Metal-Assisted Pyramidal Inversion in Metal–Phosphido Complexes

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The first systematic theoretical treatment of metal-assisted pyramidal inversion in metal–phosphido complexes is presented. We find that two effects dominate inversion barrier trends. The first effect, which is most important in early transition metal complexes, involves stabilization of the planar form through ligand-to-metal π bonding. The second effect, seen in middle and late transition metal systems, can be described as inductive destabilization of the pyramidal ground state. Both of these effects lower the inversion barriers relative to those found in PR_3 systems (R = alkyl group).

Introduction

The energetics of pyramidal inversion have been of interest to chemists since ammonia inversion was discovered in 1934.[1] Ammonia exhibits a barrier to inversion of only 6 kcal/mol, which is low enough for the process to occur rapidly at room temperature. In an analogous fashion, inversion occurs in substituted amines and phosphines, and extensive experimental and theoretical studies have focused on inversion in many of these compounds.[2-4] One characteristic of substituted amines and phosphines is that the barrier to pyramidal inversion in these systems increases as the electronegativity of the substituents increases. Thus, trifluoro-amine exhibits more than a 10-fold increase in its inversion barrier relative to ammonia.[4b] In simple AX_3 systems, this effect is well-known[4b-d] to be related to a second-order Jahn–Teller distortion arising from mixing of the HOMO and the LUMO in the planar D_{3h} transition states. Highly electronegative substituents stabilize the a_1 LUMO more that the a_2'' HOMO, which reduces the HOMO–LUMO gap and increases the degree of HOMO–LUMO mixing. This stabilizes the pyramidal form. Similar arguments can be made if the electronegativity of the central atom is reduced.[2b-d] Thus, phosphines generally have much greater barriers than the corresponding amines.

In general, the only inversion barriers which have been experimentally determined are those in which the barriers are small (such as the 6 kcal/mol barrier of ammonia) or when the invertomers have different physical properties. Therefore many of the accurately known inversion barriers have been determined theoretically, often by utilizing Hartree–Fock calculations and sometimes including electron correlation. Correlation corrections to inversion barriers are known to be small for a number of systems.[2e,5-10]

In addition to substituted amines and phosphines, pyramidal inversion also occurs at the phosphorus center in transition-metal phosphido complexes. Phosphorus most often appears in transition-metal complexes in the form of phosphine ligands, which coordinatively donate the phosphorus lone pair into an empty metal orbital. In contrast, phosphido ligands differ from the more common phosphine ligands by having only two substituents and a lone pair on the phosphorus center.

M—P with R and R substituents
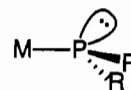
Thus metal–phosphido complexes may be viewed as substituted phosphines which have as one of their substituents a transition metal. Whereas the analogous amido complexes, NR_2^-, are typically planar with the nitrogen lone pair involved in some degree of π bonding with the metal,[11,12] phosphido complexes are characterized by a pyramidal geometry about the phosphorus, and they exhibit metal–phosphorus bond distances which are longer than the M–P bond lengths typical of the more common tertiary phosphines. The pyramidal phosphido ligand, which is nucleophilic and can be described as a PR_2^- anion, stands in contrast to the planar phosphenium ligand, which is electrophilic and can be described as a PR_2^+ cation and may be thought of as having a $d\pi$–$p\pi$ bond. Table 1 contrasts the phosphine, phosphido, and phosphenium ligands. One of the most important features of phosphido complexes, emphasized by Table 1, is the presence of an uncoordinated lone pair which causes these systems to be nucleophilic and very reactive, and a rich chemistry for compounds of this class is emerging.[13]

Table 2 lists the experimentally determined pyramidal inversion barriers for metal–phosphido complexes. The most prominent feature of these known barriers is that they are substantially

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(3) More recent work on pyramidal inversion about phosphorus, including the discovery of the unique T-shaped transition state in PF_3 and related systems, may be found in: Dixon, D. A.; Arduengo, A. J.; Fukunaga, T. *J. Am. Chem. Soc.* 1986, *108*, 2461.
(4) Work from our laboratory includes: (a) Marynick, D. S. *Chem. Phys. Lett.* 1980, *71*, 101–103. (b) Marynick, D. S. *J. Chem. Phys.* 1980, *73*, 3939–3943. (c) Marynick, D. S.; Dixon, D. A. *J. Phys. Chem.* 1982, *86*, 914–917. (d) Jolly, C. A.; Chan, F.; Marynick, D. S. *Chem. Phys. Lett.* 1990, *174*, 320–323. (e) Dixon, D. A.; Marynick, D. S. *J. Am. Chem. Soc.* 1977, *99*, 6101.
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(11) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 3.
(12) (a) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Martin, J. D.; Streib, W. E. *J. Am. Chem. Soc.* 1992, *114*, 557–570. (b) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* 1987, *109*, 905–906.

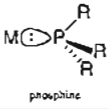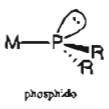**Table 1.** Three Forms of Phosphorus Coordination to a Transition Metal

PR₃	PR₂⁻	PR₂⁺
lone pair coordinated to metal	lone pair localized on P	multiple M–P bond ($d\pi$–$p\pi$)
pseudotetrahedral	pyramidal about P	planar about P
	long M–P bond length	short M–P bond length
	small M–P–R bond angle (<114°)	large M–P–R bond angle (~130°)

Table 2. Known Inversion Barriers for Metal–Phosphido Complexes (kcal/mol)

complex	inversion barrier	ref
CpW(CO)₂(PMe₃)–P(i-Pr)₂	14.4	14
CpRe(NO)(PPh₃)–PRR′	12.6–14.9	15
R = Ph, R′ = H	11.5	
R = R′ = p-C₆H₄CH₃	13.0	
Cp₂Hf(PR₂)₂ (R = Et, c-hexyl, Ph)	6	16
Cp{1,2-C₆H₄(PMePh)₂}Fe–PHPh	14.3	17

lower than the inversion barriers for the substituted phosphines described above. Whereas alkyl- and halo-substituted phosphines exhibit inversion barriers in the range of 35 kcal/mol and above, metal–phosphido complexes possess inversion barriers on the order of 11–15 kcal/mol, leading one investigator to note that the presence of a transition metal "lowers the barrier of inversion extraordinarily."[14] One complex in Table 2, Cp₂Hf(PR₂)₂, has an even lower inversion barrier of 6 kcal/mol.[16] A remarkable feature of this hafnium complex is that it contains both a phosphido and a phosphenium ligand, which, as discussed below, interconvert rapidly on the NMR time scale in solution.

X-ray structural results indicate that the M–P bond length for the planar phosphenium ligand in this complex is 2.488 Å, while the corresponding bond length for the pyramidal phosphido ligand is almost exactly 0.2 Å longer. Despite this rather significant difference in bond lengths, the presence of only one ³¹P NMR peak at room temperature indicates that the complex is fluxional with the planar and pyramidal phosphorus groups undergoing interconversion. This fluxional process provides another example of the surprising ease with which inversion occurs in phosphido complexes.

Table 3. Calculated Inversion Barriers and Geometries for Substituted Phosphines (kcal/mol, Å, deg)

	calcd	ab initio values	ref
	P(CH₃)₃		
inversion barrier	52.0	47.5	4d
P–C	1.82	1.85	22
C–P–C	100.0	98.6	22
	P(C₆H₅)₃		
inversion barrier	36.0	35.1	4d
P–C	1.83	1.83	23
C–P–C	103.5	103.0	23

Why are inversion barriers in transition-metal phosphido complexes so much lower than those generally present in substituted phosphines? This paper, the first theoretical study of inversion barriers in transition-metal phosphido complexes, addresses this issue. In order to explore a full range of metal complexes, we will use theoretical methods to examine phosphido complexes in early transition metals in high oxidation states (including Ti(IV) and Ti(III) complexes), as well as a middle transition metal with an intermediate oxidation state, namely Fe(II), and finally we will consider a model Zn complex to explore the effect of a late transition metal on the inversion process. While we restricted most of our calculations to closed-shell complexes for ease of computation, we have also studied a Ti(III) complex, Cp₂(PMe₃)TiPPh₂, which is an experimentally characterized system.[18]

Calculations

All geometry optimizations and total energy determinations were performed using the approximate molecular orbital method Partial Retention of Diatomic Differential Overlap (PRDDO).[19] PRDDO has been used effectively in a number of analyses of conformational and fluxional processes in organo-transition-metal chemistry.[20] In the PRDDO geometry optimizations, standard PRDDO basis sets were employed with two exceptions. First, for the calculations on systems containing iron, we used optimized exponents for the 3d orbitals on iron which were derived from atomic optimizations of the ⁵D state of Fe²⁺ (3d⁴4s²).[21] Second, we determined the 3s and 3p exponents for phosphorus by allowing them to vary in such a way as to obtain both optimal geometries and reasonable inversion barriers in simple phosphines. This was necessary since the built-in PRDDO constraint that the s and p exponents be equal tends to result in barriers that are too high. As a result, the 3s and 3p exponents for phosphorus were set to 1.8, slightly smaller than the standard value of 1.9. Table 3 illustrates that our calculated inversion barriers and geometries for P(CH₃)₃ and P(C₆H₅)₃ are reasonable.

Having determined appropriate phosphorus exponents for these systems, we next performed extensive geometry optimizations of all structures.

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(20) For example, see: (a) Rogers, J. R.; Kwon, O.; Marynick, D. S. *Organometallics* **1991**, *10*, 2816–2823. (b) Lawless, M. S.; Marynick, D. S. *Organometallics* **1991**, *10*, 543–545. (c) Lawless, M. S.; Marynick, D. S. *Inorg. Chem.* **1991**, *30*, 3547–3551. (d) Lawless, M. S.; Marynick, D. S. *J. Am. Chem. Soc.* **1991**, *113*, 7513–7521.

(21) The 3d exponents and contraction coefficients which we used for iron were as follows: 3d exponent = 3.091 40 with contraction coefficient of 0.782 998; 3d′ exponent = 6.563 04 with contraction coefficient of 0.368 48.

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We allowed the systems complete freedom with the following exceptions: all cyclopentadienyl and phenyl rings were constrained to planarity with C–H bond distances fixed at 1.07 Å, and cyclopentadienyl rings were constrained to an η^5 bonding mode to the metal. C–C distances in cyclopentadienyl ligands were fixed at 1.3895 Å, while C–C distances in phenyl ligands were fixed at 1.3967 Å. In the titanium systems studied, Ti–Cp(centroid) distances were fixed at 2.0975 Å, and in all iron systems studied, the following constraints were maintained: Fe–CO = 1.775 Å, Fe–C–O = 180°, C–O = 1.14 Å, and Fe–Cp(centroid) = 1.725 Å. For the systems which have been structurally characterized, our optimized molecular geometries are in close agreement with the known structures. Specific comparisons will be detailed below. Many of the ground-state structures for the phosphido complexes were determined to have pyramidal geometries (i.e., local pseudo C_{3v} symmetry) about the phosphorus atom. (Electron-deficient Ti(IV) complexes serve as important exceptions to this statement, as we shall see.) In order to determine the inversion barriers for each pyramidal phosphido system, we approximated the transition-state structure by constraining the system to a planar geometry about the phosphorus atom (i.e., local pseudo D_{3h} symmetry) while allowing the rest of the molecule to relax within the constraints listed above. Since the phosphido fragment was allowed rotational freedom relative to the metal fragment when both the ground state and transition state were optimized, the inversion barriers which we report are characteristic of the full inversion-rotation surface. Although some phosphine complexes are known to undergo inversion through nonclassical transition states (e.g., PHF_2 and PF_3 invert through T-shaped transition states[3]), we do not find nonclassical transition states for these systems.

For each optimized structure, a full Mulliken population analysis was performed, along with an analysis of the degrees of bonding between the metal and the ligands.[24] This latter quantity is especially useful, since it can be thought of as the bond order between bonded atoms. For a coordinated phosphido ligand, the degrees of bonding should be close to unity, while a metal–phosphenium bond should display a bond order approaching two.

In addition to the inversion barriers, we also calculated the barriers to rotation of the phosphido groups for the Ti(IV) and Fe(II) systems that had pyramidal ground states about phosphorus. For a given complex, the rotational barrier was estimated by setting all bond lengths equal to the values determined in the ground-state optimization. Then the R–P–Ti–X dihedral angle was incremented by 10° and all other bond angles and dihedral angles were allowed to relax. The rotational barriers for Ti(IV) complexes were found to be slightly higher than the corresponding inversion barriers, while those for the Fe(II) systems were found to be substantially lower than the Fe(II) inversion barriers.

Results and Discussion

Titanium(IV)–Phosphido Complexes. We begin our analysis of metal-assisted pyramidal inversion in phosphido complexes by considering systems which contain Ti(IV), a d^0 metal. The complexes studied include Cl_3TiPR_2, $CpCl_2TiPR_2$, and $Cp_2ClTiPR_2$ (where R = H, CH_3, CF_3, or C_6H_5). The dominant feature of these systems is expected to be the interaction of the phosphorus lone pair with the metal fragment. Since a phosphido ligand can be viewed as either a two- or four-electron donor, depending upon whether or not the lone pair is coordinated to the metal, the electron count of these complexes ranges from eight, for pyramidal Cl_3TiPR_2, to eighteen, for planar $Cp_2ClTiPR_2$. Table 4 summarizes the calculated inversion barriers for these complexes, while Tables 5–7 display the important optimized geometrical parameters.

These titanium complexes all have a common feature: an excess of unoccupied acceptor orbitals which should stabilize an electron-rich substituent such as PR_2^-. Metal moieties such as Cl_3Ti and $CpCl_2Ti$ are, in fact, so electron deficient that PR_2 is expected to act as a planar phosphenium group. The planar geometry about phosphorus results in a lone pair with 100% p character which can be stabilized by ligand-to-metal π bonding, thus increasing the electron count around the metal. Indeed, with one

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Table 4. Calculated Inversion Barriers for Titanium(IV)– and Titanium(III)–Phosphido Complexes

complex	calcd inversion barrier[a]
Cl_3TiPR_2[b]	
R = H	•
R = CH_3	•
R = C_6H_5	•
R = H, C_6H_5	•
$CpCl_2TiPR_2$	
R = H	•
R = CH_3	•
R = CF_3	8.5
R = C_6H_5	•
R = H, C_6H_5	•
$Cp_2ClTiPR_2$	
R = H	6.7
R = CH_3	2.6
R = CF_3	11.0
R = C_6H_5	•
R = H, C_6H_5	•
$Cp_2[P(CH_3)_3]TiP(C_6H_5)_2$	9.0
$[Cp_2\{P(CH_3)_3\}TiP(C_6H_5)_2]^+$	•

[a] In those complexes marked with an asterisk, the planar conformation was calculated to be the ground-state structure. [b] In addition, we examined the $Cl_3TiP(CF_3)_2$ complex, which optimized to a structure in which the $P(CF_3)_2$ ligand was chelated to the metal center.

Table 5. Cl_3TiPR_2 Optimized Geometries (Å, deg, kcal/mol)[d]

	R			
	H, H	CH_3	C_6H_5	C_6H_5, H
Ti–P	2.248	2.241	2.236	2.251
Ti–Cl$_{av}$	2.195	2.204	2.207	2.200
P–R	1.387	1.822	1.805	1.800[a]
				1.386[b]
angle sum[c]	360.0	360.0	360.0	360.0

[a] P–C. [b] P–H. [c] In this and all other tables in this paper, the angle sum represents the sum of M–P–R, M–P–R', and R–P–R' angles. [d] In each case the planar conformation was calculated to be the ground-state structure.

exception, all complexes of Cl_3Ti and $CpCl_2Ti$ which we have studied are planar in the ground state. The dominant electronic feature is best illustrated by the calculated degrees of bonding for the Ti–P interactions, which are in the range of 1.57–1.73 for the planar complexes. This is clearly indicative of strong Ti–P double-bond character. The only nonplanar species found for the Cl_3Ti and $CpCl_2Ti$ systems is $CpCl_2TiP(CF_3)_2$, which is weakly pyramidal, with an inversion barrier of only 8.5 kcal/mol. This is not particularly surprising, since the strongly electron-withdrawing CF_3 groups would be expected to stabilize the pyramidal form.

As we increase the electron count around the metal, the number of acceptor orbitals on the metal is reduced, and their detailed nature (size, shape, energy) become important. For the Cp_2ClTi species, it is useful to consider how the PR_2 group would interact with the Cp_2Ti fragment. The first three orbitals of the Cp_2Ti fragment are well-known[25] and are shown as follows:

a   b   c
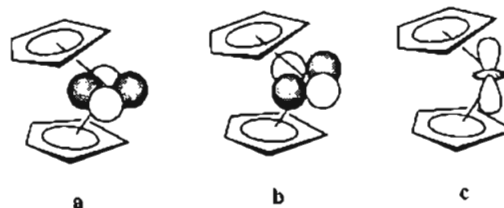
The orbitals are ranked by energy, with a the lowest. The PR_2 group bonds in the following coordination site:

(25) Albright, T. A.; Burdett, J. K.; Whangbo, M. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985; Chapter 20.

**Table 6.** CpCl$_2$TiPR$_2$ Optimized Geometries (Å, deg, kcal/mol)

	R									
	H, H		CH$_3$		CF$_3$		C$_6$H$_5$		C$_6$H$_5$, H	
	pyr	planar	pyr	planar	pyr	planar	pyr	planar	pyr	planar
Ti–P		2.240		2.240	2.464	2.272		2.254		2.246
Ti–Cl$_{av}$		2.245		2.268	2.203	2.231		2.264		2.256
P–R	1.805^a	1.384		1.819	1.892	1.904		1.814		
	1.385^b									
angle sum		360.0		360.0	298.2	360.0		360.0		360.0
ΔE		c		c	8.5			c		c

^{a} P–C. ^{b} P–H. ^{c} The planar conformation was calculated to be the ground-state structure.

Table 7. Cp$_2$ClTiPR$_2$ Optimized Geometries (Å, deg, kcal/mol)

	R									
	H		CH$_3$		CF$_3$		C$_6$H$_5$		C$_6$H$_5$, H	
	pyr	planar	pyr	planar	pyr	planar	pyr	planar	pyr	planar
Ti–P	2.468	2.282	2.470	2.277	2.505	2.325		2.295		2.280
Ti–Cl	2.351	2.414	2.351	2.433	2.302	2.384		2.425		2.426
P–R	1.390	1.381	1.832	1.830	1.910	1.922		1.827		
	1.805^a									
	1.386^b									
angle sum	305.6	360.0	318.1	360.0	316.3	360.0		360.0		360.0
ΔE	6.7		2.6		11.0			c		c

^{a} P–C. ^{b} P–H. ^{c} The planar conformation was calculated to be the ground-state structure.
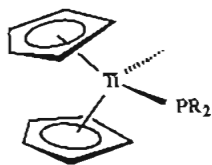
In this orientation, orbitals **b** and **c** have the appropriate local symmetry to be involved in the Ti–P and/or Ti–Cl bonds, while orbital **a** has local π symmetry with respect to the Ti–P internuclear axis. Thus, the planar forms of these species can be stabilized by π donation of the phosphorus lone pair into orbital **a**; however, the resultant complex would be an 18-electron system. Although 18-electron systems are generally the norm in transition-metal chemistry, Ti(IV) species are almost always characterized by configurations with 16 or fewer electrons. Therefore it is not surprising to find that the 16-electron, nonplanar forms of these systems are favored, although not by very much. For those species which are pyramidal, the calculated inversion barriers range from 2.6 to 11.0 kcal/mol, and are essentially determined by the electron-withdrawing ability of the phosphorus substituent. The fact that Cp$_2$Ti is still capable of participating in π bonding to phosphorus is evident when one examines Cp$_2$ClTiP(C$_6$H$_5$)$_2$, which is computed to be planar, with a calculated Ti–P degree of bonding of 1.57, very similar to the values seen for the more electron-deficient species discussed previously. The planarity of this species is likely due to two effects. First, the steric bulkiness of the phenyl substituents opens up the bond angles about phosphorus, making the phosphorus more nearly planar and thus lowering the inversion barrier. Second, the phenyl groups are capable of resonance stabilization of the p-type lone pair in the planar species, and one of the phenyl groups is oriented in the proper position to maximize π overlap of the lone pair (see Figure 1). These effects have been previously noted for simple organophosphines, where it is found that the inversion barrier of P(C$_6$H$_5$)$_3$ is 35.1 kcal/mol, while that of P(CH$_3$)$_3$ is 47.5 kcal/mol.[4d]

In each of the Ti(IV) complexes which exhibit inversion, the fact that π bonding plays an important role in stabilizing the planar transition state is illustrated by the calculated Ti–P degree of bonding, which in all cases increases from ~1.1 in the pyramidal conformation to ~1.6 in the planar conformation. In addition,
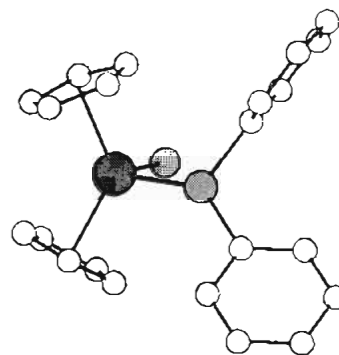
Figure 1. Planar Cp$_2$ClTiP(C$_6$H$_5$)$_2$. Hydrogens are omitted for clarity. Note that the phenyl ring located in the lower part of the figure is oriented such that π overlap with the lone pair is maximized.

the Ti–P distances are all approximately 0.2 Å longer in the pyramidal structures than in the planar transition states (see Tables 6 and 7). This corresponds almost exactly to the difference in bond lengths exhibited by the Hf complex described in the Introduction which has both phosphido and phosphenium ligands. It is evident that the generally low barriers in these systems are due to stabilization of the planar form via metal–ligand π interactions; however, the substituent effects on the inversion barriers are clearly related to the relative energies of the HOMO's in the planar and pyramidal forms. Thus, a plot of the calculated inversion barrier vs $E_{(HOMO, planar)} - E_{(HOMO, pyramidal)}$ yields an essentially perfect linear correlation (Figure 2) for CpClTiPR$_2$ (R = H, CH$_3$, CF$_3$). A similar correlation for simple alkyl-substituted phosphines has been previously reported.[4d]

Finally, we note that the fact that there is only one acceptor orbital in the Cp$_2$Ti fragment capable of ligand-to-metal π bonding dictates the rotational conformation of the PR$_2$ group. The lone pair of the PR$_2$ group must lie in the same plane as orbital **a**. Figure 3 illustrates this rotational conformation for Cp$_2$ClTiPH$_2$. This orientation is, in fact, commonly observed in these species. For example, in Cp$_2$Hf(PEt$_2$)$_2$, described in the Introduction, the alignment of a lone pair of electrons on one of the phosphorus atoms in the HfP$_2$ plane maximizes the overlap of the lone pair with the analogous orbital on Hf(IV), affording substantial π bonding.[16] Barriers to PR$_2$ rotation were calculated for all of the Ti(IV) pyramidal species and are compared to the inversion
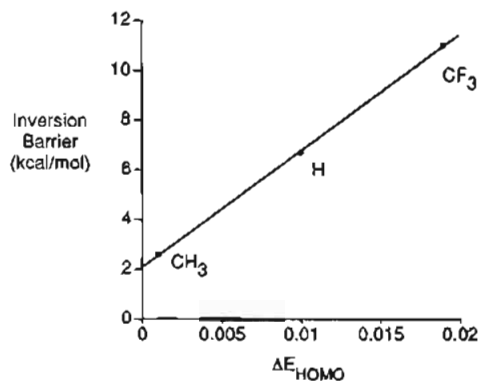
Figure 2. Calculated inversion barriers as a function of $E_{(HOMO, planar)} - E_{(HOMO, pyramidal)}$ for CpClTiPR$_2$ (R = H, CH$_3$, CF$_3$).

(a)

(b)
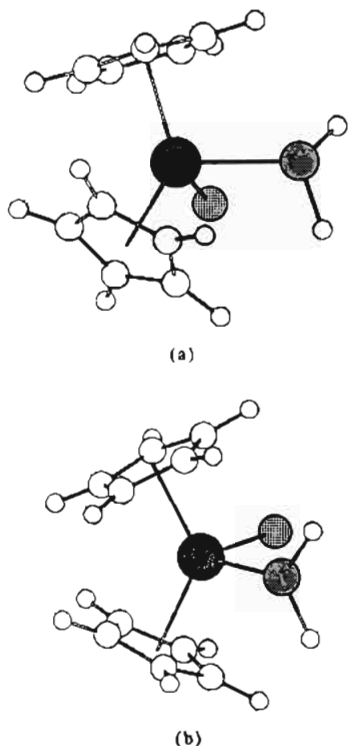
Figure 3. (a) Pyramidal Cp$_2$ClTiPH$_2$. (b) Planar Cp$_2$ClTiPH$_2$.

Table 8. Comparison of Inversion Barriers and Rotational Barriers in Pyramidal Ti(IV)–Phosphido Complexes

Ti(IV) complex	inversion barrier (kcal/mol)	rotational barrier (kcal/mol)
CpCl$_2$TiP(CF$_3$)$_2$	8.5	14.7
Cp$_2$ClTiPH$_2$	6.7	8.8
Cp$_2$ClTiP(CH$_3$)$_2$	2.6	11.5
Cp$_2$ClTiP(CF$_3$)$_2$	11.0	11.8

barriers in Table 8. The rotational barriers were all found to be somewhat higher than the calculated inversion barriers.[26] The fact that rotational barriers are competitive with inversion barriers suggests that even in the ground-state pyramidal structures there is some interaction between the lone pair and the empty metal orbital which becomes the acceptor orbital in the planar conformation. This interaction is further supported by the Ti–P degrees of bonding for the pyramidal ground states which are calculated to be slightly greater than unity (1.11 ± 0.05).

A Titanium(III)–Phosphido Complex. Recently the structural characterization of Cp$_2$(PMe$_3$)TiPPh$_2$, a Ti(III)–phosphido

(26) For comparison, we note that Cp(CO)$_2$WP(*t*-Bu)$_2$, which is planar about the P, has a rotational barrier of 10.3 kcal/mol: Jörg. K.; Malisch, W.; Reich, W.; Meyer, A.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1986,** 25, 92–93.

Table 9. Comparison of Calculated and Observed geometries for Cp$_2$(PMe$_3$)TiPPh$_2$

	exptl[a]	pyramidal	planar
Ti–PPh$_2$	2.681	2.603	2.445
Ti–PMe$_3$	2.6363	2.657	2.656
Ti–Cp(centroid)		2.119	2.158
Ti–C$_{Cp}$(mean)	2.400	2.420	2.455
P–C(Me)	1.834–1.867	1.828–1.830	1.828–1.833
P–C(Pb)	1.858–1.867	1.827–1.835	1.812–1.828
P–Ti–P	85.9	89.5	86.8
Ti–P–C(Me)	112.1	111.1	113.4
	118.9	114.2	117.0
	119.7	116.4	117.5
Ti–P–C(Ph)	111.6	116.3	119.5
	114.3	116.3	119.7
C(Ph)–P–C(Ph)	98.8	102.9	106.0
C(Me)–P–C(Me)	100.5–101.3	102.0–102.9	101.9–102.5

[a] Reference 18.

Table 10. Calculated Inversion Barriers for Iron(II) Complexes (kcal/mol)

complex	calcd inversion barrier
Cp(CO)$_2$FePR$_2$	17.8
R = H	20.5
R = CF$_3$	23.0
R = C$_6$H$_5$	15.8
R = H, C$_6$H$_5$	16.4
Cp{P(CH$_3$)$_3$}$_2$FePH(C$_6$H$_5$)	13.0
CpZnPH$_2$	24.5
Cl(CO)$_2$ZnPH$_2$	28.6

complex, was reported, representing the first structural study of a mononuclear titanium–phosphido system.[18] This complex is interesting in that it exhibits a pyramidal diphenylphosphido ligand, though no inversion barrier was reported. We optimized the pyramidal ground state and the planar transition state of this complex using the UHF formalism within PRDDO. Results of this optimization, reported in Table 9, depict a ground state in remarkable agreement with the crystallographically determined structure.

In contrast to the Ti(IV) complexes with P(C$_6$H$_5$)$_2$ described above, which are all planar, the inversion barrier of this species was calculated to be 9.0 kcal/mol. When the phosphido group is pyramidal and donates two electrons, Cp$_2$(PMe$_3$)TiPPh$_2$ can be viewed as a 17-electron complex. The π accepting orbital (orbital a above) is half-occupied, and the π accepting ability of Ti is therefore reduced. This is clearly reflected in the Ti–P degree of bonding for the planar form, which is 1.11, compared to ~1.6 for similar Ti(IV) species. Thus by adopting a pyramidal conformation about the phosphorus, this complex avoids a 19-electron configuration and exhibits a barrier to inversion. In order to confirm this interpretation, we determined the ground-state conformation for the analogous Ti(IV) cation, Cp$_2$(PMe$_3$)TiPPh$_2$$^+$, and found, as expected, a planar conformation with no inversion barrier.

Iron(II)–Phosphido Complexes. We next examined a series of Fe(II)–phosphido complexes, and their calculated inversion barriers are reported in Table 10. The Fe(II) complexes are all pyramidal in their ground states and possess inversion barriers in the range of 13–23 kcal/mol, slightly higher than those found in the titanium systems but still significantly lower than found in alkylphosphines. The experimentally known[17] inversion barrier of 14.3 kcal/mol for Cp{1,2-C$_6$H$_4$(PMePh)$_2$}Fe–PHPh is practically identical to our calculated value of 13.0 kcal/mol for the analogous Cp{P(CH$_3$)$_3$}$_2$Fe–PHPh system. One of these compounds has been crystallographically characterized, and Table 11 demonstrates that the PRDDO-optimized geometry is in close

(27) (a) Barrow, M. J.; Sim, G. A.; Dobbie, R. C.; Mason, P. R. *J. Organomet. Chem.* **1974,** 69, C4–C6. (b) Barrow, M. J.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1975,** 291–295.

Table 11. Comparison of Calculated and Observed Geometries of $Cp(CO)_2FeP(CF_3)_2$ (Å, deg)

	calcd	obsd[a]
Fe–P	2.286	2.265
P–R[c]	1.910	1.878
Fe–C(Cp)	2.091[b]	2.097[c]
Fe–C(carbonyl)	1.775[b]	1.768[c]
C–O	1.140[b]	1.138[c]
OC–Fe–CO	93.6	94.3
Fe–P–C[c]	103.1	107.4
C–P–C	95.9	94.5

[a] Reference 27. [b] These distances were fixed in the PRDDO optimization. [c] Average values.

agreement with the known structure. Whereas the presence of one or more energetically accessible π acceptor orbitals resulted in the extremely low inversion barriers, or even planar ground states, found in the electron-deficient Ti(IV) systems, two observations make it clear that electronic stabilization of the planar lone pair is not the dominant factor in these systems. First, the Fe–P bond length does not decrease substantially in the planar transition states of these systems. This can be seen in Table 12 which compares the important geometrical parameters for the series of complexes $(Cp)(CO)_2FePR_2$ (R = H, CH₃, CF₃, C₆H₅). As was pointed out previously, planar phosphenium complexes tend to have M–P bonds approximately 0.2 Å shorter than pyramidal phosphido complexes when M = Ti or Hf, and since the Fe–P bond length is essentially the same in both the pyramidal and planar conformations, metal–ligand π bonding does not appear to be important. A second observation which discounts electronic stabilization in the Fe(II) complexes concerns the Fe–P degrees of bonding. In stark contrast to the titanium systems, the Fe–P degrees of bonding are actually about 11% *smaller* in the planar transition states than in the pyramidal ground states. These trends are not surprising in light of the fact that each of these Fe(II) complexes is an eighteen-electron system if PR₂ is pyramidal. Therefore, stabilization of the planar lone pair by forward donation cannot occur since there exist no low-lying acceptor orbitals in eighteen-electron systems. In fact, a detailed analysis of the relevant orbitals in $Cp(CO)_2FePH_2$ demonstrates that electronic effects of the type seen in the titanium systems are not important here.
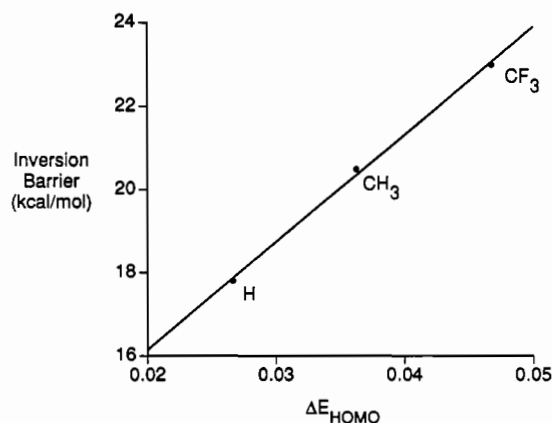
Could a fluxional cyclopentadienyl ring be assisting in the stabilization of the planar transition state? Since Cp rings are known to exhibit fluxional hapticity, or ring slippage, in a number of systems, we considered the possibility that the transition state might involve an η^3-cyclopentadienyl ligand, formally donating only four electrons and thus allowing for stabilization of the phosphorus lone pair via forward donation into an empty metal orbital. We did this by optimizing $(\eta^3-Cp)(CO)_2FePH_2$, while constraining it to planarity about P. Since this structure optimized to a conformation with the Cp bound in an η^5 fashion, we concluded that fluxional hapticity of the Cp is not an important contribution to the lower inversion barrier in these species.

Before addressing the issue of inversion barrier lowering in Fe(II) systems, let us consider the effect of the alkyl substituents on the phosphorus atom. Substituent effects on the calculated

Figure 4. Calculated inversion barriers as a function of $E_{(HOMO, planar)} - E_{(HOMO, pyramidal)}$ for $Cp(CO)_2FePR_2$ (R = H, CH₃, CF₃).

inversion barriers are clearly visible and again correlate linearly with the energy differences between the HOMOs in the planar and pyramidal forms (Figure 4) for R = H, CH₃, and CF₃. However, this correlation does not hold for R = phenyl, which has the lowest inversion barrier in the series. It is likely that the same two phenomena contribute to this substituent effect that we saw previously: namely, the bulkiness of the phenyl group and the resonance stabilization of the lone pair. The bulkiness of the phenyl groups is reflected in the sum of the three angles around phosphorus, which is significantly greater for the phenyl derivative than for any other derivative in this system (Table 12).

To further probe the nature of the iron substituent effect, we have done additional calculations on a model system, $CpZnPH_2$. This species is similar to the iron systems in that the metal is formally in the +2 oxidation state; however, the bonding in the zinc system is expected to be much more covalent than that of the iron species. The calculated inversion barrier is considerably larger (25 kcal/mol). A comparison of the population analyses and HOMO eigenvalues of $Cp(CO)_2FePH_2$ and $CpZnPH_2$ is presented in Table 13.

It is clear from the Mulliken charges that the bonding in $CpZnPH_2$ is considerably more covalent than in $Cp(CO)_2FePH_2$. Additionally, the M–P degrees of bonding are about 1.0 for Zn–P but significantly less for Fe–P, as expected for a more ionic system. It is also clear that the d orbital occupancies are not changing significantly between the planar and pyramidal forms for either complex. However, the eigenvalues of the highest occupied molecular orbitals change significantly, and the change is greater for the pyramidal form than the planar geometry. (For comparison, we note that the HOMO eigenvalues of C_{3v} and D_{3h} PH₃ are –0.309 and –0.230 au, respectively.) These data are completely consistent with an explanation based on inductive effects. The more electropositive iron substituent inductively destabilizes the HOMO in the pyramidal form. This raises the HOMO eigenvalue and lowers the barrier. A similar, but smaller, effect is seen on the HOMO of the planar form. This is expected, since the HOMO of the planar form is essentially a pure p orbital, which is much less susceptible to inductive stabilization or

Table 12. $Cp(CO)_2FePR_2$ Optimized Geometries[a] (Å, deg, kcal/mol)

	R									
	H, H		CH₃		CF₃		C₆H₅		C₆H₅, H	
	pyr	planar	pyr	planar	pyr	planar	pyr	planar	pyr	planar
Fe–P	2.282	2.274	2.283	2.260	2.286	2.283	2.285	2.270	2.281	2.268
P–R	1.400	1.393	1.846	1.835	1.910	1.887	1.845	1.820	1.824	1.800
angle sum[b]	308.5	360.0	311.4	360.0	302.0	360.0	320.8	360.0	312.3	360.0
ΔE	17.8		20.5		23.0		15.8		16.4	

[a] The following geometrical parameters were fixed: Fe–Cp(centroid) = 1.725, Fe–CO = 1.775, C–C(centroid) = 1.3895, Fe–C(Cp) = 2.0911, Fe–C–O = 180°, C–H = 1.07, C–O = 1.140. The cyclopentadienyl ligand was kept planar. [b] This represents the sum of the three angles Fe–P–R, Fe–P–R′, and R–P–R′.

Table 13. Comparison of the Electronic Properties of $Cp(CO)_2FePH_2$ and $CpZnPH_2$

	$Cp(CO)_2FePH_2$ pyramidal	$Cp(CO)_2FePH_2$ planar	$CpZnPH_2$ pyramidal	$CpZnPH_2$ planar
Mulliken charges				
M	1.149	1.193	0.607	0.666
Cp	−0.587	−0.573	−0.337	−0.357
P	−0.348	−0.408	−0.172	−0.287
PH_2	−0.501	−0.458	−0.269	−0.309
M–P degree of bonding	0.695	0.588	1.006	1.043
sum of d orbital occupancies	5.901	5.921	9.994	9.994
HOMO eigenvalues	−0.204	−0.177	−0.242	−0.193

Table 14. Comparison of Energetics for $Cp(CO)_2FePR_2$ (kcal/mol)

	inversion barrier	rotation barrier
$Cp(CO)_2FePH_2$	17.8	2.1
$Cp(CO)_2FeP(CH_3)_2$	20.5	4.5
$Cp(CO)_2FeP(CF_3)_2$	23.0	6.1
$Cp(CO)_2FeP(C_6H_5)_2$	15.8	8.6
$Cp(CO)_2FePHPh$	16.4	3.3

destabilization. Indeed, $Cp(CO)_2FePH_2$, $CpZnPH_2$, and PH_3 show a near linear correlation between the eigenvalue of the HOMO in the pyramidal form and the inversion barrier.

Finally, we compared the energetics of pyramidal inversion to those of rotation of the phosphido ligand. Rotational barriers for $Cp(CO)_2FePR_2$, given in Table 14, are all substantially lower than the corresponding inversion barriers. In fact, only in the case of the most bulky substituent, R = C_6H_5, is the rotation barrier more than half the inversion barrier. This is another contrast with the titanium systems whose rotational barriers were slightly higher than the inversion barriers. Because there is no donation of the phosphorus lone pair into an empty metal orbital in the iron systems, rotational orientation is not as important, and barriers to rotation are quite small.

Conclusions

We have examined points along the inversion-rotation surfaces of a number of early, middle, and late transition metal phosphido complexes in order to understand the origin of their reduced inversion barriers relative to substituted phosphines. Two effects dominate inversion barrier trends in these transition metal complexes and contribute to the lower barriers. The first effect involves stabilization of the planar form through metal–ligand π bonding. The second effect incorporates inductive destabilization of the pyramidal ground state. The first electronic effect dominates in the electron-deficient early transition metal systems, while the second inductive effect serves to lower the barriers in middle and late transition metal systems. Thus we found that in the Ti(IV) complexes, 8–12 electron systems should exhibit planar phosphenium ligands in their ground states due to metal–ligand π bonding, while 16-electron systems should possess pyramidal phosphido ligands (except for those cases where the phosphido substituent is bulky and/or when it stabilizes the planar lone pair through resonance) with very low inversion barriers. Furthermore, 17- and 18-electron systems are expected to be nonplanar because of the lack of a suitable acceptor orbital to stabilize the planar lone pair. However, 18-electron systems still exhibit low inversion barriers, and this was found to be due to purely inductive effects. These trends are particularly evident when comparing the inversion barriers of Ti(IV) complexes (0–11 kcal/mol) with Fe(II) complexes (16–23 kcal/mol) and $CpZnPH_2$ (25 kcal/mol).