

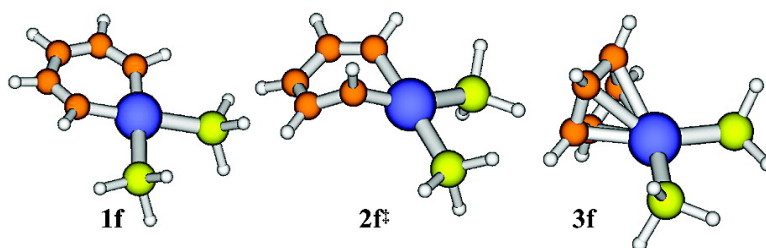
Communication

Metallabenzene versus Cp Complex Formation: A DFT Investigation

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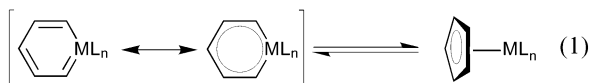
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Metallabenzenes form a class of intriguing aromatic compounds that have attracted considerable attention in recent years.^{1–8} Prior to the isolation of the first metallabenzene,^{2a} Thorn and Hoffmann in 1979 suggested that complexes of the type (C₅R₅Mn)L₄, (C₅R₅Rh)L₂Cl₂, and (C₅R₅Rh)L₃ represent viable synthetic targets.⁹ Despite the significant amount of experimental data available, few synthetic routes are known, and the desirable metalloaromatic complexes are often unstable.^{1–8} We recently investigated the mechanistic details of the cycloaddition reactions of such complexes using density functional theory (DFT).¹⁰

One reaction that metallabenzenes frequently undergo is the formation of cyclopentadienyl (Cp) complexes (eq 1). For instance, Jones and Allison were able to monitor by NMR the selective conversion of the ruthenabenzene (3,5-Ph₂-2-OEt-C₅H₂Ru)(CO)-(η⁵-Cp) to the related Cp₂Ru complex at –30 °C.^{3a} In addition, putative ferra- and rhenabenzenes were postulated to undergo Cp formation.^{3b,c} Similarly, CpIr and CpPt complexes were obtained in reactions that in related systems gave isolatable iridiabenzenes,⁵ and a platinabenzene.⁶ Stable examples of osmabenzenes,² and even osmabenzynes⁷ are also known.



It is not clear why certain metallabenzenes undergo Cp formation while others do not, nor is the reaction mechanism known. *Prima facie* there does not seem to be any apparent reason for this differing reactivity. The overall process involves a highly unusual coupling of two aromatic metal–carbon moieties.¹¹ Formally, metallabenzene complexes can be described as having a vinyl-carbene organic fragment (eq 1) even though they have aromatic characteristics. The observed cycloaddition^{5a,10} and electrophilic aromatic addition^{2b} reactivities of these complexes reflect this dual character, and Cp formation may be another example. We used DFT to investigate the mechanism of this unique C–C coupling reaction and the factors affecting the relative stability of the complexes involved.¹²

Cp complex formation was examined in the 16 model systems listed in Table 1. Many closely resemble experimental systems (**1a–d, f, g, i–j**),^{2a,3,4b,5a,6} while the others are theoretical systems that may be of much synthetic interest (**1e, h, k–p**). As an example, the calculated geometries of **1f**, **2f[‡]** and **3f** are depicted in Figure 1. The metallabenzenes (**1**) show aromatic character with nearly flat rings and little bond-length alternation. For example, in **1a** the ring bond lengths are 1.957 (Ru–C_{ortho}), 1.391 (C_{ortho}–C_{meta}) and 1.404 Å (C_{meta}–C_{para}). The C–C bond length in benzene is calculated to be 1.396 Å. The reactions were found to follow similar paths regardless of the metal center. From the metallabenzene complex (**1**), a transition state (**2[‡]**) for direct C–C coupling was found. In the three-centered transition state, the two carbon atoms are “pinched” toward each other with a C–C distance in **2a[‡]** of

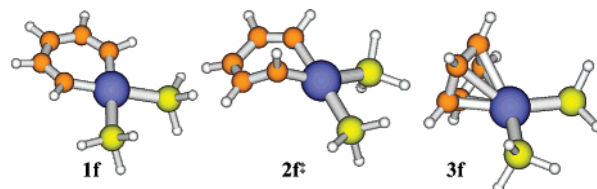


Figure 1. Calculated geometries for the Cp-formation reaction from [(C₅H₅Pt)(PH₃)₂]⁺ (**1f**). Color scheme: C: orange, H: white, Pt: blue, P: yellow.

2.175 Å. Transition state **2[‡]** exhibits an asymmetric $\overline{\text{M}=\text{C}-\text{C}=\text{C}-\text{C}=\text{C}}$ bonding scheme, where these bonds in **2a[‡]**, for example, are 1.888, 1.474, 1.350, 1.464, 1.356, and 2.131 Å, respectively. This indicates that the reaction may be classified as a carbene migratory insertion.¹³ The reaction product (**3**) is either an η¹- or η³-Cp complex (see Table 1), and in certain cases was found to undergo phosphine loss and/or Cp-slippage to give the final reaction products (**4**). The connectivity of all transition states was confirmed by intrinsic reaction coordinate (IRC) calculations.¹¹ The various ligands (Cp, CO, Cl, PH₃) on the metal center as well as the metal itself did not drastically alter the general structure of the transition state (**2[‡]**), although they did have a drastic effect on the reaction kinetics and thermodynamics (Table 1).

The calculated reaction barriers and energies (Table 1) clearly reflect the reported experimental observations. It is apparent that the Cp complexes (**3** and **4**) are generally thermodynamically favored. Remarkably, this balance is reversed in the case of **1j**.

For the ruthenabenzene **1a**, there is a relatively low barrier leading to **3a**, consistent with the reported chemistry.^{3a} Similarly, the low barriers found for Cp formation in the ferra- (**1b**) and rhenabenzene (**1c**) agree with the observations that these complexes are not stable.^{3b,c} In addition, the higher barrier found for the osmabenzene **1d** shows that it should be stable, as observed.^{2a} The analogous ruthenabenzene **1e** is not expected to be stable.

Haley postulated a cationic bis-phosphine platinabenzene analogous to **1f^{‡b}** in a reaction that in a related case gave the analogous Cp–metallabenzene complex (**1g**).⁶ The formation of platinacene (**3g**) was found to have a high barrier, while the reaction of **1f** was found to have a low barrier, in line with the experimentally observed reactivity.^{4b,6} Moreover, there is a dramatic difference in reaction energies. If one were to try to stabilize the platinabenzene moiety by preparing the cationic tris-phosphine complex (**1h**), this would be of no avail. Even though Cp formation from this complex has a significant barrier, loss of phosphine is negligible (ΔG₂₉₈ = 0.9 kcal/mol).

Cp formation in iridiabenzenes **1i, j** was also examined. Phosphine loss in **1i** is known to be highly endergonic.^{5a,10b} The barrier for C–C coupling to give the η¹-Cp complex **3i** is sufficient that the iridiabenzene is stable, even though the formation of **4i** is exergonic. Surprisingly, Cp formation is kinetically and thermodynamically unfavorable in the dichloride system (**1j**). This hints at the possibility

Table 1. Calculated Relative Energies (ΔG_{298} , kcal/mol) of the Model Systems

	1	2 ^a	3	4	ref ^b
a	(C ₅ H ₅ Ru)(CO)(η^5 -Cp)	25.2	(η^3 -Cp)Ru(CO)(η^5 -Cp)	-18.4	3a
b	(C ₅ H ₅ Fe)(CO)(η^5 -Cp)	19.2	(η^2 -Cp)Fe(CO)(η^5 -Cp)	-31.0	(η^5 -Cp) ₂ Fe -66.4 3b
c	(C ₅ H ₅ Re)(PH ₃)(CO) ₃	24.1	<i>mer</i> -(η^2 -Cp)Re(PH ₃)(CO) ₃	-30.3	(η^5 -Cp)Re(CO) ₃ -63.4 3c
d	<i>trans</i> -(C ₅ H ₅ Os)(PH ₃) ₂ (CO)Cl	27.7	<i>trans</i> -(η^1 -Cp)Os(PH ₃) ₂ (CO)(Cl) ^b	-9.4	<i>cis</i> -(η^2 -Cp)Os(PH ₃) ₂ (CO)(Cl) ^c -16.3 2a
e	<i>trans</i> -(C ₅ H ₅ Ru)(PH ₃) ₂ (CO)Cl	24.6	<i>trans</i> -(η^1 -Cp)Ru(PH ₃) ₂ (CO)(Cl) ^b	-19.0	
f	[(C ₅ H ₅ Pt)(PH ₃) ₂] ⁺	24.0	[(η^5 -Cp)Pt(PH ₃) ₂] ⁺	-37.5	4b
g	(C ₅ H ₅ Pt)Cp	45.9	(η^3 -Cp) ₂ Pt	-2.9	6
h	[(C ₅ H ₅ Pt)(PH ₃) ₃] ⁺	34.9	[(η^1 -Cp)Pt(PH ₃) ₃] ⁺	-34.4	[(η^5 -Cp)Pt(PH ₃) ₂] ⁺ -36.6
i	(C ₅ H ₅ Ir)(PH ₃) ₃	44.4	(η^1 -Cp)Ir(PH ₃) ₃	-12.5	(η^5 -Cp)Ir(PH ₃) ₂ -25.0 5a
j	(C ₅ H ₅ Ir)(PH ₃) ₂ Cl ₂	35.2	<i>trans,cis</i> -(η^3 -Cp)Ir(PH ₃) ₂ Cl ₂	10.2	<i>cis,trans</i> -(η^3 -Cp)Ir(PH ₃) ₂ Cl ₂ 7.1 5a
k	(C ₅ H ₅ Rh)(PH ₃) ₃	33.4	(η^5 -Cp)Rh(PH ₃) ₂	-20.3	(η^5 -Cp)R η (PH ₃) ₂ -45.6
l	(C ₅ H ₅ Rh)(PH ₃) ₂	20.5 ^d	(η^5 -Cp)Rh(PH ₃) ₂	-56.8	
m	(C ₅ H ₅ Rh)(PH ₃) ₂ Cl ₂	32.1	<i>trans,cis</i> -(η^3 -Cp)Rh(PH ₃) ₂ Cl ₂	-3.2	
n	[(C ₅ H ₅ Pd)(PH ₃) ₂] ⁺	19.1	[(η^5 -Cp)Pd(PH ₃) ₂] ⁺	-54.2	
o	[(C ₅ H ₅ Pd)(PH ₃) ₃] ⁺	23.6	[(η^1 -Cp)Pd(PH ₃) ₃] ⁺	-46.2	[(η^5 -Cp)Pd(PH ₃) ₂] ⁺ -56.0
p	(C ₅ H ₅ Pd)Cp	33.8	(η^3 -Cp)2Pd	-24.3	

^a References of experimental systems modeled, where applicable. ^b Square pyramidal geometry. ^c Trigonal bipyramidal geometry. ^d Phosphine dissociation from **1k** has a calculated reaction energy of $\Delta G_{298} = 11.2$ kcal/mol, leading to an overall barrier of $\Delta G_{298}^\ddagger = 31.7$ kcal/mol.

of preparing metallabenzene from metallocenes. Carbon-carbon bond activation in metal-coordinated Cp rings has been observed under mild reaction conditions.¹⁴

The results for the analogous rhodiabenzene (**11–1m**) are similar to the iridium systems, although the reaction barriers are lower. The barriers are sufficiently high that one could expect the rhodiabenzene to be stable at least for limited periods of time. The dichlororhodiabenzene **1m** might even be isolatable. Likewise, the palladiabenzene (**1n–1p**) have lower barriers than their Pt analogues, although **1p** might be a potential synthetic target. To date, there are not any reported examples of palladia- or rhodiabenzene complexes.^{1,15}

Admittedly the model systems lack the substituents on the aromatic ring and the bulkier phosphines. Nonetheless, we have observed that replacing PEt₃ ligands by PH₃ has only minimal impact on the reactivity of iridiabenzene.^{10b} In general, third-row metals give metallabenzene that are more stable than second- and first-row metals.¹ This may indicate that a higher electron density on the metal helps stabilize the metallabenzene complex. This fails, however, to explain the dramatic stabilities of **1j,m** that are in a higher oxidation state, although Cl π -bonding to the metal center may be an important stabilizing factor and the HOMO of **1j** is dominated by the Ir-(Cl)₂ π^* orbital.

In summary, Cp complex formation can proceed from metallabenzene complexes via a carbene migratory insertion regardless of the type of transition metal and ancillary ligands involved. Our calculations show that certain palladiabenzene and rhodiabenzene might be isolated prior to Cp complex formation. The Cp complex is generally the thermodynamically favored product although several metallabenzene are known to be thermally robust.^{2,5,6} Nevertheless, it should be possible to shift the thermodynamic balance toward the metallabenzene complex by proper choice of the ancillary ligands.

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Supporting Information Available: Calculated structures and full computational details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205.
- (a) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811. (b) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 750. (c) Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *J. Organomet. Chem.* **2001**, *623*, 109.
- (a) Yang, J.; Jones, W. M.; Dixon, J. K.; Allison, N. T. *J. Am. Chem. Soc.* **1995**, *117*, 9776. (b) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463. (c) Ferede, R.; Hinton, J. F.; Korfman, W. A.; Freeman, J. P.; Allison, N. T. *Organometallics* **1985**, *4*, 614.
- (a) Wu, H.-P.; Lanza, S.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2002**, *21*, 2824. (b) Jacob, V.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2002**, *21*, 5394.
- (a) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Chiang, M. Y.; Robinson, K. D.; Beatty, A. M. *Organometallics* **1997**, *16*, 606. (b) Gilbertson, R. D.; Lau, T. L. S.; Lanza, S.; Wu, H.-P.; Weakley, T. J. R.; Haley, M. M. *Organometallics* **2003**, *22*, 3279. (c) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *Chem. Eur. J.* **2000**, *6*, 437. (d) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Salazar, V.; Oñate, E.; Mereiter, K. *J. Am. Chem. Soc.* **2003**, *125*, 9898.
- Jacob, V.; Weakley, T. J. R.; Haley, M. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3470.
- (a) Wen, T. B.; Zhou, Z. Y.; Jia, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 1951. (b) Wen, T. B.; Ng, S. M.; Hung, W. Y.; Zhou, Z. Y.; Lo, M. F.; Shek, L.-Y.; Williams, I. D.; Lin, Z.; Jia, G. *J. Am. Chem. Soc.* **2003**, *125*, 884. (c) Roper, W. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2440.
- Effertz, U.; Englert, U.; Podewils, F.; Salzer, A.; Wagner, T.; Kaupp, M. *Organometallics* **2003**, *22*, 264.
- Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.
- (a) Iron, M. A.; Martin, J. M. L.; van der Boom, M. E. *Chem. Commun.* **2003**, 132. (b) Iron, M. A.; Martin, J. M. L.; van der Boom, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 11702.
- For a recent DFT investigation of vinyl-vinyl coupling, see: Ananikov, V. P.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2839.
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001. See Supporting Information for full computational details.
- 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.
- Xi, Z.; Sato, K.; Gao, Y.; Lu, J.; Takahashi, T. *J. Am. Chem. Soc.* **2003**, *125*, 9568 and references therein.
- (a) Chin, R. M.; Jones, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 357. (b) Bleeke, J. R.; Donnay, E.; Rath, N. P. *Organometallics* **2002**, *21*, 4099.

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