculated for 2, 3, and 4 based on the Δ value of complex 5 (the closest available analogue). Obviously better comparisons would be made to complexes such as $Me_2Pt[Ph_2P(CH_2)_nPPh_2]_2$, 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 PPh_2Me with δ_F −28.0 is a better analogue to 2 than to 3. If data become available for $Me_2Pt(PPh_2Et)_2$ with δ_F −13.5, obviously it should be used. The value of these Δ_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.

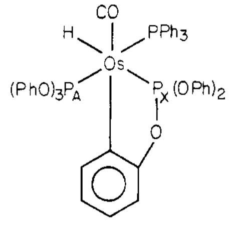
In 6, phosphorus atom P_C is metalated and trans to a triphenyl phosphite ligand. This can be directly compared to the value of δ_{P_A} which is a triphenyl phosphite ligand trans to a triphenyl phosphite ligand. Phosphorus atom P_D on the other hand is metalated but



δ_P	Δ_R
+144.2 (A)	
+149.5 (B)	
+176.4 (C)	+32.2
+180.8 (D)	+31.1

6

trans to a σ-bound phenyl group which allows direct comparison to the value of δ_{P_B} which is an unmetalated triphenyl phosphite ligand trans to a σ-bound phenyl group. Note the Δ_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 δ_{P_X} vs. δ_{P_A} would not take into account the chemical shift difference that would be caused by the different trans ligands, H and PPh_3, and would result in a Δ_R value of +38.8. A better comparison can be made to 102 which has a $P(OPh)_3$ trans to H and cis to PPh_3 with δ_P of +88.3. This comparison results in a more accurate Δ_R value of +44.2. Suffice it to say that whenever Δ_R is reported, the molecule used for analogy should be clearly delineated.



δ_P	Δ_R
+93.7 (A)	+44.2
+132.5 (X)	

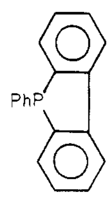
7

The theoretical aspects of Δ_R are not clear. ^{31}P chemical shifts are usually related to the C–P–C bond angle.[13] 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,[47] the only study that has compared analogus $(Ph_2P(CH_2)_nPPh_2)PdCl_2$ (n = 1–3) complexes in terms of Δ_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 Δ_R are not clear, the knowledge of its contribution to the δP value is invaluable when one makes structural assignments in phosphine transition metal complexes.

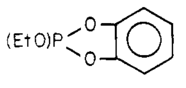
1.3. Anomalous ^{31}P Chemical Shifts in Cyclic Organophosphorus Compounds

The first place to look in trying to understand the Δ_R contribution is in the ^{31}P chemical shifts of cyclic organophosphorus complexes. The data that can be presented are inconclusive and in some ways contradictory. Very little Δ_R is observed in the series 8, 9, or 10, 11, 12, although 8 and 10 are incorporated in 5-membered rings.[19]

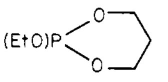


8, δ_P −12.5

Ph_3P
9, δ_P −6.0



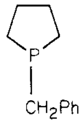
10, δ_P +136



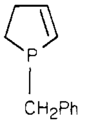
11, δ_P +130

$(EtO)_3P$
12, δ_P +138

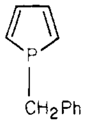
In contrast, deshielding due to phosphorus incorporation into 5-membered ring systems is observed when one compares 1-methylphosphole (δ_P −8.7) to ethyldivinylphosphine (δ_P −20.8).[20] Later[21] comparisons of 13–15 revealed that both the phospholene and the phosphole analogues possess a considerably more deshielded phosphorus than does the saturated phosphine. No conclusions were drawn as to the reasons for these shifts; however, delocalization via pπ–pπ conjugation, bond angles, and conformational and steric differences were thought to play roles in the determination of δ_P. Over a broader series of phosphole complexes a "ring contribution" to the chemical shift of +12 ppm is observed vs. acyclic analogues.[21]



13, δ_P +14.4

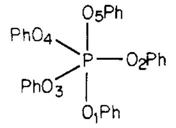


14, δ_P 0.0



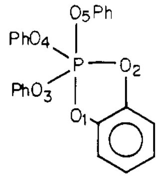
15, δ_P −7.9

Ramirez et al.[22,23] studied the ^{31}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.



O_2-P-O_3	125.5°
O_3-P-O_4	117.9°
O_3-P-O_5	87.9°

16, δ_P +88.7



O_2-P-O_3	125.5°
O_3-P-O_4	117.2°
O_3-P-O_5	93.1°

17, δ_P +60.8

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 Δ_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 Δ_R to the various aspects of ^{31}P NMR such as δ_P, $J_{P\text{-}P}$, and $J_{M\text{-}P}$ and to probe the influence

CHART II. Abbreviations Used

δ_P	observed chemical shift of the phosphorus atom under study, in ppm relative to H_3PO_4 with deshielded values being given a + sign.
δ_F	chemical shift of a free (noncoordinated) phosphine ligand.
Δ	coordination chemical shift; the change between δ_F and the δ_P observed upon coordination of the phosphorus ligand to a metal ($\Delta = \delta_P - \delta_F$).
Δ_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
n-Pr	*n*-propyl	CHT	cycloheptatriene
i-Pr	isopropyl	COD	cyclooctadiene
n-Bu	*n*-butyl	COT	cyclooctatetraene
t-Bu	*tert*-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_3	$P(CH_2CH_2PPh_2)_3$
Me-etp	$MeP(CH_2CH_2PMe_2)_2$

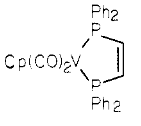
of factors such as metal radius, heteroatoms, and backbone unsaturation on the sign and size of Δ_R. In addition it is hoped that sections such as those on phosphide complexes will spur research in this area so that a more basic understanding of the Δ_R phenomenon will be possible.

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 δ_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 $Ph_2PC{\equiv}CPPh_2$ have been studied and complexes have been identified where the potentially bidentate ligands act in a bidentate, monodentate, and bridging fashion.[24] When compared to $CpV(CO)_3PPh_2Et$, the δ_P value of +112 for $CpV(CO)_2$(dppe) reveals a Δ_R of +22 indicative of chelation. The rest of the structural assignments, based on Δ_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 δ_P resonance at −25 vs. a free ligand value of −23.1. This is undoubtedly the δ_P of the uncoordinated end inadvertently misassigned. Assignment of $CpV(CO)_2$(*cis*-$Ph_2PCH{=}CHPPh_2$) with a δ_P resonance at +120 to structure **18** with a chelated diphosphine is consistent with the dppe value, while a structure assigned $[CpV(CO)_2]_2$(*trans*-$Ph_2PCH{=}CHPPh_2$)$_2$ with a δ_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 $Ph_2PC{\equiv}CPPh_2$ are thought to be **19**–**21**. Assignment of structure **19** based on δ_P values of −35 and +69 (δ_F −32.6) is consistent with free and coordinated phosphine. Assignment of structure **20** based on a δ_P resonance at +73 is reasonable; however, the δ_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 Δ_R of ~20 is also not possible since $Ph_2PC{\equiv}CPPh_2$ is a rigid ligand which is incapable of chelation.



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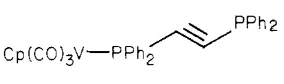

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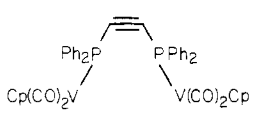

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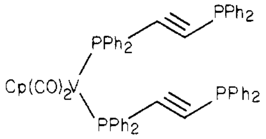

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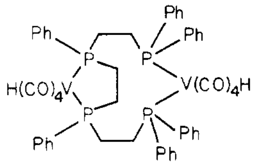
Also examined was a series of complexes of the type $HV(CO)_3L$ (L = ttp, tripod, PP_3).[25] Again, some confusion exists over structural assignments based on what we now know about δ_P and Δ_R considerations. A complex formulated $[H(CO)_4V]_2L$ with a δ_P resonance at +68 (−73 °C) is assigned structure **22** although coordinated ligand $[(Ph_2CH_2CH_2P(Ph)CH_2)_2]$ should show two distinct δ_P resonances due to P(Ph) and $P(Ph)_2$. Exchange processes must be occurring among the phosphorus atoms in this molecule.



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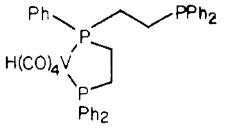
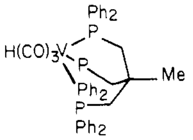


23

The δ_P resonances at +87, +76, and −15.6 support the structural assignment of **23**. The δ_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**.



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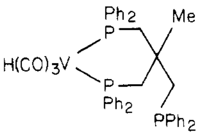

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2.2. Group 6B: Cr, Mo, W

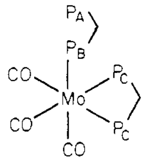
The data obtained by Grim et al.[17] for the chromium, molybdenum, and tungsten complexes of dppm, dppe, and dppp offer direct comparisons between phosphorus incorporated in 4-, 5-, and 6-membered rings (Table I). The data will be discussed later in terms of the effect of metal radius and chelate size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

TABLE I. ^{31}P Parameters for $M(CO)_4L$ Complexes[17]

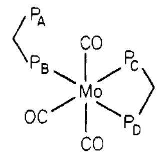
M	L	δ_P, ppm	Δ, ppm	Δ_R, ppm	chelate ring size
	dppm	−23.6			
Cr		+25.4	+49.0	−12	4
Mo		0.0	+23.6	−19.3	4
W		−23.7	0	−25.4	4
	dppe	−12.5			
Cr		+79.4	+91.9	+31.0	5
Mo		+54.7	+67.2	+24.3	5
W		+40.1	+52.6	+27.3	5
	dppp	−17.3			
Cr		+41.4	+58.7	−2	6
Mo		+21.0	+38.3	−4.6	6
W		0.0	+17.3	−8.0	6

(dppm) would assume the observed δ_P resonance represented free ligand and be hard pressed to explain why no Δ is observed. We now know that coordination deshields the δ_P resonance, and the Δ_R 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 ^{31}P NMR spectrum used to determine monodentate coordination, bridging and/or chelation.[26] 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 $Mo(CO)_3(dppm)$ have been studied.[27] The *fac* isomer **26** shows three types of phosphorus in a 1:1:2 ratio.



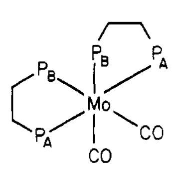
26, δ_{P_A} −25.2
δ_{P_B} +30.0
δ_{P_C} −3.0



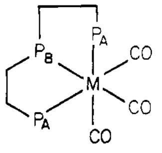
27, δ_{P_A} −24.3
δ_{P_B} +44.7
δ_{P_C} +1.8
δ_{P_D} +20.8

The chemical shift of P_C reveals a Δ_R contribution of −33 by internal comparison to the chemical shift of P_B. The Δ_R values of P_C and P_D in the *mer* complex, **27**, are calculated to be −24 and −28 by comparison to P_B (**27**) and P_B (**26**), respectively. Thus the δ_P resonance in chelated dppm is shielded ~30 ppm vs. monodentate dppm in these complexes. Complexes of the type $Mo(CHT)(CO)_xL$ (x = 1, 2; L = dppm, dppe) have also been studied.[28] For L = dppm and dppe, Δ_R values of −26.7 and +32.6 can be calculated. The effect of chelate ring size on the δ_P resonance of $M(CO)_2Cl(C_3H_5)L$ (M = Mo, W; L = dppm, dppe) reveal a 50-ppm difference between the δ_P values of phosphorus in the 4- and 5-membered rings.[29]

The ^{31}P NMR spectrum of complex **28**[16] can be compared to that of $Mo_2(CO)_6(dmpe)_3$ which has δ_P resonances at −2.5 and +24.4 for bridging and chelating phosphorus atoms, respectively, resulting in a Δ_R contribution of +26.1 to the value of δ_{P_B}. King et al.[30] recognized the additive nature of Δ_R in complexes of type **29** (M = Cr, Mo, W) where etp functions as a tridentate ligand. Thus the δ_{P_A} value where the phosphorus atoms are in a 5-membered ring is +78, whereas the δ_{P_B} value where the phosphorus is in *two* 5-membered rings is +110.2, or 30 ppm further deshielded.

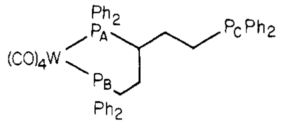


28, δ_{P_A} +42.2
δ_{P_B} +23.6



29

Reaction of $W(CO)_4(Ph_2PCH{=}CH_2)_2$ with Ph_2PH under free-radical conditions gives **30**.[31] The resonance at −20 ppm is assigned to P_C since this is close to the free ligand value of PPh_2Pr (−17.6) and the resonances at +4.0 ppm is assigned to P_B because of its resemblance to the δ_P value for $W(CO)_4(dppp)$.[17]



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2.3. Group 7B: Mn, Re

The series $M(CO)_3BrL$ (Table III) reveals a δ_P(dppm) − δ_P(dppe) of 77 for Mn and 68 for Re.[32] Although no analogues are available for calculation of Δ_R 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 $M(CO)_3L(MeCN)^+$ (M = Mn, Re; L = dppm, dppe).[33] When comparing $CpMn(CO)L$ (L = dppm[33], dppe,[33] dppp[34]), one can observe the Δ_R effect in their δ_P resonances at +58.4, +122.0, and +82.0 for the 4-, 5-, and 6-membered rings, respectively. Again no analogue such as $CpMnCO(PPh_2Et)_2$ is available for comparison.

2.4. Group VIII

2.4a. Fe, Ru, Os

Consider the series $FeCp(CO)_xL^+$ (x = 1, 2; L = dppm, dppe).[28] Comparing δ_P values of these complexes reveals a Δ_R of −69 for the chelated dppm complex and +32.3 for the dppe complex.

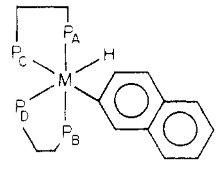
TABLE II. ^{31}P Shift Parameters of Group 6B Complexes of $Ph_2PCH_2CH_2PMe_2$[26]

complex	$\delta_{P(Ph)_2}$	$\delta_{P(Me)_2}$	$\Delta_{P(Ph)_2}$	$\Delta_{P(Me)_2}$	$\Delta_{R(P(Ph)_2)}$	$\Delta_{R(P(Me)_2)}$
L	−13.0	−31.4				
$Cr(CO)_4L$	+80.0	+65.0	+93.0	+96.4		
$Mo(CO)_4L$	+55.7	+39.0	+68.7	+70.4	+25.0	+27.7
$W(CO)_4L$	+41.0	+22.6	+54.0	+54.0	+29.1	+32.0
$[Mo(CO)_5]_2L$	+30.7	+11.3	+43.7	+42.7		
$[W(CO)_5]_2L$	+11.9	−9.4	+24.9	+22.0		

TABLE III. ^{31}P Shift Parameters for $MnBr(CO)_3L$[32]

M	L	δ_P	Δ
Mn	dppm	+10.9	+33.6
	dppe	+67.6	+80.8
Re	dppm	−38.5	−15.8
	dppe	+30.0	+43.2

CHART III



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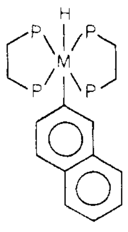
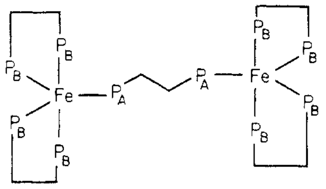
	δ_{P_A}	δ_{P_B}	δ_{P_C}	δ_{P_D}
Fe	73.3	70.5	59.8	53.6
Ru	45.4	40.1	33.3	27.4
Os	7.9	3.8	−5.0	−7.7



32, $\delta_P(Fe)$ +74
$\delta_P(Ru)$ +45.3
$\delta_P(Os)$ +9.3

Tolman et al.[35] studied a series of complexes of the type (2-naphthyl)HM(dmpe)$_2$ (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 $Fe_2(dmpe)_5$, **33**, is another one of the existing examples



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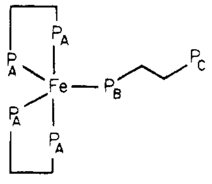
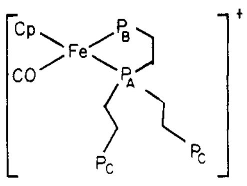
where both chelating and bridging ligand appear in the same complex; however, Δ_R cannot be calculated since the AB_4 ^{31}P spectrum indicates axial–equatorial exchange must be occurring. $Fe(dmpe)_3$ (**34**) is another



34, δ_{P_A} +60.4
δ_{P_B} +10.2
δ_{P_C} −49.8

example where a difference can be seen between the chemical shifts of chelated and nonchelated bidentate phosphines. A Δ_R value cannot be calculated since, once again, exchange is occurring.

In complex **35**, the δ_{P_A} resonance appears at +96.5, the δ_{P_B} resonance at +93.6, and the δ_{P_C} resonances at −12.5 and −13.3. Thus the bidentate nature of the potentially tetradentate ligand is substantiated.[30] In complex **36** the unsymmetrical etp ligand achieves tridentate coordination as revealed by a δ_{P_A} value of +123.1. Comparison of the δ_{P_A} value of **35** with the δ_{P_A} value of **36** reveals the δ_{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.



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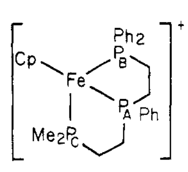
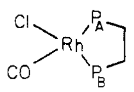


36

2.4b. Co, Rh, Ir

Caulton et al.[36] 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 δ_P resonance of $Rh(dppe)_2^+$ is at lower field than the δ_P resonance of $Ir(dppe)_2^+$. In the series $Ir(L)_2CO^+$ (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 δ_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 Δ_R effect.

From the reaction of $Rh_2Cl_2(COD)_2$ with dppm, dppe, dppp, and dppb,[37] it was learned that while dppe produces the monomeric complex **37**, the rest produce binuclear bridged complexes such as **38**.



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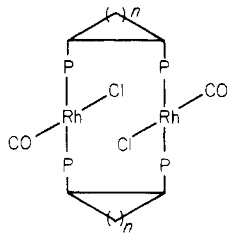
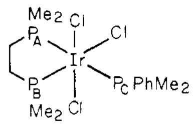


38, n = 1, 3, 4

The same trend is observed in the Ir complexes[38] which are assigned the structures $[IrCO(dppe)_2]^+$-$[IrCl_2(CO)_2]^-$, $[IrClCO(dppp)]_2$, and $[IrClCO(dppb)]_3$. The dppe chelates while dppp and dppb bridge in dimeric and trimeric complexes.

In **39**[39] comparison of the phosphorus (P_A) involved in the 5-membered chelate ring can be made internally



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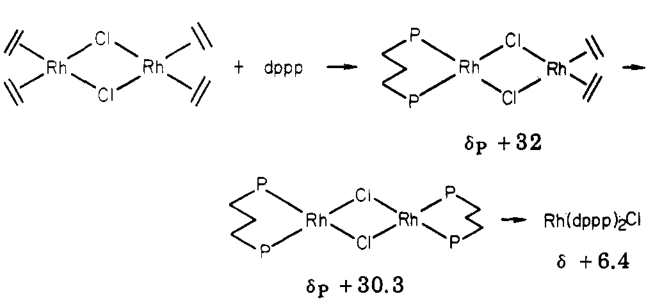
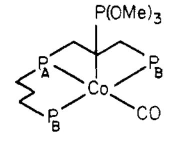


Figure 1. $\delta_{^{31}P}$ data for the intermediates in the reaction of $Rh_2Cl_2(C_2H_4)_4$ with dppp.[40]

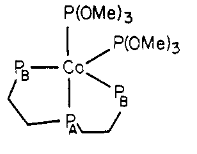
to the *trans*-PPhMe$_2$ ligand, resulting in a Δ_R of +46.3. Once again, a *trans*-PEtMe$_2$ ligand would produce a more accurate Δ_R value.

Baird et al.[40] have examined the species present during the reduction of olefins by Rh(I) complexes. The assignments of δ_P resonances were made based on two criteria: "...(a) for a given tertiary phosphine in a series of rhodium complexes, ^{31}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 ^{31}P chemical shifts of chelating diphosphines vary in a characteristic, albiet 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 δ_P value of +30.3 for P trans to Cl as in a 6-membered ring (very little Δ_R contribution) can be compared to the P trans to Cl in Rh(CO)Cl(dppe).[37] dppp was chosen as a ligand in order to avoid Δ_R contributions in any of the intermediates and allow correlations with data for monodentate phosphine systems to be made.

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



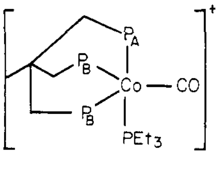
40, δ_{P_A} −6.0
δ_{P_B} +29



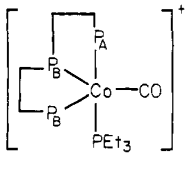
41, δ_{P_A} +108
δ_{P_B} +65

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

In such complexes Δ_R again has an additive effect, and thus the resonance due to the P_A 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



42, δ_P +21.5

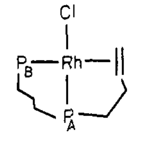


43, δ_{P_A} +109.6
δ_{P_B} +64.9

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

Again examination of **43** reveals that the ^{31}P resonance of δ_{P_A}, which is involved in two five-membered rings, is further downfield than δ_{P_B}.

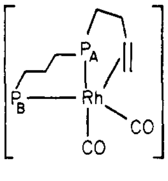
The potentially tridentate ligand $Ph_2P(CH_2)_3P(Ph)(CH_2)_2CH{=}CH_2$ (ppol) reacts with $[RhClCOD]_2$ to give RhClppol (**44**). The structure was confirmed by



44, δ_{P_A} +53.7
δ_{P_B} +5.3

a crystal structure determination.[43a] This structure is very interesting since P_B is incorporated into a 6-membered ring whereas P_A is in both a 5- and 6-membered ring. The position of the δ_{P_A} resonance appears to result from the average Δ_R of a 5- and 6-membered ring when compared to the δ_{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** (δ_{P_A} +37.3; δ_{P_B} −1.7).



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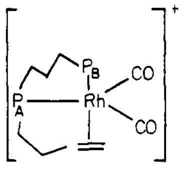

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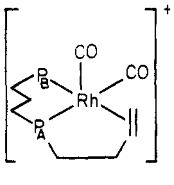

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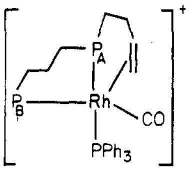
Reaction of **44** with PPh$_3$ and CO results in **48**. Since



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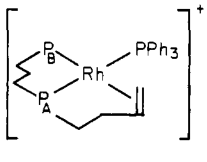

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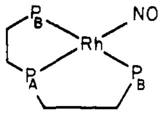
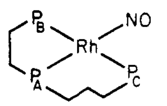
the outer lines of the AB spectrum are too weak to be observed, only a δ_{P_A} value can be obtained. Reaction of **44** with PPh$_3$ results in **49** with δ_P resonances at +29.1 and +7.3 due to P_A and P_B, respectively. These chemical shift differences are due both to Δ_R differences between a 5- and 6-membered ring and a difference in trans ligand.

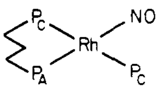
An exciting series of tridentate phosphine complexes is prepared by reaction of etp, eptp, or ttp with $Rh(PPh_3)_3NO$,[44] resulting in **50**–**52**, respectively. This



50, δ_{P_A} +89.3
δ_{P_B} +69.7



51, δ_{P_A} +56.0
δ_{P_B} +68.9
δ_{P_C} +30.2



52, δ_{P_A} +18.8
δ_{P_C} +29.2

series allows correlation of Δ_R for phosphorus incorporated in both 5- and 6-membered rings. The δ_{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 δ_{P_C} resonance for complex **51** which is in a 6-membered ring. When δ_{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 Δ_R As Observed in RhNO(L)[44]

ring size	Δ_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

[a] By comparison to $Rh(PPh_3)_3NO$, Δ 57.4.

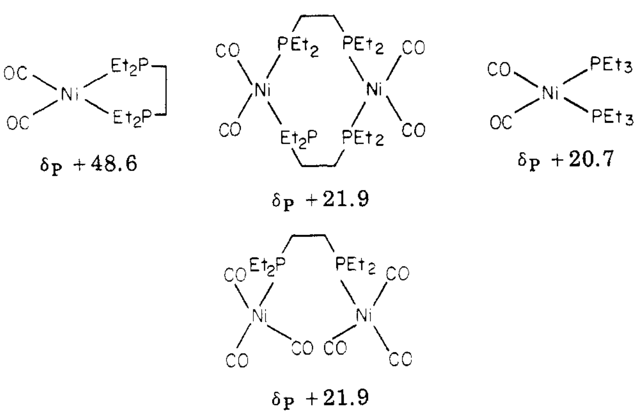


Figure 2. ^{31}P data for Merriwether's Ni carbonyl–phosphine complexes.[14]

phorus nuclei involved in two 5- vs. two 6-membered rings. If the δ_{P_A} resonance of **51** had an equal contribution from the 5- and 6-membered rings, it should appear midway between the 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 $RhNO(PPh_3)_3$ are summarized in Table IV. Note that the additive effect for 6-membered rings, derived from comparison of P_B to P_C in **52**, appears to give one-half the expected Δ_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}P of chelating diphosphines was by Merriwether, in 1961, while examining a series of nickel carbonyl-phosphine complexes.[14] He measured what we now refer to as Δ, the difference in the chemical shift (δ_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 Δ_R of +28 for the phosphorus in the 5-membered ring can be calculated.

The ^{31}P spectra of a series of Pt complexes of the type $PtMe_2L$ have been recorded.[45] Table V reveals that standard Δ_R values can be calculated from these data. The authors noted that deviations in Δ in the chelating

TABLE V. ^{31}P Data for the Series $Pt(Me)_2L$[45,47]

L	δ_P	δ_F	Δ	Δ_R	size of chelate ring
dppm[45]	−40.4	−22.7	−17.7	−52.2	4
dppe[45]	+45.4	−13.2	+58.6	+24.1	5
dppp[45]	+3.2	−17.3	+20.5	−14.0	6
dppb[47]	+18.8	−15.0	+33.8	−0.7	7
cis-$PtMe_2$-$(PPh_2Me)_2$	+6.4	−28.1	+34.5		

TABLE VI. ^{31}P Data for MCl_2L Complexes[38]

L	M	δ_P	δ_F	Δ	Δ_R
dppe	Pd	+68.3	−13.2	+81.5	+38.8
cis-$[P(Ph_2Et)_3]_2$		+30.2	−12.5	+42.7	
dppp		+12.9	−17.3	+30.2	−14.8
cis-$[P(Ph_2Pr)_3]_2$		+27.4	−17.6	+45.0	
dppb		+32.8	−15.0	+47.8	+3.8
cis-$[P(Ph_2Bu)_3]_2$		+26.6	−17.1	+43.7	
dppm	Pt	−64.3	−22.7	−41.6	−68.5
cis-$[P(Ph_2Me)_3]_2$		−1.2	−28.1	+26.9	
dppe		+45.3	−13.2	+58.5	+36.2
cis-$[P(Ph_2Et)_3]_2$		+9.8	−12.5	+22.3	
dppp		−5.6	−17.3	+11.7	−12.8
cis-$[P(Ph_2Pr)_3]_2$		+6.9	−17.6	+24.5	

TABLE VII. Important Bond Angles (Degrees) Obtained from the Crystallographic Data for the Series $PdCl_2L$[47]

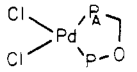
L	P–M–P	M–P–C(1)	P–C(1)–C(2)
dppm	73	94.7	93.0
dppe	85	108.5	107.9/108.2
dppp	90	115.9	112.9/118.1

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".

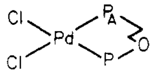
In the series MCl_2L[38] similar results are observed (Table VI). Note that there is little difference in the Δ_R values for the corresponding Pt and Pd complexes.

Comparison of $Ni(Me_2PCH_2CH_2PMe_2)_2$[46] to $Ni(PMe)_4$ results in a Δ_R of +26.4.

The δ_P values for the chelating phosphinite complexes **53** and **54** can be compared to the theoretical values[18]



53, δ_{P_A} −79.8



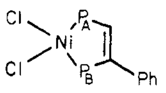
54, δ_{P_A} −11.7

calculated for *cis*-$PdCl_2L_2$ and result in Δ_R values of +52.1 and −12.3 for the 5- and 6-membered rings, respectively.

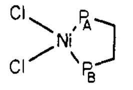
Vrieze et al.[47] have studied the ^{31}P, ^{13}C, and ^{195}Pt NMR spectra of the series $Pt(Me)_2[Ph_2P(CH_2)_nPPh_2]$ (n = 1–4) in an attempt to correlate the NMR data of various nuclei with angle strain data determined by X-ray diffraction for an analogous Pd series. These data are the same as those in Table V with the addition of data for the analogous dppb complex which results in a Δ_R of −0.7 for the 7-membered ring. Bond angles derived from crystallographic data are shown in Table VII for the analogous $PdCl_2L$ series (L = dppm, dppe, dppp). Comparison of these data reveals that in the 6-membered ring of $PdCl_2(dppp)$, the angles are larger than normal but no irregularities were found for the ^{31}P and ^{13}C NMR. On the other hand, the angles around phosphorus and carbon for PdX_2dppe are without strain and yet show remarkable downfield shifts for the Pd[38] and Pt[47] complexes. The conclusion is that angle deformations are probably not responsible for the anomalous ^{31}P shift for 5-membered ring complexes.

Another study[48] is concerned with $PtEt_2L$ (L = dppe, dppp, dppb). The data are similar to that obtained for the $PtMe_2L$ complexes[45,47] with Δ_R values of −24.8, +12.6, and −1.4 for phosphorus in the 4-, 5-, and 6-membered rings, respectively. Once again Δ_R has been obtained by comparison to *cis*-$Pt(Et)_2(PPh_2Me)_2$.

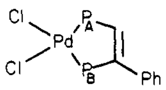
A series of phosphinoalkyne complexes *cis*-$MCl_2(Ph_2PC{\equiv}CR)_2$ (M = Pd, Pt) undergo facile 1:1 reactions with secondary phosphines to give *cis*-$MCl_2(Ph_2CH{=}CR'PR_2)$.[49] Some very interesting δ_P and J_{P-P} (to be discussed later) data can be extracted. In the series **55**–**60**, one can see δ_P 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_2 in the saturated and unsaturated rings have nearly identical δ_P values. This suggests that Δ_R 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.



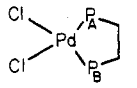
55, δ_{P_A} +43.4
δ_{P_B} +53.2



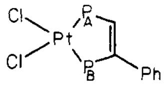
58, δ_{P_A} +46.1



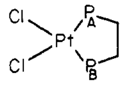
56, δ_{P_A} +32.2
δ_{P_B} +43.3



59, δ_{P_A} +35.6



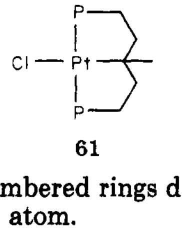
57, δ_{P_A} +30.6
δ_{P_B} +39.0



60, δ_{P_A} +32.5

Shaw et al.[50] have studied the chemistry of a comprehensive series of large chelate ring metal complexes. One of these series is represented by $PtCl_2L$ [L = $(t\text{-}Bu)_2P(CH_2)_nP(t\text{-}Bu)_2$, n = 9–12], where the δ_P values of +28.2 to +31.8 are very close to the δ_P value of +34.3 for *trans*-$PtCl_2P(n\text{-}Pr)_2(t\text{-}Bu)$.[18] These δ_P values point out that no metalation has occurred on the large ring backbone.

In a similar manner, two Pd complexes of the ligand $(t\text{-}Bu)_2PCH_2CH_2CH(Me)CH_2CH_2P(t\text{-}Bu)_2$ were isolated,[51] namely *trans*-$Pd_2Cl_4(L)_2$ (δ_P +39.0) and PtClL (δ_P +73.0). The latter downfield δ_P resonance is consistent with structure **61** where the phosphorus atoms are incorporated in 5-membered rings due to metalation of the tertiary carbon atom.

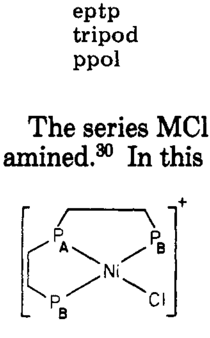


61

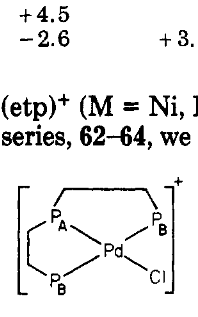
TABLE VIII. ^{31}P Data for $PtMe_2L$ (**65**)[43]

L	δ_{P_A}	δ_{P_B}	δ_{P_C}
ttp	−3.7	+3.5	−18.9
etp	+49.4	+48.5	−15.2
PP_3	+31.5	+32.4	−35.0
eptp	+44.0	+47.4	−18.9
tripod	+4.5		−28.8
ppol	−2.6	+3.4	

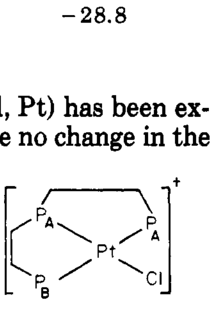
The series $MCl(etp)^+$ (M = Ni, Pd, Pt) has been examined.[30] In this series, **62**–**64**, we see no change in the δ_{P_A} value for **62** and **63** whereas a decrease of 20 ppm is noted for **64**. A steady, smaller decrease in δ_P value is noted for P_B as one descends the series.



62, δ_{P_A} +109.2
δ_{P_B} +47.1

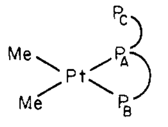


63, δ_{P_A} +109.5
δ_{P_B} +45.7



64, δ_{P_A} +86.0
δ_{P_B} +41.9

The series $Pt(Me)_2L$ was further extended to potential tridentate ligands which adopt structures similar to **65**.[43b] By the ^{31}P data in Table VIII we can distinguish 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.



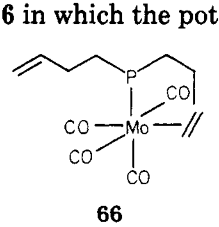
65

3. Alkenylphosphine Complexes

The majority of the ^{31}P data in this category exists in the areas of butenylphosphines, vinylphosphines, and styrylphosphines. Although reaction of the vinylphosphines results in complexes which are orthometalated, in this review they will be considered under this heading.

3.1. Butenylphosphines

Reaction of $Mo(CO)_6$ with $PhP(CH_2CH_2CH{=}CH_2)_2$ (dbp) produces **66** in which the potentially tridentate ligand achieves a bidentate coordination.[7] When this is compared to *cis*-$Mo(CO)_4[PPh(n\text{-}Bu)_2]_2$, one obtains a Δ_R of +28.6, indicating the presence of a 5-membered ring. Since common π bonding descriptions would describe this chelation as a "5$^1/_2$"-membered ring, this indicates that Δ_R 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.



66

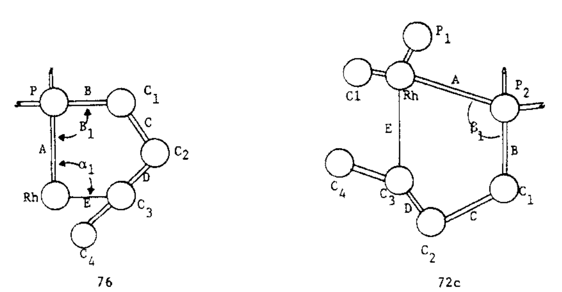
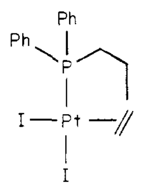
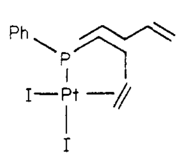


Figure 3. Bond lengths (Å) and angles (deg) for **72c**[52a] and **76**[52b]. **76**: A, 2.16; B, 1.82; C, 1.53; D, 1.50; E, 2.25; β_1, 108.2; α_1, 83.3. **72c**: A, 2.37; E, 2.35; β_1, 106.3.

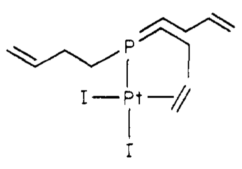
This is easily understood by examining the pertinent crystal structure parameters from butenylphosphine complexes such as **72c** and **76** (Figure 3). If one examines bond lengths A and E and envisions C_3 being substituted by PR_2, then one sees that the conformation achieved by the butenylphosphines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



67, Δ_R +26.5



68, Δ_R +40.1



69, Δ_R +41.1

A *series* of Pd(II) and Pt(II) complexes of the type MX_2L (L = mbp, dbp, tbp) was prepared.[8] These complexes adopt a square-planar geometry in which only one of the olefins is bound to the metal in the solid state. ^1H NMR reveals exchange of the olefins on the NMR time scale. The Δ_R values of the platinum complexes reveal ~14 ppm greater deshielding for the potential tri- and tetradentate ligands. Since the ^1H NMR reveals average H–H and Pt–H coupling, one could naively expect the same Δ_R for **67**–**69**. The reason the Δ_R values for **68** and **69** are equal and 14 ppm larger than Δ_R for **67** is at present unanswered. The same Δ_R difference (15 ppm) is observed for the Pd analogues of **67** and **68**.[8]

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 ^{31}P spectroscopy[9] 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 ^{31}P spectra. At 32 °C the ^{31}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.[52] 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

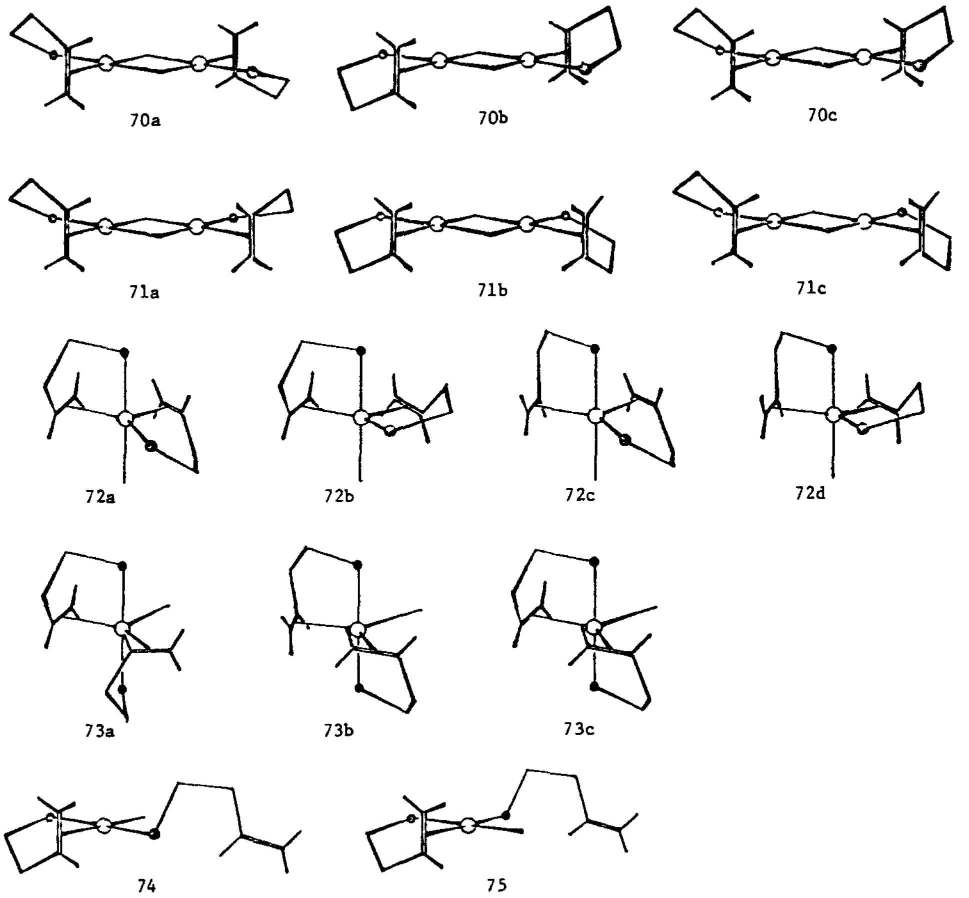


Figure 4. Possible structures of phosphine–olefin complexes.[9] Phenyls have been omitted for clarity. ● = phosphorus, ○ = Rh or Ir.

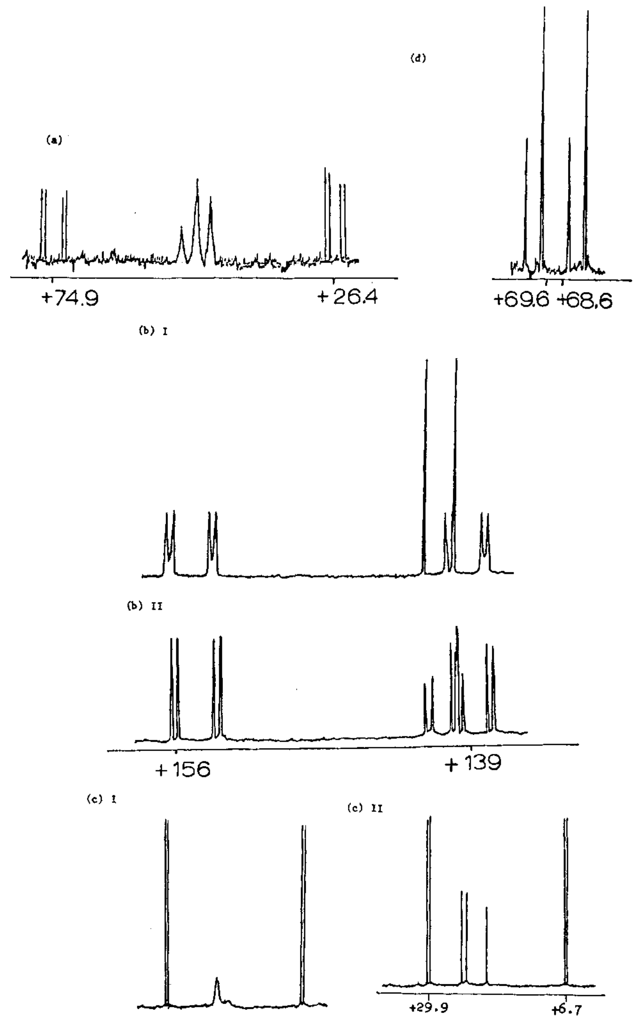
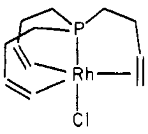


Figure 5. ^{31}P spectra of (a) RhCl(mbp)$_2$ at -75 °C, (b) RhCl(map)$_2$ at (I) 32 °C, (II) -75 °C, (c) IrCl(mbp)$_2$ at (I) 32 °C, (II) -75 °C, (d) Rh$_2$Cl$_2$(mbp)$_2$ at 32 °C.

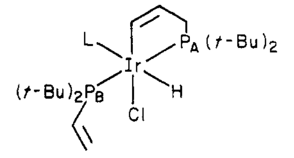
due to isomers of **73** still undergoing exchange at −75 °C. At 32 °C the ^{31}P spectrum of IrCl(mbp)$_2$ (Figure 5c) is consistent with the presence of an isomer of **72** with resonances centered at $\delta_{P(\text{axial})}$ −6.6 and $\delta_{P(\text{equatorial})}$ +29.5 with a *cis*-$^2J_{P_a-P_e}$ 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_R arguments, since the δ_P resonance of a chelated ligand should appear at ~25 ppm to lower field than that of an unchelated ligand. The ^{31}P spectrum of a solution of RhCl(map)$_2$ (Figure 5b) at 32 °C revealed an isomer of **72** whose structure was assigned in a similar manner. The ^{31}P spectrum of Rh$_2$Cl$_2$(mbp)$_2$ (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_R of +30.4 ppm when compared to Rh$_2$Cl$_2$[P(tol)$_3$]$_4$ which indicates chelating ligands are present. In a similar fashion, **76** shows a δ_P of +134, and this large coordination chemical shift is due to tetradentate coordination resulting in three times the "expected" Δ_R of 21–30.[9]



76

3.2. Allylphosphines

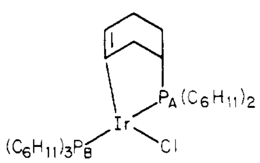
Vrieze et al.[53] studied the reaction of P(*t*-Bu)$_2$allyl with [(COT)IrCl]$_2$ in *α*-picoline (L) which resulted in **77**. The ^{31}P spectra revealed an AB pattern with large P–P coupling indicating the presence of two nonequivalent trans phosphorus atoms. At that time assignments were not made; however, we now know that the low-field resonance is due to P$_A$ and the high-field resonance to P$_B$. This results in a Δ_R of +40.9 ppm.



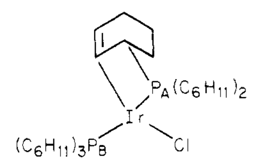
77

Reaction of Ir(acac)(C$_2$H$_4$) with P(*t*-Bu)$_2$allyl in *α*-picoline (L) resulted in (acac)[(*t*-Bu)$_2$PCH$_2$CH=CH]-Ir(H)(L). Although the stereochemistry is unknown,[10] the δ_P 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$_6$H$_{11}$)$_3$ with [(COT)IrCl]$_2$ 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.[54] These complexes contain 5^1/$_2$- and 4^1/$_2$-membered rings, respectively, and the assignments are consistent with Δ_R values of +22.7 and −17.7 ppm, respectively.



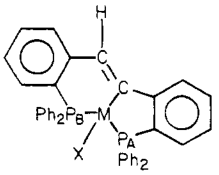
78, δ_{P_A} +35.6
δ_{P_B} +12.9



79, δ_{P_A} −20.8
δ_{P_B} −3.1

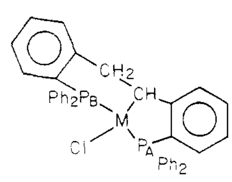
3.3. Styrylphosphines

The stilbene ligand *o*-Ph$_2$PC$_6$H$_4$CH=CHC$_6$H$_4$PPh$_2$ can lose a vinyl proton to give *σ*-vinyl chelates of type **80**.[55] P$_A$ is incorporated in a 5-membered ring while P$_B$ is in a 6-membered ring.



80

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,[56] and the resonances to lower field can be assigned to P_A.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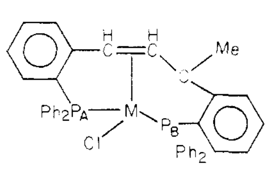
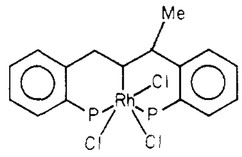
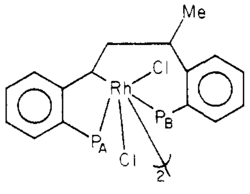

82

Reaction of **82** with HCl results in the isolation of **83** and **84**. Assignment of the resonances can be made as usual. The phosphorus atoms incorporated in the 5- and 7-membered rings in **84** should have δ_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.

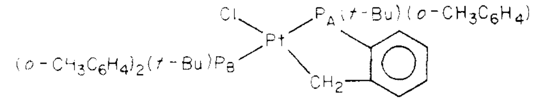

83


84

4. Orthometalated Complexes

As indicated earlier, Δ_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}P NMR spectra are usually much easier to interpret than the ^1H and ^{13}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 whereas metalation of the *tert*-butyl group would result in a 4-membered ring.[57] A δ_{P_B} resonance at +31.1 and a δ_{P_A} resonance at +52.0 result in a Δ_R value of +20.9, and this is consistent with a 5-membered ring. A similar situation exists in compound **86**,[57] where Δ_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**. δ_P resonances are observed at +67.4 and +25.9 ppm. Although the original assignment was made as structure **88**,[58] reassignment based on Δ_R of +41.5 was later made.[18] Metalation of Me_2P(naphthyl) in the 4 position of the naphthyl group gives a 5-membered ring with a resultant Δ_R of +30.8.[59]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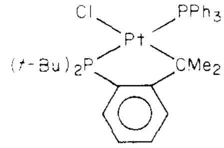
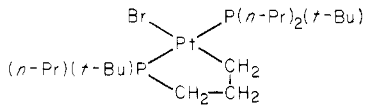

86

The Pd(II) hydride $PdHCl[P(t\text{-}Bu)_3]_2$ undergoes intramolecular metalation to produce **89**.[60] The product was identified by the loss of the hydride resonance and loss of Pd–H at 2190–2201 cm^{-1}. Comparison of the δ_P resonance of the unmetalated (+61.8 ppm) and metalated (−11.8 ppm) phosphine reveals a Δ_R of −73.6, and this is consistent with the formation of a 4-membered ring.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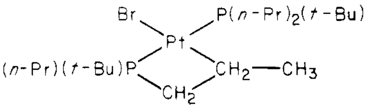
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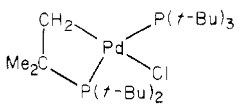
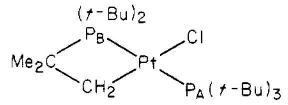
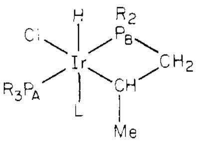
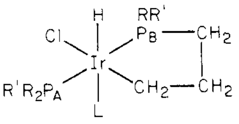

89

In a similar fashion a Δ_R of −79.6 can be calculated for **90**.[61]


90

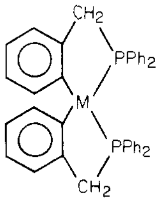
Reaction of $[CODIrCl]_2$ with $P(i\text{-}Pr)_3$ or $P(t\text{-}Bu)_2(i\text{-}Pr)$ in picoline (L) results in the isolation of **91** and **92**, respectively.


91

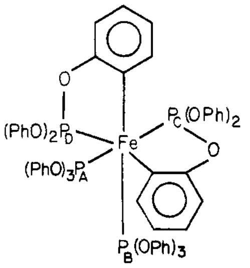

92

The assignments are consistent with Δ_R values of −41.5 ppm for the 4-membered ring in **91** and +36.6 ppm for the 5-membered ring in **92**.[62] In these cases Δ_R is a very important analytical tool in determining whether the methylene or methyl has been abstracted. ^1H NMR is complicated by the presence of resonances due to unmetalated ligand and these are less easily interpreted.

Issleib[63] prepared complexes of type **93**. Comparison of δ_P values to $(PPh_2bz)_2MCl_2$ gave the expected Δ_R values of +20.6 (Pd) and +32.9 ppm (Pt) for the phosphorus atoms incorporated in 5-membered rings.

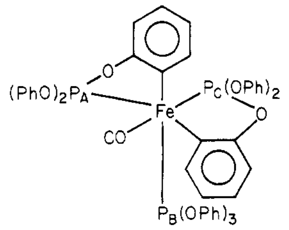

93

Tolman[5] found that reaction of $Fe(COD)_2$ with $P(OPh)_3$ resulted in **94**. The structural assignment was made based on the fact that metalated $P(OPh)_3$ lies ~30 ppm at lower fields than unmetalated ligands. By examination of the phosphorus chemical shifts, **94** obviously contains two metalated and two unmetalated



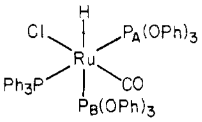
94, δ_{P_A} +144.2
δ_{P_B} +149.5
δ_{P_C} +176.4
δ_{P_D} +180.8

ligands. Reaction of **94** with CO gives **95**. From Δ_R and the splitting pattern one would again surmise the presence of two metalated and one unmetalated ligands.

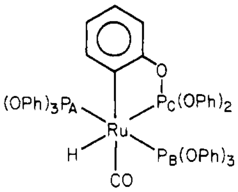


95, δ_{P_A} +186.1
δ_{P_B} +151.3
δ_{P_C} +175.7

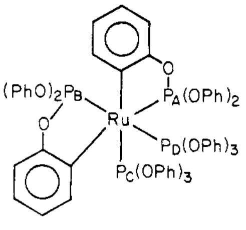
In a similar fashion structures can be assigned to **97** and **98**[64a] by comparison to **96**.



96, δ_{P_A} +129.0
δ_{P_B} +122.5

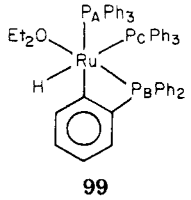


97, δ_{P_C} +165.2
δ_{P_B} +137.5



98, δ_{P_A} +155.8
δ_{P_B} +152.9
δ_{P_C} +127.8
δ_{P_D} +120.6

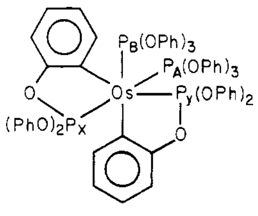
The fact that orthometalated phosphines and phosphines trans to hydride ligands resonate at lower frequencies than other phosphines allowed the unequivocal assignment of the stereochemistry to **99** (P = PPh$_3$).[65]



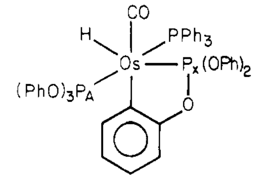
99

old assignment	new assignment
δ_{P_A} −51.4	δ_{P_A} +20.0
δ_{P_B} +20.0	δ_{P_B} −51.4
δ_{P_C} +26.1	δ_{P_C} +26.1

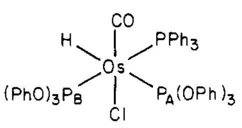
However, we now know that P$_B$ is incorporated into a 4-membered ring and should be assigned to the resonance at −51 ppm. In the series **100**–**102**,[66] metalation is indicated in **100** by Δ_R of +42.7 and in **101** (by comparison to P$_A$ in **102**) by a Δ_R of +44.2. Again, the observed splitting pattern and knowledge of Δ_R allow assignment of the stereochemistry of this molecule.



100, δ_{P_A} +71.8
δ_{P_B} +84.8
δ_{P_X} +114.5
δ_{P_Y} +119.2

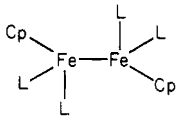


101, δ_{P_A} +93.7
δ_{P_B} +132.5

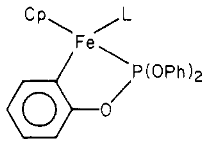


102, δ_{P_A} +88.3
δ_{P_B} +88.2

In a series of papers Stewart et al.[67–69] examined the use of ^{31}P to determine structures of triaryl phosphite complexes. Although CpFe(CO)$_2$R + P(OPh)$_3$ in the early literature was said to give **103**, the authors used Δ_R arguments to show that the structure was more likely **104**.



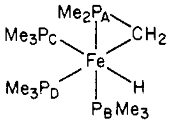
103



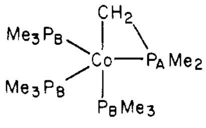
104

In a series of 5- and 6-coordinate P(OPh)$_3$ complexes of Fe, Mn, Ru, Os, Co, Pt, and Pd the authors point out Δ_R values ranging from +23 to +42 ppm (see Table IX for complexes and Δ_R values). A generalization made by these authors is that ^{31}P of unmetalated P(OPh)$_3$ lies in the range +71 to +94 ppm and is dependent on the trans ligand, whereas δ_P for metalated P(OPh)$_3$ lies in the region +114 to +133.

Complex **105** has been studied by two groups,[70,71] and their data are very similar for the δ_P of P$_A$ involved in the 3-membered ring. Note that P$_A$ is *shielded* vs. δ_P for PMe$_3$ ligand. In a similar fashion, δ_{P_A} of **106** is shielded vs. δ_{P_B}.[71]



105, δ_{P_A} −17.4
δ_{P_B} +24.1
δ_{P_C} +30.7
δ_{P_D} +38.1

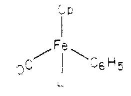
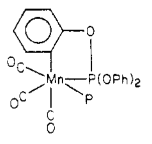
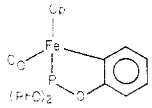
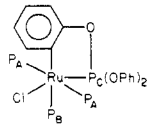
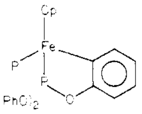
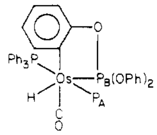
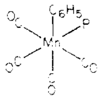
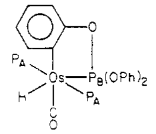
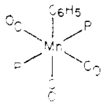
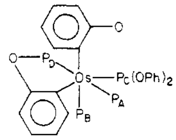
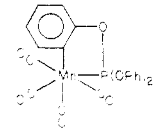
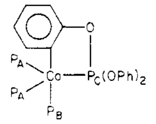
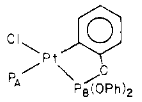


106, δ_{P_A} −30.0
δ_{P_B} +12.2

5. Phosphides

One of the newer areas in which ^{31}P data are being accumulated is that of phosphide complexes. It appears that these complexes also show Δ_R effects which can be helpful in structural assignments, although not enough

TABLE IX. ^{31}P Data for Triphenylphosphite Complexes[68]

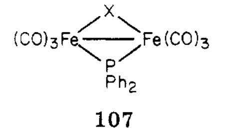
complex	δ^a	δ^b	Δ_R	complex	δ^a	δ^b	Δ_R
	+172.3				+157.1	+193.8	+36.7
		+203.4	+31.1		+114.0 (P_A) +121.0 (P_B)	+152.0 (P_C)	+38.0 +31.0
	+166.4	+200.0	+33.6		+93.7 (P_A)	+132.5 (P_B)	+38.8
	+159.8				+82.3 (P_A)	+131.2 (P_B)	+48.9
	+163.8				+71.8 (P_A) +84.8 (P_B)	+114.5 (P_C) +119.2 (P_D)	+42.7 +34.4
			+33.4		+122.0 (P_A) +144.0 (P_B)	+160.0 (P_C)	+38.0
					+112.8 (P_A)	+100.5 (P_B)	+22.9

[a] Unmetallated ligand, P = $P(OPh)_3$. [b] Metallated ligand.

TABLE X. Comparison of Fe–Fe Bond Length and Fe–P–Fe Angle with δ_P for a Variety of Iron Carbonyl Complexes

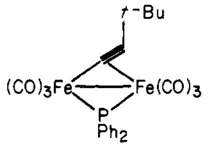
complex	Fe–Fe bond length, Å	Fe–P–Fe angle, deg	$\delta_{P(C_6H_5)_2}$
$Fe_2(CO)_6[Cl][P(C_6H_5)_2]$	2.5607 (5)	69.8 (0)	142.7
$Fe_2(CO)_6[CHC\{N(C_2H_5)_2\}\{C_6H_5\}][P(C_6H_5)_2]$	2.548 (1)	70.1 (0)	153.9
$Fe_2(CO)_6[CHC\{NHC_6H_{11}\text{-c}\}\{C_6H_5\}][P(C_6H_5)_2]$	2.576 (1)	70.5 (0)	154.0
$Fe_2(CO)_6[C\{P(OC_2H_5)_3\}C\{C_6H_5\}][P(C_6H_5)_2]$	2.671 (2)	74.0 (0)	194.5
$Fe_2(CO_6[CC\{Ph(c\text{-}C_6H_{11})_2\}\{C_6H_5\}][P(C_6H_5)_2]$	2.550 (2)	70.7 (1)	123.0
$Fe_2(CO)_6[C_2C_6H_5][P(C_6H_5)_2]$	2.597 (2)	71.64 (7)	148.4
$Fe_2(CO)_6[C\{NHC_6H_{11}\text{-c}\}CH\{C_6H_5\}][P(C_6H_5)_2]$	2.628 (1)	72.5 (0)	183.5
$Fe_2(CO)_6[C\{CN(CH_3)CH_2CH_2N(CH_3)\}C\{C_6H_5\}][P(C_6H_5)_2]$	2.644 (2)	73.4 (0)	190.3
$Fe_2Ag(CO)_6[CHC\{NHCH_3\}\{C_6H_5\}][P(C_6H_5)_2]^+ClO_4^-$	2.682 (1)	74.1 (0)	173.4
$Fe_2(CO)_6[C\{CNC(CH_3)_3\}C\{C_6H_5\}][P(C_6H_5)_2]$	2.671 (2)	74.1 (0)	194.2
$Fe_2(CO)_6[CCHC\{C_6H_5\}N\{C_6H_5\}HO][P(C_6H_5)_2]$	2.60	71	179.0
$Fe_2(CO)_6[CH_2C\{C_6H_5\}NCH_3][P(C_6H_5)_2]$	2.707 (1)	75.6 (0)	198.5
$Fe_2(CO)_6[P(C_6H_5)_2C_8F_8][P(C_6H_5)_2]$	2.791 (6)	~79	129.9
$Fe_2(CO)_4[CNC(CH_3)_3]_2[C_2C(CH_3)_3][P(C_6H_5)_2]$	2.5946 (7)	71.5 (0)	145.3
$Fe_2(CO)_6[C_2C(CH_3)_3][P(C_6H_5)_2]$	2.5959 (6)	71.7 (0)	148.3
$Fe_2(CO)_6[P(C_6H_5)_2]_2$	2.623 (3)	72.0 (1)	142.8
$Fe_2(CO)_5[P(C_6H_5)_3][C_2C_6H_5][P(C_6H_5)_2]$	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}P spectra examined[72,73] (Table X).

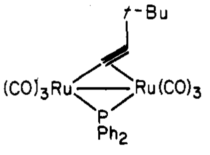


107

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.[73] Structure **110**[74] also reveals a very low field δ_P resonance

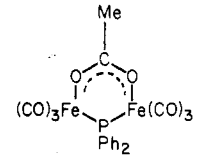


108, δ_P +148.3



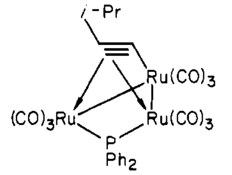
109, δ_P +123.9

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



110, δ_P +185

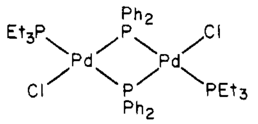
For the Δ_R effect to be valid for phosphides, one would expect phosphides bridging metals which are not involved in metal-metal bonds to be found upfield. Such is the case in structure 111[73] where the phosphorus atoms are involved in 4-membered rings.



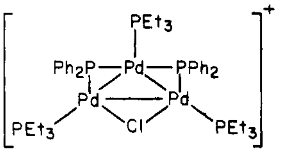
M	δ_P	∠M-P-M
Ru	−51.8	92.8°
Os	−65.4	93.2°

111

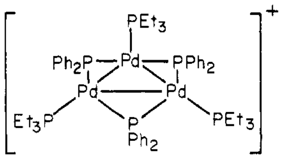
Recently[75,76] the phosphide palladium complexes 112–114 were prepared and their ^{31}P spectra examined.



112, δ_P −127



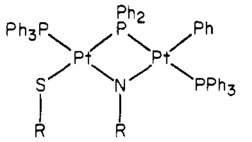
113, δ_P +204



114, δ_P +155

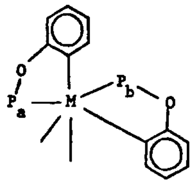
We again may compare phosphides definitely in 3-membered (113, 114) and 4-membered (112) rings. A chemical shift difference of ~300 ppm is observed between these examples, with the 3-membered ring being downfield. The authors note that such large chemical shift differences may some day allow determination 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.[77] The ^{31}P



115

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.



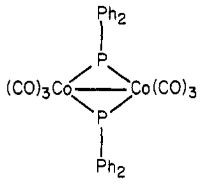
M	δP_a (ppm)	δP_b (ppm)
Fe	+180.8	+176.4
Ru	+155.6	+152.7
Os	+118.9	+113.4

Figure 6. Relationship between position in the periodic table and δ_P shifts for an orthometalated Fe series.[5]

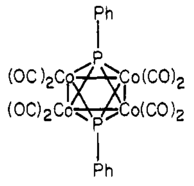
TABLE XI. Relationship between Metal Position in the Periodic Group and δ_P for $M(CO)_4L^{26}$

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 δ_P value of +62.3 for 116 can also be compared to a δ_P of +134 for 117 which can be envisioned as being involved in four 3-membered rings.[78]

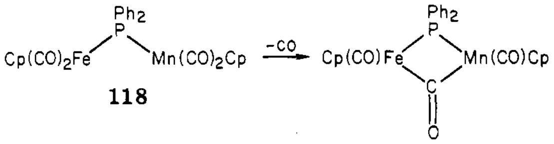


116



117

Crystallographic and ^{31}P data on a model series such as 118 and 119[79] would be useful since a downfield shift of the phosphide resonance of 119 vs. 118 would indicate the presence of an M–M bond.



118

119

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 ^{31}P resonance as one descends in a given group.[13] The same can be said for complexes which reveal a Δ_R contribution. In the orthometalated series shown in Figure 6, we clearly see a decrease in δ_P as one descends the Fe group.[5] As was previously mentioned (section 2.4a), this was also observed in 31.

Variation in δ_P also follows this trend for the Ni series 55–60 as previously described.[49] In Table XI we again see δ_P and therefore Δ_R decreasing as we descend the Cr group. Finally, in the Mn series shown in Table III, we again see a decrease in δ_P as we descend from Mn to Re.[33]

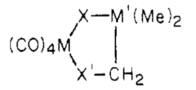
6.2. Of Heteroatoms

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

TABLE XII. ^{31}P Data for $[Ph_2P(x)CH_2PPh_2]M(CO)_4$[81]

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

TABLE XIII. Δ_R Values Obtained from 5-Membered Chelate Rings Containing Heteroatoms[82]



M	$X\text{-}M'\text{-}CH_2\text{-}X'$	Δ_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 (Δ) in $M(CO)_4Ph_2PCH_2PR_2$[83]

		Δ		
R	cone angle, deg	Cr	Mo	W
Me_2	101	+57.5	+27.3	−1.4
Ph, Me	110	+52.9	+26.1	−0.5
Ph_2	119	+49.0	+23.6	0.0
Ph, *i*-Pr	124	+48.3	+25.9	+2.0
i-Pr_2	129	+48.1	+28.0	+5.4

C in the chelate structures. As mentioned previously, Δ_R is now entrenched in the chemistry of orthometalated phosphite complexes[67–69] and chelating phosphite complexes.[17] In the series $M(CO)_4L$ (M = Cr, Mo, W; L = $Ph_2P_A(S)CH_2P_BMe_2$)[80] where S is incorporated into the 5-membered rings, a normal Δ_R is observed for 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.[81] Note that Δ_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 Δ_R values of between 10 and 30 for the 5-membered chelates.[82]

6.3. Of R Group of Phosphorus

In the series shown in Table XIV, the effect of the R group in $Ph_2PCH_2PR_2$ on δ_P was examined in relation to the cone angle extended by the PR_2 ligand.[83] It can be seen that R induces very little change in the δ_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.[49] have shown that in the case of complexes of the type **120**, δ_P values vary only slightly from the corresponding values for a saturated backbone.

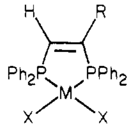
TABLE XV. Average J_{P-P} (Hz) Values for $[Ph_2P(CH_2)_nPR_2]M(CO)_4$[84]

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 $^{B}J_{P-P}$ and $^{M}J_{P-P}$ for $[Ph_2P(CH_2)_nPRR^1]M(CO)_4$[84]

M	*n*	$^{3,B}J_{P-P}$, Hz	$^{2,M}J_{P-P}$, Hz	J_{P-P} (theor),[a] Hz	J_{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] $|J_{P-P}| = |^{B}J_{P-P} \pm {}^{M}J_{P-P}|$.



120

7. Ring Contributions Observed

7.1. In P–P Coupling

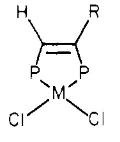
When the phosphorus atoms are chemically nonequivalent, phosphine ligands containing two or more phosphorus atoms give rise to ^{31}P spectra in which the magnitude of J_{P-P} will strongly affect the spectral appearance. A good discussion of the parameters important in determining the magnitude and sign of this coupling has been presented.[13] For our discussion here, let us note that the ^{31}P spectra of monodentate ligands reveal an algebraic increase in J_{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.[84] have suggested that the P–P coupling within a chelate ring can be divided into through-the-backbone and through-the-metal contributions $J_{P-P} = {}^{B}J_{P-P} + {}^{M}J_{P-P}$ where $^{B}J_{P-P}$ of the coordinated ligands is assumed equal to $^{B}J_{P-P}$ in the free ligand. In a 5-membered ring these contributions are nearly equal but of opposite sign, which leads to a small J_{P-P}. In a 6-membered ring $^{B}J_{P-P}$ is negligible, and thus the observed J_{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 $M(CO)_4(Ph_2P(CH_2)_nPRR')$[84] are given in Tables XV and XVI.

TABLE XVII. J_{P-P} Coupling for 122[5]

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.



121

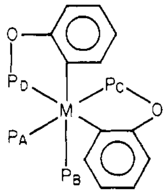
	$^2J_{P-P}$	
M	Ph	*t*-Bu
Ni	69	71
Pd	15	17
Pt	<2	<2

In a series of phosphoalkene complexes of the type 121,[49] $^2J_{P-P}$ 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 $^MJ_{P-P}$ 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 $Cl_2M(Ph_2PCH_2CH_2PPh_2)$, 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 $^MJ_{P-P}$.

In a Rh series of polyphosphine complexes,[44] the phosphorus–phosphorus coupling values reveal a relationship between chelate size in 6-membered rings where $^2J_{P-P}$ ~45–52 Hz and 5-membered rings where $^2J_{P-P}$ ~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,[43] 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, $^3J_{P-P}$ ~0 in the free ligand and the $PtMe_2L$ complex.[43] 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.[43] The Ni, Pd, and Pt complexes of $Me_2P(CH_2)_2P(Me)(CH_2)_2PMe_2$ reveal $|J_{P-P}|$ of 50, 9, and <2 Hz, respectively.[30] Whereas the PtEtCl complexes of dppe, dppp, and dppb have J_{P-P} of <2, 20.6, and 13.2 Hz,[48] their $PtMe_2L$ analogues reveal corresponding values of 34, 0, and 0 Hz.[47]

In the $HM(naphthyl)(dmpe)_2$ series, the Fe, Ru, and Os complexes revealed J_{P-P} of 105, 281, and 265 Hz, respectively,[35] while in $H_2M(dmpe)_2$, going from M = Fe to M = Ru decreases J_{P-P} from 26.5 to 21 Hz.[36]

No fewer than six J_{P-P} couplings could be obtained from structure 122.[5] 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.



122

7.2. In M–P Coupling

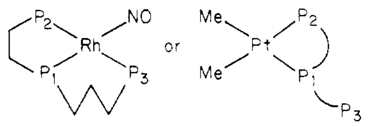
We earlier noted that there was no obvious relationship between chelation and phosphorus–metal coupling.[18] Since then further data have been compiled. In Table XVIII we see several series of W, Pt, and Rh complexes and the variation of J_{M-P} with the size of the chelate ring. Although the changes 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 $W(CO)_4L(Ph_2Pbut)_2$[17] the J_{M-P} value is identical with that of dppe; the same is found for $PtCl_2L$,[45,48] while the J_{Pt-P} value for $PtEt_2(PPh_2Me)_2$ 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 $PtMe_2L$ and $PtEt_2L$ compounds.

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

L	$W(CO)_4L$[17,a]	$WCl(CO)_2(C_3H_5)(L)$[29,a]	$PtCl_2L$[45(48),a]	$PtMe_2L$[45,a]	$PtEt_2L$[48,a]	$[NBDRhL]^+$ [a]	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
$(PPh_2Me)_2$			3616 (3620)		1667		
$(PPh_2Bu)_2$	230						

[a] In hertz.

TABLE XIX. Relationship of J_{M-P} to Chelation by Polyphosphine Ligands[43,44]



	Rh-P_1, Hz	Rh-P_2, Hz	Rh-P_3, Hz	size of ring	Pt-P_1, Hz	Pt-P_2, Hz	size of ring
etp	154	167		5, 5	1798	1900	5
ttp	154		164	6, 6	1807	1850	6
eptp	156	166	169	5, 6	1824	1841	5

TABLE XX. J_{M-P} for a Series of Orthometalated Pt Complexes[58,61]

ligand	$^1J_{Pt-P}$(unmetalated), Hz	$^1J_{Pt-P}$(metalated), Hz	size of ring
$P(OPh)_3$[b]	3229	6371	5
P(O-*o*-tolyl)$_3$[b]	3201	6409	5
PPh(*t*-Bu)$_2$[a]	2912	2222	4
P(*t*-Bu)(*n*-Pr)$_2$[a]	3086	2984[c]	5
P(*t*-Bu)$_3$[a]	2680	2360	4

[a] Phosphorus cis. [b] Phosphorus trans. [c] The *n*-Pr chain is metalated.

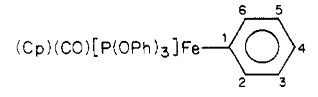
Table XIX reveals data for polydentate phosphines in a Rh[44] and a Pt[43] series. The same trends are *not* observed here. Values for the 5- and 6-membered ring systems etp, ttp, and eptp reveal little change in the J_{Rh-P} values. In the Pt series $J_{Pt-P_2(etp)}$[44] is larger than $J_{Pt-P_2(ttp)}$, but the reverse is true for J_{Pt-P_1}. One author[44] 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.

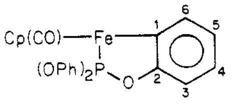
8. Comparison of ^{31}P NMR to NMR of Other Nuclei

8.1. ^{13}C

Stewart et al.[67] found that while the ^{13}C chemical shifts of the aromatic carbons in the unmetalated rings of 123 were not appreciably different from the corresponding signals in free $P(OPh)_3$, the ^{13}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_1 and C_2 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 Δ_R phenomenon is observed for these carbons incorporated into a 5-membered ring.



123



124

Hietkamp and Vrieze[47] have examined the ^{13}C spectra of a series of Me_2PtL complexes as shown in Table XXII. The aromatic parts of the ^{13}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 Δ_R trend in the ^{31}P shifts for the same compounds. The absolute values of these shifts are small and therefore could be attributed to other causes. More ^{13}C data are needed before anyone can clarify whether there is a Δ_R effect in the ^{13}C spectra of molecules such as these.

8.2. ^{195}Pt

Vrieze[47] in the aforementioned series also examined the ^{195}Pt spectra of the $PtMe_2L$ complexes. The ^{195}Pt NMR shifts shown in Table XXII are all very similar except for $PtMe_2(dppm)$, 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. ^{51}V

The ^{51}V spectra of *cis*-$CpV(CO)_2dppe$ (−1110 ppm), $Cp(CO)_3(Ph_2PC{=}CPPh_2)V$ (−1139 ppm), and $[CpV(CO)_2]_2(Ph_2PC{=}CPPh_2)$ (−1143 ppm) have been reported,[24] and one can see very little difference is observed between these chelating, nonchelating, and bridging ligands.

TABLE XXI. ^{13}C Resonances for 123 and 124[68]

	$\delta\,^{13}C$ unmetalated				$\delta\,^{13}C$ phenyl (123) or metalated (124)			
	C_1[a]	$C_{2,6}$	$C_{3,5}$	C_4	C_1	$C_{2,6}$	$C_{3,5}$	C_4
$P(OPh)_3$	+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_2) +144.2 (C_6)	+110.9 (C_3) +122.1 (C_5)	+123.9

[a] Numbered as shown in 123 and 124.

TABLE XXII. ^{13}C and ^{195}Pt Chemical Shifts for Chelating Phosphines and Their Me_2PtL Complexes[47]

ligand	metal	$\delta\,^{13}CH_2(1)^a$	$\Delta_{CH_2(1)}$	$\delta\,^{195}Pt^b$
dppm		+28.0		
	Pt	+19.7	−8.3	−703.9
dppe		+23.7		
	Pt	+29.7	+6.0	+9.2
dppp		+29.6		
	Pt	+27.4	−2.2	−4.7
dppb		+27.7		
	Pt	+28.6	+0.9	+58.6

[a] Bridging CH_2 groups adjacent to phosphorus. [b] With respect to δ_{Pt} for *cis*-$(bz)_2PtMe_2$ = 0.

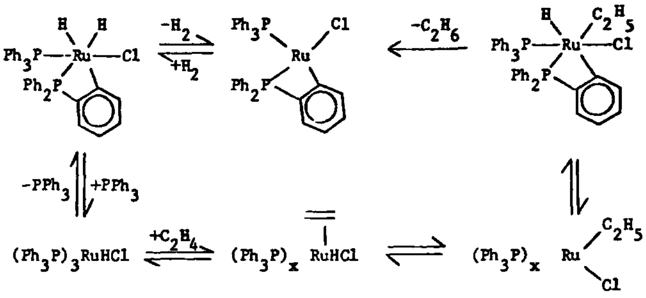


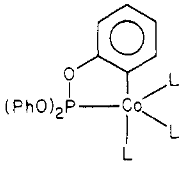
Figure 7. Proposed mechanism for ethylene hydrogeneration by $(Ph_3P)_3RuHCl$.[87]

9. Relationships

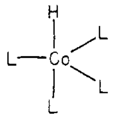
9.1. To Catalytic Reactions

A knowledge of Δ_R will better allow interpretation of the ^{31}P spectra of intermediates in catalytic reactions which involve polyphosphines or orthometalation. ^{31}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 = $P(OPh)_3$].[85]

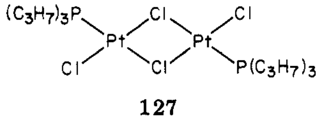


125



126

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.[86] 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_2 being necessary only to regenerate the $(Ph_3P)_3RuHCl$ catalyst.[87] Again, in compound **127** deuteration occurs in the Me group



127

which corresponds to the presence of 5-membered ring intermediates.[86] In another study the deuteration of $Ph_2P(OPh)$ by $RhHCl(PPh_3)_3$ 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.[86]

Mason and Meek[88] 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 $RhCl(PPh_3)_3$, chemical studies reveal that the Rh atom in RhCl(ttp) is quite nucleophilic and readily functions as a Lewis base, in which it mimicks $IrCl(PPh_3)_3$ more closely than $RhCl(PPh_3)_3$.

Baird[40] has used chelating phosphines to examine the species present in solution in the olefin hydrogenation catalyst $[NBDRh(diphosphine)]^+$. Knowing that a Δ_R contribution would cause upfield and downfield shifts with dppm and dppe, respectively, they chose to examine the ^{31}P spectra of a dppp system to minimize Δ_R contributions and more closely resemble the δ_P 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.[89] As such data become more prevalent and the solid-state ^{31}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.

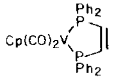
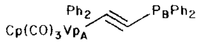
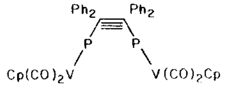
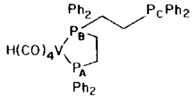
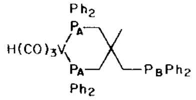
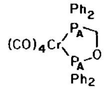
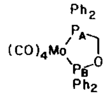
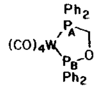
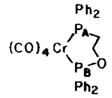
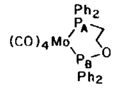
10. Conclusions

It appears that a ring contribution "Δ_R" 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_R rule are uncovered, it is likely that the theoretical reasons for Δ_R will become more clear-cut.

11. Appendix

^{31}P NMR data for diphosphine–, alkenylphosphine–, and orthometalated phosphine–transition-metal com-

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

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P'}\rvert$, Hz	J_{M-P}, Hz
24		2.1 vanadium						
	18		+120	−23.1	+143.1			δ ^{51}V = −1143
	19		(P$_A$) +69 (P$_B$) −35	−32.6	+101.6			−1334
	20		+7.3	−32.6	+105.6			−1281
25	22	H(CO)$_4$V(etp)	+68[a]					−1685
	23		(P$_A$) +87 (P$_B$) +76 (P$_C$) −15.6					
	25		(P$_A$) +27 (P$_B$) −27					
		2.2 Cr, Mo, W						
17	Table I	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	
			(P$_A$) +86.0 (P$_B$) +196.7	−14.1 −118.2	+100 +78.5		31	
			(P$_A$) +63.4 (P$_B$) +174.4	−14.1 −118.2	+77.5 +56.2		18.5	
17			(P$_A$) +49.5 (P$_B$) +154.9	−14.1 −118.2	+63.6 +36.7		11	234 260
			(P$_A$) +40.8 (P$_B$) +161.4	−22.8 −111.6	+63.6 +49.8		46.5	
			(P$_A$) +22.0 (P$_B$) +141.6	−22.8 −111.6	+44.8 +30.0		35	

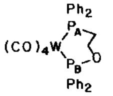
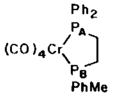
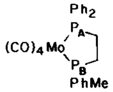
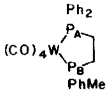
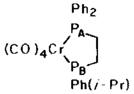
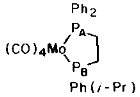
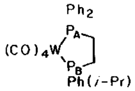
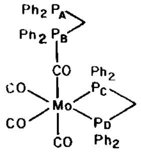
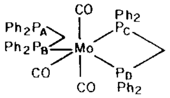
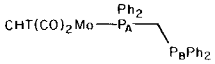
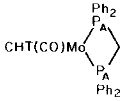
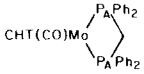
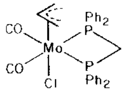
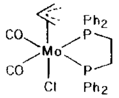
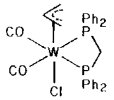
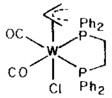
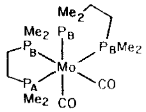
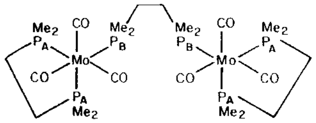
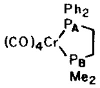
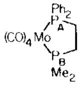
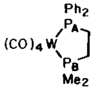
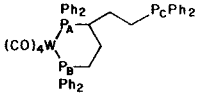
			$(\mathrm{P_A})$ $(\mathrm{P_B})$	+2.2 +116.2	−22.8 −111.6	+25.0 +4.6		31	222 261
26			$(\mathrm{P_A})$ $(\mathrm{P_B})$	+80.0 +65.0	−13.0 −31.4	+93.0 +96.4			
			$(\mathrm{P_A})$ $(\mathrm{P_B})$	+55.7 +39.0	−13.0 −31.4	+68.7 +70.4			
			$(\mathrm{P_A})$ $(\mathrm{P_B})$	+41.0 +22.6	−13.0 −31.4	+54.0 +54.0			
			$(\mathrm{P_A})$ $(\mathrm{P_B})$	+77.4 +84.8	−12.8 −2.6	+90.2 +87.4			
			$(\mathrm{P_A})$ $(\mathrm{P_B})$	+53.9 +63.6	−12.8 −2.6	+66.7 +66.2			
26			$(\mathrm{P_A})$ $(\mathrm{P_B})$	+38.9 +49.1	−12.8 −2.6	+51.7 +51.7			
27	26		$(\mathrm{P_A})$	−25.2	−22.7			$^2J_{\mathrm{P_A-P_B}}$ 34.2 $^2J_{\mathrm{P_B-P_C}}$ 24.4	
			$(\mathrm{P_B})$ $(\mathrm{P_C})$	+30.0 −3.0		+52.7 +19.7	 −27		
	27		$(\mathrm{P_A})$	−24.3	−22.7			$^2J_{\mathrm{P_A-P_B}}$ 64.4 $^2J_{\mathrm{P_B-P_C}}$ 25.6 $^2J_{\mathrm{P_B-P_D}}$ 72.4 $^2J_{\mathrm{P_C-P_D}}$ 24.4	
			$(\mathrm{P_B})$	+44.7		+67.4			
			$(\mathrm{P_C})$	+1.8		+24.5	−24		
			$(\mathrm{P_D})$	+20.8		+43.5	−28		
28			$(\mathrm{P_A})$ $(\mathrm{P_B})$	−24.9 +33.6	+21.4	 +55.0		$^2J_{\mathrm{P_A-P_B}}$ 97.7	
				+6.9	−21.4	+28.3	−26.7[b]		
				+68.3	−12.9	+81.2	−34.7[b]		

TABLE XXIII (*Continued*)

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P}\rvert$, 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_A) +42.2 (P_B) +23.6	−13.2	+55.4 +36.8	21.1[c]		
			(P_A) +24.4 (P_B) −2.5	−13.2	+37.6 +10.7			
30	Table II		(P_A) +81.2 (P_B) +55.0	−13.5 −48.4	+94.7 +103.4		15	
30			(P_A) +57.1 (P_B) +26.3		+70.6 +74.7		7	
			(P_A) +42.2 (P_B) +7.9	+55.7 +56.3			<2	
		$Cr(CO)_3(etp)$	(PPh) +110.2 (PPh_2) +77.9	−16.5 −12.9	+126.7 +90.8			12
	29	$Mo(CO)_3(etp)$	(PPh) +82.4 (PPh_2) +55.3		+98.9 +68.2			~6
		$W(CO)_3(etp)$	(PPh) +71.8 (PPh_2) +40.3		+88.3 +53.2			~6
31	30		(P_A) +17.7 (P_B) +4.0 (P_C) −20.0				$^2J_{P_A-P_B}$ 21.5 $^4J_{P_B-P_C}$ 3.6	J_{W-P_1} 221.1 J_{W-P_2} 226.5

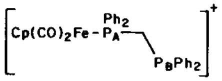
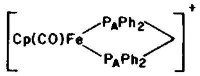
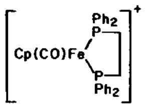
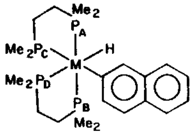
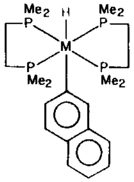
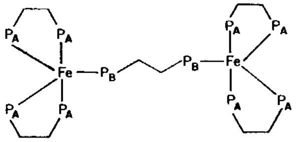
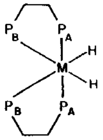
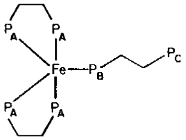
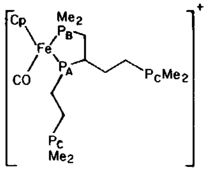
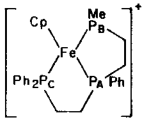
		2.3 Mn, Re						
32	Table III	$Mn(CO)_3Br(dppm)$		+10.9	−22.7	+33.6		
		$Mn(CO)_3Br(dppe)$		+67.6	−13.2	+80.8		
		$Re(CO)_3Br(dppm)$		−38.5		−15.8		
		$Re(CO)_3Br(dppe)$		+30.0		+43.2		
		$Mn(CO)_3(dppm)(MeCN)^+$		+13.7		+36.4		
		$Mn(CO)_3(dppe)(MeCN)^+$		+73.5		+86.7		
		$Re(CO)_3(dppm)(MeCN)^+$		−35.0		−12.0		
		$Re(CO)_3(dppe)(MeCN)^+$		+38.0		+51.0		
33		$(MeCpMn(CO)_2)_2(dppm)$		+91.0		+113.7		
		$MeCpMn(CO)(dppm)$		+58.4		+81.1		
		$[MeCpMn(CO)_2]_2(dppe)$		+91.0		+104.2		
		$(MeCp)Mn(CO)_2(dppe)$		+122.0		+135.2		
34		$CpMn(CO)(dppe)$		+117.3	−13.2	+130.5		
		$CpMn(CO)(dppp)$		+82.0	−17.3	+99.3		
		$CpMn(CO)(PPh_3)_2$		+92.0	−5.5	+97.5		
		2.4a Fe, Ru, Os						
28			δ_{P_A} δ_{P_B}	+33.6 −24.9	−21.7	+82.0		90.0
			δ_P	−8.9	−12.9		−69.2	
			δ_P	+92.3	−12.9		+32.3	
35	31		Fe δ_{P_A} δ_{P_B} δ_{P_C} δ_{P_D}	+73.7 +70.5 +59.8 +53.6				$^2J_{P_A-P_B}$ 105 $^2J_{P_A-P_C}$ 27 $^2J_{P_A-P_D}$ 32 $^2J_{P_B-P_C}$ 28 $^2J_{P_B-P_D}$ 18 $^2J_{P_C-P_D}$ 14
			Ru δ_{P_A} δ_{P_B} δ_{P_C} δ_{P_D}	+45.5 +40.1 +33.3 +27.4				$^2J_{P_A-P_B}$ 281 $^2J_{P_A-P_C}$ 13 $^2J_{P_A-P_D}$ 25 $^2J_{P_B-P_C}$ 13 $^2J_{P_B-P_D}$ 13 $^2J_{P_C-P_D}$ 13

TABLE XXIII (*Continued*)

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P}\rvert$, Hz	J_{M-P}, Hz
			Os δ_{P_A} +7.9 δ_{P_B} +3.8 δ_{P_C} −5.0 δ_{P_D} −7.7				$^2J_{P_A-P_B}$ 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		Feδ_P +74.2 Ruδ_P +45.3 Osδ_P +9.3					
	33		$\delta_{P_A}{}^d$ +60.4 $\delta_{P_B}{}^d$ +7.2					
			Fe $\delta_{P_A}{}^d$ +76.0 $\delta_{P_B}{}^d$ +66.3				26.5	
			Ru $\delta_{P_A}{}^d$ +49.6 $\delta_{P_B}{}^d$ +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		δ_{P_A} +96.5 δ_{P_B} +93.6 δ_{P_C} −12.5, −13.3	−20.1 −48.9	+114.0 +106.7			
	36		δ_{P_A} +123.1 δ_{P_B} +68.7	−17.9 −49.0	+141.0 +117.7		$^2J_{P_A-P_B}$ 39 $^2J_{P_A-P_C}$ 29	

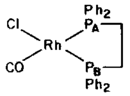
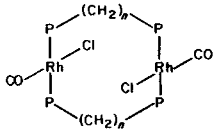
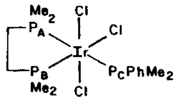
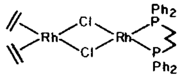
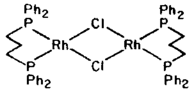
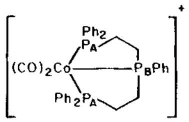
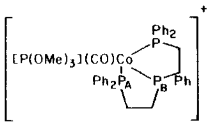
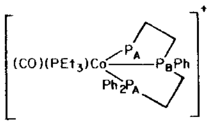
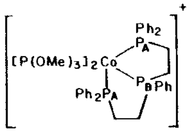
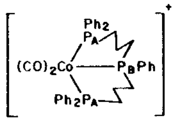
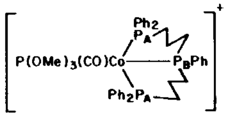
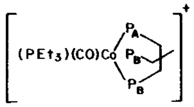
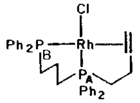
			δ_{P_C}	+104.3	−13.5	+117.8		$^2J_{P_B\text{-}P_C}$ 44	
		2.4b Co, Rh, Ir							
36		$Rh(dppe)_2^+$		+56.8	−13.2	+70.0			
		$Ir(dppe)_2^+$		+50.2	−13.2	+63.4			
		$Ir(dppm)_2CO^+$		−38.9[a]					
		$Ir(dppe)_2CO^+$	$P_a{}^l$	+28.7	−13.2	+41.9		$^2J_{P_a\text{-}P_e}$ 19.1	
			P_e	+24.4		+37.6			
		$Ir(dppp)_2CO^+$	P_a	−16.9	−17.3	+34.2		$^2J_{P_a\text{-}P_e}$ 37.1	
			P_e	−27.9		+45.2			
37	37		(P_A)	+45.1[e]				$^2J_{P_A\text{-}P_B}$ 34.5	158.5
			(P_B)	+66.7[e]					124.5
	38		$n = 1$	+96.8[e]					
			$n = 2$	+87.1[e]					125
			$n = 3$	+89.1[e]					121
38		$IrCO(dppe)_2^+IrCO_2Cl_2^-$		+28.5	−13.2	+41.7			
		$[IrCOCl(dppp)]_2$		−4.6	−17.3	+12.7			
		$[IrCOCl(dppb)]_3$		+1.7	−15.0	+16.7			
39	39		(P_A)	+4.2	−47.6	+51.8	+46.3 (P_A)		
			(P_B)	−42.1		+5.5			
40				+32	−17.0	+49.0			187
				+30.3	−17.0	+47.3			184
		$Rh(dppp)_2Cl$		+6.4[f]	−17.0	+23.4			132
40		$(NBD)RhL^+$							
			dppe	+55.6	−12.3	+67.9			157
			dppp	+14.1	−17.0	+31.1			148
			dppb	+26.8	−15.0	+41.8			152
			(−)diop	+16.2	−24.0	+40.2			153
41		$PhP_B(CH_2CH_2)P_APh_2)_2(etp)$			(P_A) −12.9 (P_B) −16.5			$^2J_{P_A\text{-}P_B}$ 27	
			(P_A)	+78.6				$^2J_{P_A\text{-}P_B}$ 48	
			(P_B)	+122.4					

TABLE XXIII (*Continued*)

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P}\rvert$, Hz	J_{M-P}, Hz
41			(P_A) +68.2 (P_B) +113.3				$^2J_{P_A-P_B}$ 38 $^2J_{P(OMe)_3-P_A}$ 88 $^2J_{P(OMe)_3-P_B}$ 211	
	43		(P_A) +64.9 (P_B) +109.6				$^2J_{P_A-P_B}$ 33 $^2J_{PEt_3-P_A}$ 53 $^2J_{PEt_3-P_B}$ 104	
41	41		(P_A) +65.6 (P_B) +108.0				$^2J_{P_A-P_B}$ 41.0 $^2J_{P_A-P(OMe)_3}$ 93.5, 110.3 $^2J_{P_B-P(OMe)_3}$ 193.5, 105.5 $^2J_{P(OMe)_3-P(OMe)_3}$ 136.5	
		$PhP_B(CH_2CH_2CH_2P_APh_2)_2$(ttp)		(P_A) −17.0 (P_B) −28.8				
			(P_A) +37.0 (P_B) −7.3				$^2J_{P_A-P_B}$ 75	
	40		(P_A) +29.0 (P_B) −6.0				$^2J_{P_A-P_B}$ 90 $^2J_{P_A-P(OMe)_3}$ 18 $^2J_{P_B-P(OMe)_3}$ 49	
	42		(P) +21.5[a]					
43a		$Ph_2P_BCH_2CH_2CH_2P_APhCH_2CH_2CH{=}CH_2$ (ppol)		(P_A) −27.1 (P_B) −18.2				
	44		(P_A) +53.7 (P_B) +5.3		+80.8 +23.5		$^2J_{P_A-P_B}$ 53	J_{Rh-P_A} 156 J_{Rh-P_B} 153

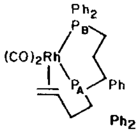
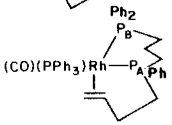
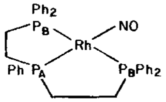
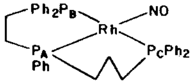
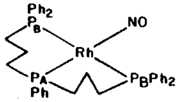
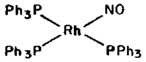
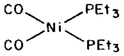
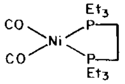
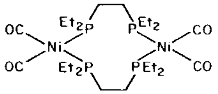
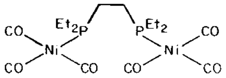
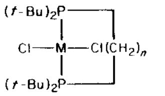
	45-47		(P_A)	+37.3			+64.4		$^2J_{P_A-P_B}$ 47	J_{Rh-P_A} 88
			(P_B)	−1.7			+16.5			J_{Rh-P_B} 115
	48-49		(P_A)	+29.1			+56.2		$^2J_{P_A-P_B}$ 49	J_{Rh-P_A} 122.5
			(P_B)	+7.3			+25.5			J_{Rh-P_B} 146
44	50		(P_A)	+89.3			+105.9		$^2J_{P_A-P_B}$ 18	154
			(P_B)	+69.7			+82.5			167
		$Ph_2P_BCH_2CH_2P_A(CH_2)_3P_CPh_2$ (eptp)			(P_A) (P_B) (P_C)	−22.4 −13.2 −18.0				
	51		(P_A)	+56.0			+78.4		$^2J_{P_A-P_B}$ 12	156
			(P_B)	+68.9			+82.1		$^2J_{P_A-P_C}$ 45	166
			(P_C)	+30.2			+48.3		$^2J_{P_B-P_C}$ 0	169
	52		(P_A)	+18.8	(P_A)	−28.8	+47.6		$^2J_{P_A-P_B}$ 48	154
			(P_B)	+29.2	(P_B)	−17.0	+46.2			164
				+48.8		−5.8	+54.6			175
		2.4c Ni, Pd, Pt								
14	Fig. 2			+20.7						
				+48.6						
				+21.9						
				+21.9						
45	Table V	*cis*-$PtMe_2(PMePh_2)_2$		+6.4		−28.1	+34.5			1851
		$PtMe_2$(dppm)		−40.4		−22.7	−17.7	−52.2		1434
		$PtMe_2$(dppe)		+45.4		−13.2	+58.6	+24.1		1794
		$PtMe_2$(dppp)		+3.2		−17.3	+20.5	−14.0		1790
47		$PtMe_2$(dppb)		+18.8		−15.0	+33.8	−0.7		

TABLE XXIII (*Continued*)

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P}\rvert$, Hz	J_{M-P}, Hz
38	Table VI	*cis*-$PdCl_2[P(Ph_2Et)_3]_2$	+30.2	−12.5	+42.7			
		$PdCl_2(dppe)$	+68.3	−13.2	+81.5	+38.8		
		cis-$PdCl_2[P(Ph_2Pr)_3]_2$	+27.4	−17.6	+45.0			
		$PdCl_2(dppp)$	+12.9	−17.3	+30.2	−14.8		
		cis-$PdCl_2[P(Ph_2but)_3]_2$	+26.6	−17.1	+43.7			
		$PdCl_2(dppb)$	+32.8	−15.0	+47.8	+3.8		
		cis-$PtCl_2[P(Ph_2Me)_3]_2$	−1.2	−28.1	+26.9			
		$PtCl_2(dppm)$	−64.3	−22.7	−41.6	−68.5		
		cis-$PtCl_2[P(Ph_2Et)_3]_2$	+9.8	−12.5	+22.3			
		$PtCl_2(dppe)$	+45.3	−13.2	+58.5	+36.2		
		cis-$PtCl_2[P(Ph_2Pr)_3]_2$	+6.9	−17.6	+24.5			
		$PtCl_2dppp$	−5.6	−17.3	+11.7	−12.8		
46		$Ni(PMe_3)_4$	+22.2	−63.3	+41.1			
		$Ni(Me_2PCH_2CH_2PMe_2)_2$	+18.1	−49.4	+67.5	−26.4		
18		*cis*-$PdCl_2(Ph_2P_ACH_2OPPh_2)_2$	(P_A) +27.0	−14.1	+41.8			
	53	$PdCl_2(Ph_2P_ACH_2OP_BPh_2)$	(P_A) +79.8	−14.1	+93.9	+52.1		
		cis-$PdCl_2(Ph_2P_ACH_2CH_2OP_BPh_2)_2$	(P_A) +24.0	−22.8	+46.8			
	54	$PdCl_2(Ph_2P_ACH_2CH_2OPPh_2)$	(P_A) +11.7	−22.8	+34.5	−12.3		
49		$Ph_2P_ACH{=}C(CF_3)P_BPh_2$		(P_A) −26.3			131	
				(P_B) −18.0				
		$Ph_2P_ACH{=}C(Ph)P_BPh_2$		(P_A) −28.1			146	
				(P_B) −7.0				
		$Ph_2P_ACH{=}C(t\text{-}Bu)P_BPh_2$		(P_A) −32.2			37	
				(P_B) −14.8				
		$Ph_2P_ACH{=}C(Ph)P_BEtPh$		(P_A) −27.8				
				(P_B) −21.1				
		$Ph_2P_ACH{=}C(CF_3)P_B(C_2H_4CN)_2$		(P_A) −23.0				
				(P_B) −32.9				
	55	$Cl_2Ni(Ph_2P_ACH{=}C(Ph)P_BPh_2)$	(P_A) +46.0	+74.1	+43.4		69	
			(P_B) +69.3	+76.3	+58.2			
		$Cl_2Ni(Ph_2P_ACH{=}C(t\text{-}Bu)P_BPh_2)$	(P_A) +43.8		+76.0	+44.0	71	
			(P_B) +72.1		+86.9	+60.6		
		$Cl_2Ni(Ph_2P_ACH{=}C(CF_3)P_BPh_2)$	(P_A) +48.0		+73.8	+43.9	66	
			(P_B) +69.9		+95.7	+65.8		
		$Cl_2Pd(Ph_2P_ACH{=}C(CF_3)P_BPh_2)$	(P_A) +56.6		+82.9	+36.5	21	
			(P_B) +73.6		+91.6	+47.8		
	56	$Cl_2Pd(Ph_2P_ACH{=}C(Ph)P_BPh_2)$	(P_A) +51.1		+79.2	+32.2	15	
			(P_B) +75.6		+82.6	+42.3		
		$Cl_2Pd(Ph_2P_ACH{=}C(Ph)P_BPhEt)$	(P_A) +51.4		+79.2	+32.3	17	
			(P_B) +80.4		+102.2	+57.4		
		$Cl_2Pd(Ph_2P_ACH{=}C(CF_3)P_B(C_2H_4CN)_2$	(P_A) +54.6		+77.6	+32.3	20	
			(P_B) +77.1		+110.0	+61.5		
		$Cl_2Pt(Ph_2P_ACH{=}C(CF_3)P_BPh_2)$	(P_A) +31.8		+58.1	+30.7	<2	
			(P_B) +48.3		+66.3	+41.6		
	57	$Cl_2Pt(Ph_2P_ACH{=}C(Ph)P_BPh_2)$	(P_A) +30.5		+58.6	+30.6	<2	3552
			(P_B) +53.1		+60.1	+39.0		3640
		$Cl_2Pt(Ph_2P_ACH{=}C(t\text{-}Bu)P_BPh_2)$	(P_A) +25.9		+58.1	+28.8	<2	3425
			(P_B) +53.2		+68.0	+44.2		3613
50		 M = Pt, n = 9	+31.0					2454
		10	+31.8					2476
		12	+28.2					2444
		M = Pd, n = 10	+43.3					

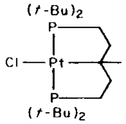
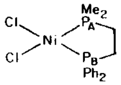
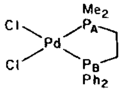
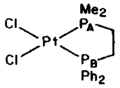
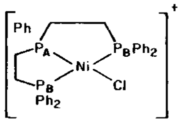
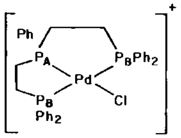
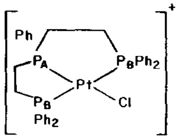
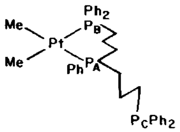
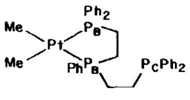
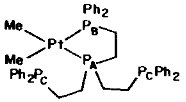
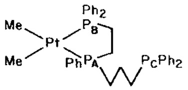
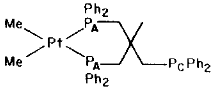
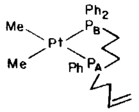
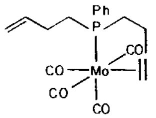
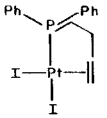
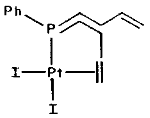
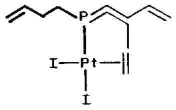
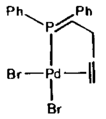
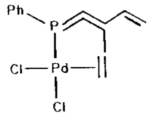
18		*trans*-$PtCl_2[P(n\text{-}Pr)_2(t\text{-}Bu)]_2$		+34.3			
51	61			+73.0			3223
30			(P_A)	+48.6	+97.0	76	
			(P_B)	+58.4	+71.9		
			(P_A)	+58.8	+107.2	10	
			(P_B)	+64.5	+78.0		
30			(P_A)	+30.8	+79.2	<2	
			(P_B)	+42.2	+55.7		
	62		(P_A)	+109.2	+125.7	50	
			(P_B)	+47.1	+70.0		
	63		(P_A)	+109.5	+126.0	10	
			(P_B)	+45.7	+68.6		
			(P_A)	+86.0	+102.5	<2	
			(P_B)	+41.9	+54.8		
43b			(P_A)	−3.7	+24.5	$J_{P_A-P_B}$ 18.0	J_{Pt-P_A} 1807
			(P_B)	+3.5	+21.6	$J_{P_A-P_C}$ 0	J_{Pt-P_B} 1850
			(P_C)	−18.9			
			(P_A)	+49.4	+66.0	$J_{P_A-P_B}$ 0.8	J_{Pt-P_A} 1838
			(P_B)	+48.5	+61.3	$J_{P_A-P_C}$ 37.5	J_{Pt-P_B} 1853
			(P_C)	−15.2			
			(P_A)	+31.5	+49.0	$J_{P_A-P_B}$ 0	J_{Pt-P_A} 1773
			(P_B)	+32.4	+45.4	$J_{P_A-P_C}$ 32.8	J_{Pt-P_B} 1853
			(P_C)	−35.0			

TABLE XXIII (*Continued*)

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P}\rvert$, Hz	J_{M-P}, Hz
			(P_A) +44.0		+66.6		$J_{P_A-P_B}$ 3.7	J_{Pt-P_A} 1824
			(P_B) +47.4		+60.0		$J_{P_A-P_C}$ 0	J_{Pt-P_B} 1841
			(P_C) −18.9					
			(P_A) +4.5		+30.1		$J_{P_A-P_C}$ 2.4	1816
			(P_C) −28.8					
			(P_A) −2.6		+24.5		$J_{P_A-P_B}$ 18.0	J_{Pt-P_A} 1789
			(P_B) +3.4		+21.6			J_{Pt-P_B} 1827
7	66		+42.5	−26.2	+67.9	+28.6 (avg)		
		cis-$Mo(CO)_4[PPh(n\text{-}Bu)_2]_2$	+14.5		+40.7			
8	67		+34.1	−16.5	+50.6	+26.6		3071
	68		+37.8	−25.4	+63.2	+40.1		3032
	69		+42.1	−30.2	+72.3	+41.1		2934
		cis-$Cl_2Pt[PPh_2(n\text{-}Bu)]_2$	+7		+24.1			
8		*cis*-$PtI_2[P(n\text{-}Bu)_3]_2$	−1.1	−32.3	+31.2			
		cis-$PtI_2[PPh(n\text{-}Bu)_2]_2$	−2.3	−25.4	+23.1			
8			+57.1	−16.5	+73.6	+29.4		
		cis-$PdBr_2[PPh_2(n\text{-}Bu)]_2$	+27.7		+44.2			
			+65.4	−25.4	+90.8	+44.8		

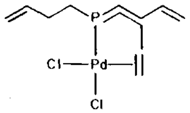
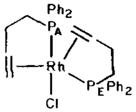
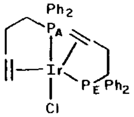
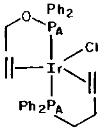
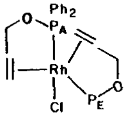
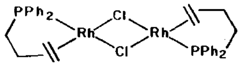
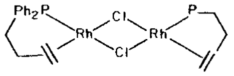
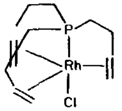
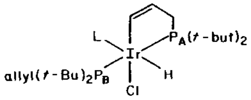
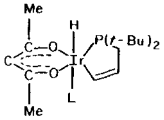
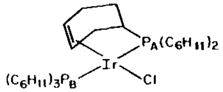
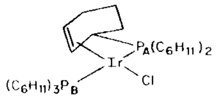
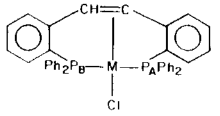
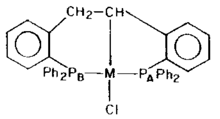
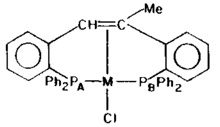
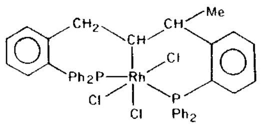
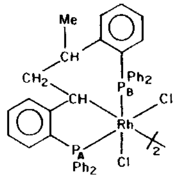
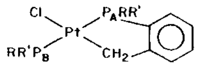
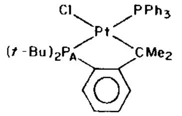
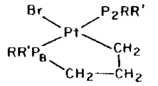
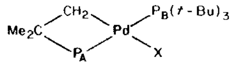
		cis-PdCl$_2$[PPh(n-Bu)$_2$]$_2$		+20.6		+46.0			
				+76.3	−30.2	+106.5			
9	72		(P$_E$) (P$_A$)	+74.9 +26.4	−16.5	+91.4 +42.9		+26.8	J_{Rh-P_E} 145 J_{Rh-P_A} 111
			(P$_E$) (P$_A$)	+29.5 +6.6	−16.5	+46.0 +23.1		+11.0	
	73		(P$_A$)	+19.3	−16.5	+35.8			
	72		(P$_E$) (P$_A$)	+156.2 +139.8	+113.0	+43.2 +26.8		+21.0	J_{Rh-P_E} 146 J_{Rh-P_A} 116
	70–71			+68.6	−16.5				188
		or							
				+69.6					189
	76			+134					
53	77		(P$_A$) (P$_B$)	+57.7 +16.8			+40.9 +40.9	365	
10				+63.9					
54	78		(P$_A$) (P$_B$)	+35.6 +12.9			+22.7	356	

TABLE XXIII (*Continued*)

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P}\rvert$, Hz	J_{M-P}, Hz
	79		(P_A) −20.8 (P_B) −3.1			−17.7	427	
55	80		M Ni (P_A) +41.4 (P_B) +26.3 Pd (P_A) +44.9 (P_B) +23.4 Pt (P_A) +43.7 (P_B) +28.9	−13.7			326 435 425	
	81		Ni (P_A) +43.5 (P_B) +14.5 Pd (P_A) +37.3 (P_B) +13.9 Pt (P_A) +43.4 (P_B) +19.0	+15.8			410 421 425	
56	82		Rh (P_A) +39.1, +40.0 (P_B) +17.3, +15.5 Ir (P_A) +34.3, +35.2 (P_B) +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_A)^g +52.0 (P_B) +31.1	−37.99	+89.99 +69.09	+20.9	409	3262 2755
	86		(P_A) +71.3				391.4	
18		*trans*-$PtCl_2[PPh(t\text{-}Bu)_2]_2$	+41.2					
	87		(P_A)^h +25.9 (P_B) +67.4	−8.74	+34.6 +76.1	+41.5	396.5	2984 3086
60	89		Cl (P_A) −11.8 (P_B) +61.8	−60.9		(P_A) −73.6		

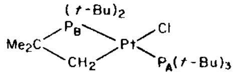
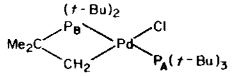
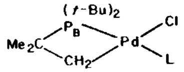
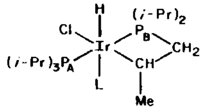
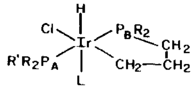
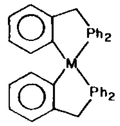
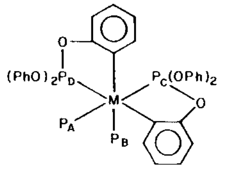
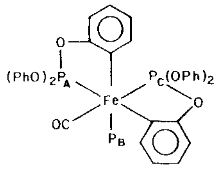
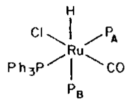
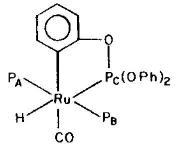
			CF$_3$COO (P$_A$)	−13.8			(P$_A$) −81.6		
			(P$_B$)	+67.8					
61	90		(P$_A$)	+66.8	−60.9	+127.7		383	2680
			(P$_B$)	−12.8		+48.1	−79.7		2360
60	89		(P$_A$)	+61.8	−60.9	+122.7			
			(P$_B$)	−11.8		+49.1	−73.6		
	89		L						
			Et$_3$P$_A$ (P$_A$)	+14.1				441	
			(P$_B$)	−14.1	−60.9	+46.8			
			P$_A$Ph$_3$ (P$_A$)	+19.6				422	
			(P$_B$)	−19.2		+41.7			
			Cy$_3$P$_A$ (P$_A$)	+14.5				409	
			(P$_B$)	−25.3		+35.6			
			Ph$_3$As	−16.2		+44.7			
			Py	+13.1		+47.8			
62	91		L						
			Py (P$_A$)	+10.5			−41.6	369.3	
			(P$_B$)	−31.2					
			CO (P$_A$)	+18.3			−48.4	308.3	
			(P$_B$)	−30.2					
			P(OPh)$_3$ (P$_A$)	+6.3, +8.6			−47.5, −51.4	315.0, 315.7	
			(P$_B$)	−41.1, −42.8					
62	92		L						
			Py (P$_A$)^h	+76.2			+36.6	360	
			(P$_B$)	+39.6					
			CO (P$_A$)	+67.8			+42.9	301	
			(P$_B$)	+24.9					
	93		Pd						
			R = Ph	+40.9			+20.8		
			t-Bu	+77.3					
			Me	+17.3			+20.3		
			Pt						
			R = Ph	+42.8			+32.9		1856
			t-Bu	+79.8					1679
			Me	+17.3			+25.7		1791
		cis-(BzR$_2$P)$_2$MCl$_2$	Pt						
			R = Ph	+9.9					3782
			Me	−8.4					3600
			Pd						
			R = Ph	+20.0					
			Me	−2.7					
5	94		M						
			Fe (P$_A$)^j	+144.2				$^2J_{P_A-P_B}$ 87	
			(P$_B$)^j	+149.5				$^2J_{P_A-P_C}$ 325	
			(P$_C$)	+176.4				$^2J_{P_A-P_D}$ 74	
			(P$_D$)	+180.8				$^2J_{P_B-P_C}$ 68	

TABLE XXIII (*Continued*)

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P} \rvert$, Hz	J_{M-P}, Hz
							$^2J_{P_B-P_D}$ 75	
							$^2J_{P_C-P_D}$ 112	
			Ru (P_A) +120.6				$^2J_{P_A-P_B}$ 53.7	
			(P_B) +127.8				$^2J_{P_A-P_C}$ 34.5	
			(P_C) +152.7				$^2J_{P_A-P_D}$ 32	
			(P_D) +155.6				$^2J_{P_B-P_C}$ 44.1	
							$^2J_{P_B-P_D}$ 68.5	
							$^2J_{P_C-P_D}$ 54.3	
			Os (P_A) +74.9				$^2J_{P_A-P_B}$ 38.3	
			(P_B) +85.9				$^2J_{P_A-P_C}$ 25	
			(P_C) +113.4				$^2J_{P_A-P_D}$ 35.3	
			(P_D) +118.9				$^2J_{P_B-P_C}$ 27.9	
							$^2J_{P_B-P_D}$ 65.1	
							$^2J_{P_C-P_D}$ 41.2	
	95		(P_A) +186.1				$^2J_{P_A-P_B}$ 68	
			$(P_B)^j$ +151.3				$^2J_{P_A-P_C}$ 110	
			(P_C) +175.7				$^2J_{P_B-P_C}$ 85	
64	96		$(P_A)^j$ +129.0				$^2J_{P_A-P_B}$ 36.8	
			$(P_B)^j$ +122.5					
	97		$(P_A)^j$ +141.5				$^2J_{P_A-P_B}$ 390	
			$(P_B)^j$ +137.5				$^2J_{P_A-P_C}$ 26	
			(P_C) +165.2				$^2J_{P_B-P_C}$ 32	

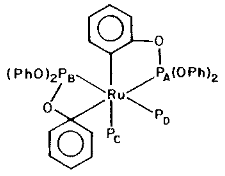
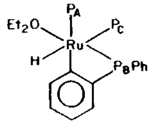
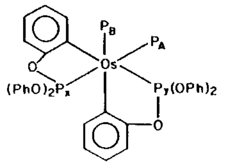
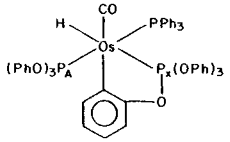
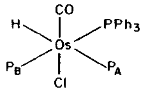
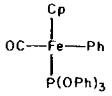
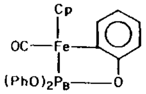
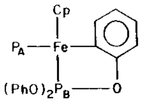
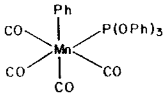
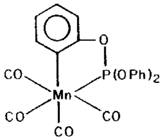
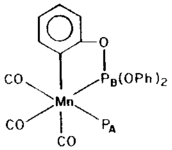
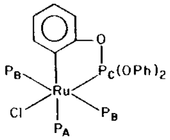
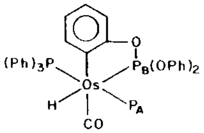
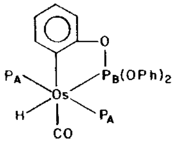
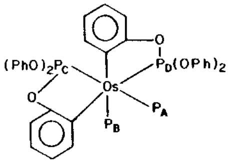
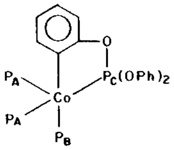
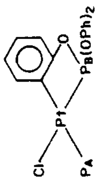
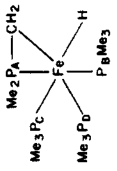
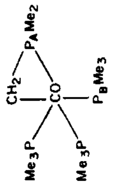
	98		(P_A) +155.8 (P_B) +152.9 (P_C)^j +127.8 (P_D)^j +120.6		$^2J_{P_A-P_B}$ 53 $^2J_{P_A-P_C}$ 35 $^2J_{P_A-P_D}$ 52 $^2J_{P_B-P_C}$ 44 $^2J_{P_B-P_D}$ 685 $^2J_{P_C-P_D}$ 54
65	99		(P_A)^k +20.0 (P_B) −51.4 (P_C)^k +26.1		$^2J_{P_A-P_B}$ 23.7 $^2J_{P_A-P_C}$ 17.7 $^2J_{P_B-P_C}$ 17.7
66	100		(P_A)^j +71.8 (P_B)^j +84.8 (P_x) +114.5 (P_y) +119.2		$^2J_{P_A-P_B}$ 41.2 $^2J_{P_A-P_x}$ 651.5 $^2J_{P_A-P_y}$ 35.3 $^2J_{P_B-P_x}$ 27.9 $^2J_{P_B-P_y}$ 25 $^2J_{P_x-P_y}$ 38.3
66	101		(P_A) +93.7 (P_x) +132.5		17.9
	102		(P_A)^j +88.3 (P_B)^j +88.2		24.0
67–69			+172.3		
			+203.4	+31.1	

TABLE XXIII (*Continued*)

ref	compd	complex	δ_P	δ_F	Δ	Δ_R	$\lvert J_{P-P}\rvert$, Hz	J_{M-P}, Hz
			$(P_A)^j$ +166.4 (P_B) +200.0			+33.6		
			+159.8					
67–69			+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		

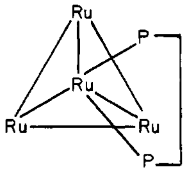
			$(P_A)^j$ +112.8 (P_B) +100.5	+22.9	
70-71	105		(P_A) −17.4 (P_B) +24.1 (P_C) +30.7 (P_D) +38.1		$^2J_{P_A\text{-}P_B}$ 34 $^2J_{P_A\text{-}P_C}$ 40 $^2J_{P_A\text{-}P_D}$ 40 $^2J_{P_B\text{-}P_C}$ 28 $^2J_{P_B\text{-}P_D}$ 28
	106		(P_A) +12.2 $(P_B)^a$ −30.0		

[a] Fluxional. [b] By comparison to Δ_{P_A} of $CHT(CO)_2Mo(dppm)$. [c] By comparison to P_A of $Mo_2(CO)_6(dmpe)_3$. [d] $\overline{P_X \quad P_X}$ = dmpe (X = A, B, or C); values for δ_P are exchange values. [e] Upfield from P_4O_6. [f] Possibly fluxional with TBP structure. [g] R = *t*-Bu, R′ = *o*-$CH_3C_6H_4$. [h] R = *t*-Bu, R′ = *n*-Pr. [i] R = *t*-Bu, *R*′ = *i*-Pr. [j] P = $P(OPh)_3$. [k] P = PPh_3. [l] a = axial; e = equatorial.

plexes are given in Table XXIII.

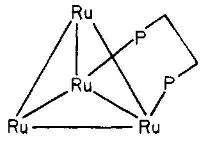
Note Added in Proof

Shapley et al.[90] were able to use Δ_R arguments to determine the mode of bonding in diphosphine-substituted tetranuclear clusters. Specifically, when the δ_P values of **128** and **129** are compared to the analogous



128

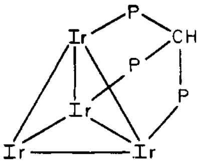
δ +70.2, +63.0



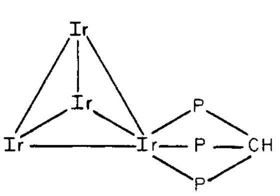
129

δ +41.8, 30.4

disubstituted PPh_2Me complex (δ 19.6), one obtains Δ_R 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 $HC(PPh_2)_3$ with $Ir_4(CO)_{12}$ is reported to give **130**.[91] We feel its δ_P value of −39.1 ppm indicates the presence of four-membered rings, and thus it is probably **131**.

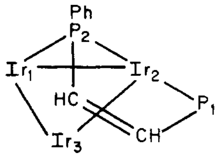


130



131

Gates and Davis[92] have recently solved the crystal structure of $Ir_3(CO)_7(PhPCH{=}CHPPh_2)$, **132**, which



132

shows a phosphide bridge between Ir_1–Ir_2 and a “phosphorus vinyl” unit bound to Ir_2–Ir_3. Although they did not assign the ^{31}P resonances at +99.4 and −22.9 ppm, it is clear from Δ_R arguments that the former is due to the phosphide and the latter to the $\overline{Ir_3{-}Ir_2{-}P_1CH{=}CH}$ unit. Omae has written a review[93] on intramolecular-coordination compounds containing phosphorus donor ligands which covers the literature through July 1979.

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