Regioselective Formation of β-Alkyl-α-phenyliridabenzenes via Unsymmetrical 3-Vinylcyclopropenes: Probing Steric and Electronic Influences by Varying the Alkyl Ring Substituent**

He-Ping Wu, Timothy J. R. Weakley, and Michael M. Haley*[a]

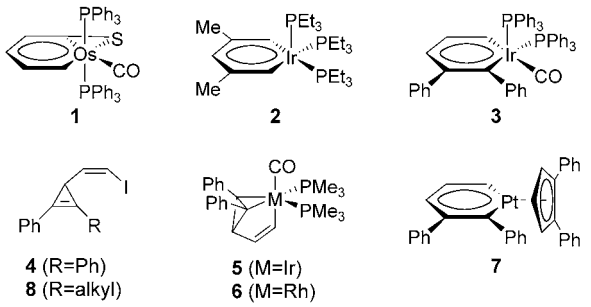
Dedicated to Professor Armin de Meijere on the occasion of his 65th birthday

Abstract: The synthesis of unsymmetrical (*Z*)-1-alkyl-3-(2-iodovinyl)-2-phenyl-1-cyclopropenes (R = Me (**8a**), Et (**8b**), *i*Pr (**8c**), and *t*Bu (**8d**)) and their reactions with Vaska's complex $[Ir(CO)Cl(PPh_3)_2]$ and its trimethylphosphine analogue $[Ir(CO)Cl(PMe_3)_2]$ were investigated. Iridabenzvalene (**13**/**20**), iridabenzene (**14**/**21**), and/or η^5-cyclopentadienyliridium complexes (**15**/**22**) were obtained in modest yields and were fully characterized by spectroscopic means. X-ray structural data was secured for iridabenzvalene **13d** and iridabenzenes **14a,b,d**. Whereas iridabenzenes **14a–c** were stable at 75 °C for 48 h, **14d**, which possesses a bulky *t*Bu group, rearranged cleanly to cyclopentadienyliridium **15d** at 50 °C over 15 h and displayed first-order kinetics. The influence of the alkyl substituent on the mechanisms of iridacycle generation, isomerization, and iridabenzene regioselectivity is discussed.

Keywords: aromaticity · iridium · metallacycles · strained molecules · valence isomerization

Introduction

Metallabenzenes are a rare class of aromatic molecules where a transition metal fragment (ML_n) has replaced one of the benzene methine (CH) units.[1] Although more than two dozen such structures have been prepared over the last 20 years or so, most examples have been stabilized by inclusion of a heteroatom (O,N,S) or by η^6-coordination to a second transition metal fragment. Until recently, only two families of discrete metallabenzenes were known, namely Roper's osmabenzenes (e.g., **1**)[2] and Bleeke's iridabenzenes (e.g., **2**);[3] nonetheless, all investigations into both families originated from compounds **1** and **2**, respectively. Very recent work on osmabenzenes[4] and irida-aromatic compounds[5] has provided a few additional examples; however, the generality of these methods has yet to be determined. Therein lies a key difficulty within this field of research: lack of versatile synthetic routes has meant that detailed, fundamental study of metallabenzenes has been problematic.



We recently reported the preparation of a third family of metallabenzenes (e.g., **3**) using 3-vinyl-1-cyclopropenes (e.g., **4**) as the source of the metallabenzene ring carbon atoms.[6] Unlike previous syntheses, this new method allows us to rationally alter variables (metal center, ligands on the metal, substituents on the C_5 backbone) to perform detailed structure–property relationship investigations. We believe such augmented studies are now possible since: 1) our route permits direct access into the metallabenzene manifold. There is no need for subsequent oxidative and/or reductive transformation(s) of the resultant organometallic species. If the metallabenzene does not form initially, simple heating iso-

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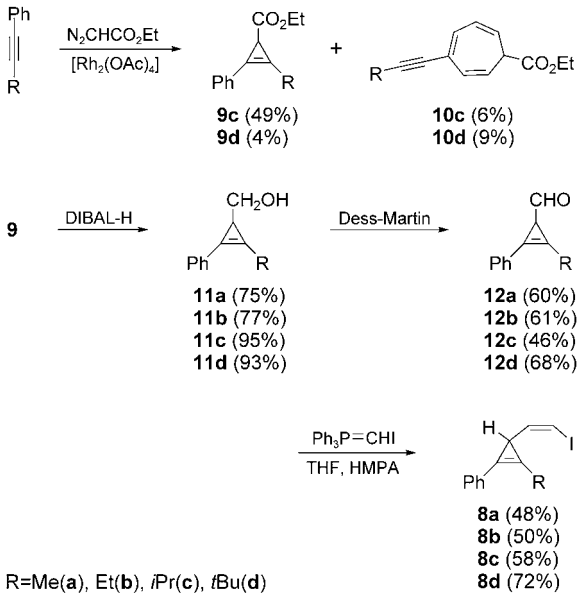
merizes the intermediate benzvalene (e.g., **5**).[7] 2) This route permits the use of a variety of starting transition metal complexes. In addition to iridabenzenes, we have very recently extended our methodology to examples containing Rh (**6**)[8] and Pt (**7**);[9] thus, this appears to be the first general pathway to metalla-aromatic formation. 3) Depending upon the vinylcyclopropene used as the C_5 backbone, a variety of substituted metallacycles,[10] previously inaccessible substitution patterns, and new metalla-aromatic topologies should become available. As an extension of our previous studies, and to elaborate further on point 3, we report herein the synthesis of several (*Z*)-1-alkyl-2-phenyl-3-(2-iodovinyl)-1-cyclopropenes (e.g., **8**) and their reactivity with Vaska's complex and its PMe_3 analogue, resulting in regioselective iridabenzene formation. We also discuss the isomerization and kinetic behavior of the resultant iridabenzvalenes and benzenes, and probe the mechanism of their interconversion by fine-tuning the alkyl substituents.

Results and Discussion

Ligand synthesis: Preparation of vinylcyclopropenes **8** was achieved by the route depicted in Scheme 1. By using the same procedure that previously produced **9a**[11] and **9b**,[12]

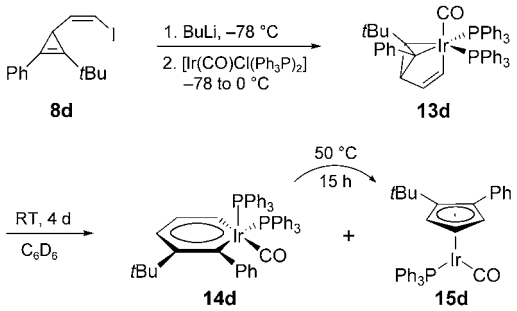


Scheme 1.

$[Rh_2(OAc)_4]$-catalyzed addition of ethyl diazoacetate to either isopropyl- or *tert*-butylphenylacetylene yielded the [2+1] cycloadducts **9c** and **9d**,[13] respectively. Interestingly, the bulky alkyl groups on the starting alkynes result in competitive carbene insertion into the benzene ring, as demonstrated by the isolation of ethyl 4-isopropyl- or 4-*tert*-butylethynyl-2,4,6-cycloheptatrien-1-yl carboxylate (**10c,d**).[14] The *tert*-butyl/phenyl derivative appears to be the upper limit of the carbene addition route as the analogous reaction failed to furnish the cyclopropene ester from di-*tert*-butylacetylene. The very low yield of **9d** is somewhat disappointing as it was hoped that the more reactive $[Rh_2(OAc)_4]$ catalyst would be superior to $CuSO_4$, the originally utilized catalyst;[13] instead, the yields of isolated material were comparable.

Reduction of esters **9** with excess DIBAL-H[15] afforded alcohols **11** in 75–95% yield. Unfortunately, use of equimolar amounts of DIBAL-H gave mixtures of the desired aldehyde **12** product along with alcohol **11** and unreacted starting material. Oxidation of **11** with the Dess–Martin reagent[16] afforded reasonable yields of aldehydes **12** as moderately stable oils. The notable exception was **12a**, where the crude isolated material was immediately subjected to the Wittig reaction because of its rather high instability. Use of $Ph_3P{=}CHI$[17] gave the vinylcyclopropenes **8** in 48–72% yield with high (>15:1 *Z*:*E*) stereoselectivity. Similar to **4**, ligands **8** can be prepared in 750 mg–1 g quantities; however, the molecules are somewhat unstable and should be stored in the dark at −20°C with a small amount hydroquinone to inhibit decomposition.

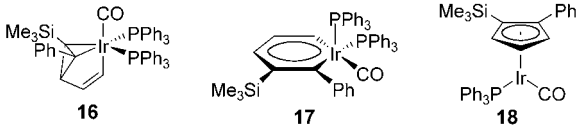
Reactions with Vaska's complex $[Ir(CO)Cl(PPh_3)_2]$: Treatment of ligand **8d** with BuLi at −78°C followed by addition of Vaska's complex produced a yellow-orange solution upon warming over 3 h from −78 to 0°C, from which iridabenzvalene complex **13d** could be isolated in 32% yield (Scheme 2). Purification of **13d** was achieved by recrystallization in toluene/cyclohexane. Although stable in the solid state, solutions of **13d** in C_6D_6 at 20°C immediately began to isomerize to an iridabenzene. After four days at 20°C, the ^1H NMR spectrum indicated that **13d** had disappeared completely to afford a mixture of iridabenzene **14d** and cyclopentadienyliridium complex **15d** in a ratio of about 3:1 in 94% combined yield. The regiochemistry of **14d** as the β-*tert*-butyl isomer was confirmed by crystallographic analysis (vide infra); the α-*tert*-butyl regioisomer was not detected in the transformation. We believed initially that **15d** was most likely derived from the thermally unstable α-regioisomer by ring contraction via "carbene migratory insertion",[18] a reac-



Scheme 2.

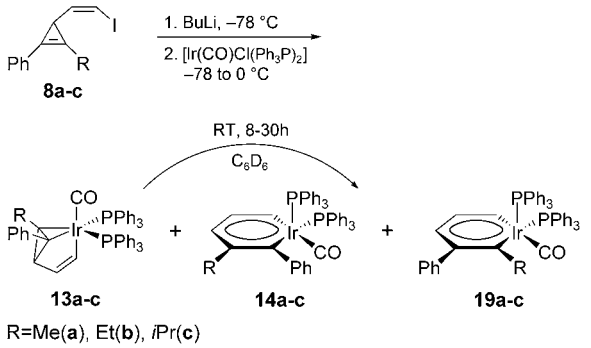
tion facilitated by the steric hindrance between the bulky *t*Bu and $[Ir(CO)(PPh_3)_2]$ moieties. To test this hypothesis, solutions of both **14d** and benzvalene **13d** in C_6D_6, respectively, were prepared and the kinetic conversion processes monitored by ^1H NMR spectroscopy under the same reaction conditions. The data showed that at 20°C **14d** rearranged into **15d** and that the rate of transformation of **14d** into **15d** was faster than that of **13d** to **15d**. These experimental results suggest that the initially formed **15d** was predominantly from the rearrangement of β-*tert*-butyl regioisomer **14d** and not from the corresponding α-isomer; therefore, the valence isomerization of unsymmetrical benzvalene **13d** to benzene **14d** appears to be highly regioselective. At 50°C for 15 h, **14d** rearranged quantitatively to **15d** with dissociation of PPh_3; however, the rearrangement could be inhibited by addition of two equivalents of PPh_3 prior to heating. In this latter case, complete transformation to **15d** took about 50 h.

Comparison of the above results with those generated from the reactions with cyclopropene **4** and the phenyl/trimethylsilyl analogue reveal some interesting trends. With Vaska's complex, the stability of the resultant iridabenzvalenes is influenced mainly by electronic donation of the substituents on the cyclopropyl ring. In the case of **13d**, its stability in solution is intermediate between the diphenyl (not detected at 20°C)[6] and phenyl/trimethylsilyl (**16**, stable for several days at 20°C)[10] systems, which is in agreement with intermediate electron donation of *t*Bu between Ph and $SiMe_3$ groups. Electron donation of the alkyl group increases



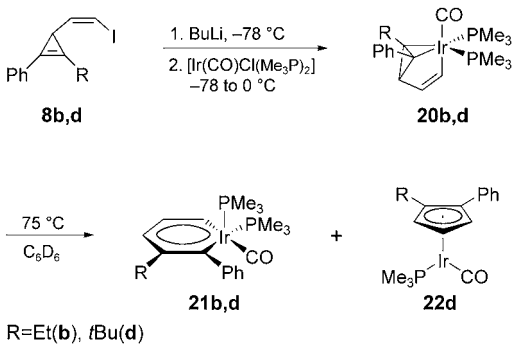
the electron density of cyclopropene double bond, which in turn strengthens the η^2-cyclopropene interaction with the iridium center. On the other hand, the contiguous arrangement of the iridium fragment and neighboring phenyl group with the bulky *t*Bu and $SiMe_3$ substituents destabilizes the resultant iridabenzene compounds. Whereas solutions of **3** are stable at 100°C over 24 h,[6] and the β-trimethylsilyl benzene **17** (stable at 20°C) rearranges to cyclopentadienyl complex **18** at 75°C over 24 h,[10] **14d** converts to **15d** even at 20°C. This difference between **14** and **17** is likely due to closer proximity of the *t*Bu group, a result of the shorter C–C bond compared to a C-Si bond (1.52 versus 1.85 Å, respectively).

Reactions of Vaska's complex with cyclopropenes **8a–c** showed the influence of alkyl substituent on both the formation of **13** and its transformation to **14** (Scheme 3). All three reactions yielded yellow solutions below 0°C, which then turned red-brown upon warming to 20°C. ^1H NMR spectroscopy showed that each crude reaction mixture was composed of the corresponding iridabenzvalene and iridabenzene. Benzvalene compounds **13a–c** were not isolated from the reaction mixture because of their relatively rapid isomerization to **14a–c**, which were isolated in about 25–30% yield. After 8 h and 30 h at 20°C in C_6D_6 solution, **13a,b** and **13c**, respectively, had isomerized completely to give **14a–c** as well as very minor amounts of the α-alkyl regioisomer **19a–c**, as detected by NMR spectroscopy of the crude reaction mixtures. Unlike **14d**, Ar-blanketed solutions of **14a–c** were stable for over 48 h at 75°C. These results suggest a trend of iridabenzvalene stability as **13a** = **13b** < **13c** < **13d**, which is in agreement with increasing electronic donation. Somewhat surprising is the independence of the stability of **13** from alkyl group sterics. On the other hand, iridabenzene stability is ordered as **14a** = **14b** > **14c** > **14d**, which is now in agreement with increasing alkyl sterics.



Scheme 3.

Reactions with $[Ir(CO)Cl(PMe_3)_2]$: Although PMe_3 ligands are known to stabilize iridabenzvalenes by stronger electronic donation compared to PPh_3,[6b,7] we wanted to examine how the decreased sterics of the $[Ir(CO)(PMe_3)_2]$ fragment influenced both the regioselectivity of isomerization of unsymmetrical benzvalene compounds and the stability of the resultant benzene compounds. Reaction of cyclopropenes **8b,d** with $[Ir(CO)Cl(PMe_3)_2]$ at −78 to 0°C over 3 h yielded the corresponding benzvalenes **20b,d** as the only product (Scheme 4). Both complexes were purified by recrystallization in hexane at −30°C and are stable at 20°C. Isomerization was observed at higher temperatures, with **20b** completely converting to β-ethyl regioisomer **21b** at



Scheme 4.

75 °C over 4 h. Under the same conditions, however, *t*Bu analogue **20d** gave a mixture composed of unreacted benzvalene, benzene **21d**, and cyclopentadienyliridium complex **22d** in a ratio of 5:10:1, as well as partial decomposition. Prolonged heating of this mixture led to complete decomposition affording unidentified materials. Interestingly, we never observe evidence for formation of the α-regioisomer of **21**, even in the NMR spectra of the crude reaction mixtures; thus, the lower sterics of PMe_3 than PPh_3 does not decrease the regioselectivity of the isomerization. The influence of the Et and *t*Bu substituents on the stability and isomerization rate of **20** is similar to that observed for corresponding PPh_3 analogs **13**. Additionally, the higher stability of the β-*t*Bu substituted **21d** compared to the corresponding PPh_3 analogue **14d** indicates that the PMe_3 ligand does stabilize the iridabenzene. Nevertheless, we have no definitive conclusions on this steric/electronic influence.

Iridabenzvalene characterization: In the ^{1}H NMR spectra of **13** and **20**, a characteristic broad signal around $\delta = 3.2$ ppm is assigned to the proton resonance of the sp^3-C*H* fragment (H3). Two complex multiplets in the ranges of $\delta = 6.05$–6.45 (H4) and 6.72–7.17 ppm (H5) are attributed to the two sp^2-C*H* groups of the bridging double bond, with the latter signal being the CH attached to the metal center. The ^{13}C NMR spectra of the benzvalenes show significant upfield shifts of the resonances for the coordinated cyclopropene double bond atoms C1 and C2, compared to the corresponding uncoordinated carbon atoms, which is commonly observed in olefin η^2-metal complexes. For example, in **20b** the resonances for C1/2 are at $\delta = 65.88$ and 71.03 ppm, versus $\delta = 110.89$ and 117.90 ppm, respectively, in **8b**. The lack of symmetry in the benzvalenes leads to a more complicated pattern of C–P couplings than in our previous work. In **20b**, coupling of the two *cis*-PMe_3 to C6 in the CO ligand and to C5 results in two triplets with coupling constants of 7.6 Hz and 15.1 Hz, respectively. Coupling of the *cis*- and *trans*-PMe_3 to C1 and C2 furnish two doublet of doublet signals with coupling constants of 72.5/4.0 and 70.5/3.0 Hz, respectively. The lack of symmetry is also exhibited in the ^{31}P NMR spectrum by the appearance of two doublets at $\delta = -0.09$ and -3.92 ppm. The absorption band of the CO group in **20b** was observed at 1966 cm^{-1} in the IR spectrum.

The structure of benzvalene **13d** was further confirmed by single crystal X-ray diffraction. Selected bond lengths and angles are given in Figure 1. The Ir atom of **13d** has a torsion trigonal-bipyramidal coordination configuration composed of carbonyl, η^2-cyclopropene double bond, two phosphine, and σ-vinyl ligands around the Ir atom. Comparison of key bond distances and bond angles with data for known benzvalenes **5**[7] and **23**[6b] (Table 1) shows that the Ir–C1 and Ir–C2 bond lengths of **13d** (2.189, 2.220 Å) are considerably longer than that in its analogues. Furthermore, the shorter C1–C2 bond length and smaller C1-Ir-C2 bond angle and Ir-C1-C2-C3 dihedral all suggest that the η^2-interaction of the cyclopropene π-bond with the Ir center in **13d** is weaker than in the analogues shown in Table 1. This

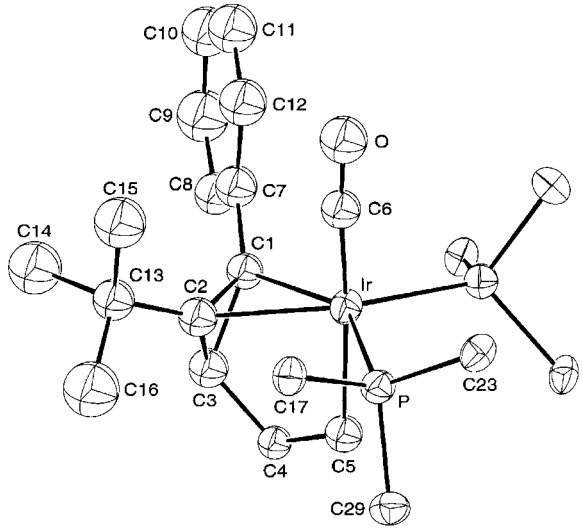
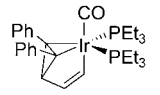


Figure 1. Molecular structure of iridabenzvalene **13d**. The thermal ellipsoids are drawn at the 30% probability level. Only the *ipso*-PPh_3 carbon atoms are shown for clarity. Selected bond lengths [Å] and bond angles [°]: Ir–P 2.353(3), Ir–C1 2.19(2), Ir–C2 2.22(2), Ir–C5 2.18(3), Ir–C6 1.73(2), C1–C2 1.41(3), C1–C3 1.56(3), C1–C7 1.47(3), C2–C3 1.57(3), C2–C13 1.49(3), C3–C4 1.40(3), C4–C5 1.38(4); P-Ir-Pi 110.4(1), P-Ir-C2 136.4(5), Pi-Ir-C1 146.6(5), C1-Ir-C2 37.1 (6), C5-Ir-C6 174(1), C1-Ir-C5 81.5(8), C2-Ir-C5 80.4(8), C3-C1-C7 130(2), C3-C2-C13 129(2), C1-C3-C2 54(1), C3-C4-C5 115(2), C4-C5-Ir 111(2).

Table 1. Selected X-ray bond lengths [Å] and bond angles [°] for iridabenzvalenes **5**, **13d**, and **23**.

	5	**23**	**13d**
Ir–C1	2.146	2.172	2.189
Ir–C2	2.143	2.159	2.220
Ir–C5	2.095	2.092	2.184
C1–C2	1.447	1.440	1.405
C1-Ir-C2	39.4	38.8	37.1
C5-Ir-C6	178.9	177.2	174.0
P-Ir-P	104.1	109.4	110.4
dihedral	116.3	116.2	109.9



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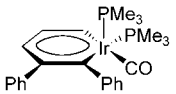

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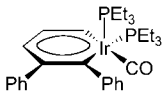

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weaker bonding is corroborated by the fact that **13d** isomerizes at room temperature to **14d**, whereas benzvalene compounds **5** and **23** similarly are stable (vide supra).

Iridabenzene characterization: The spectroscopic data of **14** and **21** resemble those for known iridabenzenes **3** and **17** with respect to chemical shifts and signal patterns.[6,10] The low-field *pseudo*-quartet in the characteristic range of $\delta =$ 10.5–11.0 ppm is assigned to H5, the proton *ortho*- to the Ir center. This dramatic downfield shift for H5 can be attributed mainly to the magnetic anisotropic effect of the heavy metal on the neighboring proton, an effect that attenuates

Table 2. Selected NMR chemical shift data for iridabenzenes.[a]

Cmpd	H3	H4	H5	C1	C2	C3	C4	C5	C6
14a	8.30	7.75	10.62	187.46	140.47	133.93	129.07	183.92	204.97
14b	8.29	7.79	10.61	187.31	140.84	139.99	129.48	184.95	204.17
14c	8.41	7.86	10.60	187.65	145.52	–[b]	129.85	185.52	203.90
14d	8.69	7.83	10.54	186.68	145.61	138.89	129.63	186.55	208.32
3	8.44	7.79	10.79	187.60	141.93	139.99	127.76	187.43	201.09
21b	8.13	7.90	10.92	188.83	138.55	135.38	129.70	174.20	181.02
21d	8.46	7.88	10.87	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]
24	8.25	7.91	11.00	189.95	141.49	136.74	129.06	176.04	189.44

[a] All data acquired in C_6D_6. Assignments based on 2D ^1H–^1H COSY and 2D ^1H–^{13}C HMQC and HMBC experiments. Atom labeling as shown in Figure 2. [b] Resonance obscured. [c] Inseparable mixture of **20d**, **21d**, and **22d** and also decomposition products precluded accurate assignment of resonances.

significantly with increasing distance.[19] The *para*- and *meta*-protons on the iridabenzene rings resonate in the range of $\delta = 8.7$–8.1 ppm and $\delta = 7.9$–7.7 ppm, respectively, values that are closer to normal resonances caused mainly by aromatic ring currents. A summary of the NMR chemical shifts for the ring proton/carbon atoms in both iridabenzenes **14** and **21** as well as comparison with related systems **3** and **24** are given in Table 2. Replacement of PPh_3 with PMe_3 on the iridium center leads to an upfield shift of the C3 ($\Delta\delta = 5.5$ ppm), C5 ($\Delta\delta = 10.8$ ppm), and C6 ($\Delta\delta = 23.2$ ppm) atom resonances, respectively, which can be rationalized in the terms of electronic influences. The stronger donating ability of PMe_3 compared to PPh_3 results in a more electron-rich metal center, which in turn increases the electron density of benzene ring and thus the upfield carbon shifts. On the other hand, small shifts for C1 ($\Delta\delta = 1.5$ ppm), C2 ($\Delta\delta = 1.4$ ppm), and C4 ($\Delta\delta = 0.2$ ppm) were observed, indicating the lack of sensitivity of these carbon atoms. The ^{31}P NMR spectra show a single resonance for the two phosphine ligands in the region of $\delta = 18.5$ ppm (PPh_3) and $\delta = -38.6$ ppm (PMe_3), respectively, due to rapid exchange between axial and basal phosphine ligands in solution at 20 °C.[3,20] The vibration frequency of CO group in iridabenzenes falls in the range between 1892–1982 cm^{-1}.

Confirmation of the structures of iridabenzenes **14a**,**b**,**d** was provided by single-crystal X-ray diffraction. The molecular structure of **14d** is shown in Figure 2 along with key bond lengths and angles. Comparison of the bond lengths and angles of complexes **14a**,**b**,**d** with analogues **3** and **25** is given in Table 3. The X-ray analyses verify that the alkyl groups on all three metallacycles are indeed at the β-position to the Ir center, in agreement with the spectroscopic assignment. The C–C bond lengths in the metallacycles are essentially equal and thus can be regarded as evidence of delocalization of the aromatic ring π electrons. The mean C–C bond lengths are extremely close—1.387 Å (**14a**), 1.389 Å (**14b**), and 1.386 Å (**14d**). The Ir–C1 and Ir–C5 bond lengths in **14a**,**b**,**d** average around 2.02 Å and are intermediate between Ir–C single and double bonds. The ring of every iridabenzene is almost planar with mean deviations of 0.011 Å (**14a**), 0.008 Å (**14b**), and 0.009 Å (**14d**). Contrary to our expectations based on reactivity, the bulky *t*Bu group does not induce greater torsion strain in the iridabenzene ring of **14d**, at least not in the solid state.

Mechanisms for iridabenzvalene formation/isomerization: The proposed mechanisms for iridabenzvalene isomerization/benzene formation have been discussed at length previously;[6b,7] thus, only salient points will be presented herein. Benzvalene formation continues to appear to be influenced preferentially by electronic factors.

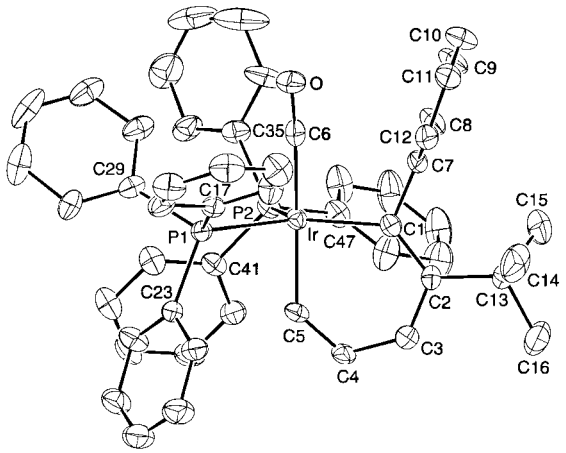


Figure 2. Molecular structure of iridabenzene **14d**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and bond angles [°]: Ir–P1 2.348(2), Ir–P2 2.306(3), Ir–C1 2.054(9), Ir–C5 2.000(9), Ir–C6 1.911(11), C1–C2 1.407(12), C2–C3 1.382(13), C3–C4 1.427(12), C4–C5 1.343(12), C1–C7 1.490(12), C2–C13 1.554(13); P1-Ir-P2 105.61(9), P1-Ir-C1 137.5(2), P2-Ir-C1 116.5(2), C5-Ir-C6 172.1(4), C1-Ir-C5 87.4(4), C1-Ir-C6 91.4(4), Ir-C1-C2 130.8(7), Ir-C1-C7 109.6(6), C1-C2-C3 119.5(9), C1-C2-C13 125.7(8), C2-C3-C4 128.2(9), C3-C4-C5 123.9(8), Ir-C5-C4 130.2(7), Ir-C6-O 174.1(8).

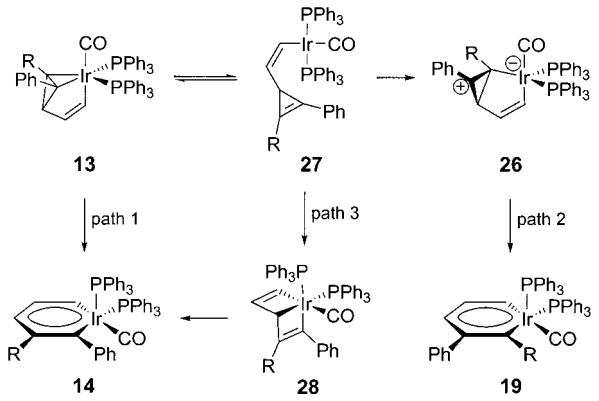
Table 3. Selected X-ray bond lengths [Å] and bond angles [°] for iridabenzenes **3**, **14a**, **14b**, **14d**, and **25**.

	14a	**14b**	**14d**	**3**	**25**
Ir–C1	2.020	2.029	2.054	2.021	2.047
Ir–C5	2.012	2.023	2.000	2.025	2.004
C1–C2	1.423	1.413	1.407	1.409	1.427
C2–C3	1.335	1.390	1.382	1.410	1.372
C3–C4	1.382	1.393	1.427	1.377	1.386
C4–C5	1.408	1.360	1.343	1.334	1.381
C1-Ir-C5	88.5	87.0	87.4	86.9	88.1
mean deviation	0.011	0.008	0.009	0.024	0.041

As mentioned above, the trend of iridabenzvalene stability for the PPh_3-containing cycles (**13a** = **13b** < **13c** < **13d** < **16**) is in agreement with increasing electronic donation of the cyclopropenyl substituents yet is seemingly independent of their steric effects.

The "valence isomerization" of **13** to **14** still presents several problems. Although a concerted process (path 1) is the

simplest explanation, and appears to be supported computationally,[21] this does not readily account for the strong preference for the β-regioisomer. If the isomerization were slightly less concerted, involving nucleophilic attack of the cyclopropene π-bond on the electron-deficient Ir center (path 2), this presumably should give favorable benzylic carbonium ion **26** (Scheme 5). Rearrangement of this stabilized



Scheme 5.

ion, however, would lead predominantly to **19**, that is, the wrong regioisomer. The remaining possibility (path 3) entails reversible dissociation of the η^2-cyclopropene in **13** to give σ-vinyliridium intermediate **27** (initially formed by nucleophilic substitution of Vaska's complex with the vinyl lithiate). Regioselective insertion of the iridium atom into the less-electron-rich C–C(Ph) σ bond leads to intermediate Dewar benzene **28**, which then affords iridabenzene **14** via rapid valence isomerization (relief of strain). In addition to these electronic factors, steric effects also appear to support path 3. Strong steric repulsion between the bulky *i*Pr/*t*Bu groups and the $[Ir(CO)(PPh_3)_2]$ fragment results in a "less efficient approach" of the iridium center to the C–C(R) bond in **27**, thus the observed decrease in the rate of valence isomerization. Detracting from this latter pathway has been our inability to isolate or even detect spectroscopically an irida-Dewar benzene complex such as **28**. It should also be noted that more than one of these pathways is possibly operational. Regardless of the exact mechanism(s) involved, isomerization of **13** to **14** and/or **15** is generally a clean, high-yield process.

Mechanism and kinetics for iridabenzene isomerization: Much more certain mechanistically is the conversion of metallabenzenes to cyclopentadienyl-metal complexes. Metallabenzenes have been implicated in a number of transformations which yielded Cp-metal complexes.[9c,22] Jones and Allison have observed the conversion of a transient ruthenabenzene to the corresponding Cp_2Ru complex using NMR spectroscopy at low temperature.[23] Our group recently reported the rearrangement of two trimethylsilyl-substituted iridabenzene isomers into the same cyclopentadienyliridium complex (**18**) at 75 °C.[10] Iridabenzene **14d** provided us with an opportunity to study the kinetics of this transformation. NMR spectroscopy was utilized to examine the kinetics of the rearrangement of **14d** at 313, 323, and 333 K, respectively (Figure 3). The relative concentrations of **14d** and **15d** in

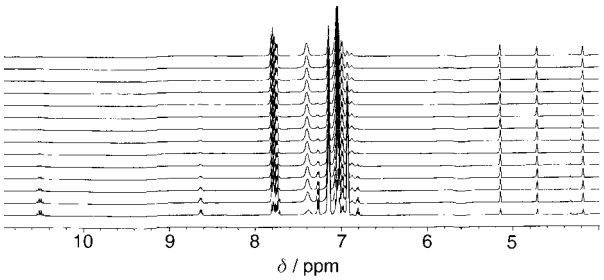
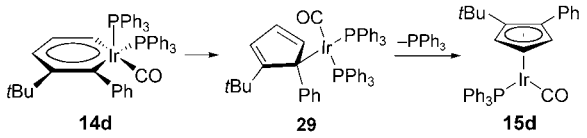


Figure 3. Time-evolved ^{1}H NMR spectra of the thermally rearrangement of **14d** to **15d** at 323 K in the C_6D_6. The bottom spectrum was recorded after heating for 1 h. The following spectra represent 2 h intervals with top spectrum corresponding to 27 h reaction time. For clarity, the signals from 0 to 4 ppm were omitted.

the course of the reaction were calculated based on the integration of their ring proton resonances in the ^{1}H NMR spectra. The rate constants of the reaction were determined by plotting $\ln[C]_i/[C]_o$ versus time. In every case, the data was linear, indicating first-order kinetics. The slopes of the lines were taken as the rate constants and were $(1.76\pm0.06)\times10^{-5}$, $(1.04\pm0.02)\times10^{-4}$, and $(3.76\pm0.16)\times10^{-4}\,s^{-1}$ at 313, 323, and 333 K, respectively. An Erying plot of the data from the rate measurements was linear and gave the following activation parameters: $\Delta H^{\neq}=31.2\pm1.9$ kcal mol^{-1}, $\Delta S^{\neq}=9.3\pm36$ cal K^{-1} mol^{-1}. These numbers are in good agreement with a recent computational study on the conversion of metallabenzene complexes to cyclopentadienyl-metal complexes.[21b,24]

The plausible mechanism for this transformation is shown in Scheme 6. Carbene migratory insertion[18,25] of **14d** leads



Scheme 6.

to formation of coordinatively unsaturated η^1-cyclopentadienyl intermediate **29**. Subsequent loss of PPh_3 yields energetically more stable η^5-cyclopentadienyliridium complex **15d**. It is reasonable to assume that the interaction of the contiguous *tert*-butyl substituent, phenyl group, and metal fragment may cause some degree of torsion in the metallabenzene ring in solution and thus lead to the observed carbene migration in **14d** and **21d**.

Conclusion

The reactions of unsymmetrical (*Z*)-1-alkyl-3-(2-iodovinyl)-2-phenyl-1-cyclopropenes **8a–d** with Vaska's complex produced initially iridabenzvalenes **13a–d**. Subsequent isomerization in a highly regioselective manner furnished α-phenyl-β-alkyl-iridabenzene complexes **14a–d**, as well as trace amounts of the β-alkyl-α-phenyl isomers **19a–c**. The α-phenyl-β-alkyl arrangement of the substituents was confirmed by X-ray crystallography for three of the iridabenzenes. Use of $[Ir(CO)Cl(PMe_3)_2]$ afforded benzvalene complexes **20b/d** and benzenes **21b/d**. The trend of the isomerization rate of alkyl-substituted benzvalene to benzene complexes is **13a** = **13b** > **13c** > **13d** > **20b** > **20d** that is in agreement with increase of both electronic donation and sterics of the alkyl group as well as electron donation and/or reduced sterics of the phosphine ligand. Whereas **14a–c** and **20b** were stable at 75 °C for 48 h, iridacycle **14d** possessing a bulky *t*Bu group was unstable and rearranged cleanly via carbene migratory insertion to cyclopentadienyliridium complex **15d** at 50 °C over 15 h and displayed first-order kinetics. Iridabenzene stability was ordered as **21b** > **14a** = **14b** = **14c** > **21d** > **14d** in agreement with a decrease of sterics of the alkyl group and as well as electron donation and/or less sterics of the phosphine ligand. Future work will focus on the preparation of irida-aromatics with different substituents, as well as reaction of cyclopropene ligands **8a–d** with additional transition-metal complexes. The results of these studies will be reported shortly.

Experimental Section

3-Methyl-1-phenyl-1-butyne,[26] 3,3-dimethyl-1-phenyl-1-butyne,[27] 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one,[16] iodomethyltriphenylphosphonium iodide,[17] and $[Ir(CO)Cl(PMe_3)_2]$[28] were prepared according to the literature. All other compounds were purchased from commercial suppliers and used as received. Column chromatography was performed on Whatman reagent grade silica gel (230–400 mesh). Manipulation of organometallic reagents was carried out using either a Vacuum Atmospheres inert atmosphere glove box or standard Schlenk techniques. THF, Et_2O, and hexanes were distilled from Na/benzophenone and C_6D_6 distilled from $LiAlH_4$. All dried solvents were degassed by three freeze/pump/thaw cycles prior to use. NMR spectra were recorded on a Varian Unity-INOVA 300 spectrometer at ambient temperature. ^1H, ^{13}C, and ^{31}P NMR spectra were acquired at 299.95, 75.43, and 121.42 MHz, respectively. Chemical shifts for ^1H and ^{13}C NMR spectra are reported in parts per million (δ) downfield from tetramethylsilane using the residual solvent signal ($CDCl_3$: ^1H 7.26, ^{13}C 77.00; C_6D_6: ^1H 7.16, ^{13}C 128.39) as an internal standard. The ^{31}P NMR spectrum is referenced relative to external H_3PO_4 or PPh_3. Coupling constants are reported in hertz. FT-IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrometer. Melting points were determined by using a Mel-Temp II capillary melting point apparatus equipped with a thermocouple and digital thermometer. Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

Ethyl 2-alkyl-3-phenyl-2-cyclopropene-1-carboxylate (9) and Ethyl 4-alkylethynyl-2,4,6-cycloheptatriene-1-carboxylate (10): General procedure:[12] To a solution of alkyne (50 mmol) and $[Rh_2(OAc)_4]$ (398 mg, 0.9 mmol) in CH_2Cl_2 (20 mL) was added a mixture of ethyl diazoacetate (4.0 g, 35 mmol) in CH_2Cl_2 (5 mL) at a rate of 0.4 mL h^{-1} by means of a syringe pump. Upon completion of the addition, stirring was continued for 3 h. The solution was then filtered through a small column of silica gel to remove the catalyst. Concentration of the filtrate and purification of the crude material by column chromatography on silica gel (hexanes/Et_2O, 6:1) afforded compounds **9** and **10** as colorless oils, with **9** eluting first.

9c: 49%; ^1H NMR ($CDCl_3$): δ = 7.50–7.28 (m, 5H), 4.24–4.06 (m, 2H), 2.98 (sept, J = 6.9 Hz, 1H), 2.45 (s, 1H), 1.32 (d, J = 6.9 Hz, 3H), 1.31 (d, J = 6.9 Hz, 3H), 1.25 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 175.92 (CO), 129.41, 128.58, 128.53, 126.95, 115.17, 103.59, 60.00, 26.22, 21.87, 20.67, 14.35 ppm; IR (Et_2O):: $\tilde{\nu}$ = 1731 (CO) cm^{-1}.

10c: 6%; ^1H NMR ($CDCl_3$): δ = 6.81 (d, J = 6.4 Hz, 1H), 6.25–6.18 (m, 2H), 5.48–5.35 (m, 2H), 4.24 (q, J = 7.2 Hz, 2H), 2.72 (sept, J = 6.9 Hz, 1H), 2.58 (t, J = 5.6 Hz, 1H), 1.29(t, J = 7.2 Hz, 3H), 1.21 ppm (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 172.59 (CO), 134.35, 127.84, 125.96, 125.41, 116.73, 115.72, 96.66, 80.62, 61.01, 43.18, 22.86, 21.03, 14.12 ppm; IR (Et_2O): $\tilde{\nu}$ = 1730 (CO) cm^{-1}.

9d: 4%; ^1H NMR ($CDCl_3$): δ = 7.51–7.29 (m, 5H), 4.22–4.07 (m, 2H), 2.45 (s, 1H), 1.33 (s, 9H), 1.23 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 175.91(CO), 129.55, 128.60, 128.52, 126.99, 117.93, 102.35, 59.96, 31.85, 28.36, 21.78, 14.37 ppm; IR (Et_2O): $\tilde{\nu}$ = 1744 (CO) cm^{-1}.

10d: 9%; ^1H NMR ($CDCl_3$): δ = 6.82 (d, J = 6.2 Hz, 1H), 6.25–6.19 (m, 2H), 5.48–5.35 (m, 2H), 4.26 (q, J = 7.2 Hz, 2H), 2.60 (t, J = 5.8 Hz, 1H), 1.31 (t, J = 7.2 Hz, 3H), 1.28 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 172.73 (CO), 134.39, 128.00, 126.06, 125.48, 116.73, 115.70, 99.48, 79.96, 61.09, 43.26, 30.94, 27.91, 14.18 ppm; IR (Et_2O) $\tilde{\nu}$ = 1742 (CO) cm^{-1}.

1-Alkyl-3-hydroxymethyl-2-phenyl-1-cyclopropene (11): General procedure: To a mixture of ester **9** (5.0 mmol) and dry THF (30 mL) cooled to 0 °C was added DIBAL-H (11 mL, 1 M in hexane, 11 mmol) by syringe over 5 min. After stirring for 3 h at 0 °C, the solution was transferred to a separatory funnel containing potassium sodium tartrate (Rochelle's salt, 2.0 g) dissolved in H_2O (10 mL). After shaking, the gel formed was extracted with Et_2O (3 × 25 mL). The combined organic phase was dried ($MgSO_4$) and concentrated. Column chromatography over silica gel (hexanes/Et_2O, 3:1) gave **11** as a colorless oil.

11a: 75%; ^1H NMR ($CDCl_3$): δ = 7.51 (d, J = 7.9 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 3.72 (d, J = 4.6 Hz, 2H), 2.54 (s), 2.02 (t, J = 4.6 Hz, 1H), 1.55 ppm (br, 1H); ^{13}C NMR ($CDCl_3$): δ = 129.65, 128.82, 128.54, 127.76, 114.86, 112.98, 67.96, 22.79, 11.77 ppm; IR (Et_2O) ν 3496 (OH) cm^{-1}.

11b: 77%; ^1H NMR ($CDCl_3$): δ = 7.55 (d, J = 7.9 Hz, 2H), 7.42 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 3.78–3.71 (m, 2H), 2.72 (q, J = 7.5 Hz, 2H), 2.06 (t, J = 4.7 Hz, 1H), 1.43 (br, 1H), 1.36 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 129.54, 128.96, 128.56, 127.82, 120.22, 112.31, 68.29, 22.61, 20.14, 12.60 ppm; IR (Et_2O): $\tilde{\nu}$ = 3491 (OH) cm^{-1}.

11c: 95%; ^1H NMR ($CDCl_3$): δ = 7.56 (d, J = 7.9 Hz, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 3.76 (dd, J = 10.7, 4.7 Hz, 1H), 3.66 (dd, J = 10.7, 4.7 Hz, 1H), 2.99 (sept, J = 6.8 Hz, 1H), 2.05 (t, J = 4.7 Hz, 1H), 1.50 (br, 1H, OH), 1.33 (d, J = 6.8 Hz, 3H), 1.31 ppm (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 129.47, 129.14, 128.55, 127.82, 124.07, 111.46, 68.55, 26.86, 22.38, 21.25, 21.17 ppm; IR (Et_2O): $\tilde{\nu}$ = 3493 (OH) cm^{-1}.

11d: 93%; ^1H NMR ($CDCl_3$): δ = 7.55 (d, J = 7.9 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.3 Hz, 1H), 3.78 (dd, J = 10.5, 4.7 Hz, 1H), 3.62 (dd, J = 10.5, 4.7 Hz, 1H), 2.03 (t, J = 4.7 Hz, 1H), 1.58 (br s, 1H), 1.31 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 129.45, 129.36, 128.60, 127.86, 126.87, 110.08, 68.72, 31.86, 28.86, 22.31 ppm; IR (Et_2O): $\tilde{\nu}$ = 3497 (OH) cm^{-1}.

2-Alkyl-3-phenyl-2-cyclopropene-1-carboxaldehyde (12): General procedure: A solution of alcohol **11** (5.0 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a mixture of 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one (2.8 g, 7.0 mmol) and CH_2Cl_2 (30 mL). After stirring for 30 min at 20 °C, the reaction mixture was treated with 1 N NaOH (50 mL). The mixture was extracted with Et_2O (2 × 50 mL) and the organic phase washed with saturated NaCl solution, dried ($MgSO_4$), and concentrated. Column chromatography over silica gel (hexanes/Et_2O, 5:1) furnished **12** as a colorless, moderately stable oil. The exception was **12a**, where the crude isolated material was immediately subjected to the Wittig reaction because of its rather high instability.

12a: 60%; ^{1}H NMR ($CDCl_3$): δ = 8.87 (d, J = 7.3 Hz, 1H), 7.27–6.99 (m, 5H), 2.61 (d, J = 7.3 Hz, 1H), 2.36 ppm (s, 3H).

12b: 61%; ^{1}H NMR (C_6D_6): δ = 8.97 (d, J = 7.3 Hz, 1H), 7.27–6.98 (m, 5H), 2.61 (d, J = 7.3 Hz, 1H), 2.10 (dq, J = 7.5, 2.6 Hz, 2H), 0.86 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR (C_6D_6): δ = 203.51, 130.82, 129.60, 129.04, 128.91, 112.24, 105.51, 35.24, 19.76, 11.89 ppm; IR (Et_2O): $\tilde{\nu}$ = 1707 (CO) cm^{-1}.

12c: 46%; ^{1}H NMR ($CDCl_3$): δ = 8.89 (d, J = 7.6 Hz, 1H), 7.53–7.37 (m, 5H), 3.05 (sept, J = 6.8 Hz, 1H), 2.64 (d, J = 7.6 Hz, 1H), 1.36 (d, J = 6.8 Hz, 3H), 1.32 ppm (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 205.68, 129.49, 129.18, 128.78, 127.02, 115.62, 104.01, 35.13, 26.64, 20.67, 20.63 ppm; IR (Et_2O): $\tilde{\nu}$ = 1708 (CO) cm^{-1}.

12d: 68%; ^{1}H NMR ($CDCl_3$): δ = 8.89 (d, J = 7.6 Hz, 1H), 7.56–7.39 (m, 5H), 2.67 (d, J = 7.6 Hz, 1H), 1.37 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 205.62, 129.64, 129.19, 128.82, 127.00, 118.45, 102.71, 35.09, 31.73, 28.26 ppm; IR (Et_2O): $\tilde{\nu}$ = 1706 (CO) cm^{-1}.

(*Z*)-1-Alkyl-3-(2-iodoethenyl)-2-phenyl-1-cyclopropene (8): General procedure: Iodomethyltriphenylphosphonium iodide was dried under vacuum at 100°C for 30 min prior to use. The dry salt (1.6 g, 3.0 mmol) was dissolved in THF (10 mL) and $NaN(SiMe_3)_2$ (3 mL, 1.0 M in THF, 3.0 mmol) was added by syringe. The reaction was stirred for 5 min, giving a yellow solution, and then it was cooled to −78°C. To the cold reaction was successively added HMPA (2.0 mL) and a solution of aldehyde **12** (3.0 mmol) in THF (5 mL). The reaction was warmed to −30°C and stirred for 45 min. Et_2O (30 mL) was added to the reaction, the resultant suspension filtered, and the filter cake washed with additional Et_2O. The filtrate was washed with 10% HCl solution, saturated NaCl solution, and 10% Na_2CO_3 solution. The organic phase was dried ($MgSO_4$), filtered, and concentrated to give an light brown semi-solid. Chromatography on silica gel (hexanes) gave **8** as a colorless oil. The vinyl iodide was stored at −30°C with a small amount (~1 mg) of hydroquinone to prevent decomposition.

8a: 48%; ^{1}H NMR ($CDCl_3$): δ = 7.46 (d, J = 7.8 Hz, 2H), 7.23–7.07 (m, 3H), 5.93 (d, J = 7.5 Hz, 1H), 5.65 (t, J = 7.5 Hz, 1H), 2.91 (d, J = 7.5 Hz, 1H), 1.90 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 145.91, 129.29, 129.15, 128.83, 128.25, 112.74, 111.60, 76.07, 28.38, 11.01 ppm; IR (Et_2O): $\tilde{\nu}$ = 1865 (cyclopropene C=C) cm^{-1}.

8b: 50%; ^{1}H NMR ($CDCl_3$): δ = 7.44 (d, J = 7.7 Hz, 2H), 7.24–7.07 (m, 3H), 5.88 (d, J = 7.5 Hz, 1H), 5.60 (t, J = 7.5 Hz, 1H), 2.85 (d, J = 7.5 Hz, 1H), 2.26 (q, J = 7.5 Hz, 2H), 0.98 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 146.18, 129.42, 129.06, 128.86, 127.18, 117.90, 110.89, 75.82, 28.17, 19.97, 12.26 ppm; IR (Et_2O): $\tilde{\nu}$ = 1862 (cyclopropene C=C) cm^{-1}.

8c: 58%; ^{1}H NMR ($CDCl_3$): δ = 7.51 (d, J = 7.9 Hz, 2H), 7.45–7.29 (m, 3H), 5.99 (d, J = 7.3 Hz, 1H), 5.82 (t, J = 7.3 Hz, 1H), 3.00 (sept, J = 7.0 Hz, 1H), 2.65 (d, J = 7.3 Hz, 1H), 1.33 ppm (d, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 146.18, 129.17, 128.81, 128.60, 128.17, 121.63, 109.33, 75.29, 27.53, 26.94, 21.04, 20.89 ppm; IR (Et_2O): $\tilde{\nu}$ = 1852 (cyclopropene C=C) cm^{-1}.

8d: 72%; ^{1}H NMR ($CDCl_3$): δ = 7.51 (d, J = 8.0 Hz, 2H), 7.46–7.31 (m, 3H), 6.00 (d, J = 7.3 Hz, 1H), 5.85 (t, J = 7.3 Hz, 1H), 2.67 (d, J = 7.3 Hz, 1H), 1.35 ppm (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 146.23, 129.32, 128.62 (2C), 128.16, 124.30, 107.88, 75.26, 32.14, 28.56, 27.39 ppm; IR (Et_2O): $\tilde{\nu}$ = 1854 (cyclopropene C=C) cm^{-1}.

Iridabenzvalene 13d: A flamed-dried Schlenk flask was charged with cyclopropene **8d** (240 mg, 0.74 mmol) and Et_2O (20 mL) and cooled to −78°C. To this was added BuLi (330 μL, 2.5 M, 0.82 mmol) at −78°C over 5 min. After stirring for 15 min at −78°C, the resulting mixture was transferred over 5 min by a double-ended needle to a −78°C stirred suspension of $[Ir(CO)Cl(PPh_3)_2]$ (580 mg, 0.74 mmol) in Et_2O (5 mL), and then slowly warmed over a 3 h period to 0°C. The solvent was removed under vacuum and the residue purified by flash chromatography over silica gel (hexanes/Et_2O, 4:1), giving **13d** (211 mg, 32%) as a pale yellow solid. X-ray quality crystals of **13d** were obtained by recrystallization from a mixture of toluene and hexane. ^{1}H NMR (C_6D_6): δ = 7.75–7.69 (dt, J = 8.2, 1.5 Hz 6H), 7.50–7.41 (m, 6H), 7.36 (d, J = 7.0 Hz, 2H), 7.08–6.91 (m, 21H), 6.76–6.69 (m, 1H), 6.05 (dq, J = 8.1, 2.7 Hz, 1H), 3.20 (br s, 1H), 1.11 ppm (s, 9H); ^{13}C NMR (C_6D_6): δ = 181.86 (dd, J = 7.9, 5.2 Hz), 149.50 (dd, J = 15.5, 12.5 Hz), 144.09 (d, J = 4.0 Hz), 143.12 (t, J = 8.1 Hz), 136.85 (d, J = 43.3 Hz), 134.81 (d, J = 43.3 Hz), 133.96 (d, J = 11.1 Hz), 133.21 (d, J = 11.1 Hz), 128.62 (d, J = 1.9 Hz), 128.24 (d, J = 1.8 Hz), 126.79 (s), 126.77 (d, J = 10.1 Hz), 126.63 (d, J = 9.1 Hz), 122.62 (s), 81.32 (dd, J = 71.4, 6.0 Hz), 65.26 (dd, J = 62.2, 4.5 Hz), 54.72 (t, J = 3.7 Hz), 35.24 (t, J = 4.0 Hz), 29.46 ppm (d, J = 2.0 Hz) (2 aromatic resonances obscured); ^{31}P NMR (C_6D_6): δ = −0.09 (d, J = 28.1 Hz), −3.92 ppm (d, J = 28.1 Hz); IR (CH_2Cl_2): $\tilde{\nu}$ = 1971 (CO) cm^{-1}; elemental analysis calcd (%) for $C_{52}H_{47}IrOP_2$: C 66.29, H 5.03; found: C 65.97, H 4.77.

Iridabenzene 14d and cyclopentadienyliridium 15d: Benzvalene **13d** (188 mg, 0.2 mmol) was dissolved in benzene (5 mL) and kept at 20°C over four days until **11d** had completely disappeared. The resultant brown solution was concentrated and the residue redissolved in hexane/Et_2O (1:1; 10 mL) which was then stored overnight at −30°C. The solid was collected and washed with cold Et_2O to give **14d** (130 mg, 71%) as red crystals. **14d**: ^{1}H NMR (C_6D_6): δ = 10.54 (q, J = 11.1 Hz, 1H), 8.69 (q, J = 6.8 Hz, 1H), 7.84 (dd, J = 9.6, 8.3 Hz, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.20–7.15 (m, 12H), 7.10 (t, J = 7.7 Hz, 2H), 6.94–6.89 (m, 18H), 6.85 (t, J = 7.4 Hz, 1H), 1.58 ppm (s, 9H); ^{13}C NMR (C_6D_6): δ = 208.32 (t, J = 51.9 Hz), 186.68 (t, J = 6.1 Hz), 186.55 (s), 172.21 (t, J = 3.4 Hz), 145.61 (t, J = 5.5 Hz), 138.89 (s), 136.68–136.24 (m), 134.42 (t, J = 5.4 Hz), 129.63 (t, J = 4.2 Hz), 129.48 (s), 125.21 (s), 124.16 (t, J = 6.7 Hz), 122.94 (s), 39.76 (t, J = 3.0 Hz), 35.77 ppm (s) (1 aromatic resonance obscured); ^{31}P NMR (C_6D_6): δ = 18.24 ppm (s); IR (CH_2Cl_2): $\tilde{\nu}$ = 1981 (CO) cm^{-1}; elemental analysis calcd (%) for $C_{52}H_{47}IrOP_2$: C 66.29, H 5.03; found: C 66.09, H 4.92.

The filtrate from above was concentrated and the residue purified by chromatography on silica gel (hexanes/Et_2O, 5:1) to give compound **15d** (32 mg, 23%) as a yellow solid. **15d**: ^{1}H NMR (C_6D_6): δ = 7.88–7.78 (m, 8H), 7.14–6.96 (m, 12H), 5.18 (t, J = 2.2 Hz, 1H), 4.76 (t, J = 2.2 Hz, 1H), 4.18 (dt, J = 2.7, 1.1 Hz, 1H), 1.34 ppm (s, 9H); ^{13}C NMR (C_6D_6): δ = 179.83 (d, J = 17.1 Hz), 138.12 (s), 137.12 (d, J = 35.3 Hz), 134.44 (s), 134.29 (d, J = 12.1 Hz), 129.92 (d, J = 3.0 Hz), 127.99 (d, J = 11.1 Hz), 127.81 (s), 127.27 (s), 115.37 (d, J = 7.1 Hz), 108.61 (d, J = 6.4 Hz), 88.26 (s), 82.07 (s), 79.56 (s), 32.65 (s), 32.15 ppm (s); ^{31}P NMR (C_6D_6): δ = 17.80 ppm (s); IR (CH_2Cl_2): $\tilde{\nu}$ = 1918 (CO) cm^{-1}; elemental analysis calcd (%) for $C_{34}H_{32}IrOP$: C 60.07, H 4.74; found: C 60.14, H 4.55.

Thermolysis of 14d: Complex **14d** (50 mg, 0.053 mmol) was dissolved in benzene (3 mL) and heated at 50°C for 15 h. Concentration of the solution and chromatography of the residue as above afforded **15d** (33 mg, 97%). The spectral data were identical to those given above.

Iridabenzene 14a: Cyclopropene **8a** (250 mg, 0.89 mmol) was allowed to react with BuLi (430 μL, 2.5 M, 1.07 mmol) and $[Ir(CO)Cl(PPh_3)_2]$ (691 mg, 0.89 mmol) as described above for **13d**. After warming to 0°C over 3 h, the reaction was filtered under an argon atmosphere to remove the precipitated lithium salts. NMR analysis of the crude material showed formation of a 3:2 mixture of **13a**:**14a** along with protonated vinylcyclopropene and a minute amount of **19a**. Partial NMR data for **13a**: ^{1}H NMR (C_6D_6): δ = 6.25 (dq, J = 8.2, 2.9 Hz, 1H), 3.10 (br s, 1H), 1.96 (s, 3H); ^{31}P NMR (C_6D_6): δ = 0.43 (d, J = 30.2 Hz), −1.23 ppm (d, J = 30.2 Hz). Partial NMR data for **19a**: ^{1}H NMR (C_6D_6): δ = 11.9 (q, J = 11.8 Hz, 1H), 8.29–8.23 ppm (m, 1H); ^{31}P NMR (C_6D_6): δ = 21.17 ppm (s).

The filtrate from above was kept at 20°C for 8 h and then cooled to −30°C overnight. The solid was collected and washed with cold Et_2O to give **14a** as red crystals. Chromatography of the concentrated mother liquor over neutral alumina (hexanes/Et_2O, 3:1) gave additional material (186 mg total, 23%). **14a**: ^{1}H NMR (C_6D_6): δ = 10.62 (q, J = 10.8 Hz, 1H), 8.30 (q, J = 6.3 Hz, 1H), 7.75 (dd, J = 10.0, 7.9 Hz, 1H), 7.26–7.12 (m, 16H), 6.98–6.88 (m, 19H), 2.69 ppm (s, 3H); ^{13}C NMR (C_6D_6): δ = 204.97 (t, J = 50.9 Hz), 187.46 (t, J = 5.6 Hz), 183.92 (s), 170.02 (t, J = 3.5 Hz), 140.47 (t, J = 8.1 Hz), 137.11–136.33 (m), 134.38 (t, J = 5.5 Hz), 133.93 (t, J = 5.5 Hz), 129.50 (s), 129.06 (t, J = 3.8 Hz), 127.88 (s), 127.13 (s), 123.39 (s), 122.34 (t, J = 7.1 Hz), 24.17 ppm (t, J = 3.0 Hz); ^{31}P NMR (C_6D_6): δ = 18.03 ppm (s); IR (CH_2Cl_2): $\tilde{\nu}$ = 1982 (CO) cm^{-1}; elemental analysis calcd (%) for $C_{49}H_{41}IrOP_2$: C 65.39, H 4.59; found: C 64.82, H 4.59.

Iridabenzene 14b: Cyclopropene **8b** (200 mg, 0.68 mmol) was allowed toreact with BuLi (330 μL, 2.5 M, 0.81 mmol) and $[Ir(CO)Cl(PPh_3)_2]$ (530 mg, 0.68 mmol) as described above for **14a**. NMR analysis of the crude material showed formation of a 10:3:1 mixture of **13b**:**14b**:**19b** along with protonated vinylcyclopropene. Partial NMR data for **13b**: ^{1}H NMR (C_6D_6): $\delta = 6.25$ (dq, $J = 8.0$, 2.8 Hz, 1H), 3.20 (br s, 1H); ^{31}P NMR (C_6D_6): $\delta = -0.05$ (d, $J = 31.8$ Hz), −1.38 ppm (d, $J = 31.8$ Hz). Partial NMR data for **19b**: ^{1}H NMR (C_6D_6): $\delta = 11.20$ (q, $J = 11.7$ Hz, 1H), 8.18 (q, $J = 6.3$ Hz, 1H), 1.49 ppm (t, $J = 7.3$ Hz, 3H); ^{31}P NMR (C_6D_6): $\delta = 20.61$ ppm (s).

The filtrate of the above mixture was kept at 20 °C for 8 h and then cooled to −30 °C overnight. The solid was collected and washed with cold Et_2O to give **14b** as red crystals. Careful chromatography of the mother liquor over neutral alumina (hexanes/Et_2O, 3:1) furnished additional pure **14b** (131 mg total, 21 %). **14b**: ^{1}H NMR (C_6D_6): $\delta = 10.61$ (q, $J = 10.9$ Hz, 1H), 8.29 (q, $J = 6.1$ Hz, 1H), 7.79 (dd, $J = 10.2$, 7.8 Hz, 1H), 7.32 (d, $J = 7.0$ Hz, 2H), 7.23–7.12 (m, 14H), 6.96–6.87 (m, 19H), 3.01 (q, $J = 7.4$ Hz, 2H), 1.35 ppm (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (C_6D_6): $\delta = 204.17$ (t, $J = 50.4$ Hz), 187.31 (t, $J = 5.5$ Hz), 184.95 (s), 169.35 (t, $J = 3.5$ Hz), 140.84 (t, $J = 6.0$ Hz), 139.99 (t, $J = 8.1$ Hz), 137.14–136.36 (m), 134.38 (t, $J = 5.5$ Hz), 129.48 (s), 129.36 (t, $J = 4.6$ Hz), 127.89 (s), 126.66 (s), 123.34 (s), 122.90 (t, $J = 6.5$ Hz), 29.52 (t, $J = 3.1$ Hz), 19.23 ppm (s); ^{31}P NMR (C_6D_6): $\delta = 18.65$ ppm (s); IR (CH_2Cl_2): $\tilde{\nu} =$ 1892 (CO) cm^{-1}; elemental analysis calcd (%) for $C_{50}H_{43}IrOP_2$: C 65.70, H 4.74; found: C 65.42, H 4.92.

Iridabenzene 14c: Cyclopropene **8c** (141 mg, 0.50 mmol) was allowed to react with BuLi (240 μL, 2.5 M, 0.60 mmol) and $[Ir(CO)Cl(PPh_3)_2]$ (390 mg, 0.50 mmol) as described above for **14a**. NMR analysis of the crude material showed formation of a 13:2:1 mixture of **13c**:**14c**:**19c** along with protonated vinylcyclopropene. Attempts to isolate/purify **13c** resulted in isomerization to **14c**. Partial NMR data for **13c**: ^{1}H NMR (C_6D_6): $\delta = 6.22$ (dq, $J = 8.2$, 2.9 Hz, 1H), 2.80 ppm (br s, 1H); ^{31}P NMR (C_6D_6): $\delta = -0.86$ (d, $J = 30.5$ Hz), −2.03 ppm (d, $J = 30.5$ Hz). Partial NMR data for **19c**: ^{1}H NMR (C_6D_6): $\delta = 10.75$ ppm (q, $J = 11.8$ Hz, 1H); ^{31}P NMR (C_6D_6): $\delta = 20.11$ ppm (s).

The filtrate of the above mixture was kept at 20 °C for 30 h and then cooled to −30 °C overnight. The solid was collected and washed with cold Et_2O to give **14c** (134 mg, 29 %) as red crystals. **14c**: ^{1}H NMR (C_6D_6): $\delta = 10.61$ (q, $J = 10.9$ Hz, 1H), 8.41 (q, $J = 6.3$ Hz, 1H), 7.85 (dd, $J = 10.0$, 7.9 Hz, 1H), 7.29 (d, $J = 7.7$ Hz, 2H), 7.23–7.11 (m, 14H), 6.97–6.88 (m, 19H), 3.56 (sept, $J = 6.7$ Hz, 1H), 1.41 ppm (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (C_6D_6): $\delta = 203.52$ (t, $J = 50.4$ Hz), 187.27 (t, $J = 6.0$ Hz), 185.14 (s), 169.68 (t, $J = 3.2$ Hz), 145.14 (t, $J = 6.0$ Hz), 137.01–136.93 (m), 136.57 (t, $J = 8.0$ Hz), 134.40 (t, $J = 5.5$ Hz), 129.47 (s), 128.92 (s), 126.75 (s), 123.28 (s), 122.58 (t, $J = 7.0$ Hz), 30.44 (t, $J = 3.0$ Hz), 26.54 ppm (s) (1 aromatic resonance obscured); ^{31}P NMR (C_6D_6): $\delta = 18.79$ ppm (s); IR (CH_2Cl_2): $\tilde{\nu} =$ 1886 (CO) cm^{-1}; elemental analysis calcd (%) for $C_{51}H_{45}IrOP_2$: C 66.00, H 4.89; found: C 65.75, H 4.86.

Iridabenzvalene 20b: Reaction of cyclopropene **8b** (220 mg, 0.74 mmol) with BuLi (0.33 μL, 2.5 M, 0.82 mmol) and $[Ir(CO)Cl(PMe_3)_2]$ (302 mg, 0.74 mmol) as described for **13d** gave benzvalene **20b** (164 mg, 41 %) as light yellow crystals. **20b**: ^{1}H NMR (C_6D_6): $\delta = 7.64$ (d, $J = 8.5$ Hz, 2H), 7.28 (t, $J = 7.9$ Hz, 2H), 7.21–7.14 (m, 1H), 7.06 (t, $J = 7.0$ Hz, 1H), 6.50–6.40 (m, 1H), 3.34 (br s, 1H), 2.61 (t, $J = 7.3$ Hz, 2H), 1.24 (d, $J = 9.0$ Hz, 9H), 1.20 (t, $J = 7.3$ Hz, 3H), 1.10 ppm (d, $J = 9.0$ Hz, 9H); ^{13}C NMR (C_6D_6): $\delta = 179.72$ (t, $J = 7.6$ Hz), 147.67 (m), 146.40 (t, $J = 4.0$ Hz), 140.17 (t, $J = 15.1$ Hz), 127.17 (s), 127.14 (s), 123.40 (s), 71.03 (dd, $J = 72.5$, 4.0 Hz), 65.88 (dd, $J = 70.5$, 3.0 Hz), 58.80 (t, $J = 4.0$ Hz), 28.18 (t, $J = 4.0$ Hz), 20.85 (dd, $J = 30.2$ Hz, 3.0 Hz), 20.07 (dd, $J = 30.2$, 2.0 Hz), 14.71 ppm (d, $J = 3.0$ Hz); ^{31}P NMR (C_6D_6): $\delta = -52.11$ (d, $J = 32.7$ Hz), −54.62 ppm (d, $J = 32.7$ Hz); IR (CH_2Cl_2): $\tilde{\nu} =$ 1966 (CO) cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{31}IrOP_2$: C 44.35, H 5.77; found: C 43.89, H 5.79.

Iridabenzvalene 20d: Reaction of cyclopropene **8d** (240 mg, 0.74 mmol) with BuLi (0.33 μL, 2.5 M, 0.82 mmol) and $[Ir(CO)Cl(PMe_3)_2]$ (302 mg, 0.74 mmol) as described for **13d** gave benzvalene **20d** (244 mg, 58 %) as light yellow crystals. **20d**: ^{1}H NMR (C_6D_6): $\delta = 7.63$ (d, $J = 7.3$ Hz, 2H), 7.20 (t, $J = 7.6$ Hz, 2H), 7.13–7.06 (m, 1H), 7.01 (t, $J = 7.0$ Hz, 1H), 6.43–6.37 (m, 1H), 3.32 (br s, 1H), 1.34 (s, 9H), 1.29 (d, $J = 9.0$ Hz, 9H), 1.04 ppm (d, $J = 9.0$ Hz, 9H); ^{13}C NMR (C_6D_6): $\delta = 181.02$ (t, $J = 7.1$ Hz), 147.99 (m), 146.34 (d, $J = 8.1$ Hz), 140.00 (t, $J = 16.1$ Hz), 127.79 (s), 127.76 (s), 123.46 (s), 83.14 (dd, $J = 73.5$, 4.0 Hz), 65.83 (dd, $J = 66.5$, 2.5 Hz), 54.87 (t, $J = 4.0$ Hz), 35.37 (t, $J = 4.0$ Hz), 31.24 (d, $J = 2.0$ Hz), 21.70 (dd, $J = 30.2$, 4.0 Hz), 19.35 ppm (dd, $J = 29.2$, 2.0 Hz); ^{31}P NMR (C_6D_6): $\delta = -53.98$ (d, $J = 35.1$ Hz), −55.38 ppm (d, $J = 35.1$ Hz); IR (CH_2Cl_2): $\tilde{\nu} =$ 1960 (CO) cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{35}IrOP_2$: C 46.38, H 6.19; found: C 45.96, H 6.19.

Iridabenzene 21b: A solution of **20b** (54 mg, 0.1 mmol) in degassed C_6D_6 (1 mL) was placed into an NMR tube and heated at 75 °C over 24 h, resulting in complete isomerization. The solvent was removed and the solid redissolved in 1:1 hexane/Et_2O. After the mixture had been cooled at −30 °C overnight, the red solid was collected and washed with cold Et_2O to give **21b** (48 mg, 89 %) as air-sensitive red crystals. **21b:** ^{1}H NMR (C_6D_6): $\delta = 10.92$ (dq, $J = 11.4$. 1.2 Hz, 1H), 8.13 (dq, $J = 6.2$, 1.2 Hz, 1H), 7.90 (dd, $J = 9.6$. 8.4 Hz, 1H), 7.43–7.31 (m, 4H), 7.08 (t, $J = 7.1$ Hz, 1H), 2.85 (q, $J = 7.5$ Hz, 1H), 1.26 (t, $J = 7.5$ Hz, 3H), 1.07 ppm (d, $J = 10.3$ Hz, 18H); ^{13}C NMR (C_6D_6): $\delta = 190.79$ (t, $J = 50.4$ Hz), 188.84 (t, $J = 5.0$ Hz), 174.20 (s), 169.29 (t, $J = 3.0$ Hz), 138.56 (t, $J = 5.0$ Hz), 135.38 (t, $J = 8.1$ Hz), 129.70 (t, $J = 4.0$ Hz), 126.23 (s), 123.86 (t, $J = 6.0$ Hz), 123.08 (s), 29.32 (t, $J = 4.0$ Hz), 20.91 (dd, $J = 14.3$, 2.0 Hz), 18.82 ppm (s); ^{31}P NMR (C_6D_6): $\delta = -38.56$ ppm (s); elemental analysis calcd (%) for $C_{20}H_{31}IrOP_2$: C 44.35, H 5.77; found: C 42.98, H 5.67.

Iridabenzene 21d and cyclopentadienyliridium complex 22d: A solution of **20d** (57 mg, 0.1 mmol) in degassed C_6D_6 (1 mL) was heated at 75 °C for 48 h leading to a mixture of unreacted **20d**, **21d**, and **22d** (5:10:1) along with numerous other decomposition products. Continue heating led to complete decomposition of the sample. **21d**: ^{1}H NMR (C_6D_6): $\delta =$ 10.87 (q, J = 12.0 Hz, 1H), 8.46 (q, J = 6.2 Hz, 1H), 7.88 (d, J = 9.7 7.9 Hz, 1H), 7.66–6.94 (m, 5H), 1.47 (s, 9H), 1.05 ppm (d, J = 10.0 Hz); ^{31}P NMR

Table 4. Crystal data for compounds **13d**, **14a**, **14b**, and **14d**.

	13d	**14a**	**14b**	**14d**
mol formula	$C_{52}H_{47}IrP_2{\cdot}2C_7H_8$	$C_{49}H_{41}IrOP_2$	$C_{50}H_{43}IrOP_2$	$C_{52}H_{47}IrOP_2$
mol. wt.	1126.4	900.0	914.1	942.1
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	*I*2/*a*	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	22.602(3)	10.979(3)	10.880(2)	11.626(2)
b [Å]	11.3221(13)	10.983(3)	11.130(2)	20.564(5)
c [Å]	23.853(5)	18.209(3)	17.883(2)	18.529(5)
α [°]	90	100.69(2)	89.59(1)	90
β [°]	106.01(2)	95.74(2)	83.42(1)	106.75(2)
γ [°]	90	110.79(3)	70.65(2)	90
V [Å^3]	5867(2)	1983.9(11)	2028.6(8)	4242.2(2)
Z	4	2	2	4
F_{000}	2296	900	916	1896
$2\theta_{max}$ [°]	46	23	48	23
independent reflections	4386	6233	6354	7688
observed [$I \geq \sigma(I)$]	4095	6229	6352	7441
used in refinement	3591	5160	5280	4835
refined parameters	245	478	487	505
$R(F)/wR$ [$I \geq \sigma(I)$]	0.063, 0.074	0.050, 0.047	0.036, 0.041	0.063, 0.052
$R(F^2)/wR(F^2)$ (all)	0.112, 0.146	0.087, 0.098	0.062, 0.086	0.097, 0.103

(C_6D_6): $\delta = -38.79$ ppm (s). Partial data for **22d**: $\delta = 5.26$ (br s, 1H), 4.72 (br s, 1H), 4.54 (br s, 1H), 1.35 ppm (s, 9H).

Kinetics of the rearrangement of iridabenzene 14d to cyclopentadienyliridium complex 15d: Solutions of **14d** in C_6D_6 were prepared in three NMR tubes under N_2 and heated at 40, 50, and 60 °C, respectively. The reaction progress was monitored by ^{1}H NMR spectroscopy. Integration of the proton resonance signals was used to calculated $\ln[C]/[C]_o$. A plot of $\ln[C]/[C]_o$ versus time gave a straight line for the data at each different temperature. The first order constants were obtained from the slopes of these lines.

X-ray structure determinations: Data were collected on an Enraf-Nonius CAD-4 Turbo diffractometer using $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; graphite monochromator; $T = 296$ K; scan mode ω–2θ. Pertinent crystallographic data and refinement parameters are given in Table 4. Structure refinement (C atoms anisotropic, H atom riding) was accomplished with the teXsan program suite (version 1.7 for SGI workstations). CCDC-218966 (**13d**), CCDC-218968 (**14a**), CCDC-218967 (**14b**), and CCDC-218965 (**14d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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