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Platinabenzenes: Synthesis, Properties, and Reactivity Studies of a Rare Class of Metalla-aromatics[†]

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Lithium−halogen exchange of (*Z*)-1,2-diphenyl-3-(2-iodoethenyl)cyclopropene (**1**) and subsequent addition to (η^4-1,5-cod)PtCl$_2$ yields the platinabenzene (η^5-C$_5$H$_3$Ph$_2$)[PtC$_5$H$_3$Ph$_2$] (**7**), in which the metallacyclic ring and C$_5$H$_3$Ph$_2$ (Cp′) unit are both derived from the cyclopropene skeleton. Starting instead with (η^5-C$_5$Me$_5$)Pt(CO)I, treatment with three nucleophilic (*Z*)-3-(2-lithiovinyl)cyclopropenes provides platinabenzenes (η^5-C$_5$Me$_5$)[PtC$_5$H$_3$PhR] (R = Ph (**8**), *t*-Bu (**9**), Me (**10**)) in low to modest yield. All platinabenzenes have been fully characterized by NMR spectroscopy and X-ray crystallography. Intermediate σ-vinyl complexes (η^5-C$_5$Me$_5$)Pt(σ-C$_5$H$_3$PhR) (R = Ph (**14**), *t*-Bu (**15**)) are also isolated from the reaction mixtures and convert cleanly to the corresponding platinabenzenes in near quantitative yield. Reactivity studies of (η^5-C$_5$Me$_5$)-[PtC$_5$H$_3$Ph$_2$] with a variety of reagents/conditions are also reported.

Introduction

For the past decade we have been examining the synthesis of metallabenzenes[1,2] and their valence isomers starting from (*Z*)-3-(2-iodoethenyl)cyclopropenes such as **1**.[3−8] Treatment of **1** with BuLi and subsequent addition to Vaska-type metal complexes possessing small and/or electron-donating phosphines furnished iridabenzvalenes (e.g., **2**), compounds with a σ-bond to the vinyl group of the vinylcyclopropene and π-coordination of the cyclopropene C=C double bond.[5−8] Cyclopropene−vinylalkylidene rearrangement,[9−11] initiated either through gentle heating of the intermediate benzvalene or by using larger phosphines on the starting organometallic complexes, led to formation of the corresponding iridabenzenes (e.g., **3**).[3,4] Inclusion of large, less electron-donating phosphines resulted in direct formation of the iridabenzene. In certain instances, the iridabenzenes were not thermally stable and underwent a carbene migratory insertion to yield η^5-cyclopentadienyliridium complexes (e.g., **4**),[6−8] which is a known decomposition pathway of metallabenzenes.[12]

Since the vinylcyclopropene route has successfully generated a large variety of iridabenzenes and iridabenzvalenes, we wished to extend our methodology to include other metals. Moving up to the second-row metals proved to be problematic. Starting with Rh complexes, we could detect rhodabenzenes in the crude reaction mixtures; however, these studies to date have afforded only rhodabenzvalenes such as **5**.[13] All attempts to isomerize these molecules to the corresponding rhodabenzenes have instead furnished either Cp′Rh

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[†] Metallabenzenes and Valence Isomers 10. For part 9, see ref 7.

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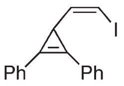

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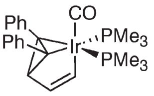

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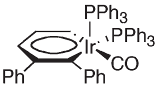

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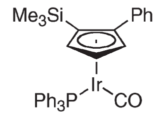

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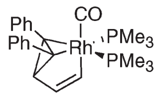

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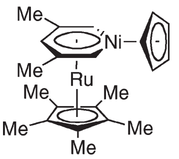

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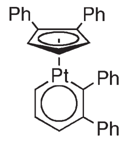

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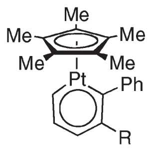
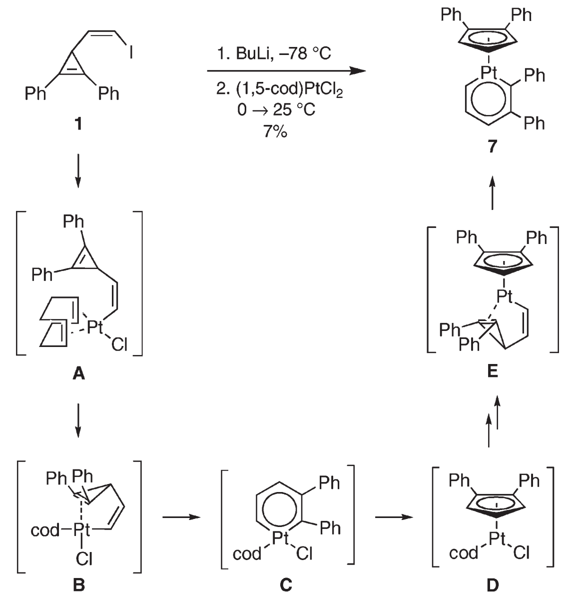


8 (R = Ph)
9 (R = *t*-Bu)
10 (R = Me)
11 (R = Et)
12 (R = *i*-Pr)

Scheme 1



complexes or unidentifiable mixtures. Efforts with Ru led not to ruthenabenzenes but instead to ruthenocenes.[1b] Somewhat surprisingly, prior to our initial[14] and follow-up[15] communications, there was only a single report in the literature of a metallabenzene incorporating a group 10 metal, namely, nickelabenzene **6**.[16] This molecule, however, most likely required the stabilization afforded by the η^6-bound Cp*Ru unit in order to be isolable. In fact, a large number of known metallabenzenes are η^6-coordinated to a second transition-metal fragment.[1a] We therefore sought to prepare stable, uncoordinated metallabenzenes containing a group 10 metal. This paper details our successful synthesis and characterization of metallacycles **7**–**10**, the first examples of platinabenzenes, and describes attempts in extending this method to structural analogues **11** and **12**. We also report the isolation and characterization of intermediate σ-vinyl complexes **14** and **15**, which upon heating afford quantitatively arenes **8** and **9**, respectively.

Results and Discussion

Initial Studies Using (η^4-1,5-cod)PtCl$_2$. Although we investigated several Pt(II) complexes[17] as possible starting points,[18] we found success with one of the simplest, (η^4-1,5-cod)PtCl$_2$. Lithium–halogen exchange of **1** (Scheme 1) and addition of the resultant vinyl lithiate to an ether suspension of (cod)PtCl$_2$ produced a dark brown slurry, from which platinabenzene **7** was isolated as a red solid after column chromatography, albeit in only 7% yield. Interestingly, both the η^5-1,2-diphenylcyclopentadienyl (Cp′) ring and metalla-aromatic ring in **7** must be derived from **1** in its reaction with (cod)PtCl$_2$.

Subsequent attempts in our lab utilizing *cis*-Pt(PEt$_3$)$_2$MeI as the Pt source failed to yield platinabenzenes and instead furnished cationic (η^3-1,2-diphenylcyclopentadienyl)Pt(II) complexes.[19] Again, the cyclopentadienyl ring in these complexes was derived from **1**. The apparent preference for the formation of the Cp′Pt fragment in this system, a result corroborated by DFT calculations,[12] led us to conclude that a Pt complex containing a coordinated Cp ring should be a viable starting material in platinabenzene synthesis.

Second-Generation Arenes From Cp*Pt(CO)I. Interestingly, compounds containing a (cyclopentadienyl)(halogen)-Pt(II) fragment, the moiety needed to undergo ligand metathesis with lithiated **1**, are limited to very few examples.[20] After a few unsuccessful trials with these compounds, we elected to start with previously unknown Cp*Pt(CO)I (**13**), obtained by iodine oxidation[21] of Boag's dimer [Cp*Pt(CO)]$_2$ (Scheme 2).[22] After the lithium–halogen exchange on **1**, the vinyl lithiate was added into the violet slurry of **13** in dry Et$_2$O at −78 °C, which resulted in a color change to light orange. After standing overnight at −30 °C, the reaction was worked up and chromatographed on silica to furnish platinabenzene **8**, isolated as a red-orange solid in 14% yield. A second compound, σ-vinyl complex **14**, which is the immediate precursor to **8**, was also isolated in 24% yield. Arene **8** is presumably formed by CO loss from the 18-electron complex **14**, followed by coordination of the cyclopropene π-bond and then rearrangement of the strained three-membered ring to give the aromatic platinacycle.

As shown in Figure 1, **14** could be converted to **8** cleanly in C$_6$D$_6$ solution at room temperature with no evidence of intermediate species. Only two signals for the Cp* methyl

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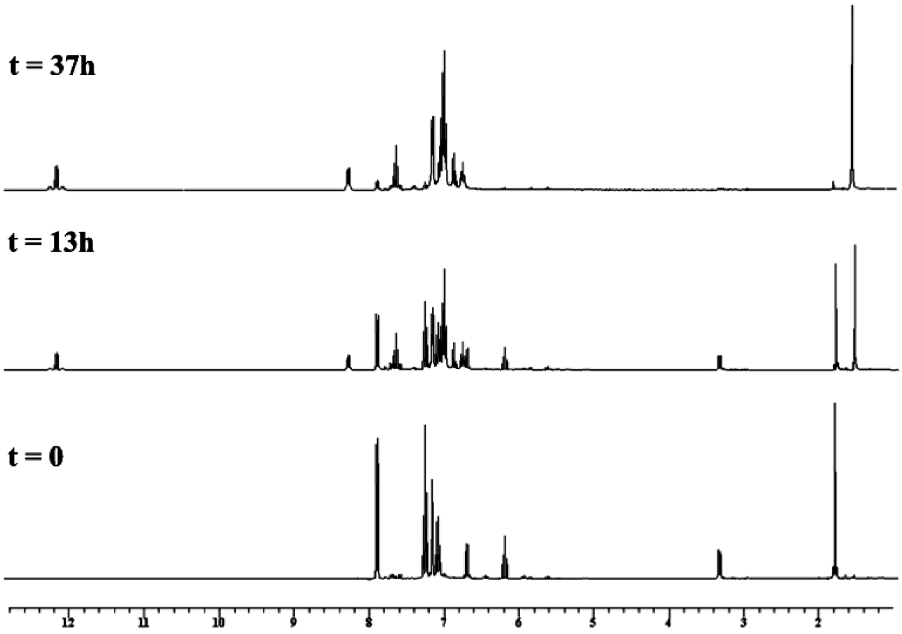
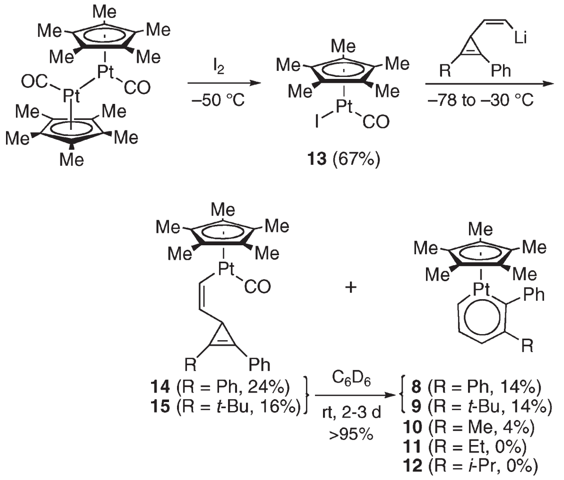


Figure 1. Conversion of **14** to **8** at room temperature monitored by ^{1}H NMR spectroscopy in C_6D_6.

Scheme 2



protons of **14** [δ 1.84 ($J_{\mathrm{Pt-H}} = 14$ Hz)] and **8** [δ 1.59 ($J_{\mathrm{Pt-H}} = 8$ Hz)] are observed throughout the whole conversion.

On the basis of this successful rational synthesis of platinabenzene **8** and taking into account the results of theoretical studies on platinabenzenes, we can now postulate a plausible mechanism of formation for platinabenzene **7** (Scheme 1). Exchange of one of the chloride ligands by the organolithium reagent, a commonly used method for the synthesis of Pt-σ-alkyl compounds,[17] would give σ-bonded vinylcyclopropene complex **A**. Intramolecular displacement of one of the 1,5-cyclooctadiene double bonds by the cyclopropene double bond should afford **B**. Subsequent ring-opening of the strained cyclopropene would ideally lead to **C**. Both computational[12] and experimental[19] studies have shown that square-planar platinabenzenes like **C** are thermally unstable and readily undergo carbene migratory insertion to give either η^3- or η^5-cyclopentadienylplatinum complexes such as **D**. Repetition of the first three mechanistic steps with a second equivalent of vinyl lithiate—as required for the formation of platinabenzene **8**—would furnish platinabenzene **7** via intermediate **E**.

Stability of Platinabenzenes. Heating solutions of **7** or **8** at 100 °C for 48 h resulted in no noticeable decomposition in the ^{1}H NMR spectrum. This finding is in contrast to the reactivity of many iridabenzenes[6−8] (and putative platinabenzenes similar to **C**),[19] which easily undergo carbene migratory insertion to afford Cp complexes such as **4**. Van der Boom and Martin performed calculations on the stability of several platinabenzene complexes toward this deleterious pathway.[12] On the basis of their results, inclusion of the cyclopentadienyl ligand appears to stabilize the platinabenzene by increasing the energy barrier for carbene migratory insertion. In the case of $C_5H_5Pt(PH_3)_2^+$, a computational analogue of **C**, the transition state to forming (η^5-Cp)Pt-$(PH_3)_2^+$ was only 24.0 kcal mol^{-1}, which corroborates our earlier experimental results.[19] For the Cp complex C_5H_5-PtCp, the computational analogue of **7**−**10**, the transition state for forming (η^3-Cp)$_2$Pt was considerably higher, calculated to be 45.9 kcal mol^{-1}. De Proft and Geerlings utilized the isomerization method to predict the aromatic stabilization energy (ASE) of the platinabenzene ring in model system Pt($C_5H_3Me_2$)(η^3-$C_5H_3Me_2$).[23] They obtained a calculated value of 23.4 kcal mol^{-1}, approximately two-thirds of the reported ASE for benzene (33.8 kcal mol^{-1}). Fernández and Frenking recently used their energy decomposition analysis method, which provides a quantitative measure for the strength of conjugation in cyclic molecules, to examine a number of metallabenzenes.[24] Their computed ASE value for C_5H_5PtCp (37.6 kcal mol^{-1}) was higher than the ASE values of any of the other metallabenzenes studied and was just slightly lower than their ASE value for benzene (42.5 kcal mol^{-1}). As a whole, these computational results clearly corroborate our experimental findings: inclusion of a cyclopentadienyl moiety as part of the overall platinabenzene structure affords a thermodynamically robust, strongly aromatic metallacycle.

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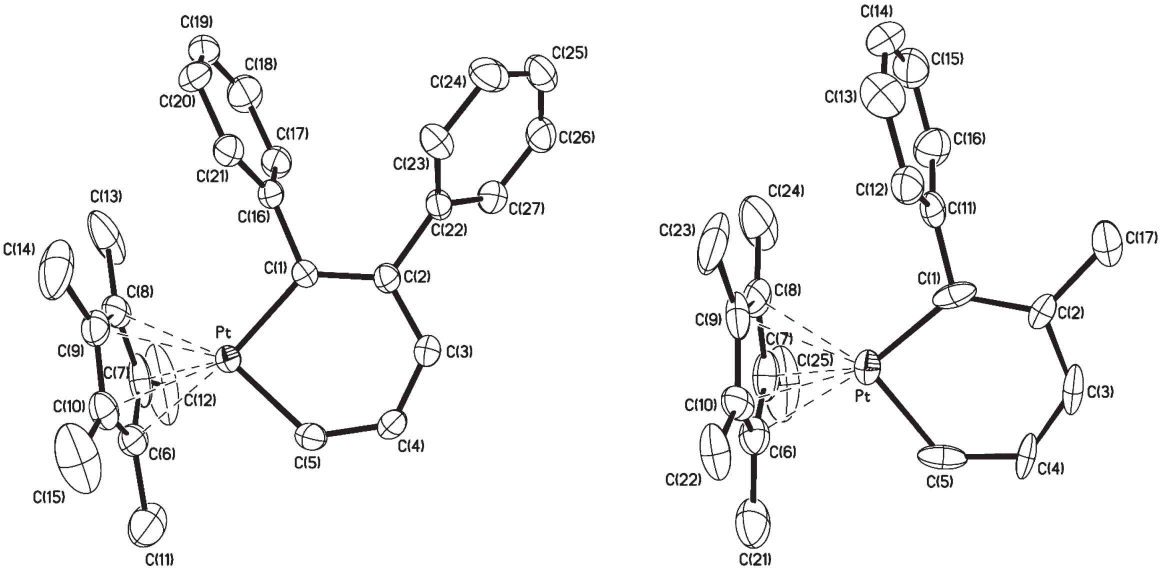

Figure 2. X-ray structure of platinabenzenes **8** (left) and **10** (right); ellipsoids at 30% probability level.

Platinabenzenes Derived from Unsymmetrical Precursors. In a manner similar to **8**, reaction of **13** with the lithiated 1-*tert*-butyl-2-phenyl analogue[7] of **1** afforded platinabenzene **9** and σ-vinyl complex **15** in 14% and 16% yield, respectively. Although the yields of platinabenzene initially isolated from the reaction mixtures were 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 **14** and **15**. Analogous to **14**, near quantitative isomerization of **15** to the corresponding arene could be accomplished by storing the σ-vinyl complex in a benzene solution at room temperature for 2−3 days, giving ca. 30% overall yield of the metalla-aromatic.

As exciting as the results were for **8/9** and **14/15**, we encountered problems when attempting to extend this synthetic strategy to the other known 1-alkyl-2-phenyl analogues[7] of **1**. The major difference between **8/9** and **10**−**12** is the presence of hydrogen atoms on the carbon atoms directly attached to the platinacycle. In the case of the methyl analogue, only a small amount of platinabenzene **10** (4% yield) could be isolated. No evidence of the corresponding σ-vinyl complex was found. In the cases of the ethyl and isopropyl analogues, only minute amounts of platinabenzenes **11** and **12**, respectively, could be detected, as shown by the presence of a small proton resonance around 12 ppm in the ^{1}H NMR spectrum. All attempts to isolate these arenes were unsuccessful. The difficulty in synthesizing these complexes appears to be related to the formation of side products like Boag's dimer and the regenerated starting vinyl iodides, which were identified in the reaction mixtures. Control experiments showed that these latter compounds were indeed re-formed during the reaction and did not originate from incomplete lithium−iodine exchange. While a number of potential deleterious mechanisms abound, these are beyond the context of the current synthetic study and will be the subject of future work.

Table 1. ^{1}H NMR Chemical Shifts of the Ring Protons for Platinabenzenes 7−10[a]

cmpd	H5	H4	H3
7	12.76	7.42	8.20
8	12.09	7.63	8.25
9	11.83	7.60	8.54
10	11.93	7.57	8.10

[a] Data obtained in C_6D_6 and given in ppm.

Spectroscopic Data. Unlike most metallabenzenes, arenes **7**−**10** are air-stable for several days in solution and in the solid state; thus, their spectroscopic data can be easily secured. The ^{1}H NMR spectrum for platinabenzene **8** exhibits the characteristic resonances for the ring protons of a metallabenzene.[1a,1b] The peak for proton H5 (see Figure 2 for atom labeling) is shifted considerably downfield due primarily to the multiple (π) bonding between the metal and carbon (12.09 ppm, $J_{\mathrm{Pt-H}} = 50$ Hz). The comparable resonance on complex **7** appears at 12.76 ppm ($J_{\mathrm{Pt-H}} = 65$ Hz). Additionally, a pseudotriplet and a doublet show up at 7.63 and 8.25 ppm, respectively, assignable to protons H4 and H3, respectively, of **8**. The methyl protons on the Cp* ring resonate at 1.59 ppm. In the ^{13}C NMR spectrum of **8**, the signals for the carbon atoms directly connected to the Pt center appear at 188.7 (C5) and 200.6 (C1) ppm and are comparable to those in **7** (194.9 and 204.0 ppm).

Comparison of the ^{1}H NMR signals of the ring protons reveals some clear trends in the platinabenzene series (Table 1). Essentially, the more electron-donating substituents cause proton H5 to shift upfield. The biggest difference comes from replacing the diphenylcyclopentadiene (Cp′) in **7** with the pentamethylcyclopentadiene (Cp*) in **8**. For this change alone the H5 proton resonance shifts 0.67 ppm upfield, illustrating how much more electron donating the Cp* unit is compared to the Cp′ group. Replacement of the phenyl group in **8** with a *tert*-butyl group as in **9** again shifts the H5 resonance upfield from 12.09 ppm to 11.83 ppm. The less electron-donating methyl substituent on **10** shows an H5 resonance in between at 11.93 ppm.

Interestingly, the opposite trend is observed for the H3 proton signals in **7**−**9**. In this case the more electron-donating substituents apparently cause the signals for H3 to appear further downfield. The H3 signal for the most electron-rich arene, *t*-Bu-substituted **9**, resonates at 8.54 ppm, whereas the least electron-rich ring, arene **7**, shows the analogous proton resonance at 8.20 ppm. This trend does not hold for **10**, however, as the H3 signal appears the furthest upfield at 8.10 ppm. A plausible explanation for this trend (**10** < **7** < **8** < **9**) is due to steric effects of the contiguous, coplanarized Cp′/Cp*, Ph, and Ph/*t*-Bu/Me substituents; the most sterically congested substitution pattern (Cp*, Ph, *t*-Bu) affords the furthest downfield H3 proton signal.

Complexes **14** and **15** can be identified by the characteristic ^{1}H NMR shifts of the σ-bound vinyl groups.[19] For example, the proton neighboring the Pt center in **14** resonates at 6.69 ppm as a Pt-coupled doublet ($J_{\mathrm{Pt-H}}$ = 14 Hz). The vinyl proton next to the cyclopropenyl ring appears as a pseudotriplet at 6.20 ppm. The comparable resonances for **15** appear at 6.57 and 6.10 ppm, respectively. The IR spectra for **14** and **15** exhibit bands for carbonyl stretching at 2001 and 2002 cm^{-1}, respectively.

X-ray Crystal Structures. As a new class of metallabenzenes, the solid-state structures of **7**–**10** are of considerable interest. Recrystallization of the red solids from hexanes afforded X-ray quality crystals of all four platinacycles. The molecular structures of **8** and **10** are shown in Figure 2, and selected bond lengths and bond angles for **7**–**10** are given in Table 2.

Comparison of the X-ray data of the four platinabenzenes (Table 2) illustrates the similarities between them. The sums of the respective platinacycle bond angles are remarkably close to the 720° required for a perfectly planar hexagon (deviation from mean plane ≤0.02 Å). Such planarity is common for about half of the known metallabenzenes.[1,12b,25] The largest angles in the platinacycles are found around the two carbon atoms next to Pt (129.2–129.8°), while the smallest bond angles are centered around the Pt metal (89.3–91.0°). The Pt–C bonds are 1.926–1.937 and 1.951–1.975 Å in length, which compare well with Pt–C bonds in other Pt(II) carbene complexes. The C–C bonds in the metallacycles have an average length of 1.382–1.396 Å, approximately the same length as observed in benzene, with no appreciable bond alternation. The Cp ring in each system is η^5-coordinated to Pt, with Pt–$\mathrm{C_{Cp}}$ distances in the range 2.257–2.342 Å.

Crystals suitable for X-ray analysis were also obtained for σ-complex **14**, and its structure is shown in Figure 3. The Pt–C(1) distance is 2.049(6) Å, which is similar to other Pt–C single bonds.[19,26] The carbonyl Pt–C(11) bond length is 1.813(7) Å. This shortened Pt–C bond is indicative of efficient back-bonding from the electron-rich metal center to the carbonyl π^* orbital. The cyclopropene double bond, C(4)–C(5), is 1.293(8) Å in length, which is comparable to other uncoordinated 1,2-diphenylcyclopropenes prepared in this lab.[19]

Reactivity Studies. To determine the stability/reactivity of this new class of metalla-aromatics, platinabenzene **8** was subjected to a variety of conditions (Scheme 3). Arene **8** is water stable, with no reaction either on direct exposure to water or in solutions of methanol and water. Slow decomposition was observed in solutions exposed to oxygen over the course of a week, but no specific products were isolable. Exposure to elemental bromine led to decomposition, but again, no specific products were isolable. This result contrasts those reported for the iridabenzenes, where oxidative addition to the metal is usually observed.[1a]

One interesting reaction that did occur was the formal [4 + 2] cycloaddition of **8** with maleic anhydride to produce **16**. While both isomers (*syn* and *anti* with respect to the phenyl groups) were observed, the ^{1}H NMR spectrum of the crude reaction mixture showed that one isomer is formed preferentially (>20:1). This major product was isolated and characterized and is provisionally assigned as the *anti* isomer **16**. It is reasonable to assume that the Ph groups perpendicular to the metallacycle plane direct the anhydride into the *anti* orientation. Similar [4 + 2] reactivity has been observed for iridabenzenes.[1a] Interestingly, dimethyl acetylenedicarboxylate (DMAD) failed to undergo an analogous cycloaddition, even when heated to 50 °C. This may be due to steric hindrance of the large Cp* group on **8**, which prevents the proper orientation of the acetylene required for the [4 + 2] addition. Similarly, solutions of **8** in acetone at 50 °C also failed to react in a [4 + 2] manner, as metallapyrilliums do with acetone.[1a]

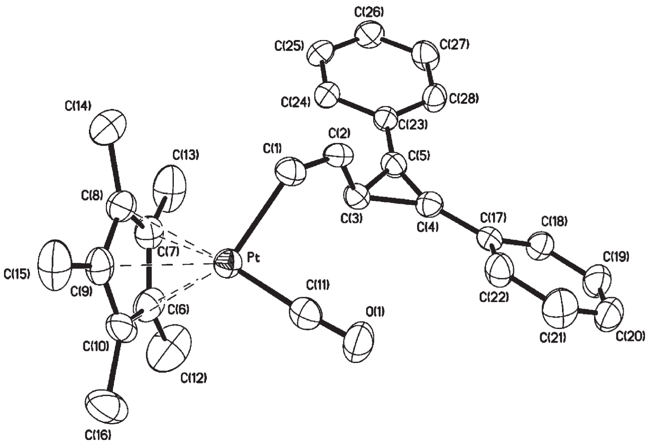

Figure 3. X-ray structure of σ-complex **14**; ellipsoids at 30% probability level. Selected bond lengths (Å) and angles (deg): Pt–C(1) 2.049(6), Pt–C(11) 1.813(7), C(1)–C(2) 1.315(8), C(2)–C(3) 1.482(8), C(3)–C(4) 1.512(8), C(3)–C(5) 1.525(8), C(4)–C(5) 1.293(8), C(11)–O 1.142(7), C(1)–Pt–C(11) 87.8(3), Pt–C(1)–C(2) 128.1(5), C(1)–C(2)–C(3) 127.0(6), C(4)–C(3)–C(5) 50.4(3).

Like several other metalla-aromatics, platinabenzene **8** reacted with Mo-arene complexes to produce Mo-coordinated metallabenzenes. A red THF solution of (toluene)Mo(CO)$_3$ rapidly turned purple upon addition of **8**, yielding η^6-complex **17** (Scheme 3). Reaction with (mesitylene)Mo(CO)$_3$ also afforded **17**, but required several days to reach completion. Because the Mo(CO)$_3$ fragment favors the more electron-rich arene, this result suggests that platinabenzenes are electron-rich species.

The crystal structure of **17** (Figure 4) reveals modest change in the Pt–C bond lengths upon coordination to the Mo(CO)$_3$ unit (Table 2). The larger changes upon coordination are lengthening of the C(2)–C(3) and C(3)–C(4) bonds (ca. 0.05–0.06 Å) and shortening of the C(1)–C(2) bond (0.036 Å). The C(4)–C(5) bond length is essentially unchanged. The Mo–Pt bond length is 2.819(2) Å, which is slightly longer than the average Mo–C(ring) distances of 2.377 Å.

As is the norm with metal arene complexes, the metallacycle ring ^{1}H NMR signals are shifted upfield significantly. The proton signal for H5 moves from 12.09 ppm in uncoordinated **8** to 8.45 ppm in coordinated **17**. Similarly, the H4 resonance shifts from 7.63 ppm to 5.11 ppm and the proton signal for H3 from 8.25 ppm to 6.43 ppm. Two bands

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(25) Zhu, J.; Jia, G.; Lin, Z. *Organometallics* **2007**, *26*, 1986–1995.

(26) Howard, W. A.; Bergman, R. G. *Polyhedron* **1998**, *17*, 803–810.

Scheme 3

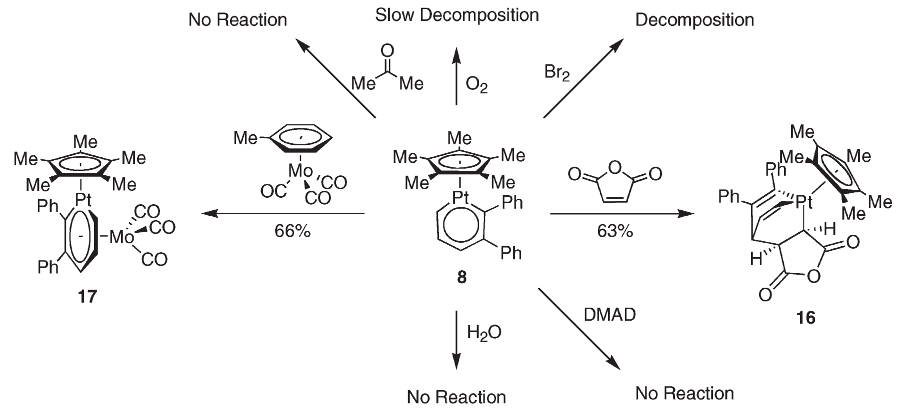

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Platinabenzenes 7−10 and η^6-Mo(CO)$_3$ Platinabenzene Complex 17

	7[a]	**8**	**9**[b,c]	**10**[b]	**17**
Pt−Cp[d]	1.965(4)	1.959(5)	1.957(5)	1.948(14)	1.958(12)
Pt−C(1)	1.959(3)	1.951(4)	1.975(5)	1.951(13)	1.973(11)
Pt−C(5)	1.929(4)	1.937(5)	1.926(5)	1.932(13)	1.916(11)
C(1)−C(2)	1.387(5)	1.401(6)	1.406(7)	1.424(15)	1.365(13)
C(2)−C(3)	1.392(5)	1.395(6)	1.389(7)	1.405(15)	1.444(14)
C(3)−C(4)	1.381(6)	1.363(7)	1.387(8)	1.374(15)	1.428(14)
C(4)−C(5)	1.364(6)	1.387(7)	1.350(8)	1.379(15)	1.388(14)
C=C mean	1.382(6)	1.387(7)	1.383(8)	1.396(15)	1.406(14)
Pt−C(1)−C(2)	129.2(3)	129.2(3)	129.8(4)	129.7(9)	130.6(9)
C(1)−C(2)−C(3)	122.6(3)	122.3(4)	124.1(5)	120.7(11)	123.2(11)
C(2)−C(3)−C(4)	124.8(4)	125.2(4)	126.9(5)	125.5(12)	123.3(11)
C(3)−C(4)−C(5)	124.1(4)	124.5(5)	119.8(5)	125.2(13)	120.3(12)
C(4)−C(5)−Pt	130.0(3)	128.9(4)	129.8(4)	127.8(10)	134.2(9)
C(1)−Pt−C(5)	89.3(2)	89.7(2)	89.4(2)	91.0(6)	87.8(5)
sum of angles	720.0	719.8	719.8	719.9	719.4

[a] Ref 14. [b] Average values for two independent molecules. [c] Ref 15. [d] Distance from the Pt center to the centroid of the Cp ring.

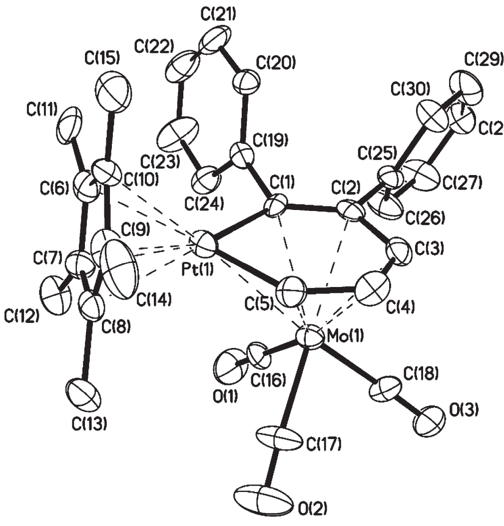

Figure 4. X-ray structure of η^6-complex **17**; ellipsoids at 30% probability level.

for carbonyl stretching vibrations appear at 1959 and 1894 cm^{-1}. The analogous bands for (toluene)Mo(CO)$_3$ (1984 and 1916 cm^{-1}) are higher in energy,[27] which suggests that the Mo center is more electron rich in the platinabenzene complex.

Conclusion

Four platinabenzenes have been synthesized and fully characterized in solution and in the solid state. Compounds **7**−**10** exhibit downfield shifts of the metallacycle ring protons and no bond alternation and form arene π-complexes, factors that are consistent with other known metallabenzenes. In this class of metallabenzenes, the Pt center lies in the plane of the ring, leading to highly planar structures. In addition to platinabenzenes, σ-vinyl complexes **14** and **15** have been isolated and characterized. Upon standing in solution, the σ-vinyl species cleanly isomerize to the respective platinabenzenes. The reactivity of platinabenzene **8** to a variety of reagents and conditions was examined. While **8** was essentially unreactive to water and acetone, it decomposed slowly upon exposure to oxygen or rapidly to bromine. [4 + 2]-Cycloaddition occurred with maleic anhydride, but not with DMAD. Reaction of **8** with (toluene)Mo(CO)$_3$ produced the arene complex **17**, which was characterized by FTIR, ^{1}H NMR, and X-ray crystallography. Our experimental studies and published computational results confirm that Cp-capped platinabenzenes such as **7**−**10** are thermodynamically robust, highly aromatic molecules.

Experimental Section

General Procedures. Reactions were carried out using standard Schlenk techniques in an inert atmosphere (dry Ar or N$_2$) when necessary. THF, toluene, and Et$_2$O were distilled from Na/benzophenone under N$_2$ prior to use. Unless stated otherwise solvents and reagents were purchased commercially and used as received. (*Z*)-1,2-Diphenyl-3-(2-iodoethenyl)cyclopropene (**1**),[4] (*Z*)-1-*tert*-butyl-3-(2-iodoethenyl)-2-phenylcyclopropene,[7] (*Z*)-1-ethyl-3-(2-iodoethenyl)-2-phenylcyclopropene,[7] (*Z*)-1-isopropyl-3-(2-iodoethenyl)-2-phenylcyclopropene,[7] (*Z*)-1-methyl-3-(2-iodoethenyl)-2-phenylcyclopropene,[7] and [(η^5-C$_5$Me$_5$)Pt(CO)]$_2$[22] were prepared according to literature methods. ^{1}H (299.94 or 500.10 MHz) and ^{13}C (75.43 or 125.76 MHz) NMR spectra were recorded using a Varian Inova 300 or 500 NMR spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane (CDCl$_3$, ^{1}H: 7.26 ppm and ^{13}C: 77.0 ppm; C$_6$D$_6$, ^{1}H: 7.15 ppm and ^{13}C: 128.0 ppm,). Coupling constants are expressed in Hz. IR spectra were recorded using a Nicolet Magna-FTIR 550 spectrometer. Melting points were determined on a Meltemp II apparatus and are uncorrected. Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

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[27] Wagner, G. W.; Hanson, B. E. *Organometallics* **1987**, *6*, 2494–2498.

Platinabenzene 7. Cyclopropene **1** (688 mg, 2.0 mmol) was dissolved in dry Et$_2$O (20 mL) under Ar and cooled to −78 °C. BuLi (0.8 mL, 2.5 M in hexanes, 2.0 mmol) was added dropwise, and the resulting yellow solution was stirred at −78 °C for 15 min. This solution was added dropwise to a stirred, ice-cooled suspension of (cod)PtCl$_2$ (374 mg, 1.0 mmol) in Et$_2$O (5 mL). The resulting dark brown suspension was allowed to warm to room temperature and stirred for 12 h before filtration. The filtrate was evaporated to give a dark brown solid that was chromatographed twice on silica (30:1 hexanes/EtOAc). Evaporation of the red band afforded **7** (45 mg, 7%) as a red solid. Mp: 168 °C (dec). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 5.09 (t, $^3J_{HH}$ = 2.7 Hz, 1H, CpH), 5.36 (d, $^3J_{HH}$ = 2.7 Hz, 2H, CpH), 6.74 (br t, $^3J_{HH}$ = 7.5 Hz, 1H, C$_6H_5$), 6.85−6.94 (m, 3H, C$_6H_5$), 6.94−6.98 (m, 6H, C$_6H_5$), 6.99 (t, $^3J_{HH}$ = 7.7 Hz, 2H, C$_6H_5$), 7.07 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C$_6H_5$), 7.13 (d, $^3J_{HH}$ = 7.3 Hz, 2H, C$_6H_5$), 7.25−7.30 (m, 4H, C$_6H_5$), 7.42 (t, $^3J_{HH}$ = 7.7 Hz, $^3J_{PtH}$ = 150 Hz, 1H, *H4*), 8.20 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, *H3*), 12.76 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, $^2J_{PtH}$ = 65 Hz, 1H, *H5*). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 96.09 (s, $CH_{Cp'}$), 97.83 (s, $CH_{Cp'}$), 114.97 (s, $CPh_{Cp'}$), 124.51, 125.00, 125.46, 125.72, 126.19, 128.51, 130.54, 130.92, 132.22 (s each; C$_6$H$_5$ and *C4*), 135.73 (s), 140.99 (s, $^3J_{PtC}$ ≈ 150 Hz, *C3*), 144.17 (s), 161.74 (s, *C2*), 194.96 (s, $^1J_{PtC}$ = 1330 Hz, *C5*), 204.01 (s, $^1J_{PtC}$ = 1400 Hz, *C1*) (2 signals obscured by solvent peaks). Anal. Calcd for C$_{34}$H$_{26}$Pt: C, 64.86; H, 4.16. Found: C, 64.95; H, 4.29.

η^5-Cp*Pt(CO)I (13). [(η^5-Cp*)Pt(CO)]$_2$ (450 mg, 0.63 mmol) was dissolved in dry toluene (15 mL) under Ar and cooled to −30 °C. Solid I$_2$ (168 mg, 0.66 mmol) was added, and the reaction mixture was allowed to warm slowly to room temperature. After stirring for 10 min at room temperature, the brown solution was evaporated to a volume of ca. 5 mL and chromatographed on silica (toluene). The violet band (R_f ≈ 0.6) was collected and evaporated to give **13** (410 mg, 67%) as a purple solid. Mp: 118 °C (dec). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.63 (s, $^2J_{PtH}$ = 17 Hz, 15H, CH_3). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 10.61 (s, CH$_3$), 108.98 (s, $^2J_{PtC}$ = 28 Hz, CCH$_3$), 166.13 (s, $^1J_{PtC}$ = 2440 Hz, CO). IR (toluene): ν 2029 cm^{-1}. Anal. Calcd for C$_{11}$H$_{15}$IOPt: C, 27.23; H, 3.12; Pt, 40.20. Found: C, 27.42; H, 2.93; Pt, 40.09.

Platinabenzene 8 and σ-Vinyl Complex 14. (*Z*)-1,2-Diphenyl-3-(2-iodoethenyl)cyclopropene (**1**, 167 mg, 0.485 mmol) was dissolved in dry Et$_2$O (20 mL) under Ar and cooled to −78 °C. BuLi (0.20 mL, 2.5 M in hexanes, 0.50 mmol) was added dropwise, and the resulting yellow solution was stirred at −78 °C for 15 min. The lithiate solution was transferred into a −50 °C cooled Schlenk flask containing Cp*Pt(CO)I (**13**, 195 mg, 0.40 mmol). A clear light red solution formed immediately. The solution was allowed to warm to −20 °C and stirred for 12 h at this temperature to give a dark brown suspension. The mixture was evaporated and chromatographed on silica (30:1 hexanes/EtOAc). Concentration of a yellow fraction (R_f ≈ 0.7 using 9:1 hexanes/EtOAc) furnished **14** (71 mg, 24%) as a yellow solid. Mp: 116 °C (dec). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.84 (s, $^2J_{PtH}$ = 14 Hz, 15H, CH_3), 3.38 (d, $^3J_{HH}$ = 8.1 Hz, 1H, CH_{pr}), 6.20 (pseudo t, $^3J_{HH}$ = 8.1 Hz, $^3J_{PtH}$ = 150 Hz, 1H, CH═CH), 6.69 (d, $^3J_{HH}$ = 8.1 Hz, $^2J_{PtH}$ = 14 Hz, 1H, PtCH), 7.07 (tt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2H), 7.25 (pseudo t, $^3J_{HH}$ = 7.7 Hz, 4H), 7.88 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 4H). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 9.7, 28.9, 103.9, 106.5, 117.3, 128.5, 129.0, 130.0, 137.0, 143.7, 167.1 (s, J_{PtC} = 1180 Hz). IR (toluene): ν 2001 cm^{-1}. Anal. Calcd for C$_{28}$H$_{28}$OPt: C, 58.43; H, 4.90; Pt, 33.89. Found: C, 58.73; H, 4.89; Pt, 33.47.

A red band (R_f ≈ 0.4 using 9:1 hexanes/EtOAc) was collected next and evaporated to afford arene **8** (31 mg, 14%) as an orange-red solid. Mp: 186 °C (dec). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.59 (s, $^3J_{PtH}$ = 8 Hz, 15 H, CH_3), 6.74 (tt, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 6.86 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 6.95−7.01 (m, 4H), 7.02−7.07 (m, 2H), 7.13−7.17 (m, 2H), 7.63 (pseudo t, $^3J_{HH}$ = 7.8 Hz, $^3J_{PtH}$ = 143 Hz, 1H, *H4*), 8.25 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, *H3*), 12.09 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.8 Hz, $^2J_{PtH}$ = 50 Hz, 1H, *H5*). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 9.03 (s, $^2J_{PtC}$ = 17 Hz, CH$_3$), 107.5 (s, CCH$_3$), 124.6, 124.9, 125.09, 125.5 (C$_6$H$_5$ and *C4*), 127.1, 127.7, 131.6 (C6H$_5$), 137.2 (s, $^2J_{PtC}$ = 43 Hz), 135.1 (s, $^3J_{PtC}$ = 163 Hz, *C3*), 146.40 (s, $^3J_{PtC}$ = 73 Hz), 159.4 (s, $^2J_{PtC}$ = 24 Hz, *C2*), 188.7 (s, $^1J_{PtC}$ = 1330 Hz, *C5*), 200.6 (s, $^1J_{PtC}$ = 1370 Hz, *C1*). Anal. Calcd for C$_{27}$H$_{28}$Pt: C, 59.22; H, 5.15; Pt, 35.62. Found: C, 59.11; H, 5.10; Pt, 35.74.

Platinabenzene 9 and σ-Vinyl Complex 15. Using the conditions described above, reaction of (*Z*)-1-*tert*-butyl-3-(2-iodoethenyl)-2-phenylcyclopropene (309 mg, 0.95 mmol), BuLi (0.41 mL, 2.5 M in hexanes, 1.03 mmol), and Cp*Pt(CO)I (420 mg, 0.86 mmol) afforded a red-brown semisolid, which was chromatographed on silica beginning with hexanes and gradually increasing in polarity to 9:1 hexanes/Et$_2$O. Isolation of a yellow band and evaporation gave **15** (78 mg, 16%) as a viscous yellow oil. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.32 (s, 9H, CH_3), 1.83 (s, $^2J_{PtH}$ = 16 Hz, 15H, CH_3), 3.02 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH_{pr}), 6.10 (pseudo t, $^3J_{HH}$ = 8.2 Hz, $^2J_{PtH}$ = 167 Hz, 1H, CH═CH), 6.57 (d, $^3J_{HH}$ = 8.3 Hz, $^2J_{PtH}$ = 10.4 Hz, 1H, PtCH), 7.04 (tt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 7.22 (pseudo t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.77 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, 2H). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 9.9, 29.0, 29.4, 32.9, 104.1, 104.2, 111.5, 127.9, 129.0, 130.0, 130.9, 145.7, 167.0 (s, J_{PtC} = 1190 Hz). IR (toluene): ν 2002 cm^{-1}. HRMS (MALDI) for C$_{26}$H$_{32}$OPt [M]$^+$: calcd 555.2101, found 555.2087.

A red band (R_f ≈ 0.4 using 9:1 hexanes/Et$_2$O) was collected next and evaporated to afford arene **9** (72 mg, 14%) as an orange-red solid. Mp: 150 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.23 (s, 9H, CH_3), 1.56 (s, $^3J_{PtH}$ = 9 Hz, 15H, CH_3), 6.83 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 7.01−7.08 (m, 2H), 7.08−7.16 (m, 3H), 7.60 (pseudo t, $^3J_{HH}$ = 7.9 Hz, $^3J_{PtH}$ = 151 Hz, 1H, *H4*), 8.54 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, *H3*), 11.83 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.6 Hz, $^2J_{PtH}$ = 41 Hz, 1H, *H5*). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 8.9 (s, CH$_3$), 35.1 (s, C(CH$_3$)$_3$), 38.8 (s, C(CH$_3$)$_3$), 107.9 (s, CCH$_3$), 124.5, 124.7, 126.3, 126.8 (C$_6$H$_5$ and *C4*), 134.1 (s, $^3J_{PtC}$ = 134 Hz, *C3*), 139.9 (s, $^2J_{PtC}$ = 43 Hz, *C2*), 161.2 (s, $^2J_{PtC}$ = 48 Hz), 187.8 (s, $^1J_{PtC}$ = 1338 Hz, *C5*), 203.7 (s, $^1J_{PtC}$ = 1370 Hz, *C1*). Anal. Calcd for C$_{25}$H$_{32}$Pt: C, 56.91; H, 6.11; Pt, 36.97. Found: C, 56.79; H, 6.35; Pt, 36.54.

Platinabenzene 10. Using the conditions described above, reaction of (*Z*)-1-methyl-3-(2-iodoethenyl)-2-phenylcyclopropene (180 mg, 0.64 mmol), BuLi (0.28 mL, 2.5 M in hexanes, 0.70 mmol), and Cp*Pt(CO)I (281 mg, 0.58 mmol) afforded a red-brown semisolid, which was chromatographed on silica beginning with hexanes and gradually increasing in polarity to 9:1 hexanes/Et$_2$O. A red band was collected and evaporated to give platinabenzene **10** (11 mg, 4%). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.61 (s, $^3J_{PtH}$ = 8.3 Hz, 15H, CH$_3$), 2.29 (s, 3H, CH$_3$), 6.97 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.20 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.26 (t, $^3J_{HH}$ = 8.2 Hz, 2H), 7.57 (pseudo t, $^3J_{HH}$ = 7.6 Hz, $^3J_{PtH}$ = 147.1 Hz, 1H, *H4*), 8.10 (d, $^3J_{HH}$ = 7.6 Hz, 1H, *H3*), 11.93 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, $^2J_{PtH}$ = 48.0 Hz, 1H, *H5*). MS (APCI): *m*/*z* (%) 486.2 (M$^+$ + H, 100). Anal. Calcd for C$_{22}$H$_{26}$Pt: C, 54.42; H, 5.40; Pt, 40.18. Found: C, 54.59; H, 5.35; Pt, 39.97.

Transformation of 14/15 into 8/9. σ-Vinyl complex **14** or **15** (30 mg) was dissolved in C$_6$D$_6$ (0.6 mL) and stored at room temperature under Ar in an NMR tube. The conversion was monitored by proton NMR spectroscopy and proved to be complete after 36−48 h. During the course of this conversion identifiable side products were not formed, nor was significant decomposition observed. Platinabenzene **8** or **9** was obtained in >95% yield.

Cycloadduct 16. Platinabenzene **8** (20 mg, 0.036 mmol) and maleic anhydride (5.5 mg, 0.056 mmol) were dissolved in dry Et$_2$O (2 mL). This mixture was stirred overnight at room temperature and then cooled to −30 °C. The solvent was removed via cannula, leaving behind **16** (15 mg, 63%) as a light

Table 3. Crystallographic Data and Summary of Data Collection and Structure Refinement

	8	10	14	17
formula	$C_{27}H_{28}Pt$	$C_{22}H_{26}Pt$	$C_{28}H_{28}OPt$	$C_{30}H_{28}MoO_3Pt$
fw	547.61	485.52	575.62	727.55
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
T, K	296	296	296	296
λ, Å	0.71073	0.71073	0.71073	0.71073
a, Å	10.575(3)	12.194(5)	15.981(3)	14.384(6)
b, Å	16.979(3)	18.709(7)	8.1257(11)	11.007(4)
c, Å	12.445(2)	16.940(6)	18.673(6)	18.438(7)
β, deg	101.32(2)	104.47(1)	98.35(2)	112.62(1)
V, Å^3	2190.8(7)	3742(2)	2399.1(8)	2695(2)
Z,Z'	4,1	8,2	4,1	4,1
D_{calc}, g cm^{-3}	1.660	1.724	1.594	1.793
μ, mm^{-1}	6.39	7.50	5.84	5.68
reflns measd	5749	22 836	5522	13 042
indep reflns	5281 [R_{int} = 0.015]	2800 [R_{int} = 0.134]	3051 [R_{int} = 0.015]	2290 [R_{int} = 0.118]
R_1	0.028	0.0395	0.034	0.0547
wR_2	0.039	0.0698	0.044	0.0728
GOF on F^2	1.48	0.76	1.29	0.93
largest diff peak and hole, e Å^{-3}	1.28/−0.80	1.04/−1.30	1.29/−0.90	0.75/−0.64

yellow powder. ^{1}H NMR (300 MHz, C_6D_6): δ 1.22 (s, 15H, CH_3), 2.36 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.4 Hz, Pt satellites obscured, 1H), 3.07 (dd, $^3J_{HH}$ = 8.9 Hz, $^3J_{PtH}$ = 145.8 Hz, 1H), 4.22−4.26 (m, 1H), 6.30−6.36 (m, 1H), 6.44 (t, $^3J_{HH}$ = 6.4 Hz, 1H), 6.57 (d, $^3J_{HH}$ = 6.0 Hz, 1H), 6.67 (dd, $^3J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 3.6 Hz, 2H), 6.77 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 6.92 (t, $^3J_{HH}$ = 7.8 Hz, 2H) 7.08−6.97 (m, 4H). ^{13}C NMR (75 MHz, C_6D_6): δ 8.1, 15.9, 16.4, 44.4, 58.8, 66.2, 108.2, 125.4, 125.9, 127.6, 129.5, 129.7, 130.2, 133.9, 135.7, 143.6, 148.5, 172.6, 180.4. IR (KBr): ν 1831 (CO), 1766 (CO) cm^{-1}. Anal. Calcd for $C_{31}H_{30}O_3Pt$: C, 57.67; H, 4.68. Found: C, 57.81; H, 4.53.

Molybdenum Complex 17. Platinabenzene **8** (24 mg, 0.044 mmol) and (toluene)Mo(CO)$_3$ were placed in a flask under N_2; then THF (5 mL) was added. Within 5 min the color of the solution changed from red-orange to deep violet. After stirring overnight, the THF was removed under reduced pressure and hexanes was added. The hexanes was slowly evaporated under a stream of N_2 to precipitate **17** (21 mg, 66%) as violet crystals. ^{1}H NMR (300 MHz, C_6D_6): δ 1.46 (s, 15H), 5.11 (tt, J_{PtH} = 132.7 Hz, $^3J_{HH}$ = 7.3 Hz, 1H, *H4*), 6.43 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HH}$ = 1.5 Hz, Pt coupling obscured, 1H, *H3*), 6.60 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.57−6.83 (m, 6H), 6.99 (d, $^3J_{HH}$ = 6.7 Hz, 2H), 7.08 (t, $^3J_{HH}$ = 6.4 Hz, 1H), 8.43 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, $^3J_{PtH}$ = 48.0 Hz, 1H, *H5*). IR (CCl_4): ν 1959 (CO), 1894 (CO) cm^{-1}. Anal. Calcd for $C_{30}H_{28}MoO_3Pt$: C, 49.52; H, 3.88. Found: C, 49.21; H, 3.99.

X-ray Crystallography. X-ray diffraction intensities were collected on Enraf-Nonius CAD-4 (**8** and **14**) and Bruker SMART Apex CCD (**10** and **17**) diffractometers at room temperature using Mo Kα radiation. The crystallographic data and some details of the data collections and refinements of the structures are given in Table 3. Absorption corrections were applied by psi-scan and SADABS for **8**/**14** and **10**/**17**, respectively. Structures were solved using direct methods or the Patterson function, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. All non-H atoms were refined with anisotropic thermal parameters. H atoms were refined in calculated positions in a rigid group model. All calculations for **8**/**14** and **10**/**17** were performed using the SIR92[28] and Bruker SHELXTL[29] packages, respectively.

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Supporting Information Available: X-ray structure cif files for compounds **8**, **10**, **14**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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