

Alkane Dehydrogenation by Sequential, Double C–H Bond Activation by $\text{Tp}^{\text{Br}^3}\text{Ir}(\text{C}_2\text{H}_4)_2$ (Tp^{Br^3} = hydrotris(3,4,5-tribromo)pyrazolylborate)

Pilar Rodríguez,[†] M. Mar Díaz-Requejo,[†] Tomás R. Belderrain,[†]
Swiatoslaw Trofimenko,[‡] M. Carmen Nicasio,^{*,†} and Pedro J. Pérez^{*,†}

Departamento de Química y Ciencia de los Materiales, Universidad de Huelva,
Campus de El Carmen, 21007 Huelva, Spain, and Department of Chemistry and Biochemistry,
University of Delaware, Newark, Delaware 19716

Received October 17, 2003

The new complex $\text{Tp}^{\text{Br}^3}\text{Ir}(\text{C}_2\text{H}_4)_2$, **1**, photochemically activates the C–H bonds of *n*-pentane in a two-step process, the first one being the formation of an isolable alkyl-hydride intermediate of composition $\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_{11})$, **3a**, that subsequently undergoes β -hydride elimination to generate a terminal olefin complex, $\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})_2(\text{C}_5\text{H}_{10})$, **4a**. The reaction can also be extended to diethyl ether. In this case, the reaction proceeds by the activation of one of the β -C–H bonds (with respect to the O-ether atom) with formation of the alkyl-hydride **3b** and the dehydrogenation product **4b**. These processes also compete with the intramolecular C–H activation of one of the coordinated ethylene ligand by the Ir(I) center in **1**, which affords the hydride-vinyl complex $\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_4)$, **2**. Attempts to thermally induce the above transformations has led to the exclusive formation of a mixture of the hydride- α,ω -butenyl complex $\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$, **5**, and the hydride-crotyl complex $\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\text{C}_4\text{H}_7)$, **6**.

Introduction

The selective activation of carbon–hydrogen bonds in alkanes by transition metal complexes still finds an enormous interest in many researchers due to the potential application of such methodology in the development of new catalytic routes to valuable products.¹ Among the processes based on such activation, the dehydrogenation of *n*-alkanes to give the corresponding 1-alkenes (α -olefins) is particularly interesting given the great versatility of alkenes as organic feedstock. It is generally accepted² that the addition, or elimination, of C–H bonds to, or from, the metal core is a requisite step for the catalytic alkane dehydrogenation reaction. However, in most of the reported systems³ the direct observation or isolation of the alkyl-hydride intermediates has been precluded. Seminal work by Crabtree⁴ and co-workers led to the first examples of stoichiometric alkane dehydrogenation. Catalytic cycles were later

reported by Crabtree,^{5a} Goldman,^{5b,c} and Jensen.^{6a} Kaska and Jensen have also reported a very efficient catalytic system based on iridium with pincer-type ligands,^{6b} with a very high activity that only very recently has been improved by Brookhart et al.^{6c}

Group 9 metal complexes appear in most of the reported systems regarding the activation of C–H bonds in the last two decades. In the early 1980s the first examples were achieved by Bergman,⁷ Graham,⁸ and Jones,⁹ in all cases a Cp^*ML ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L} = \text{CO}, \text{PMe}_3$) fragment being responsible for the process. Later in that decade the activation of olefinic C–H bonds by oxidative addition to the metal was also accomplished, not only with the Cp^*ML core¹⁰ but also with the isoelectronic Tp^xML unit (Tp^x = trispyrazolylborate ligand,¹¹ $\text{L} = \text{olefin}, \text{CO}$). Graham,^{12a} Crabtree,^{12b} and Oro^{12c} demonstrated the capabilities of this fragment to induce the

* Corresponding author. Tel: + 34 959 019956. Fax: 34 959 019942.
E-mail: perez@dqcm.uhu.es.

[†] Universidad de Huelva.

[‡] University of Delaware.

(1) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. (c) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.

(2) (a) Benson, M. T.; Cundari, T. R. *Inorg. Chim. Acta* **1997**, *259*, 91. (b) Niu S.; Hall, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 3992. (c) Haenel, M. W.; Oevers, S.; Angermund, K.; Kaska, W. C.; Fan, H.-J.; Hall, M. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3596. (d) Renkema, K. B.; Kissin Y. V.; Goldman, A. S. *J. Am. Chem. Soc.* **2003**, *125*, 7770.

(3) (a) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083. (b) Xu, W.-W.; Rosini, G. P.; Gupta, M.; Jensen, C.; Kaska, W. C.; Krogh-Jespersen, K.; Goldman, A. S. *Chem. Commun.* **1997**, 2273.

(4) (a) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738–7740. (b) Baudry, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. *J. Organometallics* **1984**, *3*, 816–817.

(5) (a) Burk, M. W.; Crabtree, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 8025–8032. (b) Maguire, J. A.; Goldman, A. S. *J. Am. Chem. Soc.* **1991**, *113*, 6706–6708. (c) Maguire, J. A.; Petrillo, A.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 9492–9498.

(6) (a) Belli, J.; Jensen, C. M. *Organometallics* **1996**, *15*, 1532–1534. (b) Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *Chem. Commun.* **1996**, 2083. (c) Göttker-Schnetmann, I.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* ASAP.

(7) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(8) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.

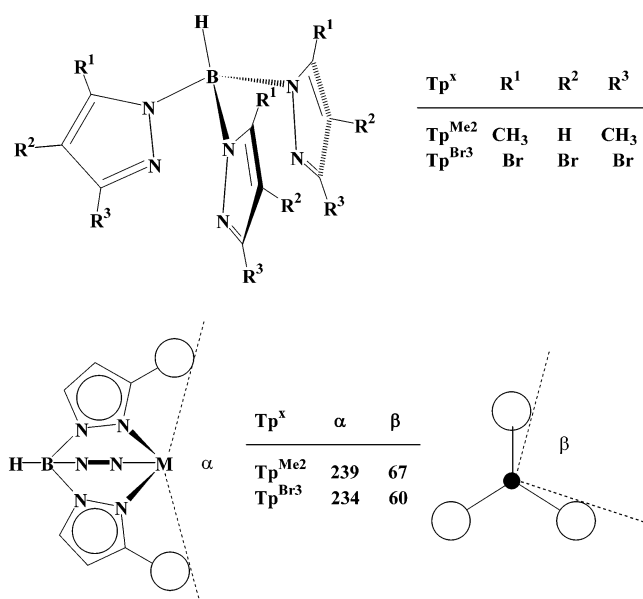
(9) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650.

(10) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

(11) Trofimenko, S. *Scorpionates, The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(12) (a) Ghosh, C. K.; Hoyano, J. K.; Krentz, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1989**, *111*, 5480. (b) Tanke, R. H.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444. (c) Fernández, M. J.; Rodríguez, M. J.; Oro, L. A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2073.

Chart 1



activation of olefinic C–H bonds to produce hydrido-vinyl derivatives. Since then, a number of contributions involving the activation of carbon–hydrogen bonds by complexes containing the Tp^xM unit (M = Rh, Ir) have appeared in the literature.¹³ An especially interesting system is based on Carmona's complex Tp^{Me2}Ir(C₂H₄)₂. This bis(ethylene) iridium(I) compound has been found to induce a considerable number of thermal activation processes.^{13,14} In the case of ethers (cyclic and noncyclic) and aliphatic amines, a double α-CH activation has been observed, leading to the formation of Fischer-type carbene complexes.¹⁵

In recent years, we have been working in the area of the functionalization of carbon–hydrogen bonds with the methodology based on the metal-catalyzed insertion of diazo compounds. We have obtained particularly good results with Tp^{Br3}Cu(NCMe) as the catalyst,¹⁶ a complex that contains the perbromo hydrotris(3,4,5-tribromo)pyrazolylborate ligand, Tp^{Br3} (Chart 1). The ligands Tp^{Me2} and Tp^{Br3} display similar values for the cone (α) and wedge (β) angles,¹¹ and therefore the steric demand induced around the metal center should be similar (see Chart 1). However, the distinct nature of the groups attached to the ligand skeleton should infer any influence in terms of electron density. Actually, the complexes Tp^xCu(CO) (Tp^x = Tp^{Me2}, Tp^{Br3}) showed different values for the ν(CO) in the IR spectrum (Nujol mull).¹⁷ The perbromo derivative displayed the absorption band centered at 2105 cm⁻¹, whereas in the Tp^{Me2} analogue this band appeared at 2056 cm⁻¹. The differences in

(13) Slugovc, C.; Padilla-Martinez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129.

(14) (a) Alvarado, Y.; Daff, P. J.; Pérez, P. J.; Poveda, M. L.; Sánchez-Delgado, R.; Carmona, E. *Chem. Eur. J.* **1997**, *3*, 860. (b) Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Carmona, E. *Chem. Eur. J.* **1998**, *4*, 2236. (c) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538.

(15) Carmona, E.; Paneque, M.; Poveda, M. L. *Dalton Trans.* **2003**, 4022.

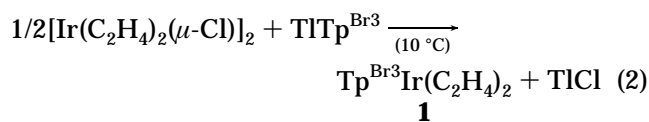
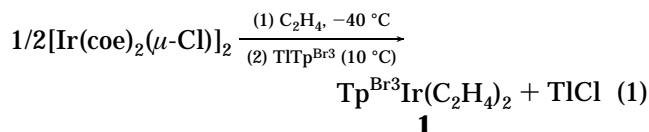
(16) Caballero, A.; Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 1446.

(17) Morilla, M. E.; Molina, M. J.; Díaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *Organometallics* **2003**, *22*, 2914.

electronics and the similarities in sterics motivated us to prepare the complex Tp^{Br3}Ir(C₂H₄)₂, **1**, analogous to Carmona's complex, to study the effect, if any, of those differences in the activation of carbon–hydrogen bonds by the Tp^xIr core.

Results and Discussion

Activation of Pentane by Tp^{Br3}Ir(C₂H₄)₂ (1**).** The complex Tp^{Br3}Ir(C₂H₄)₂ (**1**) was obtained, in high yield, following a procedure similar to that described for the Tp^{Me2} derivative^{9a} (eq 1) or, alternatively, by using [Ir(C₂H₄)₂Cl]₂¹⁸ as the starting material (eq 2).



Like the Tp^{Me2} analogue, compound **1** displayed fluxional behavior in solution. The ethylene groups gave rise to only one resonance, in both the ¹H and the ¹³C-{¹H} NMR spectra (C₆D₆, 20 °C), at δ 2.56 and 32.6 ppm, respectively, the latter being shifted to the downfield region as compared to the Tp^{Me2} complex.^{14a} Only three resonances were observed in the ¹³C{¹H} NMR spectrum for the nine quaternary carbons of the pyrazolyl rings of the Tp^{Br3} moiety centered at δ 133.6, 124.6, and 104.4. In addition, we observed a value of 2596 cm⁻¹ for ν(B–H) in the IR spectrum of complex **1**, supporting the presence of a κ³-Tp^{Br3} ligand in the molecule.¹⁹ These spectroscopic data are in good agreement with those reported for the structurally characterized Tp^{Me2}Ir(C₂H₄)₂, for which a trigonal bipyramidal structure in the solid state has been found.^{14a}

Carmona's complex chemistry has been explained in terms of accessible Ir(III) species from the bis(ethylene) Ir(I) starting material. The irradiation of solutions of Tp^{Me2}Ir(C₂H₄)₂ with an UV lamp provided high-yield conversions into the hydrido-vinyl complex Tp^{Me2}Ir(CH=CH₂)(H)(C₂H₄). Under the same conditions, our perbromo analogue **1** decomposed massively, with no identified products being observed from the reaction mixture. However, irradiation of cyclohexane solutions under sunlight (visible) for 20 min led to the formation of the product derived from the C–H vinylic activation, Tp^{Br3}Ir(CH=CH₂)(H)(C₂H₄) (**2**), in 80% yield (with 20% of the bis(ethylene) still unreacted). Complex **2** showed NMR patterns similar to those of the Tp^{Me2} derivative (see Experimental Section). But when irradiation was carried out in *n*-pentane, with the temperature maintained at –10 °C, the results were quite different (Scheme 1). Photolysis for 40 min induced the total consumption of the bis(ethylene) complex and the formation of two new species, **3a** (41%) and **4a** (33%),

(18) Arthurs, M. A.; Bickerton, J.; Stobart, S. R.; Wang, J. *Organometallics* **1998**, *17*, 2743.

(19) For a discussion on the hapticity of the Tp ligand based on ν(B–H) values see: Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121.

Scheme 1. Photochemical Activation of 1

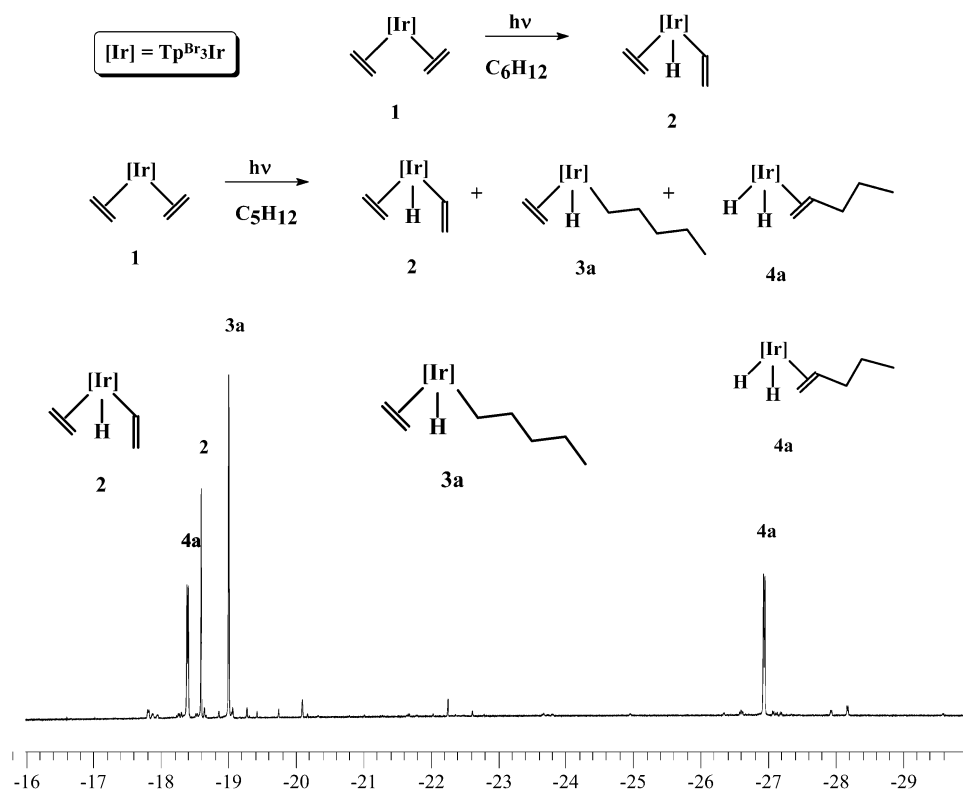


Figure 1. Hydride resonances of the mixture of **2**, **3a**, and **4a**.

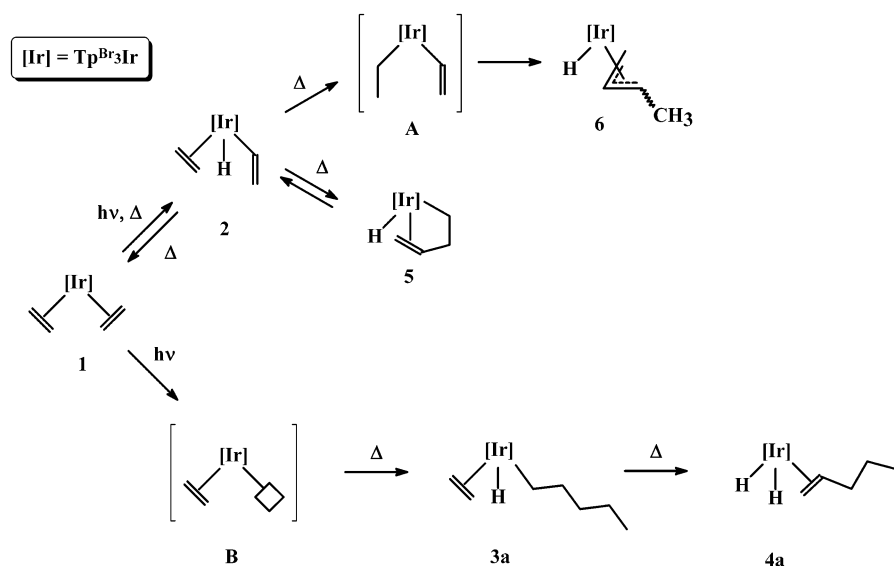
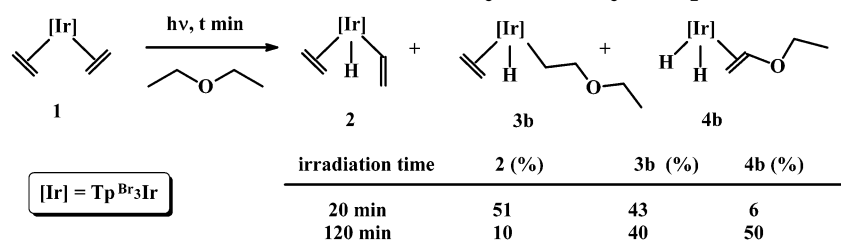
accounting for 74% of the species in solution, the remaining 26% being covered by **2**. Figure 1 shows the high-field region (hydride resonances) of the ^1H NMR spectrum of the reaction mixture. On the basis of an extensive NMR study we have been able to obtain unambiguous information about their compositions. Thus, complex **3a** has been identified as the hydrido-pentyl complex $\text{Tp}^{\text{Br}_3}\text{Ir}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)(\text{H})(\text{C}_2\text{H}_4)_2$, derived from the activation of a C–H bond of the methyl group in pentane. The ^1H NMR (C_6D_6 , 20°C) exhibited a hydride resonance at $\delta -19.01$ ppm and two resonances at $\delta 2.79$ (m) and 4.19 ppm (m) due to a static ethylene molecule. The *n*-pentyl unit displayed several multiplet resonances: the diastereotopic protons of the methylene group bonded to iridium appeared as two multiplets centered at 2.56 and 0.58 ppm, whereas other signals in the $\delta 0.65$ – 1.29 ppm range corresponded to the remaining CH_2 groups, and a triplet at $\delta 0.82$ ($J_{\text{HH}} = 7$ Hz) to the methyl group. The observation of resonances at $\delta -7.0$ (CH_2 –Ir), 14.6, 22.6, 31.6, and 43.4 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3a** confirmed the presence of a five-carbon chain attached to the Ir(III) center, the resonance at 46.7 ppm being assigned to the ethylene ligand. It is also worth mentioning that the nine quaternary carbons supporting the nine bromine atoms have also been observed, as evidence of the octahedral, nonsymmetric geometry of the molecules of **3a**.

The second compound formed in this reaction has been characterized as the dihydride $\text{Tp}^{\text{Br}_3}\text{Ir}(\text{H})_2(\text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3)$ (**4a**). The ^1H NMR spectrum showed two doublets in the high-field region assigned to Ir–H groups (-18.39 , d; -26.94 , d; $J_{\text{HH}} = 7.6$ Hz). In addition, characteristic resonances for a terminal olefin

group were also observed at $\delta 2.55$ (d, $J_{\text{HH}} = 8.2$ Hz), 3.65 (d, $J_{\text{HH}} = 11.6$ Hz), and 5.36 (ddt, $J_{\text{HH}} = 7.3$ Hz). The formation of this compound could be explained as the consequence of a β -elimination reaction in the pentyl chain in **3a** and ethylene loss. Prolonged irradiation (75 min overall time) effected a change in the **2**:**3a**:**4a** ratio from 26:41:33 to 15:35:50, with no secondary C–H activation products nor isomerization of the terminal olefin in complex **4a** being observed under these conditions. To our knowledge, the formation of C–H activation products from alkane substrates has not been observed with the Tp^{Me_2} -containing bis(ethylene) complex.²⁰ It has been mentioned above that group 9 transition metal unsaturated species of the type $\text{CpM}(\text{L})$ ($\text{M} = \text{Rh}, \text{Ir}$) or $\text{RhTp}(\text{L})$ have been reported to promote the activation of C–H bonds of hydrocarbons under thermal or photochemical conditions. One interesting case is that of the cationic Ir(III) derivative, $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{Me})]^+$, described by Bergman et al.²¹ This complex was found to be very active and selective toward the activation of C–H bonds of saturated hydrocarbons at very mild conditions. However, the thermal activation of *n*-pentane in the presence of the above-mentioned Ir(III) complex produced the α -alkene complex as the sole product, the alkyl-hydride complex being proposed as an intermediate, although it could not be detected. Thus, the system we report herein could constitute an example of a sequential double dehydrogenation of alkanes. But for this purpose, it seems necessary to verify that **4a** forms directly from **3a**.

(20) Carmona, E. Personal communication.

(21) (a) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970. (b) Luecke, H. F.; Arndtsen, B. A.; Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 2117.

Scheme 2. Activation of Olefinic and Aliphatic C–H Bonds by Complex 1**Scheme 3. Activation of Diethyl Ether by Complex 1**

isoprene)^{24a} indeed activates the α -C–H bonds of Et₂O to generate a hydride ethoxy carbene derivative, and a similar transformation has been observed for platinum.^{24b} Bergman's complex [Cp*Ir(PMe₃)(Me)]⁺ promoted the dehydrogenation²¹ of diethyl ether to produce a vinyl ether complex similar to **4b**. This reaction was postulated to proceed by the initial addition of a β -C–H bond of the diethyl ether molecule to the Ir(III) center to form an unobserved cationic methyl-activated intermediate similar to **3b**, which then rearranges by rapid β -H elimination to the isolated hydride (ethyl vinyl ether) complex. In our case, we believe that the overall reaction mechanism depicted in Scheme 2 finds application in the diethyl ether system. Similar experiments were carried out to demonstrate this proposal: (i) heating of the solution enriched in **2** and **3b** induced the independent conversions of **2** into **5** and **6** as well as that of **3b** into **4b**; (ii) a diethyl ether solution heated at 140 °C did not provide detectable amounts of **3b** and/or **4b**, again evidencing the need of photolysis to induce the ethylene extrusion necessary to initiate the activation reaction.

Conclusions

The results described in this contribution demonstrate the distinct chemical behavior toward C–H bond activation processes of the complexes Tp^{Br3}Ir(C₂H₄)₂ and Tp^{Me2}Ir(C₂H₄)₂. These differences must be related to the electronic effect induced by the Tp^x ligand in the iridium

center, since their steric properties are quite similar. The perbromo ligand generates a more electron-poor complex, compared to the Tp^{Me2} analogue, that must be responsible for the differences in the observed chemical behavior. Complex **1** induced the dehydrogenation of pentane and diethyl ether, similarly to the cationic complex [Cp*Ir(PMe₃)(Me)]⁺. We interpret this similarity in terms that a decrease in the electron density at iridium seems to be a requirement for this reaction to occur. Finally, our system has allowed the stepwise observation of the dehydrogenation process, for both *n*-pentane and diethyl ether, demonstrating that the alkyl-hydrido complexes **3** are intermediates in the formation of **4**.

Experimental Section

All manipulations were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen with the appropriate drying agents and degassed before use. [Ir(coe)₂Cl]₂²⁵ and Tl[Tp^{Br3}]¹¹ were prepared as reported in the literature. NMR spectra were recorded in a Varian Mercury 400 MHz spectrometer. Infrared spectra were recorded as Nujol mulls in KBr using a ATI Mattson Genesis Series FTIR spectrometer. Photolysis experiments were carried out using a conventional tungsten 300 W lamp and a water cooling system.

Synthesis of Tp^{Br3}Ir(C₂H₄)₂, 1. Procedure A. [Ir(coe)₂Cl]₂ (0.45 g, 0.5 mmol) was dissolved in THF (40 mL) and the solution cooled to –40 °C. Ethylene was bubbled through the solution for 15 min, and TlTp^{Br3} (1.13 g, 1.01 mmol) was added. The reaction mixture was maintained at 10 °C to give a golden

(24) (a) Slugovc, C.; Mereiter, K.; Trofimenko, S.; Carmona, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 2158. (b) Holtcam, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848.

(25) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 19.

yellow suspension, which was stirred at that temperature for 3 h. After filtration, the volatiles were removed under vacuum. Complex **1** was obtained in quantitative yield and needed no further purification.

Procedure B. $[\text{Ir}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (0.30 g, 0.47 mmol) was dissolved in THF (30 mL) and the resulting red solution cooled at 0 °C. TTP^{Br^3} (1.06 g, 0.94 mmol) was then added. The resulting brown suspension was stirred for 3 h at 10 °C. The solvent was pumped off and the residue extracted with $\text{CH}_2\text{-Cl}_2$ (20 mL) and filtered off. The yellow solution was taken to dryness, yielding complex **1** in quantitative yield. IR (Nujol): $\nu(\text{B-H})$ 2596 cm^{-1} . ^1H NMR (400 MHz, C_6D_6): δ 2.56 (s, 8 H, C_2H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 104.4, 124.6, 133.6 (CBr), 32.6 (C_2H_4).

Synthesis of $\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\text{C}_2\text{H}_4)(\text{CH}=\text{CH}_2)$, **2.** A solution of **1** (0.08 g, 0.07 mmol) in cyclohexane (20 mL) was irradiated at 10 °C for 20 min. The resulting dark yellow solution was evaporated under vacuum, and the solid residue was analyzed by ^1H NMR spectroscopy, which confirmed the presence of the hydride-vinyl **2** in 80% yield (the starting material accounted for the remaining 20% yield). IR (Nujol): $\nu(\text{Ir-H})$ 2220 cm^{-1} . ^1H NMR (400 MHz, C_6D_6): δ 6.59 (1 H, Ir-CH=CH₂, dd, $J_{\text{HH}} = 17.4$ and 9.9 Hz), 5.29 (1 H, d, Ir-CH=CH₂), 4.44 (m, 2 H, AA' part of a AA'XX' spin system, C_2H_4), 4.33 (1 H, d, Ir-CH=CH₂), 3.05 (m, 2 H, XX' part of a AA'XX' spin system, C_2H_4), -18.57 (s, 1 H, Ir-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 135.1, 133.3, 132.3, 124.6, 124.0, 123.3 (CBr), 121.1 (Ir-CH=CH₂), 119.3 (IrCH=CH₂), 104.8, 104.0, 103.1 (CBr), 49.4 (C_2H_4).

Synthesis of the Complexes **3a and **4a**.** A solution of **1** (0.2 g, 0.17 mmol) in *n*-pentane (60 mL) was irradiated for 40 min at 10 °C. The solvent was removed in vacuo, and the residue analyzed by ^1H NMR, which confirmed the presence of **2**, **3a**, and **4a** in 26:41:33 ratio. Similar results were obtained using **2** as the starting material. We have failed in separating these two compounds, either by fractional crystallization or by column chromatography, the characterization being accomplished by 1D and 2D NMR studies of the reaction mixture.

$\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\text{C}_2\text{H}_4)(\text{C}_5\text{H}_{11})$, **3a.** ^1H NMR (400 MHz, C_6D_6): δ 4.19 (m, 2 H, AA' part of a AA'XX' spin system, C_2H_4), 2.79 (m, 2 H, XX' part of a AA'XX' spin system, C_2H_4), 2.35, 0.58 (m, 1 H each, Ir-CH₂Bu), 1.29 (m, 2 H, Ir(CH₂)₂CH₂Et), 1.20 (m, 2 H, Ir(CH₂)₃CH₂CH₃), 0.82 (t, 3 H, Ir(CH₂)₄CH₃), $J_{\text{HH}} = 7$ Hz), 0.78 and 0.65 (m, 1 H each, IrCH₂CH₂Pr), -19.01 (s, 1 H, Ir-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 135.3, 133.9, 131.8, 124.3, 124.1, 123.4, 104.4, 102.9, 102.6 (CBr), 46.7 (C_2H_4), 43.4 (Ir(CH₂)₂CH₂Et), 31.6 (IrCH₂CH₂Pr), 22.6 (Ir(CH₂)₃CH₂CH₃), 14.6 (Ir(CH₂)₄CH₃), -7.0 (Ir-CH₂Bu).

$\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})_2(\text{C}_5\text{H}_{10})$, **4a.** ^1H NMR (400 MHz, C_6D_6): δ 5.36 (ddt, 1 H, CH₂=CHPr, $J_{\text{HH}} = 11.6$ and 8.2 Hz, $J_{\text{H-CH}_2} = 7.2$ Hz), 3.65 (d, 1 H, CHH=CHPr) 2.55 (d, 1 H, CHH=CHPr), 2.30-2.40 (m, 2 H, CH₂=CHCHHPr), 1.89 (m, 1 H, CH₂=CHCH₂CHHMe), 1.76 (m, 1 H, CH₂=CHCH₂CHHMe), 1.07 (t, 3 H, CH₂=CH(CH₂)₂CH₃, $J_{\text{HH}} = 7$ Hz), -18.39 (d, 1 H, Ir-H, $J_{\text{HH}} = 7.6$ Hz), -26.94 (d, 1 H, Ir-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 136.0, 134.8, 132.4, 123.7, 123.2, 122.4, 103.3, 102.7,

102.2 (CBr), 68.8 (CH₂=CHPr), 43.4 (CH₂=CHPr), 42.7 (CH₂=CHCH₂Et), 27.2 (CH₂=CHCH₂CH₂Me), 14.2 (CH₂=CH(CH₂)₂CH₃).

Synthesis of the Complexes **3b and **4b**.** A solution of **1** (0.15 g, 0.13 mmol) in Et₂O (60 mL) was irradiated at 10 °C for 20 min. The solvent was pumped off and the residue studied by ^1H NMR, which showed the formation of **2**, **3b**, and **4b** in a 51:43:6 ratio. We have characterized **3b** and **4b** by 1D and 2D NMR studies of the reaction mixture.

$\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\text{C}_2\text{H}_4)(\text{C}_4\text{H}_9\text{O})$, **3b.** ^1H NMR (400 MHz, C_6D_6): δ 4.24 (m, 2 H, AA' part of a AA'XX' spin system, C_2H_4), 3.25 and 3.23 (dq, 1 H each, Ir(CH₂)₂OCH₂Me, $J_{\text{HH}} = 10$ and 7 Hz), 2.94-2-91 (m, 2 H, IrCH₂CH₂OEt), 2.87 (m, 2 H, XX' part of a AA'XX' spin system, C_2H_4), 2.71 (td, 1 H, IrCHHCH₂OEt, $J_{\text{HH}} = 10.4$ and 5.6 Hz), 1.11 (m, 1 H, IrCHHCH₂OEt), 1.07 (t, 3 H, Ir(CH₂)₂OCH₂CH₃, $J_{\text{HH}} = 7$ Hz), -19.17 (s, 1 H, Ir-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 135.8, 134.3, 132.0, 124.4, 123.8, 123.6, 104.5, 103.5, 103.1 (CBr), 73.1 (IrCH₂CH₂OEt), 65.3 (Ir(CH₂)₂OCH₂Me), 49.2 (C_2H_4), 15.9 (Ir(CH₂)₂OCH₂CH₃), -9.3 (Ir-CH₂CH₂OEt).

$\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})_2(\text{C}_4\text{H}_8\text{O})$, **4b.** ^1H NMR (400 MHz, C_6D_6): δ 7.50 (ddd, 1 H, IrCH₂=CHOEt, $J_{\text{HH}} = 9.5$ and 5 Hz, $J_{\text{HH}} = 1.8$ Hz), 4.17 (dq, 1 H, CH₂=CHOC(H)Me, $J_{\text{HH}} = 9.5$ and 7 Hz), 4.04 (dd, 1 H CHH=CHOEt), 3.74 (dq, 1 H, CH₂=CHOC(H)Me, $J_{\text{HH}} = 7$ Hz), 2.28 (dd, 1 H CHH=CHOEt), 1.21 (t, 3 H, CH₂=CHOCH₂CH₃, $J_{\text{HH}} = 7$ Hz), -18.63 (dd, 1 H, Ir-H, $J_{\text{HH}} = 7.3$ Hz), -26.79 (d, 1 H, Ir-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 136.4, 135.5, 134.0, 124.2, 123.4, 122.3, (CBr), 106.9 (CH₂=CHOEt), 103.4, 102.7, 102.1 (CBr), 69.2 (CH₂=CHOCH₂Me), 28.2 (CH₂=CHOEt), 14.7 (CH₂=CHOCH₂CH₃).

Synthesis of the Complexes **5 and **6**.** A solution of **1** (0.1 g, 0.085 mmol) in cyclohexane was heated at 60 °C for 4 h. The solvent was removed under vacuum, and the solid residue was investigated by ^1H NMR, confirming the formation of **5** and **6** in 4:1 ratio.

$\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$, **5.** IR (Nujol): $\nu(\text{Ir-H})$ 2210 cm^{-1} . ^1H NMR (400 MHz, C_6D_6): δ 5.12 (m, 1 H, CH=CH₂), 4.30 (d, 1 H, CH=CHH, $J = 11.3$ Hz), 3.99 (m, 1 H, Ir-CH₂CHH), 3.00 (m, 1 H, Ir-CH₂CHH), 2.44 (d, 1 H, CH=CHH, $J = 7.6$ Hz), 1.95 (m, 1 H, IrCHHCH₂), 1.09 (dt, 1 H, IrCHHCH₂, $J = 14.6$ and 8 Hz), -20.08 (d, 1 H, Ir-H, $J = 2.1$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 134.2, 132.9, 132.3, 123.9, 123.0, 122.7, 104.3, 103.6, 101.9 (CBr), 49.2 (CH₂=CH), 31.4 (Ir-CH₂CH₂), 18.5 (CH₂=CH), -46.8 (Ir-CH₂CH₂).

$\text{Tp}^{\text{Br}^3}\text{Ir}(\text{H})(\eta^3\text{-CH}_2\text{CHCHMe})$, **6.** Only the major isomer (>85%) was detected^{14a} by ^1H NMR (400 MHz, C_6D_6): δ 5.58 (dt, 1 H, CH₂CHCHMe, $J = 11$ and 7.1 Hz), 4.58 (dq, 1 H, CH₂CHCHMe, $J_{\text{H-CH}_3} = 6.5$ Hz), 3.44 and 2.85 (dd, 2 H each, CH₂CHCHMe, $J = 1.6$ Hz), -31.76 (s, 1 H, Ir-H).

Acknowledgment. We thank MCyT (BQU2002-01114) and Junta de Andalucía for financial support. Thanks are also due to the Servicio de RMN de la Universidad de Huelva.

OM034242U