

Coupling of Internal Alkynes in $\text{Tp}^{\text{Me}_2}\text{Ir}$ Derivatives: Selective Oxidation of a Noncoordinated Double Bond of the Resulting Iridacycloheptatrienes

Eleuterio Álvarez,[†] Margarita Gómez,[†] Margarita Paneque,^{*,†} Cristina M. Posadas,[†] Manuel L. Poveda,[†] Nuria Rendón,[†] Laura L. Santos,[†] Susana Rojas-Lima,[‡] Verónica Salazar,[‡] Kurt Mereiter,[§] and Caridad Ruiz^{||}

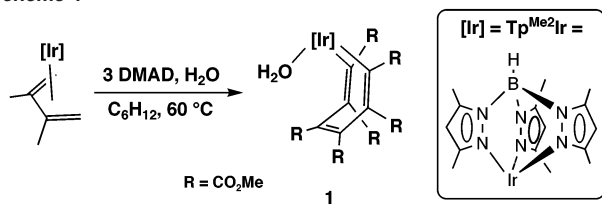
Instituto de Investigaciones Químicas, Consejo Superior de Investigaciones Científicas-Universidad de Sevilla, Avda. Américo Vespucio s/n, Isla de la Cartuja, 41092 Sevilla, Spain, Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca-Tulancingo Km 4.5, Pachuca, Hidalgo, México, Department of Chemistry, Vienna University of Technology, Getreidemarkt 9/164, A-1060 Vienna, Austria, and Instituto de Ciencia de Materiales de Madrid, CSIC, Campus de Cantoblanco, 28049 Madrid, Spain

Received October 22, 2002; E-mail: paneque@iiq.csic.es

Alkynes are common, versatile reagents that are frequently employed as building blocks in C—C bond-forming reactions mediated by transition metal compounds.^{1,2} O'Connor and co-workers have reported recently in this journal³ the facile generation of iridacyclopentene and iridacyclopentadiene units upon reaction of $\text{TpIr}(\text{C}_2\text{H}_4)_2$ with DMAD (Tp = hydrotris(pyrazolyl)borate; DMAD = dimethyl acetylenedicarboxylate). Prompted by these results, we report different results for the reactions of DMAD with related iridium complexes of the bulkier Tp^{Me_2} ligand (Tp^{Me_2} = hydrotris(3,5-dimethylpyrazolyl)borate). Unusual iridacycloheptatrienes, models for the proposed intermediates of the metal-catalyzed cyclotrimerization of alkynes,⁴ are produced under mild conditions. Most remarkably, some of these unsaturated iridacycles undergo a mild, regioselective oxidation which involves a distant C=C bond (that at the 3–4 position of the metallacyclic linkage) to yield unprecedented iridacyclohexadienes with a pendant, coordinated ketone functionality.

The Ir(I) butadiene derivative $\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^4\text{-CH}_2\text{=C}(\text{Me})\text{C}(\text{Me})\text{=CH}_2)$,⁵ when reacted with 3 equiv of DMAD at 60 °C (Scheme 1)

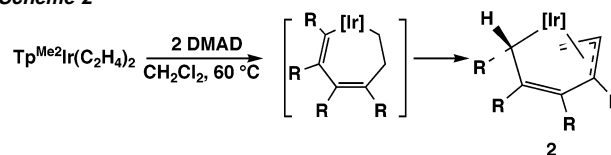
Scheme 1



quantitatively generates complex **1**,⁶ an iridacycloheptatriene⁷ resulting from the coupling of three molecules of the alkyne. A molecule of adventitious water completes the metal coordination. NMR monitoring reveals that the diene is cleanly extruded, but no intermediates can be detected even if only 1 equiv of the alkyne is used.

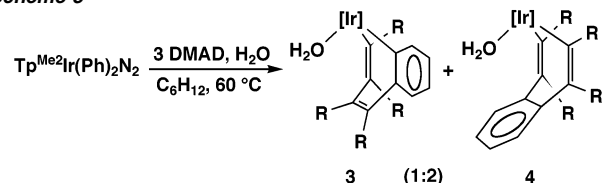
At variance with this result, the analogous reaction of $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$ ⁸ and DMAD affords compound **2**.⁶ As shown in Scheme 2, the newly generated six-carbon organometallic ligand formally results from the coupling of two molecules of DMAD and one of ethylene followed by the isomerization of the metallacyclic moiety (stereospecific hydrogen shift) to give the observed hydrocarbyl chain that consists of an alkyl and an allyl terminus.

Scheme 2



To gain further insight into these C—C bond-coupling processes, the reaction of $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2(\text{N}_2)$ ⁹ and DMAD has been investigated. Using cyclohexane as the reaction solvent (Scheme 3) a 1:2

Scheme 3

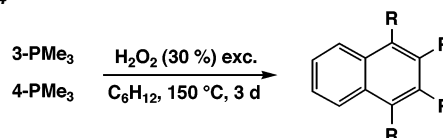


mixture of complexes **3** and **4**,⁶ readily separable by column chromatography, is obtained.

These isomeric compounds contain a benzannulated iridacycloheptatriene linkage that formally results from the cycloaddition of one benzyne and two DMAD units.¹⁰ Once more, metal coordination is completed by a molecule of H_2O . Thus, **3** and **4** are closely related to **1**. The water ligand of **1**, **3**, and **4** is easily replaced by other Lewis bases, resulting in the adducts **1**·L, **3**·L, and **4**·L (L = CO, PMe_3 , and NCMc; C_6H_{12} , 25–60 °C, excess L).

As in the reaction leading to **1**, no intermediates can be detected along the way to **3** and **4**, even if a deficiency of the alkyne is used. It appears plausible that a benzoiridacyclopentadiene complex ($[\text{Ir}]\text{-}o\text{-C}_6\text{H}_4\text{-C}(\text{R})\text{=C}(\text{R})\text{-}$) is generated, which finally yields the two observed products, namely **3** and **4**, by the insertion of a second molecule of the alkyne into the Ir-alkenyl or the Ir-aryl bond, respectively. It is worth mentioning that, when subjected to very drastic oxidation conditions, the adducts **3**· PMe_3 and **4**· PMe_3 give rise to 1,2,3,4-tetra(carboxymethyl)naphthalene,¹¹ i.e., the product of reductive elimination of the hydrocarbyl ligand (Scheme 4).

Scheme 4



The lability of the water ligand in **1**, **3**, and **4** permits the facile oxidation of their hydrocarbon chains. Oxidants such as O_2 , H_2O_2 ,

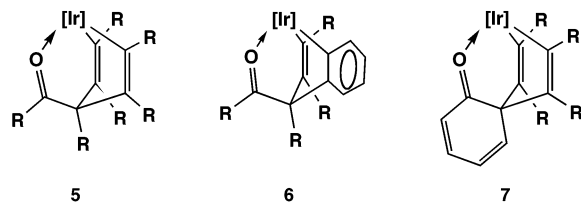
[†] CSIC and Universidad de Sevilla.

[‡] Universidad Autónoma del Estado de Hidalgo.

[§] Vienna University of Technology.

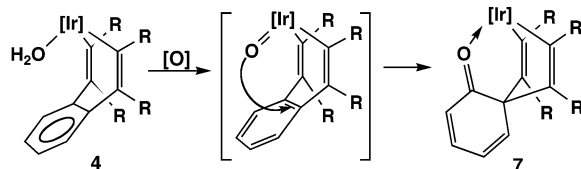
^{||} CSIC, Madrid.

pyridine-*N*-oxide, and particularly *t*-BuOOH prove effective in this regard. The latter reagent is able, at room temperature, to oxidize **1**, **3**, and **4** to the remarkably thermally stable (C₆H₁₂, 200 °C) products **5**, **6**, and **7**, respectively.⁶ Dioxygen requires more forcing conditions (C₆H₁₂, 3 atm, 60 °C, 24 h) to effect this transformation.



As can be seen, one of the carbon atoms of the distant carbon–carbon double bond within the metallacycle (vide infra), namely that at the 3,4-position, is regioselectively oxidized. Using the 4-to-7 transformation as a model, the oxidation may occur as represented in Scheme 5. A highly reactive Ir(V)–oxo derivative (see ref 12

Scheme 5



for a unique Ir(V)–oxo organometallic complex) could be responsible for the oxidation of the carbon atom; the transfer of the O atom to the double bond could produce an O-coordinated epoxide, which would ultimately rearrange to the ketone-like product.¹³ This and other mechanistic possibilities will be discussed in full in due course.^{14,15}

Although this proposal is inevitably speculative, it finds support in the following observations: (i) in accord with the inertness of the PMe₃ ligands toward substitution in Tp^{Me2}Ir(III)–PMe₃ compounds, adducts **3**·PMe₃ and **4**·PMe₃ do not undergo this oxidation. (ii) Complexes **6** and **7** may be alternatively generated directly if the reaction of Scheme 3 (i.e. that leading to **3** and **4**) is effected in the presence of oxygen. This route utilizes milder conditions than those required for the dioxygen-induced oxidations of **3** and **4** (vide supra) due to preferred coordination of the oxygen relative to water. (iii) As already noted, the seemingly distant C=C bond of the iridacycle is selectively oxidized; note however that the boat conformation adopted by these ring systems places this C=C bond close to the vacant coordination site at iridium (following H₂O dissociation) and thus close to the oxo ligand of the purported Ir(V)–oxo intermediate.¹⁶

In summary, the chemistry reported here provides new entries into metallacycles resulting from metal-induced coupling of alkynes. We have succeeded in isolating novel iridacycloheptatriene structures which are useful models for the metal-catalyzed cyclotrimerization of alkynes. Moreover we have demonstrated that C atoms of distant C=C bonds, including aromatic ones, can selectively be converted to the corresponding keto functionality under mild conditions.

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Supporting Information Available: Synthetic procedures and spectroscopic and analytical data for complexes **1–7**; structure and refinement data, ORTEP representations (PDF) and X-ray crystallographic files in CIF format (compounds **1**, **2**, **4**, **6**, and **7**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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