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Metallabenzenes and Valence Isomers. 3. Unexpected Rearrangement of Two Regioisomeric Iridabenzenes to an (η^5-Cyclopentadienyl)iridium(I) Complex

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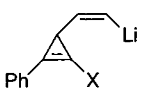
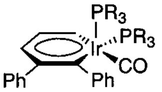
*Summary: The reaction of (Z)-1-phenyl-2-(trimethylsilyl)-3-(2-lithiovinyl)cyclopropene (**4**) with Vaska's complex generates the iridabenzvalene **8**, the iridabenzene **9**, and the cyclopentadienyl complex **10** in a 10:2:3 ratio. Heating this mixture to 75 °C converts **8** and **9** to **10**. NMR studies over a 24 h period at 75 °C show that samples containing pure **8** isomerize to **10** in high yield and generate regioisomeric iridabenzene **11** as an intermediate.*

Metallabenzenes,[1] organic/transition-metal "hybrids" which possess aromatic properties, have been shown to exhibit many similarities to heterobenzenes—downfield chemical shifts for ring protons, planarity of the six-membered metallacycle, no alternation of bond lengths, arene displacement from (arene)Mo complexes, and even electrophilic aromatic substitution.[2,3] The transition-metal center, however, exerts significant influence on the chemistry of the system by undergoing oxidative-addition, ligand-dissociation, and electron-transfer processes. Unfortunately, the limited number of metallabenzenes and the lack of a general synthetic route to this class of metallacycles have restricted detailed systematic studies. Recently, we described a direct path to generate metallabenzenes, which involved an intramolecular, metal-promoted cyclopropene rearrangement. This method has been applied successfully to generate iridabenzenes (e.g., **1**) by reactions of nucleophilic (*Z*)-1,2-diphenyl-3-(2-lithiovinyl)cyclopropene (**2**) with Vaska's complex[4] and several Vaska-type complexes.[5] In addition, the first metallabenzene valence isomers, namely iridabenzvalenes (e.g., **3**), can be generated and isomerized cleanly to iridabenzenes.[5] Extension of this new route to other metals and other cyclopropenes should permit access to numerous metallabenzenes bearing a variety of substituents on the carbon backbone. In this latter regard, we present herein the reaction of lithiate **4** with Vaska's complex, resulting in formation of an iridabenzvalene and two regioisomeric iridabenzenes, and their facile rearrangement to an (η^5-cyclopentadienyl)iridium(I) complex.



2 (X=Ph)
4 (X=SiMe$_3$)



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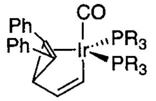

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The choice of cyclopropene **5** (Scheme 1) as the ligand for this study was inspired by three factors. We wished to see (1) how replacement of one of the phenyl units with a trimethylsilyl group would influence the overall chemistry of metallabenzene formation, (2) what would be the regiochemical outcome using an unsymmetrical cyclopropene, and (3) if removal of the trimethylsilyl group by fluoride ion could lead to monosubstituted metallaaromatics. Compound **5** was prepared by reduction of ester **6**[6] with DIBAL-H and subsequent oxidization with Dess−Martin periodinane.[7] The Wittig reaction of aldehyde **7** with $Ph_3P{=}CHI$[8] gave **5** with high stereoselectivity (>15:1 *Z*:*E*). Lithium−iodine exchange with 1 equiv of butyllithium in Et_2O at −78 °C generated lithiate **4**. Addition of this intermediate to $(Ph_3P)_2Ir(CO)Cl$ at −78 °C and then warming to ambient temperature over a 3 h period resulted in a mixture of products. Fast chromatography on silica gel gave a 47% yield of purified mixture of **8**, **9**, and **10** in a ratio of 10:2:3. Complexes **8** and **10** could be isolated independently through chemical methods (by treatment of the purified mixture with MeI and with heat (vide infra), respectively); nevertheless, samples of **9** always contained significant amounts of either **8** or **10**. Solutions of **8** and **10** are stable at room temperature for several weeks, while solutions of **10** "enriched" with **9** show that the signals for **9** slowly disappear over 1 week at 0 °C.

The composition of complexes **8** and **9** was determined by comparison of their NMR chemical shifts with those of structurally similar analogues **3** (R = Me)[5a] and **1** (R = Ph),[4] respectively. Resonance peaks in the $^1H/^{13}C$ NMR spectra corresponding to the three CH groups in iridabenzvalene **8** are observed at δ_H/δ_C 6.66, 6.33, 3.08/

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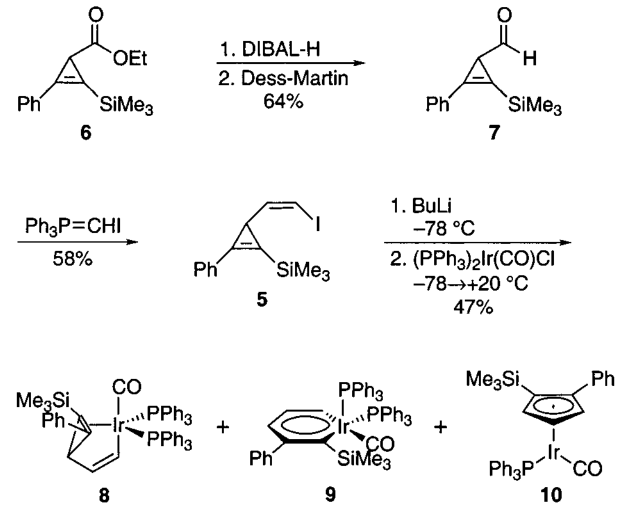
Scheme 1



151.25, 144.15, 56.97 ppm, which are close to those reported previously for **3** (R = Me) (δ_H/δ_C 7.25, 6.55, 3.82/146.76, 141.79, 60.83 ppm).[5a] The upfield shift of ring protons in **8** are attributed to stronger shielding by the $-SiMe_3$ group. It is noteworthy that iridacycle **8**, which has bulkier, less donating phosphines compared to **3** (R = Me), forms as the major product of this reaction, whereas the corresponding diphenyl-substituted molecule from Vaska's complex (**3**, R = Ph) is never observed. A possible explanation is that the longer carbon−silicon bond makes the cyclopropene π-bond accessible for bonding to the electron-deficient Ir center, as well as increased electron density of the π-bond due to the electron-donating $-SiMe_3$ group. Typical of metallabenzenes, the ^1H NMR spectrum of **9** exhibits downfield resonance peaks of the hydrogens ortho and para to the iridium at 10.45 and 8.14 ppm, which are comparable to the analogous signals in **1** (R = Ph) at 10.79 and 8.44 ppm, respectively.[4] The signals for the meta H and the remaining protons of **9** were not observed because of the small amount of material, the instability of the compound, and overlap with the phenyl resonances of **8** and **10**.

Complex **10** was unambiguously characterized by ^1H and ^{13}C NMR spectroscopy and by single-crystal X-ray diffraction. The $^1H/^{13}C$ NMR resonances of the three −CH groups in the cyclopentadienyl ring of **10** appear at δ_H/δ_C 5.40, 4.67, 4.54/91.06, 89.67, 85.47 ppm. Signals at 111.85 and 92.25 ppm are attributed to the two quaternary C atoms. The IR spectrum shows a band at 1936 cm^{-1} for the CO stretching frequency. X-ray-quality crystals of **10** were grown from hexane. Selected bond lengths and angles are listed in Figure 1.[9] In comparison to the parent CpIr(CO)PPh$_3$ complex,[10] the carbon−carbon bonds in the cyclopentadienyl moiety are lengthened on average about 0.035 Å. The effect of steric interactions between the bulky trimethylsilyl and phenyl groups is reflected in a slightly larger Si−C3−C2 bond angle (130.9(3)°) compared to Si−C3−C4 (123.9(3)°).

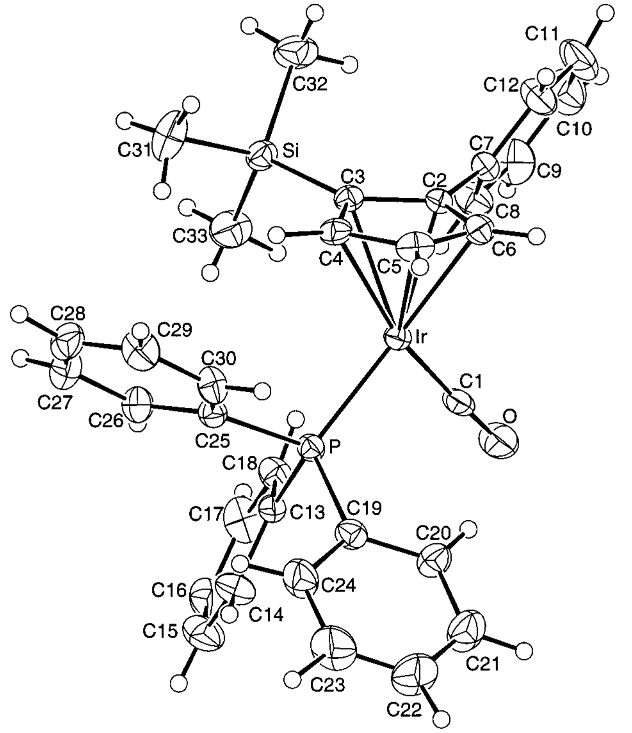
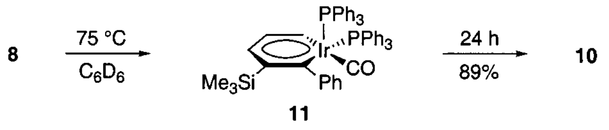


Figure 1. Molecular structure of complex **10**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ir−P = 2.235(1), Ir−C1 = 1.814(4), Ir−C2 = 2.251(3), Ir−C3 = 2.306(3), Ir−C4 = 2.254(4), Ir−C5 = 2.310(4), Ir−C6 = 2.284(4), C3−Si = 1.872(4), C2−C3 = 1.433(5), C2−C6 = 1.437(5), C2−C7 = 1.498(5), C3−C4 = 1.438(5), C4−C5 = 1.420(6), C5−C6 = 1.395(6); P−Ir−C1 = 90.3(1), P−Ir−Cp = 133.4(1), C1−Ir−Cp = 136.3(2), Ir−C1−O = 177.4(3), C3−C2−C6 = 108.7(3), C3−C2−C7 = 125.3(3), C6−C2−C7 = 125.3(3), Si−C3−C2 = 130.9(3), Si−C3−C4 = 123.9(3), C2−C3−C4 = 105.1(3), C3−C4−C5 = 109.9(3), C4−C5−C6 = 107.6(3), C2−C6−C5 = 108.5(3).

Scheme 2



In an attempt to prepare a pure sample of **9**, we heated a benzene-d_6 solution of **8** at 75 °C for 24 h. Although valence isomerization to yield **9** was the expected transformation, ^1H NMR analysis of the reaction mixture showed exclusive and essentially quantitative formation of **10**. This result is surprising, given the ease with which benzvalene **3** (R = Me) can be converted to **1** (R = Me). Closer inspection of the thermal chemistry of these complexes showed multiple conversions. Analysis of a sample of **8** heated at 75 °C for 1 h revealed, in addition to unreacted **8** and a small amount of **10**, the characteristic ^1H NMR signals for an iridabenzene; however, these resonances were at 10.85 and 8.78 ppm, suggesting the formation of a different iridabenzene. The assignment of **11** as the regioisomer

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(9) Crystal data for **10**: $C_{33}H_{32}IrOPSi$, M_r = 695.9, monoclinic, $P2_1/a$, a = 9.1428(17) Å, b = 32.708(3) Å, c = 9.7927(9) Å, β = 94.344(12)°, V = 2920.0(6) Å^3, Z = 4, D_{calcd} = 1.583 g cm^{-3}, μ = 47.0 cm^{-1}, F(000) = 1376, Mo Kα radiation (λ = 0.710 73 Å), T = 300 K, $2\theta_{max}$ = 50°, 5114 independent reflections scanned, 5114 reflections in refinement on F^2, 463 parameters, $R(F)$ = 0.022 ($I = \sigma(I)$), $R_w(F^2)$ = 0.052 (all data). Data were collected on an Enraf-Nonius CAD-4 Turbo diffractometer. Structure refinement (C atoms anisotropic, H atoms isotropic) was accomplished with the teXsan program suite (version 1.7 for SGI workstations).

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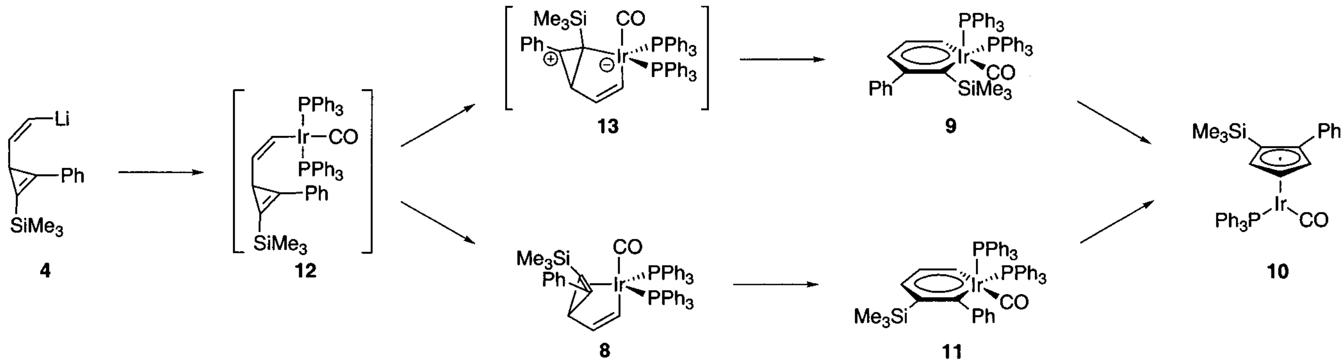
Scheme 3



depicted in Scheme 2 is based on ^{1}H$-$^{29}Si gHMQC NMR experiments, which indicate that the para proton at 8.78 ppm is coupled to a silicon nucleus.[11] Careful monitoring of the reaction showed that the concentration of **11** peaked after 8−10 h and then steadily decreased. Benzvalene **8** was completely consumed after 15 h, with total conversion of **8** and **11** to **10** after 24 h at 75 °C in 89% isolated yield. Heating the purified mixture of **8**−**10** furnished similar results. After 1 h, the resonances of **9** had disappeared and been replaced by signals for **11**. The intensity of the signals for **8** and **10** had decreased and increased, respectively, suggesting that **9** goes to **10** and **8** goes to **11**. The disappearance of **8** and **11** progressed as described above upon further heating. After 24 h, transformation to **10** (with concomitant formation of PPh_3) was complete with a color change from red-brown to yellow.

The observed results and possible conversion pathways are summarized in Scheme 3. Addition of **4** to Vaska's complex furnishes the η^1-vinyl species[12] **12** which, upon coordination of the cyclopropene π-bond, yields predominantly benzvalene **8**. The small amount **9** and **10** in the initial reaction mixture could likely come from **13**, which may or may not be directly along the pathway to **8**. An intermediate such as **13** seems plausible, as the carbocation is stabilized by both the α-phenyl and the β-trimethylsilyl moieties. Subsequent ring opening results in regioselective formation of iridabenzene **9**. Similar regioselective addition of an unsymmetrical disubstituted cyclopropene has been observed in a metal-mediated cyclopropene ring rearrangement.[13] Complex **9**, however, is sterically destabilized by having the trimethylsilyl group adjacent to the bulky iridium fragment and thus undergoes a facile carbene migratory insertion[14] followed by dissociation of a Ph_3P ligand, leading to the formation of (cyclopentadienyl)iridium complex **10**.

Once formed, benzvalene **8** is stable at room temperature but slowly isomerizes to iridabenzene **11** upon heating. Although much less thermally labile than **9**, **11** also undergoes carbene migratory insertion at elevated temperatures to give **10**. It is possible that **9** is also an intermediate in the conversion of **8** to **10**; however, **9** was not detected during the isomerization of pure samples of **8**. The conversion of **9** and **11** to **10** is quite unexpected, since all other iridabenzenes that we[4,5] and others[1,2d,e] have previously studied have not undergone a similar rearrangement. For example, samples of **3** (R = Me, Et, *i*-Bu) can be cleanly and quantitatively isomerized to **1** with no evidence of subsequent rearrangement or decomposition.[5] In fact, iridabenzene **1** (R = Ph) is thermally stable to ca. 200 °C. Nevertheless, metallabenzenes have been implicated as intermediates in several reactions, yielding cyclopentadienyl−metal complexes.[15] The transformations described above are, to the best of our knowledge, the first documented examples of iridabenzenes rearranging to an (η^5-cyclopentadienyl)iridium(I) complex.

Further work will focus on the steric and electronic influence of substituents on the cyclopropene and on the phosphine ligands at the Ir center. The results of these studies will be reported shortly.

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Supporting Information Available: Text giving experimental details and spectral data for **8**−**11** and description of the X-ray structure of **10**, including structure refinement details and tables of atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, and mean planes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) In addition to the NMR experiments, compound **11** can be intercepted by a second iridium fragment, which is only produced at elevated temperatures needed to give **10**. The structure of the resultant dinuclear complex has been confirmed by X-ray crystallography: Wu, H.-P.; Weakley, T. J. R.; Haley, M. M. Unpublished results.

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