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Formation of Indanone from an Iridanaphthalene Complex

M. Talavera,[†] S. Bolaño,^{*,†} J. Bravo,[†] J. Castro,[†] S. García-Fontán,[†] and J. M. Hermida-Ramón[‡]

[†]Departamento de Química Inorgánica and [‡]Departamento de Química Física, Universidad de Vigo, Campus Universitario, E-36310 Vigo, Spain

Supporting Information

ABSTRACT: The first example of evolution of an iridanaphthalene into an indanone through an intermediate indenyl is reported, serving as a good example of starting material to obtain indanones. Two new iridanaphthalenes are obtained by intramolecular C–H activation of a phenyl ring of a carbene ligand in $[IrCp^*{=C(OMe)CH=CPh_2}(L)]PF_6$ $(L = PPh_2Me, PMe_3)$ complexes. It is demonstrated that these iridanaphthalene complexes can undergo a thermal reaction to give indenyl complexes and 3-phenylindanone.

M etallacyclic aromatic compounds incorporating transition metals are a subject of great interest, since they display a behavior that includes properties from both aromatic organic and organometallic compounds. Although many metallabenzenes of osmium, iridium, platinum, and ruthenium are known, to the best of our knowledge only two metallanaphthalenes have been reported, one with osmium¹ and another with iridium.² The importance of this type of metal-organic functionality is emphasized by the fact that metal cyclopentadienyls can be formed from transitory metallabenzenes.³ Analogously, an osmanaphthalene has been proposed as intermediate leading to an indenyl complex.⁴

Recently, we have reported that the new (methoxy)alkenylcarbeneiridium complex [IrCp*Cl{=C(OMe)CH= CPh₂}(PPh₂Me)]PF₆ (1a) reacts with amines to undergo the unexpected cleavage of the O-CH₃ bond instead of the usual aminolysis.⁵ This peculiar behavior has prompted us to further explore the reactivity of these types of compounds. Here, we report that treatment of [IrCp*Cl{=C(OMe)CH=CPh₂}-(L)]PF₆ (L = PPh₂Me (1a), PMe₃ (1b)) with AgPF₆ gives high yields of the iridanaphthalene complexes [IrCp*{=C(OMe)-CH=C(o-C₆H₄)(Ph)}(L)]PF₆ (L = PPh₂Me (2a), PMe₃ (2b)) through an intramolecular C-H activation of one of the phenyl rings of the carbene ligand (eq 1).



The structures of both iridanaphthalene complexes have been confirmed by single-crystal X-ray diffraction (see the Supporting Information). Figure 1 shows the complex cation **2a**. The iridium atom becomes part of a metallanaphthalene moiety and the metal





Figure 1. ORTEP view of the cation $[IrCp^*{=C(OMe)CH=C(o-C_6H_4)(Ph)}(PPh_2Me)]^+$ (**2a**) drawn at the 50% probability level. P1 represents a PPh₂Me ligand, and the hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Ir-P(1), 2.2968(9); Ir-CT, 1.9306(2); Ir-C(11), 1.966(4); Ir-C(22), 2.068(3); C(11)-Ir-C(22), 89.52(14). CT refers to the centroid of the Cp* ligand.

coordination sphere is completed with a pentamethylcyclopentadienyl (Cp*) and a phosphane ligand.

The NMR spectra support the solid-state structures of 2a,b (see the Supporting Information).

Remarkably, the iridanaphthalene moiety is not stable and refluxing 2 in 1,2-dichloroethane or toluene for 24 h gives 3-phenylindanone (4) (eq 2). The same transformation occurs also at longer reaction times in dichloromethane at 35 °C (eq 2).

 Received:
 July 17, 2013

 Published:
 July 30, 2013



The nature of 4,⁶ which was isolated in excellent yield, was confirmed by ¹H and ¹³C{¹H} NMR spectroscopy (see the Supporting Information). The transformation of 2 to give 4 is, to the best of our knowledge, the first example of indanone formation from a metallanaphthalene. We prepared a solution of 2 (0.013 M) in dichloromethane, and in order to shed light on the mechanism of this reaction the transformation of 2 into 4 was followed at 35 °C by NMR spectroscopy. After 8 days, integration of the ³¹P{¹H} peaks showed a partial transformation of 2 into the new complex [IrCp*{ η^3 -(C₉H₅)(OMe)(Ph)}(L)]-PF₆ (3) (3:7 ratio). ¹H NMR confirms the presence of 4 in addition to 2 and 3. Extraction of 4 with diethyl ether gives 3a (L = PPh₂Me) (or 3b (L = PMe₃)) contaminated with 2a (30%) (or 2b (5%)).

Multidimensional and multinuclear NMR analysis of the mixture formed by **2** and **3** confirms the formulation of **3** as the indenyl complex. The ¹H NMR spectrum for **3a** shows the presence of signals at 3.84 (s, 3H, OCH₃) and 6.01 (d, 1H, ${}^{3}J_{H-P} = 10.8 \text{ Hz}, C^{2}$ -H) ppm, while for **3b** the same signals appear at 3.78 (s, 3H, OCH₃) and 5.96 (d, 1H, ${}^{3}J_{H-P} = 10.7 \text{ Hz}, C^{2}$ -H) ppm. The ${}^{13}C{}^{1}H{}$ NMR spectrum for **3a** reveals the existence of resonances at 49.4 (s, C^{3}), 56.3 (s, C^{2} -H), 132.3 (s, C^{9}), 161.0 (s, C^{8}), and 186.3 (s, C^{1}) ppm, while the peaks for **3b** appear at 50.1 (s, C^{3}), 55.3 (s, C^{2} -H), 132.3 (s, C^{9}), 161.3 (s, C^{8}) and 185.5 (s, C^{1}) ppm. The { ${}^{1}H, {}^{13}C{}$ HMBC NMR experiment further confirms the existence of the indenyl ligand, showing correlations between η^{3} -C²H and C³, C¹, C⁸, and C⁹ (Figure 2).



Figure 2. Section of the {¹H, ¹³C} HMBC NMR experiment of **3a** showing correlations between η^3 -C²H and C³, C¹, C⁸, and C⁹ resonances. Signals marked with an asterisk correspond to the presence of **2a** as an impurity.

Since chemical shifts ranging between 140 and 160 ppm are typical for C^8 and C^9 in η^3 -indenyl ligands,⁷ the NMR data suggest the structure displayed in Scheme 1 for complex 3, showing an η^3 hapticity of the indenyl ligand. The crystal structure of 3a confirms that this formulation is retained in the solid state, with the iridium atom coordinated to a phosphane

Scheme 1. Proposed Mechanism for the Formation of 3 and 4



ligand (PPh₂Me), to a η^{5} -pentamethylcyclopentadienyl ligand, and to η^{3} -1-methoxy-3-phenylindene (Figure 3). The noteworthy



Figure 3. ORTEP view of the cation $[IrCp^*{\eta^3-(C_9H_5)(OMe)(Ph)}-(PPh_2Me)]^+$ (**3a**) drawn at the 20% probability level. P1 represents a PPh₂Me ligand, and the hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Ir-CT, 1.896(2); Ir-P(1), 2.280(7); Ir-C(11), 2.92(2); Ir-C(12), 2.17(2); Ir-C(13), 2.25(2); CT-Ir-C(12), 142.6(6); CT-Ir-C(13), 133.6(7); CT-Ir-C(14), 106.9(5). CT refers to the centroid of the Cp* ligand.

geometrical feature of the structure is the strongly slipped indenyl group, in which the average of the Ir–C(14) and Ir–C(15) distances is 3.23(3) Å. This value is 24% longer than the average value of the Ir–C(11), Ir–C(12), and Ir–C(13) distances, 2.45(2) Å. On the other hand, the C(12)–C(13) and C(12)–C(11) distances are 1.42(3) Å, as expected. Bond distances and angles are given in the Supporting Information.

The interception of complex **3** along the transformation of complex **2** shed light on the possible mechanism for the formation of **4**. The iridanaphthalene **2** could undergo carbene migratory insertion, leading to the 16e intermediate **A** (not observed),⁸ which after switching from η^1 to η^3 hapticity leads to the more stable

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18e complex 3, stabilized with respect to A by aromatization of the benzene ring. Formation of 4 from 3 recalls the formation of indene from the indenyl complex,^{7a} but in our case the final product is an indanone (Scheme 1). This implies not only the heterolytic cleavage of the O-CH₂ bond but also the hydrogenation of the remaining double bond. The solvent does not seems to play any role in the reaction, since it occurs irrespective of solvent polarity (dichloromethane, 1,2-dichloroethane, methanol, chloroform, and toluene) and in aprotic solvents (carbon tetrachloride) or when the presence of water is rigorously avoided.⁹ In keeping with this hypothesis, repeating the reaction in deuterated solvents (CD₂Cl₂, CDCl₂) does not result in any deuterium incorporation in the final products. Therefore, complex 3 is the only species initially involved in the formation of 4, and the methyl group possibly bonded to the iridium atom after the heterolytic cleavage of the O-CH₃ bond seems to be involved in the hydrogenation.

In summary, we have synthesized the iridanaphthalene 2 by a intramolecular C–H activation of one phenyl ring of the carbene ligand in complex 1 and shown that 2 selectively transforms into the indenyl compound 3. When the reaction is carried out at low concentration in a low-boiling-point solvent, a mixture of 2 and 3 is formed, suggesting a rationale for the mechanism of the evolution from to 2 to 4. The formation of the indanone 4 from compound 2 suggests that indenyl complexes could be relevant intermediates to obtain these organic compounds, which are important for their medical applications.¹⁰ Further studies tackling the preparation of other iridanaphthalenes are in progress in our laboratory, aimed at addressing the full scope of the reaction.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, tables, and CIF files giving experimental procedures and full spectroscopic data for all new compounds and crystallographic data for compounds $2a \cdot BPh_4$, $2b \cdot BPh_4$, $2b \cdot PF_6$, and $3a \cdot BPh_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for S.B.: bgs@uvigo.es.

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

We thank the University of Vigo CACTI services for collecting X-ray data and recording NMR spectra.

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(8) Formation of Cp complexes from metallabenzenes is known, and also this rearrangement was proposed for obtaining an indenyl osmium complex (see refs 3 and 4).

(9) All solvents were dried by the usual procedures (Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Butterworth/ Heinemann: London/Oxford, 1988) and, prior to use, distilled under argon.

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