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Metallabenzenes and Valence Isomers. 5. Synthesis and Structural Characterization of a Rhodabenzvalene: A Rare η^2-Cyclopropene/σ-Vinylrhodium(I) Complex

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

Department of Chemistry, University of Oregon, Eugene, Oregon 97403-1253

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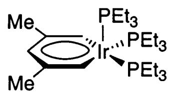
*Summary: Treatment of cis-1,2-diphenyl-3-(2-lithioethenyl)cyclopropene (**2**) with $(Me_3P)_2Rh(CO)Cl$ gives the corresponding rhodabenzvalene **5**, which contains rare η^2-cyclopropene and σ-vinylic linkages to Rh. The successful preparation of this metallacycle can be attributed to the synergistic combination of intramolecular π-bonding of the cyclopropene and σ-vinylic linkage to the Rh atom, both of which in turn inhibit decomposition of the other respective moiety.*

A major limitation of research on metallabenzenes[1] and their valence isomers has been the inability to rationally alter variables (metal center, C_5 backbone, other ligands on the metal) in order to perform detailed structure−property relationship studies. Invariably, each new metallabenzene synthesis leads to only one molecule via that particular route.[1] To fully understand the many subtleties affecting the formation and reaction chemistry of metallaaromatics, researchers must prepare a number of structurally similar molecules, systematically altering the parameters. Of the known metallabenzenes, only complex **1** has been studied much beyond routine characterization; even then, all of the investigations were initiated from this single metallacycle.[2] To allow an augmented study of this class of molecules, we recently reported a new method using nucleophilic 3-vinyl-1-cyclopropenes (e.g., **2**) that permits direct entry into the metallabenzene manifold, yielding iridacycles such as **3** and **4**, without the need for subsequent chemical transformation(s).[3] More importantly, the new route should allow for the introduction of a variety of transition-metal fragments[4] and thus offer a general pathway for metallaaromatic and valence isomer formation. With this idea in mind, we have investigated the reaction of **2** with Rh complexes, which like Ir contain a group 16 element and thus often have similar chemical properties and reactivities, such as nucleophilic substitution reactions with anions, coordination of olefins, etc.[5] We report herein the versatility of our synthetic method by the formation and complete characterization by NMR spectroscopy and X-ray crystallography of rhodabenzvalene **5**, which contains η^2-cyclopropene and σ-vinylic linkages rarely found in Rh complexes (vide infra).[6]



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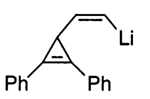

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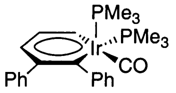

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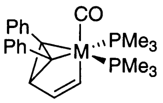
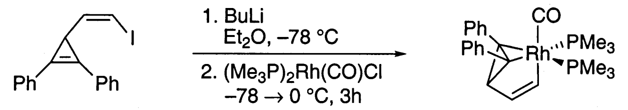


4 (M=Ir)
5 (M=Rh)

Scheme 1



6 **5**

Compound **5** was synthesized as shown in Scheme 1. Lithium−iodine exchange of cyclopropene **6**[3a] with 1 equiv of BuLi at −78 °C followed by addition to a stirred suspension of $(Me_3P)_2Rh(CO)Cl$[7] at −78 °C produced a yellow-orange solution that was warmed to 0 °C over a 3 h period. Both ^1H and ^{31}P NMR spectra of the crude reaction mixture showed that compound **5** was formed as the only organometallic product.[8] Pale yellow crystals of **5** were obtained in 48% yield by recrystallization from ether and hexanes at −30 °C. Although **5** is moderately stable in the solid state, it is thermally unstable in

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[*] To whom correspondence should be addressed. E-mail: haley@oregon.uoregon.edu. Fax: 541-346-0487.

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(8) Spectroscopic data for **2**: ^1H NMR (500 MHz, C_7D_8, −20 °C) δ 7.67 (d, $J = 7.6$ Hz, 4H, *Ph*), 7.19 (t, $J = 7.6$ Hz, 4H, *Ph*), 6.99 (t, $J = 7.6$ Hz, 3H, *Ph* and *H5*), 6.18−6.12 (m, 1H, *H4*), 2.99 (br s, 1H, *H3*), 0.95 (d, $J = 7.5$ Hz, 18H, P*Me*$_3$); ^{13}C NMR (125 MHz, C_7D_8, −20 °C) δ 195.71 (dt, $J_{Rh,C} = 47.2$ Hz, $J_{P,H} = 10.2$ Hz, *C*O), 155.06 (q, $J = 18.5$ Hz, *C5*), 145.82 (s, *C4*), 142.57 (s), 128.29 (s), 127.04 (s), 124.25 (s), 85.83 (m, 2C, *C1/C2*), 51.92 (s, *C3*), 19.35 (m, P*Me*$_3$); ^{31}P NMR (107 MHz, C_7D_8, −20 °C) δ −12.89 (d, $J_{Rh,P} = 127.7$ Hz, PMe_3); IR (Et_2O) ν 1980 (s, CO) cm^{-1}. Anal. Calcd for $C_{24}H_{31}RhOP_2$: C, 57.61; H, 6.24. Found: C, 57.41; H, 6.24.

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solution. ^{1}H NMR spectra showed that, at room temperature, **5** completely decomposed to an unidentified mixture after 12 h; however, ^{1}H NMR spectra of solutions kept at −30 °C did not exhibit any noticeable change over a 2 week period.

Spectroscopic data obtained from the recrystallized material support the formation of **5** as the symmetric rhodabenzvalene. The ^{1}H NMR spectrum shows three sets of arene protons, indicating that the phenyl groups are equivalent. The methyl proton resonances of the PMe_3 ligand appear as a doublet (δ 0.95, $J = 7.6$ Hz), and the ^{31}P NMR spectrum contains only one signal at −12.89 ppm ($J_{Rh,P} = 127.7$ Hz). The other proton signals are characteristic of benzvalene-type[9] structures, with the bridged sp^3 *C*H group appearing as a broad singlet at 2.99 ppm and the two sp^2 C*H* groups as complex multiplets at 6.15 and 6.99 ppm; however, the latter resonance is barely discernible because of overlap with one set of phenyl protons. Although the NMR data are similar to those observed in the corresponding iridabenzvalene **4**,[3b] they are complicated by coupling with the Rh nucleus. For example, the carbonyl resonance in the ^{13}C NMR spectrum appears as a doublet of triplets at 195.7 ppm, which indicates coupling to both Rh and P nuclei ($J_{Rh,C} = 47.2$ Hz, $J_{P,C} = 10.2$ Hz). These values are very close to those of the known four-coordinate square-planar Rh(I) complexes [Rh(σ-CR=CHR′)(CO)(P-*i*-Pr_3)$_2$] (R = H, alkenyl, alkynyl; R′ = H, Ph): in C_6D_6, δ 195.5−197.8 ppm ($J_{Rh,C} = 53.2$−54.7 Hz, $J_{P,C} = 13.8$−16.9 Hz).[10] The IR spectrum shows the CO stretching band at 1980 cm^{-1}.

The structure of rhodabenzvalene **5** was unambiguously confirmed by single-crystal X-ray diffraction (Figure 1).[11] Selected bond lengths and angles are listed in Table 1. The coordination geometry around rhodium is trigonal bipyramidal with the two phosphines and η^2-olefin equatorial and the CO and σ-vinyl ligands axial. The bond lengths of Rh−C1 and Rh−C2 are 2.139 and 2.167 Å, respectively, and are bracketed well by other known Rh−C single-bond lengths in η^2-olefin−Rh(I) complexes (2.105−2.195 Å).[12] In comparison to a typical cyclopropene double bond (~1.29 Å),[13] C1−C2 is elongated (1.414 Å), indicating substantial metal-to-olefin π-back-bonding. This phenomenon also results in an increase of the apical C1−C3−C2 bond angle (55.1°), compared to ~50° in a typical cyclopropene, leading to a reduction of ring strain.[13,14]

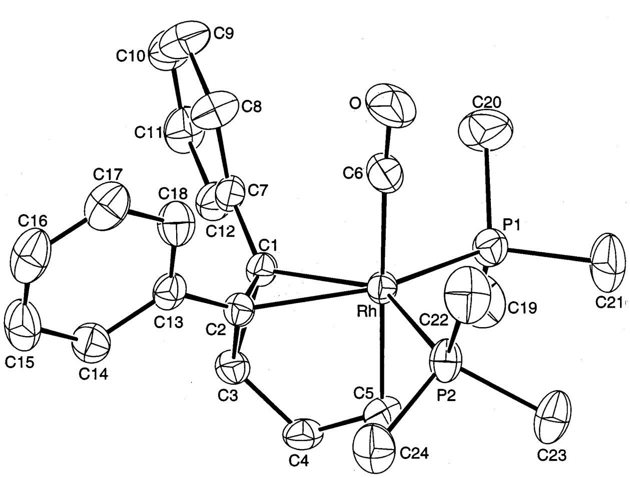

Figure 1. Molecular structure of rhodabenzvalene **5**. Ellipsoids were drawn at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Rhodabenzvalene 5 and Comparison to Values for Iridabenzvalene 4

	5	**4**[a]		**5**	**4**[a]
M−P1	2.315(1)	2.306(3)	P1−M−P2	111.0(1)	104.1(1)
M−P2	2.302(1)	2.318(3)	P1−M−C1	101.7(1)	109.4(2)
M−C1	2.139(2)	2.146(10)	P2−M−C2	107.0(1)	105.9(3)
M−C2	2.167(2)	2.143(8)	C1−M−C2	38.3(1)	39.4(3)
M−C5	2.060(2)	2.095(11)	C5−M−C6	178.8(1)	178.9(4)
M−C6	1.902(3)	1.870(10)	C1−M−C5	83.7(1)	83.1(4)
C1−C2	1.414(3)	1.447(12)	M−C5−C4	112.3(2)	111.4(7)
C1−C3	1.522(3)	1.529(12)	C1−C3−C2	55.1(1)	56.5(5)
C2−C3	1.536(3)	1.526(12)	C3−C1−C7	130.0(2)	126.8(9)
C3−C4	1.469(3)	1.466(13)	C3−C2−C13	128.6(2)	127.9(8)
C4−C5	1.313(3)	1.322(13)	dihedral[b]	119.3	115.8

[a] Reference 3b. [b] The angle between plane 1 (C1,C2,C3) and plane 2 (C7,C1,C2,C13).

Other than the metal center, benzvalenes **4** and **5** are completely isostructural and thus direct comparison between the two metallacycles can be made (Table 1). Although most bond lengths and bond angles are similar, the main differences between the structures arise as a consequence of the differing binding affinities for the cyclopropene π-bond. Second-row metals are known to back-bond less efficiently. This is reflected in the shorter C1−C2 bond in **5** (1.414 vs 1.447 Å in **4**). As a result, C1 and C2 are less like sp^3-hybridized carbons; therefore, the C3−C1−C7 and C3−C2−C13 bond angles are larger than those in **4** and thus the corresponding dihedral angle between the plane of the three-membered ring and the plane formed by the phenyl ipso carbons and the cyclopropene π-bond is greater (119.3 vs 115.8°). The weaker coordination also translates into a much larger P1−M−P2 angle, which is nearly 7° greater in **5**. Regardless, formation of the η^2-cyclopropene−Rh moiety is unique, as oxidative addition to the strained σ-bond is the exclusive reactivity observed in previous studies of cyclopropenes with Rh.[15]

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(9) Alternatively, **5** can be depicted as an η^2-cyclopropene complex; however, because of metal to olefin π-back-bonding, the metallacyclopropane resonance form is preferable. For a detailed discussion, see ref 3b.

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(11) Crystal data for **5**: $C_{24}H_{31}OP_2Rh$, $M_r = 500.4$, monoclinic, $P2_1/n$, $a = 10.312(3)$ Å, $b = 16.800(5)$ Å, $c = 14.309(5)$ Å, $\beta = 95.82(3)°$, $V = 2466(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.348$ g cm^{-3}, $\mu = 8.3$ cm^{-1}, $F(000) = 1032$, Mo Kα radiation ($\lambda = 0.710$ 73 Å), $T = 296$ K, $2\theta_{max} = 53°$, 5299 independent reflections scanned, 5088 nonabsent reflections in refinement on F^2, 254 parameters, $R(F) = 0.028$ ($I \geq \sigma(I)$), $R_w(F^2) = 0.066$ (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).

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Almost equally rare are σ-vinyl/vinylic–Rh(I) complexes.[10] The bond lengths in the Rh–σ-vinyl group of **5** are Rh–C5 = 2.060 Å and C4–C5 = 1.313 Å, both of which are similar to those of *trans*-[$(i\text{-}Pr_3P)_2Rh\{\sigma\text{-}(Z)\text{-}C(CH{=}CH_2){=}CHPh\}(CO)$] (**7**)[10d] (2.088 and 1.356 Å, respectively). The C4–C5–Rh bond angle (112.3°), however, is considerably smaller than in **7** (128.1°), undoubtedly due to the intramolecular nature of the vinylcyclopropene ligand of **5**. The scarcity of σ-vinyl–Rh(I) complexes is attributable to poor thermal stability, which varies markedly depending upon the ligands around Rh and the σ-vinylic ligands. The few known examples all require the steric bulk of $i\text{-}Pr_3P$ for stabilization.[10] Vinylic Rh complexes prepared by the reaction of *trans*-2-lithio-2-butene with $(Ph_3P)_2Rh(CO)Cl$ rapidly undergo hydride rearrangements, yielding products derived from isomerization to η^3-crotyl complexes.[16] While complexes obtained in the reaction of $(i\text{-}Pr_3P)_2Rh(CO)Cl$ with RMgBr (R = $CH{=}CH_2$, Ph) are stable even at 50 °C,[10c] their $(i\text{-}Pr_3P)_2Rh(C{=}CHR')R$ analogues rearrange readily to η^3-allyl complexes.[10b]

In summary, the successful preparation of **5** can be attributed to the synergistic combination of intramolecular π-bonding of the cyclopropene and a σ-vinylic linkage to the Rh atom, both of which in turn inhibit decomposition of the other respective moiety. Future work will focus on rhodabenzene formation by thermal isomerization or metal-catalyzed ring opening of **5**,[3] as well as the influence of phosphine ligands and the effects of cyclopropene substituents on rhodabenzvalene formation.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-0075246) for support of this research.

Supporting Information Available: A figure giving the X-ray structure of **5**, text giving 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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