1174 *Organometallics* **2004,** *23,* 1174−1176

Communications

Rational Synthesis of Platinabenzenes[†]

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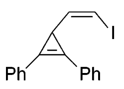
Received December 15, 2003

*Summary: Treatment of Cp*Pt(CO)I (**8**) with two nucleophilic (Z)-3-(2-lithiovinyl)cyclopropenes provides a rational synthesis of platinabenzenes **6** and **7**. The intermediate σ-vinyl complexes **9** and **10** are also isolated from the reaction mixtures and convert cleanly to the corresponding platinabenzenes in near-quantitative yield.*

For the last several years we have been exploring a general procedure for the synthesis of metallabenzenes[1] and their valence isomers starting from (*Z*)-3-(2-iodoethenyl)cyclopropenes such as **1**.[2−4] Treatment of **1** with BuLi and subsequent addition to Vaska-type complexes possessing small and/or electron-donating phosphines yielded iridabenzvalenes (e.g., **2**) with a σ-bond to the vinyl group of the vinylcyclopropene and π-coordination of the cyclopropene C=C double bond.[3,4] Cyclopropene−vinylalkylidene rearrangement,[5] initiated either through gentle heating of the intermediate benzvalene or by use of larger phosphines on the starting organometallic complex, led to formation of the corresponding iridabenzenes (e.g., **3**).[2] As part of our efforts to extend this methodology to other metal complexes,[6] we recently reported the first example of a platinabenzene (**4**)[7] in which an (η^5-1,2-diphenylcyclopentadienyl)platinum(II) unit was part of the metalla-aromatic ring. Interestingly, both the cyclopentadienyl (Cp′) and metalla-aromatic rings in **4** were derived from **1** in its reaction with (η^4-1,5-cod)PtCl$_2$. Subsequent attempts utilizing *cis*-Pt(PEt$_3$)$_2$MeI as the Pt source failed to yield platinabenzenes and instead furnished cationic (η^3-cyclopentadienyl)platinum(II) complexes such as **5**,[8] again with the cyclopentadienyl ring derived from **1**. The apparent preference for the formation of the Cp′Pt fragment, a result that has been very recently corroborated by DFT calculations,[9] led us to conclude that a platinum complex containing a coordinated Cp ring should likely be a viable starting material. We report herein the rational synthesis and characterization of platinabenzenes **6** and **7** starting from Cp*Pt(CO)I.



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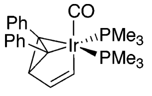

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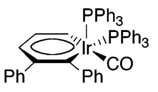

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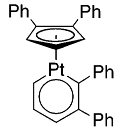

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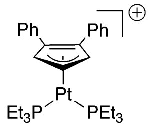

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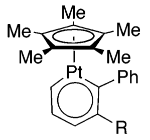

6 (R = Ph)
7 (R = *t*-Bu)

Surprisingly, compounds containing a (cyclopentadienyl)(halogen)platinum(II) fragment, the requisite unit needed to undergo ligand metathesis with lithiated **1**, are limited to a handful of examples. Of these, the best described complexes are Cp*Pt(CO)X (X = Cl, Br),[10] both of which are derived from the known platinum dimer [Cp*Pt(CO)]$_2$.[11] Reaction of lithiated **1** with Cp*Pt(CO)Cl and subsequent workup afforded mainly protonated **1** and recovered Pt complex along with trace amounts of a platinabenzene, on the basis of the presence of very small, low-field signals in the proton NMR spectrum. Apparently, ligand metathesis is extremely slow under the reaction conditions.

With Cp*Pt(CO)I (**8**) as the starting material, obtained by iodine oxidation[12] of [Cp*Pt(CO)]$_2$, the reaction proceeded via a different course (Scheme 1). After the lithium−halogen exchange on **1**, the vinyl lithiate was cannulated into the violet slurry of **8** in dry ether at −78 °C, the color of which changed to a transparent

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[†] Metallabenzenes and Valence Isomers. 7. Part 6: ref 2b.

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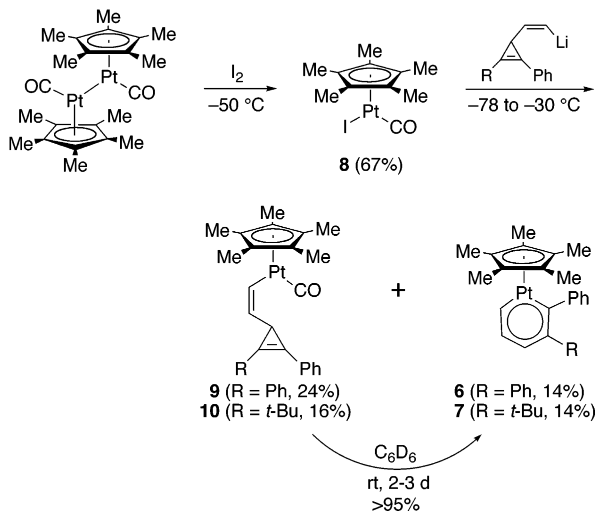
10.1021/om034371a CCC: $27.50

Scheme 1



orange. After standing overnight at −30 °C, the reaction mixture was worked up and flash-chromatographed on silica to furnish platinabenzene **6** as a red-orange solid in 14% isolated yield. The arene is presumably formed by CO loss from the 18-electron complex followed by coordination of the π-bond and then rearrangement of the cyclopropene moiety to give the aromatic platinacycle. A second compound, the σ-vinyl complex **9**, which is the immediate precursor to **6**, can also be isolated in 24% yield. In a similar manner, reaction of **8** with the lithiated 1-*tert*-butyl-2-phenyl analogue[13] of **1** afforded platinabenzene **7** and σ-vinyl complex **10** in 14% and 16% yields, respectively. Although the yields of platinabenzene initially isolated from the reaction mixtures were rather low, the relative ratio of benzene to σ-vinyl complex varied depending upon the length of time the material was in solution. Shorter reaction times and faster workups favored **9** and **10**. More importantly, though, near-quantitative isomerization of **9** and **10** to the corresponding arenes could be accomplished by storing the σ-vinyl complexes in a benzene solution at room temperature for 2−3 days, giving ca. 30−35% overall yield of the metalla-aromatics. Unlike most metallabenzenes, arenes **6** and **7** (and **4**) are air stable for several days both in solution and in the solid state.

The ^{1}H NMR spectrum for platinabenzene **7** exhibits the telltale resonances for the ring protons of a metallabenzene.[1] The peak for the proton ortho to platinum is shifted considerably downfield, due to the anisotropy of the platinum metal (11.83 ppm, $J_{\mathrm{Pt-H}} = 41$ Hz). The comparable resonance on complex **4** appears at 12.76 ppm ($J_{\mathrm{Pt-H}} = 65$ Hz). Additionally, a pseudotriplet and a doublet show up at 7.60 and 8.54 ppm, respectively, assignable to the meta and para protons, respectively. The methyl protons for the Cp* ring resonate at 1.56 ppm. In the ^{13}C NMR spectrum of **7**, the signals for the ortho carbons with respect to platinum appear at 187.72 and 203.65 ppm and are comparable to those in **4** (194.96 and 204.01 ppm).

The structure of **7** was confirmed by X-ray diffraction of the red solid recrystallized from hexanes, as shown in Figure 1.[14] Selected bond lengths and bond angles are given in Table 1. The compound crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell. The six-membered platinabenzene ring is essentially planar, as expected for an aromatic ring, with a mean deviation of 0.014 Å out of the plane. No significant bond alternation is present. The C−C bond lengths in the platinabenzene ring lie between 1.352 and 1.411 Å (average 1.387 Å), approximately the same length as observed in benzene. The Pt−C bond lengths are 1.972 and 1.930 Å. A similar average C−C bond length (1.385 Å) and similar Pt−C bond lengths (1.929 and 1.959 Å) are observed for **4**. Pt−C$_{\mathrm{Cp^*}}$ distances are in the range of 2.257−2.337 Å and thus corroborate the η^5 coordination of the Cp* ligand. Analogous to **4**, the cyclopentadienyl group is tilted slightly away (ca. 5°) from the Ph/*t*-Bu substituents on the arene backbone.

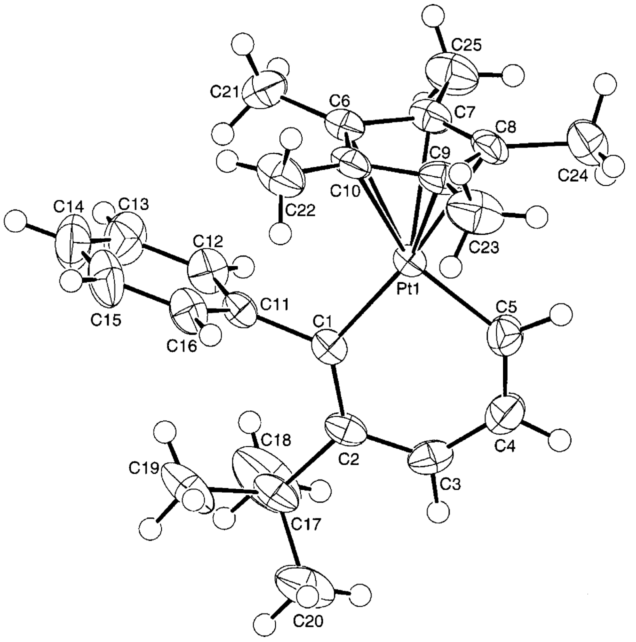


Figure 1. Molecular structure of platinabenzene **7**. Ellipsoids are drawn at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Platinabenzenes 4 and 7

	7[a]	4[b]		7[a]	4[b]
Pt−C1	1.972(5)	1.959(3)	C3−C4	1.392(8)	1.381(6)
Pt−C5	1.930(5)	1.929(4)	C4−C5	1.352(8)	1.364(6)
Pt−C6	2.337(6)	2.342(3)	C1−Pt−C5	89.7(2)	89.3(2)
Pt−C7	2.271(7)	2.327(3)	Pt−C1−C2	129.8(4)	129.2(3)
Pt−C8	2.257(7)	2.289(4)	C1−C2−C3	119.8(5)	122.6(3)
Pt−C9	2.265(6)	2.270(4)	C2−C3−C4	127.0(5)	124.8(4)
Pt−C10	2.324(6)	2.299(4)	C3−C4−C5	124.0(5)	124.1(4)
C1−C2	1.411(7)	1.387(5)	C4−C5−Pt	129.7(4)	130.3(3)
C2−C3	1.391(7)	1.395(5)			

[a] Average values for two independent molecules. [b] Reference 4.

In summary, the rational synthesis of two platinabenzenes by the reaction of Cp*Pt(CO)I with nucleophilic (*Z*)-3-(2-lithiovinyl)cyclopropenes has been accom-

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[13] Wu, H.-P.; Weakley, T. J. R.; Haley, M. M. Manuscript in preparation.

[14] Crystal data for **7**: $C_{25}H_{32}Pt$, $M_r = 527.6$, triclinic, $P\bar{1}$, $a = 10.569(4)$ Å, $b = 11.656(3)$ Å, $c = 18.575(8)$ Å, $\alpha = 80.39(3)°$, $\beta = 80.61(3)°$, $\gamma = 76.28(3)°$, $V = 2173.4(14)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.612$ g cm^{-3}, $\mu = 64.4$ cm^{-1}, $F(000) = 1040$, Mo Kα radiation ($\lambda = 0.710\ 73$ Å), $T = 217$ K, $2\theta_{\max} = 52°$, 8513 independent reflections scanned, 7288 nonabsent reflections in refinement on F^2, 469 parameters, $R(F) = 0.031$ ($I \geq \sigma(I)$), $R_w(F^2) = 0.076$ (all data). Data were collected on an Enraf-Nonius CAD-4 Turbo diffractometer. Structure refinement (non-C atoms anisotropic, H atoms riding, isotropic) was accomplished with the teXsan program suite (version 1.7 for SGI workstations).

plished. In addition, intermediate Cp*Pt(σ-vinyl) complexes can be isolated and characterized from the reaction mixtures. With several new 3-vinylcyclopropene ligands in hand,[13] this new route should lend itself to the preparation and detailed study of a number of platinabenzenes. The results of this work will be reported in due course.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-0075246) for support of this research. V.J. gratefully acknowledges the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship. We thank Dr. Alex Blumenfeld (University of Idaho) for acquisition of the HMBC and HMQC NMR spectra.

Supporting Information Available: Text giving experimental details and spectral data for **6**−**10** and a description of the X-ray structure of **7**, including a figure of **7**, text giving structure refinement details, and tables of atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, and mean planes; crystallographic data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

OM034371A