Synthesis, Characterization, and Isomerization of an Iridabenzvalene

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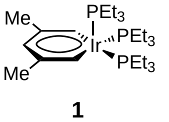
Abstract: Metal–halogen exchange of vinylcyclopropene **4** followed by addition of $[(Me_3P)_2Ir(CO)Cl]$ produced iridabenzvalene **5**. The metallabenzene valence isomer was characterized by NMR and IR spectroscopy and by X-ray crystallography. Isomerization of complex **5** to iridabenzene derivatives **6** and **13** was accomplished by thermolysis and by Ag^+ ions, respectively. The former transformation was a clean and quantitative process that displayed first-order kinetics.

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

Introduction

The valence isomers of benzene have been the subject of a myriad of experimental and theoretical studies.[1] The parent hydrocarbons, as well as numerous derivatives of Dewar benzene, benzvalene, prismane, and bicycloprop-2-enyl, have been thoroughly investigated throughout the latter half of the 20th century.[2] The valence isomers of some heteroaromatic compounds are also known, although there are considerably fewer studies of these systems. For example, the Regitz group has utilized stable cyclobutadienes and azacyclobutadienes to prepare valence isomers of azabenzene (pyridine) and phosphabenzene (phosphinine).[3] The valence isomers of metallabenzenes, perhaps the rarest class of aromatic compounds, are as yet unknown. Metallabenzenes, in which one of the methine groups in benzene has been replaced with an isoelectronic transition metal fragment,[4] have been shown by ^1H NMR spectroscopy and X-ray crystallography to indeed possess aromatic properties.[5] Unfortunately, detailed systematic studies involving these aromatic systems have been limited by the lack of general preparative routes to the metallacycles. Although several metallabenzenes that are stabilized by η^6 coordination of the metallacyclic ring to a second metal fragment have been reported,[6] only two families of stable metallabenzenes have been prepared. In addition to Bleeke's iridabenzene **1** and its derivatives,[5c–f] osmabenzene complex **2** has been reported by Roper et al. along with several analogues.[5a, b]



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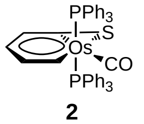

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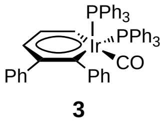

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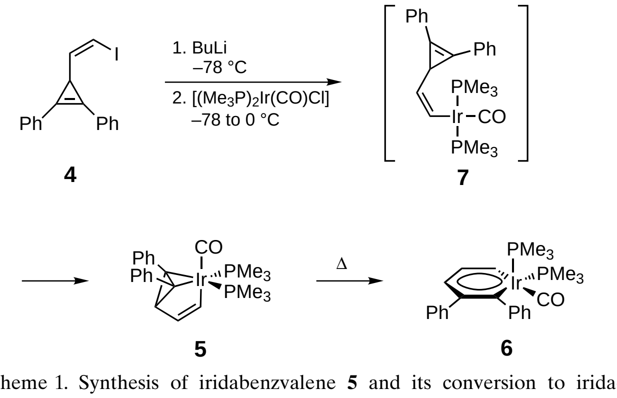
Recently, we reported the synthesis of iridabenzene **3** which utilizes an intramolecular cyclopropene rearrangement.[7] Metal–halogen exchange on cyclopropene **4** followed by the addition of Vaska's complex resulted in the direct formation of **3**. In an effort to expand the scope of this chemistry, we have performed the reaction with other Vaska-type iridium complexes that possess alkylphosphine ligands. Herein we report the preparation and structural characterization of a metallabenzene valence isomer, iridabenzvalene **5**, and the thermally promoted isomerization of **5** to the corresponding iridabenzene **6**. We also present the results of the isomerization/oxidation of **5** with Ag^+ ions.

Results and Discussion

Iridabenzvalene **5** was prepared from cyclopropene **4** and $[(Me_3P)_2Ir(CO)Cl]$ (Scheme 1). In contrast to the preparation of **3**,[7] the crude mixture from the reaction showed no evidence of metallabenzene products in the ^1H NMR spectrum (peaks which are attributed to ring protons in iridabenzenes are quite obvious as they generally appear at



Scheme 1. Synthesis of iridabenzvalene **5** and its conversion to iridabenzene **6**.

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$\delta = 7-11$).[5, 7] The crude orange oil was taken up in diethyl ether, filtered, and cooled to $-35\,^{\circ}C$ whereupon light yellow crystals formed in 50% yield.

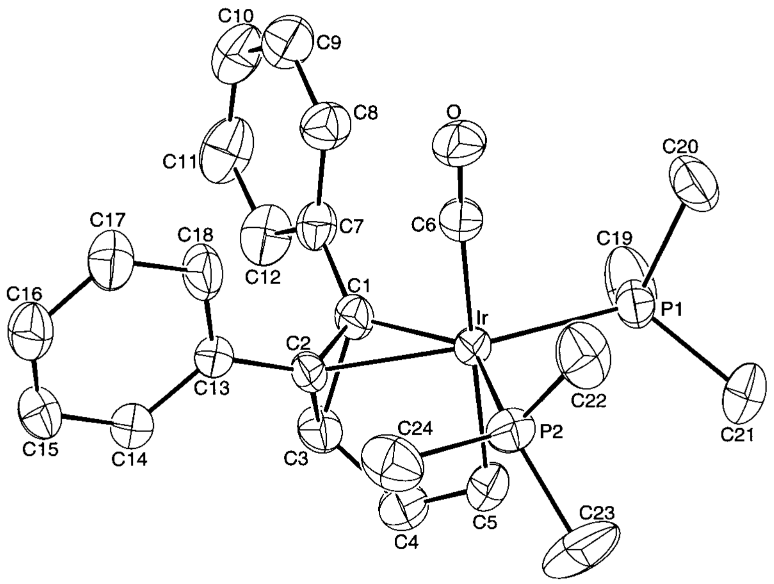
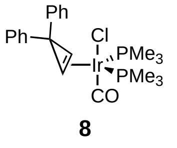


Figure 1. Molecular structure of iridabenzvalene complex **5**; ellipsoids drawn at the 30% level. Selected bond lengths [Å] and angles [°]: Ir–P1 2.306(3), Ir–P2 2.318(3), Ir–C1 2.15(1), Ir–C2 2.143(8), Ir–C5 2.10(1), Ir–C6 1.87(1), C1–C2 1.45(1), C1–C3 1.53(1), C2–C3 1.53(1), C3–C4 1.47(1), C4–C5 1.32(1), C6–O 1.15(1); P1-Ir-P2 104.1(1), P1-Ir-C1 109.4(2), P2-Ir-C2 105.9(3), Ir-C1-C2 70.2(5), Ir-C2-C1 70.4(5), C1-C2-C3 61.9(6), C2-C1-C3 61.6(6), C1-C3-C4 116.4(8), C2-C3-C4 116.4(8), C3-C4-C5 115.5(9), Ir-C5-C4 111.4(7), C5-Ir-C6 178.9(4), Ir-C6-O 178.1(9).

Spectral data obtained from the recrystallized product suggested the formation of the symmetrical structure **5**. The ^1H NMR spectrum had only one resonance in the alkyl region where signals from a PMe_3 ligand would be expected, a doublet with an integral value of 18H. Additionally, the ^1H NMR spectrum showed that both of the phenyl groups were equivalent. Other notable features in the ^1H NMR spectrum of **5** included a complex multiplet at $\delta = 3.82$ corresponding to the bridgehead cyclopropyl proton, and multiplets corresponding to the vinylic protons at $\delta = 6.55$ and 7.23. The latter multiplet was partially obscured by overlap with a resonance from the phenyl groups. The ^{31}P NMR spectrum contained a single peak at $\delta = -54.36$, while the carbonyl group of **5** had a stretching frequency of $\tilde{\nu} = 1955\,cm^{-1}$ in the IR spectrum. These observations are all consistent with a trigonal-bipyramidal arrangement of ligands around the iridium center in **5** (Scheme 1). Presumably, the initial nucleophilic substitution of the iridium center by the vinyl lithiate produces complex **7**.[8] Complex **5** is then formed by coordination of the π bond of the cyclopropene to the iridium center. The basic structure of **5** is not unprecedented in the literature. Several η^2-cyclopropene transition metal complexes have been prepared,[9] including a series generated from 3,3-diphenylcyclopropene and Vaska-type iridium compounds.[10] The PMe_3 analogue of this series (**8**) was characterized by single-crystal X-ray crystallography. Furthermore, a molybdenum complex (**9**) with an intramolecular cyclopropene ligand coordinated to the metal center in an η^2 fashion has been reported by Hughes et al.[11]



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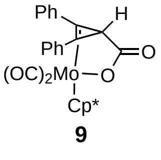

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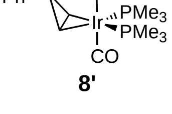
The structure of **5** was confirmed by a single-crystal X-ray diffraction study (Figure 1). The axis of the olefinic cyclopropene bond in **5** lies in the equatorial plane of the complex, which is typical of a trigonal-bipyramidal d^8 complex.[12] The Ir–C1 (2.15(1) Å) and Ir–C2 (2.143(8) Å) bond lengths of **5** are similar to the corresponding bond lengths reported for complex **8** (2.116(6) Å, 2.118(6) Å).[10] The length of the C1–C2 bond (1.45(1) Å) in **5** is greater than that of a typical cyclopropene (≈1.29 Å).[13] This type of bond elongation is characteristic of transition metal olefin complexes that have a significant backbonding contribution from the metal center.[12] In the case of η^2-cyclopropene transition metal complexes, the elongation of the π bond results in an increase in the apical angle of the three-membered ring, and hence, a reduction in the strain of the cyclopropene ring.[9, 10, 14] The apical bond angle in a typical cyclopropene is ≈50°,[13] whereas in **5** the C1-C3-C2 bond angle is 56.5(5)° (the corresponding angle in **8** is 56.7(4)°).[10] Another consequence of complexation of the cyclopropene to the iridium center is that the phenyl substituents of the cyclopropene are bent out of the ring plane.[14] In complex **5**, the C1-C2-C3 plane intersects with the C1-C2-C7-C13 plane at an angle of 63.7°. For comparison, the cyclopropene substituents of $[(PPh_3)_2Pt(1,2\text{-diphenylcyclopropene})]$ and $[(PPh_3)_2Pt(3,3\text{-diphenylcyclopropene})]$ are bent away from the plane of the three-membered ring by angles of 59.1° and 72.1°, respectively.[14b] The orientation of the cyclopropene plane in **5**, with respect to the iridium center, is significantly restrained compared to complex **8**. The Ir-C1-C2-C3 torsion angle in **5** is 110.3(5)°, whereas the corresponding angle in **8** is 126.3(4)°.[10] The constraint of this angle in **5** is undoubtedly an effect of the intramolecular nature of the cyclopropene ligand. In comparison, the corresponding angle in benzvalene is 106°.[15]

When viewed in the limiting resonance form of a metallacyclopropane,[9, 12] the structure of complex **8′** resembles that of strained bicyclo[1.1.0]butane (**10**).[10] By the same analogy, complex **5** closely resembles the structure of benzvalene



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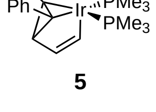

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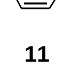

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(**11**).[15] The structure of alkenes which are η^2-coordinated to transition metals can vary between the limiting resonance forms of an olefin complex and a metallacyclopropane and is dependent on a number of factors.[12] In the olefin-type structure, the transition metal is usually highly oxidized and the alkene ligand is predominantly a σ donor. Since there is little, if any, backbonding in this type of structure, the bond lengths and hybridization of the alkene are very similar to the free alkene. Variables that favor the metallacyclopropane limiting structure include a transition metal in a low oxidation state, electron-withdrawing substituents on the olefin, and strain in the olefin. In a low-oxidation state, the transition metal is more apt to facilitate backbonding and, hence, the olefins in this type of structure are predominantly π acceptors and exhibit bond elongation and hybridization close to sp^3. Considering all of these factors and the crystallographic data from Figure 1, it is appropriate, at least from a structural point of view, to refer to **5** as a metallabenzvalene since its structure is more like that of a metallacyclopropane than an olefin complex.

In view of the structural similarities of **5** and **11**, and the propensity of η^2-cyclopropene transition metal complexes to rearrange into metal carbenes,[14a, 16] we were interested in the reactivity of **5**. In particular, we were interested in the possibility that complex **5** could be induced to rearrange into an iridabenzene complex. The analogous rearrangement of benzvalene to benzene has been promoted thermally and can also be catalyzed by silver ions.[17] Complex **5** is indefinitely stable in the solid state at ambient temperature, and no noticeable decomposition was observed after exposure of the solid to atmospheric oxygen for a period of several days. In refluxing benzene, however, **5** was converted cleanly and quantitatively (measured by ^1H NMR spectroscopy) to iridabenzene **6**. No other reaction products were observed in the ^1H, ^{13}C, or ^{31}P NMR spectra during this reaction. Solutions of **5** in benzene or toluene are nearly colorless; however, after conversion to **6** has occurred, the same solutions take on a reddish hue, which is consistent with iridabenzene **3**[7] as well as other iridabenzene complexes.[5]

The conversion of **5** into iridabenzene **6** is quite apparent in the ^1H and ^{31}P NMR spectra (Figure 2). During the course of the reaction, the resonances at $\delta = 3.62$ and 6.55 (resulting from the cyclopropyl proton and one of the vinyl protons in **5**) disappear, while three new signals, consistent with iridabenzene ring protons, appear at $\delta = 11.00$, 8.25, and 7.91 (H5, H3, and H4, respectively). The ^{31}P NMR spectrum shows a new resonance at $\delta = -39.33$ which is attributed to iridabenzene **6**, while the resonance from complex **5** at $\delta = -54.36$ disappears. The rate of the isomerization was measured by NMR spectroscopy. The concentration of **5** during the course of the reaction was determined from the integral value of the cyclopropyl proton. The rate constants at 331.32, 343.38, and 353.84 K were determined by plotting $\ln[\mathbf{5}]/[\mathbf{5}]_0$ versus time (Table 1). In all cases the data was linear, which indicates first-order kinetics. The slopes of the lines were taken as the rate constant. An Eyring plot of the data obtained from the rate measurements was linear and gave the following activation parameters: $\Delta H^{\neq} = 25.3 \pm 5.3\ \mathrm{kcal\,mol^{-1}}$, $\Delta S^{\neq} = -5.6 \pm 15$ eu. The corresponding values for benzvalene (**11**) are $25.9 \pm 0.2\ \mathrm{kcal\,mol^{-1}}$ and 1.6 ± 0.7 eu, respectively.[17]

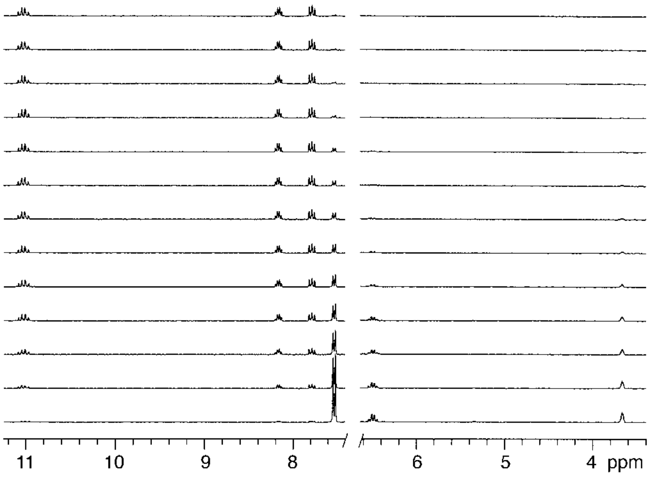
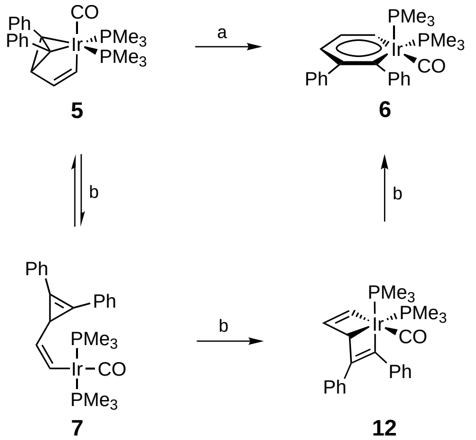


Figure 2. Time-evolved ^1H NMR spectra of the thermally promoted isomerization of **5** to **6** at 58.2 °C in [D$_8$]toluene. The bottom spectrum was recorded after 1 h, and the following spectra represent 3 h intervals with the top spectrum representing a reaction time of 37 h. For clarity, the region between $\delta = 6.6$ and 7.5, which corresponds to numerous aromatic resonances of **5**, **6**, and the toluene solvent, has been omitted. The PMe_3 region has also been omitted.

Table 1. Rate constants for the thermolysis of **5** in [D$_8$]toluene.

Temperature	Rate constants [s^{-1}]
331.32 K	$3.46 \pm 0.12 \times 10^{-5}$
341.38 K	$7.11 \pm 0.22 \times 10^{-5}$
351.84 K	$3.22 \pm 0.04 \times 10^{-4}$

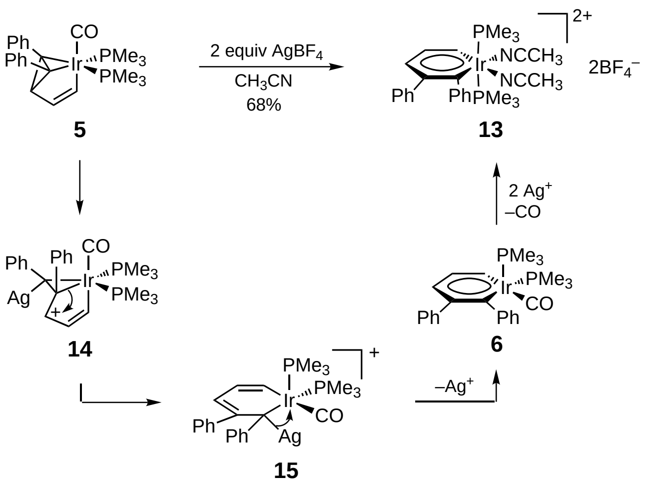
Two plausible mechanistic pathways for the thermally promoted isomerization of **5** are given in Scheme 2. If **5** is viewed as an iridabenzvalene complex, then the simplest mechanistic explanation is a concerted rearrangement of the metallabicyclobutane moiety which would give iridabenzene



Scheme 2. Two plausible mechanistic pathways for the thermally promoted isomerization of **5**.

6 directly (Path a). A concerted rearrangement of **5** would be analogous to the thermally promoted isomerization of benzvalene to benzene.[15] Alternatively, the isomerization of **5** may proceed in a stepwise fashion (Path b). Cyclopropene ligands in complexes prepared from Vaska-type iridium complexes, such as **8**, are relatively labile. For example, the cyclopropene in **8** can be exchanged quantitatively at ambient temperatures with a deuterated version of the cyclopropene, or with electron-deficient olefins, such as tetracyanoethylene or dimethyl maleate.[10] If the cyclopropene portion of **5** dissociated from the iridium center, it would produce **7** (incidentally, the same intermediate presumably formed in the initial step in Scheme 1). Complex **7** would very likely be a highly reactive intermediate considering that it is a coordinatively unsaturated, 16 e^- species. Oxidative addition of a cyclopropene σ bond in **7** to the iridium center would give the metalla–Dewar benzene **12**. A rapid valence isomerization of **12** to iridabenzene **6** should be a facile process due to the release of strain energy.

The isomerization of **5** to a metallabenzene can also be promoted by Ag^+ ions (Scheme 3). When complex **5** was treated with two equivalents of $AgBF_4$ in acetonitrile, the color of the solution gradually turned blue and Ag metal was deposited on the walls of the flask. Filtration of the solution and removal of the solvent gave **13** as a blue oil.[18] When catalyzed by Ag ions, the ring opening of cyclopropenes occurs either through initial electrophilic attack of the Ag cation at the π bond of the cyclopropene, or by attack at one of the cyclopropene σ bonds.[19] The electrons of the π bond in **5** are coordinated to the iridium center which means that the electrophilic attack of the Ag^+ ion at the π bond is unlikely. Hence, in the case of **5**, initial attack of the Ag^+ is most likely to occur at one of the σ bonds to give a cationic intermediate, such as **14** (Scheme 3), which is stabilized by allylic resonance. Attack of a transition metal at one of the cyclopropene σ bonds was proposed in the rearrangement of complex **8** to a metallacyclobutene.[10] The subsequent rearrangement of **14** to intermediate **15** is probably driven by the relief of the strain energy in the bicyclic system of **14**. Loss of the Ag substituent in **15** leads to the production of metallabenzene **6** and regeneration of the Ag^+ ion. The oxidation of metallabenzene **6** by two equivalents of Ag^+ then produces a dicationic metallabenzene complex (**13**) with the loss of a CO ligand and accounts for the deposition of Ag metal on the reaction vessel.



Scheme 3. The isomerization of **5** to a metallabenzene, which is promoted by Ag^+ ions.

A similar oxidation of metallabenzene **1** to a dicationic complex with two equivalents of Ag^+ was first observed by Bleeke et al.[5e]

Conclusions

We have prepared and characterized an iridabenzvalene complex (**5**). In a similar manner to its purely hydrocarbon analogue (**11**), complex **5** can be cleanly isomerized to iridabenzene derivatives by thermolysis (**6**) and by a two-step Ag-mediated rearrangement/oxidation procedure (**13**). The mechanism of the reaction is currently under investigation to discover whether the former process is a true "valence isomerization" (Scheme 2, Path a) or if it proceeds through an alternative route (Path b). Attempts to detect intermediates **7** and **12** and/or trap these species are in progress.

Experimental Section

General: Cyclopropene **4** and $[(PMe_3)_2Ir(CO)Cl]$ were prepared according to the literature.[7, 20] A solution of butyllithium (2.5 M) in hexanes was purchased from the Aldrich Chemical Company. Manipulations of organometallic reagents were carried out in either an inert-atmosphere glove box (Vac Atmosphere) or by standard Schlenk techniques. Diethyl ether, toluene, and hexanes were distilled from sodium/benzophenone and degassed by three freeze/pump/thaw cycles prior to use. Acetonitrile was distilled from CaH_2 and degassed as above prior to use. $[D_6]$Acetone and $[D_8]$toluene were purchased in 0.5 mL ampoules from Aldrich and used as received. NMR spectra were recorded on a Varian Unity-INOVA 300 spectrometer at ambient temperature, unless otherwise noted. ^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 downfield from tetramethylsilane with the residual solvent signal as an internal standard. The ^{31}P NMR spectra are referenced relative to external H_3PO_4. Coupling constants are reported in Hertz. FT-IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer.

Iridabenzvalene 5: In an inert-atmosphere glove box, a flame-dried Schlenk flask was charged with cyclopropene **4**[7] (0.185 g, 0.537 mmol) and Et_2O (5 mL). The solution was cooled to −78 °C under an argon atmosphere and a solution of BuLi in hexanes (0.21 mL, 0.53 mmol, 2.5 M) was added with a syringe. The resulting solution was stirred at −78 °C for 15 min, then a solution of $[(PMe_3)_2Ir(CO)Cl]$[20] (0.204 g, 0.5 mmol) in Et_2O (20 mL), precooled to −78 °C, was added over a period of 5 min by means of a double-ended needle under Ar pressure. The solution was stirred at −78 °C for 30 min, then allowed to equilibrate to ambient temperature over a period of 1 h. The color of the solution changed from yellow to orange during this time and a white precipitate (LiCl) was formed. Ethanol (95 %, 0.10 mL) was added by syringe and the suspension was filtered through a glass frit (medium porosity). The solvent was removed in vacuo to give an orange oil which was taken up in Et_2O and filtered through Celite. The ethereal solution was cooled to −35 °C whereupon light yellow crystals of **5** (0.047 g) formed. Two additional crops of crystals were subsequently collected for a combined total yield of 0.148 g (50 %). ^1H NMR ($[D_6]$benzene): $\delta = 7.63$ (d, $J = 7.3$ Hz, 4H), 7.26–7.17 (m, 5H), 7.00 (t, $J = 7.3$ Hz, 2H), 6.55 (H4: ddt, $J(H4,H5) = 8.2$, $J(H4,H3) = 2.6$, $J(H4,P) = 8.8$ Hz, 1H), 3.83–3.80 (H3: m, $J(H3,H4) = 2.6$, Hz, 1H), 1.11 ($P(CH_3)_3$, d, $J = 9.0$ Hz, 18H); ^{13}C NMR ($[D_6]$benzene): $\delta = 180.48$ (t, $J = 6.5$ Hz, CO), 146.76 (t, $J = 4.0$ Hz), 146.52 (t, $J = 7.5$ Hz), 141.79 (t, $J = 15.1$ Hz), 128.15 (s), 124.53 (s), 70.92 (m), 60.83 (t, $J = 3.5$ Hz), 20.49 (m, $P(CH_3)_3$) (one resonance is obscured by the solvent signals); ^{31}P NMR ($[D_6]$benzene): $\delta = -54.36$; IR (KBr): $\tilde{\nu} = 1955$ cm^{-1} (CO); anal. calcd (%) for $C_{24}H_{31}IrP_2O$: C 48.89, H 5.30; found: C 48.74, H 5.37.

Iridabenzene 6: Complex **5** (0.014 g, 0.023 mmol) was dissolved in $[D_6]$benzene (0.75 mL) and flame-sealed in a 5 mm NMR tube. The NMR tube was heated in a sand bath at 100 °C for 1 h. The solution changed from pale yellow to red during the isomerization. At the end of the heating period, an analysis of the NMR spectrum of the sample showed quantitative conversion to metallabenzene **6**. The solvent was removed in vacuo to give a deep red solid, which was taken up in Et_2O. The ethereal solution was cooled to $-35\,^{\circ}C$ whereupon red-orange crystals of **6** formed. M.p. 145 °C (decomp); ^1H NMR ([D_6]benzene): $\delta = 11.00$ (H5: ddt, J(H5,H4) = 10.1, J(H5,H3) = 1.3, J(H5,P) = 12.3 Hz, 1 H), 8.25 (H3: ddt, J(H3,H4) = 8.0, J(H3,H5) = 1.3, J(H3,P) = 6.0 Hz, 1 H), 7.91 (H4: ddt, J(H4,H3) = 8.0, J(H4,H5) = 10.1, J(H4,P) = 0.9 Hz, 1 H), 7.28 (t, J = 8.8 Hz, 4 H), 7.12–7.00 (m, 4 H), 6.90–6.79 (m, 2 H), 1.03 ($P(CH_3)_3$, d, J = 7.2 Hz, 18 H); ^{13}C NMR ([D_6]benzene): $\delta = 191.42$ (t, J = 51.4 Hz, CO), 189.95 (t, J = 5.0 Hz, C1), 176.04 (s, C5), 169.02 (t, J = 3.1 Hz), 148.94 (t, J = 4.0 Hz), 141.49 (t, J = 4.5 Hz), 136.74 (t, J = 8.6 Hz), 131.92 (s), 129.06 (t, J = 4.0 Hz), 127.50 (s), 126.59 (t, J = 6.0 Hz), 126.16 (s), 124.87 (s), 123.44 (s), 21.20 (d, J = 33.6 Hz, $P(CH_3)_3$); ^{31}P NMR ([D_6]benzene): $\delta = -39.33$ (s); anal. calcd (%) for $C_{24}H_{31}IrP_2O$: C 48.89, H 5.30; found: C 48.68, H 5.29.

Iridabenzene 13: In an inert-atmosphere glove box, a Schlenk flask was charged with $AgBF_4$ (0.020 g, 0.10 mmol) and complex **5** (0.029 g, 0.049 mmol). Acetonitrile was added to the solids and the resulting solution was stirred at room temperature for 2 h. During the reaction, the color of the solution changed to blue and metallic silver was deposited on the walls of the flask. The resulting suspension was filtered through a glass frit and the solvent was removed in vacuo to give a blue oil (0.027 g, 68 %). Repeated attempts to crystallize or precipitate the oil were only marginally successful, hence **13** was not isolated in analytically pure form. ^1H NMR ([D_6]acetone): $\delta = 13.31$ (*H5*: dd, J(H4,H5) = 8.2, J(H5,H3) = 2.1 Hz, 1 H), 8.57 (*H3*: apparent dq, J(H3,H4) = 7.9, J(H3,H5) = J(H3,P) = 2.1 Hz, 1 H). 8.01 (*H4*: apparent triplet, J(H4,H3) = J(H4,H5) = 8.0 Hz, 1 H), 7.34–7.29 (m, 2 H), 7.11–7.05 (m, 4 H), 7.00–6.95 (m, 4 H), 2.86 ($NCCH_3$, t, J(H,P) = 1.5 Hz, 3 H), 2.36 ($NCCH_3$, t, J(H,P) = 1.2 Hz, 3 H), 1.60 ($P(CH_3)_3$, d, J = 9.7 Hz, 6 H); ^{31}P NMR ([D_6]acetone): $\delta = -24.24$ (s).

Crystal structure of 5: $C_{24}H_{31}IrOP_2$, $M_r = 598.68$, yellow prisms, $0.16 \times 0.18 \times 0.36$ mm, monoclinic, space group $P2_1/c$, $a = 8.8486(9)$, $b = 15.192(2)$, $c = 18.982(2)$ Å, $\beta = 104.773(9)^{\circ}$, $V = 2467.4(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.587\,g\,cm^{-3}$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 55.7\,cm^{-1}$, $F(000) = 1160$, $T = 22\,^{\circ}C$, $2\theta_{max} = 50^{\circ}$, 4341 independent reflections scanned, 3054 reflections in refinement ($I > 1.5\sigma(I)$), structure refinement (C atoms anisotropic, H atoms riding) with teXsan (v. 1.7 for SGI workstations), 254 parameters, $R = 0.049$, $Rw = 0.046$. Data was obtained on an Enraf-Nonius CAD-4 Turbo diffractometer. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120562. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Kinetics of the thermolysis of 5: The disappearance of **5** was monitored by ^1H NMR spectroscopy by integration of the resonance corresponding to the H3 proton. The isomerization was followed at three different temperatures (331.32, 343.38, and 353.84 K). At each temperature the NMR spectrometer probe was calibrated by means of the temperature dependence of ethylene glycol. A plot of ln[**5**]/[**5**]$_0$ versus time gave a straight line for the data at each different temperature. The first-order rate constants were obtained from the slopes of these lines. An Eyring plot of the rate constants yielded a straight line from which ΔH^{+} and ΔS^{+} were determined. Since only one rate measurement was acquired at each temperature, error analysis of the Eyring parameters was determined based on a least-squares fit of the data.

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[1] For complementary historical overviews of this area, see: a) I. Gutman, J. H. Potgieter, *J. Chem. Educ.* **1994**, *71*, 222–224; b) J. H. Potgieter, *J. Chem. Educ.* **1991**, *68*, 280–281.

[2] See, for example: a) P. J. Garratt, *Aromaticity*, Wiley, New York, **1986**; b) V. I. Minkin, M. N. Glukhovtsev, B. Y. Simkin, *Aromaticity and Antiaromaticity*, Wiley, New York, **1994**; c) Y. Kobayashi, I. Kumadaki, *Top. Curr. Chem.* **1984**, *123*, 103–150; d) A. T. Balaban, *Rev. Roum. Chim.* **1966**, *11*, 1097–1116; e) D. S. Warren, B. M. Gimarc, *J. Am. Chem. Soc.* **1992**, *114*, 5378–5385.

[3] M. Regitz, H. Heydt, U. Bergsträsser in *Advances in Strain in Organic Chemistry, Vol. 5* (Ed.: B. Halton), JAI Press, London, **1996**, pp. 161–243, and references therein.

[4] D. L. Thorn, R. Hoffmann, *Nouv. J. Chim.* **1979**, *3*, 39–45.

[5] a) G. P. Elliott, W. R. Roper, J. M. Waters, *J. Chem. Soc. Chem. Commun.* **1982**, 811–813; b) G. P. Elliott, N. M. McAuley, W. R. Roper, *Inorg. Synth.* **1989**, *26*, 184–189; c) J. R. Bleeke, Y.-F. Xie, W.-J. Peng, M. Y. Chiang, *J. Am. Chem. Soc.* **1989**, *111*, 4118–4120; d) J. R. Bleeke, *Acc. Chem. Res.* **1991**, *24*, 271–277; e) J. R. Bleeke, R. Behm, Y.-F. Xie, M. Y. Chiang, K. D. Robinson, A. M. Beatty, *Organometallics* **1997**, *16*, 606–623; f) J. R. Bleeke, R. Behm, *J. Am. Chem. Soc.* **1997**, *111*, 8503–8511; g) J. Yang, W. M. Jones, J. K. Dixon, N. T. Allison, *J. Am. Chem. Soc.* **1995**, *117*, 9776–9777.

[6] a) M. S. Kralik, A. L. Rheingold, R. D. Ernst, *Organometallics* **1987**, *6*, 2612–2614; b) H. W. Bosch, H.-U. Hund, D. Nieltlispach, A. Salzer, *Organometallics* **1992**, *11*, 2087–2098; c) J. R. Bleeke, L. A. Bass, Y.-F. Xie, M. Y. Chiang, *J. Am. Chem. Soc.* **1992**, *114*, 4213–4219; d) W. Lin, S. R. Wilson, G. S. Girolami, *J. Chem. Soc. Chem. Commun.* **1993**, 284–285; e) U. Bertling, U. Englert, A. Salzer, *Angew. Chem.* **1994**, *106*, 1026–1028; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1003–1005; f) W. Lin, S. R. Wilson, G. S. Girolami, *Organometallics* **1997**, *16*, 2356–2361; g) U. Englert, F. Podewils, I. Schiffers, A. Salzer, *Angew. Chem.* **1998**, *110*, 2196–2197; *Angew. Chem. Int. Ed.* **1998**, *37*, 2134–2136.

[7] R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 2597–2598.

[8] J. Schwartz, D. W. Hart, B. McGiffert, *J. Am. Chem. Soc.* **1974**, *96*, 5613–5614.

[9] For a general review of cyclopropene transition metal complexes, see: Z. Goldschmidt in *The Chemistry of the Cyclopropyl Group, Vol. 2*, (Ed.: Z. Rappoport), Wiley, New York, **1995**, pp. 495–695.

[10] R. T. Li, S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1994**, *116*, 10032–10040.

[11] R. P. Hughes, J. W. Reisch, A. L. Rheingold, *Organometallics* **1985**, *4*, 241–244.

[12] J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, **1987**.

[13] R. Boese in *Advances in Strain in Organic Chemistry, Vol. 2* (Ed.: B. Halton), JAI Press, London, **1992**, pp. 191–254.

[14] a) L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 8130–8145; b) D. L. Hughes, G. J. Leigh, C. N. McMahon, *J. Chem. Soc. Dalton Trans.* **1997**, 1301–1307.

[15] For a review of benzvalene chemistry, see: M. Christl, *Angew. Chem.* **1981**, *93*, 515–532; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 529–546.

[16] a) P. Binger, P. Muller, R. Benn, R. Mynott, *Angew. Chem.* **1989**, *101*, 647–648; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 610–611; b) S. T. Nguyen, L. K. Johnson, R. H. Grubbs, *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975; c) M. R. Gagne, R. H. Grubbs, J. Feldman, J. W. Ziller, *Organometallics* **1992**, *11*, 3933–3935; d) B. T. Flatt, R. H. Grubbs, R. L. Blanski, J. C. Calabrese, J. Feldman, *Organometallics* **1994**, *13*, 2728–2732.

[17] N. J. Turro, C. A. Renner, T. J. Katz, K. B. Wiberg, H. A. Connon, *Tetrahedron Lett.* **1976**, 4133–4136.

[18] Repetition of this experiment without $AgBF_4$ showed that complex **5** remained unchanged after several hours in acetonitrile.

[19] A. Padwa, T. J. Blacklock, R. Loza, *J. Org. Chem.* **1982**, *47*, 3712–3721.

[20] M. J. Burk, R. H. Crabtree, *Inorg. Chem.* **1986**, *25*, 931–932.

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