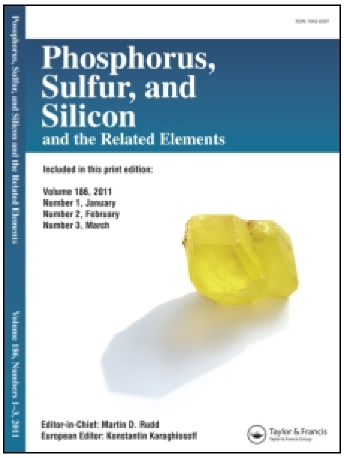

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STRUCTURES AND STRUCTURAL DISTORTIONS OF METALATED PHOSPHORANES

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STRUCTURES AND STRUCTURAL DISTORTIONS OF METALATED PHOSPHORANES

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The 15 published crystal structures of metalated phosphoranes are reviewed. For 12 such structures, the distortion from a trigonal bipyramid towards a rectangular bipyramid and a 30° turnstile geometry is calculated using the method of dihedral angles. When compared to non-metalated phosphoranes, these metalated compounds exhibit a marked preference for the trigonal bipyramidal geometry. It is suggested here that this may be due to the π-donating abilities of the metal substituents. In a few cases, the metalated phosphorane structures also exhibit distortion along the turnstile coordinate as opposed to the Berry pseudorotation mechanism followed by non-metalated phosphoranes. This appears to be due to the considerable steric demands of the metal substituents in the equatorial plane of the phosphorane in these cases.

Key words: Metalated phosphorane; Berry pseudorotation; Turnstile mechanism; trigonal bipyramid; square pyramid.

INTRODUCTION

Compounds having a pentacoordinate phosphorus center have been much studied.[1] However it has only been relatively recently that a new class of phosphorus compounds, with phosphoranide anions acting as ligands giving five-coordinate metalated phosphorus, (Figure 1) has been observed.

The first such metalated phosphorane or metal phosphoranide was prepared in 1981 by Riess et al.[2] as shown in Reaction I.

Since then, a number of other such complexes have been prepared and characterized, many by single crystal X-ray crystallography. In addition, the reactivity of metalated phosphoranes has begun to be investigated.[3–9]

One of the interesting features of pentacoordinate compounds is the structural diversity. This has been investigated thoroughly for non-metalated phosphoranes.[1,10,11] The purpose of this paper then, is to examine the known structures of metalated phosphoranes, to consider the distortion of these structures from idealized geometries and to discuss the effect of a metal substituent of the structure of pentacoordinate phosphorus.

PENTACOORDINATE PHOSPHORUS

There are two idealized structures for pentacoordinate phosphorus, trigonal bipyramidal (TBP) and square pyramidal (SP) as illustrated in Figure 2. (The rectangular pyramidal structure (RP) is similar to the square pyramid but having two five-membered rings, each attached to the phosphorus at the basal positions.) If

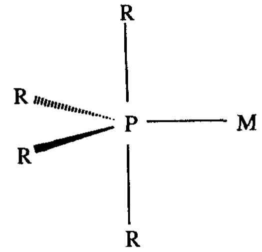
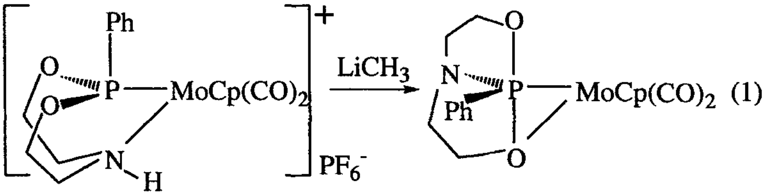


FIGURE 1 A metalated phosphorane.



(1)

REACTION I

considering interactions between substituents only, one would predict the TBP structure to be most stable, however the introduction of ring strain results in phosphorane structures spanning the complete range between the two idealized structures.

This has been illustrated by Holmes,[10,11] who measured the degree of distortion from an idealized TBP geometry towards an SP (or RP) geometry for a number of phosphoranes. The six planes of a TBP result in nine dihedral angles. Holmes' method of calculating the degree of distortion requires determining the absolute difference between each dihedral angle, δ, in the compound of interest and the corresponding dihedral angle in the idealized TBP and SP (or RP) structures. These differences are then summed giving $\Sigma|\delta(\text{structure X})-\delta(\text{TBP})|$ and $\Sigma|\delta(\text{structure X})-\delta(\text{RP})|$.

Since $\Sigma|\delta(\text{RP})-\delta(\text{TBP})| = 217.7°$, $(\Sigma|\delta(\text{structure X})-\delta(\text{TBP})|)/217.7 \times 100\%$ gives the percent deviation from a TBP structure towards an RP. Furthermore, if a structure X does lie along the Berry coordinate between the TBP and RP structures then one would expect that $\Sigma|\delta(\text{structure X})-\delta(\text{TBP})| + \Sigma|\delta(\text{structure X})-\delta(\text{RP})|$ to be equal to 217.7°. Similar calculations could also be done for distortion of a structure from a TBP towards a 30°TR, (the barrier structure along the turnstile mechanism), where $\Sigma|\delta(30\text{TR})-\delta(\text{TBP})| = 223.8°$. It was in fact found to be the

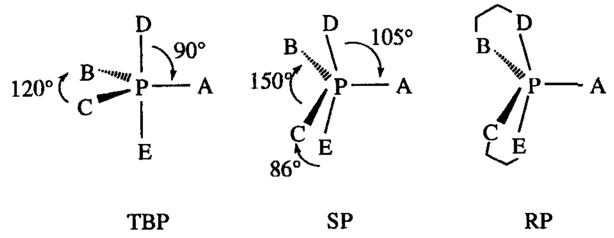


FIGURE 2 Idealized pentacoordinate phosphorus geometries.

case that for non-metalated phosphoranes any distortion from the TBP geometry tends to be towards the RP geometry and along the Berry coordinate (as opposed to the turnstile coordinate).[10] This has been used to lend support to the Berry pseudorotation mechanism as the means by which such phosphoranes exchange sites in a TBP.

In this paper Holmes' method will be applied to metalated phosphoranes in order to determine the extent and nature of distortion from an idealized TBP arrangement. Comparisons will be made with non-metalated phosphoranes.

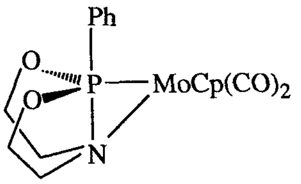
METALATED PHOSPHORANE STRUCTURES

A complete listing of metalated phosphoranes characterized by X-ray crystallography is given in Table I.

Compounds **1** and **2** were the first metalated phosphoranes to be prepared. These O-bound and N-bound linkage isomers were prepared in 1981 by Riess et al.[2,12]

Riess et al.[13,14] also prepared and structurally characterized compound **3**, which utilizes a bidentate phosphoranide ligand. This ligand coordinates to the metal through both the phosphorus and a nitrogen, and is here given the abbreviation {cyclamPN}$^-$.

The remainder of the structurally characterized transition metal phosphoranes have been prepared by Lattman and co-workers using two ligand systems. The



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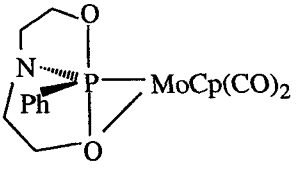

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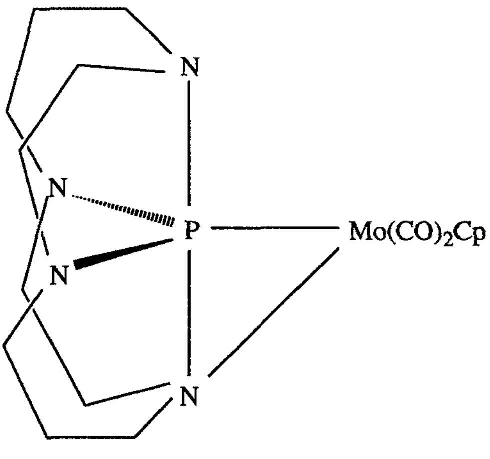

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TABLE I

Metalated phosphoranes characterized by X-ray crystallography

Compound	Formula	P-M Bond Dist. (Å)	Ref.
1	$\{N(C_2H_4O)_2PPh\}Mo(CO)_2Cp$	2.382(4)	12
2	$\{N(C_2H_4O)_2PPh\}Mo(CO)_2Cp$	2.375(2)	2
3	$\{cyclamPN\}Mo(CO)_2Cp$	2.444(2)	13,14
4	$\{(C_6H_4O_2)_2P\}Co(CO)_3(PPh_3)$	2.257(4)	15
5	$\{(C_6H_4O_2)_2P\}Mn(CO)_4\{P(OPh)_3\}$	2.350(2)	16
6	$\{cyclenPN\}Mo(CO)_2Cp$	2.431(2)	17
7	$\{cyclenPNH\}CH_2RhCl_3(PPh_3)$	2.271(2)	18
8	$\{cyclenPN\}Co(CO)_3$	2.195(2)	19
9	$\{cyclenPN\}PtCl(PPh_3)$	2.223(3)	20
10	$[\{cyclenPH_2\}PtCl_2(PPh_3)]Cl$	2.289(12)	21
11	$\{cyclenPN\}PtI(PPh_3)$	2.236(3)	22
12	$\{cyclenPN\}Pt[Co(CO)_4](PPh_3)$	2.241(3)	22
13	$\{cyclenPN\}PtBr(PPh_3)$	2.230(3)	23
14	$[\{cyclenPH_2\}PtCl(Ph_2PCH_2PPh_2)](BF_4)_2$	2.316(4)	24
15	$\{cyclenPN\}Pt[Co(CO)_3](Ph_2PCH_2PPh_2)$	2.227(2)	24

[a] Figure 6 illustrates the $\{cyclenPN\}^-$ and $\{cyclenPH_2\}^+$ phosphoranide ligands

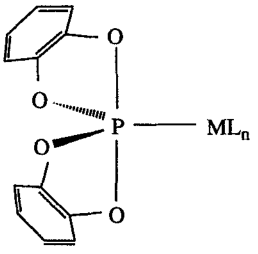


FIGURE 3 The $\{(C_6H_4O_2)_2P\}^-$ phosphoranide ligand.

$\{(C_6H_4O_2)_2P\}^-$phosphoranide ligand acts as a monodentate ligand coordinating to the metal through the phosphorus only (Figure 3). This ligand system is employed in compounds **4** and **5**.[15,16]

Lattman also used the method of proton abstraction with cyclenPH to prepare two types of metalated phosphoranes: those where the $\{cyclenPN\}^-$ phosphoranide acts as a bidentate ligand coordinating to the metal through the P and N[17–20,22–24] and those where the diprotonated $\{cyclenPH_2\}^+$ ligand coordinates through the P only[21,24] (Figure 4). (The aforementioned abbreviations for this ligand system reflect the similarity, but for ring size, with the $\{cyclamPN\}^-$ ligand in the work of Riess.)

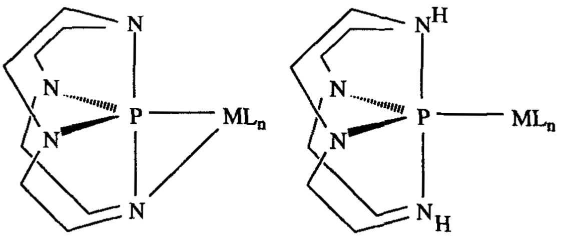
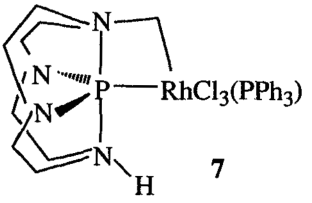


FIGURE 4 The {cyclenPN}$^-$ and {cyclenPH$_2$}$^+$ phosphoranide ligands.



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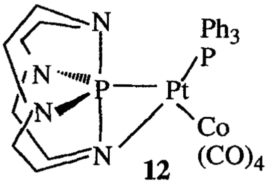

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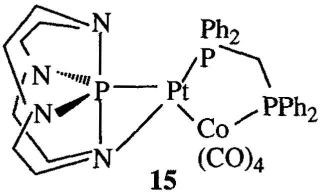

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Examples of these two applications of this phosphoranide can be seen in compounds **6** and **10**, respectively.

Compounds **12** and **15** are also examples of a {cyclenPN}$^-$ phosphoranide complex, where each features a bimetallic substituent on the phosphorus. Finally, compound **7** has a rather unusual coordination mode at the metal center.

There are other metalated phosphoranes that have been prepared and characterized, some of which will be referred to in this paper; Table I contains only those characterized by X-ray crystallography.

DISTORTION OF STRUCTURES

Holmes' method of determining the distortion of a pentacoordinate structure from a trigonal bipyramid was applied to these structurally characterized metalated phosphoranes and the calculated distortions appear in Table II.

A number of types of distortion can be identified. First of all, deviation of bond distances from unit distances can be considered a form of distortion. Therefore in calculating the distortion, unit bond distances were used, so as to consider angular distortions only. These values appear in the third column of Table II.

A second type of distortion is also evident in a number of these structures. There are two types of phosphorane structures appearing in Tables I and II, those in which the phosphoranide ligand acts as a monodentate ligand coordinated to the

TABLE II

Distortion of metalated phosphorane structures from TBP

Compd.	% Distortion towards RP[a]	% Towards RP (unit bond lengths)[a]	% Towards RP (idealized metal position)[a]	% Towards RP (idealized metal position and unit bond lengths)[a]	% Towards 30°TR[a]	% Towards 30°TR (unit bond lengths)[a]
1	Insufficient data to calculate					
2	Insufficient data to calculate					
3	20.0 (102.2)[b]	23.1 (104.2)[b]	20.5 (107.2)[b]	5.4 (100.0)[b]	19.5 (93.5)[b]	22.5 (102.2)[b]
4	27.9 (72.4)	35.2 (64.8)	–	–	27.2 (113.2)	34.3 (116.3)
5	21.5 (114.3)	11.0 (101.3)	–	–	20.9 (87.0)	10.7 (89.7)
6	26.4 (92.0)	24.9 (92.7)	18.7 (104.4)	3.2 (97.0)	25.8 (101.8)	24.3 (105.9)
7	Insufficient data to calculate					
8	33.0 (88.6)	29.3 (84.9)	12.6 (92.4)	14.0 (86.0)	31.9 (108.0)	28.4 (114.4)
9	40.0 (78.3)	37.4 (76.3)	16.2 (86.3)	20.6 (79.4)	38.8 (117.2)	36.4 (122.8)
10	17.2 (106.7)	5.1 (99.8)	–	–	17.6 (97.2)	7.9 (101.0)
11	41.9 (76.4)	38.0 (76.0)	17.2 (84.6)	22.1 (77.9)	40.8 (117.3)	36.9 (121.6)
12	35.7 (87.7)	32.3 (81.7)	13.7 (91.7)	14.9 (85.1)	35.1 (109.5)	31.5 (115.5)
13	40.3 (77.7)	38.1 (76.2)	16.6 (85.9)	21.4 (78.6)	39.3 (117.9)	37.0 (123.6)
14	26.1 (108.8)	21.9 (102.3)	–	–	17.0 (108.8)	13.8 (105.7)
15	32.0 (87.1)	32.9 (79.9)	12.7 (91.4)	15.3 (84.7)	36.4 (110.2)	32.4 (115.5)

[a] See text for explanation of calculation.

[b] Bracketed values represent percent distortions from RP or 30°TR back towards TBP.

metal center through the phosphorus only (such as compounds **4** and **5**), and those in which the phosphoranide ligand acts as a bidentate ligand coordinated through both the phosphorus and an oxygen or nitrogen atom (such as compounds **1**, **2**, and **3**). In the latter case, there is distortion resulting from the highly strained three-membered (P-N-metal or P-O-metal) ring. For such compounds the percent distortion was also calculated assuming the metal to be in an idealized location. This idealized position is one where both metal-P-axial substituent angles are equal, as are both metal-P-equatorial substituent angles. By so doing it is possible to consider the distortion of the remaining PR_4^-, phosphoranide ligand about this idealized position. The results of these calculations appear in the fourth and fifth columns of Table II (without and with unit bond lengths respectively). However, it should be noted that because the influence of the three-membered ring is not well understood, the interpretation of the data from the bidentate phosphoranide structures is less reliable.

As mentioned previously, it is also possible to calculate the degree of distortion from a TBP along the turnstile coordinate towards a 30°TR, (Figure 5) the transition state configuration along the turnstile mechanism. These percentages appear in the final two columns of Table II, again without and with unit bond lengths.

There are two noteworthy features present in the results appearing in Table II: the preferred structure of the metallophosphoranes and the preferred form of distortion (Berry versus turnstile). Firstly, all the structures appear as TBPs or slightly distorted TBPs (with the metal occupying an equatorial position on the phosphorus). The highest distortion among the monodentate phosphoranide structures is 35.2% in the case of compound **4**. Among the bidentate phosphoranides the highest distortion towards an RP structure is 41.9%, in the case of compound **11**. However this is lowered to 38.0% when unit bond lengths are used, and further lowered to 22.1% if the idealized metal position is also used.

(It should be noted that there were three metal phosphoranes which were characterized by X-ray crystallography but the number of bond angles about the phosphorus recorded was not sufficient to allow the calculation of percent distortions. These were compounds **1**, **2**, and **7**. However in each case the authors described the structure as trigonal bipyramidal.)

That the TBP structure should be so favoured is a surprising result in light of the sorts of factors which tend to favour an RP structure. Holmes lists five factors[11] which favour the formation of an RP over a TBP geometry: 1) increasing unsaturation in five-membered rings; 2) the presence of two such rings as opposed to one; 3) the two atoms bonded to the phosphorus in a ring being the same; 4) the presence of a four-membered ring; and 5) the fifth substituent in a spirobicyclic phosphorane being electropositive and sterically demanding.

Compound **4** exhibits factors 1, 2, 3 and 5 and yet is distorted a mere 35.2% along the Berry coordinate from a TBP towards an RP. This is all the more noteworthy when compared to some other $(C_6H_4O_2)_2PR$ phosphoranes.[10] When $R = CH_3$, the percent distortion is 82.4%; when R = OPh, the percentage increases further to 87.7%. Clearly there is yet another factor operative in the case of metallophosphoranes, which is responsible for the close adherence of these structures to a TBP geometry.

It is suggested here that this factor may be related to the π-bonding abilities of the fifth substituent in a spirobicyclic phosphorane. Hoffmann, Howell and Muetterties[25] performed extended Hückel calculations on PH_5 allowing for sub-

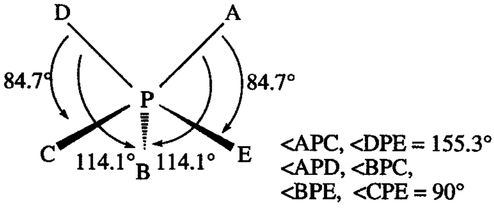


FIGURE 5 The 30°TR geometry.

stitution of π-donors in both the axial and equatorial positions of a TBP. The results indicated a preference for the equatorial sites by π-donors. This preference may represent a sixth factor to be considered when predicting the preferred geometry of a phosphorane; a π-donor as the fifth substituent in a spirobicyclic phosphorane will result in the favouring of the TBP geometry.

Consistent with this proposal are the nature of the metal substituents in the metallophosphoranes considered here and the position assumed by these metal substituents. Each metal substituent in these structures is a potential π-donor. Most significantly the metal in compound **4** (whose TBP geometry is most surprising) is Co(I), a potential π-donor. Also the position of the metal in each case is indeed the equatorial position.

The second noteworthy feature of Table II involves the type of distortion; it is possible to discern between distortion via the Berry pseudorotation mechanism and that via the turnstile mechanism. These two mechanisms are reviewed in Figures 6 and 7. The Berry pseudorotation mechanism requires an in-plane opening of an equatorial angle (B-P-C here) while the axial angle (D-P-E here) simultaneously closes down opposite to and in the plane of the remaining equatorial substituent (A here). Conversely the turnstile mechanism begins with the in-plane closing of the equatorial angle (B-P-C) to 90°. An axial substituent and the remaining equatorial substituent (A and D here) rotate relative to the other three substituents. One important difference then, between the two mechanisms involves angle B-P-

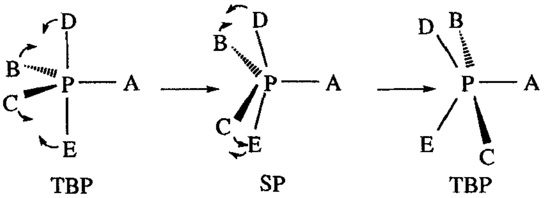


FIGURE 6 The Berry pseudorotation mechanism.

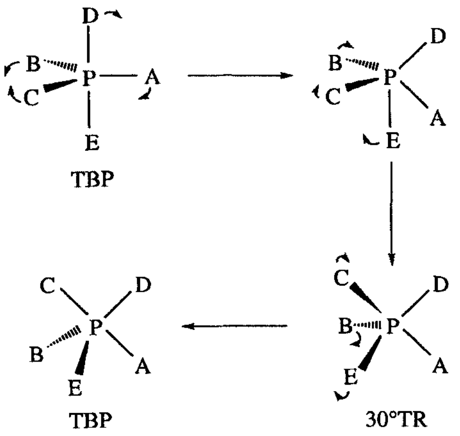


FIGURE 7 The turnstile mechanism.

C which initially decreases the turnstile mechanism but increases in the Berry mechanism.

Since the distortion of non-metalated phosphoranes in the solid-state consistently lies along the Berry coordinate,[10] it would appear likely that this mechanism has a lower energy profile as compared to the turnstile mechanism and is therefore the mechanism by which exchange of equatorial and axial sites takes place in solution.

Furthermore, there is some evidence for metalated phosphoranes also exhibiting fluxionality in solution. In the ^{13}C NMR spectrum of compound **5**, there appears only three signals.[16] This is consistent with either a rectangular pyramidal geometry in solution, or an exchange process. Since the solid-state structure is distorted TBP, Lattman concludes the latter is the case and suggests the Berry pseudorotation mechanism is implied.

Another metalated phosphorane, $[IrCl_2(PEt_3)_2CO(PF_4)]$ **16** also appears to be fluxional about the phosphorus nucleus. No solid-state structure was obtained for this compound but the $^{31}P\{^{19}F\}$ NMR spectrum becomes broad on cooling to 190 K which Ebsworth attributes to fluxionality.[26]

Finally, while not a phosphorane, $[FeCpCO(PMe_3)(SbCl_2Me_2)]$ **17** contains a metalated pentacoordinate group 15 element. Only one methyl signal is observed in the ^1H NMR spectrum and Malisch cites rapid pseudorotation about the antimony as the likely explanation.[27]

Therefore, since there is possible evidence for site exchange at the phosphorus of metalated phosphoranes, it would be of interest to consider the mechanism by which this exchange occurs. While the distortion of non-metalated phosphoranes is consistently observed to be along the Berry coordinate, this study indicates that is not necessarily the case for metalated phosphoranes. This is evidenced in part by the bracketed values in Table II which represent percent distortions from an RP or 30°TR back towards a TBP via the Berry mechanism or turnstile mechanism respectively. Ideally the sum of the bracketed and unbracketed numbers should be 100%, indicating the deviation follows closely along the Berry coordinate (or turnstile coordinate, as the case may be). If however, the bracketed value in the third column of Table II is greater than 100% for a particular compound, then the data does not suggest "Berry-like" distortion but rather "turnstile-like."

Among the bidentate phosphoranide structures, the distortion seems to be consistently towards an RP structure and following closely the Berry coordinate. The third column of Table II has bracketed values less than 100% for each bidentate case, with the exception of compound **3**. Furthermore, if the metal is placed in an idealized position as in the fifth column, the sum of bracketed and unbracketed percentages is equal to or extremely close to 100% in each case. This suggests that the distortion in these bidentate structures very closely follows the Berry mechanism (particularly when the additional distortion of the strained three-membered ring is eliminated). However, again the presence of the three-membered rings means that caution must be taken in interpreting these structures.

However, this is not necessarily the case for the monodentate phosphoranide structures. In the case of compound **5**, the distortion from a RP towards a TBP is greater than 100%. Consistent with this is the observation that the O-P-O angle made with the equatorial oxygens has decreased to 110.1° rather than increased. These results suggest that compound **5** is exhibiting distortion not along the Berry coordinate but rather along the turnstile mechanism. Indeed in the final column of Table II, when unit bond distances are used to calculate the percent distortion from TBP towards the 30°TR geometry and from the 30°TR back towards the TBP, the sum of the two values (10.7% and 89.7% respectively) comes very close to 100%. This again suggests very close adherence to the turnstile coordinate in the distortion of compound **5**.

As mentioned, Lattman reports only three resonances in the ^{13}C NMR spectrum for this compound, which is consistent with an exchange process in solution. However, the aforementioned calculations on the solid-state structure suggests that this exchange may indeed take place via the turnstile rather than the Berry pseudorotation mechanism.

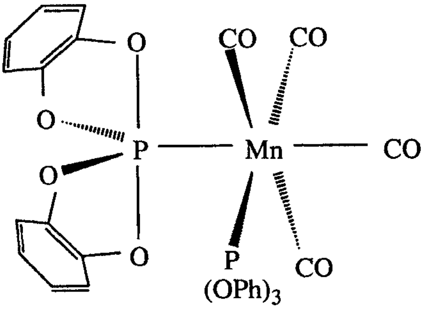
On the other hand, compound **4**, also a monodentate phosphoranide does appear to distort along the Berry coordinate. When unit bond distances are used the percent distortion from TBP to 30°TR is 35.2% and from 30°TR back to TBP is 64.8%.

For the remaining two structurally characterized monodentate metal phosphoranides, compounds **10** and **14**, it is difficult to discern based on the percent distortions of Table II, which mechanism is the preferred one.

The increased viability of the turnstile mechanism as the means of site exchange in the case of metalated phosphoranes may be explained in part by the significant steric requirements of some metal substituents bonded to the phosphorus. The importance of this factor may be seen by again considering the four monodentate phosphoranide structures.

Compound **5**, which displays distortion along the turnstile coordinate, has a very sterically demanding metal substituent bonded to the phosphorus. It is significant that the bulky phosphite ligand on the octahedral Mn is located in a cis position with respect to the phosphoranide ligand. Lattman notes that the phosphoranide and $Mn(CO)_4P(OPh)_3$ groups are "staggered" with respect to each other (the equatorial plane of the phosphorane bisects a phosphite-Mn-C angle and a C-Mn-C angle) in order to lessen the steric interactions between the Mn ligands and the phosphoranide substituents.[16] Nevertheless the phosphite group appears bulky enough to disallow the opening of the B-P-C equatorial angle in the phosphorane as required by the Berry mechanism. Instead the angle closes down and the structure follows the turnstile mechanism.

This may be contrasted with compound **4**, which shares the same phosphoranide



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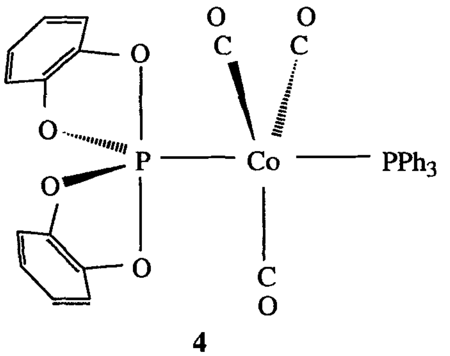

4

group as compound **5** and yet distorts instead along the Berry coordinate. Again this may be explained by the significantly reduced steric demands of the metal substituent in compound **4** as compared with **5**. Here, the metal stereochemistry is TBP with the phosphoranide and bulky triphenyl phosphine groups occupying the axial positions. This allows the phosphorane B-P-C equatorial angle to open up and the structure to follow the Berry coordinate as it distorts.

The remaining two monodentate phosphoranide structures contain metal substituents on the phosphorus which would appear to be intermediate between those of compounds **4** and **5** in terms of steric bulk. This is in keeping with the distortion in these compounds not clearly following either the Berry or the turnstile mechanism. It should be noted however that in both cases the B-P-C equatorial angle does decrease (as with compound **5**) consistent with the turnstile mechanism. In the case of compound **10**, Lattman notes that this angular contraction is due to the steric bulk of the triphenyl phosphine ligand on the platinum.[21] The significance of the steric demands of this ligand is enhanced when one notes that the coordination plane of the platinum lies very close to the equatorial plane of the phosphorane, causing this phosphine to eclipse the two equatorial substituents. The stereochemistry of compound **14** is very similar, with an η^2-$Ph_2PCH_2PPh_2$ replacing the PPh_3 and a chloride on the platinum. Again this results in the closing of the B-P-C angle.

CONCLUSIONS

Those metalated phosphoranes which have been characterized by X-ray crystallography thus far, exhibit a marked preference for the trigonal bipyramidal geometry over the square pyramidal. This preference is even more notable when compared to non-metalated phosphoranes. It may be that this is due to π-donor abilities of the metallic substituents which causes them to prefer the equatorial site of a TBP.

Furthermore, while like non-metalated phosphoranes, the metalated examples generally tend to distort along the Berry pseudorotation coordinate, there are examples of metalated phosphoranes which exhibit distortion along the turnstile coordinate. This may suggest that due to the steric demands of the metallic substituent, the turnstile mechanism is the means by which some metalated phosphoranes undergo pseudorotation in solution.

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