Organometallics 1987, 6, 1578-1581

warmed above 0 °C in acetone solution. The formation of 3 probably proceeds by coupling of C(1) and C(5) to produce [(η^4-1,3-dimethylcyclopentadiene)Ir$(\mathrm{PEt_3})_3$]$^+\mathrm{O_3SCF_3}^-$, followed by phosphine loss and transfer of the endo ring hydrogen to the iridium center.[13]

As shown in Scheme III, the reaction of 2 with $\mathrm{NMe_4I}$ or the reaction of 1 with methyl iodide produces $[\overline{\mathrm{IrCH{=}C(Me)CH{=}C(Me)CH_2}}](\mathrm{PEt_3})_3(\mathrm{I})$ (4),[14] a compound which is identical with 1, except that an iodo ligand has replaced the hydride ligand. The methyl iodide reaction probably proceeds through the intermediacy of cation 2.

The NMR spectra of 4[15] are very similar to those of 1 except for the absence of the hydride resonance at δ −13.1 in the ^{1}H NMR spectrum. The position of the iodo ligand trans to C(5) is clear from the fact that C(5) does *not* exhibit phosphorus coupling in the ^{13}C NMR spectrum. In contrast, C(1) is strongly coupled to phosphorus ($J_{\mathrm{C-P}}$ = 82.5 Hz) and must reside trans to a phosphine ligand. Compound 4, like 1, exhibits mirror plane symmetry in solution. Hence, the two protons bonded to C(5) are equivalent and the two mutually trans phosphine ligands are equivalent by NMR spectroscopy.

We are continuing to study the reactivity of these unusual iridacycles. Particularly intriguing is the possibility that they may be convertible to the corresponding iridabenzenes.[16,17]

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) is gratefully acknowledged. Washington University's High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co. We thank Professor Russell Hughes (Dartmouth College) for sharing research results prior to publication.

Registry No. 1, 108296-94-2; 2, 108296-96-4; 3, 108296-98-6; 4, 108296-99-7; $\mathrm{ClIr(PEt_3)_3}$, 91513-65-4; potassium 2,4-dimethylpentadienide-tetrahydrofuran, 72013-05-9; methyl trifluoromethanesulfonate, 333-27-7; methane, 74-82-8.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, and significant least-squares planes for 1 and 2 (16 pages); listings of observed and calculated structure factor amplitudes for 1 and 2 (45 pages). Ordering information is given on any current masthead page.

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[11] Compound **2** (0.50 g, 6.3 × 10^{-4} mol) was dissolved in 25 mL of acetone and stirred at 20 °C for several hours, during which the color of the solution lightened. After removal of the volatiles under vacuum, the residue was redissolved in a minimal quantity of acetone and cooled to −30 °C, producing colorless crystals of **3**. Yield: 0.38 g (90%). Anal. Calcd for $\mathrm{C_{20}H_{40}IrP_2SO_3F_3}$: C, 35.75; H, 6.01. Found: C, 36.13; H, 5.91.

[12] Spectroscopic Data for **3**. ^{1}H NMR ($\mathrm{(CD_3)_2CO}$, 22 °C, 300 MHz): δ 5.35 (s, 2, H(4)/H(5)), 5.30 (s, 1, H(2)), 2.32 (s, 6, $\mathrm{CH_3}$'s of Cp), 2.05–1.85 (complex m, 12, $\mathrm{CH_2}$'s of $\mathrm{PEt_3}$'s), 1.08–0.95 (m, 18, $\mathrm{CH_3}$'s of $\mathrm{PEt_3}$'s), −17.36 (t, $J_{\mathrm{H-P}}$ = 30 Hz, 1, Ir–H). ^{13}C{^{1}H} NMR ($\mathrm{(CD_3)_2CO}$, 22 °C, 75 MHz): δ 104.8 (s, C(1)/C(3)), 86.9 (s, C(2)), 83.1 (s, C(4)/C(5)), 22.2 (t, $J_{\mathrm{C-P}}$ = 19 Hz, $\mathrm{CH_2}$'s of $\mathrm{PEt_3}$'s), 14.3 (s, $\mathrm{CH_3}$'s of Cp), 8.4 (s, $\mathrm{CH_3}$'s of $\mathrm{PEt_3}$'s). ^{31}P{^{1}H} NMR ($\mathrm{(CD_3)_2CO}$, 22 °C, 121 MHz, referenced to $\mathrm{H_3PO_4}$): δ −1.7 (d, $J_{\mathrm{P-H}}$ = 22 Hz).

[13] Alternatively, the sequence of steps may involve dissociation of double bond C3–C4 and abstraction of a hydrogen from C5 by Ir to produce a transient iridabenzene (or iridacyclohexatriene) species, which then collapses to **3** with phosphine loss.

[14] Method A. $\mathrm{NMe_4I}$ (0.20 g, 1.0 × 10^{-3} mol) was added to a cold (−30 °C) solution of **2** (0.79 g, 1.0 × 10^{-3} mol) in tetrahydrofuran. After the solution was warmed to room temperature, stirred for 0.5 h, and filtered, the volume of solvent was reduced and the resulting saturated solution was cooled to −30 °C, causing **4** to crystallize as light yellow needles. Yield (crystalline): 0.46 g (60%).

Method B. $\mathrm{CH_3I}$ (0.14 g, 1.0 × 10^{-3} mol) was added dropwise with stirring to a solution of 1 (0.64 g, 1.0 × 10^{-3} mol) in 10 mL of tetrahydrofuran. The pale yellow reaction solution was cooled to −30 °C, causing **4** to crystallize from it as light yellow needles. Yield (crystalline): 0.38 g (50%). Anal. Calcd for $\mathrm{C_{25}H_{55}IrP_3I}$: C, 39.10; H, 7.23. Found: C, 39.15; H, 7.44.

[15] Spectroscopic Data for **4**. ^{1}H NMR (1:2 $\mathrm{(CD_3)_2CO/DCCl_3}$, 22 °C, 300 MHz): δ 7.98 (s, 1 H(1)), 5.35 (s, 1, H(3)), 2.79 (t of d, $J_{\mathrm{H-P}}$ = 12.16 Hz, $J_{\mathrm{H-P}}$ = 7.30 Hz, 2, H(5)'s), 2.20–1.80 (m, 18, $\mathrm{CH_2}$'s of $\mathrm{PEt_3}$'s), 1.72 (s, 3, $\mathrm{CH_3}$, 1.57 (s, 3, $\mathrm{CH_3}$), 1.22–0.93 (m, 27, $\mathrm{CH_3}$'s of $\mathrm{PEt_3}$'s). ^{13}C{^{1}H} NMR (1:2 $\mathrm{(CD_3)_2CO/DCCl_3}$, 22 °C, 75 MHz): δ 134.4 (s, C(2) or C(4)), 130.0 (d of t, $J_{\mathrm{C-P}}$ = 82.5 Hz, $J_{\mathrm{C-P}}$ = 14.9 Hz, C(1), 129.5 (s, C(3)), 127.9 (s, C(2) or C(4)), 29.6 (d, $J_{\mathrm{C-P}}$ = 7 Hz, C(6)), 28.9 (s, C(7), 21.0 (d, $J_{\mathrm{C-P}}$ = 24.0 Hz, $\mathrm{CH_2}$'s of $\mathrm{PEt_3}$), 17.7 (virtual t, $J_{\mathrm{C-P}}$ = 30.0 Hz, $\mathrm{CH_2}$'s of trans $\mathrm{PEt_3}$'s), 10.1, 9.7 (s's, $\mathrm{CH_3}$'s of $\mathrm{PEt_3}$'s), −3.8 (s, C(5). ^{31}P{^{1}H} NMR (1:2 $\mathrm{(CD_3)_2CO/DCCl_3}$, 22 °C, 121 MHz, referenced to $\mathrm{H_3PO_4}$): δ −35.0 (d, $J_{\mathrm{P-P}}$ = 19 Hz, 2), −42–3 (t, $J_{\mathrm{P-P}}$ = 19 Hz, 1).

[16] Only one metallabenzene, an osmium derivative, has been reported to date: Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811.

[17] For a theoretical treatment of metallabenzenes, see: Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

Transition-Metal-Promoted Ring-Opening Reactions of Vinylcyclopropenes. 1,2,3,5-η-Penta-2,4-dienediyl and 1,5-η-Penta-2,4-dienediyl (1-Metallacyclohexa-2,4-diene) Complexes of Rhodium(III) and Iridium(III) and Their Conversion to (η^5-Cyclopentadienyl)hydridometal Compounds

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Summary: 1,2,3-Triphenyl-3-vinyl-1-cyclopropene (**2**) reacts with "$\mathrm{MCl(PMe_3)_2}$" (M = Rh, Ir) to give novel complexes **3a,b** containing the 1,2,3,5-η-penta-2,4-dienediyl ligand, one of which, the iridium species **3b**, has been crystallographically characterized. In contrast, reaction of **2** with the bulkier reagent "$\mathrm{RhCl(P\text{-}\textit{i}\text{-}Pr_3)_2}$" yields directly the (cyclopentadienyl)hydridorhodium complex **6**. Reaction of **3a** with (acetylacetonato)thallium affords the (1,5-η-penta-2,4-dienediyl)rhodium (1-rhodacyclohexa-2,4-diene) complex **8** which has also been crystallographically characterized.

Recently we reported the isolation and structural characterization of a 1,5-η-penta-2,4-dienediyl (1-metallacyclohexa-2,4-diene) complex of platinum(II) (1), from the oxidative addition reaction of triphenylvinylcyclopropene 2 with the labile Pt(0) complex $[\mathrm{Pt}(\eta\text{-}\mathrm{C_2H_4})(\mathrm{PPh_3})_2]$.[2a] The crsytallographically characterized compound 1 contained the first reported example of this unsaturated metallacyclic skeleton. The ring is severely puckered in the solid state, and this structure is maintained in solution with a substantial activation barrier for inversion of the ring, as shown by the NMR inequivalence of the $\mathrm{CH_2}$ protons. Thermolysis of 1 resulted in reductive elimination to give free 1,2,3-triphenylcyclopentadiene, and the intermediacy of analogous metallacycles in the stepwise formation of (η^4-cyclopentadiene)rhodium and (η^4-cyclohexadienone)-

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[1] (a) Dartmouth College. (b) University of Delaware.

[2] (a) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc. Chem. Commun.* **1986**, 1694. (b) Cho, S. H.; Liebeskind, L. S. *J. Org. Chem.*, submitted for publication.

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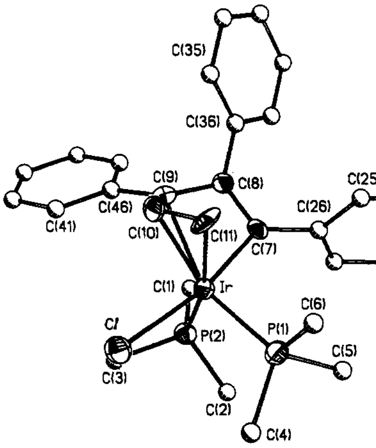


Figure 1. Molecular structure and labeling scheme for **3b**. Bond distances (Å) and angles (deg): Ir–Cl, 2.517 (4); Ir–P(1), 2.283 (4); Ir–P(2), 2.320 (3); Ir–C(7), 2.03 (1); Ir–C(9), 2.35 (1); Ir–C(10), 2.21 (1); Ir–C(11), 2.20 (1); C(7)–C(8), 1.34 (2); C(8)–C(9), 1.48 (2); C(9)–C(10), 1.41 (2); C(10)–C(11), 1.44 (2); Cl–Ir–P(1), 91.0 (1); Cl–Ir–P(2), 90.4 (1); P(1)–Ir–P(1); 102.6 (1); C(7)–C(8)–C(9), 109 (1); C(8)–C(9)–C(10), 120 (1); C(9)–C(10)–C(11), 121 (1).

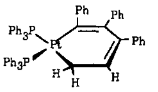
iron complexes from vinylcyclopropenes was suggested.[2a] Recent work by Liebeskind has shown that vinylcyclopropenes can be carbonylated to give phenols by using $[RhCl(CO)_2]_2$ as a catalyst,[2b] prompting us to report further studies on C–C activation in vinylcyclopropenes using Rh(I) and Ir(I) centers in the absence of CO. We now report that novel complexes of Rh(III) and Ir(III) containing the 1,2,3,5-η-penta-2,4-dienediyl ligand have been isolated and that subsequent conversion of the rhodium compound to 1,5-η-penta-2,4-dienediyl (1-metallacyclohexa-2,4-diene) complexes and to (η^5-cyclopentadienyl)-hydridometal systems has been confirmed.

1,2,3-Triphenyl-3-vinyl-1-cyclopropene (**2**)[3] reacted slowly with $[RhCl(PMe_3)_3]$[4] in benzene solution at room temperature to afford the bright yellow, air-stable Rh(III) complex **3a**,[5] which contains a 1,2,3,5-η-penta-2,4-dienediyl ligand. The reaction of **2** with "$RhCl(PMe_3)_2$", prepared in situ from $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = *cis*-cyclooctene) and PMe_3, yielded **3a** almost quantitatively and far more rapidly.[6] The corresponding reaction of **2** with "$IrCl(PMe_3)_2$" was less clean but afforded low yields of **3b**,[5] which has been structurally characterized by single-crystal X-ray diffraction methods.[7] The molecular structure of **3b** and selected bond distances and angles are shown in Figure 1, and fractional atomic coordinates are presented in Table I. The structure unambiguously defines the features of this new 1,2,3,5-η-penta-2,4-dienediyl ligand.

Table I. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for 3b

	x	y	z	U^a
Ir	1912.2 (4)	7471.3 (4)	6953.1 (3)	29.0 (1)
Cl	736 (3)	8198 (2)	7772 (2)	47 (1)
P(1)	1099 (3)	6136 (2)	7044 (2)	37 (1)
P(2)	619 (3)	8023 (2)	5611 (2)	35 (1)
C(1)	1292 (12)	8418 (9)	4833 (8)	51 (6)
C(2)	−549 (11)	7333 (9)	4894 (9)	62 (6)
C(3)	−180 (12)	8997 (8)	5720 (9)	56 (6)
C(4)	−296 (11)	6158 (10)	7222 (10)	57 (6)
C(5)	796 (13)	5331 (9)	6161 (9)	59 (7)
C(6)	2018 (13)	5487 (9)	7978 (9)	56 (6)
C(7)	3114 (10)	7082 (7)	6412 (7)	30 (4)
C(8)	3899 (10)	7738 (7)	6616 (8)	32 (4)
C(9)	3514 (11)	8402 (8)	7123 (9)	43 (5)
C(10)	3397 (11)	8194 (9)	7940 (8)	42 (5)
C(11)	3410 (11)	7293 (7)	8201 (8)	45 (5)
C(21)	2518 (7)	6124 (5)	5068 (5)	41 (5)
C(22)	2641	5356	4636	48 (6)
C(23)	3487	4731	5088	59 (7)
C(24)	4209	4874	5973	59 (7)
C(25)	4087	5642	6406	53 (6)
C(26)	3241	6267	5953	36 (5)
C(31)	5317 (8)	7512 (6)	5815 (5)	61 (6)
C(32)	6450	7566	5782	78 (9)
C(33)	7376	7917	6499	86 (11)
C(34)	7169	8214	7251	72 (8)
C(35)	6037	8160	7285	50 (6)
C(36)	5111	7809	6567	39 (5)
C(41)	3377 (7)	9397 (4)	6823 (5)	33 (4)
C(42)	2863	10021	7208	50 (6)
C(43)	2815	10901	6954	57 (7)
C(44)	3280	11158	6315	57 (6)
C(45)	3794	10535	5930	55 (7)
C(46)	3842	9654	6184	51 (6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.



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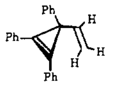

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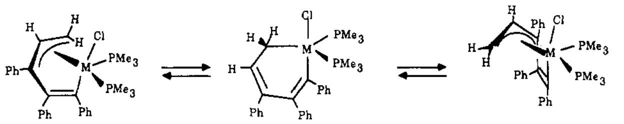

3 a. M = Rh b. M = Ir

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NMR studies of **3a,b** are consistent with a solution

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(3) Zimmerman, H. E.; Fleming, S. A. *J. Org. Chem.* **1985**, *50*, 2539 and references cited therein. Padwa, A. *Org. Photochem.* **1979**, 4, 261 and references cited therein.

(4) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 511.

(5) **3a**: 98%; ^{1}H NMR (300 MHz, $CDCl_3$, J values in Hz; at −10 °C) δ 1.14 (d, J_{HP} = 9, 18 H, PMe_3), 2.71 (dd, J_{HH} = 9, J_{HP} = 9, 1 H, CH_{anti}), 3.37 (dd, J_{HH} = 7, J_{HP} = 3, 1 H, CH_{syn}), 6.11 (dd, J_{HH} = 9, 7, 1 H, $CH_{central}$), 6.8–7.9 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ 15.61 (d, J_{CP} = 23, P*Me*$_3$), 19.3 (d, J_{CP} = 26, P*Me*$_3$), 48.27 (dd, J_{CP} = 44, $J_{C\text{-}Rh}$ = 8, *C*H$_2$), 87.23 (d, J_{CP} = 28, allylic *C*Ph), 113.51 (s, *C*H) (other resonances due to ring and Ph carbons could not be unambiguously assigned); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, negative shifts upfield relative to external H_3PO_4) δ −14.5 (dd, J_{PRh} = 143, J_{PP} = 11, PMe_3), 0.99 (dd, J_{PRh} = 168, J_{PP} = 11, PMe_3). Anal. Calcd for $C_{29}H_{36}ClP_2Rh$: C, 59.54; H, 6.21. Found: C, 59.30; H, 6.22. **3b**: 10%; ^{1}H NMR ($CDCl_3$) δ 1.25 (d, J_{HP} = 9, 9 H, PMe_3), 1.30 (d, J_{HP} = 10, 9 H, PMe_3), 2.45 (dd, J_{HH} = 9, J_{HP} = 9, 1 H, CH_{anti}), 3.29 (dd, J_{HH} = 7, J_{HP} = 3, 1 H, CH_{syn}), 5.70 [ddd, J_{HH} = 9, 7, J_{HP} = 2, 1 H, $CH_{central}$), 6.7–7.9 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14.98 (d, J_{CP} = 34, P*Me*$_3$), 18.98 (d, J_{CP} = 33, P*Me*$_3$), 37.36 (d, J_{CP} = 42, *C*H$_2$), 80.81 (d, J_{CP} = 21, allylic *C*Ph), 109.14 (s, *C*H) (other resonances due to ring and Ph carbons could not be unambiguously assigned); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −38.97 [d, J_{PP} = 6, PMe_3), −44.90 (d, J_{PP} = 6, PMe_3). Elemental composition was confirmed by an Xray crystallographic study.[7]

(6) The much slower reaction rate of **2** with $[RhCl(PMe_3)_3]$ is interpreted to imply that phosphine dissociation is required to give two coordination sites, one for initial binding of the vinylcyclopropene and the second to trigger the ring-opening reaction.

(7) Crystal data for **3b**: monoclinic, $P2_1/c$,a = 12.114 (2) Å, b = 15.207 (3) Å, c = 16.094 (4) Å, β = 111.07 (2)°, V = 2767 (1) Å^3, Z = 4, D(cald) = 1.63 g cm^{-3}, μ(Mo Kα) = 53.4 cm^{-1}, t = 293 K, T(max)/T(min) = 0.178/0.127. A yellow crystal, 0.20 × 0.25 × 0.38 mm, was obtained by crystallization from CH_2Cl_2/hexane. All specimens diffracted weakly. Of 6827 reflections collected (Nicolet R3m/μ, Mo Kα, $4° \leq 2\theta \leq 55°$), 6358 were unique (R_{int} = 2.42%) and 3167 were observed at the $3\sigma(F_o)$ level. An empirical correction for absorption was applied to the data. A Patterson synthesis provided the location of the Ir atom. With all non-hydrogen atoms anisotropic and all hydrogen atoms idealized: $R(F)$ = 4.72%, (wF) = 5.00%, GOF = 0.959, Δ/σ = 0.056, $\Delta(\rho)$ = 1.08 e Å^{-3} (0.90 Å from Ir), N_o/N_v = 12.0. All software from SHELXTL library, Nicolet Corp., Madison, WI.

structure identical with that in Figure 1.[5] In particular, the syn and anti CH_2 protons exhibit negligible geminal coupling, consistent with essentially sp^2 character for the terminal allylic carbon atom and in contrast to the significant geminal coupling observed for the formally sp^3 CH_2 group in metallacycle **1**.[2a] The resonances due to the syn and anti CH_2 protons in the rhodium complex **3a** are broad at room temperature, and only one resonance for the PMe_3 protons is observed; however, the $^{31}P\{^1H\}$ NMR spectrum does show inequivalent phosphorus environments at this temperature. Low-temperature ^1H NMR spectra exhibit sharp multiplets for the CH_2 protons, and warming the sample to 60 °C results in coalescence due to syn–anti site exchange between the CH_2 protons and interconversion of ^{31}P environments. A plausible explanation for this behavior involves a reversible $\eta^3 \rightarrow \eta^1$ transformation of the allylic part of the organic ligand, via intermediate **4**, in which a plane of symmetry bisects the H–C–H and P–Rh–P angles.

While the NMR behavior discussed above is reversible and no decomposition was observed during the NMR experiments, prolonged heating of **3a** in $CHCl_3$ solution at 70 °C resulted in loss of PMe_3 and isolation of the (η-1,2,3-triphenylcyclopentadienyl)rhodium complex **5a**[8] together with some free 1,2,3-triphenylcyclopentadiene. Furthermore, in contrast to our results using PMe_3 (vide supra), the room-temperature reaction of **2** with $[RhCl(C_8H_{14})_2]_2$ in the presence of 4 equiv of the bulkier phosphine P-*i*-Pr_3 in benzene yielded directly the orange air-sensitive (η^5-cyclopentadienyl)hydridorhodium complex **6**.[8] This in turn reacted with $CHCl_3$ at 50 °C to afford the corresponding dichloro complex **5b**.[8] These observations imply that a key step in ring closure from compounds such as **3a** involves phosphine dissociation and is consequently accelerated with bulkier phosphines such as P-*i*-Pr_3. The intimate mechanism of formation of the cyclopentadienyl ring is still unclear. A plausible sequence would involve reductive elimination from the 1-rhodacyclohexadiene **4** to give an η^4-cyclopentadiene ligand,[2] followed by oxidative addition of the endo CH bond to the metal center.[9]

While reaction of **2** with $[Rh(acac)(\eta-C_2H_4)_2]$ (acac = acetylacetonate) in the presence of 1 molar equiv of PMe_3 yielded **7**,[10] metathetical replacement of chloride with acac

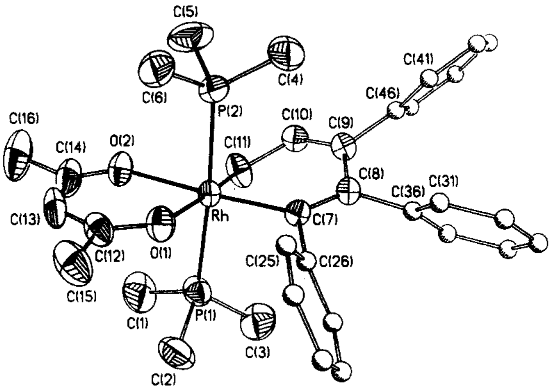
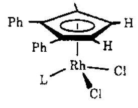
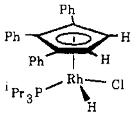


Figure 2. Molecular structure and labeling scheme for **8**. Bond distances (Å) and angles (deg): Rh–P(1), 2.321 (2); Rh–P(2), 2.324 (2); Rh–O(1), 2.194 (3); Rh–O(2), 2.157 (3); Rh–C(7), 2.032 (4); Rh–C(11), 2.064 (5); C(7)–C(8), 1.365 (6); C(8)–C(9), 1.494 (7); C(9)–C(10), 1.331 (7); C(10)–C(11), 1.491 (7); P(1)–Rh–P(2), 175.2 (1); P(1)–Rh–O(1), 89.3 (1); P(1)–Rh–O(2), 90.4 (1); P(1)—Rh–C(7), 91.7 (1); P(1)–Rh–C(11), 87.4 (2); P(2)–Rh–O(1), 90.8 (1); P(2)–Rh–O(2), 84.8 (1); P(2)–Rh–C(7), 93.1 (1); P(2)–Rh–C(11), 91.9 (2); O(1)–Rh–O(2), 85.4 (1); /(1)–Rh–C(7), 97.4 (2); O(1)–Rh–C(11), 172.3 (2); O(2)–Rh–C(7), 176.5 (2); O(2)–Rh–C(11), 87.7 (2); C(7)–Rh–C(11), 89.6 (2).

by reaction of **3a** with [Tl(acac)] in THF did not result in loss of PMe_3 to give **7** but instead produced an $\eta^3 \rightarrow \eta^1$ transformation of the allylic part of the organic ligand to give the yellow, air-stable 1-rhodacyclohexa-2,4-diene complex **8**.[10] Addition of 1 equiv of PMe_3 to **7** in C_6H_6 also yielded **8**, although traces of an isomer containing cis PMe_3



5 a. L = PMe_3
b. L = P^iPr_3



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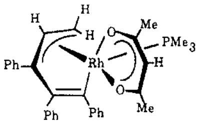

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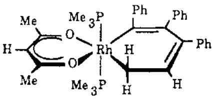
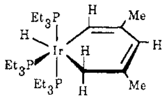


8



9

ligands could also be detected by ^{31}P NMR spectroscopy. The structure of **8** has been confirmed by single-crystal X-ray diffraction methods.[11] Its molecular structure with

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(8) **5a**: ^1H NMR ($CDCl_3$) δ 1.42 [d, J_{HP} = 12, 9 H, PMe_3), 5.43 (s, 2 H, CH), 7.1–7.5 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.7 (d, J_{CP} = 35, P*Me*$_3$), 80.3 (d, *J* = 8, *C*H), 104.8 (s, *C*–Ph), 128.1, 128.2, 128.8, 128.9, 130.2, 130.3, 131.7, 131.8 (Ph) (the third cyclopentadienyl ring resonance could not be identified unambiguously); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 22.3 (d, J_{PRh} = 128, PMe_3). **5b**: ^1H NMR ($CDCl_3$) δ 1.25 (dd, J_{HH} = 7, J_{HP} = 14, 18 H, CH*Me*$_2$), 2.80 (m, 3 H, C*H*Me$_2$), 5.58 (s, 2 H, CH_{ring}), 7.1–7.9 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 20.1 (s, CH*Me*$_2$), 26.9 (d, J_{CP} = 21, *C*HMe$_2$), 73.2 (d, *J* = 8, *C*H$_{ring}$), 112.2 (d, *J* = 5, *C*–Ph), 127.9, 128.3, 1128.5, 129.4, 130.2, 130.7, 131.7, 131.8 (Ph) (the third cyclopentadienyl ring resonance could not be identified unambiguously). Anal. Calcd for $C_{32}H_{38}Cl_2PRh$: C, 61.24; H, 6.11. Found: C, 61.16; H, 6.14. **6**: 60%; ^1H NMR (C_6D_6) δ −11.86 (dd, J_{HP} = 35, J_{HRh} = 14, 1 H, Rh–H), 0.92 (dd, J_{HP} = 14, J_{HH} = 7, 9 H, CH*Me*), 1.01 [dd, J_{HP} = 15, J_{HH} = 8, 9 H, CH*Me*), 2.09 (m, 3 H, C*H*Me), 4.44 (d, *J* = 2.4, 1 H, CH_{ring}), 5.54 [d, *J* = 1, 1 H, CH_{ring}), 6.8–8.0 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 19.8 (s, CH*Me*), 20.1 (s, CH*Me*), 27.3 (d, J_{CP} = 15, *C*HMe), 71.3 [dd, *J* = 14, 7, *C*H$_{ring}$), 87.0 (d, *J* = 15, *C*H$_{ring}$), 110.0 (s, *C*–Ph), 114.9 (s, *C*–Ph), 129.9, 130.5, 131.1, 132.8, 133.3, 133.9, 134.7 (Ph) (the fifth cyclopentadienyl ring carbon could not be located unambiguously); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 82.88 (d, J_{PRh} = 141, P-*i*-Pr_3); IR (THF) ν_{Rh-H} 2051 cm^{-1}.

(9) We cannot exclude the possibility of α-elimination from **4** to give a hydridorhodabenzene[12] (or -rhodacyclohexatriene) intermediate followed by loss of phosphine and subsequent valence isomerization to the cyclopentadienylrhodium product. Experiments designed to probe these mechanisms are in progress.

(10) **7**: 70%; ^1H NMR (C_6D_6) δ 0.84 (d, J_{HP} = 10, 9 H, PMe_3), 1.52 (s, 3 H, CH_3), 1.96 (s, 3 H, CH_3), 2.47 [b d, 1 H, CH_2), 2.54 (b d, 1 H, CH_2), 4.83 [s, 1 H, acac CH], 5.65 (b t, 1 H, CH); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 15.7 (d, J_{CP} = 27, PMe_3), 25.9 (d, J_{CP} = 16, CH_2), 28.2 (s, CH_3), 29.4 (s, CH_3), 98.5 (s, acac CH), 104.0 (d, J_{CP} = 24, allylic CPH), 107.6 (d, J_{CP} = 5, CH), 186.4 (s, CO), 187.2 (s, CO); $^{31}P\{^1H\}$ (C_6H_6) δ 14.3 (d, J_{PRh} = 201, PMe_3). Anal. Calcd for $C_{31}H_{34}O_2PRh$: C, 65.04; H, 6.00. Found: C, 65.04; H, 6.00. The solid-state structure of **7** has also been confirmed by single-crystal X-ray diffraction methods and is the isomer shown: Rheingold, A. L., unpublished observations. **8**: 60%; ^1H NMR (C_6D_6) δ 1.01 ("virtual" t, *J* = 3.3, 18 H, PMe_3), 1.62 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 2.92 (m, J_{HH} = 5, 2 H, CH_2), 4.98 (s, 1 H, CH_{acac}), 5.94 (t, J_{HH} = 5, 1 H, CH), 6.6–7.9 (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 12.7 ("virtual" t, J_{CP} = 14, P*Me*$_3$), 13.5 (dt, J_{CRh} = 26, J_{CP} = 7, *C*H$_2$), 28.3 (s, *C*H$_3$), 28.4 (s, *C*H$_3$), 98.4 (s, *C*H$_{acac}$), 164.3 (dt, J_{CRh} = 35, J_{CP} = 11, CPH), 186.5 (s, *C*–O), 188.0 (s, *C*–O) (other resonances due to ring and Ph carbons could not be unambiguously assigned); $^{31}P\{^1H\}$ NMR (C_6H_6) δ −1.49 (d, J_{PRh} = 121, PMe_3]. Anal. Calcd for $C_{34}H_{43}O_2P_2Rh$: C, 62.96; H, 6.69. Found: C, 62.78; H, 6.71.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 8

	x	y	z	U^a
Rh	2397.2 (4)	1846.8 (2)	1876.4 (2)	36.9 (1)
P(1)	1967 (2)	443.0 (9)	1797.1 (8)	57.6 (5)
P(2)	2871 (2)	3236.9 (9)	2049.1 (7)	54.8 (5)
O(1)	4519 (3)	1607 (2)	1755 (2)	55 (1)
O(2)	3103 (4)	1720 (2)	2890 (2)	59 (1)
C(1)	1873 (8)	−29 (5)	2568 (3)	99 (3)
C(2)	3254 (7)	−153 (4)	1481 (4)	89 (3)
C(3)	382 (7)	104 (4)	1317 (4)	89 (3)
C(4)	2429 (7)	3996 (4)	1428 (3)	85 (3)
C(5)	2194 (9)	3670 (5)	2727 (4)	108 (4)
C(6)	4676 (7)	3420 (4)	2262 (4)	89 (3)
C(7)	1655 (4)	2021 (3)	935 (2)	36 (2)
C(8)	460 (4)	2395 (3)	690 (2)	38 (2)
C(9)	−448 (4)	2794 (3)	1106 (2)	41 (2)
C(10)	−397 (4)	2621 (3)	1726 (2)	44 (2)
C(11)	458 (5)	1984 (4)	2103 (3)	57 (2)
C(12)	5457 (5)	1362 (3)	2190 (3)	58 (2)
C(13)	5363 (6)	1300 (4)	2846 (3)	67 (2)
C(14)	4281 (7)	1512 (4)	3151 (3)	70 (2)
C(15)	6774 (6)	1142 (4)	1952 (4)	84 (3)
C(16)	4455 (8)	1481 (6)	3870 (3)	113 (4)
C(21)	2037 (3)	1001 (2)	79 (2)	67 (2)
C(22)	2853	666	−342	102 (3)
C(23)	4146	989	−365	115 (4)
C(24)	4625	1645	32	103 (4)
C(25)	3809	1979	453	64 (2)
C(26)	2516	1657	476	46 (2)
C(31)	798 (3)	2822 (3)	−424 (2)	64 (2)
C(32)	308	2913	−1075	84 (3)
C(33)	−993	2635	−1320	88 (3)
C(34)	−1805	2265	−913	74 (2)
C(35)	−1315	2174	−262	58 (2)
C(36)	−14	2452	−17	47 (2)
C(41)	−977 (3)	4075 (2)	451 (2)	66 (2)
C(42)	−1878	4689	194	81 (3)
C(43)	−3232	4670	300	75 (3)
C(44)	−3684	4036	663	84 (3)
C(45)	−2783	3422	920	59 (2)
C(46)	−1430	3442	814	41 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

selected bond distances and angles is shown in Figure 2, and fractional atomic coordinates appear in Table II. In the solid state the metallacyclic ring is puckered and contains localized single and double bonds between carbon atoms as does its previously characterized 1-platinacyclohexa-2,4-diene relative 1.[2a] In sharp contrast to 1, whose CH_2 protons are inequivalent at room temperature,[2a] low-temperature NMR studies of 6 indicate that even at −96 °C the analogous protons are either equivalent or the ring is undergoing rapid inversion. The metallacyclic ring in octahedral 8 is significantly less puckered in the solid state than that in square-planar 1, presumably due to the presence of PMe_3 above and below the organic ring. An iridacyclohexadiene complex 9 has recently been structurally characterized by Bleeke;[13] in this compound the metallacyclic ring is essentially planar. In light of these results we feel that the puckering of the metallacyclohexadiene rings in 1 and 8 probably results from minimization of steric repulsions between the phenyl substituents.

In conclusion, our results clearly demonstrate the stepwise nature of metal-promoted ring opening/ring closure reactions of vinylcyclopropenes. Further studies on the chemistry of these new metallacycles, particularly their potential for transformation to metallabenzenes (or metallacyclohexatrienes), is in progress.

Acknowledgment. We are grateful to the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Air Force Office of Scientific Research (Grant AFOSR-86-0075) for generous support of our research. We thank Professors John Bleeke (Washington University, St. Louis) and Lanny Liebeskind (Emory University) for providing preprints of their work and for free and open discussion of their results.

Registry No. **2**, 62747-62-0; **3a**, 108560-73-2; **3b**, 108560-74-3; **5a**, 108560-76-5; **5b**, 108560-78-7; **6**, 108560-77-6; **7**, 108560-79-8; *trans*-8, 108646-09-9; *cis*-8, 108560-72-1; $RhCl(PMe_3)_3$, 36103-64-7; $[RhCl(C_8H_{14})_2]_2$, 12279-09-3; $IrCl(PMe_3)_2$, 108560-75-4; Rh(acac)(N-C_2H_4)$_2$, 12082-47-2; Tl(acac), 14219-90-0; PMe_3, 594-09-2; P-*i*-Pr_3, 6476-36-4; 1,2,3-triphenylcyclopentadiene, 108535-09-7.

Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen-atom coordinates (8 pages); listings of observed vs. calculated structure factors (54 pages). Ordering information is given on any current masthead page.

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(11) Crystal data for 8: monoclinic, $P2_1/c$, a = 9.934 (2) Å, b = 16.243 (5) Å, c = 21.070 (7) Å, β = 98.42 (2)°, V = 3361 (1) Å^3, Z = 4, D(calcd) = 1.28 g cm^{-3}, μ(Mo Kα) = 6.2 cm^{-1}, t = 294 K. A yellow crystal, 0.20 × 0.23 × 0.31 mm, was obtained by crystallization from hexane. Of 6335 reflections collected ($4° \leq 2\theta \leq 50°$), 5924 were unique (R_{int} = 1.95%) and 3989 were observed at the $3\sigma(R_o)$ level. No correction for absorption was required. A Patterson synthesis provided the location of the Rh atom. With all non-hydrogen atoms anisotropic and all hydrogen atoms idealized: $R(F)$ = 4.37%, $R(wF)$ = 5.51%, GOF = 1.113, Δ/σ = 0.013, $\Delta(\rho)$ = 0.49 e Å^{-3} (1.05 Å from Rh), N_o/N_v = 12.6. All software as in ref 7.

(12) While metallabenzenes have been the subject of theoretical studies (Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39), only one example of an osmabenzene has been reported to date (Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811).

(13) Bleeke, J. R.; Peng, W.-J. *Organometallics*, preceding paper in this issue.

New Tantalum Ylide Complexes: Crystal and Molecular Structure of (η^5-C_5Me_5)$Cl_4Ta(CH_2{=}PMePh_2)$ Containing a Neutral Phosphorus Ylide

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Summary: (η^5-C_5Me_5)$TaCl_4$ reacts with methylenephosphoranes to give the neutral ylide derivatives (η^5-C_5Me_5)$Cl_4Ta(CH_2{=}PRR'_2)$ where R = Me or Ph and R′ = Me or Ph. The X-ray crystal structure of complex with R = Me and R′ = Ph shows a pseudooctahedral geometry with the ylide ligand trans to the pentamethylcyclopentadienyl ring.

Intermediate tantalum phosphorus ylide derivatives have been formulated in alkylidene-transfer reactions from alkylidenephosphoranes,[1] but as far as we know, only two tantalum complexes containing a phosphoniomethanide fragment have been isolated.[2] Here we report the first

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(1) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, *171*, 43.