Metallacycloheptatrienes of Iridium(III): Synthesis and Reactivity

Margarita Paneque,*,† Cristina M. Posadas,† Manuel L. Poveda,*,† Nuria Rendón,†
Laura L. Santos,† Eleuterio Álvarez,† Verónica Salazar,‡ Kurt Mereiter,§ and Enrique Oñate⊥

Instituto de Investigaciones Químicas and Departamento de Química Inorgánica, Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla, Avenida Américo Vespucio 49, Isla de la Cartuja, 41092 Sevilla, Spain, Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, Carretera Pachuca a Tulancingo, Pachuca, Hidalgo, México, Department of Chemistry, Vienna University of Technology, Getreidemarkt 9/164SC, A-1060 Vienna, Austria, and Instituto de Ciencia de Materiales de Aragón, CSIC and Universidad de Zaragoza, Plaza de San Francisco s/n, Zaragoza, Spain

The Ir(I)−butadiene complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2=C(Me)C(Me)=CH_2)$ (**1**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) reacts with ≥3 equiv of DMAD ($RC≡CR$, R = CO_2Me) in CH_2Cl_2 at 60 °C, in the presence of adventitious water, with formation of the iridacycloheptatriene $Tp^{Me2}\overline{Ir(C(R)}=C(R)C\text{-}(R)=C(R)C(R)=C(R))(H_2O)$ (**2**), by the oxidative coupling of three molecules of DMAD in the metal coordination sphere. In a related process, $Tp^{Me2}IrPh_2(N_2)$ (**4**) gives two benzoannelated iridacycloheptatrienes, the symmetrical species $Tp^{Me2}\overline{Ir(C(R)}=C(R)\text{-}o\text{-}C_6H_4C(R)=C(R))(H_2O)$ (**5**) and the unsymmetrical one $Tp^{Me2}\overline{Ir(C(R)}=C(R)C(R)=C(R)\text{-}o\text{-}C_6H_4)(H_2O)$ (**6**). The water ligand in these complexes is labile, and derivatives substituted with CO, PMe_3, and NCMe have been obtained. **2**, **5**, and **6** react, at 25 °C, with oxo-transfer oxidizing reagents such as ^tBuOOH with formation of the keto-metallabicyclic products **7**−**9**, which result from the selective oxo attack to the γ,δ-C=C double bond, irrespective of this being of the benzo or the (R)C=C(R) type. In the latter case, further oxidation takes place with ^tBuOOH, at ambient temperature, with formation of an iridabenzene (**11**) and an iridanaphthalene (**12**) (with five and three electron-withdrawing CO_2Me substituents, respectively) in which the carboxylate $MeO_2CCO_2^-$ ligand completes the metal coordination sphere. Interestingly, substitution of this group by OH^- or MeO^- allows the formation of Jackson−Meisenheimer complexes, reflecting the inherent aromaticity of these electron-deficient metalloaromatics. Finally, the hydrogenation of the iridacycloheptatrienes has been studied. All new compounds have been fully characterized by microanalysis, IR and NMR spectroscopies, and, in some cases, single-crystal X-ray diffraction studies.

Introduction

Although scarce,[1] metallacycloheptatrienes are very interesting organometallic species, which are implicated in the transition metal mediated cyclotrimerization of alkynes, to give benzene derivatives.[2] According to the commonly accepted mechanism for this process, it would be possible to synthesize metallacycloheptatrienes through the reaction of a metallacyclopentadiene[3] with an alkyne, provided that the former species has, maybe transiently, a vacant, *cis*-positioned, coordination site. The resulting adduct[4] will provide the desired seven-membered metallacycle by an insertion process; if unstable, the structure can be stabilized by an incoming 2 e⁻ donor L.[5] Of course, the metal center needs not to have any tendency to experience a

reductive elimination under the reaction conditions, or otherwise a benzenoid ligand will be formed instead. The $Tp^{Me2}Ir(III)$ system (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate)[6] is

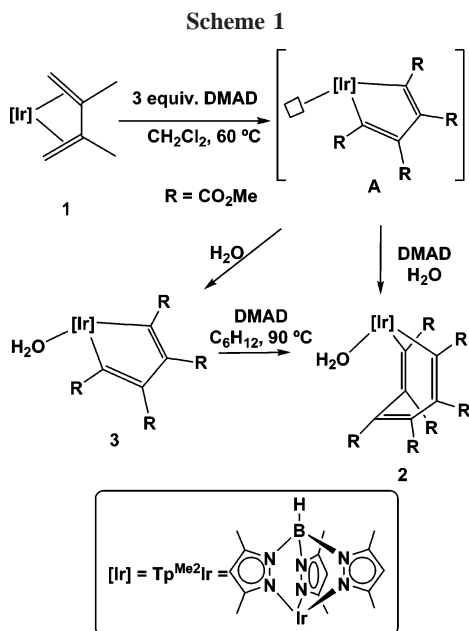* To whom correspondence should be addressed. E-mail: paneque@iiq.csic.es.

† Universidad de Sevilla and Consejo Superior de Investigaciones Científicas.

‡ Universidad Autónoma del Estado de Hidalgo.

§ Vienna University of Technology.

⊥ Universidad de Zaragoza.

(1) (a) Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31. (b) Browning, J.; Green, M.; Laguna, A.; Smart, L. E.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1975**, 723. (c) Agh-Atabay, N. M.; Davidson, J. L.; Douglas, G.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1989**, 549.

(2) (a) Collman, C. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Keruza, S.; Tanaka, S.; Ohe, T.; Nakaya, Y.; Takeuchi, R. *J. Org. Chem.* **2006**, *71*, 543. (c) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901. (d) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, Chapter 7.3. (e) Kirchner, K.; Calhorda, M. J.; Schmid, R.; Veiros, L. F. *J. Am. Chem. Soc.* **2003**, *125*, 11721. (f) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143. (g) Kakeya, M.; Fujihara, T.; Kasaya, T.; Nagasawa, A. *Organometallics* **2006**, *25*, 4131.

(3) For some iridacyclopentadienes see: (a) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298. (b) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.-L; Eisenstein, O.; Jackson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010. (c) O'Connor, J. M.; Closson, J.; Gantzel, P. *J. Am. Chem. Soc.* **2002**, *124*, 2434. (d) Martin, M.; Sola, E.; Torres, O.; Plou, P.; Oro, L. A. *Organometallics* **2003**, *22*, 5406. (e) Álvarez, E.; Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *Chem.−Eur. J.* **2007**, in press.

(4) Diercks, R.; Eaton, B. E.; Gürtzgen, S.; Jalisatgi, S.; Matzger, A. J.; Radde, R. H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1998**, *12*, 8247.

(5) For other structural outcomes, see: (a) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525. (b) Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holman, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*, 1275, and ref 3b.

Scheme 1

particularly well suited in this regard, and in this paper we report on the synthesis and reactivity of some unusual iridacycloheptatrienes. Part of this work has been briefly communicated.[7]

Results and Discussion

**Synthesis and Characterization of Iridacycloheptatrienes.** The reactions of the Ir(I) complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2=C(Me)C\text{-}(Me)=CH_2)$ (**1**)[8a] with a series of Lewis bases L have been studied,[8b–d] and depending on the nature of L, simple η^2:σ,σ butenediyl Ir(III) adducts are formed (some of them reversibly, e.g., with C_2H_4),[8b] or the diene is coupled to the entering molecule.[8c,d] As for alkynes, we have reported that $Me_3SiC\equiv CSiMe_3$ rearranges to a vinylidene ligand,[8e] while $PhC\equiv CPh$ couples with the diene to give a bicyclic alkyl—allyl complex.[8f] By contrast, **1** reacts with ≥3 equiv of dimethyl acetylenedicarboxylate (DMAD = $MeO_2CC\equiv CCO_2Me$) in CH_2Cl_2 at 60 °C with extrusion of the butadiene and formation, as a water adduct,[9] of the iridacycloheptatriene **2** (Scheme 1), the result of the oxidative coupling of three DMAD molecules on the Ir coordination sphere. From the composition of complex **2**, it is obvious that water is needed in the reaction medium, but we have shown[3e] that if a large excess of it is present, preferential trapping of intermediate **A** by H_2O takes place and the iridacyclopentadiene **3** is obtained instead. This is not an

important synthetic problem, as the latter compound reacts with further DMAD, although under more forcing conditions, to give **2**.[3e] When the latter reaction is carried out with an excess (5 equiv) of DMAD-d_6, **2**-d_6 is obtained (eq 1), clearly indicating that formation of the iridacycloheptatriene is irreversible under the conditions depicted in Scheme 1.
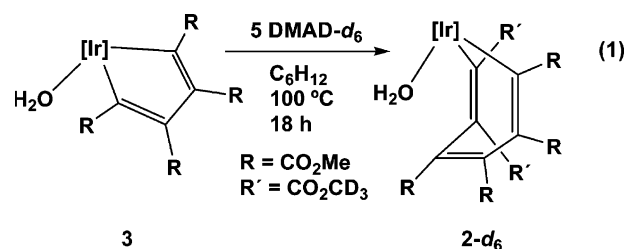
Compound **2** has been fully characterized by microanalysis, IR and NMR spectroscopies, and, in addition, by single-crystal X-ray analysis (see below). The symmetrical nature of the metallacycle is clearly reflected in both the ^1H and $^{13}C\{^1H\}$ NMR spectra, with three different CO_2Me groups being observed. The ^{13}C nuclei of the ring appear at 156.1, 135.9, and 134.9 ppm, but these resonances cannot be confidently assigned to any particular position. **2** undergoes slow thermal decomposition, in C_6H_{12} at 150 °C, to give a number of unidentified products, none of them being $C_6(CO_2Me)_6$, the expected result of a reductive elimination process. It is also worth noting that this complex has no tendency to lose water with formation of a 1-iridabicyclo[3.2.0]heptatriene derivative.[10]

Two more interesting isomeric benzoannelated iridacycloheptatrienes, complexes **5** and **6**, are obtained (2:1 ratio) upon treatment of the dinitrogen complex $Tp^{Me2}IrPh_2(N_2)$ (**4**)[11] with an excess of DMAD in C_6H_{12} at 60 °C (eq 2). These species can be cleanly separated by chromatography on silica gel, and this has allowed an easier characterization. The symmetrical and unsymmetrical nature of **5** and **6** is reflected in their NMR spectra, but otherwise the data obtained are similar and compare well with those reported for **2**.
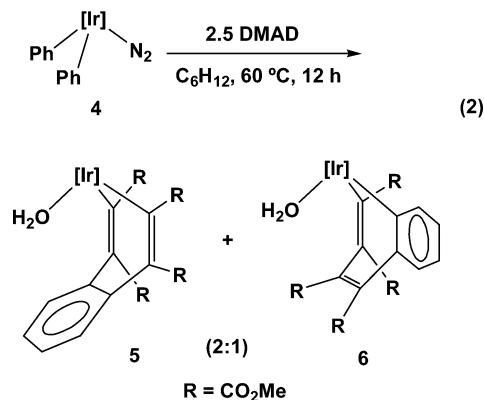
Complexes **5** and **6** are clearly the result of the formal coupling, with different regioselectivity, of two molecules of DMAD and C_6H_4 (benzyne) in the Ir coordination sphere. In fact, a mechanism in which the two Ir—phenyl groups are converted into a benzyne ligand[12] could be invoked for their formation, but this would imply a reduction in the oxidation

(6) Trofimenko, S. *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(7) (a) Álvarez, E.; Gómez, M.; Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Rojas-Lima, S.; Salazar, V.; Mereiter, K.; Ruiz, C. *J. Am. Chem. Soc.* **2003**, *125*, 1478. (b) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Salazar, V.; Oñate, E.; Mereiter, K. *J. Am. Chem. Soc.* **2003**, *125*, 9898.

(8) (a) Boutry, O.; Poveda, M. L.; Carmona, E. *J. Organomet. Chem.* **1997**, *528*, 143. (b) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V. *Organometalllics* **2000**, *19*, 3120. (c) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 248. (d) Paneque, M.; Poveda, M. L.; Salazar, V.; Taboada, S.; Carmona, E. *Organometallics* **1999**, *18*, 139. (e) Ilg, K.; Paneque, M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Carmona, E.; Mereiter, K. *Organometallics* **2006**, *25*, 2230. (f) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *Organometallics* **2007**, *26*, 1900.

(9) (a) Amouri, H.; Guyard-Duhayon, C.; Vaissermann, J. *Inorg. Chem.* **2002**, *41*, 1397. (b) Miranda-Soto, V.; Parra-Hake, M.; Morales-Morales, D.; Toscano, R. A.; Boldt, G.; Koch, A.; Grotjahn, D. B. *Organometallics* **2005**, *24*, 5569.

(10) Paneque, M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *J. Am. Chem. Soc.* **2004**, *126*, 1610.

(11) Gutiérrez-Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Carmona, E. *Chem.—Eur. J.* **1998**, *4*, 2225.

(12) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 6492.
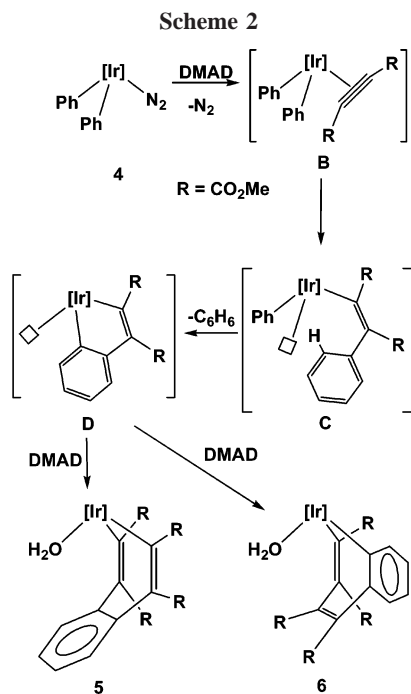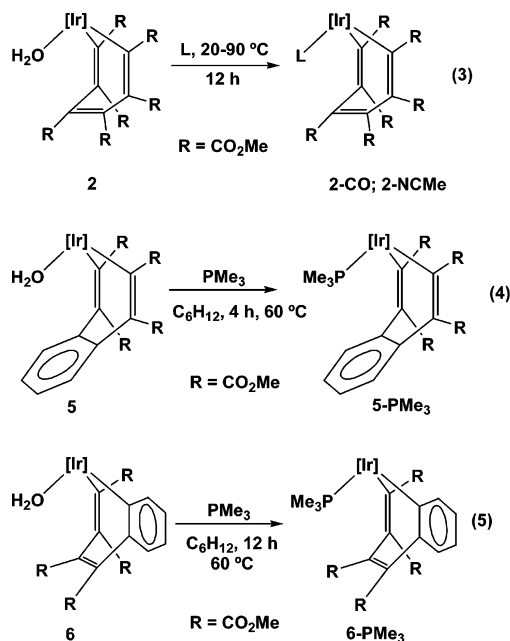
Scheme 2

state of the iridium center from +3 to +1, and we have shown this to be a very unlikely situation in the Tp^{Me2}Ir system.[11,13] Therefore, we prefer to propose instead the mechanism depicted in Scheme 2, which is partially based on the reaction outcome of complex **4** with C$_2$H$_4$.[11]

As can be observed, DMAD inserts into an Ir–Ph bond of adduct **B**, and then the phenyl group of the resulting *cis*-alkenyl ligand in **C** undergoes an *o*-metalation process, giving C$_6$H$_6$ and the unsaturated benzoiridacyclopentadiene **D**. If this is true, and as the formation of **5** and **6** has been shown to be irreversible, the observed ratio of these two complexes reflects the different reactivities of the two Ir–C$_{sp2}$ bonds in **D** toward DMAD insertion. Attempts to detect any of the intermediates depicted in Scheme 2 were made by monitoring the reaction by NMR spectroscopy, but these were unsuccessful even when 1 equiv of DMAD was used. It is important to point out that the process depicted in eq 2 quite closely resembles the reaction of CrPh$_3$(THF)$_3$ with DMAD, which gives naphthalene species, and was studied in depth years ago by Whitesides et al.[14] In this work, no organometallic compounds were obtained, but structures related to **5** and **6** were proposed as intermediates.

As expected,[3e,10] the water ligand in complexes **2**, **5**, and **6** is labile and easily replaced by other Lewis bases such as CO, NCMe, and PMe$_3$ (eqs 3–5). The resulting adducts have been completely characterized by microanalysis and IR and NMR spectroscopies. Interestingly, the rotation around the Ir–P bond in complexes **5·PMe$_3$** and **6·PMe$_3$** is slow, on the NMR time scale, at room temperature (see Experimental Section).

Oxidation Reactions. In an effort to liberate the organic fragments of complexes **2**, **5**, and **6** from the metal, we submitted them to the action of oxidizing reagents, a method to induce reductive eliminations that has precedents in Cp′Ir(III) chem-

(13) (a) Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem.–Eur. J.* **1997**, *3*, 860. (b) Carmona, E.; Paneque, M.; Poveda, M. L. *Dalton Trans.* **2003**, 4022. (c) Carmona, E.; Paneque, M.; Santos, L. L.; Salazar, V. *Coord. Chem. Rev.* **2005**, *294*, 1729. For some exceptions to this norm, see ref 8b and: Posadas, C. M. Ph.D. Thesis, University of Seville, 2006.

(14) Whitesides, G. M.; Ehmann, W. J. *J. Am. Chem. Soc.* **1970**, *92*, 5625.

(3)

(4)

(5)

istry.[15] However, quite different results were obtained for these Tp^{Me2}Ir(III) derivatives when the oxidation was carried out with oxo-transfer species. Thus, the reaction of complex **2** with an excess (5 equiv) of ^{t}BuOOH in CH$_2$Cl$_2$ at 20 °C furnishes the keto-ester compound **7** (eq 6). The symmetrical nature of product **7** is clearly manifested in both the ^{1}H and ^{13}C{^{1}H} NMR spectra, with the more important data being the resonances at 209.3 and 73.3 ppm corresponding to the ^{13}C nuclei of the keto group bonded to the metal and of the aliphatic *C*(CO$_2$Me) moiety, respectively.
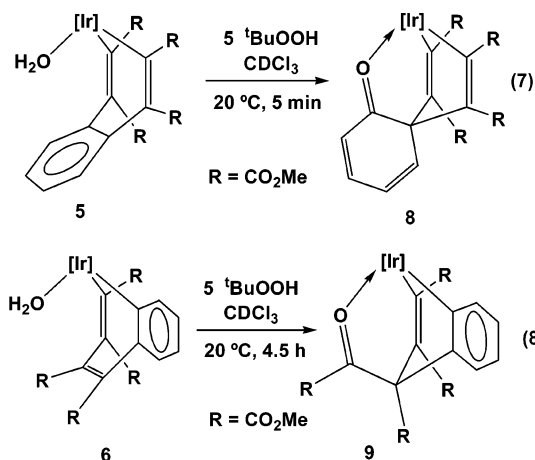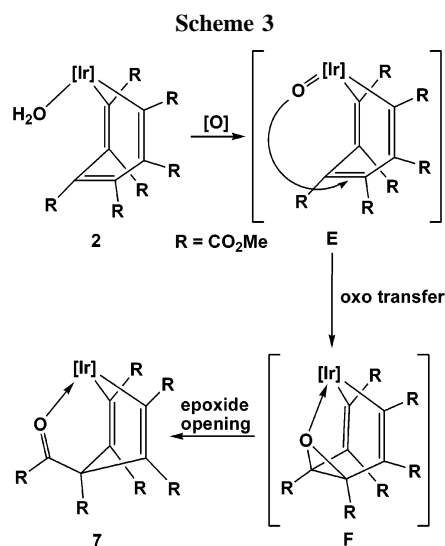

(6)
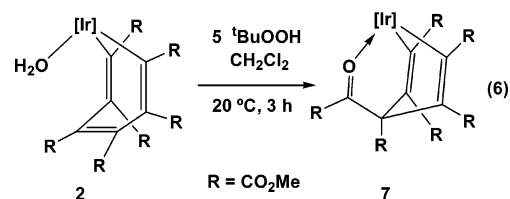
In related processes, the benzoiridacycloheptatrienes **5** and **6** gave compounds **8** and **9**, respectively (eqs 7 and 8), and it is notable that in the first case the aromaticity of the benzenoid ring is lost. Although ^{t}BuOOH is the reagent of choice for these oxidations, due to the mild requirements of the reactions, other reagents such as H$_2$O$_2$, pyridine oxide, and even O$_2$ are capable of effecting these transformations (see Experimental Section). The reactions shown in eqs 6–8 have to be carefully monitored, as overoxidations with ^{t}BuOOH are easy processes, which will be described below. However, once isolated, the three oxidized species **7**, **8**, and **9** are very stable thermally, and their solutions in C$_6$H$_{12}$, in the absence of O$_2$, can be heated to 150 °C without evident decomposition.

We have found that the presence of radical inhibitors such as cyclohexadiene or hydroquinone did not affect the oxidations shown in eqs 6–8, and they are most easily explained by invoking the mechanism depicted in Scheme 3 (for clarity the **2** → **7** transformation is the one represented). In the first step, an oxo derivative of Ir(V) (**E**)[16] is formed following H$_2$O extrusion. As expected, this species would be highly unstable[17] and transfers the oxygen, regio- and stereoselectively, to the

(15) Diversi, P.; Marchetti, F.; Ermini, V.; Matteoni, S. *J. Organomet. Chem.* **2000**, *593*, 154.

(7)

(8)

more distant C=C double bond, giving the epoxide **F**, which then, by virtue of its interaction with the Lewis acidic Ir(III) center, experiences an opening process[18] to give a keto group that remains bonded to the metal. Interestingly, the epoxidizing power of the oxo ligand present in **E** and related intermediates must be very strong, as double bonds carrying two e$^-$ accepting, hence deactivating, substituents such as the CO$_2$Me group, are usually reluctant to participate in this kind of oxidation, and the same is true for benzenoid C=C bonds.[19] In accord with

Scheme 3

the proposed mechanism, the PMe$_3$ derivatives **5·PMe$_3$** and **6·PMe$_3$** (having nonlabile phosphine ligands) did not react with H$_2$O$_2$ even at 130 °C. However, for the first case and under more forcing conditions (eq 9), a mixture was obtained from which the naphthalene **10**[20] (the expected product of the reductive elimination of the metallacycle) could be isolated by column chromatography.

(9)
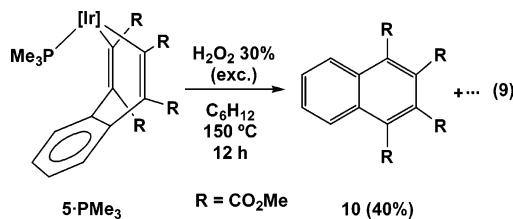
As commented above, the oxidation of the iridacycloheptatrienes **2**, **5**, and **6** with an excess of ^{t}BuOOH does not stop with the formation of derivatives **7**, **8**, and **9**. For the case of **2** and **6** (or **7** and **9**) the reactions were quite clean, at ambient temperature, and the metalloaromatics **11** and **12** were obtained in very high yields (eqs 10 and 11). The coordination sphere of the iridium is completed in both cases with a methyloxalate ligand.

(10)

(11)
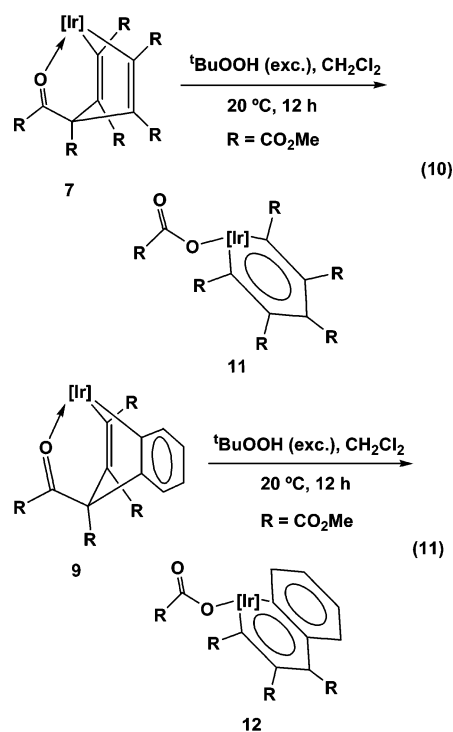
Complexes **11** and **12** add to the growing family of metallabenzenes[8e,21] and related metalloaromatics, and **12**

(16) The monomeric Ir(O)(mesityl)$_3$ is known and has been characterized, among other methods, by X-ray diffraction studies. See: (a) Hay-Motherwell, R. S.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1993**, *12*, 2009. (b) Jacobi, B. G.; Laitar, D. S.; Pu, L.; Wargocki, M. F.; DiPasquale, A. G.; Fortner, K. C.; Schuck, S. M.; Brown, S. N. *Inorg. Chem.* **2002**, *41*, 4815.

(17) Oxo-terminal derivatives, L$_n$M=O, of 8−10 transition metal groups are very unstable entities mainly due to the great number of d electrons available. In Wilkinson's compound[16] geometrical factors prevent the antibonding orbitals of the double bond Ir=O from being populated (although it is very reactive and easily transfers the oxo ligand to other reagents). Quite recently M=O derivatives for Pd and Pt have been described in which the double bond is protected by encapsulation. See: (a) Anderson, T. M.; Neiwert, W. A.; Kirk, M. L.; Piccoli, P. M. B.; Schultz, A. J.; Koetzle, T. F.; Musaev, D. G.; Morokuma, K.; Cao, R.; Hill, C. L. *Science* **2004**, *306*, 2074. (b) Anderson, T. M.; Cao, R.; Slonkina, E.; Hedman, B.; Hodgson, K. O.; Hardcastle, K. I.; Neiwert, W. A.; Wu, S.; Kirk, M. L.; Knottenbelt, S.; Depperman, E. C.; Keita, B.; Nadjo, L.; Musaev, D. G.; Morokuma, K.; Hill, C. L. *J. Am. Chem. Soc.* **2005**, *127*, 11948.

(18) Smith, M. B.; March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 5th ed.; Wiley: New York, 2001.

(19) Somasekar, R. A. In *Comprehensive Organic Chemistry*; Ley, S. V., Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 7, Chapter 3.1.

(20) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827.

(21) (a) Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205. (b) Landorf C. W.; Haley, M. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3914. (c) Thorn, D. L.; Hoffman, R. *Nouv. J. Chim.* **1979**, *3*, 39. (d) Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811. (e) Bleeke, J. R.; Xie, Y.-F.; Peng, W.-J.; Chiang, M. Y. *J. Am. Chem. Soc.* **1989**, *111*, 4118. (f) Gilbertson, R. D.; Weakley, T. J. R.; Haley, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 2597. (g) Jacob, V.; Weakley, T. T. R.; Haley, M. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3470. (h) Chin, C. S.; Lee, H. *Chem.−Eur. J.* **2004**, *10*, 4518. (i) Xia, H.; He, G.; Zhang, H.; Wen, T. B.; Sung, H. H. Y. *J. Am. Chem. Soc.* **2004**, *126*, 6862. (j) Barrio, P.; Esteruelas, M. A.; Oñate, E. *J. Am. Chem. Soc.* **2004**, *126*, 1946. (k) Álvarez, E.; Paneque, M.; Poveda, M. L.; Rendón, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 474. (l) Clark, G. R.; Johns, P. M.; Roper, W. R.; Wright, L. J. *Organometallics* **2006**, *25*, 1771.

Scheme 4

Scheme 5
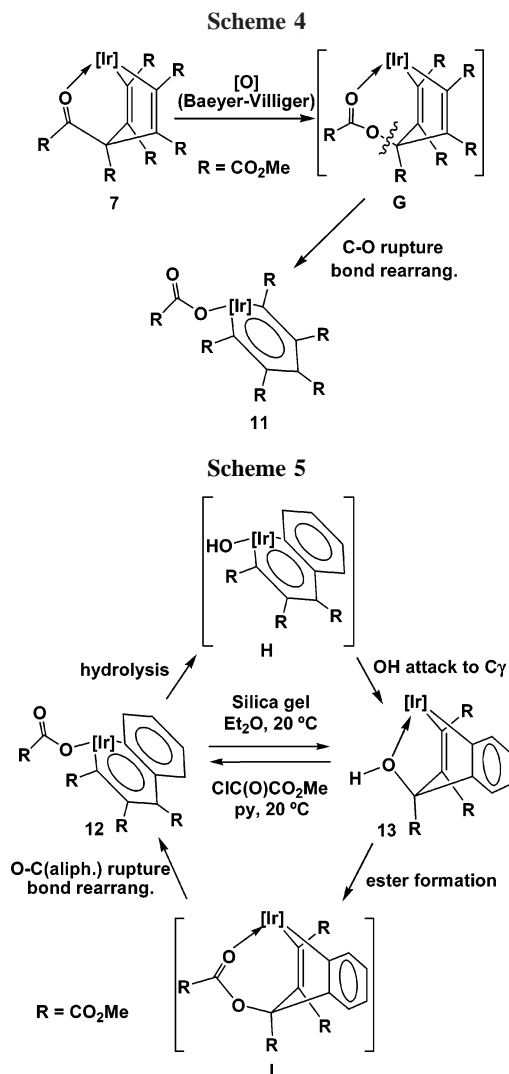
represents the first transition metal metallanaphthalene. They are also unusual for the presence of quite a number of electron-withdrawing substituents (five CO_2Me in the case of **11**), which are not normally thought of as stabilizers of this kind of structure. **11** and **12** have been completely characterized by microanalysis, IR and NMR spectroscopies, and single-crystal X-ray studies, presented below. For compound **11** the two carbon nuclei bonded to Ir are equivalent (in accord with aromatic delocalization) and resonate in the $^{13}C\{^1H\}$ NMR spectrum at 229.3 ppm, a reasonable value if a 50% carbene character is taken into consideration. In the case of **12** the IrC(CO_2Me) nucleus appears at lower field, specifically at δ 255.0, while the other carbon bonded to iridium resonates at 177.9 ppm, clearly indicating that the first of these Ir—C bonds has more Ir=C contribution. A more detailed analysis will be postponed until the X-ray structure of this complex is presented (see below).

With respect to the mechanism of the formation of these metallabenzenes, we propose that their formation occurs as depicted in Scheme 4 (exemplified for the **7 → 11** transformation). A Baeyer—Villiger oxidation[18] of the C(=O)—C(R) bond gives rise to an unstable ester **G**, which rearranges to the observed product by C—O rupture and bond reorganization.

Interestingly, complex **12** readily undergoes hydrolysis upon chromatography on silica gel, and the bicyclic compound **13**, containing a tertiary alcohol functionality bonded to the Ir(III) center, is isolated. The carbon that supports the OH resonates at 98.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum, while the OH

functionality was apparent by IR spectroscopy as an absorption at 3380 cm^{-1}. Scheme 5 shows this transformation along with a plausible mechanism for it. Hydrolysis of the methyloxalate ligand in **12** will give a hydroxo complex **H**, from which, upon nucleophilic attack of the OH to the C_γ of the benzene ring, **13** is formed. In that way this last species can be viewed as an internal neutral Jackson—Meisenheimer[22] complex and adds support to the already reported aromaticity of the iridanaphthalene. Complex **13** reverts to **12** upon reaction with the acid chloride ClC(=O)CO_2Me, and this process presumably takes place by the intermediacy of ester **I** (related to **G**, Scheme 4), which, as suggested before, decomposes by C—O bond rupture.

Hydrolysis of the iridabenzene **11** with silica gel was not successful, but a compound related to **13** was obtained, although in very low yield, in THF—H_2O in the presence of p-MeC$_6H_4$-SO$_3H$ (eq 12). The new complex **14** is formulated as a symmetrical (NMR evidence) p-toluenesulfonic acid adduct, for which we propose that the H$^+$ is forming a bifurcated hydrogen bond between two CO_2Me groups. Treatment of this species with ClC(=O)CO_2Me regenerates complex **11**. When the acid hydrolysis of **11** is carried out in MeOH, the formation, in low yield, of the ether derivative **15** was observed (eq 13). The coordinated methoxy group gives rise to a singlet at 3.55 ppm and to a resonance at 55.9 ($^1J_{CH}$ = 144 Hz) ppm in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. An acid adduct of this species has been observed with HBF$_4$, from which neutral **15** could be regenerated by treatment with NaOH (eq 14). In fact, a series of experiments have shown that the two complexes **15** and **15·HBF$_4$** are in fast equilibrium, with respect to the NMR time scale, in CDCl$_3$ solution at 25 °C.

(12)

(13)

(14)
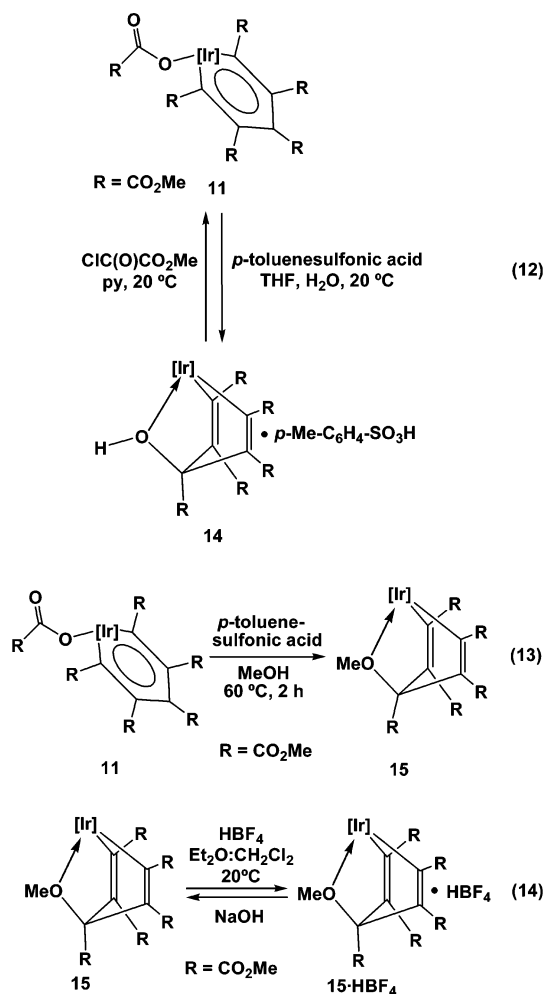
Hydrogenation Reactions. In an attempt to induce the rupture of one, or both, of the Ir−C bonds in **2**, its reaction with H_2 was studied. In fact, under the conditions depicted in eq 15 (C_6H_{12}, 60 °C, 3 atm), hydrogenolysis occurs, and the iridacyclohexadiene **16** is cleanly formed.


(15)
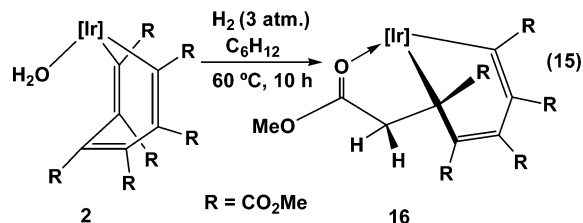
As can be observed, 1 mol of H_2 has been added to one of the C_α with concomitant ring contraction of the metallacycle. The water ligand is no longer present, and coordination of the ester group of the pending CH_2CO_2Me substituent completes the metal 18 e^- count. The different nature of this CO_2Me group is reflected in the $^{13}C\{^1H\}$ NMR spectrum, as the quaternary carbon resonates at δ 197.8, ca. 20−30 ppm downfield of the other CO_2Me substituents. The CH_2 group and the aliphatic carbon bonded to iridium appear at 53.5 and 17.0 ppm, respectively. A possible mechanism for this hydrogenation is shown in Scheme 6, where the hydride-alkene complex $J \rightleftharpoons J'$

Scheme 6
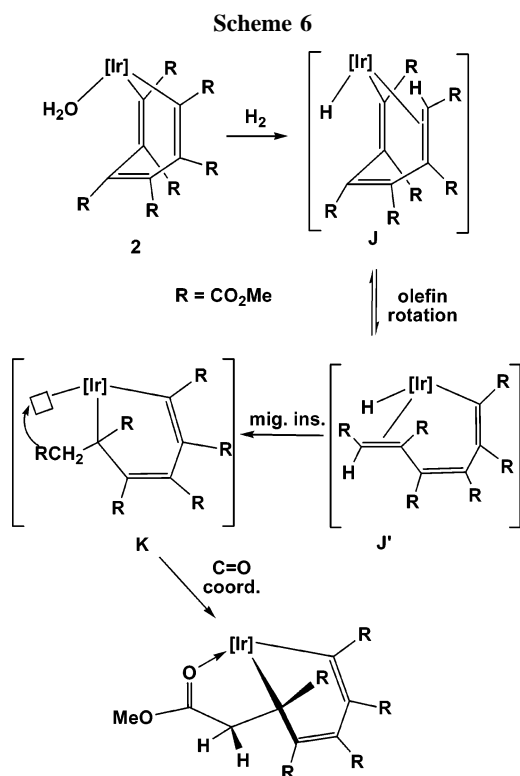
is proposed as an active intermediate. A migratory insertion of the olefin into the Ir−H bond, with subsequent coordination of the CH_2CO_2Me group, furnishes complex **16**. A similar reaction takes place with complex **5**, and the related benzoiridacyclohexadiene **17** is obtained (eq 16).

Finally, and in order to complete these studies, the hydrogenation of the iridacyclopentadiene **3** was also carried out. In this case two isomeric products, the hydrides **18** and **19**, are formed, in a 70:30 ratio, each of them being the result of the addition of 2 mol of H_2 to the starting material (eq 17). As can

(22) Terrier, F. *Chem. Rev.* **1982**, *82*, 77.

(16)
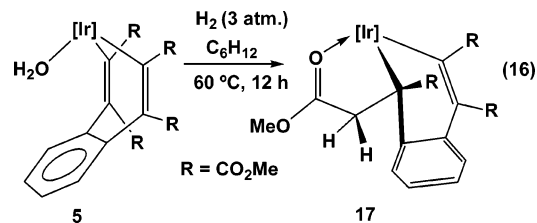
be observed, both complexes have a configurationally identical alkenylic chain (i.e., the hydrogenation is stereospecific), but they differ in which CO_2Me group, acting as 2 e^- donors, completes the metal coordination sphere. Complexes **18** and **19** can be separated by chromatography and have been completely characterized by microanalysis and IR and NMR (including NOESY experiments) spectroscopies. Scheme 7 shows the proposed mechanism for the formation of these compounds. The first step closely resembles that reported for the hydrogenation of the iridacycloheptatriene **2** with formation of the unsaturated intermediate **L** (akin to **K** of Scheme 6), but in this case, and probably as a consequence of the strained nature of this iridacyclobutene, the Ir−C_{alkyl} bond is cleaved by another molecule of H_2 to give **M**, which gives rise to each of the observed products by coordination of one of the two different CO_2Me groups more easily available. Interestingly, and as a series of control experiment showed, formation of complexes **18** and **19** is under kinetic control and no interconversion between them, once separated and pure, takes place when subjected to the reaction conditions depicted in eq 17. This finding is somewhat surprising and is probably due to the strength of the Ir←O≡C(OMe)− bonds and to the chelate effect.


(17)

Scheme 7
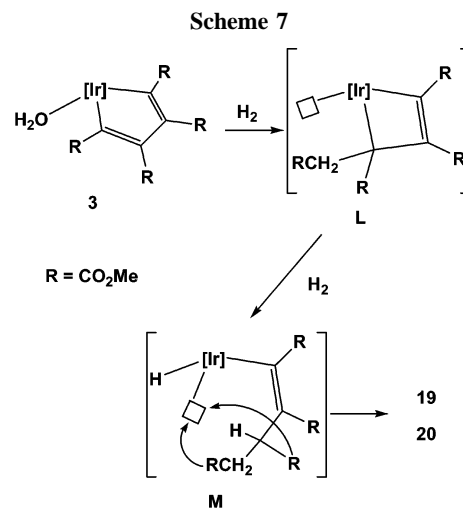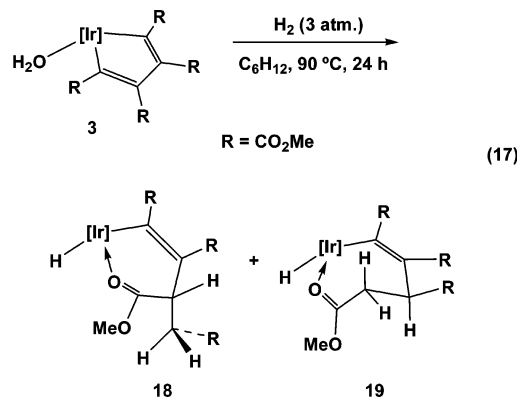
X-ray Diffraction Studies. Table 1 contains crystal data and data collection details for all compounds analyzed in this section.

Table 1. Crystal Data and Data Collection and Refinement Details for Complexes 2, 8, 11, 12, 13, and 18

	2	8	11	12	13	18
formula	$C_{33}H_{42}BIrN_6O_{13}\cdot$ $H_2O\cdot CHCl_3$	$C_{33}H_{38}BIrN_6O_9$	$C_{33}H_{40}BIrN_6O_{14}\cdot$ $0.25\ CH_2Cl_2$	$C_{33}H_{38}BIrN_6O_{10}\cdot$ CH_2Cl_2	$C_{30}H_{36}BIrN_6O_7$	$C_{27}H_{38}BIrN_6O_8$
mol wt	1071.12	865.70	968.95	966.63	795.66	777.64
color, habit	yellow, block	plate, red	red, block	red, block	colorless, prism	yellow, prism
symmetry,	monoclinic,	monoclinic,	triclinic,	monoclinic,	monoclinic,	monoclinic,
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a, Å	10.663(2)	7.9871(5)	11.2272(14)	10.8289(7)	10.439(3)	17.0603(7)
b, Å	23.173(4)	21.0604(14)	18.882(2)	31.296(2)	35.341(10)	9.7334(4)
c, Å	16.987(39)	21.0566(14)	19.527(3)	11.2884(7)	17.675(5)	18.5643(7)
α, deg	90	90	75.816(2)	90	90	90
β, deg	90.103(3)	95.072(1)	78.055(2)	103.605(1)	98.729(5)	94.062(1)
γ, deg	90	90	75.870(2)	90	90	90
V, Å^3	4197.5(13)	3528.1(4)	3844.0(8)	3718.3(4)	6445(3)	3074.9(2)
Z	4	4	4	4	8	4
D_{calcd}, g cm^{-3}	1.695	1.630	1.674	1.727	1.640	1.680
μ, mm^{-1}	3.443	3.846	3.582	3.800	4.198	4.399
θ range, deg	1.2−30.0	2.2−28.5	1.9−28.5	1.3−28.6	2.0−25.2	2.2−30.0
temp, K	123(2)	100(2)	100(2)	100(2)	297(2)	173(2)
no. of data collected	58 702	40 068	46 509	45 100	60 972	45 236
no. of unique data	12 102 (R_{int} = 0.031)	8455 (R_{int} = 0.062)	17 776 (R_{int} = 0.067)	8912 (R_{int} = 0.062)	11 187 (R_{int} = 0.054)	8924 (R_{int} = 0.020)
no. of params/ restraints	552/4	461/0	1021/23	500/0	835/4	398/0
R_1^a ($F^2 > 2\sigma(F^2)$)	0.0320	0.0351	0.0420	0.0446	0.0364	0.0195
wR_2^b (all data)	0.0706	0.0658	0.0731	0.0971	0.0746	0.0436

Complex 2. Figure 1 shows an ORTEP view of a molecule of **2**, while Table 2 collects selected bond lengths and angles.
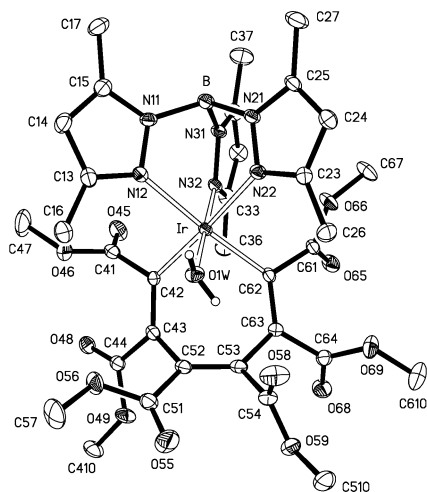

Figure 1. ORTEP view of complex **2** (50% ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 2

Ir−N(12)	2.127(3)	C(42)−C(43)	1.361(4)
Ir−N(22)	2.140(3)	C(43)−C(52)	1.481(4)
Ir−N(32)	2.038(3)	C(52)−C(53)	1.343(4)
Ir−C(42)	2.029(3)	C(53)−C(63)	1.470(4)
Ir−C(62)	2.047(3)	C(62)−C(63)	1.356(4)
Ir−O(1W)	2.113(2)		
C(42)−Ir−N(32)	90.7(1)	C(62)−Ir−N(12)	175.9(1)
C(42)−Ir−C(62)	90.4(1)	O(1W)−Ir−N(12)	87.5(1)
N(32)−Ir−C(62)	87.5(1)	C(42)−Ir−N(22)	175.7(1)
C(42)−Ir−O(1W)	92.4(1)	N(32)−Ir−N(22)	91.0(1)
N(32)−Ir−O(1W)	176.4(1)	C(62)−Ir−N(22)	93.7(1)
C(62)−Ir−O(1W)	94.5(1)	O(1W)−Ir−N(22)	85.8(1)
C(42)−Ir−N(12)	93.2(1)	N(12)−Ir−N(22)	82.9(1)
N(32)−Ir−N(12)	90.4(1)		

The iridacycle skeleton has a boat conformation with the γ,δ-C=C double bond pointing to the water ligand, and in fact this latter group is involved in a hydrogen bond with the carboxyl of one of the CO$_2$Me substituents of the mentioned double bond,

specifically the one at C(53). As expected the C−Ir−C bite angle of the metallacycloheptatriene (90.4°) is significantly wider than that observed[3e] in the iridacyclopentadiene **3** (79.3°), while the Ir−C bond lengths of these two compounds have rather similar values (2.04 Å av for the former vs 2.02 Å av for the latter). With respect to the three C=C double bonds present in the seven-membered ring, all have almost equivalent lengths (1.35 Å av). Finally, and as is the norm in this type of complex,[3e] the Ir−N(pyrazolyl) bond *trans* to the hard water ligand (2.04 Å) is shorter than the other two (2.13 Å av).

Complex 8. In Figure 2, the molecular structure of complex **8** is represented, while Table 3 collects selected bond lengths
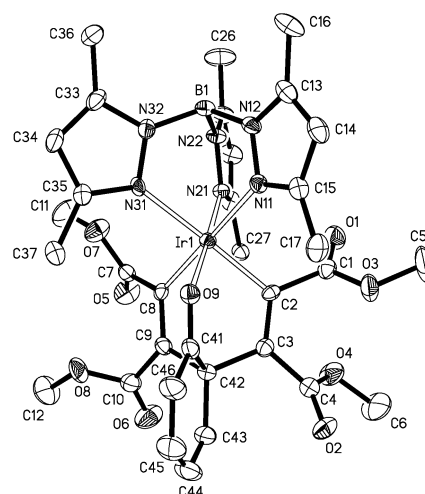
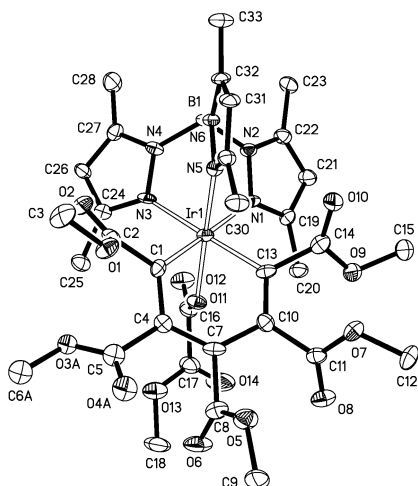**Figure 2.** ORTEP for **8** (40% ellipsoids).

and angles. The iridacycle present in **8** is six-membered and, as compared with compound **2**, the C−Ir−C bite angle is consequently somewhat reduced to 86.5°. That the original benzenoid ring has lost its aromaticity is clearly shown by the value of the C(41)−C(42) bond length of 1.54 Å, which is in the expected range for a typical C−C single bond.[8e] The keto group (C−O = 1.26 Å) bonded to iridium behaves as a hard ligand, as reflected in the Ir−N(pyrazolyl) bond distance *trans*

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex 8

Ir(1)−N(11)	2.144(3)	C(2)−C(3)	1.332(5)
Ir(1)−N(21)	2.045(3)	C(3)−C(42)	1.560(5)
Ir(1)−N(31)	2.152(3)	C(9)−C(42)	1.560(6)
Ir(1)−O(9)	2.052(3)	C(8)−C(9)	1.341(5)
Ir(1)−C(2)	2.018(4)	C(41)−O(9)	1.256(5)
Ir(1)−C(8)	2.020(4)	C(41)−C(42)	1.538(6)
C(2)−Ir(1)−C(8)	86.46(15)	N(21)−Ir(1)−N(11)	89.10(12)
C(2)−Ir(1)−N(21)	96.16(14)	O(9)−Ir(1)−N(11)	91.29(12)
C(8)−Ir(1)−N(21)	93.27(14)	C(2)−Ir(1)−N(31)	174.97(14)
C(2)−Ir(1)−O(9)	85.75(14)	C(8)−Ir(1)−N(31)	94.62(14)
C(8)−Ir(1)−O(9)	86.30(13)	N(21)−Ir(1)−N(31)	88.69(12)
N(21)−Ir(1)−O(9)	178.02(12)	O(9)−Ir(1)−N(31)	89.42(12)
C(2)−Ir(1)−N(11)	94.54(14)	N(11)−Ir(1)−N(31)	84.17(12)
C(8)−Ir(1)−N(11)	177.31(14)		

to it of 2.05 Å, which is significantly shorter than the other two (2.15 Å av).

Complex 11. Figure 3 shows an ORTEP view of this compound, and Table 4 collects selected bond lengths and angles. This species is very significant because it represents the

Figure 3. ORTEP for **11** (40% ellipsoids, only one of the two independent molecules is shown).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex 11 (dimensions for the first of two crystallographically independent molecules)

Ir(1)−N(1)	2.115(5)	Ir(1)−O(11)	2.047(4)
Ir(1)−N(3)	2.104(5)	C(1)−C(4)	1.401(8)
Ir(1)−N(5)	2.041(5)	C(4)−C(7)	1.393(8)
Ir(1)−C(1)	1.921(6)	C(7)−C(10)	1.441(8)
Ir(1)−C(13)	1.957(6)	C(10)−C(13)	1.359(7)
C(1)−Ir(1)−C(13)	89.3(2)	N(5)−Ir(1)−N(3)	89.9(2)
C(1)−Ir(1)−N(5)	91.9(2)	O(11)−Ir(1)−N(3)	93.5(2)
C(13)−Ir(1)−N(5)	92.8(2)	C(1)−Ir(1)−N(1)	177.7(2)
C(1)−Ir(1)−O(11)	84.7(2)	C(13)−Ir(1)−N(1)	92.5(2)
C(13)−Ir(1)−O(11)	84.1(2)	N(5)−Ir(1)−N(1)	89.5(2)
N(5)−Ir(1)−O(11)	175.4(2)	O(11)−Ir(1)−N(1)	94.0(2)
C(1)−Ir(1)−N(3)	95.7(2)	N(3)−Ir(1)−N(1)	82.4(2)
C(13)−Ir(1)−N(3)	174.2(2)		

first metallabenzene where all five substituents are of electron-withdrawing nature, specifically CO_2Me groups. The six-membered ring is not planar, as the iridium deviates ca. 0.75 Å from the mean plane of the five carbon atoms (rms nonplanarity 0.040 Å) (see below). On the other hand the Ir−C(1) and Ir−C(13) bond distances have similar values (1.92 and 1.96 Å, respectively) and reflect the expected intermediate bond order of ca. 1.5 between the metal and the carbon atoms.[8e,21k]

Complex 12. The structure of this complex, the first example of a metallanaphthalene of a transition metal, is shown in Figure 4, while selected bond lengths and angles are collected in Table 5. Interestingly the Ir−C(30) bond distance (1.98 Å), i.e., that
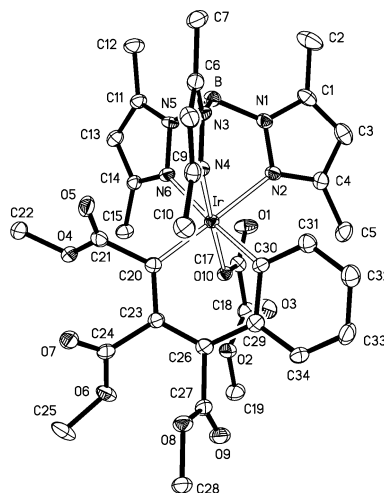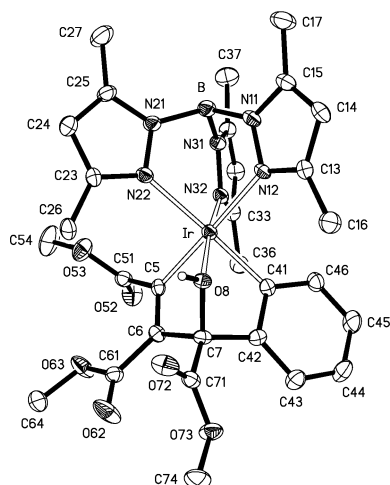

Figure 4. ORTEP for **12** (40% ellipsoids).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex 12

Ir−N(2)	2.131(5)	C(26)−C(29)	1.430(8)
Ir−N(4)	2.028(5)	C(29)−C(30)	1.445(8)
Ir−N(6)	2.147(5)	C(29)−C(34)	1.403(8)
Ir−O(10)	2.058(4)	C(30)−C(31)	1.401(8)
Ir−C(20)	1.930(6)	C(31)−C(32)	1.377(8)
Ir−C(30)	1.981(6)	C(32)−C(33)	1.404(9)
C(20)−C(23)	1.402(8)	C(33)−C(34)	1.351(9)
C(23)−C(26)	1.396(8)		
C(20)−Ir−C(30)	90.1(2)	N(4)−Ir−N(2)	87.0(2)
C(20)−Ir−N(4)	92.5(2)	O(10)−Ir−N(2)	93.3(2)
C(30)−Ir−N(4)	90.8(2)	C(20)−Ir−N(6)	94.5(2)
C(20)−Ir−O(10)	87.2(2)	C(30)−Ir−N(6)	175.2(2)
C(30)−Ir−O(10)	85.7(2)	N(4)−Ir−N(6)	90.5(2)
N(4)−Ir−O(10)	176.5(2)	O(10)−Ir−N(6)	93.1(2)
C(20)−Ir−N(2)	178.6(2)	N(2)−Ir−N(6)	84.3(2)
C(30)−Ir−N(2)	91.2(2)		

corresponding to the benzenoid ring, is longer than the Ir−C(20) of 1.93 Å. Again the iridium atom deviates significantly (0.77 Å) from the main plane formed by the C atoms of the six-membered ring (C(20), C(23), C(26), C(29), and C(30); rms nonplanarity 0.028 Å. A very recent theoretical DFT calculation study[23] points toward steric effects of the Tp^{Me2} ligand as well as the unsymmetrical ligand environment above and below the six-membered metal-containing ring to explain the nonplanarity observed for compounds **11** and **12**. Other aspects of the structure of **12** essentially show that, although the metallanaphthalene is distinctly bent, the relatively homogeneous C−C bond length spectrum is consistent with a metallanaphthalene.

Complex 13. An ORTEP view of this molecule is shown in Figure 5, and selected bond lengths and angles are collected in Table 6. In this species the two Ir−C(sp2) bonds have similar lengths,[3e,8e] 1.99 Å for the Ir(alkenyl) and 2.00 Å for the Ir-(phenyl) with the C−Ir−C bite angle being 87.3°. The Ir−O(8) bond distance amounts to 2.08 Å, somewhat shorter than the Ir−OH₂ bond length found in complex **2** (2.11 Å), and correspondingly the Ir−N(pyrazolyl) *trans* to the former (2.00 Å) is shorter than to the latter (2.04 Å).

(23) Zhu, J.; Jia, G.; Lin, Z. *Organometallics* **2007**, *26*, 1986.

Figure 5. ORTEP for **13** (30% ellipsoids, only one of the two independent complexes is shown).

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Complex 13 (dimensions for the first of two crystallographically independent molecules)

Ir−C(5)	1.988(5)	C(5)−C(6)	1.338(7)
Ir−C(41)	1.997(5)	C(6)−C(7)	1.529(7)
Ir−N(32)	2.001(4)	C(7)−C(42)	1.503(7)
Ir−O(8)	2.085(3)	C(41)−C(42)	1.409(7)
Ir−N(12)	2.121(4)	C(7)−O(8)	1.470(5)
Ir−N(22)	2.157(4)		
C(5)−Ir−C(41)	87.3(2)	N(32)−Ir−N(12)	86.1(2)
C(5)−Ir−N(32)	99.0(2)	O(8)−Ir−N(12)	95.5(1)
C(41)−Ir−N(32)	97.1(2)	C(5)−Ir−N(22)	92.8(2)
C(5)−Ir−O(8)	79.8(2)	C(41)−Ir−N(22)	172.7(2)
C(41)−Ir−O(8)	76.7(2)	N(32)−Ir−N(22)	90.0(2)
N(32)−Ir−O(8)	173.8(2)	O(8)−Ir−N(22)	96.1(1)
C(5)−Ir−N(12)	174.3(2)	N(12)−Ir−N(22)	84.5(2)
C(41)−Ir−N(12)	94.7(2)		

Complex 18. The molecular structure of this compound is shown in Figure 6, while selected bond lengths and angles are collected in Table 7. This X-ray structure confirms the stere-
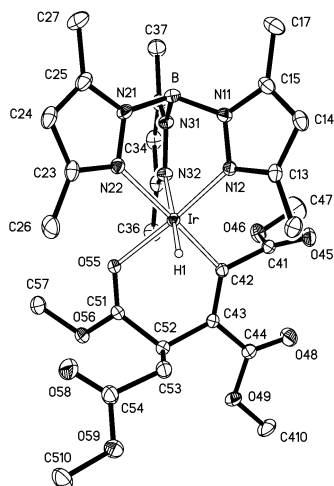
Figure 6. ORTEP for **18** (30% ellipsoids).

ochemistry at C(52) that was deduced from NOESY experiments. A CO_2Me group is bonded to the iridium through the carboxyl, and the Ir−O(55) bond distance of 2.07 Å is almost equal to that found for the Ir−O(R)H group in complex **13**. Finally, in this complex the three Ir−N(pyrazolyl) bond lengths are notably dissimilar depending on the nature of the group *trans* to them: shorter (2.02 Å) for the ester, intermediate (2.10 Å) for the alkenyl, and longer (2.18 Å) for the hydride.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for Complex 18

Ir−N(12)	2.021(2)	Ir−C(42)	2.008(2)
Ir−N(22)	2.100(2)	C(42)−C(43)	1.363(3)
Ir−N(32)	2.182(2)	C(43)−C(52)	1.525(3)
Ir−H(1)	1.49(3)	C(51)−C(52)	1.506(3)
Ir−O(55)	2.074(1)	C(51)−O(55)	1.230(2)
C(42)−Ir−N(12)	97.4(1)	O(55)−Ir−N(32)	87.6(1)
C(42)−Ir−O(55)	86.6(1)	C(42)−Ir−H(1)	86.6(10)
N(12)−Ir−O(55)	175.9(1)	N(12)−Ir−H(1)	89.3(10)
C(42)−Ir−N(22)	177.8(1)	O(55)−Ir−H(1)	91.7(10)
N(12)−Ir−N(22)	84.7(1)	N(22)−Ir−N(32)	85.6(1)
O(55)−Ir−N(22)	91.2(1)	N(22)−Ir−H(1)	93.6(10)
C(42)−Ir−N(32)	94.2(1)	N(32)−Ir−H(1)	178.9(10)
N(12)−Ir−N(32)	91.2(1)		

Conclusions

An iridacycloheptatriene complex has been synthesized by the oxidative coupling of three molecules of $MeO_2CC≡CCO_2$-Me (DMAD), while related, symmetrical and unsymmetrical, benzoannelated derivatives are the result of the corresponding formal coupling of two DMAD with "benzyne". Oxidation of these species with ^tBuOOH allows the formation of unusual metalloaromatics, specifically an iridabenzene and an iridanaphthalene, with five and three electron-withdrawing CO_2Me groups, respectively. The formation of neutral internal Jackson−Meisenheimer complexes is in accord with the aromaticity of these six-membered iridacycles.

Experimental Section

General Procedures. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained from a Bruker Vector 22 spectrometer. The NMR instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 0 ppm) using the residual protio solvent peaks as internal standards (^1H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free dinitrogen, following conventional Schlenk techniques. The complexes $Tp^{Me2}Ir(\eta^4-CH_2=C(Me)C(Me)=CH_2)$ **(1)**,[8a] $Tp^{Me2}IrPh_2(N_2)$ **(4)**,[11] and $Tp^{Me2}Ir(C(R)=C(R)C(R)=C(R))(H_2O)$ **(3)** (R = CO_2Me)[3e] were obtained by published procedures.

Complex 2. To a solution of $Tp^{Me2}Ir(\eta^4-CH_2=C(Me)C(Me)=CH_2)$ **(1)** in cyclohexane (1 g, 1.75 mmol; 15 mL) was added $MeO_2CC≡CCO_2Me$ (0.64 mL, 5.24 mmol) and the mixture stirred at 60 °C for 12 h. After removing the solvent under reduced pressure, quantitative conversion into the new product **2** was ascertained by ^1H NMR spectroscopy. Yellow crystals of **2** were obtained in 77% yield by crystallization from hexane−CH_2Cl_2 (1:2) at −20 °C. ^1H NMR (CDCl$_3$, 25 °C): δ 5.75, 5.61 (s, 2:1, 3 CH$_{pz}$), 4.73 (s, 2 H, OH$_2$), 3.77, 3.64, 3.07 (s, 6 H each, 6 CO_2Me), 2.36, 2.34, 2.14, 2.05 (s, 1:2:2:1, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C): δ 175.8, 171.9, 165.8 (CO_2Me), 156.1, 135.9, 134.9 (CCO$_2$Me), 155.9, 151.9, 144.4, 143.7 (1:2:1:2, C$_{qpz}$), 107.1 (CH$_{pz}$), 53.4, 52.0, 51.0 (CO$_2$*Me*), 17.7, 13.7, 13.5, 12.7 (1:2:2:1, Me$_{pz}$). IR (Nujol): ν-(OH) 3396 cm^{-1}. Anal. Calcd for $C_{33}H_{42}BN_6O_{13}Ir·CH_2Cl_2$: C, 40.1; H, 4.3; N, 8.3. Found: C, 40.3; H, 4.3; N, 8.2.

Complex 2·CO. Compound **2** was suspended in cyclohexane (0.05 g, 0.053 mmol; 4 mL) and transferred into a Fischer−Porter vessel, which was pressurized with CO (2 atm). After stirring at 90 °C for 12 h, a pale brown precipitate was observed and the solvent was removed under reduced pressure. Quantitative conversion into **2·CO** was ascertained by ^1H NMR spectroscopy, and the

crude product was crystallized from a mixture of pentane−CH$_2$Cl$_2$ (1:1) at −20 °C (pale yellow crystals). ^{1}H NMR (CDCl$_3$, 25 °C): δ 5.80, 5.75 (s, 2:1, 3 CH$_{pz}$), 3.78, 3.66, 3.09 (s, 6 H each, 6 CO$_2$-Me), 2.34, 2.33, 2.26, 2.16 (s, 1:2:2:1, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 172.3, 167.6, 166.1 (*C*O$_2$Me), 163.3 (CO), 154.9, 152.8, 144.4, 144.3 (1:2:1:2, C$_{qpz}$), 144.9, 138.5, 138.5 (*C*CO$_2$Me), 107.7, 107.2 (1:2, CH$_{pz}$), 52.8, 52.4, 51.4 (CO$_2$*Me*), 17.4, 14.9, 13.6, 12.8 (1:2:1:2, Me$_{pz}$). IR (Nujol): ν(CO) 2066 cm^{-1}. Anal. Calcd for C$_{34}$H$_{40}$BN$_6$O$_{13}$Ir·0.5CH$_2$Cl$_2$: C, 42.0; H, 4.2; N, 8.5. Found: C, 42.3; H, 4.2; N, 8.6.

Complex 2·NCMe. A solution of compound **2** in NCMe (0.02 g, 0.021 mmol; 2 mL) was stirred at room temperature for 12 h. After this period of time, the volatiles were removed in vacuum and quantitative conversion into **2·NCMe** was ascertained by ^{1}H NMR spectroscopy. Upon crystallization from hexane−CH$_2$Cl$_2$ at −20 °C, an analytically pure sample was obtained (yellow crystals). ^{1}H NMR (CDCl$_3$, 25 °C): δ 5.73, 5.65 (s, 2:1, 3 CH$_{pz}$), 3.75, 3.63, 3.06 (s, 6 H each, 6 CO$_2$Me), 2.47 (s, 3 H, MeCN), 2.34, 2.33, 2.20, 2.11 (s, 1:2:2:1, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 175.1, 169.8, 166.8 (*C*O$_2$Me), 155.4, 151.6, 143.7,143.4 (1:2:1:2, C$_{qpz}$), 151.7, 136.3, 135.8 (*C*CO$_2$Me), 121.9 (N*C*Me), 107.1, 106.8 (2:1, CH$_{pz}$), 52.6, 52.0, 51.0 (CO$_2$*Me*), 17.6, 14.4, 13.5, 12.8 (1:2:1:2, Me$_{pz}$), 5.1 (NC*Me*). IR (Nujol): ν(CN) 2246 cm^{-1}. Anal. Calcd for C$_{35}$H$_{43}$BN$_7$O$_{12}$Ir: C, 43.9; H, 4.5; N, 10.2. Found: C, 43.7; H, 4.8; N, 9.8.

Complexes 5 and 6. To a solution of Tp^{Me2}IrPh$_2$(N$_2$) (**4**) in C$_6$H$_{12}$ (0.30 g, 0.45 mmol; 7 mL) was added MeO$_2$CC≡CCO$_2$Me (0.164 mL, 1.34 mmol) and the mixture stirred at 60 °C for 12 h. After this period, a brown precipitate was formed and the volatiles were removed in vacuum to give a crude solid consisting of a ca. 2:1 mixture of **5** and **6** (^{1}H NMR). Separation of the two compounds was accomplished by column chromatography on silica gel, using a 1:5 mixture of petroleum ether−Et$_2$O as eluent: 0.09 g (pale yellow crystals) of **5** (23%) and 0.16 g (yellow crystals) of **6** (42%) were obtained.
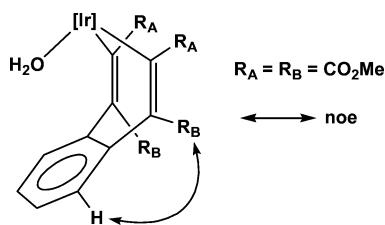
5: R_f = 0.12 [silica gel, petroleum ether−Et$_2$O (1:5)]. ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.20 (s, 4 H, 4 CH$_{ar}$), 5.69, 5.56 (s, 2:1, 3 CH$_{pz}$), 3.55 (s, 6 H, 2 CO$_2$Me (R$_B$)), 3.01 (s, 6 H, 2 CO$_2$Me (R$_A$)), 2.34, 2.32, 2.03, (s, 1:2:3, 6 Me$_{pz}$). The H$_2$O resonance has not been located. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 176.0, 170.0 (*C*O$_2$Me of R$_A$ and R$_B$, respectively), 153.8, 151.3, 144.0, 142.7 (1:2:1:2, C$_{qpz}$), 142.9, 141.2 (*C*R$_A$ and *C*R$_B$, respectively), 136.1 (C$_{qar}$), 131.0, 127.2 (CH$_{ar}$), 106.7, 106.4 (1:2, CH$_{pz}$), 51.8, 50.6 (CO$_2$*Me* of R$_B$ and R$_A$, respectively), 16.6, 13.4, 12.8, 12.4 (1:1:2:2, Me$_{pz}$). IR (Nujol): ν(OH) 3520 cm^{-1}. Anal. Calcd for C$_{33}$H$_{40}$BN$_6$O$_9$Ir·Et$_2$O: C, 47.1; H, 5.3; N, 8.9. Found: C, 46.9; H, 5.4; N, 9.1. **6**: R_f = 0.26 [silica gel, petroleum ether−Et$_2$O (1:5)]. ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.39, 6.84, 6.59, 6.09 (d, t, t, d, 1 H each, $^3J_{HH}$ ≈ 8 Hz, 4 CH$_{ar}$), 5.83, 5.71, 5.59 (s, 1 H each, 3 CH$_{pz}$), 4.58 (s, 2 H, OH$_2$), 3.90, 3.70, 3.59, 3.04 (s, 3 H each, 4 CO$_2$Me), 2.42, 2.41, 2.39, 2.27, 1.44, 1.26 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 177.4, 175.9, 169.4, 164.2 (*C*O$_2$Me), 161.6, 142.5, 131.2, 130.8 (*C*CO$_2$Me), 154.5, 152.1, 150.1, 144.2, 143.7, 143.2 (C$_{qpz}$), 143.2, 126.5, 125.3, 122.5 (CH$_{ar}$), 139.5, 138.4 (C$_{qar}$), 107.5, 107.3, 106.8 (CH$_{pz}$), 53.4, 52.2, 51.3, 50.4 (CO$_2$*Me*), 17.1, 13.4, 13.1, 12.8, 12.4 (1:1:1:1:2, Me$_{pz}$). Anal. Calcd for C$_{33}$H$_{40}$BN$_6$O$_9$Ir·Et$_2$O: C, 47.1; H, 5.3; N, 8.9. Found: C, 46.9; H, 5.3; N, 9.1.

Complex 5·PMe$_3$. Compound **5** was suspended in cyclohexane (0.075 g, 0.086 mmol; 6 mL), and PMe$_3$ was added (0.43 mL, 1 M

solution in THF). The mixture was stirred at 60 °C for 4 h, when a pale yellow suspension was obtained and the volatiles were removed under reduced pressure. Quantitative conversion into **5·PMe$_3$** was ascertained by ^{1}H NMR (pale yellow solid).
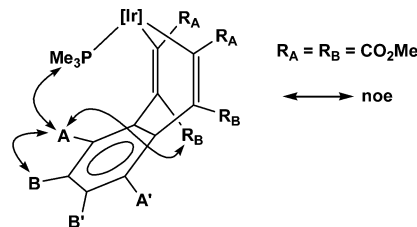
^{1}H NMR (CDCl$_3$, 25 °C): δ 7.42, 7.20 (m, 2 H each, AA′BB′ spin system, A and B, respectively), 5.74, 5.60 (s, 2:1, 3 CH$_{pz}$), 3.61 (s, 6 H, 2 CO$_2$Me (R$_B$)), 3.02 (s, 6 H, 2 CO$_2$Me (R$_A$)), 2.37, 2.29, 2.17, 2.11 (s, 2:1:2:1, 6 Me$_{pz}$), 0.99, 0.45 (br s, 2:1 ratio (due to restricted rotation of the ligand around the Ir−P bond), 9 H, PMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 174.8, 172.0 (*C*O$_2$Me of R$_A$ and R$_B$, respectively), 152.9, 152.3, 143.5, 143.0 (1:2:2:1, C$_{qpz}$), 145.5 (C$_{qar}$), 136.7, 134.4 (s, d, $^2J_{CP}$ = 7 Hz, *C*R$_B$ and *C*R$_A$, respectively), 132.0, 126.8 (CH$_A$ and CH$_B$, respectively), 107.6, 106.8 (s, d, 2:1, $^4J_{CP}$ = 3 Hz, CH$_{pz}$), 51.9, 50.8 (CO$_2$*Me* de R$_B$ and R$_A$, respectively), 19.8, 18.3 (br s, 2:1 ratio (due to restricted rotation of the ligand around the Ir−P bond), $^1J_{CP}$ = 36 Hz, PMe$_3$), 17.8, 16.4, 13.2, 13.1 (2:1:1:2, Me$_{pz}$). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ −62.9. Anal. Calcd for C$_{36}$H$_{47}$BN$_6$O$_8$PIr: C, 46.7; H, 5.1; N, 9.1. Found: C, 46.6; H, 5.1; N, 9.1.
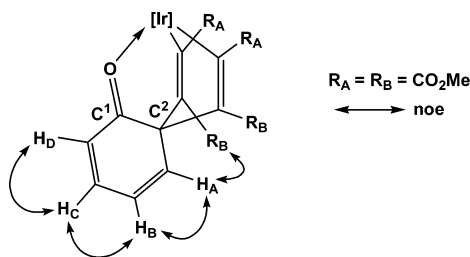
Complex 6·PMe$_3$. Compound **6** was suspended in cylohexane (0.070 g, 0.081 mmol; 7 mL), and PMe$_3$ was added (0.4 mL, 1 M solution in THF). The mixture was heated at 60 °C for 12 h, and after this period of time the solvent was removed under reduced pressure. Quantitative conversion into **6·PMe$_3$** was ascertained by ^{1}H NMR, and an analytically pure sample was obtained by crystallization from a mixture of hexane−CH$_2$Cl$_2$ at −20 °C (yellow crystals). ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.31, 6.79, 6.54, 6.45 (d, t, t, d, 1 H each, $^3J_{HH}$ ≈ 7 Hz, 4 CH$_{ar}$), 5.85, 5.75, 5.53 (s, 1 H each, 3 CH$_{pz}$), 3.90, 3.73, 3.56, 2.92 (s, 3 H each, 4 CO$_2$Me), 2.43, 2.41, 2.30, 2.29, 1.68, 1.08 (s, 3 H each, 6 Me$_{pz}$), 1.61 (br (due to restricted rotation of the ligand around the Ir−P bond), 9 H, PMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 175.1, 172.1, 168.4, 168.3 (*C*O$_2$-Me), 153.0, 152.4, 150.6, 144.2, 143.5, 143.3 (s, d, s, s, s, s, J_{CP} = 4 Hz, C$_{qpz}$), 148.0, 142.7, 136.8, 128.4 (s, d, s, s, J_{CP} = 7 Hz, *C*CO$_2$-Me), 145.9, 127.9, 126.2, 122.2 (CH$_{ar}$), 140.2, 136.8 (s, d, J_{CP} = 13 Hz, C$_{qar}$), 108.4, 107.6, 107.4 (s, s, d, J_{CP} = 3 Hz, CH$_{pz}$), 52.4, 52.2, 51.6, 50.6 (CO$_2$*Me*), 18.9 (br (due to restricted rotation of the ligand around the Ir−P bond), PMe$_3$), 18.2, 18.2, 15.4, 13.2, 13.1 (1:1:1:2:1, Me$_{pz}$). ^{31}P{^{1}H} NMR (CDCl$_3$, 25 °C): δ −58.1. Anal. Calcd for C$_{36}$H$_{47}$BN$_6$O$_8$PIr: C, 46.7; H, 5.1; N, 9.1. Found: C, 46.2; H, 4.7; N, 8.9.

Complex 7. To a solution of compound **2** in CH$_2$Cl$_2$ (0.1 g, 0.107 mmol; 6 mL) was added ^{t}BuOOH (0.051 mL, 0.535 mmol) and the mixture stirred at room temperature for 3 h. After this period of time the solvent was removed under reduced pressure; several portions of Et$_2$O were added to the residue and subsequently evaporated, to force the elimination of the excess of peroxide. Quantitative conversion into compound **7** was ascertained by ^{1}H NMR, and it was crystallized from hexane−CH$_2$Cl$_2$ (1:1) at −20 °C as a red microcrystalline solid in 75% yield.
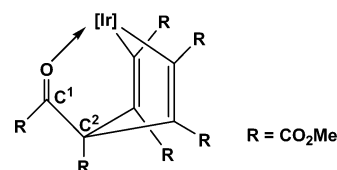
^{1}H NMR (CDCl$_3$, 25 °C): δ 5.82, 5.66 (s, 1:2, 3 CH$_{pz}$), 4.02, 3.75, 3.64, 3.23 (s, 1:1:2:2, 6 CO$_2$Me), 2.45, 2.31, 2.02, 1.65 (s, 1:2:1:2, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 209.3 (C^1), 172.3, 168.6, 165.6, 163.3 (2:1:2:1, CO$_2$Me), 159.3, 128.2 (CCO$_2$-Me), 156.6, 151.9, 144.1, 144.0 (1:2:2:1, C$_{qpz}$), 107.1, 106.9 (2:1, CH$_{pz}$), 73.3 (C^2), 53.9, 52.8, 52.4, 51.2 (1:1:2:2, CO$_2$$Me$), 17.8, 13.6, 13.2, 12.7 (1:1:2:2, Me$_{pz}$). Anal. Calcd for C$_{33}$H$_{40}$BN$_6$O$_{13}$Ir: C, 42.5; H, 4.3; N, 9.0. Found: C, 42.6; H, 4.4; N, 8.8.

Complex 8. (a) To a solution of compound **5** (0.01 g, 0.012 mmol) in CDCl$_3$ (0.4 mL) was added ^{t}BuOOH (0.007 mL, 0.070 mmol), and the color of the solution changed from yellow to black immediately. Quantitative conversion into **8** was ascertained by ^{1}H NMR. (b) A solution of complex **5** (0.020 g, 0.022 mmol) in CH$_2$Cl$_2$ (5 mL) was placed in a Fischer–Porter vessel, and the stirred mixture was heated under 1 atm of O$_2$ at 60 °C for 2 days. The volatiles were evaporated under vacuum, and quantitative conversion into **8** was ascertained by ^{1}H NMR. (c) A stirred suspension of complex **5** (0.010 g, 0.012 mmol) and H$_2$O$_2$ (30%, 0.15 mL) in cyclohexane (3 mL) was heated at 60 °C for 3 days. After this time, the solvent was distilled off under reduced pressure and a ^{1}H NMR spectrum showed formation of **8** in 90% yield. Complex **8** could be purified by column chromatography on silica gel, using a 40:75 mixture of petroleum ether–Et$_2$O as eluent and subsequent crystallization from hexane–CH$_2$Cl$_2$ at −20 °C (black crystals).

R_f = 0.1 [silica gel, petroleum ether–Et$_2$O (40:75)]. ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.43, 7.10, 6.51, 6.43 (d, dd, dd, d, 1 H each, $^3J_{HH} \approx$ 9 and 6 Hz, H$_A$, H$_C$, H$_B$, H$_D$, respectively), 5.69 (s, 3 H, 3 CH$_{pz}$), 3.63 (s, 6 H, 2 CO$_2$Me (R$_B$)), 3.17 (s, 6 H, 2 CO$_2$Me (R$_A$)), 2.43, 2.36, 1.78, 1.66 (s, 1:2:1:2, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 208.1 (C^1), 171.6, 167.6 (CO$_2$Me of R$_A$ and R$_B$, respectively), 153.7, 151.2, 143.3, 142.9 (1:2:1:2, C$_{qpz}$), 152.6, 129.0 (CR$_A$ and CR$_B$, respectively), 146.9, 146.5 (CH$_C$ and CH$_A$, respectively, $^1J_{CH}$ = 162 and 170 Hz), 120.9, 120.4 (CH$_D$ and CH$_B$, respectively, $^1J_{CH}$ = 170 and 167 Hz), 106.5, 106.2 (2:1, CH$_{pz}$), 65.9 (C^2), 52.0, 50.9 (CO$_2$$Me$ of R$_B$ and R$_A$, respectively), 15.8, 13.2, 12.6, 12.4 (1:1:2:2, Me$_{pz}$). Anal. Calcd for C$_{33}$H$_{38}$BN$_6$O$_9$Ir: C, 45.7; H, 4.4; N, 9.7. Found: C, 45.1; H, 4.1; N, 9.6.

Complex 9. (a) To a suspension of complex **6** (0.020 g, 0.023 mmol) in CDCl$_3$ (0.5 mL) was added ^{t}BuOOH (0.04 mL, 0.47 mmol). The resulting mixture was kept at room temperature, and ^{1}H NMR monitoring revealed quantitative formation of complex **9** after 4.5 h. (b) A suspension of complex **6** (0.020 g, 0.023 mmol) in cyclohexane (10 mL) was transferred into a Fischer–Porter vessel, which was pressurized with O$_2$ (3 atm). After 12 h at 60 °C, the volatiles were removed in vacuum and the mixture formed was purified by column chromatography (silica gel) to give compound **9** in 40% yield (red crystals).
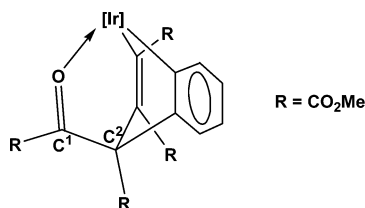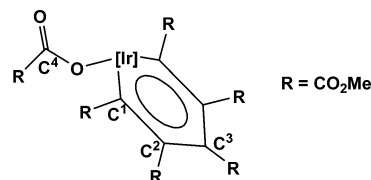

R_f = 0.22 [silica gel, petroleum ether–Et$_2$O (40:75)]. ^{1}H NMR (CDCl$_3$, 25 °C): δ 6.97, 6.88, 6.70, 6.66 (d, t, t, d, 1 H each, $^3J_{HH}$

$\approx$ 8 Hz, 4 CH$_{ar}$), 5.78, 5.73, 5.63 (s, 1 H each, 3 CH$_{pz}$), 3.95, 3.94, 3.67, 3.27 (s, 3 H each, 4 CO$_2$Me), 2.49, 2.38, 2.37, 1.73, 1.50, 0.87 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 209.4 (C^1), 173.7, 170.8, 165.4, 163.2 (CO$_2$Me), 162.7, 125.9 (CCO$_2$-Me), 154.1, 151.8, 150.8, 144.0, 143.4, 143.2 (C$_{qpz}$), 142.1, 130.0 (C$_{qar}$), 139.1, 126.2, 124.9, 123.3 (CH$_{ar}$), 107.2, 107.0, 106.7 (CH$_{pz}$), 76.3 (C^2), 53.3, 52.4, 51.9, 50.7 (CO$_2$$Me$), 17.4, 13.3, 13.0, 12.4, 12.4, 11.7 (Me$_{pz}$). Anal. Calcd for C$_{33}$H$_{38}$BN$_6$O$_9$Ir: C, 45.7; H, 4.4; N, 9.7. Found: C, 45.1; H, 4.3; N, 9.7.

Compound 10. To a solution of complex **5·PMe$_3$** in cyclohexane (0.08 g, 0.086 mmol; 6 mL) was added H$_2$O$_2$ (30%, 0.3 mL), and the resulting mixture was heated at 150 °C for 3 days. After this time, the solvent was evaporated under reduced pressure and the title compound was purified by chromatography on silica gel using Et$_2$O–hexane (3:1) as eluent and finally by crystallization from hexane–CH$_2$Cl$_2$ (colorless crystals, 39% yield). The NMR data obtained for **10** matched those found in the literature.[20]

Complex 11. This compound was prepared from the bicyclic ketone **7**, by addition of ^{t}BuOOH (5 equiv) to its CH$_2$Cl$_2$ solutions and stirring at room temperature for 10 h. Nevertheless, it is more practical to perform this synthesis starting from the precursor **2**, without isolation of the intermediate species **7**: (a) To a solution of **2** in CH$_2$Cl$_2$ (0.2 g, 0.21 mmol; 10 mL) was added ^{t}BuOOH (0.15 mL, 1.1 mmol), and the mixture was stirred at room temperature for 12 h. The dark red solution was pumped off to dryness, and the residue was treated with several portions of Et$_2$O, which were subsequently evaporated, in order to force the elimination of the peroxide. Quantitative conversion into compound **11** was ascertained by ^{1}H NMR. Red crystals of analytical purity were obtained by cooling its solutions in hexane–CH$_2$Cl$_2$ (1:1) at −20 °C. Yield: 81%. (b) Compound **2** was dissolved in CH$_2$Cl$_2$ (0.05 g, 0.053 mmol; 4 mL) in a Fischer–Porter vessel, which was pressurized with O$_2$ (1 atm). After stirring at 60 °C for 24 h the solvent was removed under reduced pressure and the ^{1}H NMR spectrum of the crude of the reaction showed formation of **11** in 80% yield.

^{1}H NMR (CDCl$_3$, 25 °C): δ 5.80, 5.60 (s, 2:1, 3 CH$_{pz}$), 3.89, 3.76, 3.69, 3.24 (s, 1:2:1:2, 6 CO$_2$Me), 2.57, 2.48, 1.87, 1.19 (s, 1:2:2:1, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 229.3 (C^1), 177.2, 168.9, 165.2, 160.0 (2:1:2:1, CO$_2$Me), 163.2, 162.6 (C^3, C^4), 154.8, 151.6, 145.2, 144.8 (2:1:2:1, C$_{qpz}$), 143.0 (C^2), 107.9, 105.7 (2:1, CH$_{pz}$), 53.2, 53.1, 52.1 (2:1:3, CO$_2$$Me$), 14.4, 13.5, 12.9 (2:1:3, Me$_{pz}$). Anal. Calcd for C$_{33}$H$_{40}$BN$_6$O$_{14}$Ir: C, 41.8; H, 4.2; N, 8.9. Found: C, 41.6; H, 4.2; N, 8.7.

Complex 12. To a solution of compound **9** in CH$_2$Cl$_2$ (0.1 g, 0.11 mmol; 6 mL) was added ^{t}BuOOH (0.3 mL, 2.2 mmol) and the mixture stirred at room temperature for 30 h. After this period of time, the solvent was removed under reduced pressure; several portions of Et$_2$O were added to the residue and subsequently evaporated, to force the elimination of the excess peroxide, and quantitative conversion into compound **12** was ascertained by ^{1}H NMR. The residue was crystallized by the slow diffusion of hexane into a dichloromethane solution at −20 °C (red crystals).
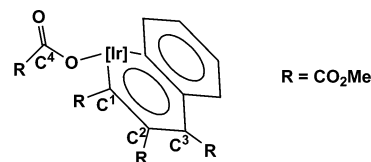
¹H NMR (CDCl₃, 25 °C): δ 8.12, 7.12, 7.03, 6.60 (d, t, t, d, 1 H each, $^3J_{HH} \approx 8$ Hz, 4 CH$_{ar}$), 5.80, 5.77, 5.60 (s, 1 H each, 3 CH$_{pz}$), 4.05, 3.79, 3.64, 3.29 (s, 3 H each, 3 CO₂Me), 2.56, 2.52, 2.49, 1.84, 1.26, 0.79 (s, 3 H each, 6 Me$_{pz}$). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 255.0 (C¹), 181.1, 170.4, 163.2, 160.1 (*C*O₂Me), 177.9 (IrC$_{qar}$), 137.0 (C$_{qar}$), 163.8, 163.7 (C³, C⁴), 153.4, 153.2, 151.0, 144.7, 144.0 (1:1:1:2:1, C$_{qpz}$), 141.8 (C²), 142.1, 135.3, 128.6, 126.3 (CH$_{ar}$), 108.3, 106.8, 106.2 (CH$_{pz}$), 52.8, 52.7, 51.7, 51.5 (CO₂*Me*), 13.9, 13.5, 13.3, 12.9, 12.7, 12.6 (Me$_{pz}$). Anal. Calcd for C₃₈H₃₈-BN₆O₁₀Ir·CH₂Cl₂: C, 42.2; H, 4.1; N, 8.7. Found: C, 42.3; H, 3.9; N, 8.9.

Complex 13. When compound **12** was passed through a column of silica gel, using a mixture of hexane−Et₂O (1:2) as eluent, an orange band was collected, which contained compound **13**. After evaporation of the solvent, the orange residue was crystallized by slow diffusion of hexane into a dichloromethane solution at room temperature in 42% yield (orange crystals). R_f = 0.38 [silica gel, hexane−Et₂O (10:1)]. ¹H NMR (CDCl₃, 25 °C): δ 8.10, 6.98, 6.94, 6.83 (d, t, d, t, 1 H each, $^3J_{HH} \approx 7$ Hz, 4 CH$_{ar}$), 5.82, 5.72, 5.60 (s, 1 H each, 3 CH$_{pz}$), 4.02, 3.64, 3.39 (s, 3 H each, 3 CO₂Me), 2.42, 2.40, 2.35, 2.32, 1.62, 1.13 (s, 3 H each, 6 Me$_{pz}$). The OH resonance was not located. ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 176.1, 172.8, 171.1 (*C*O₂Me), 161.4, 135.8 (*C*$_{olef}$CO₂Me), 152.6, 151.4, 151.1 (C$_{qpz}$), 143.9, 143.6, 143.5, 143.2 (C$_{qpz}$, C$_{qar}$), 138.2 (C$_{qar}$) 137.7, 124.7, 122.1, 121.9 (CH$_{ar}$), 107.1, 106.7 (2:1, CH$_{pz}$), 98.4 (COH), 53.4, 51.8, 50.9 (CO₂*Me*), 17.2, 14.4, 13.2, 12.5, 12.4, 12.3 (Me$_{pz}$). IR (Nujol): ν(OH) 3380 cm⁻¹.

Formation of 12 from 13. To a solution of compound **13** (0.02 g, 0.04 mmol) in pyridine (6 mL) was added an excess of ClC-(O)CO₂Me in pyridine. The resulting mixture was stirred for 18 h at room temperature, and after this period the solvent was evaporated under vacuum. The solid residue was treated with a mixture of CH₂Cl₂−H₂O, and the organic phase was separated, dried with MgSO₄, and filtered. After removal of the solvent under reduced pressure, the ¹H NMR spectrum of the residue revealed the presence of compound **12** in almost pure form.

Complex 14. To a solution of compound **11** in THF (0.1 g, 0.106 mmol; 3 mL) were added a few crystals of *p*-toluenesulfonic acid and some water (∼10 drops). The red resultant mixture was stirred at room temperature, and after 2.5 h the solution turned yellow. The solvent was evaporated under reduced pressure, the residue was dissolved in CH₂Cl₂, dried with Na₂SO₄, and centrifuged, and the solvent was evaporated. The ¹H NMR spectrum of the residue showed the presence of a mixture in which complex **14** was present. This complex was isolated by column chromatography on silica gel using a mixture of Et₂O−AcOEt (10:1) → AcOEt as eluent (yield: 10%, yellow solid). ¹H NMR (CD₃OD, 25 °C): δ 5.65 (s, 3 H, 3 CH$_{pz}$), 3.68, 3.65, 3.29 (s, 2:1:2, 5 CO₂Me), 2.38, 2.35, 2.27, 1.57 (s, 1:2:2:1, 6 Me$_{pz}$). The OH signal has not been located, and the resonances corresponding to the *para*-toluenesulfonic acid are not reported. ¹³C{¹H} NMR (CD₃OD, 25 °C): δ 179.1, 174.6, 169.5 (2:1:2, *C*O₂Me), 161.3, 149.7 (*C*CO₂Me), 154.2, 151.8, 143.7, 142.9 (2:1:1:2, C$_{qpz}$), 107.2, 106.0 (2:1, CH$_{pz}$), 99.6 (COH), 52.1, 51.9, 51.1 (1:2:2, CO₂*Me*), 14.8, 14.3, 13.0, 12.5 (1:2:1:2, Me$_{pz}$). The signals corresponding to the *para*-toluenesulfonic acid are not reported.

Complex 15. To a solution of compound **11** in methanol (0.02 g, 0.021 mmol; 0.5 mL) were added a few crystals of *p*-toluenesulfonic acid. The solution was stirred at 60 °C for 2 h and cooled at room temperature. An orange solid precipitated, which was separated from the mother liquor and dried under vacuum (yield: 15%, orange solid). ¹H NMR (CDCl₃, 25 °C): δ 5.71, 5.65 (s, 2:1, 3 CH$_{pz}$), 4.06, 3.74, 3.18 (s, 1:2:2, 5 CO₂Me), 3.55 (s, 3 H, OMe), 2.40, 2.35, 1.79, 1.78 (s, 1:2:2:1, 6 Me$_{pz}$). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 179.5, 172.0, 167.5 (1:2:2, *C*O₂Me), 154.2, 151.0, 143.3, 143.2 (1:2:2:1, C$_{qpz}$), 147.9, 135.0 (*C*CO₂Me), 106.5,

106.2 (2:1, CH$_{pz}$), 90.6 (*C*OMe), 57.0, 52.2, 50.9 (1:2:2, CO₂*Me*), 55.9 (CO*Me*, $^1J_{CH}$ = 144 Hz), 15.9, 13.2, 13.1, 12.5 (1:1:2:2, Me$_{pz}$).

Complex 15·HBF₄. To a solution of compound **15** in Et₂O−CH₂Cl₂ (1:1) (0.02 g, 0.023 mmol; 4 mL) was added a drop of HBF₄ (54% weight in Et₂O), and the resulting solution was stirred at room temperature for 3 h. The orange solution was dried in vacuum, and quantitative conversion into **15·HBF₄** was ascertained by ¹H NMR. ¹H NMR (CDCl₃, 25 °C): δ 5.78, 5.60 (s, 2:1, 3 CH$_{pz}$), 4.09, 3.80, 3.20 (s, 1:2:2, 5 CO₂Me), 3.62 (s, 3 H, OMe), 2.40, 2.38, 1.78, 1.50 (s, 2:1:2:1, 6 Me$_{pz}$). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 179.9, 171.7, 171.6 (1:2:2, *C*O₂Me), 152.9, 152.8 (C$_{qpz}$, *C*CO₂Me), 151.2, 144.1, 143.5 (2:1:2, C$_{qpz}$), 134.4 (*C*CO₂Me), 106.8, 106.7 (2:1, CH$_{pz}$), 91.6 (*C*OMe), 57.5, 57.4 (CO*Me*, CO₂*Me*), 54.2, 51.8 (CO₂*Me*), 14.7, 13.4, 13.2, 12.8 (1:1:2:2, Me$_{pz}$).

Complex 16. Compound **2** was suspended in cyclohexane (0.05 g, 0.053 mmol; 4 mL) and transferred into a Fischer−Porter vessel, which was pressurized with H₂ (3 atm). The mixture was stirred at 60 °C for 10 h, and after this period of time the volatiles were removed under vacuum. An ¹H NMR spectrum of the crude of the reaction showed quantitative conversion into compound **16**, which was crystallized from a mixture of hexane−CH₂Cl₂ (1:1) at −20 °C in 40% yield (yellow crystals).
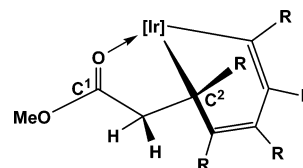
¹H NMR (CDCl₃, 25 °C): δ 5.71, 5.60 (s, 2:1, 3 CH$_{pz}$), 4.44, 3.32 (d, 1 H each, $^2J_{HH}$ = 20.9 Hz, CH₂), 3.83 (s, 3 H, C¹O₂Me), 3.70, 3.66, 3.61, 2.95, 2.81 (s, 3 H each, 5 CO₂Me), 2.40, 2.31, 2.30, 2.18, 2.09, 2.07 (s, 3 H each, 6 Me$_{pz}$). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 197.8 (C¹), 181.2, 177.1, 170.5, 168.3, 167.0 (*C*O₂Me), 156.5, 151.1, 149.8, 144.4, 143.9, 142.9 (C$_{qpz}$), 144.8, 138.6, 135.0, 134.5 (*C*CO₂Me), 109.6, 108.6, 107.5 (CH$_{pz}$), 56.4 (C¹O₂*Me*), 52.5, 52.3, 50.8 (1:2:2, CO₂*Me*), 53.5 (CH₂, $^1J_{CH}$ = 133 Hz), 17.0 (C²), 15.3, 15.1, 13.6, 13.3, 13.3, 12.8 (Me$_{pz}$). IR (Nujol): ν(CO₂Me) 1716 (br) cm⁻¹. Anal. Calcd for C₃₃H₄₂BN₆O₁₂Ir: C, 43.2; H, 4.6; N, 9.2. Found: C, 43.5; H, 4.7; N, 8.6.

Complex 17. Compound **5** was suspended in cyclohexane (0.250 g, 0.288 mmol; 6 mL) and transferred into a Fischer−Porter vessel, which was pressurized with H₂ (3 atm). The mixture was stirred at 60 °C for 24 h, when a pale yellow precipitate was observed, and the volatiles were removed under reduced pressure. The yellow residue was dissolved in a mixture of Et₂O−CH₂Cl₂ (1:1), and the resulting solution was cooled at −20 °C to give **17** as a pale yellow solid in almost quantitative yield.
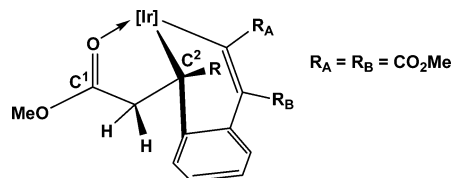
¹H NMR (CD₂Cl₂, 25 °C): δ 7.19, 7.12, 7.04 (m, d, d, 2:1:1, $^3J_{HH} \approx 7$ Hz, 4 CH$_{ar}$), 5.83, 5.80, 5.53 (s, 1 H each, 3 CH$_{pz}$), 4.53, 2.54 (d, 1 H each, $^2J_{HH}$ = 20.8 Hz, CH₂), 3.83 (s, 3 H, C¹O₂Me), 3.75, 3.00 (s, 3 H each, CO₂Me of R$_B$ and R$_A$, respectively), 2.80 (s, 3 H, C²CO₂Me), 2.47, 2.40, 2.39, 2.20, 2.17, 1.46 (s, 3 H each, 6 Me$_{pz}$). ¹³C{¹H} NMR (CD₂Cl₂, 25 °C): δ 197.3 (C¹), 182.8 (C²*C*O₂Me), 177.7, 171.1 (*C*O₂Me of R$_A$ and R$_B$, respectively), 155.4, 150.6, 150.3, 144.5, 144.4, 142.8 (C$_{qpz}$), 145.8, 136.3 (C$_{qar}$), 139.8, 128.8 (*C*$_{olef}$R$_B$ and *C*$_{olef}$R$_A$, respectively), 128.4, 128.0, 125.5, 125.3 (CH$_{ar}$), 109.0, 108.1, 107.2 (CH$_{pz}$), 56.2 (C¹O₂*Me*), 55.2 (CH₂,

$^1J_{CH}$ = 130 Hz), 52.2, 50.7 (CO$_2$*Me* of R$_B$ and R$_A$, respectively), 50.6 (C^{2}CO$_2$*Me*), 19.5 (C^2), 14.8, 14.4, 13.5, 13.3, 13.0, 12.6 (Me$_{pz}$).

Complexes 18 and 19. Compound **3** was suspended in cyclohexane (0.6 g, 0.76 mmol; 10 mL) and transferred into a Fischer—Porter vessel, which was pressurized with H$_2$ (3 atm). The resulting mixture was stirred at 90 °C for 24 h, and after this period of time a pale yellow precipitate was formed and the solvent was evaporated to dryness. A ^{1}H NMR spectrum of the crude of the reaction showed formation of complexes **18** and **19**, in a 7:3 ratio, as the main products. Separation of these two compounds was accomplished by column chromatography on silica gel, using a 1:1 mixture of hexane—Et$_2$O as eluent (**18**, 32% yield, pale yellow crystals; **19**, 10% yield, pale yellow crystals).
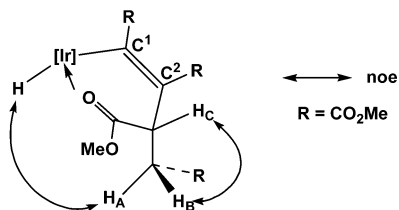
R = CO$_2$Me

18: R_f = 0.34 [silica gel, hexane—Et$_2$O (1:3)]. ^{1}H NMR (CDCl$_3$, 25 °C): δ 5.76, 5.74, 5.67 (s, 1 H each, 3 CH$_{pz}$), 4.74 (dd, 1 H, $^3J_{CA}$ = 10.9, $^3J_{CB}$ = 6.0 Hz, H$_C$), 4.46 (dd, 1 H, $^2J_{BA}$ = 14.3 Hz, H$_B$), 3.84, 3.70, 3.64, 3.13 (s, 3 H each, 4 CO$_2$Me), 2.97 (dd, 1 H, H$_A$), 2.40, 2.34, 2.33, 2.16, 2.03, 1.85 (s, 3 H each, 6 Me$_{pz}$), −20.70 (s, 1 H, Ir—H). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 182.9, 178.1, 171.8, 163.5 (CO$_2$Me), 169.4 (C^1), 153.5, 151.3, 150.4, 144.0, 143.6, 142.5 (C$_{qpz}$), 121.0 (C^2), 106.5, 105.6, 105.5 (CH$_{pz}$), 55.0, 51.8, 51.6, 50.2 (CO$_2$*Me*), 43.7 (CH$_C$, $^1J_{CH}$ = 134 Hz), 30.9 (CH$_A$H$_B$, $^1J_{CH}$ = 134 Hz), 17.2, 13.8, 13.0, 12.5, 12.4 (1:1:2:1:1, Me$_{pz}$). IR (Nujol): ν(Ir—H) 2167 cm^{-1}. Anal. Calcd for C$_{27}$H$_{38}$BN$_6$O$_8$Ir: C, 41.7; H, 4.9; N, 10.8. Found: C, 41.7; H, 4.8; N, 10.8.
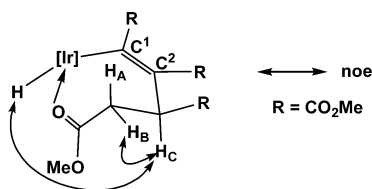
R = CO$_2$Me

19: R_f = 0.41 [silica gel, hexane—Et$_2$O (1:3)]. ^{1}H NMR (CDCl$_3$, 25 °C): δ 5.72, 5.68, 5.27 (s, 1 H each, 3 CH$_{pz}$), 5.04 (dd, 1 H, $^3J_{CA}$ = 11.7, $^3J_{CB}$ = 3.4 Hz, H$_C$), 3.85, 3.72, 3.60, 3.18 (s, 3 H

each, 4 CO$_2$Me), 3.53 (dd, 1 H, $^2J_{AB}$ = 18.4 Hz, H$_A$), 2.99 (dd, 1 H, H$_B$), 2.39, 2.35, 2.33, 2.18, 2.05, 1.75 (s, 3 H each, 6 Me$_{pz}$), −20.98 (s, 1 H, Ir—H). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 182.8, 176.7, 173.1, 164.4 (CO$_2$Me), 169.4 (C^1), 153.5, 151.3, 150.5, 143.6, 143.4, 142.9 (C$_{qpz}$), 122.8 (C^2), 106.2, 105.6, 105.5 (CH$_{pz}$), 55.5, 51.8, 51.3, 50.2 (CO$_2$*Me*), 48.8 (CH$_C$, $^1J_{CH}$ = 128 Hz), 32.8 (CH$_A$H$_B$, $^1J_{CH}$ = 136 Hz), 17.2, 13.9, 13.3, 13.0, 12.5, 12.3 (Me$_{pz}$). IR (Nujol): ν(Ir—H) 2167 cm^{-1}. Anal. Calcd for C$_{27}$H$_{38}$BN$_6$O$_8$Ir: C, 41.7; H, 4.9; N, 10.8. Found: C, 41.7; H, 4.9; N, 10.6.

X-ray Structure Determination. X-ray data of complexes **2**, **8**, **11**, **12**, **13**, and **18** (the following compounds were solvates: **2**·H$_2$O·CHCl$_3$, **11**·0.25CH$_2$Cl$_2$, **12**·CH$_2$Cl$_2$) were collected on Bruker CCD area detector diffractometers using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames covering complete spheres of the reciprocal space with θ$_{max}$ = 25−30°. After data integration with the program SAINT corrections for absorption, λ/2 effects, and crystal decay were applied with the program SADABS.[24] The structures were solved by direct methods, expanded by Fourier syntheses, and refined on F^2 with the program suite SHELX97.[25] All non-hydrogen atoms were refined anisotropically. Most H atoms were placed in calculated positions and thereafter treated as riding. A torsional parameter was refined for each pyrazole-bound methyl group. The hydride H atom in **18** was refined in x,y,z and U_{iso} without restraints. Moderate disorder in **11**·0.25CH$_2$Cl$_2$ (solvent and two COOMe groups) was taken into account. Crystal data and experimental details are given in Table 1.

Supporting Information Available: Complete crystallographic data and technical details in CIF format for complexes **2**, **8**, **11**, **12**, **13**, and **18**, and pdf file containing ^{1}H and ^{13}C{^{1}H} NMR spectra of complexes **13**, **14**, **15**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM061036O

(24) Bruker programs: *SMART*, version 5.629; *SAINT+*, version 6.45; *SADABS*, version 2.10; *SHELXTL*, version 6.14; Bruker AXS Inc.: Madison, WI, 2003.
(25) Sheldrick, G. M. *SHELX97*: Program System for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997.