C–H Bond Activation

A Measureable Equilibrium between Iridium Hydride Alkylidene and Iridium Hydride Alkene Isomers**

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Dedicated to Professor H. Werner on his 70th birthday

Rearrangement between isomeric M–olefin and M–alkylidene units (in which M is a transition-metal atom) is a fundamental transformation key to many homogeneous and heterogeneous catalytic processes.[1] However, whereas conversion of a metal alkylidene into the corresponding metal alkene has been known for some time, particularly for cationic electrophilic metal alkylidenes,[2,3] the reverse transformation is a rarely observed process, known only for a few transition-metal complexes that have few d electrons.[4] Moreover, detection of a thermoneutral (or almost thermoneutral) redistribution of this kind, that is, a process whereby the alkene and the alkylidene isomers exist in equilibrium, finds little precedent and appears to be limited to some complexes of the early transition metals.[5] We report herein that a d^6 $Tp^{Me_2}Ir^{III}$ fragment allows attainment of an equilibrium mixture of the hydride alkylidene and hydride alkene structures **1** and **2a** (Scheme 1), through a reaction that implies the activation of sp^3 C–H bonds of *o*-$C_6H_4(OH)CH_2CH_3$.

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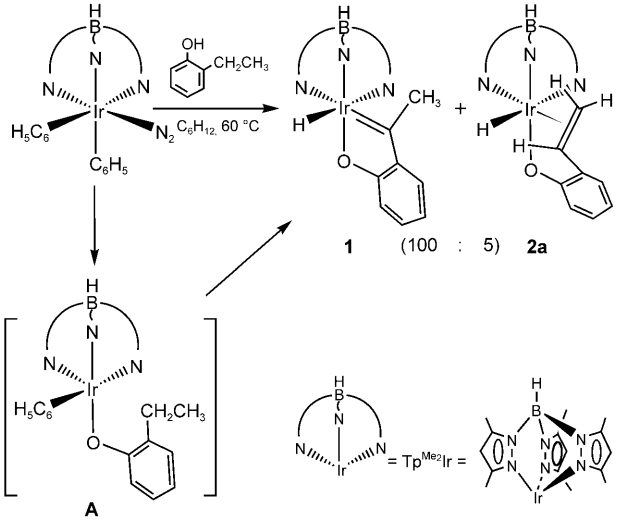
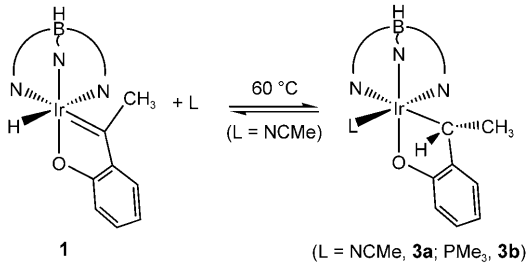


Scheme 1. Double sp^3 C–H bond activation of *o*-$C_6H_4(OH)C_2H_5$.

The thermal reaction of $Tp^{Me_2}Ir(C_6H_5)_2(N_2)$[6a] and 2-ethylphenol (ca. 1:2.5 molar ratio, cyclohexane solvent, 60 °C) produces the hydride alkylidene **1** (Scheme 1) as the main product (95% conversion into products as determined by NMR spectroscopy; 90% yield of isolated **1**). Presumably, the reaction starts with alcoholysis of one of the Ir–C_6H_5 bonds (structure **A**, Scheme 1), and this is then followed by a facile, double activation[6,7] of the methylenic C–H bonds of the *ortho* ethyl substituent. The C–H bond cleavage is highly regioselective. Monitoring by ^{1}H NMR spectroscopy reveals that under kinetic control, the alternative reaction product, namely the hydride alkene isomer **2a** that derives from β- as opposed to α-hydride elimination in the last C–H activation step, amounts to only about 5% of the total reaction product (Ir–H signals at $\delta = -20.40$ for **1** and −17.49 ppm for **2a**, with intensity ratio of ca. 100:5).

Characterization of **1** from the analytical and spectroscopic data is unequivocal (see Experimental Section). Lewis bases, such as NCMe or PMe_3, induce a stereospecific 1,2-hydrogen shift to yield the corresponding adducts, **3a** and **3b**, respectively (Scheme 2); the latter has been characterized by X-ray crystallography (Figure 1).[8] The 1,2-hydrogen shift is reversible;[7,9,10] heating the acetonitrile adduct **3a** in C_6H_{12} at 100 °C for 1 h cleanly restores the hydride alkylidene structure (only trace amounts of compound **2a** are detected under these conditions). It seems clear, therefore, that an α-agostic intermediate of type **B** (Scheme 3) can be reached from **1**



Scheme 2. Reversible 1,2-hydrogen shift of hydride alkylidene **1**.

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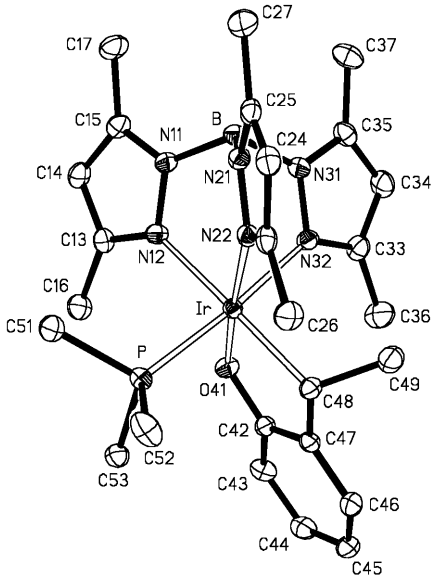
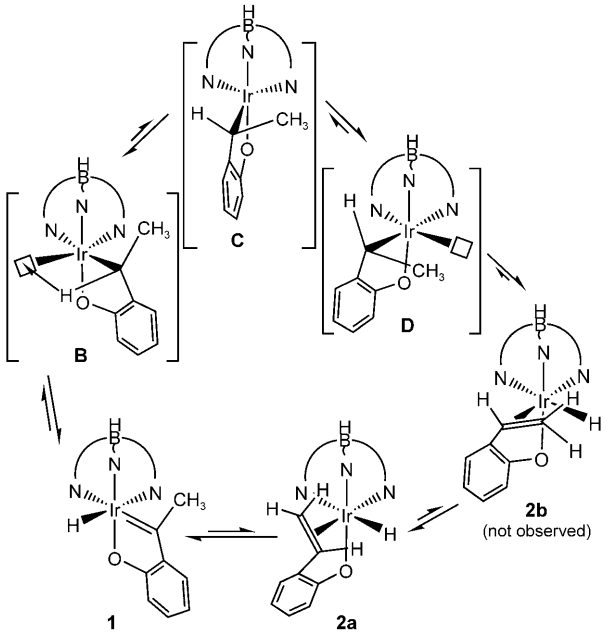


Figure 1. Molecular structure of **3b** in **3b**·CH_2Cl_2 (50% ellipsoids, H atoms and CH_2Cl_2 omitted for clarity). Selected bond lengths [Å] and angles [°]: Ir-P 2.2526(7), Ir-N(12) 2.205(2), Ir-N(22) 2.106(2), Ir-N(32) 2.159(2), Ir-O(41) 2.035(2), Ir-C(48) 2.091(2), O(41)-C(42) 1.343(3), C(47)-C(48) 1.515(3), C(48)-C(49) 1.544(3); O(41)-Ir-C(48) 84.02(8), O(41)-Ir-P 89.61(5), C(48)-Ir-P 89.28(7), N(22)-Ir-P 95.62(5).



Scheme 3. Thermal equilibration of compounds **1** and **2a**.

under mild conditions.[11] Access to structure **D** (that would precede β-hydride elimination[11,12] to generate the hydride alkene isomer **2b**) requires, assuming chiral integrity of the alkyl carbon, metal inversion through a five-coordinate structure such as **C**. This is expected to be energetically costly,[13] and accordingly, the **1**–**2a** isomerization requires prolonged heating at temperatures around 100 °C. The equilibrium constant shows little temperature dependence ($K_{eq} \approx 8$ in C_6D_{12}, temperature range 90–130 °C) and favors the hydride alkylidene **1**.

Despite its low equilibrium concentration, the hydride alkene **2** can be isolated, although only diastereomer **2a** can be detected. Coordination of the other enantiotopic face of the alkene,[2c,14] **2b**, appears to be sterically hindered, although it is accessible upon heating (Scheme 3). A strong correlation signal between the olefinic *H*C= resonance ($\delta =$ 6.88 ppm, dd, 8.3 and 11.2 Hz; see Experimental section) and the hydride signal ($\delta = -17.53$ ppm) found in the NOESY spectrum supports the coordination mode shown in **2a** for the olefin.

Pure samples of **2a**, namely, the minor component of the **1**–**2a** equilibrium, equilibrate upon heating (measurements between 90 and 130 °C, with intervals of 10 °C) to provide K_{eq} values identical to those obtained when the equilibrium is approached starting from **1**. The equilibration rates follow first-order kinetics (^{1}H NMR spectroscopic monitoring in C_6D_{12}) through about 75% conversion. From the gradient of the slopes obtained by plotting $\ln(c\text{-}c_e/c_o\text{-}c_e)$ versus time[15] and from the value of K_{eq} at each temperature, the forward (k_1, **2a**→**1**) and reverse (k_{-1}) rate constants have been determined (at 100 °C, $k_1 = 4.5 \times 10^{-5}$, $k_{-1} = 4.7 \times 10^{-6}\ s^{-1}$). An Eyring plot gives $\Delta H^{\neq} = 21.3$ kcal mol^{-1} and $\Delta S^{\neq} = -21$ cal mol^{-1} K^{-1}.

The mechanistic hypothesis outlined in Scheme 3 has been analysed by means of theoretical calculations (see Experimental Section). The relative energies of alkylidene **1** and alkene **2a** are 0.0 and 1.8 kcal mol^{-1}, respectively, therefore providing a theoretical justification for the almost thermoneutral character of the **1**–**2a** equilibrium. Calculations show that the detected alkene diastereoisomer, **2a**, is 8.2 kcal mol^{-1} more stable than **2b**, which is in full agreement with the experimental results. Alkene **2a** has the double bond slightly closer to the metal center, with Ir–C bond lengths of 2.185 Å and 2.253 Å for **2a**, and 2.252 Å and 2.243 Å for **2b**.

The other postulated intermediates for the isomeric interconversion reaction (Scheme 3) are located as minima in the potential-energy surface. Structure **B** is 19.6 kcal mol^{-1} above the alkylidene, and contains a clear α-agostic interaction, with a C–H bond length of 1.191 Å and an Ir-C-H angle of 76.1°. The energy of intermediate **D** is 21.5 kcal mol^{-1}. Its structure shows neither an α- nor a β-agostic interaction, the three C–H bond lengths range from 1.090 Å to 1.098 Å. The calculated energies for these intermediates are within the expected range given the experimental value of the activation enthalpy, therefore supporting the proposed mechanism. Moreover, the accuracy of energies obtained by density functional theory (DFT) has been checked by MP2 single-point calculations. MP2 energies were similar to DFT energies for all the determined structures. Their values are 0.0 kcal mol^{-1} for **1**, −0.6 kcal mol^{-1} for **2a**, 5.2 kcal mol^{-1} for **2b**, 19.5 kcal mol^{-1} for **B**, and 20.8 kcal mol^{-1} for **D**.

In conclusion, we have presented an example of an unusual double activation of sp^3 C–H bonds that gives rise to a kinetic mixture of a hydride alkylidene, **1**, and the isomeric hydride alkene **2a** of about 20:1. The kinetic predominance of the alkylidene product **1** may result from the preferential

activation of the methylene hydrogen atom of the presumed structure **A** (Scheme 1) that leads to the α-agostic intermediate **B**. Interestingly, the hydride alkylidene **1** is thermodynamically somewhat more stable than the hydride alkene compound **2a**, possibly as a result of the combination of a favorable alkylidene conformation within the five-membered chelate ring in **1**, with a strained olefin coordination in **2a**. Isolated samples of either of these complexes convert into equilibrium mixtures of the two, therefore demonstrating that alkene and alkylidene functionalities can be readily interconverted by d^6, $Tp^{Me_2}Ir^{III}$ fragments.

Experimental Section

1: A suspension of $[Tp^{Me_2}Ir(C_6H_5)_2(N_2)]$ (0.10 g, 0.15 mmol) and 2-ethylphenol (0.023 mL, 0.194 mmol) in C_6H_{12} (6 mL) was heated at 60 °C for 14 h. The solvent was then removed in vacuo, to leave a dark green residue, which was dissolved in 10 mL of CH_2Cl_2. Excess of the phenol was eliminated by successive washings with aquous solutions of NaOH (10%), NH_4OH (saturated), and brine. The CH_2Cl_2 solution was dried over Na_2SO_4, the solvent removed in vacuo, and the resulting solid material (ca. 95%) was subjected to chromatography through silica (hexane:Et_2O mixtures, from 5:1 to 1:5) to yield pure **1** as a dark-green solid (ca. 90% yield of isolated product). IR (Nujol): $\tilde{\nu} = 2519$ (B-H), 2146 cm^{-1} (Ir-H); ^1H NMR ($CDCl_3$, 25 °C): $\delta = 7.50$, 7.27, 7.17, 6.56 (dd, ddd, d, ddd, 1H each, $^3J(H,H) \approx 8$, $^4J(H,H) \approx 1$ Hz, 4 CH_{ar}), 5.88, 5.87, 5.57 (s, 1H each, 3 CH_{pz}), 2.87 (s, 3H, Ir=CCH_3), 2.58, 2.44, 2.39, 2.37, 2.09, 1.27 (s, 3H each, 6 Me_{pz}), −20.42 ppm (s, 1H, IrH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 274.2$ (Ir=C), 189.6, 151.9 (C_qO and C_qC=Ir resp.), 152.9, 152.5, 152.2, 144.7, 144.3, 143.3 (C_{qpz}), 137.4, 123.0, 117.5, 114.1 (CH_{ar}), 106.8, 106.7, 106.6 (CH_{pz}), 35.3 (Ir=CCH_3, $^1J(C,H) = 126$ Hz), 16.9, 14.4, 13.4, 12.6, 12.5, 11.8 ppm (Me_{pz}); elemental analysis calcd (%) for $C_{23}H_{30}BN_6OIr \cdot 1/2\,Et_2O$: C 46.4, H 5.4, N 13.0; found: C 46.8, H 5.6, N 13.0.

2a: A solution of **1** in C_6H_{12} (0.54 g, 0.90 mmol; 20 mL) was heated at 90 °C for 22 h. The volatile products were removed in vacuo and the resulting **1**:**2a** mixture (ca. 88:12) was subjected to chromatography (silica gel, hexane:Et_2O eluent) to give **2a** (0.060 g, 11%) and 0.45 g of **1** (83%). Compound **2a** was isolated as a pale-green microcrystalline solid by crystallization from a 3:1 mixture of pentane:CH_2Cl_2 at −20 °C. IR (Nujol): $\tilde{\nu} = 2528$ (B-H), 2180 cm^{-1} (Ir-H); ^1H NMR ($CDCl_3$, 25 °C): $\delta = 7.20$, 6.84, 6.50, 6.47 (d, t, d, t, respectively, 1H each, $^3J(H,H) \approx 8$ Hz, 4 CH_{ar}), 6.89 (dd, 1H, $^3J(A,C) = 11.2$, $^3J(A,B) = 8.3$ Hz, CH_A=CH_BH_C), 5.90, 5.83, 5.64 (s, 1H each, 3 CH_{pz}), 4.28 (d, 1H, H_C), 3.29 (d, 1H, H_B), 2.44, 2.38, 2.35, 2.29, 1.95 (s, 1:2:1:1:1:1, 6 Me_{pz}), −17.53 ppm (s, 1H, IrH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 173.6$, 131.3 (C_qO and C_qC=H resp.), 152.4, 150.8, 144.1, 143.8, 143.4 (1:2:1:1:1, C_{qpz}), 127.9, 125.9, 115.7, 114.4 (CH_{ar}), 108.2, 107.2, 106.9 (CH_{pz}), 77.0 (CH_A, $^1J(C,H) = 165$ Hz), 46.2 (CH_BH_C, $^1J(C,H) = 162$ Hz), 14.0, 13.8, 12.9, 12.4, 12.3, 12.2 ppm (Me_{pz}); elemental analysis calcd for $C_{23}H_{30}BN_6OIr$: C 45.3, H 4.9, N 13.8; found: C 45.6, H 4.9, N 13.7.

Calculations: The calculations were performed by using the Gaussian 98 program.[16] All geometries were fully optimized at the ONIOM(BHandH:UFF) level.[17] The Ir, 2-ethylphenolate, and three NH=CH_2 groups that represent the Tp^{Me_2} ligand were described at the DFT by level using the BHandH functional,[16] whereas the rest of the Tp^{Me_2} ligand was described at the molecular-mechanics level by using the UFF force field[18]. For the Ir atom, the lanl2dz[19] effective core potential was used to replace the inner electrons, whereas its associated double-ζ basis set[16,19] was employed to describe the 15 outer electrons. The 6-31g(d) basis set was used for the others.[20] The energies presented in the text were obtained by full quantum mechanics at both BHandH and MP2 levels on the real molecules by using the ONIOM(BHandH:UFF) optimized geometries.

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