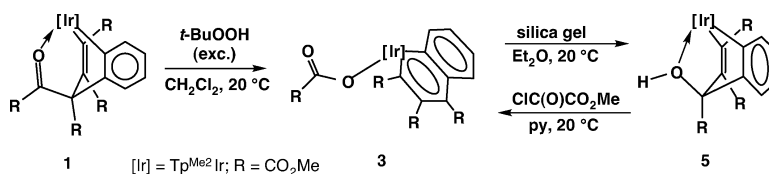


Formation of Unusual Iridabenzene and Metallanaphthalene Containing Electron-Withdrawing Substituents

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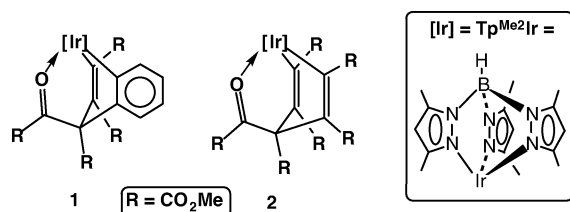
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Metallabenzene are a very attractive family of organometallic complexes,¹ which has recently received increasing attention,² particularly after convenient routes to different compounds of this type have been designed. The first reported examples include neutral and cationic osmabenzene³ derivatives, as well as a family of iridabenzene,⁴ the latter being derived from transient η^1 -pentadienyl-iridium species. More recently, Ir⁵ and Pt⁶ metallabenzene have been produced starting from the C₅ precursor Z-3-(2-iodovinyl)-1,2-diphenylcyclopropene. Apart from these three types, most of the known metallabenzene display η^6 -coordination to a second transition-metal fragment.² Transient metallabenzene have been proposed as intermediates in reactions leading to metal-cyclopentadienyls,^{6,7} thereby highlighting the importance of this type of metal-organic functionality. Notwithstanding, and to the best of our knowledge, higher metalla-aromatics of the transition elements, viz. metallanaphthalene or metallanthracene, have not been isolated.⁸ Following our earlier report⁹ on the formation of the bicyclic iridium derivatives **1** and **2** (Chart 1) we now wish to describe their transformation under very mild conditions into the irida-aromatic complexes **3** and **4**, respectively. As discussed below, the latter constitutes an unusual example of an Ir(III) metallabenzene, whereas the former represents the first transition element metallanaphthalene structure to be reported in the literature.

Chart 1



Compounds **1** and **2** react smoothly at room temperature with an excess of *t*-BuOOH to give their respective oxidized products, **3** and **4**, which contain a methoxalate ligand (Scheme 1). An X-ray study¹⁰ on compound **3** shows that the Tp^{Me2}Ir fragment is part of a somewhat bent metallanaphthalene unit. The iridium atom shows a deviation of 0.76 Å with respect to the mean plane defined by the five carbon atoms that compose the metallacyclic structure, possibly as a result of steric hindrance (vide infra). The two Ir–C distances amount to 1.930(6) and 1.981(6) Å, and are intermediate between Ir–C single and double bonds.¹¹

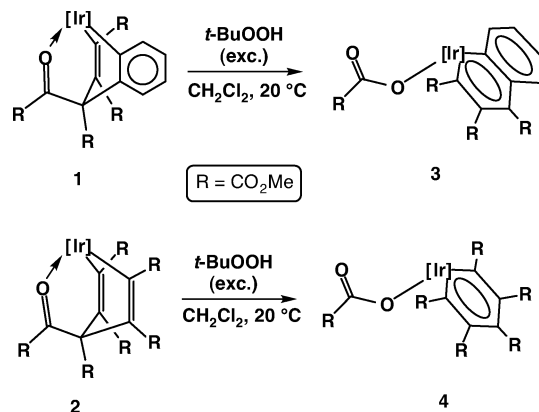
[†] CSIC and Universidad de Sevilla.

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[§] Universidad de Zaragoza and CSIC.

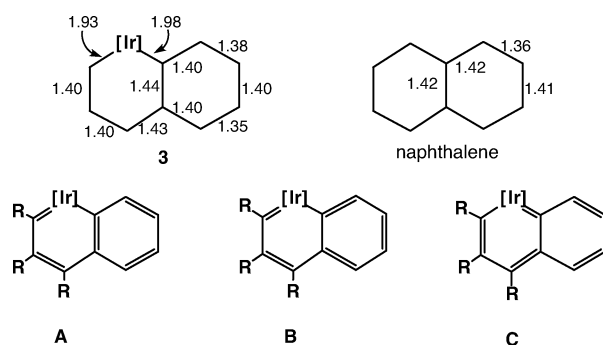
^{||} Vienna University of Technology.

Scheme 1



The four C–C bonds of this IrC₅ linkage, as well as all the C–C distances of the fused benzenic ring compare well with those found in naphthalene.¹² This suggests a similar, delocalized electronic structure, which may actually be described in terms of canonical forms **A–C**, (Chart 2) with larger contributions from the first two. In solution, a low field resonance (δ 255 ppm) in the ¹³C NMR spectrum,¹⁰ can be attributed to Ir–C(CO₂Me). This low field chemical shift value is indicative of appreciable carbene character for this carbon atom (canonical forms **A** and **B**).

Chart 2

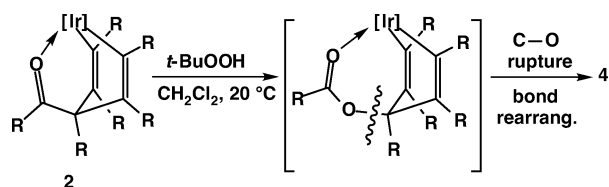


The metallacyclic moiety of **4** exhibits similar structural features to those of the related unit in **3**. As in the latter complex, the iridium atom of **4** deviates appreciably from the mean plane defined by the five carbon atoms of the ring (0.74 Å). This is probably due to steric interactions involving the CO₂Me substituents and the very bulky Tp^{Me2} auxiliary ligand. It may be noted in this regard that in Bleeker's iridabenzene Ir(CHC(Me)CHC(Me)CH)-(PR₃)₃, the devia-

tion of the iridium atom from the mean metallacyclic plane increases from 0.17 Å in the PMe_3 compound to 0.24 Å in the analogous PEt_3 derivative.¹³ In **4** the two Ir–C distances are very similar (1.921(6) and 1.957(6) Å, and 1.919(6) and 1.984(6) Å, respectively for each independent molecule in the unit cell) and intermediate between Ir–C bonds of single and double character.¹¹ In solution these carbon atoms give rise to a ^{13}C singlet at δ 229 ppm, that compares well with the value of 215 ppm found for previously reported Ir(III) benzenoid derivatives.¹⁴ It is worth noting that compounds **3** and **4** are the only metalla-aromatic species known that contain electron-withdrawing CO_2Me groups (three and five, respectively).

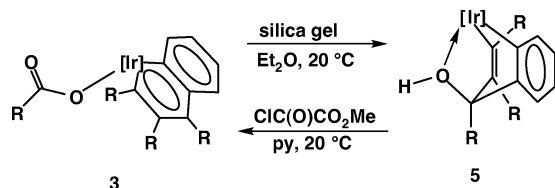
Although no intermediates have been observed in these transformations, the oxidation of **1** and **2** to **3** and **4**, respectively, can be proposed to occur by a Baeyer–Villiger process,¹⁵ to yield an unstable ester derivative, in which the rupture of the O–C(aliph) bond would finally form the observed products (Scheme 2, exemplifying the transformation from **2** to **4**).

Scheme 2



Both **3** and **4** are thermally stable in solution and exhibit interesting reactivity. For instance, column chromatography of **3** through silica gel produces the benzannulated iridacyclohexadiene structure **5** (Scheme 3), fully characterized by spectroscopy and X-ray diffraction.¹⁰

Scheme 3



It seems likely that hydrolysis gives rise to a hydroxo complex intermediate which undergoes nucleophilic attack at the γ -carbon atom of the electron-poor iridanaphthalene structure.¹⁶ Compound **5** can be viewed as a kind of internal neutral Jackson–Meisenheimer complex,¹⁷ its formation being in support of the aromatic nature of **3**. Interestingly, this transformation can be reversed. Thus, when **5** is treated with $\text{ClC(O)CO}_2\text{Me}$, in the presence of pyridine, **3** is cleanly formed, this observation being in support of the intermediate species proposed in Scheme 2.

In conclusion, we have disclosed a new route to iridanaphthalene and iridabenzene derivatives, consisting in the oxidation of bicyclic compounds. Compound **3** is unique as it contains the previously

unknown iridanaphthalene structure. Moreover, both **3** and **4** are unusual metalla-aromatic derivatives that possess electron-withdrawing carboxymethyl substituents. Hydrolytic cleavage of the Ir–carboxylate moiety of **3** regenerates the bicyclic structure by means of the nucleophilic attack of the resulting hydroxide ligand onto the γ -carbon of the iridanaphthalene unit, a process that can be reversed under appropriate conditions.

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Supporting Information Available: Synthetic procedures and spectroscopic and analytical data; structure and refinement data, ORTEP representations (PDF). X-ray crystallographic file in CIF format (compounds **3**–**5**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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