

Computational Evidence of the Importance of Substituent Bulk on Agostic Interactions in $\text{Ir}(\text{H})_2(\text{P}^t\text{Bu}_2\text{Ph})_2^+$

Gregori Ujaque, Alan C. Cooper, Feliu Maseras,* Odile Eisenstein,* and Kenneth G. Caulton*

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405-4001, and LSDSMS UMR 5636, Université de Montpellier 2, 34095 Montpellier Cedex 5, France

Received August 25, 1997

Abstract: While $\text{Ir}(\text{H})_2(\text{P}^t\text{Bu}_2\text{Ph})_2^+$ has been shown experimentally to have two agostic ^tBu groups, ab initio B3LYP calculations on $\text{IrH}_2[\text{P}(\text{Et})\text{H}_2]_2^+$ show that the CH_3 group of the phosphine ligand does not form any agostic bond with the strongly electron-deficient (14-valence electron) metal. In contrast, integrated molecular mechanics/molecular orbital (IMOMM) calculations on the full complex $\text{Ir}(\text{H})_2(\text{P}^t\text{Bu}_2\text{Ph})_2^+$ duplicate the experimentally observed agostic interaction. Thus, at least in this case, the agostic interaction is due in part to the trapping of a C–H bond in the vicinity of the metal by the steric effects of the other groups of the bulky phosphine. This necessity of steric “constraint” identifies an additional influential factor for the agostic interaction.

Introduction

Following their initial discovery¹ and subsequent categorization,² agostic interactions have been found to be extremely common, provided a metal has a low-lying empty valence orbital. In fact, there has been little scrutiny of what factors can assist in stabilizing agostic interactions. Every complex with an empty coordination site is a candidate for an agostic bond. It is also implicit that such a bond is always due to an attraction between the electron-deficient metal center and the C–H bond acting as a weak Lewis base. Experimental³ and computational⁴ studies have revealed interaction energies in the range 10–15 kcal/mol. In addition, the few well-studied cases which show that the agostic bond forms at the expense of a significant geometrical distortion within the ligand^{5,6} (e.g., bending at CH_2 and lengthening of C–H) were important landmarks. These results suggested that the agostic bond could be associated with sufficient stabilization energy to overcome

geometrical distortions⁷ at carbon far larger than the history of carbon chemistry could have suggested (e.g., 90° angle at acyclic four-coordinate C). Thus, the occurrence of an empty site and the presence of a C–H bond in “reasonable proximity” to the empty site could be thought to be the necessary and sufficient conditions for occurrence of an agostic interaction. In the case where no agostic bonds were observed, it was thought that the main reason was due to ancillary ligands decreasing the acidity of the metal center.

The present study suggests a more subtle situation. When the attraction between the metal and the C–H bond is not sufficiently strong to overcome the intrinsic conformation preference of the ligand bearing the potentially agostic group, substituents within this group can be “tuned” to facilitate agostic bonding.

In the course of our efforts to synthesize and characterize transition metal complexes of Ru(II) and Ir(III), d^6 configuration, with two empty metal valence orbitals (“14-electron complexes”), we discovered unprecedented examples where one substituent R in each phosphine of $\text{L}_n\text{M}(\text{PR}'_2\text{R})_2^+$ donates to the empty orbitals (Figure 1a): the Lewis acidity of the 14-electron complex is high enough to elicit nucleophilic behavior from two methyl hydrogens.⁸

As we began to discover other examples of such “double agostic” complexes, we were able to establish the relative ability of ^tBu , cyclohexyl, phenyl, and methyl as agostic donors. An aspect of formation of agostic interactions in $\text{M}(\text{PR}'_2\text{R})$ which has not been adequately explored is the influence of steric pressure of the two pendent groups R' on the ability of R to donate to an empty metal orbital. Despite accumulation of considerable experimental data on a range of doubly agostic complexes, the inevitable simultaneous introduction of several changes at a time makes it difficult to isolate single factors which

(1) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, 250, 395.

(2) (a) Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, 36, 1. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, 28, 299.

(3) (a) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, 112, 1566. (b) Crabtree, R. H. *Chem. Rev. (Washington, D.C.)* **1985**, 85, 245. (c) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, 7, 2429. (d) Zhang, K.; Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Hoff, C. D.; Kubat-Martin, K. A.; Barnhart, D.; Kubas, G. J. *J. Am. Chem. Soc.* **1991**, 113, 9170.

(4) (a) Lohrenz, J. C. W.; Woo, T. K.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, 117, 12793. (b) Margl, P.; Lohrenz, J. C. W.; Ziegler, T.; Blöchl, P. E. *J. Am. Chem. Soc.* **1996**, 118, 4434. (c) Kawamura-Kuribayashi, H.; Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1992**, 114, 2359. (d) Thomas, J. L. C.; Hall, M. B. *Organometallics* **1997**, 16, 2318. (e) Musaev, D. G.; Froese, R. D. J.; Svensson, M.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, 119, 367. (f) Han, Y.; Deng, L.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, 119, 5939. (g) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, 119, 6177.

(5) Dawoodi, Z.; Green, M. L. H.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1982**, 802.

(6) Cracknell, R. B.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1005.

(7) (a) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, 112, 1289. (b) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, 32, 325.

(8) Cooper, A. C.; Streib, W. E.; Eisenstein, O. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, 119, 9069.

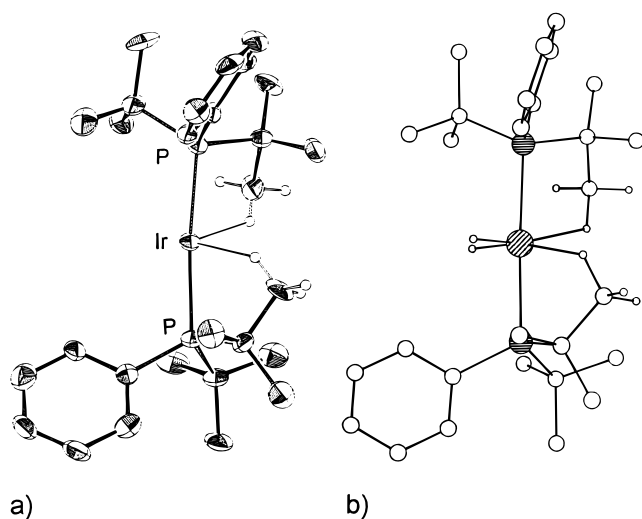


Figure 1. (a) Observed structure of $\text{Ir}(\text{H})_2(\text{PtBu}_2\text{Ph})_2^+$; hydrogens were not located by X-ray diffraction, and the agostic hydrogens shown were placed in idealized positions, assuming staggered conformations. (b) Optimized geometry of the same cation from the IMOMM (B3LYP:MM3) method.

influence agostic donation. This is an ideal situation to combine emerging experimental results with several “computational experiments”, using integrated molecular orbital and molecular mechanics (IMOMM) methodology.^{9,10,11} This is a recently proposed⁹ hybrid method that uses quantum mechanics and molecular mechanics descriptions for different parts of the same system, and it has been proven to be successful in the quantification of electronic and steric effects in a number of transition metal systems.¹⁰ In the present case, the IMOMM method enables a deeper understanding of the subtle interplay of electronic and steric factors in the occurrence of an agostic interaction.

Computational Details

Pure quantum mechanics calculations on the model systems $\text{Ir}(\text{H})_2[\text{P}(\text{Et})\text{H}_2]_2^+$ and $\text{Ir}(\text{H})_2[\text{P}(\text{Et})\text{H}(\text{CH}_2\text{CH}_2)]_2^+$ are carried out with Gaussian 94.¹² Two different basis sets, I and II, are used. In both of them, quasirelativistic effective core potentials replace the 60-electron core of the Ir atom¹³ and the 10-electron core of the P atoms.¹⁴ Basis set I is valence double- ζ for all atoms,^{14,15} with the addition of a polarization

(9) Maseras, F.; Morokuma, K. *J. Comput. Chem.* **1995**, *9*, 1170.

(10) (a) Matsubara, T.; Maseras, F.; Koga, N.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 2573. (b) Ujaque, G.; Maseras, F.; Lledos, A. *Theor. Chim. Acta* **1996**, *94*, 67. (c) Barea, G.; Maseras, F.; Jean, Y.; Lledos, A. *Inorg. Chem.* **1996**, *35*, 6401. (d) Wakatsuki, Y.; Koga, N.; Werner, H.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 360. (e) Ogasawara, M.; Maseras, F.; Gallego-Planas, N.; Kawamura, K.; Ito, K.; Toyota, K.; Streib, W. E.; Komiya, S.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1997**, *16*, 1979. (f) Ujaque, G.; Maseras, F.; Eisenstein, O. *Theor. Chem. Acc.* **1997**, *96*, 146.

(11) (a) Svensson, M.; Humbel, S.; Morokuma, K. *J. Chem. Phys.* **1996**, *105*, 3654. (b) Matsubara, T.; Sieber, S.; Morokuma, K. *Int. J. Quantum Chem.* **1996**, *60*, 1101.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, Pennsylvania, 1995.

(13) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(14) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(15) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.

d shell on phosphorus atoms.¹⁶ Basis set II corresponds to a further extension including polarization shells on carbon and hydrogen atoms¹⁷ involved in the agostic interaction.

IMOMM calculations were performed on the real system $\text{Ir}(\text{H})_2[\text{P}^i\text{-Bu}_2\text{Ph}]_2^+$ with a program built from modified versions of two standard programs: Gaussian 92/DFT¹⁸ for the quantum mechanics (QM) part and mm3(92)¹⁹ for the molecular mechanics (MM) part. The QM part was always carried out on the $\text{Ir}(\text{H})_2[\text{P}(\text{Et})\text{H}_2]_2^+$ system with the computational level described in the previous paragraph. For the MM part, the MM3(92) force field was used.²⁰ van der Waals parameters for the iridium atom are taken from the UFF force field,²¹ and torsional contributions involving dihedral angles with the metal atom in the terminal position are set to zero. All geometrical parameters are optimized without symmetry restrictions except the bond distances between the QM and MM regions of the molecules. The frozen values are 1.420 (P–H), 1.112 (C–H), 1.101 Å in the QM part and 1.843 (P–C) and 1.5247 (C–C) in the MM part. The starting point of all geometry optimizations was the X-ray structure of one of the three independent molecules of $\text{Ir}(\text{H})_2(\text{P}^i\text{Bu}_2\text{Ph})_2^+$ present in the crystal unit cell. Therefore all comparisons with experiment are done with this particular structure, which presents only conformational differences with respect to the other two.

Results

The complex $\text{Ir}(\text{H})_2(\text{P}^i\text{Bu}_2\text{Ph})_2^+$ is a remarkable candidate for an agostic bond. It is a 14-electron species with two empty orbitals, a positive charge to increase the Lewis acidic character of the metal, numerous CH bonds to donate to the electron-deficient Ir, and no π -donor ligand to stabilize the high electron deficiency. It is thus not surprising that the crystal structure of the complex reveals two agostic bonds. The crystal structure shows three independent molecules in the unit cell which differ by orientation within the phosphines. The three molecules present similar agostic structures, and only one of them was computed and will be analyzed.

To theoretically characterize the agostic interaction, we initially calculated, at the DFT Becke3LYP level, a highly simplified system in which we kept only those atoms involved in the agostic interaction and the groups around the metal which are necessary to properly describe the ligand field. The calculations were thus carried out on $\text{Ir}(\text{H})_2(\text{PH}_2\text{Et})_2^+$. The results of the full optimization with no symmetry constraints are shown in Figure 2 and Table 1. The two phosphine ligands behave very similarly, so discussion will be limited to one of them. Satisfactorily, the geometry of the atoms directly bonded to Ir is identical with that of an even simpler model, $\text{Ir}(\text{H})_2(\text{PH}_3)_2^+$, which confirms that the saw-horse shape of this complex is determined by the bonds to the metal (Ir–P and Ir–hydride) and the d^6 configuration at the metal and not by the presence of the agostic bonds.⁸ The two empty sites are clearly apparent trans to the hydride ligands. What is highly surprising is the *lack* of any agostic interaction with the terminal CH bond of CH_3 in this purely ab initio calculation. This is evident from several structural parameters. The shortest $\text{Ir}\cdots\text{C}$

(16) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(17) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92/DFT*; Gaussian, Inc.: Pittsburgh, Pennsylvania, 1993.

(19) Allinger, N. L. *mm3(92)*; QCPE: Bloomington, IN, 1992.

(20) (a) Allinger, N. L.; Yuh, Y. H.; Lii, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 8551. (b) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566. (c) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.

(21) Rappé, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024.

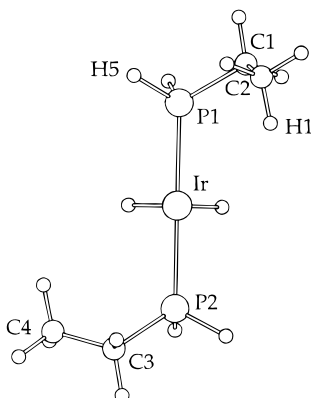


Figure 2. Optimized geometry (B3LYP) of the model complex $\text{Ir}(\text{H})_2[\text{P}(\text{Et})\text{H}_2]_2^+$. The H–Ir–H bond angle is 87.5°.

Table 1. Selected Geometrical Parameters (Å and deg) from Pure QM Calculations on the Model Complex $\text{Ir}(\text{H})_2[\text{P}(\text{Et})\text{H}_2]_2^+$ and IMOMM Calculations on the Full Complex $\text{Ir}(\text{H})_2(\text{P}^i\text{Bu}_2\text{Ph})_2^{+a}$

	exp	QM/I	QM/II	IMOMM/I	IMOMM/II
Ir–H1		3.511	3.476	2.446	2.379
Ir–C2	2.811	4.000	3.976	3.138	3.083
C2–H1		1.097	1.097	1.109	1.111
C–H (av) ^b		1.095	1.095	1.094	1.094
Ir–P1–C1	97.0	118.8	118.4	102.6	101.7
Ir–P1–X5 ^c	114.3	114.2	114.3	110.5	111.2
P1–C1–C2	102.7	112.6	112.3	106.8	106.2
C1–C2–H1		111.8	111.8	111.5	111.5
C2–C1–P1–Ir	29.7	58.5	57.8	31.7	31.2
Ir–C4	2.936	4.033	4.023	3.321	3.279
Ir–P2–C3	99.0	119.5	119.4	104.7	104.2

^a Results are presented from calculations with two different basis sets, I and II. X-ray results for the experimental system are also provided for comparison. Atom labeling is defined in Figure 1. ^b Average of the four non-agostic C–H bonds in the two β -methyl groups. ^c X5 corresponds to H5 in the model system, and to the α -carbon of the non-agostic ^tBu group in the real system.

distance is 4.0 Å (compared to 2.811 Å in the X-ray structure) leading to a $\text{Ir}\cdots\text{H}$ distance of 3.511 Å, which is much too long for establishing any significant interaction; this is also evident from the essentially equal distance for all CH bonds of CH_3 (1.096–1.097 Å). The structural parameters which are responsible for the longer $\text{Ir}\cdots\text{C}-\text{H}$ distance with respect to the experimental structure are the angle Ir–P1–C1 (118.8° in the calculation vs 97.0 in the experimental structure) and a twist of the C2–C1–P1–Ir dihedral angle (58.5° in place of 29.7°) which moves the CH_3 group away from the metal (0° dihedral angle corresponds to Ir–P1 eclipsing C1–C2). The P1–C1–C2 angle is also more open in the calculated structure (112.6°) than in the experimental system (102.7°) but the deviation is smaller than for the angle at P1. Bond distances are all unremarkable.

Improvements to the model were done in several ways. One H of PH_2Et was replaced by a vinyl group, as a model of the phenyl group. No changes in the optimized structure were obtained. This suggests that changes in the basicity of the phosphine ligand by introducing more carbon atoms at the phosphorus do not lead to sufficient electronic changes at the metal or at the C–H bonds to result in the occurrence of an agostic interaction. We also added polarization functions to C and H with no visible changes in the geometry (Table 1). It thus appears that, while the level of calculations seemed appropriate, these models are unable to describe the agostic interactions. These calculations, however, fail to represent the steric bulk of the phosphine ligands.

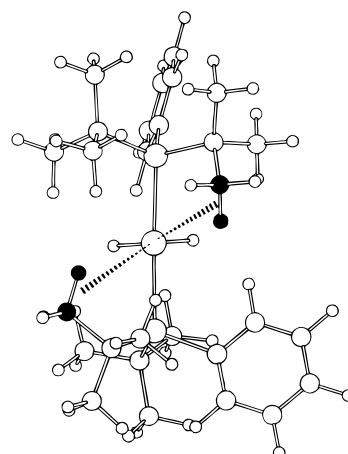


Figure 3. Optimized geometry of the complex $\text{Ir}(\text{H})_2(\text{P}^i\text{Bu}_2\text{Ph})_2^+$ with the IMOMM (B3LYP:MM3) method. The *ab initio* part is carried out on the $\text{Ir}(\text{H})_2[\text{P}(\text{Et})\text{H}_2]_2^+$ fragment with basis set I. C and H atoms involved in agostic interactions are highlighted in black. The H–Ir–H bond angle is 87.6°.

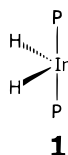
The entire character of the ligand was thus introduced in the calculations by using the IMOMM methodology. The results of the full optimization of $\text{Ir}(\text{H})_2(\text{P}^i\text{Bu}_2\text{Ph})_2^+$, starting close to the experimental structure, are shown in Figure 3 and Table 1. Figure 1b shows another view, allowing direct comparison to the experimental structure. Introduction of polarization functions on C and H of the QM part gives similar results (Table 1). The saw-horse shape around the metal is again found with no major change in the position of hydride and phosphorus atoms. The ligand conformation is very similar to the experimental one, suggesting that packing forces in the solid-state structure do not greatly modify the conformation within the phosphine ligands. The striking difference with the calculation on the model systems presented above resides in the clear formation of an agostic interaction. Discussion will be limited to one phosphine ligand. The $\text{Ir}\cdots\text{C}2$ nonbonding distance is now 3.138 Å (3.083 Å with polarization functions), which is still a bit longer than the experimental value of 2.811 Å, but is significantly shorter than the 4.0 Å distance calculated in $\text{Ir}(\text{H})_2(\text{PH}_2\text{Et})_2^+$. The corresponding $\text{Ir}\cdots\text{H}$ distance is also relatively short: 2.446 Å (2.379 Å with polarization). The structural parameter that has contributed most to the decrease of the $\text{Ir}\cdots\text{C}2-\text{H}1$ distance is the Ir–P1–C1 angle (102.6°, 101.7° with polarization), which is only 5° larger than the experimental value of 97.0°. This is a drastic reduction from the 118.8° value in $\text{Ir}(\text{H})_2(\text{PH}_2\text{Et})_2^+$. There is also a change in the Ir–P1–C1–C2 dihedral angle (31.7° vs 29.7° experimentally) accompanying the change in angles at the phosphine, showing the agostic CH_3 gets closer to the metal by rotating the C1–C2 bond toward Ir. In contrast, the angles at C1 are much less perturbed by the full implementation of all substituents in the phosphine ligand. The variation in angle goes in the right direction and the calculated P1–C1–C2 angle (106.8°, 106.2° with polarization) is no more than 4° larger than the experimental values.

Although the steric bulk of the phosphine plays a central role in constraining the agostic C–H bond in proximity to the iridium, there is a real interaction of this bond with the metal. This can be seen by comparing the computed values for the two Ir–P1–C(^tBu) angles of the same phosphine. That corresponding to the ^tBu carrying the agostic interaction, Ir–P1–C1, is smaller by 8.9° (10.5° with polarization) than that corresponding to the other ^tBu, Ir–P1–C5, again mimicking experiment. The final proof of the existence of agostic

interactions comes from the C–H distances, which are stretched to 1.109 Å (1.111 Å with polarization) and are significantly longer than the other C–H bonds of the CH₃ groups (average 1.094 Å). Other bond length variations are unremarkable.

It thus appears that a simplified representation of the phosphine ligand does not lead to a structure with agostic interactions. The presence of an empty site at the metal is not by itself sufficient to maintain a C–H in bonding proximity at the expense of unfavorable deformation of the carbon chain. A more complete representation of the ligand, incorporating intraligand nonbonded interactions, leads to a structure with agostic interactions. Since the additional groups are represented at the molecular mechanics level, the basicity of the C–H of the CH₃ terminal group is not modified. Only steric factors have been changed. The motion of a CH₃ group is clearly more limited in the bulky P^tBu₂Ph than in the model PH₂Et system. The large bulk of the phosphine thus constrains the CH₃ to a small region close to the metal, in which the Ir···C–H interaction takes place. The pendent ^tBu and Ph groups and the two geminal methyl groups are thus essential to forming the agostic ^tBu interaction in the computation and, by extension of this computational experiment, in reality.

At this point, it must be recognized that the total number of valence electrons is not sufficient to indicate the presence of an energetically low LUMO that could lead to Lewis acid character. For example, Ir(H)₂L₂⁺ has a saw-horse shape (**1**)



and an energetically low LUMO made of x^2-y^2 character (x and y pointing along the Ir–H vectors) and pointing away from the cis hydrides. The next higher empty orbital lies along the C₂ axis, but its p contribution leads to higher energy. In contrast, linear L₂Pt and R₂M (M = Zn, Hg) have a high-lying LUMO pointing along the Pt–P or M–C bonds and a next higher empty orbital made of the intrinsically high (but system-dependent) p metal orbital perpendicular to the M–P vector; they thus have only one “functional” empty orbital, and its high energy explains the absence of an agostic interaction.²² Similarly, the LUMO of a d₈ square-planar complex lies along the M–L bond vectors, where it is sterically unsuitable for agostic acceptance, despite its 16-electron count.²³

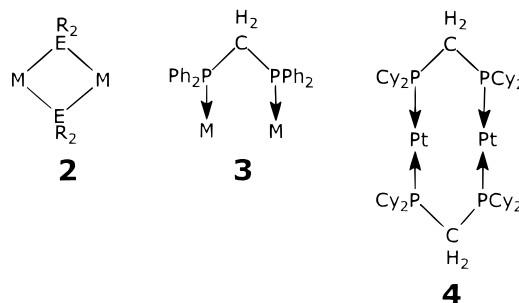
Discussion

The results reported here should be viewed in a larger context. Thorpe and Ingold have identified an influence of increasing steric bulk in R of a CR₂ group on ring formation involving this CR₂: bulky R, by increasing the angle R–C–R, favors the kinetics and thermodynamics of formation of rings, especially small rings, containing the CR₂ group.²⁴ This effect is clearly generalizable to any ER₂ group where E is a tetrahedral atom, and indeed Shaw has elaborated the idea for PR₂R'

(22) Frederic, P.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030.
(23) (a) Yao, W.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chim. Acta* **1997**, *254*, 105. (b) Braga, D.; Grepioni, F.; Tedesco, E.; Biradha, K.; Desiraju, G. *Organometallics* **1997**, *16*, 1846.

(24) Eliel, E. L.; Wilen, S. H.; Mander, L. N. In *Stereochemistry of Organic Compounds*; Wiley: New York, 1994; p 682.

ligands,²⁵ where he has been a pioneer in using bulky groups R. Bulky substituents R encourage ring closure,²⁶ bridging (see **2**), and *ortho* metalation²⁷ when R' = C₆H₅. Agostic interaction and *ortho*-metalation have been shown to be linked.²⁸ Note also that the ligand Ph₂PCH₂PPh₂ shows a distinct aversion to be bidentate to a single metal,²⁹ but is most often found bridging two metals (**3**); evidently two phenyl groups lack the bulk to



enforce formation of the four-membered ring M(η^2 -Ph₂PCH₂-PPh₂). When R = ^tBu^{30,31,32} or Cy,³³ the (bent) monomeric two-coordinate complexes Pt(η^2 -R₂PCH₂PR₂) are transients, highly reactive toward oxidative addition of a variety of substrates, ring opening and transformation to long-lived, less-reactive (linear geometry at Pt) dimers **4** occurs, where a larger ring has the phosphine bridging two metals. For sterically less-demanding groups R, four-membered-ring structures apparently do not have sufficient stability to allow their experimental generation as reactive intermediates.

A number of platinum alkyl cations with β -agostic Pt–H–C bonding have been characterized by using variable-temperature ¹H and ³¹P NMR spectroscopy.^{34,35} For these complexes, [Pt(CH₂CHRR')(L–L)]⁺ (L–L = Bu₂P(CH₂)₃PBu₂), interpretation of the chemical shifts and coupling constants suggests that the β -agostic bonding is weakest when R = R' = H, stronger for R = H, R' = ^tBu, and strongest for R = Me, R' = ^tBu.

It is possible to work with a certain class of molecules without clear recognition of the characteristics of such molecules which confer either limitations (“boundary conditions”) or benefits. This can be the case for those molecules containing at least two bulky ligands such as P^tPr₃, PCy₃, P^tBu₃, P^tBu₂R, P^tPr₂R, etc. For example, it is clearly recognized that such ligands

(25) (a) Shaw, B. L. *J. Am. Chem. Soc.* **1975**, *97*, 3856. (b) Shaw, B. L. *J. Organomet. Chem.* **1980**, *200*, 307.

(26) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972.

(27) (a) Bottomley, A. R. H.; Crocker, C.; Shaw, B. L. *J. Organomet. Chem.* **1983**, *250*, 617. (b) Mason, R.; Textor, M.; Al-Salem, N.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1976**, 292.

(28) (a) Albeniz, A. C.; Schulte, G.; Crabtree, R. H. *Organometallics* **1992**, *11*, 242. (b) Cooper, A. C.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1997**, *16*, 1974. (c) Jiménez-Cataño, R.; Hall, M. B. *Organometallics* **1996**, *15*, 1889.

(29) (a) Gao, Y.; Holah, R. G.; Hughes, A. N.; Spivak, G. J.; Havighurst, M. D.; Magnuson, V. R.; Polyakov, V. *Polyhedron* **1997**, *16*, 2797. (b) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99. (c) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191.

(30) Hofmann, P.; Unfried, G. *Chem. Ber.* **1992**, *125*, 659.

(31) Hofmann, P.; Heib, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880.

(32) Hofmann, P.; Heib, H.; Müller, G. *Z. Naturforsch.* **1987**, *B42*, 395.

(33) Notheis, U.; Hofmann, P. Private communication.

(34) Carr, N.; Mole, L.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2653. Spencer, J. L.; Mhinzi, G. S. *J. Chem. Soc., Dalton Trans.* **1995**, 3819.

(35) Appleton, T. J.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

permit isolation of five-coordinate species of Ru^{II} , Os^{II} , Rh^{III} , and Ir^{III} , even when halide-bridged dimers might confer an 18-electron configuration. We have reported³⁶ the phosphine substituent dependence of enthalpies for addition of small ligands to such species, in an attempt to establish differences among phosphines which might otherwise all be categorized as "bulky". We have also reported the ease of *ortho*-metalation of $\text{P}^i\text{Bu}_2\text{Ph}$ to Ir^{I} ,³⁷ in contrast to the rarity of *ortho*-metalation involving the smaller phosphine PMe_2Ph .³⁸ It is therefore important to recognize that using, among others, the bulky phosphines listed above can have the consequence of metal attack on normally inert C–H bonds (C–C or P–C bond scission might also³⁹ be anticipated), to give either new products or products of MD/C–H isotopic scrambling. Examples of cyclohexyl C–H oxidative addition⁴⁰ and cyclohexyl⁴¹ and *i*Pr dehydrogenation are known. A rare case of conversion of $\text{PPh}_3 + \text{C}_2\text{H}_4$ to $\text{PPh}_2(o\text{-C}_6\text{H}_4\text{Et})$ while attached to osmium proceeds by insertion of C_2H_4 into an *ortho*-metalated phosphine phenyl group.⁴² The double agostic complexes reported here are shown to rely on bulky pendent phosphine substituents to "encourage" formation of weakly bound cycles (rings). The examples of Milstein⁴³ and of Shaw⁴⁴ on oxidative addition to metals of C–C and C–H bonds within the connecting unit G in $\text{R}_2\text{P}-\text{G}-\text{PR}_2$

(36) Li, C.; Ogasawara, M.; Nolan, S. P.; Caulton, K. G. *Organometallics* **1996**, *15*, 4900.

(37) (a) Cooper, A. C.; Caulton, K. G. *Inorg. Chim. Acta* **1996**, *251*, 41. (b) Hauger, B. E.; Caulton, K. G. *J. Organomet. Chem.* **1993**, *450*, 253.

(38) Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. *J. Organomet. Chem.* **1981**, *218*, C39.

(39) Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A.; Tolosa, J. I. *Organometallics* **1997**, *16*, 1316.

(40) Arliguie, T.; Chaudret, B.; Jalon, F.; Lahoz, F. J. *J. Chem. Soc., Chem. Commun.* **1988**, 998.

(41) (a) Heitkamp, S.; Stufkens, D. J.; Vrieze, K. *J. Organomet. Chem.* **1978**, *152*, 347. (b) Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527.

(42) Desrosiers, P. J.; Cai, L.; Halpern, J. *J. Am. Chem. Soc.* **1989**, *111*, 8513.

can be attributed to this same effect. A number of the C–F oxidative additions to low-valent W involve C–F bonds of an aryl substituent on a bulky, rigid ligand.⁴⁵ In summary, it will be useful to be alert to how two of the E-substituents R' in $\text{MER}'_2\text{R}$ can influence the interaction of M with R (e.g., $\text{ER}'_2\text{R} = \text{C}(\text{SiMe}_3)_3$ or $\text{C}(\text{SiMe}_3)_2\text{H}^{46}$), as well as cases where (at least) stabilization of unusual species can result, as in the 14-electron complexes we have sought. Finally, cases where such bond-scission or agostic interactions do *not* occur (e.g., 14-electron $\text{Pt}(\text{P}^i\text{Bu}_3)_2$ or M^iBu_2 where $\text{M} = \text{Zn}$ or Hg) are equally important for what they imply about the *lack* of strong Lewis acidity as a result of linear geometry raising the energy of the LUMO with respect to a bent situation. On the computational side, the IMOMM methodology is a potent tool for evaluating the importance of steric factors in transition metal systems, where lack of parameters for metal/ligand bonding prevents use of pure molecular mechanics methods.

Acknowledgment. This work was supported by the U.S. National Science Foundation and the Université de Montpellier 2 and French CNRS, including an international NSF/CNRS (PICS) grant for US/France collaboration. F.M. thanks the CNRS for a position of research associate. G.U. thanks the Spanish DGES for financial support under project No. PB95-0639-C02-01.

JA9729894

(43) (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699. (b) Rybtchinski, B.; Vignalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1996**, *118*, 12406.

(44) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 387.

(45) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev. (Washington, D.C.)* **1994**, *94*, 373.

(46) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637.