

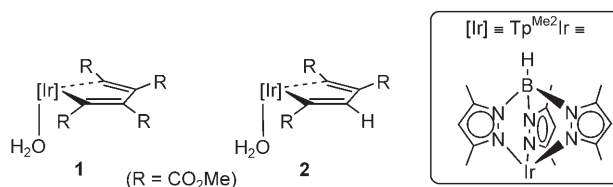
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Formation of Iridabenzenes by Coupling of Iridacyclopentadienes and Alkenes**

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Metallabenzenes are interesting structural units that have attracted broad attention.^[1] Recently, formation of iridabenzenes by a [2+2+1] cyclotrimerization of alkynes via iridacyclopentadiene intermediates was demonstrated,^[2] constituting a valuable addition to previous synthetic methodologies.^[1a,3] Herein we describe new iridabenzene structures prepared by a novel synthetic procedure, namely the coupling of an alkene with iridacyclopentadienes.

Two iridacyclopentadiene structures were chosen as probes to test this reactivity: the known^[4] compound **1** and the related derivative **2**.



Both **1** and **2** react with C₂H₄ to give the allyl derivatives **4a** and **4b** via intermediate hydride alkenes **3a** and **3b**, respectively (Scheme 1).^[5] Compound **4a** was reported previously.^[6] Notably, C₂H₄ inserts regioselectively into the Ir–C bond with the H substituent in the β-position.

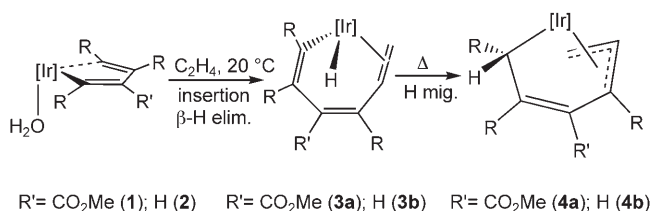
In contrast, complex **1** reacts with propene at 20°C to form the new derivative **5** as a result of the regioselective insertion of MeCH=CH₂ into one of the equivalent Ir–C bonds. Interestingly, the insertion of propene is reversible, and upon standing at room temperature for several hours, solutions of **5** in CDCl₃ revert to **1** and propene. However, when the reaction of **1** and propene is effected at 60°C, the

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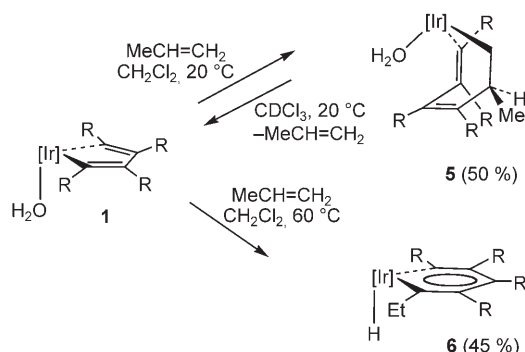


Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.



Scheme 1. Formation of allylic species by the reaction of **1** and **2** with C_2H_4 .

iridabenzene **6** is formed in approximately 45 % yield, as determined by ^1H NMR spectroscopy (Scheme 2).^[7]



Scheme 2. Reaction of compound **1** with propene at different temperatures.

The Ir-bonded ^{13}C nuclei of **6** resonate at $\delta = 274.2$ (Ir-C(Et)) and 202.1 (Ir-C(CO_2Me)) ppm. Both δ values indicate partial double-bond character of the Ir–C bonds,^[8] with a higher stabilization of the alkylidene functionality by the more strongly electron-donating alkyl group. This is also reflected in the solid-state structure, determined by X-ray crystallographic methods (Figure 1). As observed previously for a related $\text{Tp}^{\text{Me}_2}\text{Ir}^{\text{III}}$ (see **1** and **2** for structure of Tp^{Me_2}) metallabenzene, the Ir atom deviates considerably (0.57 Å) out of the plane defined by the five carbon atoms of the ring.^[3c]

While a simple olefin insertion can explain the formation of **5** (Scheme 2), generation of iridabenzene **6** requires a more complex reaction pathway proposed to consist of isomerization of the coordinated alkene to a propylidene ligand as in **A**, followed by migratory insertion to give **B**^[9] and α -hydride elimination (Scheme 3).

Alkene to alkylidene rearrangement is a rare but known event^[10] and, similarly, the migratory insertion^[11] and the α -hydride-elimination^[12–14] steps find ample literature precedent.

The analogous reaction of propene with iridacycle **2** demonstrates a surprising and unexpected effect of the nature of the iridacycle substituents in the course of the reaction. Thus, treatment of **2** (with H instead of CO_2Me at one of the β -carbon atoms) with propene gives the iridabenzene **7**, which, unlike **6**, is not a hydride but bears, instead, an iridium-bound methyl group (Scheme 4).

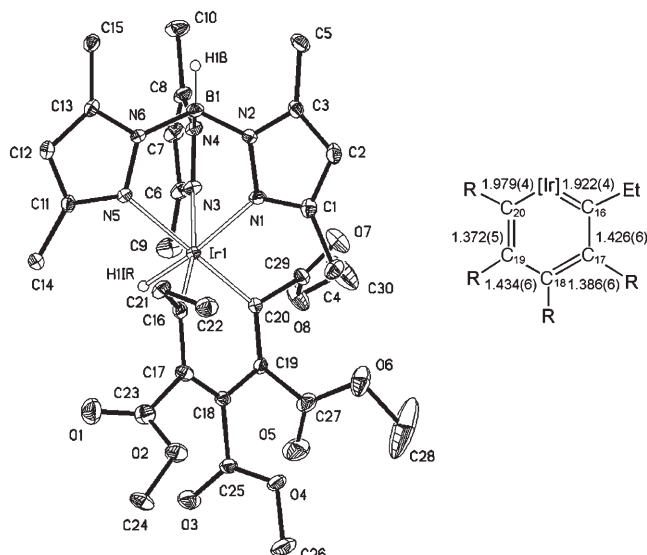
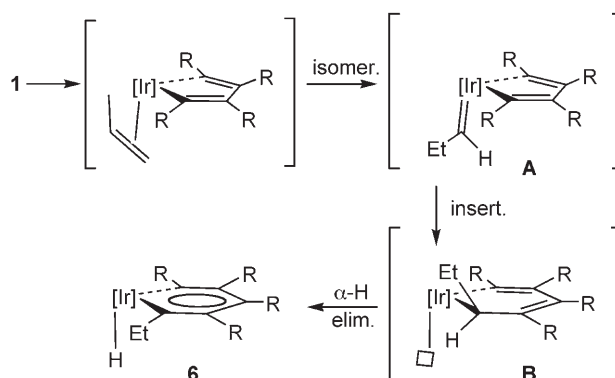
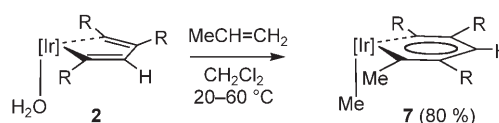


Figure 1. Molecular structure of **6** (30% ellipsoids, H atoms other than the hydride ligand omitted for clarity). Selected bond lengths [Å] and angles [°]: Ir–C(16) 1.922(4), Ir–C(20) 1.979(4); C(16)–Ir–C(20) 90.51(17), C(17)–C(18)–C(19) 125.0(4).



Scheme 3. Proposed mechanism for the formation of **6**.



Scheme 4. Reaction of complex **2** with propene.

In the temperature range from 20 to 60 °C, compound **7** is practically the only reaction product. The NMR spectroscopic and X-ray crystallographic data for **7** confirm this structure. Figure 2 contains an ORTEP representation for this compound, for which the structural features are similar to those of **6** (see above). In this case, the Ir atom deviates by 0.70 Å out of the plane defined by the five carbon atoms of the metallacycle.

The intermediate metal–alkylidene resulting from the isomerization of the propene ligand is also suggested in a possible route to compound **7** (Scheme 5), but for subtle

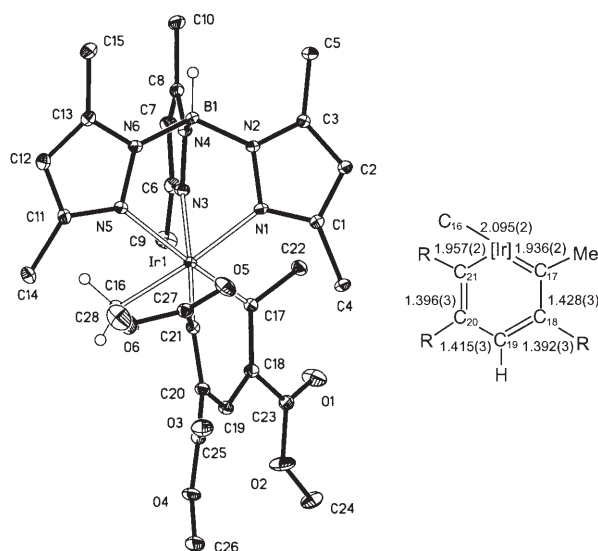
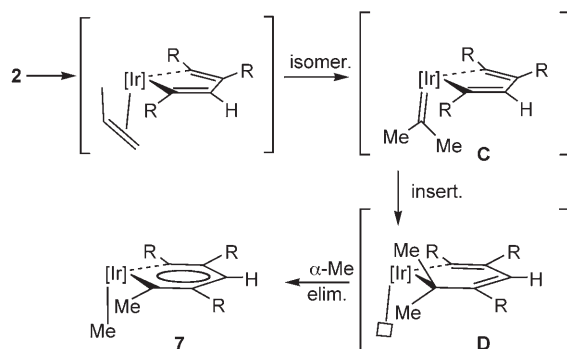


Figure 2. Molecular structure of **7** (30% ellipsoids, H atoms other than those of the methyl ligand omitted for clarity). Selected bond lengths [Å] and angles [°]: Ir–C(16) 2.095(2), Ir–C(17) 1.936(2), Ir–C(21) 1.957(2); C(17)–Ir–C(21) 90.87(9), C(18)–C(19)–C(20) 127.0(2).

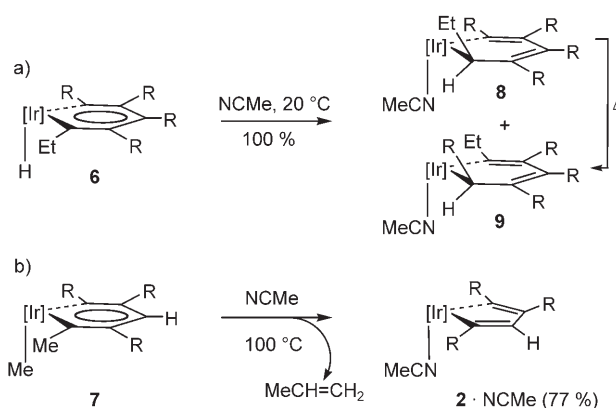


Scheme 5. Proposed mechanism for the formation of **7**.

reasons that are not presently understood, the dimethylcarbene unit, $=\text{CMe}_2$ as in **C**, appears to be favored over the linear propylidene, $=\text{C}(\text{H})\text{Et}$. This isomerization would be followed by regioselective migration of the alkenyl carbon atom adjacent to the CH group onto the alkylidene carbon atom to give **D**^[9] and by an unusual α -Me elimination.^[15]

Preliminary studies on the reactivity of iridabenzene **6** and **7** reveal interesting differences. Thus, the hydride compound **6** reacts with NCMe at 20 °C to give a 6:1 kinetic mixture of **8** and **9**, the products of the migration of the hydride ligand onto the two Ir–C bonds (Scheme 6a).^[16] By heating these mixtures, in C_6H_6 or C_6H_{12} at 90 °C with a drop of NCMe, **8** transforms completely into the thermodynamically more favored **9**, possibly via **6**.^[17] In contrast, the methyl derivative **7**, does not react with acetonitrile at 20 °C, but at 100 °C it mainly reverts to the iridacycle **2**, isolated in the form of the NCMe adduct **2**·NCMe (Scheme 6b).^[18] This clearly demonstrates that the reaction of **2** with propene represented in Scheme 4 is a reversible process.

In conclusion a new route to iridabenzene involving the coupling of the primary alkene $\text{MeCH}=\text{CH}_2$ with iridacycles **1**



Scheme 6. Reaction of compounds **6** and **7** with acetonitrile. a) Compound **6** reacts with NCMe at 20 °C to give a mixture of **8** and **9**. b) The methyl derivative **7** does not react with acetonitrile at 20 °C and at 100 °C it mainly reverts to the iridacycle **2**.

and **2** has been demonstrated. Transient iridium alkylidenes, resulting from the isomerization of iridium alkenes, appear to be key intermediates of this rearrangement that involves the formation of new carbon–carbon bonds. In one instance, namely the generation of compound **7** from **2** and $\text{MeCH}=\text{CH}_2$, the C–C bond-forming reaction is reversible.

Experimental Section

6: Compound **1** (0.5 g, 0.63 mmol) was dissolved in CH_2Cl_2 (12 mL), $\text{MeCH}=\text{CH}_2$ was bubbled through the solution for 7 min, and the resulting solution was stirred under propene in a closed vessel for 12 h at 60 °C. After this period the solvent was removed under reduced pressure, and the formation mainly of a mixture of two isomeric compounds was ascertained by ^1H NMR spectroscopy (iridabenzene/isomer ratio: 5:1, $\approx 65\%$ yield). Compound **6** was separated by column chromatography (silica gel) by using hexane/ Et_2O (1:1) as eluant (34 % yield). Compound **6** was crystallized from pentane/ CH_2Cl_2 (1:1) at -20°C (23 %) as green crystals. The second isolated product was formulated as in reference [7].

7: Compound **2** was dissolved in CH_2Cl_2 (0.32 g, 0.44 mmol; 10 mL), $\text{MeCH}=\text{CH}_2$ was bubbled through the solution for 5 min, and the solution was stirred under propene in a closed vessel for 15 h at room temperature. After this period of time the solution changed from dark yellow to green. The yield of the product **7** was ascertained to be about 80 % by ^1H NMR spectroscopy. This compound was purified by chromatography on silica gel with hexane/ Et_2O (2:1) and isolated in 54 % yield. Crystallized from hexane/ Et_2O (2:1) at -20°C gave the product as thin, dark green needles (45 %).

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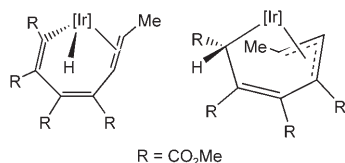
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