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Synthesis and Reactivity of Iridacycles Containing the $Tp^{Me2}Ir$ Moiety

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Dedicated to Prof. Kurt Mereiter on the occasion of his retirement

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The $Tp^{Me2}Ir$ moiety has proven to easily promote the formal oxidative addition reactions of unsaturated molecules, with or without concomitant formation of carbon–carbon bonds, to form metallacyclic species. The ring sizes may range between having 5- and 7 members, and these metallacycles exhibit a rich reactivity. Some of these metallacycles represent stable models of intermediates proposed in catalytic processes such as alkyne cyclotrimerization or olefin/alkyne coupling. The stability of these $Tp^{Me2}Ir^{III}$ species allows the mechanistic investigation of the reactions observed, by way of the isolation and/or trapping of intermediates.

Introduction

Transition-metal metallacycles are very interesting and ubiquitous species in organometallic chemistry. They may adopt a multitude of structural modes, and their synthesis and reactivity are highly dependent on the nature of the metal and the substituents in the ring.

Over the past twenty years, our research group has been involved, along with other lines of research, in developing the organometallic chemistry of Ir compounds containing the Tp^{Me2} ligand [Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)-borate].[1,2] In this review, we describe some of the most interesting and recent results obtained from studying the synthesis and reactivity of iridacyclopentene, -pentadiene, -heptadiene, -heptatriene and -benzenoid derivatives.

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Margarita Paneque obtained a Ph. D. degree from the University of Sevilla (1986, E. Carmona, M. L. Poveda) and carried out postdoctoral work with Prof. P. M. Maitlis in Sheffield. In 1989, she joined the Spanish Council for Scientific Research (CSIC) and currently works at the Instituto de Investigaciones Químicas (Sevilla) as a Research Professor. Her research interests include different aspects of organometallic chemistry, as for instance the study of elemental processes for potential applications.

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Nuria Rendón (Sevilla, 1978) got her Ph. D. in Chemistry in 2005 at the University of Sevilla (Margarita Paneque and M. L. Poveda) with a thesis on the reactivity of $Tp^{Me2}Ir$ complexes towards alkynes. Later she moved to the Laboratoire de Chemie Organometallique de Surface (CNRS, CPE Lyon, Villeurbanne, France) for a postdoctoral stay with Dr. Christophe Copéret. In January 2009, she returned as a "Ramon y Cajal" fellow to the University of Sevilla. Her present research interests are focussed on the development of catalysts with bulky ligands and their support on silica using surface organometallic chemistry.

Generation and Reactivity of Iridacyclopent-3-ene Derivatives

Metallacyclopent-3-enes of structure **A** can be viewed as an extreme variation of the normal coordination mode of butadiene (η^4, with **B** and **C** as resonance structures) in which the π interaction does not exist (Figure 1).

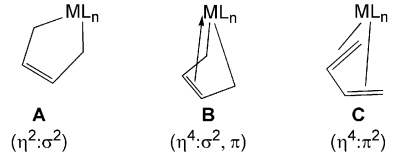


Figure 1. Coordination modes of butadiene.

Coordination mode **C** usually occurs for middle and late transition metals,[3] while type **B** has often been encountered in compounds of the more electropositive early transition and actinide metals.[4,5] In this coordination mode, the hydrocarbyl ligand exhibits considerable σ^2-diyl character, but there is always additional bonding interaction of the metal with the central carbon–carbon double bond. Although very unusual in stable compounds of transition metals, coordination mode **A** has been frequently invoked to explain the fluxional NMR behaviour and other properties of compounds with ground-state geometry **B**. Only a few examples were known[6,7] before the publication of our first report on iridacyclopentenes with this type of structure,[8] but none had derived from the formal oxidative addition of a η^4-butadiene derivative upon reaction with a Lewis base.

In our case, this turned out to be a typical transformation, observed in a variety of reactions of Ir^I-butadiene derivatives with the composition $Tp^{Me2}Ir[CH_2{=}C(R){-}C(R'){=}CH_2]$ (R = R′ = H, butadiene **1**; R = H, R′ = Me, isoprene **2**; R = R′ = Me, 2,3-dimethylbutadiene **3**),[9] {Figure 2; in this and in the following figures [Ir] means $Tp^{Me2}Ir$, that is, hydrotris(3,5-dimethylpyrazolyl)borate iridium}, with different substrates that can act, in principle, as Lewis bases.

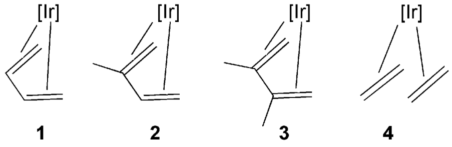
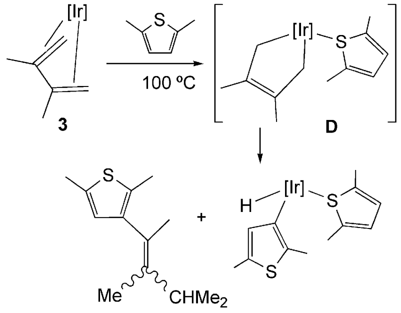


Figure 2. Schematic drawing of compounds **1**–**4**.

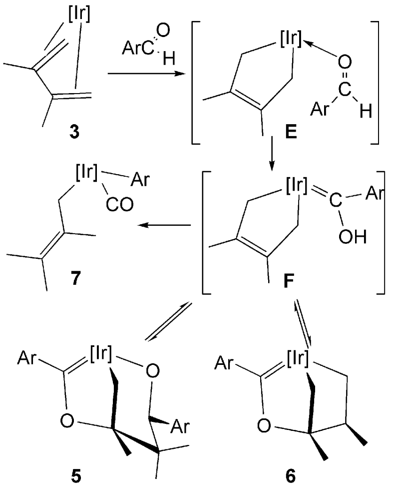
As an extension of our studies on the C–H activation of organic molecules with the $Tp^{Me2}Ir(C_2H_4)_2$ (**4**) species,[10] we studied the reactivity of the diene derivatives **1**–**3**. We already knew that the bis(ethylene) complex **4** experiences a very easy (60 °C) intramolecular C–H bond activation to generate the Ir^{III} derivative $Tp^{Me2}Ir(H)(CH{=}CH_2)(C_2H_4)$,[10] which was responsible for the C–H activation observed with, for instance, benzene or cyclic ethers.[11] In addition, we also knew that the butadiene derivatives **1**–**3** were thermally quite stable, only experiencing intramolecular C–H activation under UV irradiation to form allyl species.[9]

Interestingly, upon heating the 2,3-dimethylbutadiene derivative **3** with 2,5-dimethylthiophene,[12] we observed the formation of organic products that derived from the coupling of the diene ligand and the thiophene. NMR monitoring of the reaction reveals the presence, in the reaction mixture, of an intermediate species assigned as **D** (Scheme 1). This species exhibits a very characteristic set of signals in the ^{1}H NMR spectrum, between 2.9–3.4 ppm, that corresponds to the AB spin system of the Ir–CH_2 protons ($^2J_{HH}$ = 13.3 Hz), which allows us to propose the η^2-diyl structure (**D**).



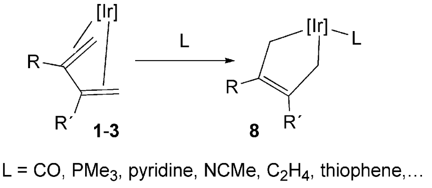
Scheme 1.

We also studied the highly complex reaction of **3** with aromatic aldehydes,[8] and again we were able to detect by ^{1}H NMR spectroscopy the presence of two kinds of intermediates, both with the same kind of AB spin system (structures **E** and **F** in Scheme 2). These derivatives evolved to reach the final products of the reaction (**7**), which are the result of the formal decarbonylation of the aldehyde that proceeds through two additional kinds of kinetic intermediates (**5** and **6**), which results from the coupling of two molecules and one molecule, respectively, of the aldehyde with the diene ligand. These species revert back to **F**, which eventually yields the thermodynamic products of the reaction, **7**.

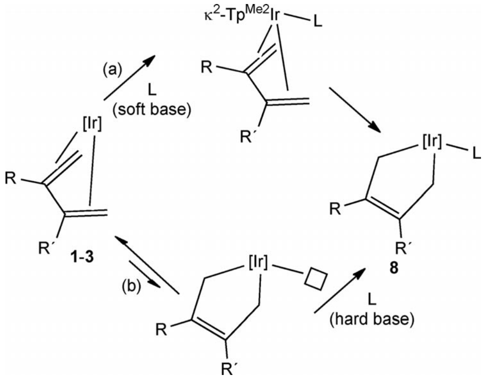


Scheme 2.

Thus, we decided to study in detail the reactivity of the diene compounds **1**–**3** with a variety of Lewis bases (CO, PMe_3, pyridine, NCMe, C_2H_4, thiophene, to name a few) to form the adducts **8** (Scheme 3).[13] From the results obtained in these studies we propose that these reactions could follow two different pathways, one of which [path (a) of Scheme 4] was assumed to be taken by the reaction with soft bases (CO, PMe_3) and would imply the initial coordination of the Lewis base to an unsaturated diene compound, with subsequent oxidative addition of the diene moiety. Temporary decoordination of one of the pyrazolyl arms of the Tp′ ligand [Tp′ = any type of hydrotris(pyrazolyl)borate derivative] in the Ir^I derivatives to form an unsaturated $16e^-$ species is a well-documented fact, and it allows, for instance, the occurrence of associative substitution reactions.[14] The other mechanistic way [path (b)] was invoked to explain the reactions of Ir-dienes **1**–**3** with hard Lewis bases (NCMe, pyridine, etc.).



Scheme 3.



Scheme 4.

The two different mechanisms shown in Scheme 4 may also account for the different types of processes in which the 2,3-dimethylbutadiene derivative **3** (the most reactive among **1**–**3**, and hence the most studied) takes part. Because of its relevance as a precursor for other metallacycles, as will be seen in subsequent sections, the reactivity of **3** is described in some detail in the next paragraphs.

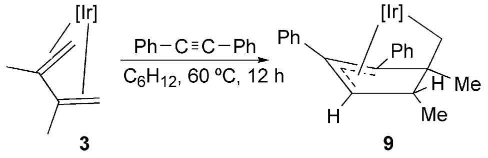
Three different types of processes have been observed in the reactions of **3** with organic substrates: (i) the diene simply oxidatively adds to the metal centre and forms stable iridacyclopent-3-ene derivatives; (ii) the diene, having not transformed, is displaced unreacted; and (iii) the carbon skeleton of the diene experiences some type of coupling with the substrate added.

Examples of the first type (i) are the reactions summarized in Scheme 3.[13] It is worth mentioning briefly that some adducts of **3**, i.e. with NCMe and SC_4H_8, are thermally unstable, and revert to **3** upon heating in solution at sufficiently high temperatures. This observation is important because it represents the first example in which a $Tp^{Me2}Ir^{III} \rightarrow Tp^{Me2}Ir^{I}$ reduction process takes place (see above). Most of the $Tp^{Me2}Ir^{III}$ compounds we have investigated are extremely reluctant to evolve through Ir^I intermediates or to result in Ir^I reaction products. In the compounds mentioned, the reversibility of the reaction may have some relation to the special stability expected for the Ir^I-η^4-dimethylbutadiene moiety.

For the second group of reactions, a representative example might be the interaction of **3** with dimethylacetylenedicarboxylate (DMAD),[15] where the diene is displaced by two molecules of the alkyne. This reaction will be discussed in detail in the next section.

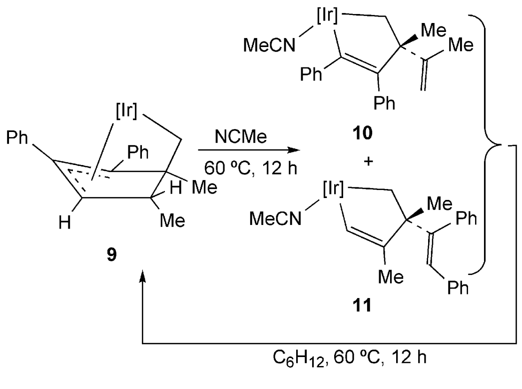
With regard to the third type of process, two examples have already been mentioned, those corresponding to the reactions with 2,5-dimethylthiophene[12] and with aromatic aldehydes.[8] In both cases, the reactions proceed through intermediate iridacyclopent-3-ene derivatives.

We had also studied the reaction of the 2,3-dimethylbutadiene derivative **3** with diphenylacetylene,[16] in which the diene and the alkyne were shown to form a compound (**9**) having an elaborate new ligand (Scheme 5).

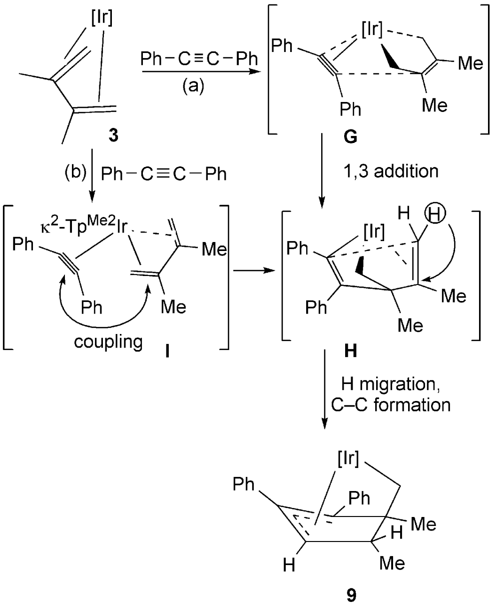


Scheme 5.

No intermediates were detected in the reaction, and the complexity of the chelating ligand present in **9** made it difficult to propose a reliable mechanistic pathway for its formation, but the reaction of **9** with NCMe (Scheme 6) provided valuable information and facilitated, at least in part, this task. This reaction yielded two isomeric acetonitrile adducts, **10** and **11**, both being iridacyclopent-2-ene species. Their formation was reversible, since, when heated in cyclohexane (60 °C), NCMe dissociated with the formation of the allyl precursor **9**. Their structure and behaviour allowed us to propose the mechanism for the formation of compound **9** from **3** and PhC≡CPh represented in Scheme 7.



Scheme 6.



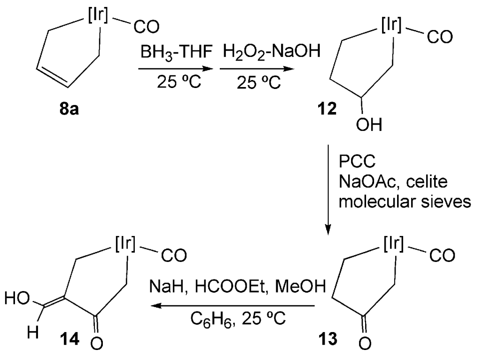
Scheme 7.

The initial coordination of the alkyne, as in path (a), produces the Ir^{III} species **G**, an additional example of the η^4:π^2 to η^2:σ^2 rearrangement of the butadiene ligand discussed before. Intermediate **G** can then experience a 1,3-addition[17] of the alkyne to the metallacycle to form **H**, a bicyclic structure with a coordinated olefinic terminus. Alternatively, path (b) results from the initial coordination of the alkyne to an unsaturated Ir^I intermediate, provided by a coordination change of the Tp^{Me2} ligand from κ^3 to κ^2. This Ir^I intermediate will result in **H** by a [2+2] oxidative coupling and restoration of κ^3-Tp^{Me2} binding. Finally, stereospecific migration of one of the terminal olefinic H atoms of **H** to the adjacent carbon atom and a C–C bond-forming process would yield the observed product **9**. Unfortunately, we were unable to get experimental evidence to disclose which of the paths (a) or (b) was acting in this reaction.

The organometallic skeleton proposed for **H** is identical to that found in one of the NCMe adducts, **10**, obtained from **9**, and this would imply that the **H**→**9** transformation is reversible, intermediate **H** being trapped by the Lewis base to result in **10**. The other NCMe adduct **11** was assumed to be formed by isomerization of this intermediate species **H**, either directly, by H transfer from the coordinated olefin to the alkenyl end of the metallacycle, or through the final product **9** by a different H to allyl migration.

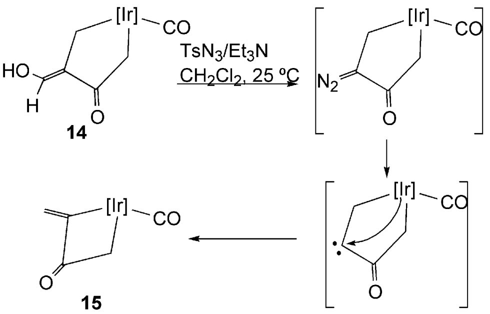
“Organic” Reactivity of the Iridacyclopent-3-ene [Tp^{Me2}Ir(CH$_2$C(H)=C(H)C^{4}H$_2$)(CO)(*Ir–C^4*)]

A final comment on the reactivity of the iridacyclopentenes **8** is appropriate. When the Lewis base added is tightly coordinated to iridium (as is the case for CO and PMe$_3$), the organometallic unit is so stable that these compounds allow the development of “organic” chemistry in the metallacycle, without breaking any of the Ir–C bonds. Preliminary results for this type of reaction have shown that the unsubstituted iridacyclopent-3-ene **8a**, [Tp^{Me2}Ir(CH$_2$C(H)=C(H)C^{4}H$_2$)(CO)(*Ir–C^4*)], can be transformed in a stepwise manner to the α-formyl-3-iridacyclopentanone **14**, shown in Scheme 8.[18]



Scheme 8.

Interestingly, species **14** underwent an unusual rearrangement to yield the contracted four-membered iridacycle **15** when treated with TsN$_3$ (Scheme 9). We expected to obtain a diazoalkane, which may in fact be acting as an intermediate species in the formation of the observed product. The putative carbene intermediate that should form after elimination of N$_2$ is attacked by the iridium centre, with preference over the alternative attack to the carbonyl function, a normal process under these Wolff rearrangement conditions. This is an important finding because heteroatom migration under Wolff reaction conditions is very uncommon, to the point that transition-metal migration was in fact unprecedented before this report.



Scheme 9.

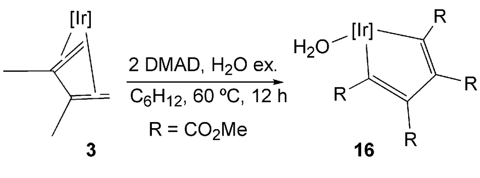
Synthesis and Reactivity of Iridacyclopentadienes

As a class of metallacycles, metallacyclopentadiene derivatives are very interesting functionalities in organometallic chemistry, which exhibit a rich reactivity.[3,19] These species can be formed, among other synthetic procedures, by the oxidative coupling of two molecules of alkyne to a metal centre. They are likely to be stable toward the formation of a more elaborate ligand when the incorporation of more alkyne groups is disfavoured, either by steric hindrance of coligands or by the presence of bulky substituents in the alkyne. Nevertheless, if the incorporation of a third alkyne molecule is highly probable, they are usually difficult to isolate, unless particular precautions are followed.

Metallacyclopentadienes[3,19] are also involved, as common intermediates, in transition-metal-mediated synthesis of highly conjugated organic products, such as the cyclotrimerization of alkynes (to yield benzene derivatives),[20] the coupling of alkyne and nitriles (for the synthesis of pyridines),[21] the coupling of alkyne and olefins (for the formation of cyclohexadienes),[21,22] amongst others.[19g,23] In particular, addition of alkenes or alkynes to metallacyclopentadienes may lead to metallacycloheptadienes or metallacycloheptatrienes, postulated often as reaction intermediates in the co-oligomerization of alkynes and olefins and in the cyclotrimerization of alkynes, respectively, although sometimes these reactions lead to complexes of unexpected structure. In the next paragraphs we describe our findings in this field with the $Tp^{Me2}Ir$ system.

Synthesis of the Iridacyclopentadienes $[Tp^{Me2}Ir(C(R){=}C(R')C(R){=}C^4R)(L)(Ir{-}C^4)]$ (R = CO_2Me; R′ = CO_2Me, H; L = H_2O, CO, NCMe)

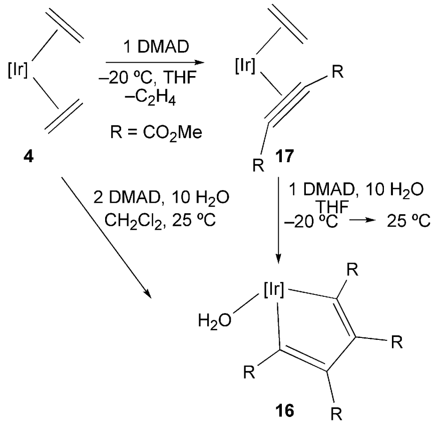
We have used the compound $Tp^{Me2}Ir[\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2]$ (**3**) as the $Tp^{Me2}Ir$ source for the synthesis of iridacyclopentadienes. As already shown previously, this species can incorporate the hydrocarbyl chain to the products formed upon reaction with PhC≡CPh, but when reacted with 2 equiv. DMAD, it was displaced, to result in the iridacyclopentadiene **16**.[15] This iridacycle[24] completes the 18-electron metal count by the coordination of a molecule of added water,[25] which is essential for the isolation of the iridacyclopentadiene. In fact, by using normally dried solvents (only adventitious water being present), the reaction did not stop in the formation of **16**, but continued to give an iridacycloheptatriene (see below), with starting material remaining (Scheme 10).



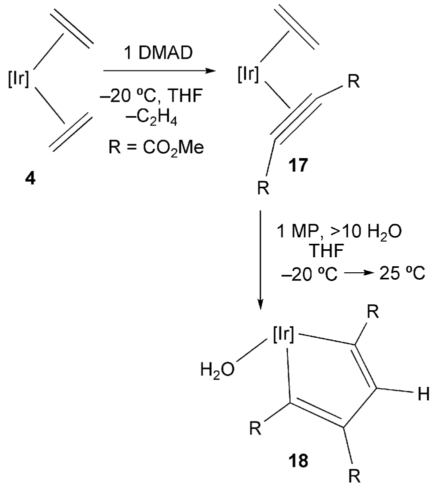
Scheme 10.

This metallacyclopentadiene **16** could also be prepared from $Tp^{Me2}Ir(C_2H_4)_2$ (**4**),[15] but again requiring a large excess of water. Important mechanistic information was obtained by carrying out the reaction at low temperatures and with deuterated DMAD. These studies ruled out any interconversion between the iridacyclopentadiene and a bis(alkyne)Ir^I species, and this was in accord with the findings observed in a related system.[24b]

Thus, the reaction of **4** with DMAD at –20 °C resulted in the formation of the Ir^I adduct $[Tp^{Me2}Ir(C_2H_4)(MeO_2CC{\equiv}CCO_2Me)]$ (**17**),[15] generated by a molecule of DMAD substituting one of the ethylene ligands in **4** (Scheme 11).[26] Compound **17** was stable up to 10 °C, but above that temperature it reacted with a second molecule of DMAD to form either metallacycle **16**, if the reaction mixture contained enough water, or an hydride–alkene species (**21** in the next section) when normal anhydrous conditions were employed. In a related process, the sequential addition to **4**, at low temperature, of 1 equiv. DMAD and 1 equiv. methyl propiolate $HC{\equiv}CCO_2Me$ (MP) in the presence of added water (10 equiv.) regioselectively yielded the iridacyclopentadiene **18**[15] (Scheme 12).

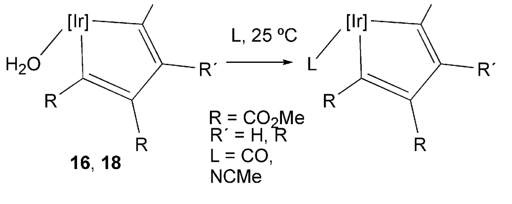


Scheme 11.



Scheme 12.

The water ligand of **16** and **18** is labile and was easily displaced by Lewis bases such as NCMe or CO (Scheme 13). This lability permits the incorporation of

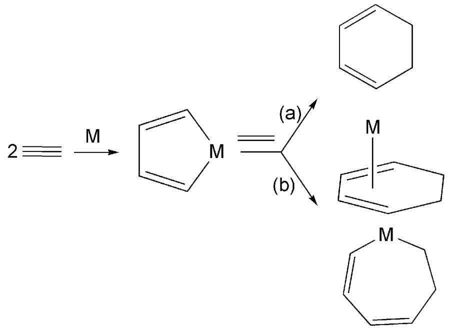


Scheme 13.

other unsaturated molecules to the cycle. In the next section, the reactivity of **16** and **18** towards olefins and alkynes is presented and discussed.

Reactivity of the Iridacyclopentadienes [Tp^{Me2}Ir(C(R)=C(R′)C(R)=C^{4}R)(H_2O)(*Ir–C^4*)] (R = CO_2Me; R′ = CO_2Me or H) towards Olefins

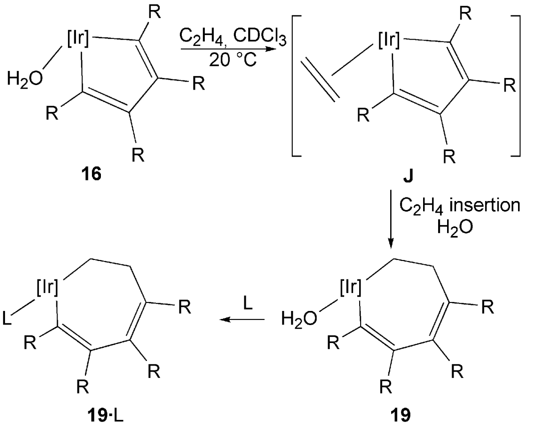
As mentioned above, metallacyclopentadienes are known to participate in a variety of coupling processes. Thus, they act as intermediates in the coupling of two alkynes and an alkene to form cyclohexadienes in a catalytic process or result in cyclohexadiene ligands or metallacycloheptadienes in its stoichiometric version (Scheme 14).



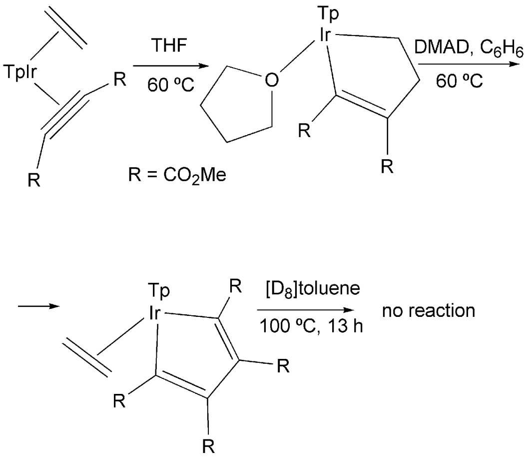
Scheme 14.

Reactions with Ethylene

Upon reaction with ethylene,[15] complex **16** formed the iridacyclohexadiene **19**, probably through the intermediacy of intermediate **J**, a very reactive species (see below) that could be stabilized by other Lewis bases such as CO or NCMe, which substitute for the labile water ligand (Scheme 15). It is worth mentioning the ease with which the ethylene inserts itself into the Ir–C bond of the presumed intermediate **J**. In the case of the related, isolable compound with the unsubstituted Tp ligand [Tp = hydrotris(pyrazolyl)borate], no insertion was observed up to 110 °C (Scheme 16).[24a] This is in agreement with the known decreased reactivity of the TpIr compounds, as compared with those containing Tp^{Me2}Ir, in activation processes. In the Tp^{Me2}Ir system, we have observed cases in which C_2H_4 easily inserts itself into an Ir–C bond, for example in its reaction with Tp^{Me2}Ir(C_6H_5)$_2$(N_2).[11] However, we also found complexes that are unreactive in this respect, such as the iridacyclopentene [Tp^{Me2}Ir($CH_2C(Me)=C(Me)C^4H_2$)(C_2H_4)(*Ir–C^4*)] (**8**-C_2H_4), which, upon heating, dissociates the coordinated ethylene[13] or the very reactive Tp^{Me2}Ir(H)(CH=CH_2)(C_2H_4), which has been shown to yield a C_4 chain by the coupling of the two C_2 ligands. The latter, however, follows a mechanistic pathway different from the insertion of ethylene into the Ir–C bond.[10]

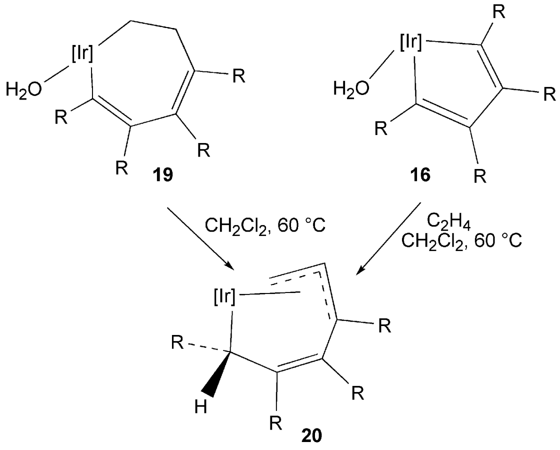


Scheme 15.



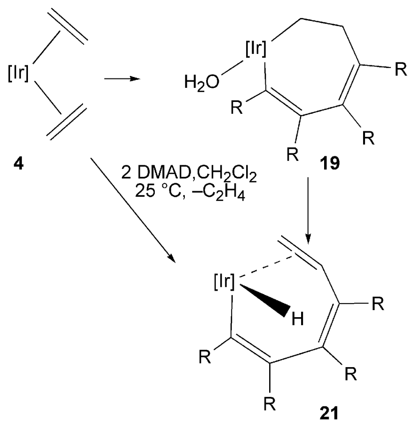
Scheme 16.

Interestingly, heating solutions of **19** or its precursor reagents (**16** + C_2H_4) with ethylene at 60 °C resulted in the clean formation of the allyl derivative **20** (Scheme 17).



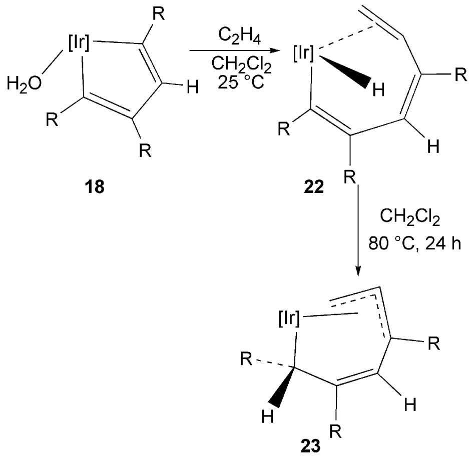
Scheme 17.

Formation of this derivative had been observed previously in our group in the reaction of the Ir^I bis(ethylene) complex **4**, with 2 equiv. DMAD at 60 °C.[15] Soon we realized that both processes took place by common intermediates and actually compound **19** was observed in the reaction **4**→**20** when an excess of water was added to the reaction mixture. Once more, water reveals itself as an interesting and appropriate trapping reagent in these $Tp^{Me2}Ir^{III}$ systems. Additionally, another intermediate was detected when the reaction of complex **4** and DMAD took place at room temperature. In that case, immediate consumption of **4** was observed with formation of **21**, a compound having a chelating hydrocarbyl–alkene ligand (Scheme 18). The carbon skeleton of this species is generated by a β-H elimination process in metallacycle **19**, which takes place as soon as water is released from this complex. As expected, when the transformation **4**→**21** was carried out in the presence of excess H_2O, compound **16** was formed in almost quantitative yield.



Scheme 18.

The less-substituted iridacyclopentadiene **18** reacted similarly and very favourably with ethylene, with the regio- and stereoselective formation of the hydrido–olefin derivative **22** (Scheme 19) as the only observable product at room temperature. Isomerization to the corresponding allyl derivative **23** required harsher conditions and took place at 80 °C.

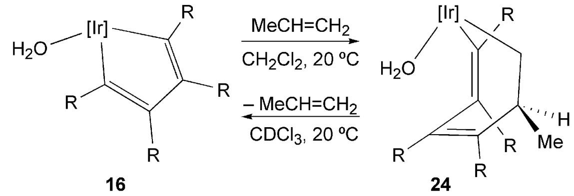


Scheme 19.

Reactions with Propene

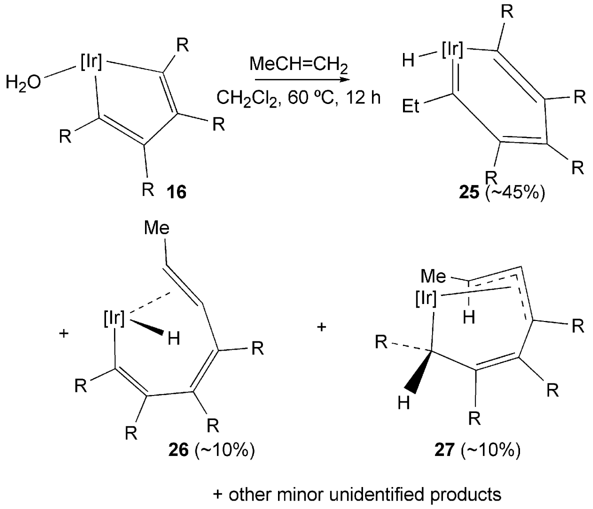
In contrast with the identical outcome when **16** and **18** react with ethylene, a different and unusual chemistry has been observed when each was treated with propene or 1-butene. It is remarkable that a simple modification of one of the substituents in the metallacycle allows the reactivity described below.

Reaction of **16** with propene at room temperature took place with the highly selective formation of only one of the four possible stereoisomers derived from the simple 1,2-migratory insertion of the olefin into one of the Ir–C bonds (Scheme 20).



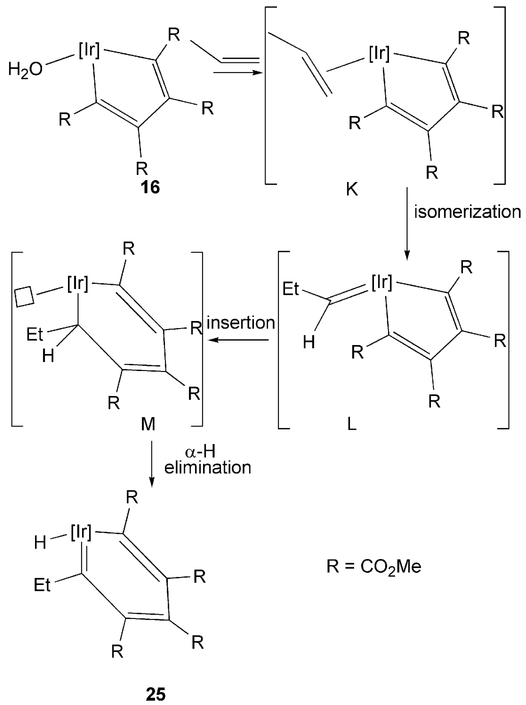
Scheme 20.

However, quite a different result was observed when the reaction was carried out at 60 °C, as shown in Scheme 21. It yielded a mixture of products of which the major product, **25**, had an iridabenzene structure. This compound added to the small but recently growing family of metallabenzenes, and this procedure represents a new method for the synthesis of these species, namely the coupling of an alkene and a metallacyclopentadiene.



Scheme 21.

Formation of **25** clearly implied the insertion of a C_1 unit derived from the olefin into one of the Ir–C bonds of the iridacycle. Hence, for this process we proposed that, at 60 °C, the propene ligand isomerizes to an alkylidene moiety and then inserts itself (Scheme 22).

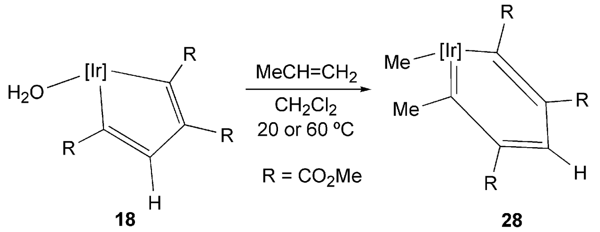


Scheme 22.

The alkene to alkylidene rearrangement is not a common process, but it has precedent in the literature[27] (several of them in our own Tp^{Me2}Ir systems[27c]); the migratory insertion of the alkylidene into the Ir–C bond,[28] and the α-hydride elimination,[29] also already find quite ample precedent in the Tp^{Me2}Ir chemistry developed in our group.

With regard to the minor products of Scheme 21, it was evident that the hydride–olefin **26**, related to **21**, is derived from an iridacycloheptadiene isomer of **24** that resulted from the insertion of propene with the opposite regioselectivity and which instead formed at high temperatures. This species then sequentially gave **26** and the allyl species **27**. Notice that the stereochemistry of **24** did not allow for a β-H elimination to yield a hydride product.

The iridacyclopentadiene **18** reacted differently with propene. In fact, in this case (Scheme 23) only one process, a new one, was observed from 20 to 60 °C. Iridabenzene **28** was obtained, which contains a methyl ligand bound to iridium. The change in the course of the reaction might be because of a preference for the formation of an intermediate with a dimethyl carbene unit, =CMe_2, over the linear propylidene, =C(H)Et, that was proposed in Scheme 22 for the formation of **25**. Formation of **28** then took place by the insertion of the carbene followed by an unusual α-Me elimination process.[30]



Scheme 23.

Reactions with 1-Butene

The reaction of the iridacycles **16** and **18** with 1-butene provided the iridabenzenes **29** and **30**, respectively, although with very low selectivity in the latter case where **30** is accompanied by a very complex mixture of unidentified products (Figure 3).

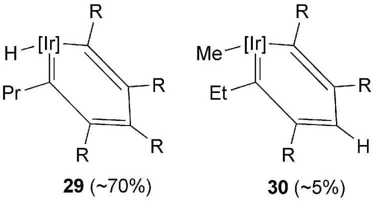
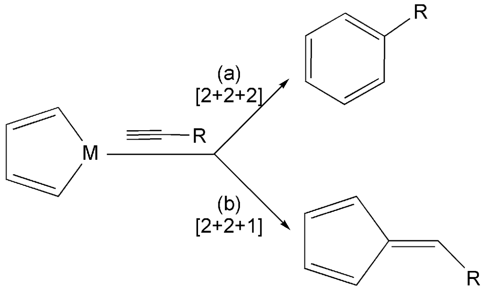


Figure 3. Structure of the iridabenzenes formed by the reactions of **16** and **18** with 1-butene.

Reactivity of the Iridacyclopentadiene [Tp^{Me2}Ir(C(R)=C(R)-C(R)=C^{4}R)(H_2O)(*Ir–C*^{4})] towards Alkynes

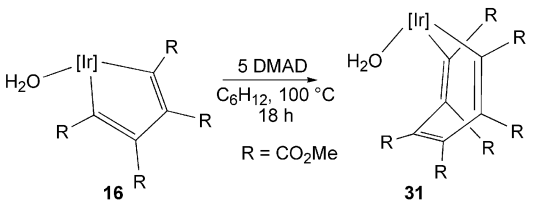
Metallacyclopentadienes can also react with alkynes to form cyclic products, which result from the formal trimerization of C≡C triple bonds. It seems reasonable that the first step of this reaction is the alkyne coordination with the formation of a metallacyclopentadiene–alkyne species. In general, and as a final result of the reaction, aromatic benzene derivatives are formed by a [2+2+2] cycloaddition reaction [Scheme 24, path (a)]. However, it has been found that, in a specific iridium system, depending on the nature of the alkyne, fulvene derivatives can be obtained as the result of a [2+2+1] cyclization, which most likely takes place through the formation of a vinylidene ligand from the alkyne [Scheme 24, path (b)].[31]



Scheme 24.

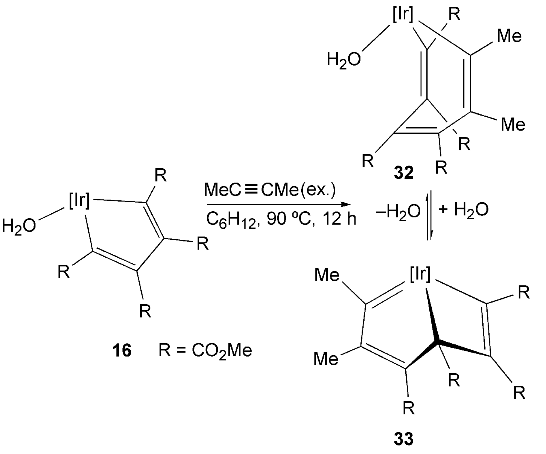
Reactions with MeC≡CMe and PhC≡CPh

Even before the synthesis of compound **16**, we had prepared a family of iridacycloheptatrienes, among them the derivative **31**,[32] which derived from the insertion of a third molecule of DMAD into an Ir–C bond of metallacycle **16**. If no added water was present in the reaction leading to **16**, formation of **31** directly from **3** was quite easy, but once the water adduct **16** had been formed, its formation required quite harsh conditions (excess DMAD, 100 °C) (Scheme 25). This shows that water competes strongly with the alkyne for metal coordination. Complex **31** represents a model for the proposed intermediates of the metal-catalyzed cyclotrimerization of alkynes. This type of metallacycles will be discussed in more detail in the next section.



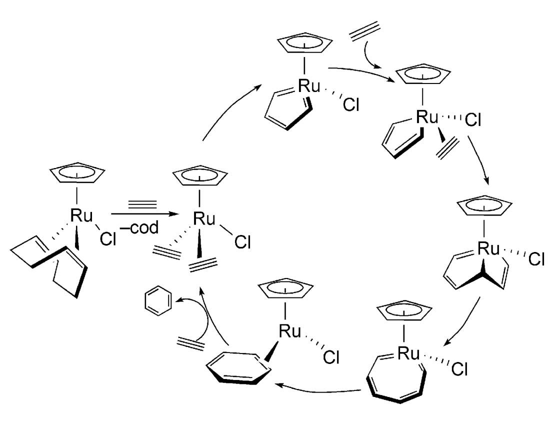
Scheme 25.

Interestingly, the reaction of iridacycle **16** with alkynes did not in most cases yield this type of seven-membered metallacycles, but rather different species, depending on the nature of the alkyne. Thus, with 2-butyne, not only the metallacycloheptatriene complex **32** was obtained, but also the unexpected derivative **33** with a metallabicyclo[3.2.0]-heptatriene structure (Scheme 26).

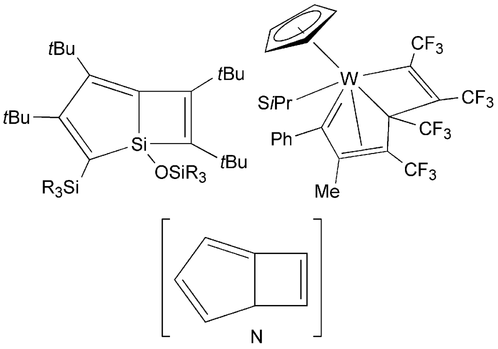


Scheme 26.

The structure of **33** represents the first experimental example of a bicyclo[3.2.0]heptatriene structure in transition-metal chemistry.[33] This type of compound has been theoretically postulated as an active intermediate in the process of cyclotrimerization of alkynes catalyzed by Ru. Specifically, a ruthenabicyclo[3.2.0]heptatriene was proposed[20d,20e] as an intermediate in the transformation of a ruthenacyclopentadiene–alkyne in a ruthenacycloheptatriene (Scheme 27). Besides these theoretical examples of bicyclo[3.2.0]heptatriene structures, related isolable species have been found in the literature, for example, a silicon compound stabilized by very bulky substituents[34] and a tungsten complex with a similar bicycle skeleton but with a more complicated bonding pattern.[35] This structural backbone is unusual not only in organometallic chemistry; although the parent pure organic compound [3.2.0]hepta-1,3,6-triene, **N**, has been proposed to be implicated in a number of chemical reactions as a highly unstable transient species,[36] it has never been detected (Scheme 28).

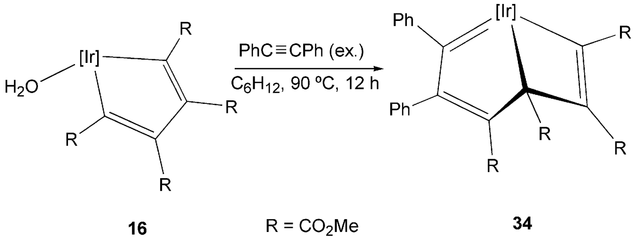


Scheme 27.



Scheme 28.

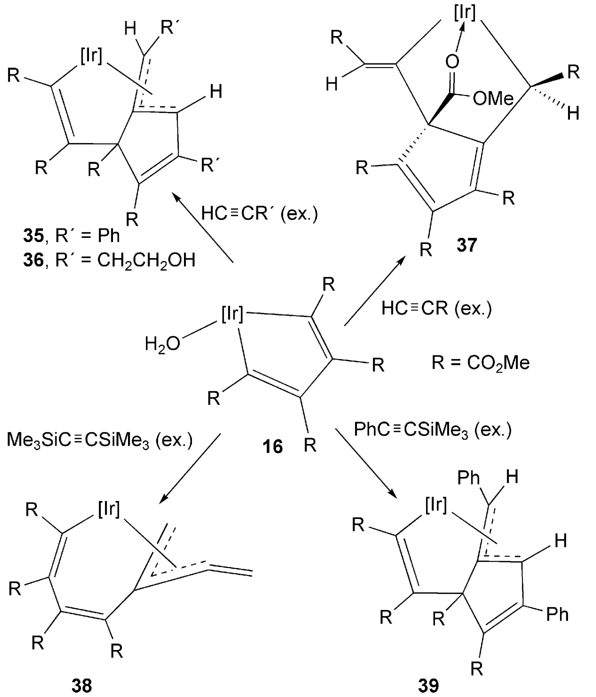
Complexes **32** and **33** interconverted easily into each other, and their proportion in the reaction mixture depended on the water content. From a mechanistic point of view, and because of the fact that equilibrium between **32** and **33** is faster than the reaction shown in Scheme 26, it is not possible to know which of them is formed first. The transformation of **32** into **33** is regioselective as there is no evidence for the formation of an isomeric species in which a –C(Me)=C(Me)– unit is on the four-membered iridacycle, and this may be due, at least partially, to the stabilization that a donor substituent, such as the methyl group, confers to the electrophilic carbene.[29a,37] In accord with this reasoning, the iridacycloheptatriene **31**,[32] in which all the substituents are CO_2Me groups, did not result in a bicyclic compound related to **33** when its solutions in C_6D_6 were heated in the presence of molecular sieves (60 °C, 48 h), in spite of the lability of the water ligand under these conditions.[32] On the other hand, diphenylacetylene provided a related bicycle **34** as the main product and, in this case, no iridacycloheptatriene derivative was observed even upon heating its solutions at 90 °C with an excess of added H_2O (Scheme 29).



Scheme 29.

Reactions with $HC{\equiv}CR$ (R = Ph, CH_2CH_2OH, CO_2Me) and $Me_3SiC{\equiv}CR$ (R = Ph, $SiMe_3$)

The outcome of the reaction changed drastically when terminal alkynes were employed. In the reaction of **16** with excess $HC{\equiv}CPh$, $HC{\equiv}CCH_2CH_2OH$ and $HC{\equiv}CCO_2Me$, chelating structures were formed, that derived from the incorporation of two molecules of the corresponding alkyne into the iridacycle of **16**.[33b] In the two first cases, the alkenyl–allyl complexes **35** and **36** were isolated, having had two molecules of the added alkyne inserted consecutively into an Ir–C bond of the metallacycle with eventual formation of an allyl end and ring contraction. By contrast, for the case of the reaction with methyl propiolate, the first molecule of alkyne was incorporated into one of the Ir–C bonds of complex **16**, and the second into the other. Interestingly, the two $SiMe_3$ alkynes $Me_3SiC{\equiv}CSiMe_3$ and $Me_3SiC{\equiv}CPh$ behaved as terminal groups, in spite of being internal groups, in the sense that they provided structures **38** and **39**, in which two molecules of the corresponding alkyne were incorporated. However, in the final products, the $SiMe_3$ groups had been replaced by hydrogen atoms, clearly the result of an easy hydrolysis (Scheme 30).



Scheme 30.

All these reactions seemed to require one step of formation of vinylidene ligands from the alkyne to be incorporated, an usual transformation for terminal alkynes, also accessible to $SiMe_3$ derivatives {for example[38] the complex $Tp^{Me2}Ir(C_6H_5)_2(N_2)$ reacts with $Me_3SiC{\equiv}CSiMe_3$ with the formation of $Tp^{Me2}Ir(C_6H_5)_2[C{=}C(SiMe_3)_2]$, but surprisingly the C–$SiMe_3$ bonds are very difficult to hydrolyze}. For the case of $Me_3SiC{\equiv}CPh$, the hydrolysis of the C–$SiMe_3$ bonds probably took place in a late step, since this product yielded an isomer of the compound formed with $HC{\equiv}CPh$, but with a different stereochemistry of the CHPh terminus of the allyl moiety; most likely, the $SiMe_3$ group had forced a different stereochemistry in the reaction, before being hydrolyzed.

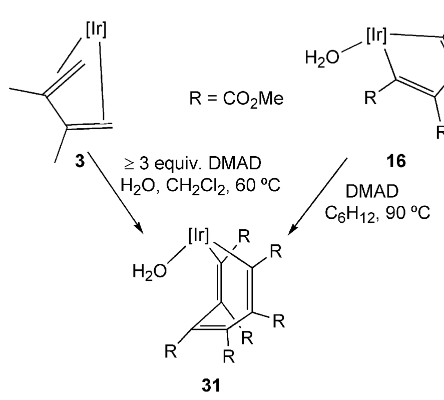
Synthesis of the Iridacycloheptatriene $[Tp^{Me2}Ir(C(R){=}C(R)C(R){=}C(R)C(R){=}C^6R)(H_2O)(\mathit{Ir}{-}C^4)]$ (R = CO_2Me) and Related Species

Although scarce,[35,39] metallacycloheptatrienes are very interesting organometallic species, which are implicated in the transition-metal-mediated cyclotrimerization of alkynes to yield benzene derivatives.[3,20] According to the commonly accepted mechanism for this process, these metallacycles can result from the insertion of an alkyne into a metallacyclopentadiene[40] and by filling, if necessary, the generated new vacant by an incoming $2e^-$ donor ligand.[41] Of course, the metal centre must not have any tendency to experience a reductive elimination under the reaction conditions or otherwise a benzenoid unit will be formed instead. Because of the high reactivity of the Tp^{Me2} iridacyclopentadienes described above and the inertness of these $Tp^{Me2}Ir^{III}$ species towards reductive elimination, this system has been shown to be especially well suited for the synthesis of iridacycloheptatriene derivatives. Some examples have already been commented on in previous sections.

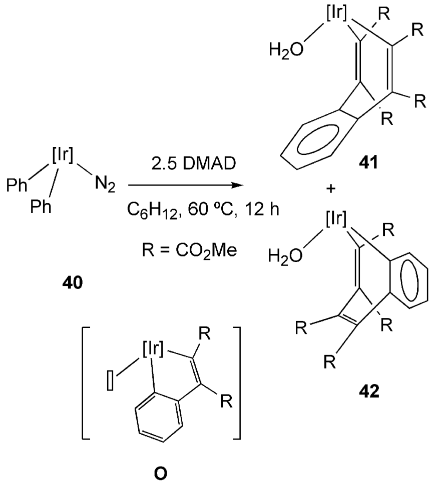
As already described, the reaction of the metallacyclopentadiene **16** with DMAD led to the irreversible formation of complex **31**, a very thermally stable iridacycloheptatriene with six CO_2Me substituents, which could also be prepared straightforwardly from the butadiene derivative **3** (Scheme 31).

Two related iridacycloheptatrienes had been obtained upon treatment of the dinitrogen complex $Tp^{Me2}IrPh_2(N_2)$ (**40**)[11] with excess DMAD.[32] The symmetrical and unsymmetrical benzoannelated iridacycloheptatrienes **41** and **42** are clearly the result of the coupling, with different regioselectivities, of 2 molecules of DMAD and formally "C_6H_4" (benzyne) in the Ir coordination sphere. This reaction seems to proceed through the intermediacy of an unsaturated, benzoiridacyclopentadiene **O**, which has very recently been successfully trapped as the NCMe adduct when the reaction was carried out with di-*tert*-butylacetylene dicarboxylate (Scheme 32).[42]

It is important to point out that structures related to **41** and **42** were proposed years ago[43] as intermediates in the reaction of $CrPh_3(THF)_3$ with 2-butyne to give naphthalene

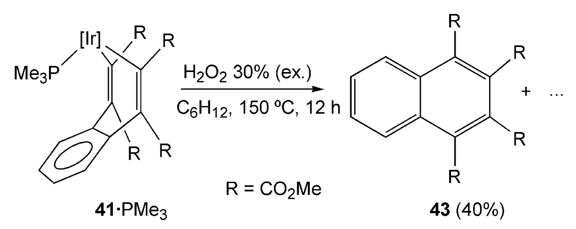


Scheme 31.



Scheme 32.

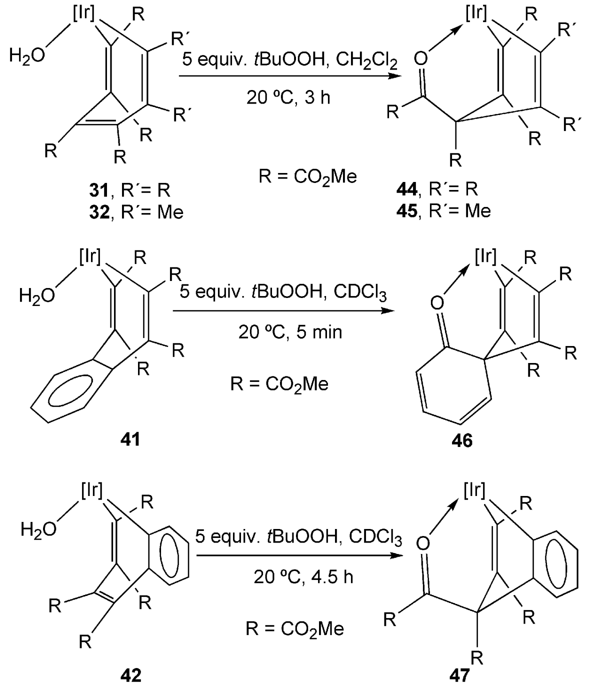
derivatives. As anticipated, derivatives **41** and **42** were very reluctant to reductive elimination. In spite of that, the PMe_3 adduct of **41** provided the corresponding naphthalene derivative under rather forced oxidative conditions (Scheme 33).



Scheme 33.

Reactivity of the Iridacycloheptatrienes

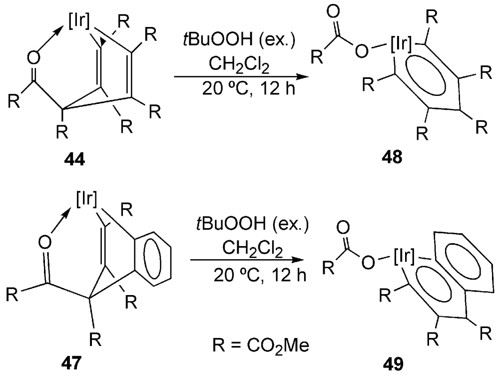
The most interesting reaction of complexes **31**, **32**, **41** and **42** was the oxidation that took place when any one of these metallacycles were subjected to the action of oxygen, or other oxidizing reagents, to give species **44**–**47**. In the case of the formation of **46**, it is important to highlight the loss of aromaticity of the benzenoid ring. In every case, ketone derivatives were formed, as shown in Scheme 34, which specifically indicates the conditions required when *t*BuOOH was employed as the oxidant. These reactions needed heating at 60 °C to proceed with 2 bar of molecular oxygen, although very recently it has been shown that the complexes related to **41** and **42** that contain CO_2tBu substituents are easily oxidized in air at room temperature, which indicates that the coordinated water is much more easily displaced in these bulkier derivatives.



Scheme 34.

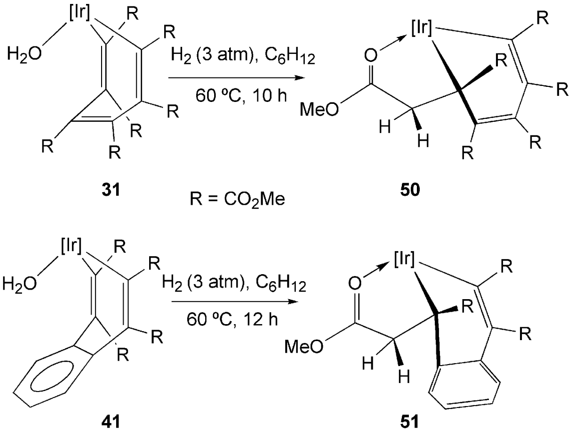
The oxidized species **44**–**47**, once isolated, were very thermally stable, and their solutions in C_6H_{12}, in the absence of O_2, could be heated up to 150 °C without evident decomposition. However, these oxidation reactions have to be carefully monitored as overoxidation with *t*BuOOH can take place. In fact, for iridacycloheptatrienes **31** and **42**, reaction with *t*BuOOH did not stop with the formation of complexes **44** and **47**, as a clean overoxidation was observed with the formation of complexes **48** and **49** (Scheme 35). These latter species are unusual metalla-aromatic species in which the coordination sphere of the iridium centre is completed with a methyloxalate ligand. Both complexes **48** and **49**, together with other iridabenzene derivatives in the Tp^{Me2} system, will be discussed in the next section, but it is worthy to remark at this point that complex **49** represented the first example of a transition-metal metallanaphthalene.

In an attempt to induce the rupture of one, or both, of the Ir–C bonds in the iridacycloheptatriene derivatives **31** and **41**, their hydrogenation was studied, and the clean formation of iridacyclohexadienes **50** and **51** observed (Scheme 36). They were the result of two hydrogen atoms being added to one of the C_α atoms with concomitant ring contraction of the metallacycle. The water ligand was no longer present, and coordination of the ester group of the

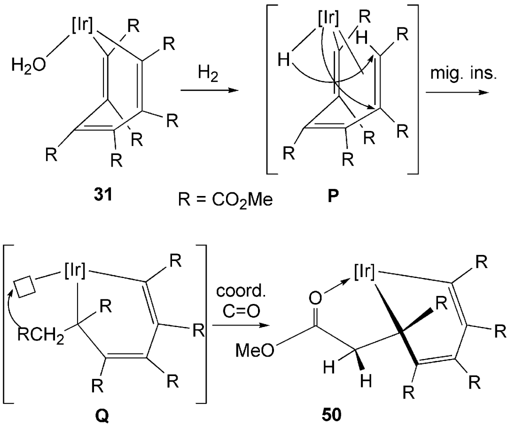


Scheme 35.

pending CH_2CO_2Me substituent completed the metal 18e$^-$ count. These reactions may, in fact, proceed by the initial hydrogenation of an Ir–C bond, but they further evolve, probably by the sequence of steps illustrated in Scheme 37 for the transformation **31**→**50**, to yield the observed products.



Scheme 36.



Scheme 37.

Generation and Reactivity of Benzenoid Iridacycles

Since 1982 when Roper et al. described the first stable and isolable osmabenzene,[44] a number of different metallabenzenes[45] have been prepared,[46] but the last decade has shown an increasing interest in this type of species, as new aromatic topologies as well as new versatile synthetic procedures have been reported. Our Tp^{Me2}-containing benzenoid compounds (Figure 4) have all been prepared in a serendipitous manner, and they can be grouped by the method of formation:

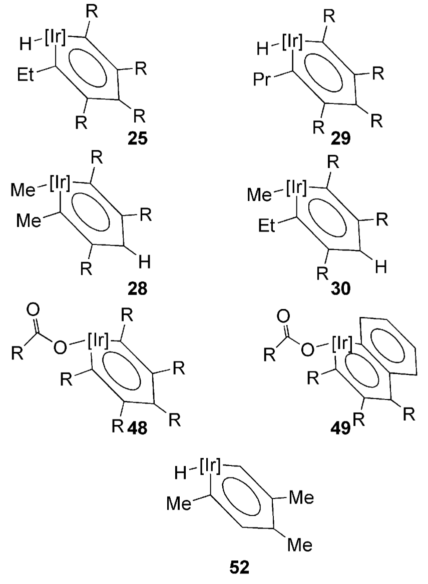


Figure 4. Iridaaromatics found in the Tp^{Me2}Ir system.

(i) Compounds **25**, **28**, **29** and **30** were synthesized by the coupling of iridacyclopentadienes with olefins, a process that might be considered an interesting variation of the formal [2+2+1] alkyne cyclization already described.[47] Interestingly, the reaction outcome depended strongly on the substitution pattern of the five-membered metallacycle and the nature of the olefin (propene and 1-butene are efficient as metallabenzene generators, while ethylene yielded only products derived from the 1,2-insertion of the olefin into the Ir–C bonds). (ii) The aromatic iridacycles **48** and **49** were obtained upon the oxidation with *t*BuOOH of two different chelating ketone complexes (see Scheme 35). Higher homologues of metallabenzenes were unknown until **49** was isolated, and they are still very rare; only last year a second metallanaphthalene was described in the literature, an osmanaphthalene, which transforms into an osmanaphthalyne, thus representing the first example of conversion of a metallabenzene into a metallabenzyne.[48] (iii) Finally, another iridabenzene **52**, which has not been commented on in this review was formed by an acid-catalyzed migratory insertion of a vinylidene ligand into a Tp^{Me2}-iridacyclopentene derivative.[38]

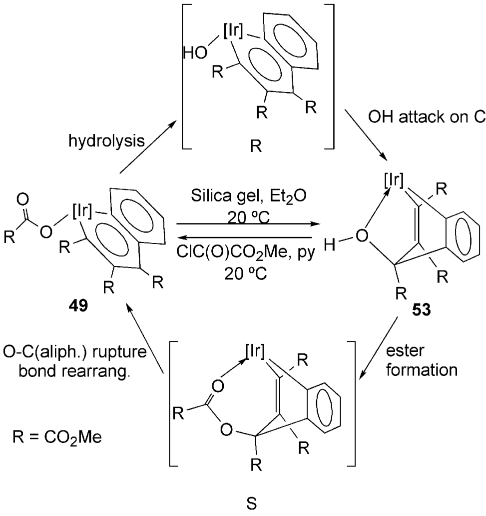
Because it had been predicted that π donors, especially those *ortho* and *para* to the metal, would stabilize aromatic metallacycles,[49] iridanaphthalene **49** and iridabenzenes **25**, **28**, **29**, **30**, **48** were unexpected in view of the presence of a considerable number of electron-withdrawing substituents on the ring, namely CO_2Me. They were the first examples of metalla-aromatic species substituted with electron-withdrawing groups. A number of metallabenzenes have been synthesized with π donors *ortho* to the metal fragment.[44,50] Other examples of metallabenzenes bearing electron-withdrawing groups include the phosphonium-substituted osmabenzenes and ruthenabenzenes reported by Jia et al.,[51] but these moieties are located at the less influential *meta* positions.

Structural features of aromaticity are ring planarity and π-bond delocalization. Usually metallacycles have planar or nearly planar structures, and delocalization of the π electrons is evidenced by C–C bond lengths in the central ring that are very similar and range between single and double C–C bonds and by M–C bond lengths that are intermediate between those corresponding to typical single and double bonds. For the case of the irida-aromatics described in this section, delocalization along the rings was also inferred from the structural data, although their values are not commented on in detail here. NMR spectroscopic data also supported this fact, since the corresponding ^{13}C NMR signals for the Ir–C nuclei were shifted to low fields, between 200–280 ppm [with the exception of the benzenic C atom bound to iridium (without the R substituent) of compound **49**, whose chemical shift is 177.9 ppm].

The bulkiness of the metal fragment often distorts the six-membered ring from planarity,[32,52] and this also the case for these irida-aromatics, for which the iridium atom lies between 0.50 and 0.76 Å out of the plane defined by the five carbon atoms. Subtle electronic factors may also contribute to this deviation.[53]

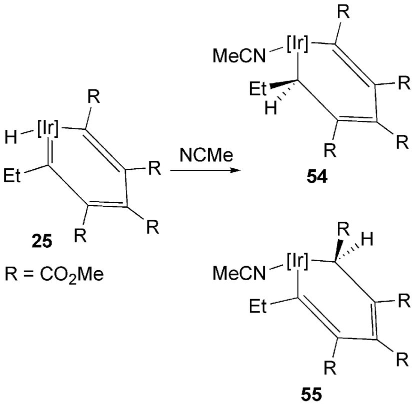
With regard to the reactivity of metallabenzenes, and owing in part to the reactivity of the metal centres, some electrophilic aromatic substitutions have been reported only occasionally.[45a,54] Other reactions in support of the aromatic character of these type of compounds have been the formation of arene-coordinated complexes.[55] Both types of reactions are, in general, hardly feasible in the case of our irida-aromatics, because of the substitution pattern and the bulkiness of the ring environment. Nevertheless, a somewhat sophisticated reaction came to support the aromatic nature of some of these compounds.

Column chromatography of complex **49** on silica gel resulted in the hydrolysis of the ester ligand, with loss of the metalla-aromaticity, to yield the bicyclic compound **53** that contains a tertiary alcohol functionality O-bonded to the Ir^{III} centre. Scheme 38 shows this transformation along with a plausible mechanism involving an intermediate hydroxy complex, which subsequently experiences an intramolecular nucleophilic attack of the OH at the C_γ atom of the iridanaphthalene ring to finally result in complex **53**. This last compound can be viewed as a kind of internal neutral Jackson–Meisenheimer complex,[56] and its formation supports the aromaticity of the iridanaphthalene **49**. Interestingly, this transformation could be reversed, and the reaction of **53** with the acid chloride $ClC(=O)CO_2Me$ in the presence of pyridine gave back **49**, which demonstrates the plausibility of the proposed mechanism.



Scheme 38.

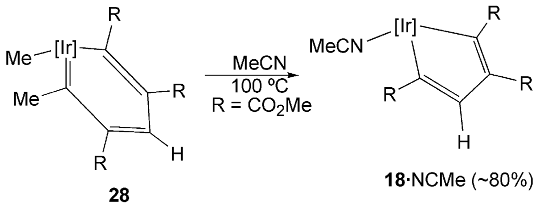
Finally, we have also studied the reaction of some of these iridabenzenes with NCMe at room temperature. The hydride **25** reacted in an expected way,[57] with migration of this ligand to both α-carbon atoms to form a kinetic mixture of adducts (Scheme 39) that slowly evolved to the thermodynamically favoured isomer **55**, probably through **25**. Compound **54** represents the NCMe adduct of the probable intermediate formed, before generation of **25**, in the reaction of iridacyclopentadiene **16** and propene (see Scheme 22).



Scheme 39.

More unpredictable (or less predictable) was the reaction of NCMe with the iridabenzene **28**, which contains a Me ligand. This reaction required heating at 100 °C to proceed and produced the fragmentation of the ring, with liberation of propene and regeneration of the original iridacyclopentadiene, isolated as the NCMe adduct **18**·NCMe (Scheme 40).

As can be observed, acetonitrile destroyed the aromatic integrity of both compounds **25** and **28** by different routes; **25** underwent hydride migration to the two α-carbon atoms, and **28** gave rise to the elimination of propene, which shows the reversibility of the C–C bond formation that yields **28**.



Scheme 40.

Conclusions

The synthesis and reactivity of Tp^{Me2}-containing iridacyclopentene, -pentadiene, -heptadiene, -heptatriene, and -benzenoid derivatives have been described. Upon recognizing the incredibly ample scope and tolerance of modern organic reactions to the presence of different substituents and/or functionalities, it is surprising the variability of reactivities we have found in simple metallacycle chemistry, thus proving that our knowledge of chemical reactivity is very far from satisfactory, and inspiring our interest in continuing research.

Acknowledgments

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