

# Double Activation of the Geminal Carbon–Hydrogen Bonds in 1,3-Butadiene by a Diiridium Complex

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**Summary:** The binuclear complex  $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\text{dppm})_2][\text{CF}_3\text{SO}_3]$  (**1**) ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) reacts with 1,3-butadiene at ambient temperature over a 48 h period to give the vinylvinylidene-bridged product  $[\text{Ir}_2(\text{CH}_3)(\text{H})(\text{CO})_2(\mu\text{-H})(\mu\text{-CC}(\text{H})\text{C}(\text{H})\text{CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$  (**2**). At  $-55^\circ\text{C}$  the same reactants yield the 1,3-butadiene adduct  $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\mu\text{-}\eta^2\text{-H}_2\text{C}=\text{C}(\text{H})\text{C}(\text{H})=\text{CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$  (**3**), in which the diolefin binds in an *s-trans* geometry on one face of the complex. A proposal is advanced rationalizing the conversion of **3** to **2** upon warming.

The activation of vinylic carbon–hydrogen bonds by transition-metal complexes has attracted considerable interest.<sup>1,2</sup> In the majority of cases the activating complex is a highly reactive, coordinatively unsaturated species that has been generated by ligand loss through photolysis,<sup>1,2d,3</sup> or thermolysis,<sup>2c,d,3b,4</sup> or by prior substrate hydrogenation by a polyhydride precursor complex.<sup>5</sup> In most cases the activation of only a single olefinic C–H bond occurs. However, there have been a few reports of *double* C–H activation of an olefin to give either dimetallaolefin or vinylidene products.<sup>6</sup> Double C–H activation of ethers to give Fischer carbenes<sup>7</sup> and the activation of a single C–H bond in two separate olefin molecules<sup>5b,d</sup> have also been reported. In this paper we

report the double C–H activation of one set of geminal C–H bonds in 1,3-butadiene by a diiridium complex under ambient conditions, in which prior activation of the complex by ligand loss is not required.

Our previous studies have shown that the reaction of  $[\text{Ir}_2(\text{CH}_3)(\text{CO})_2(\text{dppm})_2][\text{CF}_3\text{SO}_3]$  (**1**;  $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) with a variety of substrates resulted in C–H bond cleavage of the methyl ligand by the adjacent metal, yielding the methylene-bridged hydride products  $[\text{Ir}_2\text{H}(\text{L})(\text{CO})_2(\mu\text{-CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$  ( $\text{L} = \text{CO}, \text{SO}_2, \text{PR}_3, \text{CNR}$ ).<sup>8</sup> In addition, reaction with unsaturated organic substrates yielded vinyl carbenes, and these have also been proposed to proceed via methylene-bridged intermediates.<sup>9</sup> The present study was initiated as part of a continuation of the reactivity studies of **1**, in which olefins were investigated as the substrates.

Although compound **1** reacts with the monoolefins ethylene and tetrafluoroethylene to give simple olefin-adducts in which the olefin was either bound to one metal or bridging the two,<sup>10</sup> it reacts very differently with 1,3-butadiene. At ambient temperature, over a 48 h period compound **1** reacts with a butadiene-saturated  $\text{CH}_2\text{Cl}_2$  solution to give the dihydrido vinylvinylidene-bridged product  $[\text{Ir}_2(\text{CH}_3)(\text{H})(\text{CO})_2(\mu\text{-H})(\mu\text{-CC}(\text{H})\text{C}(\text{H})\text{CH}_2)(\text{dppm})_2][\text{CF}_3\text{SO}_3]$  (**2**),<sup>11</sup> as shown in Scheme 1. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum three resonances are observed for the vinylvinylidene fragment; the two at  $\delta$  145.8 and 112.0 are typical of olefinic moieties,<sup>12</sup> and the resonance at  $\delta$  196.0 shows the usual downfield shift characteristic of the  $\alpha$ -carbon of a bridging vinylidene group.<sup>13</sup> The signal for the  $\beta$ -carbon is not observed and

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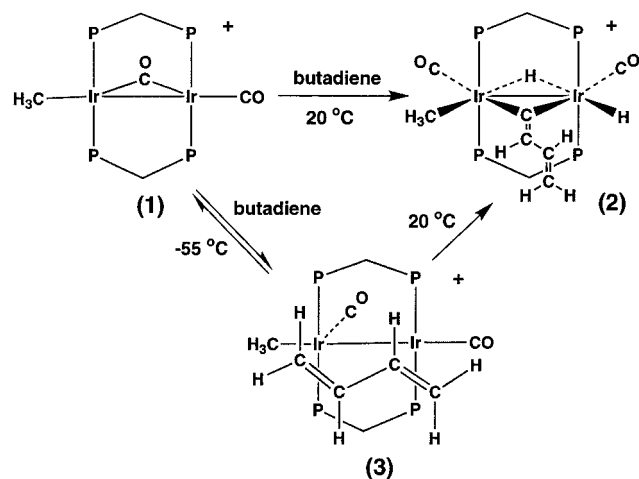
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(11) Spectroscopic data for **2**:  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  6.79 (d,  $^3J_{\text{HH}} = 10.0$  Hz, 1H), 5.28 (ddd,  $^3J_{\text{HH}} = 16.5$ , 10.0, 10.0 Hz, 1H), 4.91 (d,  $^3J_{\text{HH}} = 16.5$  Hz, 1H), 4.38 (d,  $^3J_{\text{HH}} = 10.0$  Hz, 1H), 3.75 (m, 2H), 2.63 (m, 2H),  $-0.51$  (t, 3H),  $-12.64$  (t,  $^2J_{\text{PH}} = 17$  Hz, 1H),  $-13.90$  (q,  $^2J_{\text{PH}} = 6$  Hz, 1H);  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$   $-4.9$  (m), 13.1 (m);  $^{13}\text{C}\{^1\text{H}\}$  (natural abundance)  $\delta$  196.0 (q,  $^2J_{\text{PC}} = 9.5$  Hz,  $\mu\text{-C}=\text{CHCHCH}_2$ ), 173.6 (t,  $^2J_{\text{PC}} = 9.8$  Hz, CO), 173.2 (t,  $^2J_{\text{PC}} = 9.2$  Hz, CO), 145.8 (s,  $\mu\text{-C}=\text{CHCH}=\text{CH}_2$ ), 112.0 (s,  $\mu\text{-C}=\text{CHCH}=\text{CH}_2$ ),  $-9.9$  (b,  $\text{CH}_3$ ); IR 2014, 2003  $\text{cm}^{-1}$ .

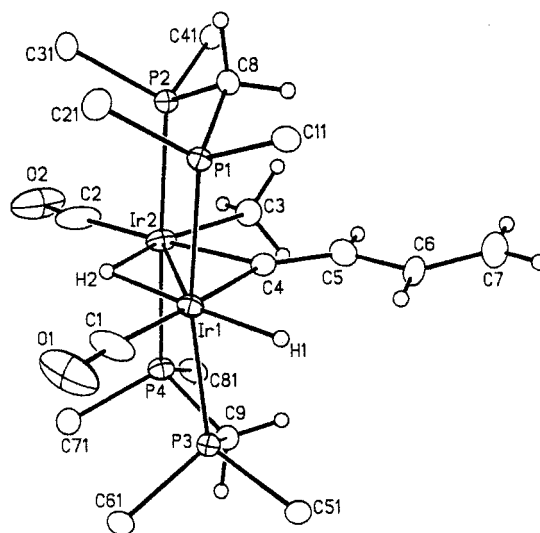
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Scheme 1

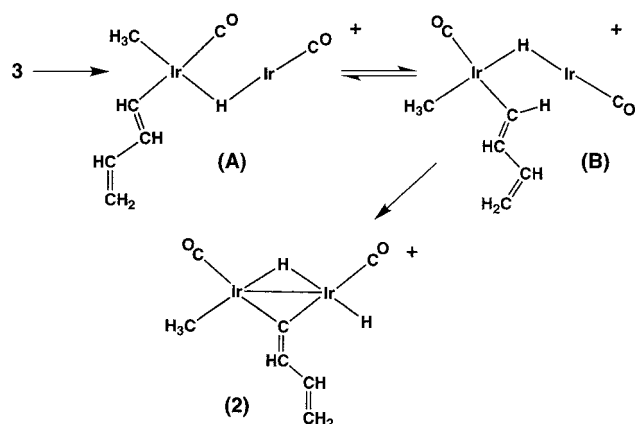


is presumably obscured by the phenyl resonances. Similarly, the hydrogen resonances for the vinylvinylidene group are as expected. The hydrido ligands appear in their typical high-field positions, and their couplings to the phosphines indicate that one is terminally bound while the other is bridging. Confirmation of this structural proposal comes from the X-ray determination,<sup>14</sup> the results of which are shown in Figure 1. The vinylvinylidene group bridges the metals symmetrically, and all parameters within this group are consistent with the 1,3-diolefin formulation. The Ir–Ir bond length (2.9339(4) Å) shows the lengthening expected when involved in a three-center, Ir( $\mu$ -H)Ir interaction (compare: 2.7775(5) Å in the precursor **1**).<sup>8</sup>

In an attempt to discover how this unusual double oxidative addition occurred and to determine the effects of the adjacent metals in the C–H activation steps, the reaction was carried out at low temperature, reacting about 30% excess of the diene with **1**, in an effort to observe intermediates in the transformation. At temperatures between –50 and –95 °C the diolefin adduct [Ir<sub>2</sub>(CH<sub>3</sub>)(CO)<sub>2</sub>( $\mu$ - $\eta^2$ : $\eta^2$ -H<sub>2</sub>C=CH–CH=CH<sub>2</sub>)(dppm)<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>] (**3**) was observed<sup>15</sup> in equilibrium with compound **1** and free butadiene. At –55 °C the equilibrium constant for formation of the butadiene adduct (**3**) is approximately 105 M<sup>–1</sup>, as determined by NMR. At ambient temperature the equilibrium favors the starting materials and **3** is not observed. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3** indicates that all phosphorus atoms are chemically inequivalent. Although the appropriate num-



Scheme 2



(protons exhibiting NOE are indicated by the double-headed arrows). NOE was also observed between each of  $H_c$  and  $H_d$  and one hydrogen of each of the dppm methylene groups, consistent with the structure shown. The  $^{13}\text{C}$  chemical shifts for  $C_B$ ,  $C_C$ , and  $C_D$  (between  $\delta$  47.88 and 72.14) and the C–H coupling constants involving the attached hydrogens (between 147 and 161 Hz) appear typical for a coordinated olefin;<sup>16</sup> however, the  $^{13}\text{C}$  chemical shift for  $C_A$  ( $\delta$  –3.50) is at unusually high field and together with the associated C–H coupling constants ( $^1J_{\text{CH}} = 139$  Hz) suggests a substantial rehybridization of this carbon toward  $\text{sp}^3$ .

Although the direct transformation of compound **3** to **2** cannot be observed, since **3** is only detectable at low temperatures, at which C–H activation of the butadiene ligand does not occur, we propose that **3** is an intermediate in the formation of **2**. We suggest that C–H activation occurs stepwise, with the first activation occurring at the iridium having the methyl group attached. This metal should be more electron rich and more susceptible to oxidative addition owing to the electron-donor properties of the methyl ligand; the adjacent metal should be less prone to oxidative addition owing to its positive charge. These suggestions are consistent with the proposed rehybridization noted earlier for  $C_A$ , indicating greater back-donation to this end of the diolefin. Although structure **3** has a carbonyl on each metal, C–H activation might be accompanied by carbonyl transfer from one metal to the other, generating the necessary unsaturation. Oxidative addition of the first C–H bond would yield a vinyl hydride as shown in structure **A** of Scheme 2 (dppm ligands, perpendicular to the plane of the drawing, are not shown). Activation of a single terminal vinylic C–H bond of 1,3-butadiene by a binuclear species to give a bridging butadienyl moiety has previously been observed.<sup>19</sup> Inversion of the “ $\text{Ir}_2(\mu\text{-H})$ ” core, as diagrammed, is common<sup>20</sup> and would yield a species such as **B** in which the hydride ligand is now on the opposite face of the  $\text{Ir}_2\text{P}_4$  plane from the resulting hydrocarbyl

fragment, as observed in the structure of the final product **2**. This “hydride inversion” brings the vinyl group into proximity with the adjacent metal, leading to activation of the second C–H bond to give **2**.

The possibility of initial C–H activation of the methyl group, as previously observed or proposed in reactions of **1** with various substrates,<sup>8,9</sup> has been tentatively ruled out by experiments involving  $\text{CD}_3$ -labeled **1**, in which no deuterium incorporation into the butadiene ligand of **3** or into the hydride or vinylvinylidene ligands of **2** was observed.

Support for our proposal, that precoordination of butadiene at both metals precedes the double C–H activation, comes from attempted reactions of **1** with monosubstituted butadienes. Therefore, compound **1** in the presence of 2-methyl-1,3-butadiene or either *cis*- or *trans*-1,3-pentadiene results in no reaction after several days at ambient temperature or after 24 h in refluxing  $\text{CH}_2\text{Cl}_2$  or THF. The failure of the pentadiene compounds to give a C–H activation product strongly suggests that coordination of *both* olefin functionalities is required; otherwise substitution at one end of the butadiene unit would not be expected to inhibit C–H activation at the *other* end. Although 2-methyl-1,3-butadiene does not form an adduct at temperatures down to –95 °C, both pentadiene isomers form weak adducts at this temperature. Unfortunately the exchange occurring at this temperature has not allowed us to carry out the necessary 2D NMR studies in order to determine the orientations of the pentadiene molecules; these studies are continuing. Additional support that prior coordination of *both*  $\pi$  bonds of butadiene facilitates the C–H activation observed comes from the reaction with ethylene, which does not give C–H activation products, yielding only a  $\pi$  complex.<sup>10</sup>

The activation of *both* geminal C–H bonds of butadiene is unusual enough; however, activation by a binuclear complex *without* prior activation of the complex by ligand loss is quite remarkable. Currently we are carrying out DFT calculations on the butadiene-bridged adduct (**3**) in attempts to obtain additional insights into the proposed transformation of this species into the doubly C–H activated product (**2**) and are investigating related systems in an effort to obtain additional support for this proposed transformation.

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**Supporting Information Available:** Crystallographic information (PDF) is available free of charge via the Internet at <http://pubs.acs.org>.

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