

C–H Bond Activations by New Labile η^6 -Arene Complexes of Iridium

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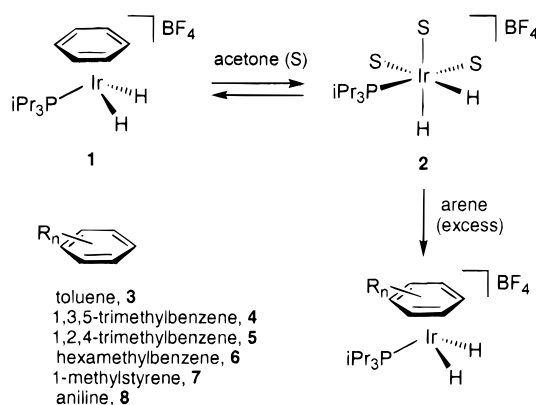
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The activation of C–H bonds of hydrocarbons by transition metal complexes is a process of central interest since it may lead to the functionalization of unreactive compounds.¹ To achieve these challenging functionalizations, the C–H activating compounds should remain reactive after the activation step, allowing further transformations with the participation of the activated substrate. However, this requirement is frequently not fulfilled by the C–H activating metal complexes hitherto reported, which in most cases are unable to create adequate coordination vacancies after activation. This is the case of half-sandwich complexes of iridium containing Cp* ligands which, despite their remarkable capabilities for C–H bond activation, can only create coordination vacancies through the elimination of the activated substrate.² In an attempt to overcome the limitations of these iridium complexes, we searched for C–H activating species containing labile ligands. This search has led us to the new half-sandwich η^6 -arene complexes of iridium³ reported here.

Compound **1**⁷ is obtained as a white solid in 70% yield, in a one-pot synthesis, by treatment of the dimer $[\text{Ir}(\mu\text{-OMe})(\text{cod})]_2$ with the phosphonium salt $[\text{HP}^i\text{Pr}_3]\text{BF}_4$ in acetone/benzene solution, followed by reaction with hydrogen. The benzene ligand of **1** is readily substituted by solvent molecules in acetone solution, giving rise to the tris-acetone compound **2**,⁸ in equilibrium with **1** (Scheme 1). The equilibrium constant for the formation of the solvato species **2** ($K = [2]/[\text{C}_6\text{H}_6][1]$) has been estimated by ¹H NMR as 0.45 mol, in acetone-*d*₆ at 293 K. The treatment of the

Scheme 1



1/2 equilibrium mixture with an excess of arenes other than benzene readily affords products of arene substitution, as shown in Scheme 1 for a variety of arenes. In the case of aniline, the synthesis of complex **8** requires the use of the stoichiometric amount of this ligand since the excess leads to the replacement of the η^6 -aniline by three N-bonded anilines giving the cation $[\text{IrH}_2(\text{NH}_2\text{Ph})_3(\text{P}^i\text{Pr}_3)]^+(\mathbf{9})$, analogous to species **2**, in equilibrium with **8**.

The spectroscopic data of the complexes shown in Scheme 1 are consistent with the fast rotation of the arene ligand around the Ir–arene axis. This rotation results in the chemical equivalence of the hydride ligands in the 293 K ¹H NMR spectra, except for complex **5** in which the asymmetry of the arene ligand allows the observation of nonequivalent hydrides showing a mutual coupling constant of 5.1 Hz. The structure of the mesitylene derivative **4** determined by X-ray diffraction is shown in Figure 1.⁹

In contrast to that shown for 1-methylstyrene in Scheme 1, the reaction of **1** with styrene does not give the arene substitution product. In turn, styrene is hydrogenated to ethylbenzene, which remains coordinated to the final reaction product **10** (Scheme 2).¹⁰ This reaction suggests the potential use of complex **1** as a homogeneous hydrogenation catalyst, which has been successfully tested for substrates such as alkenes and ketones.

In addition, this hydrogenation capability can be used with synthetic purposes in the preparation of Ir(I)–alkene complexes, as shown in Scheme 2 for the ethylene complex **11**.¹¹ Although the solutions of **11** in acetone do not show any detectable product of arene replacement by solvent molecules, the treatment of these solutions with an excess of arenes such as mesitylene leads to the product of arene substitution **12** (Scheme 2). This complex can be also conveniently prepared by treatment of the dihydride **4** with ethylene in acetone. The spectroscopic data of the ethylene derivatives **11** and **12** at room temperature are consistent with

(8) Characterization data for **2**: ¹H NMR (acetone-*d*₆, 253 K, 300 MHz) δ –31.08 (d, $J_{\text{HP}} = 23.7$ Hz, 2H, Ir–H), 1.15 (dd, $J_{\text{HP}} = 13.5$ Hz, $J_{\text{HH}} = 6.8$ Hz, 18H, PCHCH₃), 2.12 (m, 3H, PCHCH₃); ³¹P{¹H} NMR (acetone-*d*₆, 253 K, 121 MHz) δ 31.32 (s); ¹³C{¹H} NMR (acetone-*d*₆, 253 K, 75 MHz) δ 16.49 (s, PCHCH₃), 22.53 (d, $J_{\text{CP}} = 35.2$ Hz, PCHCH₃). The tris-acetonitrile analogue to complex **2** has been reported: Sola, E.; Bakhamutov, V. I.; Torres, F.; Elduque, A.; López, J. A.; Lahoz, F. J.; Werner, H.; Oro, L. A. *Organometallics* **1998**, *17*, 683.

(9) Crystallographic data for **4**: crystals are monoclinic, *P*2₁; a transparent colorless irregular block was used (0.36 × 0.24 × 0.18 mm). Cell parameters $a = 8.1477(7)$ Å, $b = 13.8943(12)$ Å, $c = 10.1659(9)$ Å, $\beta = 109.454(10)^\circ$; $Z = 2$; data collected at 150 K. All non-hydrogen atoms refined with anisotropic adp's; organic hydrogens included in calculated positions. Hydride ligands obtained from difference Fourier maps and refined with low-angle data ($2\theta \leq 40^\circ$); in the last cycles they were refined riding on the Ir atom with two free isotropic thermal parameters. $R_1 = 0.0345$ (3675 reflections, $I \leq 2\sigma(I)$) and $wR_2 = 0.0833$; GOF = 1.079 (SHELXL-97 program).

(10) An analogous reaction leading to the cation $[\text{Ir}(\eta^6\text{-C}_6\text{H}_5\text{Et})(\text{PPh}_3)_2]^+$ was reported in ref 6a.

- (1) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.
 (2) (a) Arndsten, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154 and references therein. (b) Arndsten, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (c) Lohrenz, J. C.; Jacobsen, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1305.
 (3) The iridium η^6 -arene complexes reported so far are restricted to Ir(III) derivatives of general composition $[\text{CpIr}(\text{arene})]^{2+}$ (ref 4) and Ir(I) species of formulas $[\text{Ir}(\text{arene})(\text{diene})]^+$ (ref 5) and $[\text{Ir}(\text{arene})(\text{P}_2)]^+$ (ref 6).
 (4) (a) White, C.; Maitlis, P. M. *J. Chem. Soc. A* **1971**, 3322. (b) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654. (c) Grundy, S. L.; Maitlis, P. M. *J. Organomet. Chem.* **1984**, *272*, 265. (d) Rybinskaya, M. I.; Kudinov, A. R.; Kaganovich, V. S. *J. Organomet. Chem.* **1983**, *246*, 279. (e) Herebian, D. A.; Schmidt, C. S.; Sheldrick, W. S.; van Wüllen, C. *Eur. J. Inorg. Chem.* **1988**, 1991. (f) Amouri, H.; Besace, Y.; Le Bras, J.; Vaissermann, J. *J. Am. Chem. Soc.* **1998**, *120*, 6171.
 (5) (a) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339. (b) Osborn, J. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1971**, *93*, 3089. (c) Dragget, P. T.; Green, M. L.; Lowrie, S. F. E. *J. Organomet. Chem.* **1977**, *135*, C60. (d) Bianchi, F.; Gallazzi, M. C.; Porri, L.; Diversi, P. *J. Organomet. Chem.* **1980**, *202*, 99. (e) Usón, R.; Oro, L. A.; Cabeza, J.; Foces-Foces, C.; Cano, F. H.; García-Blanco, S. *J. Organomet. Chem.* **1983**, *246*, 73. (f) Usón, R.; Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H.; García-Blanco, S.; Vázquez de Miguel, A. *J. Organomet. Chem.* **1984**, *273*, 111. (g) Oro, L. A.; Valderrama, M.; Cifuentes, P.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1984**, *276*, 67.
 (6) (a) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (b) Schnabel, R. C.; Roddick, D. M. *Organometallics* **1996**, *15*, 3550.

(7) Characterization data for **1**: IR (Nujol mull) 2208, 2237 $\nu(\text{Ir–H})$; ¹H NMR (CDCl₃, 293 K, 300 MHz) δ –16.66 (d, $J_{\text{HP}} = 27.2$ Hz, Ir–H), 1.08 (dd, $J_{\text{HP}} = 15.6$ Hz, $J_{\text{HH}} = 7.2$ Hz, 18H, PCHCH₃), 2.14 (m, 3H, PCHCH₃), 6.71 (s, 6H, C₆H₆); ³¹P{¹H} NMR (CDCl₃, 293 K, 121 MHz) δ 51.23 (s); ¹³C{¹H} NMR (CDCl₃, 293 K, 75 MHz) δ 19.78 (d, $J_{\text{CP}} = 1.3$ Hz, PCHCH₃), 28.16 (d, $J_{\text{CP}} = 34.4$ Hz, PCHCH₃), 97.99 (d, $J_{\text{CP}} = 2.3$ Hz, C₆H₆); MS (FAB+, *m/z* (%)) 433 (100) [M⁺]; Λ_M (5×10^{-4} M, acetone) = 135 Ω^{-1} cm² mol⁻¹ (1.1). Anal. Calcd for C₁₅H₂₉BF₄IrP: C, 34.69; H, 5.63. Found: C, 34.28; H, 5.87.

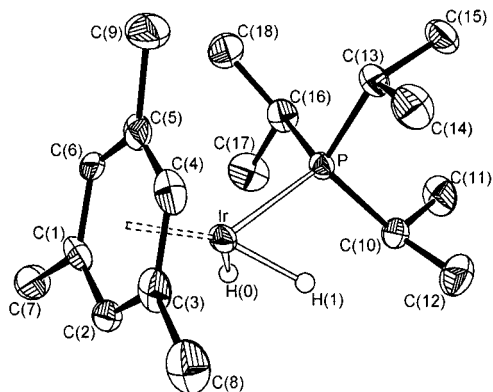
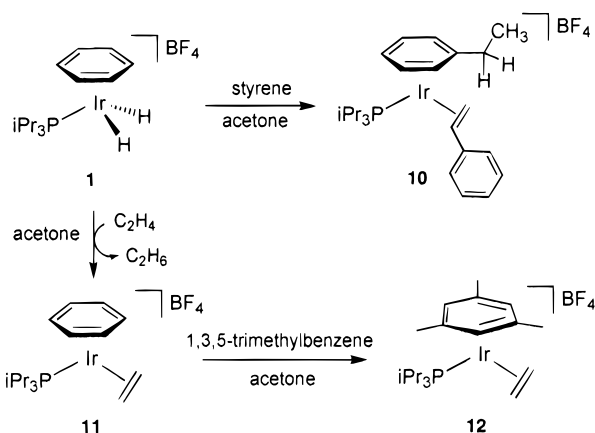


Figure 1. Molecular structure of the cation of complex $[(\eta^6\text{-}1,3,5\text{-C}_6\text{H}_3\text{(Me)}_3)\text{IrH}_2(\text{P}^i\text{Pr}_3)]\text{BF}_4$ (**4**) together with atom labeling scheme used. Hydride ligands have been drawn at refined positions. Selected bond lengths (Å) and angles (deg) are as follows: Ir–P 2.270(2), Ir–C(mesitylene) 2.246(9)–2.367(9), Ir–G 1.832(11), Ir–H(0) 1.49, Ir–H(1) 1.50; P–Ir–G 141.6(3), P–Ir–H(0) 75, P–Ir–H(1) 63, G–Ir–H(0) 127, G–Ir–H(1) 149, H(0)–Ir–H(1) 68.0 (G is the centroid of the C(1)–C(6) ring).

Scheme 2

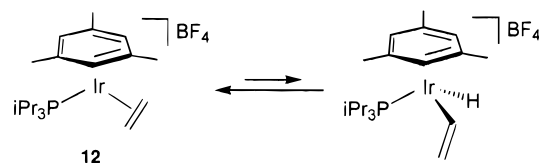


the presence of a fast rotating η^6 -arene ligand and a nonrotating ethylene, which is disposed parallel to the arene ring.

In the acetone- d_6 solutions containing equilibrium mixtures of **1** and the tris-acetone complex **2**, the hydride ligands of these compounds undergo H/D scrambling with the solvent giving rise, after a period of several hours at room temperature, to isotopomeric mixtures observable by NMR.¹² Such scrambling processes with acetone have been previously observed for other cationic hydrido complexes of iridium(III),^{8,13} being attributed to the Brønsted acidity of these species.¹⁴ After longer reaction time, the ^2H NMR spectra of the mixtures show that the H/D scrambling

(11) Characterization data for **11**: ^1H NMR (CDCl_3 , 293 K, 300 MHz) δ 1.60 (dd, $J_{\text{HP}} = 14.1$ Hz, $J_{\text{HH}} = 7.2$ Hz, 18H, PCHCH_3), 2.07 (part A of a $\text{AA}'\text{MM}'\text{X}$ spin system ($\text{X} = ^3\text{P}$): $J_{\text{AA}'} = 8.5$ Hz, $J_{\text{AM}} = 11.3$ Hz, $J_{\text{AM}'} = 2.3$ Hz, $J_{\text{AX}} = 4.9$ Hz, 2H, CH_2), 2.39 (m, 3H, PCHCH_3), 3.32 (part M of a $\text{AA}'\text{MM}'\text{X}$ spin system ($\text{X} = ^3\text{P}$): $J_{\text{MM}'} = 8.5$ Hz, $J_{\text{MX}} = 0.8$ Hz, 2H, CH_2), 7.01 (s, 6H, C_6H_6); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, 121 MHz) δ 22.43 (s); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K, 75 MHz) δ 19.31 (d, $J_{\text{CP}} = 1.4$ Hz, PCHCH_3), 19.53 (d, $J_{\text{CP}} = 2.2$ Hz, C_2H_4), 24.43 (d, $J_{\text{CP}} = 32.2$ Hz, PCHCH_3), 95.89 (d, $J_{\text{CP}} = 2.2$ Hz, C_6H_6); MS (FAB+, m/z (%)) 459 (100) [M^+]; Λ_{M} (5×10^{-4} M, acetone) = $129 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (1:1). Anal. Calcd for $\text{C}_{17}\text{H}_{32}\text{BF}_4\text{IrP}$: C, 37.37; H, 5.90. Found: C, 37.02; H, 5.55.

Scheme 3



is extended to the benzene moieties and to the phosphine ligands, indicating that the system formed by complexes **1** and **2** activates C–H bonds. As for other electrophilic complexes, these C–H bond activations may involve either an oxidative addition or a σ -bond metathesis mechanism, although for Ir(III) complexes there is a preponderance of evidence supporting the participation of Ir(V) intermediates.¹⁵

On the other hand, the solutions of the electron-rich iridium(I) complex **12** in acetone- d_6 at room temperature show slow deuterium incorporation into the ethylene ligand.¹⁶ This is in contrast to the behavior of the less basic benzene derivative **11**, which, apparently, does not undergo evolution in this solvent. Taking into account the aforementioned Brønsted acidity of the iridium(III) dihydrides, this H/D scrambling affecting the ethylene ligand could be explained through the participation of an iridium(III) hydrido-vinyl species, formed by the C–H oxidative addition of ethylene (Scheme 3).

The proposal of Scheme 3 implies not only that the nucleophilic Ir(I) derivative **12** activates ethylene C–H bonds, but also that the lifetime of the Ir(III) species generated in this activation is long enough to allow intermolecular H/D scrambling. Whether or not this lifetime will allow other intermolecular reactions leading to the functionalization of the activated ethylene is being currently investigated.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica for the support of this research (Project Nos. PB94-1186 and PB95-0318).

Supporting Information Available: Synthetic procedures and spectroscopic and analytical data for complexes **1** to **12**; tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **4** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) The hydride resonance of the ^1H NMR spectrum and the $^{31}\text{P}\{^1\text{H}\}$ NMR signal corresponding to the HD isotopomer of **2** show downfield isotopic shifts of 0.04 and 0.19 ppm, respectively, which compare well to those found in related octahedral iridium(III) compounds (see refs 8 and 13). The deuteration of one hydride of **1** does not produce any detectable isotopic shift in the hydride ^1H signal, whereas, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the isotopomeric mixture is observable but not well resolved (isotopic shifts can be estimated as about +0.02 ppm). The $^2\text{H}\{^1\text{H}\}$ NMR spectrum in CH_2Cl_2 of a sample of **1** isolated after treatment with acetone- d_6 shows a high-field doublet at $\delta -16.36$ with a D–P coupling constant of 4.2 Hz, which may correspond to an unresolved mixture of the two expected isotopomers.

(13) Jiménez, M. V.; Sola, E.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Chem. Eur. J.* **1998**, *4*, 1398.

(14) Kristjánssdóttir, S. S.; Norton, J. R. *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York 1992; p 309.

(15) Alaimo, P. J.; Bergman, R. G. *Organometallics* **1999**, *18*, 2707.

(16) The deuteration of the ethylene ligand of **12** results in complex resonances for the ethylene hydrogens and carbons in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, showing the formation of several isotopomers (a maximum of 8 isotopomers can be formed). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these isotopomeric mixtures display two signals corresponding to deuterated isotopomers ($\Delta\delta = +0.05$ and $+0.1$ ppm), suggesting that not every H/D substitution in the nonrotating ethylene provokes observable isotopic shifts in the ^{31}P signal.