

## Isolation of a Stable 1-Iridabicyclo[3.2.0]hepta-1,3,6-triene and Its Reversible Transformation into an Iridacycloheptatriene

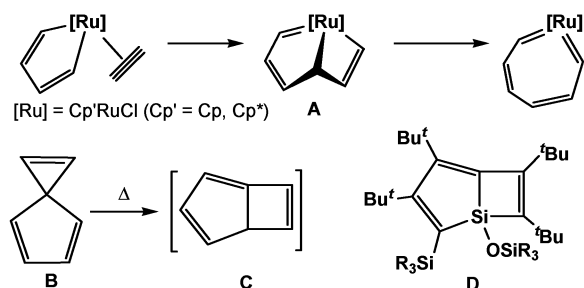
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The transition-metal-catalyzed [2 + 2 + 2] cyclotrimerization of alkynes, as a selective and efficient route to produce substituted benzenes, continues receiving increasing attention.<sup>1</sup> Besides broadly accepted reaction mechanisms, two very recent theoretical studies, published in this journal by Kirchner and Calhorda and by Yamamoto, on the cyclotrimerization of alkynes by the Cp'RuCl fragments (Cp' = Cp, Cp\*)<sup>2,3</sup> have found a novel ruthenabicyclo[3.2.0]heptatriene intermediate **A**, on the way from an alkyne-metallacyclopentadiene to a seven-membered metallacycle (Chart 1). To the best of our knowledge, no complexes with structure **A** have been reported to date.<sup>4</sup> The parent hydrocarbon, bicyclo[3.2.0]hepta-1,3,6-triene **C**, a highly strained and reactive olefin, has not even been detected, despite intense efforts,<sup>5,6</sup> and only very recently a sila-derivative (**D**), stabilized by very bulky substituents, which prevent dimerization, has been isolated and characterized.<sup>7</sup>

Chart 1



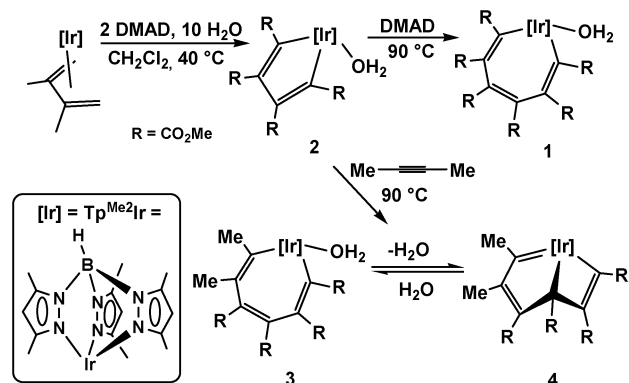
Prompted by these findings, we report herein on the synthesis and full characterization of an Ir complex of structure **A** and its reversible transformation into an iridacycloheptatriene derivative. We have reported that the reaction of  $\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^4\text{-CH}_2=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2)$  with 3 equiv of dimethylacetylene dicarboxylate (DMAD) affords the iridacycloheptatriene derivative **1** (Scheme 1),<sup>8</sup> which is stabilized by the coordination of a molecule of adventitious water.

Now we have found that if this reaction is carried out in the presence of an excess of water ( $\geq 10$  equiv), a metallacyclopentadiene<sup>9</sup> complex **2**, fully characterized by spectroscopy and X-ray diffraction,<sup>10</sup> is isolated in almost quantitative yield (Scheme 1). It cleanly reacts with more DMAD to give **1**, the reaction being, as expected, retarded by the addition of water.

Interestingly, **2** reacts with an excess of  $\text{MeC}\equiv\text{CMe}$  to give a mixture of mainly two complexes **3** and **4** ( $\geq 80\%$ , Scheme 1), whose relative ratio is dependent on the amount of water present in the reaction mixture.

Complex **3**, a yellow crystalline solid, is related to **1**, i.e., it is the result of the formal insertion of the alkyne into an Ir–C bond,

Scheme 1



and it is also stabilized by the coordination of a molecule of water. The other compound formed is green in color, is formulated as the bicyclic derivative **4**, and represents the first example of this kind of compound.

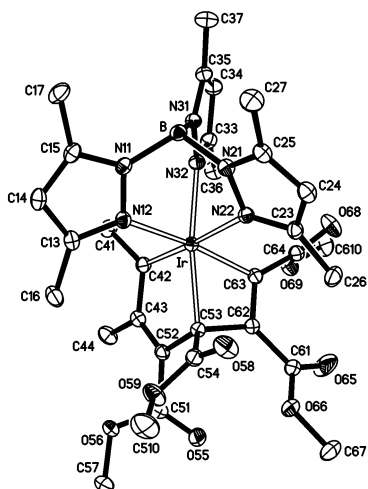
Compounds **3** and **4** transform easily into each other by simple variation of the amount of water present in their solutions. Thus, when **3** is dissolved in dry solvents (for instance,  $\text{C}_6\text{D}_6$ ), the solution becomes green, and compound **4** is formed. In turn, when **4** is dissolved in  $d_6$ -acetone, the initially green solution becomes yellow after a little  $\text{D}_2\text{O}$  is added, and an  $^1\text{H}$  NMR spectrum reveals the formation of the metallacycle **3** (data for the **3** to **4** +  $\text{H}_2\text{O}$  equilibrium:  $\Delta H = 6.5 \text{ kcal}\cdot\text{mol}^{-1}$ ,  $\Delta S = 19.1 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , acetone- $d_6/\text{D}_2\text{O}$  (0.6 M), 40–70 °C).

While the NMR data for **3** are very similar to those of the related compound **1**, the most relevant features for **4** are the resonance for the carbene carbon, at 275.1 ppm,<sup>11</sup> and a resonance at 20.5 ppm, which accounts for the bridging, aliphatic quaternary carbon. The observation of a long-range heterocoupling between the protons of both Me groups derived from the former 2-butyne and the carbene carbon supports the formulation of the depicted regioisomer.

Compounds **3** and **4** have been further characterized by X-ray diffraction studies. The structure found for **3** is closely related to that of **1**,<sup>8</sup> and will be reported elsewhere. Figure 1 shows an ORTEP representation of the structure found for **4**. The distance of 1.905(3) Å for the Ir–C(42) bond is in good agreement with its double bond character.<sup>11</sup> The other two distances, Ir–C(53) (2.136(2) Å) and Ir–C(63) (2.025(2) Å), correspond to single bonds, the first of them being clearly larger, probably reflecting the ring strain of the bicyclic framework,<sup>3</sup> in agreement with its facility to break and form the corresponding iridacycloheptatriene compound **3**. As expected, the C(63)–Ir–C(53) bond angle (in the four-membered ring) of 66.04(10)° is smaller than the corresponding C(53)–Ir–C(42) bond angle (in the five-membered ring) of 81.82(10)°.

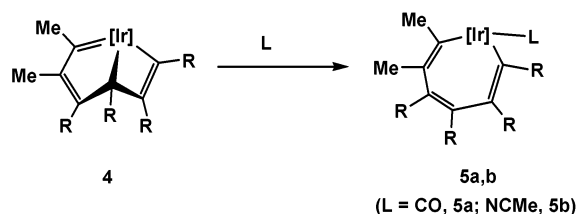
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**Figure 1.** Thermal ellipsoid plot (20% ellipsoids) of compound **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir–C(42) 1.905(3), Ir–C(53) 2.136(2), Ir–C(63) 2.025(2). Selected bond angles (deg): C(63)–Ir–C(53) 66.04(10), C(53)–Ir–C(42) 81.82(10).

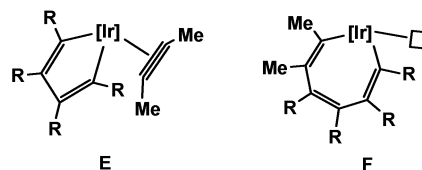
#### Scheme 2



The **3** to **4** transformation is regioselective, this fact being probably due to the stabilizing effect of the Me substituent on the carbene carbon, in comparison with the presence of an attracting CO<sub>2</sub>Me group. In fact, **1** does not provide a derivative related to **4** when dissolved in dry solvents, even in the presence of molecular sieve (C<sub>6</sub>D<sub>6</sub>, 60 °C, 2 days).

The transformation of the bicyclic arrangement in **4** to the metallacycle in **3** can also be achieved by the addition of other Lewis bases, such as NCMe and CO, to give derivatives **5a,b** (Scheme 2), which are inert to the extrusion of the Lewis base (C<sub>6</sub>D<sub>6</sub>, 60 °C, 15 h).

It has to be mentioned in connection with the catalytic cycles proposed for the Ru systems,<sup>2,3</sup> that we cannot establish whether **3** or **4** is formed first from the purported intermediate [Tp<sup>Me2</sup>Ir(C(R)=C(R)C(R)=C(R))(MeC≡CMe)] (R = CO<sub>2</sub>Me) (**E**), since they are formed at high temperature, during which they transform into each other very fast. With respect to the **3** to **4** transformation, we favor the intermediacy of species **F**, which we formulate as a coordinatively unsaturated 16 e Ir(III) species,<sup>12</sup> rather than a saturated 18 e Ir(I) biscarbene complex related to the Ru species mentioned above. **F** may undergo ring contraction to give **4** or receive a ligand L to give **3** or **5a,b**.



In summary, by employing a very stable Tp<sup>Me2</sup>Ir system, we have isolated a compound, **4**, which lends a first experimental support to the very recent theoretically predicted intermediate on the cyclotrimerization of alkynes by Cp'Ru compounds.<sup>2,3</sup> Furthermore, compound **4** represents the first example of an organometallic derivative with the structure of bicyclo[3.2.0]hepta-1,3,6-triene.

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**Supporting Information Available:** Synthetic procedures and spectroscopic and analytical data, structure and refinement data, and ORTEP representation (PDF), and X-ray crystallographic file for compounds **2** and **4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) See the Supporting Information for experimental procedures, analytical and spectroscopic data, and for the X-ray diffraction studies of compounds **2** and **4**.
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