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Water-Promoted Generation of a Diazairida Homobarrelene by C–C Coupling Between an Iridacyclic Alkylidene and Acetonitrile**

María F. Espada, Joaquín López-Serrano, Manuel L. Poveda, and Ernesto Carmona**

***Abstract:** The stable cationic iridacyclopentenylidene $[Tp^{Me2}\overline{Ir(=CHC(Me)=C(Me)C}H_2(NCMe)]PF_6$ (**A**; Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) has been obtained by α-hydride abstraction from the iridacyclopent-2-ene $[Tp^{Me2}\overline{Ir(CH_2C(Me)=C(Me)C}H_2)(NCMe)]$. Complex **A** exhibits Brønsted–Lowry acidity at the Ir–CH_2 and proximal (relative to Ir–CH_2) methyl sites. The coordination of an extra molecule of acetonitrile to the iridium center initiates the reversible isomerization of the chelating carbon chain of **A** to the monodentate butadienyl ligand of complex $[Tp^{Me2}Ir(CH=C(Me)C(Me)=CH_2)(NCMe)_2]PF_6$, which is capable to engage in a water-promoted C–C coupling with the MeCN co-ligands. The product is an aesthetically appealing bicyclic structure that resembles the hydrocarbon barrelene.*

Cationic carbene–Ir^{III} complexes of the type $[L_nIr=C(R)(R')]^+$, in which the carbene ligand is devoid of heteroatom substituents (R and R′ are hydrogen or hydrocarbyl groups), are rare species because of the high reactivity of the strongly electrophilic alkylidene carbon atom.[1,2] Iridium compounds of this kind have been studied mainly by our group, taking advantage of the stabilizing properties provided by ancillary C_5Me_5[3] and Tp^{Me2}[4] ligands (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate). We now wish to report on the generation of the cationic iridacyclopentenylidene complex $[Tp^{Me2}\overline{Ir(=CHC(Me)=C(Me)C}H_2)(NCMe)]PF_6$ (**2**), which, despite the existence of iridium–alkylidene and iridium–alkyl termini, exhibits remarkable thermal stability. The investigation of its chemical behavior in solution showed that the cation of species **2** features an unusual Brønsted–Lowry acidity at the Ir–CH_2 and proximal (relative to Ir–CH_2) methyl sites. These properties and the well-known versatility of nitriles as ligands[5] allowed the clean, water-promoted transformation (MeCN/H_2O, 100 °C) into an iridabicyclic complex with an aesthetically attractive structure that resembles that of the organic molecule barrelene[6] (HC(CH=CH)$_3$CH; Figure 1).

The known iridacyclopent-2-ene complex $[Tp^{Me2}\overline{Ir(CH_2C(Me)=C(Me)C}H_2)(NCMe)]$ (**1**)[7] reacted with $Ph_3C^+PF_6^-$ (CH_2Cl_2, 25 °C) to produce the cationic iridacyclopentenylidene complex **2** in almost quantitative yield (Scheme 1). It is important to note that despite its weak donor ability,[5a] the σ-electron-donating properties of MeCN are crucial for the success of the reaction, as the CO-bearing analogue of **1** underwent no reaction with $Ph_3C^+PF_6^-$ under identical conditions.

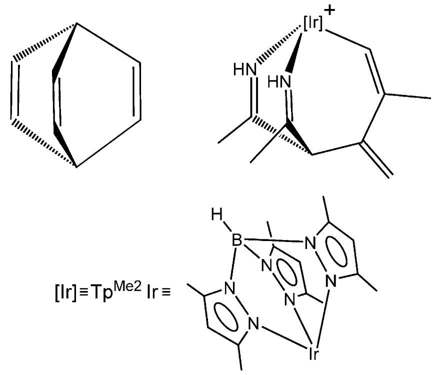
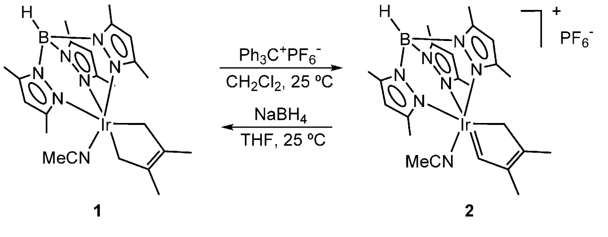


Figure 1. Structures of barrelene (left) and the cation of the iridabicyclic complex **4** (right).

Complex **2** was characterized by microanalysis and NMR spectroscopy (in $CDCl_3$). Similar to recently reported alkyl/alkylidene platinum[1f] and iridium[3a] complexes, the resonances for the Ir=CH and Ir–CH_2 protons were sufficiently separated. The former proton appears at 16.04 ppm, while the latter two protons give doublets centered at 3.67 and 0.70 ppm



Scheme 1. Synthesis of the alkylidene **2** by hydride abstraction from complex **1** and its back conversion to the latter species by reaction with $NaBH_4$.

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[+] DFT calculations

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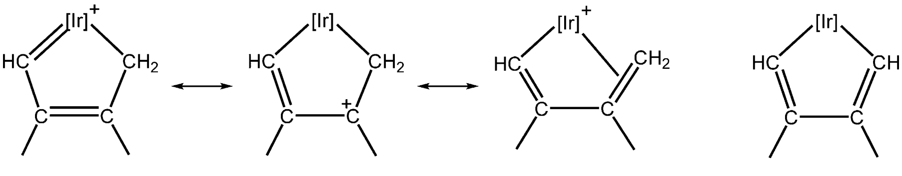
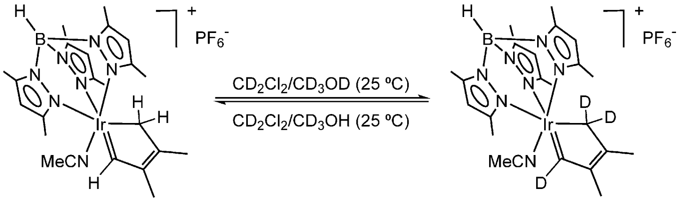
($^{2}J_{\mathrm{HH}}=20.5$ Hz). The corresponding ^{13}C NMR signals appear at 276.2 ($^{1}J_{\mathrm{CH}}=140$ Hz) and 20.1 ppm ($^{1}J_{\mathrm{CH}}=129$ Hz), respectively. However, in marked contrast to the above-mentioned platinum and iridium species, which undergo C–C coupling reactions at low temperature, and also in contrast to cationic hydride/alkylidene complexes of iridium, which experience reversible 1,2-H shifts under mild conditions,[4c] complex **2** is remarkably stable toward these decomposition pathways (in CH_2Cl_2, up to 80 °C). This is most likely due to considerable strain in the four-membered iridium-bound cyclobutenyl entity that would result from a carbene migratory insertion in **2**. Calculations in the gas phase confirmed this assumption, giving an energy of 38.2 kcal mol^{-1} for the high-tension transition state (Figure S6). Moreover, β-H elimination from the alleged alkyl product would generate a high-energy molecule of 1,2-dimethyl cyclobutadiene.[8] Nevertheless, the electrophilicity of the Ir=CH functionality of **2** was demonstrated by the easy hydride addition that took place upon treatment with $NaBH_4$ to restore compound **1** (Scheme 1).[9]

A natural bond orbital (NBO) analysis of the metallacyclic linkage of **2** disclosed the expected strong electron delocalization within its $\overline{\mathrm{Ir^{+}{=}CHC(Me){=}C(Me)CH_2}}$ moiety and furthermore showed that the carbocationic electronic structure **II** (Figure 2) is essentially equivalent to the iridacyclopentenylidene formulation (structure **I**; see the Supporting Information). In support of these findings, the ^{13}C resonance corresponding to the carbon atom bearing the positive charge in **II** is strongly deshielded, appearing at 223.7 ppm (compared with 166.9 ppm, exhibited by the olefinic carbon atom that is bound to it). Brønsted–Lowry acidity can thus be expected for both the CH_2 and CH_3 groups in α position to the positively charged carbon atom. Indeed, compound **2** underwent facile CH→CD exchanges (in CD_2Cl_2 in the presence of CD_3OD) at the two methylene and the methyne (alkylidene) positions with approximately the same rate (25 °C, 4 M solutions of CD_3OD in CD_2Cl_2, ca. 20 % incorporation of deuterium per proton site after 35 min). The isotopic exchange was considerably retarded by the addition of acid, which is in agreement with methanol acting as a base (Scheme 2). An unobserved symmetrical iridacyclopentadiene species (structure **IV**, Figure 2) might act as the conjugated base of **I** and could therefore be deuterated by an acid to give [D^{1}]-**2**, with deuterium incorporation at either one of the Ir–CH= termini. Thus, this proposal explains also the deuteration of the non-acidic alkylidene site, although it implicitly admits that the diastereotopic Ir–CH_2 sites are deuterated with the same rate.



I **II** **III** **IV**

Figure 2. Different electronic formulations (**I**–**III**) and Brønsted conjugated base structure (**IV**) of the iridacyclic unit of complex **2**. [Ir] = Tp$^{\mathrm{Me2}}$Ir(NCMe).



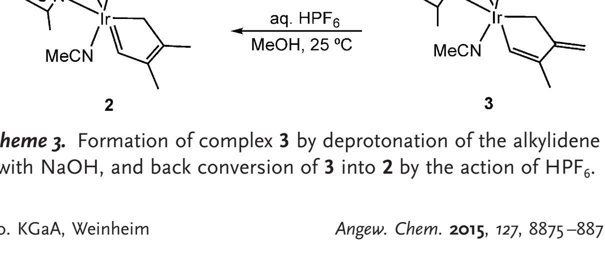
2 [D$_3$]-**2**

Scheme 2. CH⇄CD exchanges observed when solutions of the isotopomers **2** and [D$_3$]-**2** in CD_2Cl_2 were treated with CD_3OD and CD_3OH, respectively (25 °C).

A much faster reaction occurred when NaOH was utilized as the base in methanol at room temperature. As shown in Scheme 3, this almost instantaneous reaction led to the neutral complex **3**, as a result of the deprotonation of the methyl group directly bound to the cationic carbon atom in structure **II** (Figure 2). Not unexpectedly, the reaction could be reversed and treatment of compound **3** with aqueous HPF_6 in the same solvent re-established the conjugated acid **2**.

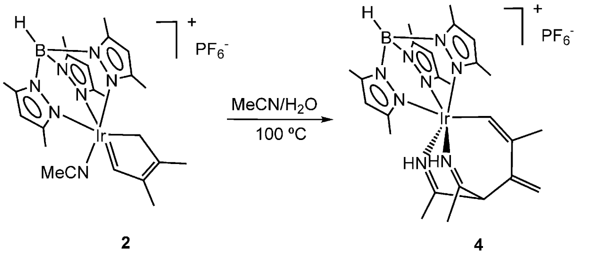
Complex **3** was characterized by NMR spectroscopy (see the Supporting Information). It is worth remarking that the formation of **3** by NaOH-promoted deprotonation of **2** is undoubtedly much faster than the isotopic exchange in **2** with CD_3OD. As a matter of fact, when the reaction of **2** with NaOH was performed in CD_3OD, the resulting complex **3** did not contain any deuterium. As definite conclusions on the nature of the thermodynamic deprotonation product (i.e. **IV** or **3**) could not be drawn from the available experimental data, DFT calculations were undertaken. Nonetheless, the results were ambiguous, as the two species were computed to have similar stability (see the Supporting Information).

Nitriles are an important family of ligands with well-recognized coordination properties and chemical reactivity.[5,10–14] Arguably, much more interesting reactivity ensued when complex **2** was heated for about 16 hours at 100 °C, employing a MeCN/H_2O mixture (ca. 6:1 v/v) as the solvent. A three-component reaction[15] that involved two molecules of MeCN took place and afforded cleanly and almost quantitatively the symmetrical iridabicyclic complex **4**, in a process that required the formation of two C–C bonds (Scheme 4).



2 **3**

Scheme 3. Formation of complex **3** by deprotonation of the alkylidene **2** with NaOH, and back conversion of **3** into **2** by the action of HPF_6.



Scheme 4. Formation of complex **4** by thermal treatment (100 °C, 16 h) of alkylidene **2** in a MeCN/H_2O mixture (6:1 v/v).

Complex **4** was fully characterized by elemental analysis, NMR spectroscopy, and X-ray analysis. With reference to its metallacyclic fragment, a ^{13}C NMR resonance located at 182.6 ppm can be confidently attributed to the C=N nuclei, whereas the >CH−C(=CH$_2$)−C(Me)=CH− chain gives rise (from left to right) to ^{13}C NMR signals at 62.5 ($^1J_{CH} = 140$ Hz), 135.0, 117.4 ($^1J_{CH} = 158$ Hz), 137.2, 26.9 ($^1J_{CH} = 126$ Hz), and 129.0 ppm ($^1J_{CH} = 143$ Hz). Figure 3 shows an ORTEP diagram of the cation of complex **4**. As it can be seen, the iridabicyclic structure consists of one six-membered ring (composed of Ir1, the nitrogen atoms N1 and N2, and the three carbon atoms C4, C5, and C6), and two seven-membered metallacycles. Each of the latter cycles comprises the iridium atom, one nitrogen atom, and five carbon atoms. The length of the Ir1−C1 bond is 2.019(2) Å, and the five Ir1−N bonds have lengths that range between 1.99–2.16 Å, with the longest distance (Ir1−N6, ca. 2.16 Å) corresponding to the Ir−N bond in *trans* position to the alkenyl terminus (Ir1−C1), which has the highest *trans* influence.[16] Bond angles between atoms in *trans* position with respect to the metal, that is N1-Ir1-N4 (177.9(7)°), N2-Ir1-N8 (178.8(7)°), and C1-Ir1-N6 (176.0(8)°), are very close to the ideal 180° value. As illustrated in Figures 1 and 3, the iridabicyclic moiety of compound **4** is reminiscent of the structure of barrelene. Specifically, the structure corresponds to a rather symmetrical trimethyl-substituted diazametalla homobarrelene that possesses an exocyclic methylene group bound to the extra carbon atom. As expected, computational studies showed that just as barrelene,[6] the metallabicyclic part of **4** does not have an electronically delocalized structure (see the Supporting Information).

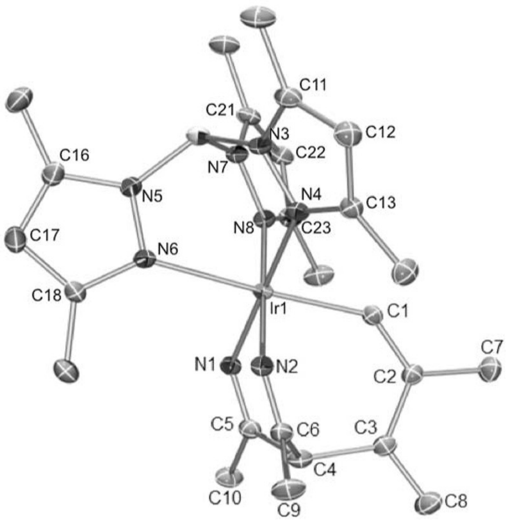
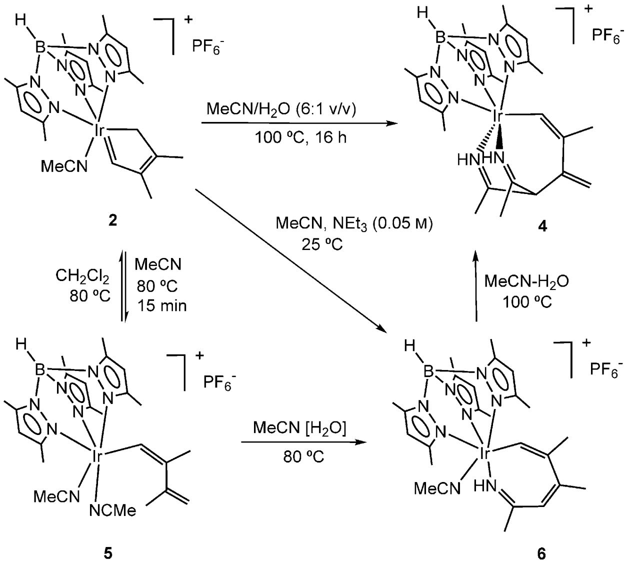


Figure 3. ORTEP view of the cation of complex **4**. H atoms are excluded for clarity and thermal ellipsoids are set at 50%. Selected bond distances [Å] and angles [°]: Ir1–N1 = 2.0054(19), N1–C5 = 1.283(3), C5–C4 = 1.522(3), C4–C3 = 1.538(3), C3–C2 = 1.465(3), C2–C1 = 1.354(3), Ir1–C1 = 2.019(2); N2-Ir1-N1 = 87.89(8), N1-Ir1-C1 = 88.37(8), C5-N1-Ir1 = 124.98(16), C5-C4-C3 = 109.82(18), C2-C3-C4 = 120.08(19), C1-C2-C3 = 124.8(2), C6-C4-C5 = 115.56(19), C2-C1-Ir1 = 136.11(17).

Monitoring by ^{1}H NMR spectroscopy provided useful mechanistic information on the reaction path that leads from complex **2** to complex **4**. Two independent experiments were performed, one in CD$_3$CN and the other in a CD$_3$CN/H$_2$O solvent mixture. The two experiments disclosed the formation of two intermediates (**5** and **6**; Scheme 5), which are formed in sequential, well-differentiated chemical events. Compound **5** contains two coordinated molecules of MeCN and a monodentate, σ-bound butadienyl ligand that is isomeric to the chelating alkyl/alkylidene fragment of **2**. It seems reasonable to propose that the unusual ring-opening reorganization of the hydrocarbon-based ligand of iridacycle **2** is driven by the coordination of an additional molecule of acetonitrile to iridium. As discussed below, complex **5** reverted partially to **2** in the absence of additional acetonitrile.



Scheme 5. Formation of complex **4** by the thermal treatment (100 °C) of the alkylidene **2** in MeCN/H_2O mixtures and of the two isolated intermediates **5** and **6** under different reaction conditions.

The structure proposed for complex **5** (see Scheme 5) finds strong support in the obtained NMR data. In particular, the sp^2-hybridized ^{13}C nuclei of the −CH=C(Me)C(=CH$_2$)Me hydrocarbyl chain give rise (from left to right) to resonances at 103.2 ($^1J_{CH} = 143$ Hz), 148.7, 143.8, and 111.8 ppm ($^1J_{CH} = 157$ Hz).

Additional heating at 80 °C of solutions of compound **5** in acetonitrile led to the slow formation of complex **6** as a consequence of formal nucleophilic attack of the *exo* methylene carbon atom of **5** to the carbon atom of a coordinated molecule of MeCN, followed by a 1,3-H shift. In contrast with this observation, the thermal activation of complex **5** in CH_2Cl_2 (80 °C, 16 h) resulted in a ca. 1:1 mixture of **2** and **6**, along with some decomposition products, thereby demonstrating that the formation of **5** from **2** is a reversible reaction.

Complex **6** was characterized by NMR spectroscopy and X-ray crystallography (see the Supporting Information, Figure S6). It is pertinent to note that we previously reported a somewhat similar C–C coupling reaction between an iridium vinyl fragment (Ir–CH=CH_2) and a coordinated molecule of acetonitrile to afford an iridapyrrole functionality.[4d] As in the formation of complex **6**, a 1,3-H shift ensued after the formation of the C–C bond and it required the participation of H_2O as a catalyst. We therefore believe that traces of water also catalyzed the formation of **6**. Interestingly, NEt_3 readily promoted the clean formation of complex **6** directly from **2** at 25 °C (MeCN, 0.05 M, 4 h), making this method the preferred synthetic procedure for species **6**. When monitored by NMR spectroscopy, an instantaneous deprotonation of **2** to give complex **3** was observed, with the reaction system slowly evolving to give **6**, and with no detectable amounts of species **5**. This NEt_3-assisted reaction was not restricted to MeCN as solvent, but seemed to be more general, as the use of acetone instead of acetonitrile permitted the isolation of complex **7**, with a structure akin to that of **6**, but with a coordinated molecule of acetone (see the Supporting Information).

As expected, pure samples of compound **6** were converted cleanly into the bicyclic complex **4** in MeCN/H_2O mixtures (100 °C, 2 M in water, 16 h). The new C–C bond arose formally from nucleophilic attack of the sp^2-hybridized carbon atom of **6** (in α position to the C=NH functionality) to the coordinated molecule of acetonitrile, followed by a water-catalyzed prototropic shift that now implicated the participation of a distant proton (1,5-H shift).

In conclusion we have characterized a surprisingly stable cationic iridacyclopentenylidene complex, **2**, of unusual Brønsted–Lowry acidity, that smoothly rearranges its chelating hydrocarbyl skeleton to a monodentate butadienyl isomeric structure. The latter allows interesting reactivity in C–C bond formation with the electrophilic carbon atom of coordinated molecules of MeCN. The key observation reported in this paper is the water-promoted three-component reaction that involved the C–C coupling of complex **2** with two coordinated molecules of MeCN. This reaction produced in essentially quantitative yield the iridabicyclic complex **4**, which exhibits an engaging structure that bears a likeness with that of the cyclic hydrocarbon barrelene.

Keywords: alkylidenes · C–C coupling · iridium · water catalysis

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Angew. Chem. **2015**, *127*, 8875–8879

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[1] For recent examples of electrophilic late-transition-metal alkylidenes, see the following citations and those in reference [2]: a) M. Joost, L. Estévez, S. Mellet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2014**, *53*, 14512–14516; *Angew. Chem.* **2014**, *126*, 14740–14744; b) Y. Wang, M. E. Muratore, Z. Rong, A. M. Echevarren, *Angew. Chem. Int. Ed.* **2014**, *53*, 14022–14026; *Angew. Chem.* **2014**, *126*, 14246–14250; c) M. W. Hussong, F. Rominger, P. Krämer, B. F. Straub, *Angew. Chem. Int. Ed.* **2014**, *53*, 9372–9375; *Angew. Chem.* **2014**, *126*, 9526–9529; d) R. J. Harris, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2014**, *53*, 9369–9371; *Angew. Chem.* **2014**, *126*, 9523–9525; e) D. H. Ringger, I. J. Kobylianskii, D. Serra, P. Chen, *Chem. Eur. J.* **2014**, *20*, 14270–14281; f) J. Campos, R. Peloso, E. Carmona, *Angew. Chem. Int. Ed.* **2012**, *51*, 8255–8258; *Angew. Chem.* **2012**, *124*, 8380–8383.

[2] a) A. Fürstner, *Angew. Chem. Int. Ed.* **2014**, *53*, 8587–8598; *Angew. Chem.* **2014**, *126*, 8728–8740; b) A. S. K. Hashmi, *Acc. Chem. Res.* **2014**, *47*, 864–876; c) Y. Wang, A. D. Lackner, F. D. Toste, *Acc. Chem. Res.* **2014**, *47*, 889–901; d) C. Obradors, A. M. Echevarren, *Acc. Chem. Res.* **2014**, *47*, 902–912; e) D. Zhang, X. Tang, M. Shi, *Acc. Chem. Res.* **2014**, *47*, 913–924; f) A. Fürstner, *Acc. Chem. Res.* **2014**, *47*, 925–938; g) L. Fensterbank, M. Malacria, *Acc. Chem. Res.* **2014**, *47*, 953–965; h) H. Yeom, S. Shin, *Acc. Chem. Res.* **2014**, *47*, 966–977.

[3] a) J. Campos, J. López-Serrano, E. Álvarez, E. Carmona, *J. Am. Chem. Soc.* **2012**, *134*, 7165–7175; b) J. Campos, M. F. Espada, J. López-Serrano, E. Carmona, *Inorg. Chem.* **2013**, *52*, 6694–6704; c) J. Campos, E. Carmona, *Organometallics* **2015**, DOI: 10.1021/om500910t.

[4] a) F. M. Alías, M. L. Poveda, M. Sellin, E. Carmona, *J. Am. Chem. Soc.* **1998**, *120*, 5816–5817; b) M. Besora, S. F. Vyboishchikov, A. Lledós, F. Maseras, E. Carmona, M. L. Poveda, *Organometallics* **2010**, *29*, 2040–2045; c) F. M. Alías, M. L. Poveda, M. Sellin, E. Carmona, E. Gutiérrez-Puebla, A. Monge, *Organometallics* **1998**, *17*, 4124–4126; d) Y. Alvarado, P. J. Daff, P. J. Pérez, M. L. Poveda, R. Sánchez-Delgado, E. Carmona, *Organometallics* **1996**, *15*, 2192–2194.

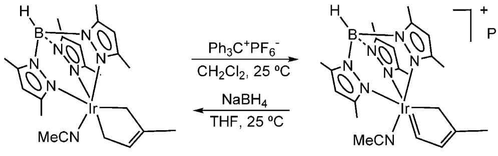
[5] a) R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299–338; b) V. Y. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771–1802.

[6] a) H. E. Zimmerman, R. M. Paufler, *J. Am. Chem. Soc.* **1960**, *82*, 1514–1515; b) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, M. A. Sherwin, *J. Am. Chem. Soc.* **1969**, *91*, 2330–2338.

[7] M. Paneque, M. L. Poveda, V. Salazar, E. Gutiérrez-Puebla, A. Monge, *Organometallics* **2000**, *19*, 3120–3126.

[8] a) D. J. Cram, M. E. Tanner, R. Thomas, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1024–1027; *Angew. Chem.* **1991**, *103*, 1048–1051; b) G. Maier, S. Pfriem, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 520–521; c) G. Maier, A. Alzérreca, *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 1015–1016; *Angew. Chem.* **1973**, *85*, 1057–1058; d) S. Masamune, N. Nakamura, M. Suda, H. Ona, *J. Am. Chem. Soc.* **1973**, *95*, 8481–8483.

[9] The related isoprene-derived Ir^{III} complex $[Tp^{Me}\overline{Ir(CH_2CH{=}C(Me)CH_2})(NCMe)]$ also experienced a similar formal H^- abstraction by $Ph_3C^+PF_6^-$ to give complex 2-H. As shown in the scheme below, this process was completely regioselective and the latter species was also converted into the starting material by reaction with $NaBH_4$. The characterization of complex 2-H is given in the Supporting Information, but no further studies of this species were undertaken.



1-H

2-H

[10] a) G. Yan, X. Wu, M. Yang, *Org. Biomol. Chem.* **2013**, *11*, 5558–5578; b) N. A. Bokach, V. Y. Kukushkin, *Russ. Chem. Rev.* **2005**, *74*, 153–170; c) N. A. Bokach, M. L. Kuznetsov, V. Y. Kukushkin, *Coord. Chem. Rev.* **2011**, *255*, 2946–2967.

[11] a) J. Lasri, S. Gupta, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Inorg. Chem. Commun.* **2012**, *18*, 69–72; b) M. N. Kopylovich, K. V. Luzyanin, M. Haukka, A. J. L. Pombeiro, V. Y. Kukushkin, *Dalton Trans.* **2008**, 5220–5224; c) K. V. Luzyanin, A. J. L. Pombeiro, M. Haukka, V. Y. Kukushkin, *Organometallics* **2008**, *27*, 5379–5389; d) P. V. Gushchin, K. V. Luzyanin, M. N. Kopylovich, M. Haukka, A. J. L. Pombeiro, V. Y. Kukushkin, *Inorg. Chem.* **2008**, *47*, 3088–3094.

[12] a) J. Vicente, J. A. Abad, M.-J. López-Sáez, P. G. Jones, *Angew. Chem. Int. Ed.* **2005**, *44*, 6001–6004; *Angew. Chem.* **2005**, *117*, 6155–6158; b) J. Vicente, M. T. Chicote, M. A. Beswick, M. C. Ramirez de Arellano, *Inorg. Chem.* **1996**, *35*, 6592–6598; c) J. Vicente, M.-T. Chicote, M.-C. Lagunas, P. G. Jones, *Inorg. Chem.* **1995**, *34*, 5441–5445.

[13] a) J. J. García, P. Zerecero-Silva, G. Reyes-Rios, M. G. Crestani, A. Arévalo, R. Barrios-Francisco, *Chem. Commun.* **2011**, *47*, 10121–10123; b) A. Arévalo, J. J. García, *Eur. J. Inorg. Chem.* **2010**, 4063–4074; c) T. A. Ateşin, T. Li, S. Lachaize, W. W. Brennessel, J. J. García, W. D. Jones, *J. Am. Chem. Soc.* **2007**, *129*, 7562–7569; d) J. J. García, N. M. Brunkan, W. D. Jones, *J. Am. Chem. Soc.* **2002**, *124*, 9547–9555.

[14] a) M. G. Crestani, A. Steffen, A. M. Kenwright, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *Organometallics* **2009**, *28*, 2904–2914; b) X. Wang, H. Chen, X. Li, *Organometallics* **2007**, *26*, 4684–4687; c) B. de Bruin, M. J. Boerakker, R. de Gelder, J. M. M. Smits, A. W. Gal, *Angew. Chem. Int. Ed.* **1999**, *38*, 219–222; *Angew. Chem.* **1999**, *111*, 118–121.

[15] J.-R. Huang, Q. Song, Y.-Q. Zhu, L. Qin, Z.-Y. Qian, L. Dong, *Chem. Eur. J.* **2014**, *20*, 16882–16886.

[16] a) T. G. Appleton, H. C. Clark, L. E. Manzer, *Coord. Chem. Rev.* **1973**, *10*, 335–422; b) F. R. Hartley, *Chem. Soc. Rev.* **1973**, *2*, 163–179; c) L. J. Manojlovic-Muir, K. W. Muir, *Inorg. Chim. Acta* **1974**, *10*, 47–49; d) E. M. Shustorovich, M. A. Porai-Koshits, Y. A. Buslaev, *Coord. Chem. Rev.* **1974**, *17*, 1–98; e) T. G. Appleton, M. A. Bennett, *Inorg. Chem.* **1978**, *17*, 738–747; f) K. I. Purcell, J. C. Kotz, *Inorganic Chemistry*, W. B. Saunders, Co. Philadelphia, **1977**, chap. 13.

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