Metallabenzenes

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Building a Parent Iridabenzene Structure from Acetylene and Dichloromethane on an Iridium Center**

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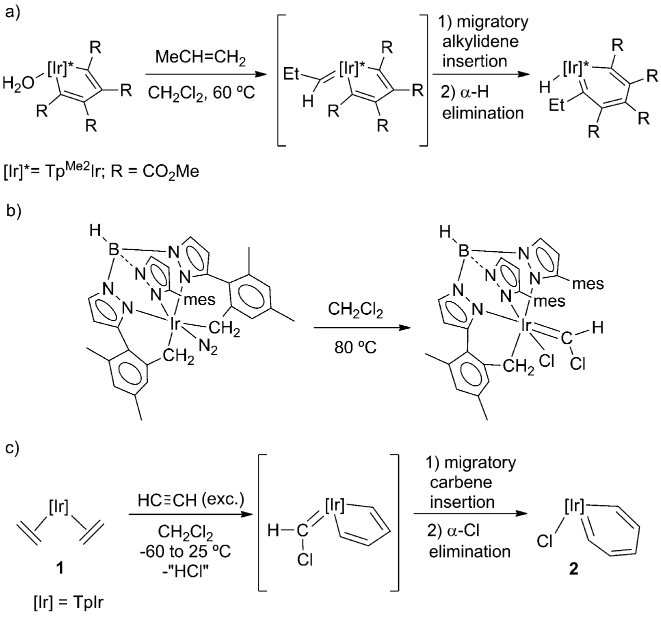
Metallabenzenes[1] are species which have attracted ample interest from the academic community because their structures,[2] electronic properties,[3] and reactivity.[4] Despite recent significant advances in this field, which have been reviewed lately,[1b,c] and the development of different synthetic methods, a parent metallabenzene, that is, a complex in which apart from the metal center, only CH units are in the aromatic six-membered ring, remains an unknown and appealing target. This situation contrasts with the related phosphabenzene and arsabenzene, for which corresponding parent structures were reported several decades ago.[5]

We have already described[6] a new synthetic route to iridabenzene units that relied on the reaction of fully CO_2Me substituted Tp^{Me2}-iridacyclopentadienes (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) with a terminal olefin, such as propene (Scheme 1 a). We explained iridabenzene formation on the basis of a rare olefin-to-alkylidene isomerization,[7] followed by migratory insertion and α-H elimination processes. Interestingly, C_2H_4 did not afford a related methyl-substituted iridabenzene but inserted instead into an Ir−C bond giving a H_2O-stabilized iridacycloheptadiene.[8]

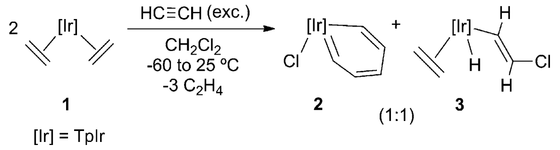
In parallel studies,[9] we also demonstrated that an Ir^{III} complex of a doubly metallated Tp^{Mes} ligand (Tp^{Mes} = hydrotris(3-mesitylpyrazolyl)borate) cleaved dichloromethane cleanly to produce a monochloro carbene ligand, :C(H)Cl, with the remaining Cl and H atoms adding to the metal and to one of the Ir−CH_2 bonds of the starting compound, respectively (Scheme 1 b).

Encompassing these two reactivity modes, we now report the formation of the first parent metallabenzene (complex **2** in Scheme 1 c) in the reaction of the compound $[TpIr(C_2H_4)_2]$ (**1**)[10] (Tp = hydrotris(pyrazolyl)borate) with acetylene in CH_2Cl_2.



Scheme 1. Previous reactivity studies on Tp′Ir^{III} systems (a),[6] and (b)[9] relevant to the iridabenzene synthesis reported herein (c). exc. = saturated.

A solution of complex **1** (50 mg, 0.1 mmol) in CH_2Cl_2 (20 mL) saturated with acetylene[11] (glass ampoule, −60 °C, 1 atm) was allowed to reacted from −60 °C to room temperature to yield quantitatively (by NMR spectroscopy) an approximately 1:1 mixture of the iridabenzene **2** and the β-chlorinated vinyl hydride complex **3** (Scheme 2). Under the above conditions, the reaction outcome is highly reproducible but the yield of the iridabenzene is highly sensitive to deviations from them, for example, if C_2H_2 saturation is carried out at −20 °C the ratio of complexes **2** and **3** becomes ca. 1:2.



Scheme 2. Reaction of complex $[TpIr(C_2H_4)_2]$ (**1**) with acetylene in CH_2Cl_2.

Complex **2** was purified by chromatography on silica gel and characterized by the usual spectroscopic and analytical methods, including single-crystal X-ray studies (Figure 1). The five carbon atoms of the metallacycle are almost coplanar, but the Ir atom is displaced from this plane by 0.29 Å. This deviation is a typical characteristic of metallabenzenes,[2] and has been documented for other iridaben-

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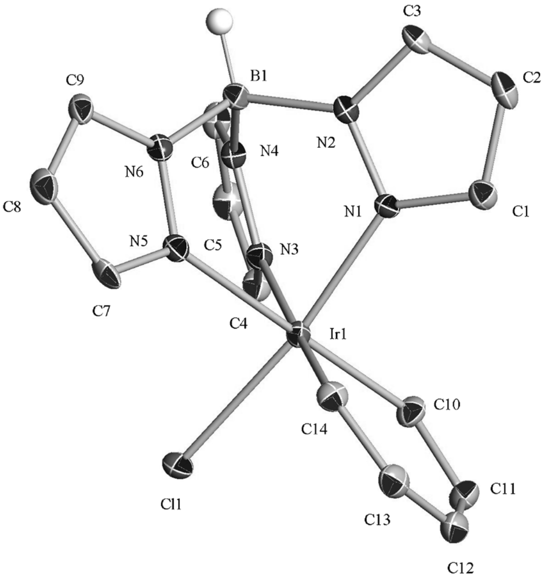


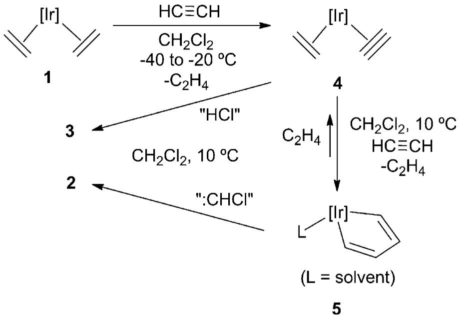
Figure 1. OTREP view of complex **2**. Thermal ellipsoids are set at 30% probability level. Selected bond lengths [Å] and angles [°]: Ir1-C14 1.947(5), Ir1-C10 1.955(5), C10-C11 1.380(7), C11-C12 1.397(9), C12-C13 1.392(9), C13-C14 1.382(8); C10-Ir1-C14 89.9(2).

zenes.[12] The two Ir–C distances are identical within experimental error and average around 1.95 Å, being therefore comparable to those found in a related $Tp^{Me2}Ir^{III}$ iridabenzene (ca. 1.94 Å).[12c] In turn, the four C–C bonds between carbon atoms C10–C14 are in the narrow range 1.38–1.40 Å, and are therefore essentially identical to the bond lengths in benzene (1.39 Å).

The aromaticity of the ring formed by the Ir1 and C10–C14 atoms becomes evident from the analysis of ^1H and ^{13}C NMR data. Thus, the two equivalent 2- and 6-CH groups feature strongly deshielded ^1H and ^{13}C resonances, with chemical shifts of $\delta = 14.67$ and 203.6 ppm, respectively, and a $^1J_{CH}$ coupling constant of 142 Hz. In addition, one of the pyrazolyl N-C-H hydrogen atoms, namely that bound to C1 (Figure 1) resonates with an unusually low frequency ($\delta = 5.69$ ppm), in all probability due to its interaction with the electronic current within the aromatic ring.

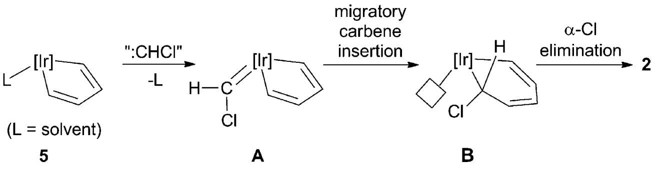
NMR spectroscopic data (^1H and ^{13}C) for complex **3** also provided unequivocal evidence for its chemical constitution. The inequivalency of the three Tp-pyrazolyl rings (see Supporting Information) indicates the chiral nature of the iridium center, which is a consequence of its additional coordination to three different monodentate ligands. The presence of a hydride is manifested by its characteristic ^1H NMR signal at $\delta = -16.2$ ppm. Then, a molecule of C_2H_4, that undergoes fast rotation around the $Ir-C_2H_4$ bond on the NMR time scale, gives rise to an AA′XX′ spin system, with $\delta_A = 3.23$ and $\delta_X = 2.95$ ppm. And, finally, a *trans*-C(H)=C(H)Cl alkenyl fragment yields two ^1H NMR doublets ($\delta = 6.78$ and 4.91 ppm, $^3J_{HH} = 13.5$ Hz) along with corresponding ^{13}C resonances at $\delta = 118.9$ ($^1J_{CH} = 143$ Hz) and 109.9 ppm ($^1J_{CH} = 198$ Hz) respectively. The hydride ligand of compound **3** was easily exchanged by bromine upon exposure to bromoform and the resulting, more robust, derivative gave satisfactory HRMS (FAB) results (see Supporting Information).

To gain mechanistic information on the formation of these two complexes acetylene was bubbled at −60 °C through a solution of **1** in CD_2Cl_2, and the reaction monitored by variable temperature ^1H NMR spectroscopy. At −40 °C, quantitative formation of the mixed species $[TpIr(C_2H_4)(C_2H_2)]$ (**4**) and free C_2H_4 was observed (Scheme 3). Similarly to its DMAD counterpart $[TpIr(C_2H_4)(DMAD)]$[13] (DMAD = dimethyl acetylenedicarboxylate) this is a highly fluxional molecule that was characterized at −40 °C (see Supporting Information). Complex **4** was stable up to about 10 °C when its characteristic resonance signals gradually disappeared, with concomitant emergence of a low field AA′XX′ spin system ($\delta = 7.31$ and 6.51 ppm) assigned to the iridacyclopentadiene species **5** (Scheme 3; L = CD_2Cl_2, acetone,[11] or adventitious water) that formed upon further reaction of **4** with acetylene. At this temperature and before full consumption of **4**, complex **5** began to disappear while resonance signals arising from **2** and **3** started to grow, until a final mixture of these products was obtained. In this experiment the **2**:**3** ratio never reached the 1:1 value depicted in Scheme 2 (a 1:2 ratio being a typical result) with the vinyl species **3** always appearing first and consequently predominating over **2** in the final reaction mixture.[14]



Scheme 3. Proposed relationship between the intermediate species **4** and **5** and the final products **2** and **3**.

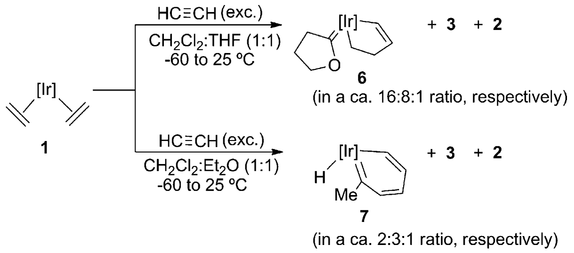
As represented in Scheme 3, these results are best explained by assuming that at 10 °C, complexes **4** and **5** are in equilibrium and CH_2Cl_2 is cleaved to generate "HCl" and the chlorocarbene ":C(H)Cl" fragments. Although mechanistic details for the formation of **3** are not yet available, in a formal sense this compound derives from "HCl" addition to complex **4**.[15] In turn, chlorocarbene coordination to **5** (with prior dissociation of L), to give **A** (Scheme 4), would lead to the iridabenzene complex **2** by means of the reaction steps



Scheme 4. Proposed mechanism for the formation of iridabenzene **2** from the iridacyclopentadiene **5**.

represented in Scheme 4, that is, through migratory carbene insertion into an Ir–C bond and α-Cl elimination of the stereoisomer **B**. In accord with this mechanism the iridabenzene **2** obtained in CD_2Cl_2 was fully deuterated in the 2 (or 6) position.[16]

The ^1H NMR monitoring experiments indicate that the formation of complex **3** is the first observed event to indicate the cleavage of CH_2Cl_2, thus the detected ratio of **2**:**3** would depend upon the efficiency with which the chlorocarbene unit, ":C(H)Cl", is trapped by **5**, which would in turn be dictated by the precise experimental reaction conditions. This conclusion is further confirmed when the outcomes of the reaction of complex **1** and acetylene carried out in 1:1 by volume mixtures of CH_2Cl_2 and other potentially reactive co-solvents (Scheme 5) are considered. These results may reflect the low affinity of species **5** for the chlorocarbene ":C(H)Cl", and/or its fleeting existence in solution.[14]



Scheme 5. Reactivity of complex **1** with acetylene in CH_2Cl_2/THF and CH_2Cl_2/Et_2O mixtures (1:1 vol.).

Thus, in the presence of THF, the Fischer's carbene **6** (Scheme 5 and Figure 2)[17] was formed along with the alkenyl complex **3**, as the main (over 95%, NMR yield) reaction products (compounds **6**, **3**, and **2** were formed in an approximately 16:8:1 ratio). Clearly, THF efficiently traps the iridacyclopentadiene **5** and transfers the two hydrogen atoms of a methylene group adjacent to the oxygen atom to one of the metallacyclic Ir-CH=CH- moieties. This proposal has been demonstrated by the use of [D$_8$]THF.[18] Similar THF activations by Ir^{III} complexes have been reported.[19]

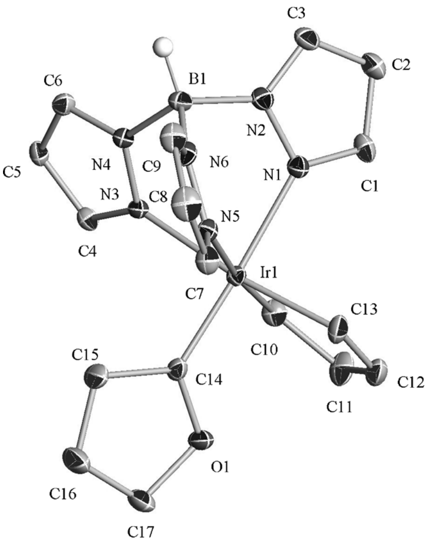
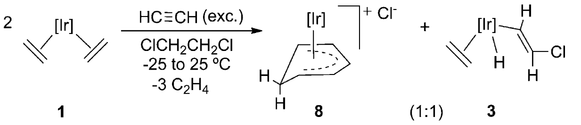


Figure 2. ORTEP view of complex **6**. Thermal ellipsoids are set at 30% probability level. Selected bond lengths [Å] and angles [°]: Ir1-C10 2.051(6), Ir1-C13 2.033(6), Ir1-C14 1.898(6); C10-Ir1-C13 80.7(3).

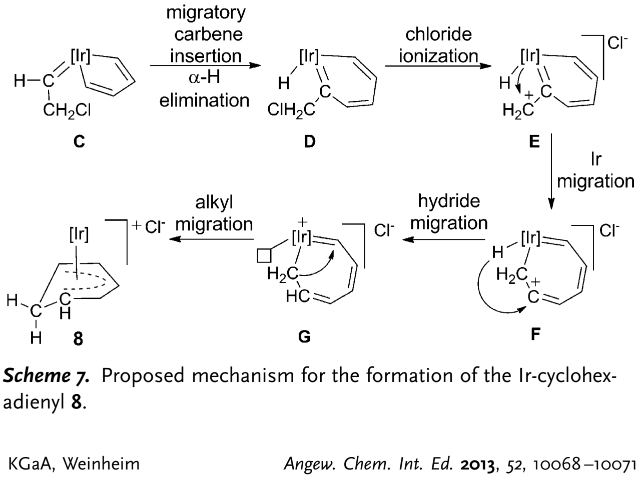
When diethyl ether was employed as the co-solvent, the formation of complex **3** was accompanied by that of two iridabenzenes, complex **2** and the new hydride **7** (Scheme 5, the ratio of **7**:**3**:**2** was ca. 2:3:1). The formation of **7** is clearly the result of ethylene entering the reaction pathway depicted in Scheme 1 a, by means of a metal-induced isomerization to ethylidene, ":C(H)CH_3".[6,7] As free ethylene was always present (1–2 equiv depending on the conditions) in all the reaction mixtures discussed above it is difficult to understand why only in the presence of Et_2O it becomes such an effective reacting species towards **5**. If CH_2Cl_2 is excluded from the reaction, **7** becomes the major product and, as expected, neither **3** or **2** are observed.

In an effort to extend the reactivity to an, in principle, less-activated alkyl chloride, the reaction of complex **1** with acetylene was performed in 1,2-dichloroethane as the solvent. In this case an approximately 1:1 mixture of the choroalkenyl complex **3** and the cationic η^5-cyclohexadienyl species **8**[20] was cleanly obtained (Scheme 6), suggesting that the mixed C_2H_4/C_2H_2 adduct **4** of Scheme 3 is also able to abstract "HCl" from $ClCH_2CH_2Cl$.



Scheme 6. Reaction of complex [TpIr(C_2H_4)$_2$] (**1**) with acetylene in 1,2-dichloroethane.

Scheme 7 shows a mechanism for the formation of compound **8** where ionization of a benzylic chloride in the expected iridabenzene **D** triggers the sequence of events. In agreement with this reaction pathway, [D$_4$]1,2-dichloroethane yielded [D$_3$]**8** in which the three deuterium atoms were part of a -CD_2CD- portion of the cyclohexadienyl ring.



Scheme 7. Proposed mechanism for the formation of the Ir-cyclohexadienyl **8**.

In summary, the first parent metallabenzene has been synthesized through the reaction of $[TpIr(C_2H_4)_2]$ (**1**) with acetylene in CH_2Cl_2 and we have shown that by simple modification of the reaction conditions other interesting reactivity modes may be achieved.

Experimental Section

2: Complex **1** (50 mg, 0.11 mmol) was dissolved in CH_2Cl_2 (20 mL) in a Schlenk tube which was then introduced into a cold bath at −60 °C. The solution was saturated with acetylene by bubbling, the cold bath removed and the solution allowed to reach room temperature. After 20 min of stirring at 25 °C the resulting red solution was evaporated to dryness and the residue was ascertained, by ^1H NMR spectroscopy, to contain an approximately 1:1 mixture of **2** and **3**. Compound **2** was isolated by column chromatography on silica gel using hexane:Et_2O (4:1) as eluent (30% yield). Red crystals of analytical purity and suitable for single-crystal X-ray studies were obtained by slow solvent evaporation from its solutions in hexane:Et_2O mixtures.

X-Ray structure for **2** and **6**: CCDC 944031 (**2**) and 944032 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) J. R. Bleeke, *Chem. Rev.* **2001**, *101*, 1205; b) A. F. Dalebrook, L. J. Wright, *Adv. Organomet. Chem.* **2012**, *60*, 93; c) J. Chen, G. Jia, *Coord. Chem. Rev.* **2013**, in press.

[2] J. Zhu, G. Jia, Z. Lin, *Organometallics* **2007**, *26*, 1986.

[3] R. W. A. Havenith, F. D. Proft, L. W. Jenneskens, P. W. Fowler, *Chem. Phys. Phys. Chem.* **2012**, *14*, 9897.

[4] a) R. Lin, H. Zhang, S. Li, J. Wang, H. Xia, *Chem. Eur. J.* **2011**, *17*, 4223; b) G. R. Clark, L. A. Ferguson, A. E. McIntosh, T. Söhnel, L. J. Wright, *J. Am. Chem. Soc.* **2010**, *132*, 13443; c) R. Lin, J. Zhao, H. Chen, H. Zhang, H. Xia, *Chem. Asian J.* **2012**, *7*, 1915.

[5] A. J. Ashe III, *Acc. Chem. Res.* **1978**, *11*, 153.

[6] a) E. Álvarez, M. Paneque, M. L. Poveda, N. Rendón, *Angew. Chem.* **2006**, *118*, 488; *Angew. Chem. Int. Ed.* **2006**, *45*, 474; b) M. Paneque, M. L. Poveda, N. Rendón, E. Álvarez, E. Carmona, *Eur. J. Inorg. Chem.* **2007**, 2711.

[7] a) P. Lara, M. Paneque, M. L. Poveda, L. L. Santos, J. E. V. Valpuesta, V. Salazar, E. Carmona, S. Moncho, G. Ujaque, A. Lledós, C. Maya, K. Mereiter, *Chem. Eur. J.* **2009**, *15*, 9046; b) O. V. Ozerov, L. A. Watson, M. Pink, K. G. Caulton, *J. Am. Chem. Soc.* **2003**, *125*, 9604; c) K. F. Hirsekorn, A. S. Veige, M. P. Marshak, Y. Koldobskaya, P. T. Wolczanski, T. R. Cundari, E. B. Lobcovski, *J. Am. Chem. Soc.* **2005**, *127*, 4809; d) L. Giannini, G. Guillemot, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa, C. Rizzoli, *J. Am. Chem. Soc.* **1999**, *121*, 2797; e) R. P. Hughes, S. M. Maddock, A. L. Rheingold, I. A. Guzei, *Polyhedron* **1998**, *17*, 1037; f) J. S. Freundlich, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1996**, *118*, 3643; g) G. A. Miller, N. J. Cooper, *J. Am. Chem. Soc.* **1985**, *107*, 709; h) J. D. Fellmann, R. R. Schrock, D. D. Traficante, *Organometallics* **1982**, *1*, 481; i) G. Parkin, E. Bunel, B. J. Burger, M. S. Trimmer, A. Van Asselt, J. E. Bercaw, *J. Mol. Catal.* **1987**, *41*, 21.

[8] M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, E. Álvarez, K. Mereiter, *Chem. Eur. J.* **2007**, *13*, 5160.

[9] J. A. López, K. Mereiter, M. Paneque, M. L. Poveda, O. Serrano, S. Trofimenko, E. Carmona, *Chem. Commun.* **2006**, 3921.

[10] a) M. J. Fernández, M. J. Rodríguez, L. A. Oro, F. J. Lahoz, *J. Chem. Soc. Dalton Trans.* **1989**, 2073; b) R. S. Tanke, R. H. Crabtree, *Inorg. Chem.* **1989**, *28*, 3444.

[11] Commercial acetylene was used without further purification. Therefore substantial amounts of acetone were present in the reaction mixture.

[12] See for example: a) R. D. Gilbertson, T. L. S. Lau, S. Lanza, H. P. Wu, T. J. R. Weakly, M. M. Haley, *Organometallics* **2003**, *22*, 3279; b) J. R. Bleeke, R. Behm, Y. F. Xie, M. Y. Chiang, K. D. Robinson, A. M. Beatty, *Organometallics* **1997**, *16*, 606; c) K. Ilg, M. Paneque, M. L. Poveda, N. Rendón, L. L. Santos, E. Carmona, K. Mereiter, *Organometallics* **2006**, *25*, 2230.

[13] J. M. O'Connor, A. Closson, P. Gantzel, *J. Am. Chem. Soc.* **2002**, *124*, 2434.

[14] The fate of the chlorocarbene, when not giving rise to complex **2**, has not been clarified.

[15] HCl“ is not free HCl as this acid reacts with complex **4** to give not **3**, but another product to be described in the full report of this work.

[16] Complex **3** obtained under these conditions was devoid from deuterium. It is believed that “DCl” easily undergoes D,H exchange with adventitious water and in fact if D_2O-saturated CD_2Cl_2 was used as solvent $[D_1]$**3**, with the deuterium scrambled among the hydride and ethylene positions, was obtained.

[17] If the reaction was carried out in neat THF only complex **6** was obtained (see Supporting Information).

[18] The stereochemical distribution of the two deuterium atoms in the iridacyclopentene ring of $[D_8]$**6** will be discussed in a forthcoming full paper.

[19] a) J. E. V. Valpuesta, E. Álvarez, J. López-Serrano, C. Maya, E. Carmona, *Chem. Eur. J.* **2012**, *18*, 13149; b) H. Werner, *Angew. Chem.* **2010**, *122*, 4822; *Angew. Chem. Int. Ed.* **2010**, *49*, 4714; c) S. Conejero, M. Paneque, M. L. Poveda, L. L. Santos, E. Carmona, *Acc. Chem. Res.* **2010**, *43*, 572; d) M. T. Whited, R. H. Grubbs, *Acc. Chem. Res.* **2009**, *42*, 1607.

[20] For related cationic C_5Me_5 Ir complexes, see: S. L. Grundy, P. M. Maitlis, *J. Organomet. Chem.* **1984**, *272*, 265.