Skeletal Rearrangement during Rhodium-Promoted Ring Opening of 1,2-Diphenyl-3-vinyl-1-cyclopropene. Preparation and Characterization of 1,2- and 2,3-Diphenyl-3,4-pentadienediyl Rhodium Complexes and Their Ring Closure to a 1,2-Diphenylcyclopentadienyl Complex

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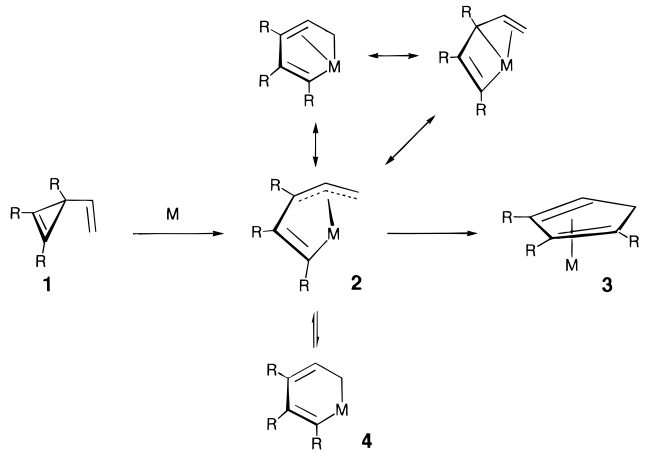
Under conditions of kinetic control, 1,2-diphenyl-3-vinyl-1-cyclopropene undergoes ring opening with the [Rh(Cl)(PMe_3)$_2$] fragment to give two isomeric η^3:η^1-1,3-pentadienediyl compounds: the expected 1,2-diphenyl isomer, and the 2,3-diphenyl isomer resulting from an apparent skeletal rearrangement reaction. The latter complex has been characterized by X-ray crystallography. Both complexes underwent ring closure to give the same 1,2-diphenylcyclopentadienyl complex on treatment with silver ion. Addition of a third equivalent of trimethylphosphine to the 2,3-diphenyl isomer produced two meridional rhodacyclohexadienes, which exhibit facile solvent-dependent chloride dissociation. In contrast, phosphine added reversibly to the 1,2-diphenyl isomer to give only the chloride-dissociated compound, and the tris(phosphine) product could only be isolated after anion exchange with hexafluorophosphate. No deprotonation to give rhodabenzene complexes could be achieved. The mechanism of rearrangement is proposed to involve a carbocation rearrangement during the ring-opening reaction and is compared to other metal-promoted reactions of vinylcyclopropenes.

Introduction

3-Vinyl-1-cyclopropenes of general structure **1** (Scheme 1) undergo thermal and photochemical ring expansion to cyclopentadienes and indenes.[2−6] Transition metal complexes also effect this ring expansion catalytically and stoichiometrically, to give cyclopentadienes, η^4-cyclopentadiene complexes, and η^5-cyclopentadienyl complexes.[7−11] On treatment with carbonyl-bearing metal complexes, cyclohexadienones, η^4-cyclohexadienone complexes, and phenols have been prepared.[7−14]

Scheme 1



In several of these closures, pentadienediyl intermediates **2** resulting from ring opening of the vinylcyclopropenes have been observed[15,16] and have been shown to be precursors to the ring-closed η^4-cyclopentadiene products **3**.[7−11,16−18] Use of selectively deuterated com-

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(9) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1578−81.
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(11) Donovan, B. T.; Hughes, R. P.; Kowalski, A. S.; Trujillo, H. A.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1038−43.
(12) Cho, S. H.; Liebeskind, L. S. *J. Org. Chem.* **1987**, *52*, 2631−4.
(13) Semmelhack, M. F.; Ho, S.; Steigerwald, M.; Lee, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 4397.
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(15) Donovan, B. T.; Egan, J. W., Jr.; Hughes, R. P.; Spara, P. P.; Trujillo, H. A.; Rheingold, A. L. *Isr. J. Chem.* **1990**, *30*, 351−60.
(16) Donovan, B. T.; Hughes, R. P.; Trujillo, H. A. *J. Am. Chem. Soc.* **1990**, *112*, 7076−7.

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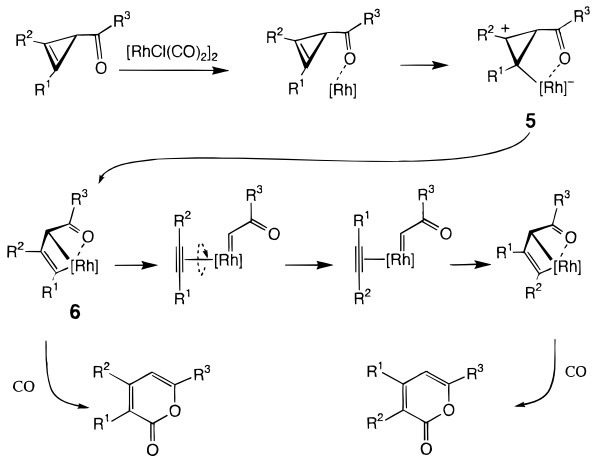
pounds has demonstrated the stereochemistry of both the ring-opening and -closure reactions.[15,16] While metallacyclohexadiene intermediates **4** may be energetically accessible in the reaction,[9,19] ring-closure reactions do not require such intermediates and have been shown to occur directly from nonplanar intermediates **2**.[7,15,16]

The corresponding reactions of cyclopropenyl ketones with Rh(I) and Rh(II) catalysts yield α-pyrones and furans.[12,14] One suggested pathway to pyrones is shown in Scheme 2;[12] the corresponding furans are the products if CO insertion is slow. A particularly interesting feature of this reaction is the regiochemistry observed in the cases of unsymmetrically substituted substrates. A ring-opening mechanism involving initial binding of rhodium to the ketone function, followed by interaction of the metal with the cyclopropene double bond, was suggested to give cationic intermediate **5**; disrotatory opening of **5** was proposed to afford **6**, which is analogous to one of the valence tautomers of the pentadienediyl species **2** we have observed. To account for some unexpected product regiochemistries, the metallacyclobutene portion of intermediate **6** was assumed to rearrange via a cycloaddition cycloreversion pathway, as shown in Scheme 2, thereby exchanging the positions of the α and β carbons and their substituents.

Here we report a different rearrangement encountered in the reaction of a symmetrically substituted vinylcyclopropene with a Rh(I) precursor, which clearly must proceed by a pathway quite different from that proposed in Scheme 2.

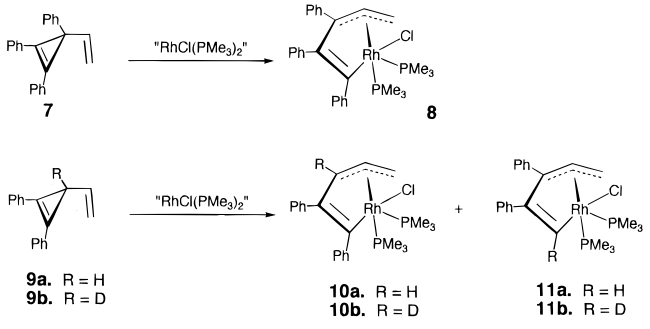
Scheme 2[a]



[a] R^1 = Me, R^2 = Ph, R^3 = OEt.

Results and Discussion

The previously observed ring opening of triphenylvinylcyclopropene **7** on reaction with the [$RhCl(PMe_3)_2$] fragment (obtained in situ by treatment of [$Rh(C_8H_{14})_2Cl]_2$ with 2 equiv of PMe_3 per Rh) cleanly affords the pentadienediyl Rh(III) complex **8**.[9] However, examination of the corresponding reaction of diphenylvinylcyclopropene **9a** with the [$RhCl(PMe_3)_2$] fragment at room temperature revealed a more complicated process. While the expected 1,2-diphenyl compound **10a** was obtained, the major product was its 2,3-diphenyl isomer **11a**; the ratio of **10a** to **11a** was 1:3. The two isomers could be separated, and on standing in solution for 2 weeks at 45 °C, a sample of pure **10a** showed no conversion to the major isomer **11a**. As the reaction in which the two compounds are formed occurs readily at room temperature, the 1:3 product ratio clearly cannot be due to an equilibration of the two compounds and is the result of kinetic control. An X-ray diffraction study of a single crystal of **11a** confirmed its structure; the ORTEP diagram shown in Figure 1 illustrates that the phenyl rings are indeed in the 2 and 3 positions of the pentadienediyl ligand. The crystallographic parameters, atomic coordinates, and selected bond lengths and angles for the structure are listed in Tables 1−3.



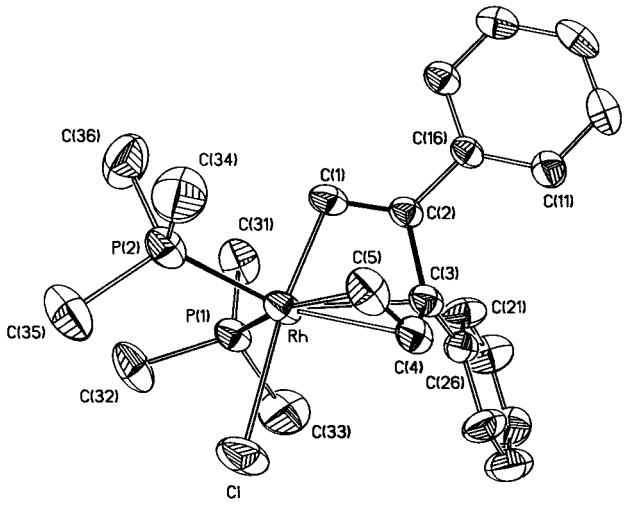


Figure 1. ORTEP diagram and numbering scheme for **11a**.

The location of the phenyl rings in the two isomers was also clear from their low-temperature proton NMR spectra. The connectivity of the four ring hydrogens in the minor isomer, **10a**, is demonstrable by COSY and by the proton−proton coupling constants. The spectra of the major isomer, **11a**, show a set of three coupled protons and an isolated proton coupled only to phosphorus and to rhodium. The lone ring hydrogen, H(1), displays a surprisingly large coupling constant to one of the phosphines. Since neither phosphine is trans to C(1) in the structure, the 17 Hz coupling may arise from the near coplanarity of the P(2)−Rh and C(1)−H(1) bonds, which form a 14.2° dihedral angle. As in triphenyl compound **8**,[9] broad room temperature NMR resonances for the geminal hydrogens and for the phosphines are consistent with an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ allyl

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Table 1. Crystal, Data Collection, and Refinement Parameters for 11a

formula	$C_{23}H_{32}ClP_2Rh$
cryst syst	trigonal
space group	$R\bar{3}$
a, Å	20.165(7)
b, Å	20.165(7)
c, Å	30.89(1)
V, Å^3	10874(7)
Z	18
D(calcd), g cm^{-3}	1.46
μ(Mo Kα), cm^{-1}	7.8
temp, °C	23
cryst dimens, mm	0.25 × 0.25 × 0.25
radiation	graphite-monochromated Mo Kα (λ = 0.710 73 Å)
diffractometer	Nicolet R3m/μ
scan speed, deg min^{-1}	variable, 6−20
scan limits, deg	$4 \le 2\theta \le 48$
scan technique	Wykoff
data collected	$+h,+k,\pm l$
weighting factor, g	0.0010
indep data	3804 (4170 collected)
indep data with $F_o \ge 5\sigma(F_o)$	2541
std rflns	3 stds/197 rflns
$R(F)$, %	4.22
$R_w(F)$, %	4.52
GOF	1.098
data/parameter	10.7
Δ/σ	0.003

Table 2. Selected Bond Distances for 11a

Rh−P(1)	2.325(2)
Rh−P(2)	2.256(2)
Rh−Cl	2.486(3)
Rh−C(1)	2.004(7)
Rh−C(3)	2.416(6)
Rh−C(4)	2.226(7)
Rh−C(5)	2.146(6)
P(1)−C(31)	1.791(10)
P(1)−C(32)	1.815(7)
P(1)−C(33)	1.817(8)
P(2)−C(34)	1.819(7)
P(2)−C(35)	1.807(9)
P(2)−C(36)	1.811(14)
C(1)−C(2)	1.321(8)
C(2)−C(3)	1.518(10)
C(2)−C(16)	1.490(7)
C(3)−C(4)	1.387(10)
C(3)−C(26)	1.491(7)
C(4)−C(5)	1.420(9)

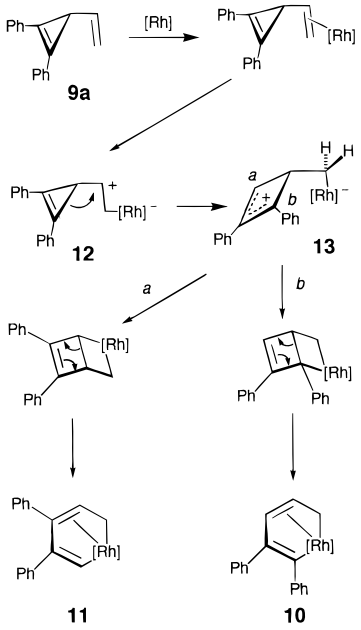
Table 3. Selected Bond Angles for 11a

P(1)−Rh−P(2)	100.5(1)	C(32)−P(1)−C(33)	101.5(4)
P(1)−Rh−Cl	86.5(1)	Rh−P(2)−C(34)	114.8(3)
P(2)−Rh−Cl	94.6(1)	Rh−P(2)−C(35)	119.3(3)
P(1)−Rh−C(1)	94.0(2)	C(34)−P(2)−C(35)	102.2(4)
P(2)−Rh−C(1)	93.0(2)	Rh−P(2)−C(36)	114.9(3)
Cl−Rh−C(1)	172.1(2)	C(34)−P(2)−C(36)	101.5(4)
P(1)−Rh−C(3)	99.6(1)	C(35)−P(2)−C(36)	101.7(5)
P(2)−Rh−C(3)	148.8(1)	Rh−C(1)−C(2)	106.5(5)
Cl−Rh−C(3)	110.2(2)	C(1)−C(2)−C(3)	108.4(6)
C(1)−Rh−C(3)	62.0(3)	C(1)−C(2)−C(16)	128.0(6)
P(1)−Rh−C(4)	126.4(1)	C(3)−C(2)−C(16)	123.2(5)
P(2)−Rh−C(4)	133.1(1)	Rh−C(3)−C(2)	83.1(3)
Cl−Rh−C(4)	88.8(2)	Rh−C(3)−C(4)	65.2(3)
C(1)−Rh−C(4)	84.6(3)	C(2)−C(3)−C(4)	117.7(5)
C(3)−Rh−C(4)	34.5(2)	Rh−C(3)−C(26)	125.5(3)
P(1)−Rh−C(5)	164.1(2)	C(2)−C(3)−C(26)	119.9(5)
P(2)−Rh−C(5)	95.3(2)	C(4)−C(3)−C(26)	122.3(6)
Cl−Rh−C(5)	94.0(2)	Rh−C(4)−C(3)	80.3(4)
C(1)−Rh−C(5)	83.4(3)	Rh−C(4)−C(5)	68.0(4)
C(3)−Rh−C(5)	65.3(2)	C(3)−C(4)−C(5)	123.3(7)
C(4)−Rh−C(5)	37.8(2)	Rh−C(5)−C(4)	74.1(3)
Rh−P(1)−C(31)	117.6(2)	C(2)−C(16)−C(11)	120.6(3)
Rh−P(1)−C(32)	117.8(2)	C(2)−C(16)−C(15)	119.3(3)
C(31)−P(1)−C(32)	102.8(4)	C(3)−C(26)−C(21)	119.4(4)
Rh−P(1)−C(33)	111.7(3)	C(3)−C(26)−C(25)	120.5(4)
C(31)−P(1)−C(33)	103.2(4)		

rearrangement process via a metallacyclohexadiene intermediate that exchanges both the syn and anti proton environments with concomitant exchange of the phosphine environments rapidly on the NMR time scale.

A mechanism consistent with the formation of **10a** and **11a** is shown in Scheme 3. Initial coordination of the metal followed by slippage would lead to structure **12**, which is poised for ring expansion to **13**. Breslow[20] has shown the ease with which such cyclopropenylcarbinyl expansions occur during solvolysis reactions, and we have provided evidence that an analogous intermediate is important in the chloropalladation reactions of other vinylcyclopropenes.[21] The importance of initial coordination to the vinyl group has been clearly demonstrated for similar reactions, in which ring expansion is significantly slowed by methylation of the vinyl group.[10,13,22] Attack of the metal at the less sterically

Scheme 3 [a]



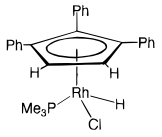
[a] [Rh] = Rh(Cl)(PMe$_3$)$_2$.

hindered site, *a*, of **13** would then lead to 2,3-diphenyl structure **11**. The formation of lesser amounts of **10** is consistent with attack at *b* being disfavored by the greater steric congestion at *b* than at *a*. When the reaction was carried out using ring-deuterated **9b**, the deuterium was observed in the appropriate positions in both compounds **10b** and **11b**, consistent with Scheme 3. Since these reactions are carried out in toluene, it is doubtful whether the metal and carbon atoms in **12** carry substantial charges, but partial charge separation may be enough to trigger ring expansion, given the ease with which analogous expansions are known to occur.[20]

As earlier demonstrated for triphenyl compound **8** and several related compounds, thermal phosphine loss triggers ring closure followed by endo-H migration to the metal, giving cyclopentadienyl compounds such as

(20) Breslow, R.; Lockhart, J.; Small, A. *J. Am. Chem. Soc.* **1962**, *84*, 2793−800.
(21) Donovan, B. T.; Hughes, R. P.; Spara, P. P.; Rheingold, A. L. *Organometallics* **1995**, *14*, 489−94.
(22) Choi, H.; Pinhas, A. R. *Organometallics* **1992**, *11*, 1.

14.[9,23] Similarly, on chloride abstraction from diphenyl compound **10a** or **11a** by silver ion, the cyclopentadienyl compound **15a** was obtained. As expected, on treatment with silver ion, the deuterated isotopomers **10b** and **11b** both gave the same product **15b**, having deuterium in a position α to a phenyl group in the cyclopentadienyl ring.



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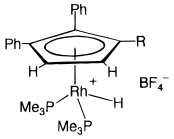
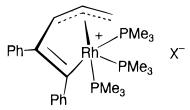


15a. R = H
15b. R = D

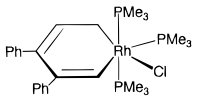


16a. X = Cl
16b. X = PF_6

Both diphenyl complexes **10a** and **11a** readily coordinate a third phosphine to afford metallacyclohexadiene complexes. When 1,2-diphenyl complex **10a** is treated with a third equivalent of trimethylphosphine, tris(phosphine) complex **16a** is formed in solution, although the third phosphine is lost on evaporation, regenerating **10a**. Similar behavior is also observed with 1,2,3-triphenyl compound **8**. Tris(phosphine) cation **16b** may be trapped, however, through exchange of chloride for an effectively noncoordinating anion, such as hexafluorophosphate. The facile loss of phosphine from tris(phosphine) complexes **16** is most likely a result of steric congestion due to the phenyl group on the carbon adjacent to the metal.

On similar treatment with a third equivalent of trimethylphosphine, the 2,3-diphenyl complex **11a** behaves differently. Instead of reversibly losing chloride to form an η^3-allyl tris(phosphine) complex, a mixture of two isomeric metallacyclohexadienes, **17** and **18**, is formed in a 2:1 ratio. Although the orientation of the ligands in the two isomers was not pursued, the observation of a $P_{eq}-H(4)$ NMR coupling in only the minor isomer ($J_{HP} = 14.0$ Hz) suggests that the equatorial phosphine lies trans to the sp^3 carbon in the minor isomer; no $P_{eq}-H(4)$ coupling is observed in the major compound. The same mixture of isomers could be obtained in a one-pot reaction from **9a** and "$Rh(PMe_3)_2Cl$" by adding an extra equivalent of PMe_3 per Rh after the ring-opening process.

On dissolution in chloroform, the **17**:**18** mixture produced a third compound. The regeneration of the original NMR spectrum, on evaporation of the chloroform sample and redissolution in benzene, suggested that the third compound, **19a**, was in equilibrium with **17** and **18** and was not the result of their decomposition in the chlorinated solvent. In nonpolar solvents such as benzene, ether, and dimethoxyethane, **17**:**18**:**19a** ratios of roughly 2.3:1:0 were observed by ^{31}P NMR. In deuteriochloroform, the ratio changed to 2.6:1:0.7, and in deuterioacetonitrile, it was 2.2:1:8.9. The maintenance of the 2:1 **17**:**18** ratio regardless of the fraction of **19a** present demonstrates that **17** and **18** are indeed in equilibrium. Both the strong dependence of the concentration of **19a** on the solvent polarity and the correspondence of the facial compound's ^{31}P NMR spectrum in acetonitrile with that of the cation **16b** obtained from **17**/**18** by chloride abstraction lead to the conclusion that the facial compound is actually a dissociation isomer of **17** and **18**. As such, **19a** may provide an interconversion path between **17** and **18**. Similarly to 1,2-diphenyl compound **16a**, **19a** may be trapped by anion exchange and isolated as its PF_6^- salt **19b**.



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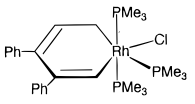

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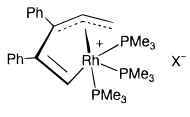
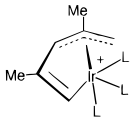
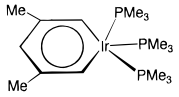


19a. X = Cl
19b. X = PF_6



20. L = PEt_3
22. L = PMe_3



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The resemblance between cation **19** and the precursor **20** to Bleeke's iridabenzene **21**[24−33] suggested that the mixture of **17**:**18**:**19a** might deprotonate to give an analogous rhodabenzene. On treatment with several strong bases (lithium diisopropylamide, lithium tetramethylpiperidide, potassium hydride) in various solvents, **17**:**18**:**19a** either decomposed or failed to react, reminiscent of Bleeke's observation that triethylphosphine complex **20** deprotonates readily, yet its trimethylphosphine analogue **22** is inert.[25]

Conclusion

To summarize, diphenylvinylcyclopropene **9** undergoes ring opening with the $[Rh(Cl)(PMe_3)_2]$ fragment to give 2,3- and 1,2-diphenyl isomers **10** and **11**, presumably by ring expansion via two different metallacyclobutenes. On treatment with silver ion, **10** and **11** both undergo ring closure to give cyclopentadienyl compound **15a**. In contrast, on treatment with a third equivalent of phosphine, **10** reversibly exchanges phosphine for chloride, to form a tris(phosphine) cation **16a**, whereas chloride dissociation from the tris(phosphine) complex **17**:**18** obtained from **11** is solvent dependent.

(23) Bleeke, J. R.; Peng, W. J.; Xie, Y. F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113−9.

(24) Bleeke, J. R.; Rohde, A. M.; Boorsma, D. W. *Organometallics* **1993**, *12*, 970−4.

(25) Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271−7.

(26) Bleeke, J. R.; Xie, Y. F.; Peng, W. J.; Chiang, M. *J. Am. Chem. Soc.* **1989**, *111*, 4118−20.

(27) Bleeke, J. R.; Behm, R.; Xie, Y.-F.; Clayton, T. W., Jr.; Robinson, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 4093−4.

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Experimental Section

General Procedures. All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried over Aquasorb. Petroleum ether (35−65 °C), other hydrocarbon solvents, and ethers were distilled under nitrogen from benzophenone ketyl; chlorinated solvents, acetonitrile, and methanol, from CaH_2. ^1H (300 MHz), $^2H\{^1H\}$ (46.1 MHz), $^{13}C\{^1H\}$ (75 MHz) and $^{31}P\{^1H\}$ (121 MHz) NMR spectra were recorded at 25 °C, unless otherwise noted. Chemical shifts are reported as parts per million downfield of either TMS (^1H, ^2H, and ^{13}C NMR, referenced to the solvent) or external 85% H_3PO_4 (^{31}P NMR). Coupling constants are reported in Hertz with estimated errors of ±0.2 Hz. Resonances are assigned using the numbering scheme of Figure 1. IR spectra were recorded on a Bio-Rad Digilab FTS-40 Fourier transform infrared spectrophotometer. Melting points of samples in capillaries sealed under vacuum were obtained using an Electrothermal device and are uncorrected. Elemental analyses were performed by Spang (Eagle Harbor, MI).

Ammonium hexafluorophosphate, diisopropylamine, lithium diisopropylamide, and potassium hydride were obtained from Aldrich; silver hexafluorophosphate from Pennwalt; and sodium hydride from Alfa. 1,2-Diphenyl-3-vinylcyclopropene (**9a**),[34] 3-deuterio-1,2-diphenyl-3-vinylcyclopropene (**9b**),[19] trimethylphosphine,[35] and $[Rh(C_8H_{14})_2Cl]_2$ (C_8H_{14} = *cis*-cyclooctene)[36] were prepared by literature routes.

Preparation of 10a and 11a and Their Deuterated Isotopomers 10b and 11b. A benzene (250 mL) solution of $[Rh(C_8H_{14})_2Cl]_2$ (1.73 g, 4.83 mmol of Rh) was treated with trimethylphosphine (0.98 mL, 9.6 mmol, 2.0 equiv) dissolved in benzene (25 mL). After the orange solution had been stirred for 5 min, a solution of **9a** (1.10 g, 5.03 mmol, 1.02 equiv) in benzene (25 mL) was added over 10 min, and the deep red solution was stirred overnight. After concentration almost to dryness and precipitation with petroleum ether (50 mL), **11a** was collected as an orange powder (2.20 g) containing traces of **10a** which could be removed by recrystallization from 1:1 CH_2Cl_2/petroleum ether. **11a** mp: 135−136 °C dec. Calcd for $C_{23}H_{32}P_2ClRh$: 54.28, C; 6.35, H. Found: 54.18, C; 6.50, H. ^1H NMR (−20 °C, $CDCl_3$): δ 6.80* (exchange d(dd), 1H, J_{HP} = 17.6, J_{RhH} = 1.3, H_1) 6.96−7.60 (m, 10H, Ph), 6.03 (ddd, 1H, J_{HH} = 9.9, 7.6, J_{HP} = 1.5, $H_{central}$), 3.18 (ddd, 1H, J_{HH} = 7.6, 0.8, J_{HP} = 4.1, H_{syn}), 2.28 (dddd, 1H, J_{HH} = 10.1, 1.0, J_{HP} = 9.9, J_{RhH} = 0.4, H_{anti}), 1.58 (d, 9H, J_{HP} = 10.0, PMe_3), 0.97 (d, 9H, J_{HP} = 8.8, PMe_3). The peak marked with an asterisk decoalesced to a dd on further cooling to −40 °C. $^{13}C\{^1H\}$ NMR ($CDCl_3$, selected CH coupling constants and multiplicities in square brackets): δ 139.56 (dd, J_{CP} = 24.3, J_{CRh} = 8.7, C_1 [d, J_{CH} = 161]), 137.98 (t, J_{CP} = 4.4, J_{CRh} = 4.4, C_2), 137.56, 132.85, 128.27, 127.74, 126.24, 125.07, 122.86 (Ph), 111.5 (d, J_{CP} = 3.2, C_4 [d, J_{CH} = 158]), 98.41 (d, J_{CP} = 28.6, C_3), 45.90 (dd, J_{CP} = 48.7, J_{CRh} = 8.5, C_5 [t, J_{CH} = 156]), 17.54 (d, J_{CP} = 29.4, PMe_3 [q, J_{CH} = 128]), 13.64 (d, J_{CP} = 24.4, PMe_3 [q, J_{CH} = 131 Hz]). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.4 (dd, 1P, J_{PP} = 12.2, J_{RhP} = 169, PMe_3), −14.4 (dd, 1P, J_{PP} = 14.4, J_{RhP} = 136, PMe_3). IR (KBr, cm^{-1}): 1150 m, 1097 m, 1019 m, 963 s, 948 vs.

On cooling to −20 °C, the benzene/petroleum ether filtrate precipitated **10a** as a yellow powder, which was recrystallized from ether for analysis: mp 142−145 °C, dec. Calcd for $C_{23}H_{32}P_2ClRh$: 54.28, C; 6.35, H. Found: 54.29, C; 6.42, H. $^1H\{^{31}P\}$ NMR (−20 °C, $CDCl_3$): δ 6.76−7.77 (m, 10H, Ph), 5.27 (m, 2H, H_3, $H_{central}$), 3.24 (d, 1H, J_{HH} = 7.0, H_{syn}), 2.55 (dd, 1H, J_{HH} = 9.2, H_{anti}), 1.65, (s, 9H, PMe_3), 1.22 (s, 9H, PMe_3). ^1H NMR (−20 °C, toluene-d_8): δ 6.71−7.18 (m, 10H, Ph), 5.50 (dt, 1H, J_{HH} = 10.4, 7.6, 7.6, $H_{central}$), 5.10 (ddd, 1H, J_{HH} = 7.4, 0.5, J_{HP} = 4.2, H_3), 3.27 (ddd, 1H, J_{HH} = 7.4, J_{HP} = 2.5, 0.5, H_{syn}), 2.56 (ddt, 1H, J_{HH} = 10.3, 0.8, J_{HP} = 8.0, J_{RhH} = 0.8, H_{anti}), 1.34 (d, 9H, J_{HP} = 8.6, PMe_3), 0.95 (d, 9H, J_{HP} = 9.7, PMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −0.4 (d, 1P, J_{PP} = 12, J_{RhP} = 170, PMe_3), −11.2 (dd, 1P, J_{PP} = 12, J_{RhP} = 139, PMe_3). IR (KBr, cm^{-1}): 943 vs, 848 m, 621 m.

Deuterated compounds **10b** and **11b** were prepared in the same manner as their protic isotopomers, using ring-deuterated vinylcyclopropene **9b**. **11b** ^1H and $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) were identical to those of protic **11a**, except for the absence of the proton resonance at δ 6.80. $^2H\{^1H\}$ NMR ($CHCl_3$): δ 6.88 (br, D_1). **10b** ^1H NMR (C_6D_6): 6.80−7.83 (m, 10H, Ph), 5.59 (t, 1H, J_{HH} = 8.6, $H_{central}$), 3.21 (br, 1H, H_{syn}), 2.68 (br, 1H, H_{anti}), 1.80 (br, 9H, PMe_3), 1.51 (br, 9H, PMe_3). $^2H\{^1H\}$ NMR (C_6H_6): δ 5.12 (br, D_3). The $^{31}P\{^1H\}$ NMR spectrum (C_6D_6) was identical to that of protic **10a**.

Attempted conversion of 10a to 11a. A yellow solution of **10a** (6.8 mg, 11.9 μmol) in C_6D_6 (0.25 mL) was freeze−pump−thaw degassed and sealed under vacuum in an NMR tube. No changes were observed visually or by ^1H and ^{31}P NMR spectroscopy after 1 day at 45 °C. After 2 weeks at 45 °C, the sample had darkened to a clear orange. ^1H and ^{31}P HMR spectra showed no changes in the sample except the formation of traces of trimethylphosphine oxide (δ ^{31}P −33.3) and a possible cyclopentadienyl compound (δ ^{31}P −2.7, d, J_{RhP} = 213).

Ring Closure Reactions To Give Compounds 15. Protic Compounds. A suspension of $AgPF_6$ (0.06 g, 0.237 mmol, 1.0 equiv) and **11a** (0.120 g, 0.237 mmol) in THF (25 mL) was stirred overnight in the dark. Filtration of the yellow-brown mixture gave a yellow solution. The filtrate was concentrated in vacuo to approximately 1−2 mL, and 5 mL of ether was added. A yellow precipitate formed and was recrystallized from methanol/ether to give **15a** as a yellow solid (0.080 g): ^1H NMR (THF-d_8): δ −12.28 (td, J_{RhH} = 22.9, J_{HP} = 32.2, 1H, RhH), 7.2−7.5 (Ph), 5.86 (d, J_{HH} = 3, 2H, lateral H_{Cp}), 5.32 (t, J_{HH} = 3, 1H, central H_{Cp}), 1.65 (filled doublet, 18H, PMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 9.2 (d, J_{RhP} = 127.8, PMe_3), −143.8 (sept, J_{PF} = 712.7, PF_6).

Deuterated Compounds. A suspension of **10b** and **11b** (22 mg, 0.043 mmol, ∼1:2) and $AgPF_6$ (9 mg, 0.04 mmol, 1 equiv) in DME (5 mL) was stirred overnight in the dark. The resulting gray suspension was filtered through Celite and evaporated. The red residue was extracted with methanol, passed through Celite, concentrated, and precipitated with ether. Filtration and drying of the solid gave **15b** as a yellow-orange solid (12 mg, 56%). $^1H\{^{31}P\}$ NMR (CD_3CN): δ 6.90−7.70 (m, 10H, Ph), 6.01 (d, 1H, J_{HH} = 2.1, lateral H_{Cp}), 5.15 (d, 1H, J_{HH} = 2.3, central H_{Cp}), 1.63 (filled d, 18 H, J_{HP} = 11.9, PMe_3), −11.9 (m, 1H, RhH). $^2H\{^1H\}$ NMR (CH_3CN): δ 5.93 (br, lateral D_{Cp}). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 12.15 (d, 2P, J_{RhP} = 126, PMe_3), −143 (sept, 1P, J_{PF} = 707, PF_6).

Rhodacyclohexadiene Complexes 17 and 18. (a) From $[Rh(C_8H_{14})_2Cl]_2$. A solution of $[Rh(C_8H_{14})_2Cl]_2$ (499 mg, 1.39 mmol Rh) in toluene (75 mL) was treated with trimethylphosphine (288 μL, 2.82 mmol, 2.0 equiv) dissolved in toluene (5 mL). After the orange solution had been stirred for 5 min, a solution of **9a** (314 mg, 1.43 mmol, 1.1 equiv) in toluene (5 mL) was added. The resulting red solution was stirred for 12 h and then treated with trimethylphosphine (150 μL, 1.47 mmol, 1.1 equiv) dissolved in toluene (5 mL). After being stirred for 20 min, the solution was evaporated nearly to dryness and precipitated with petroleum ether (50 mL) to give a yellow powder, which was washed with petroleum ether (2 × 5 mL). Recrystallization from ether gave isomers **17** and **18** as orange crystals (427 mg, 71%). Mp: 148−160 °C dec. Calcd for $C_{26}H_{41}P_3ClRh$: 53.35, C; 7.06, H. Found: 53.45, C; 7.00, H. IR (KBr, cm^{-1}): 1383 m, 1282 m, 1020 s, 947 s. **17**: ^1H NMR (C_6D_6) δ 8.31 (tdd, 1H, $J_{HP(cis)}$ = 6.4, $J_{HP(trans)}$ = 7.9, J_{RhH}

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= 3.3, H_1), 6.8−7.7 (m, 10H, Ph), 5.63 (td, J_{HH} = 5.1, J_{RhH} = 2.3, H_4), 2.26 (dddt, 2H, J_{HH} = 5.2, $J_{HP(eq)}$ = 10.1, $J_{HP(ax)}$ = 8.0, J_{RhH} = 3.6, H_5), 1.16 (virtual t, 18H, J_{HP} = 3.1, axial PMe_3), 0.92 (d, 9H, J_{HP} = 6.2, equatorial PMe_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −7.0 (dd, 2P, J_{RhP} = 109, J_{PP} = 30, axial PMe_3), −24.0 (dt, 1P, J_{RhP} = 81, J_{PP} = 30, equatorial PMe_3). **18**: ^1H NMR (C_6D_6) δ 6.83 (m, 1H, H_1), 6.8−7.7 (m, 10H, Ph), 6.52 (dtd, 1H, J_{HH} = 5.8, J_{HP} = 14.0, J_{RhH} = 1.2, H_4), 2.90 (tddd, 2H, J_{HH} = 5.7, J_{HP} = 10.1, 8.4, J_{RhH} = 3.7, H_5), 1.14 (virtual t, 18H, J_{HP} = 3.2, axial PMe_3), 1.04 (d, 9H, J_{HP} = 6.3, equatorial PMe_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −5.32 (dd, 2P, J_{RhP} = 100, J_{PP} = 31, axial PMe_3), −25.18 (dt, 1P, J_{RhP} = 79, J_{PP} = 31, equatorial PMe_3).

On slow cooling to −78 °C, the toluene/petroleum ether filtrate and washings precipitated **10a** (93 mg, 18%). Similar results were obtained when this preparation was performed in benzene.

The deuterated isomers, **17**-*d* and **18**-*d*, were prepared in the same manner, using ring-deuterated vinylcyclopropene **9b**. The ^1H and $^{31}P\{^1H\}$ NMR spectra (C_6D_6) of both isomers were identical to those of their protic isotopomers, with the exception of the missing resonances for H_1 at δ 8.31 (**17**) and 6.83 (**18**). **17**-*d*: $^2H\{^1H\}$ NMR (C_6H_6) δ 8.34 (br, D_1). **18**-*d*: $^2H\{^1H\}$ NMR (C_6H_6) δ 6.81 (br, D_1).

(b) From Bis(phosphine) Compound 11a. Trimethylphosphine (100 μL, 0.98 mmol, 1.1 equiv) dissolved in benzene (5 mL) was added to an orange solution of **11a** (450 mg, 0.885 mmol) in benzene (50 mL). The resulting yellow solution was stirred for 15 min and then evaporated. Recrystallization of the resulting yellow residue from ether gave a yellow-orange powder (674 mg, 79%) whose NMR spectra (C_6D_6) showed a 2:1 ratio of **17** to **18**. ^1H and ^{31}P NMR: identical to the spectra from the one-pot preparation above.

Complexes 16. (a) Chloride Salt. Trimethylphosphine (4.5 μL, 34 mmol, 2 equiv) was added to a yellow solution of **10a** (8.8 mg, 17 μmol) in C_6D_6 (0.5 mL). No change was observed initially either visually or by ^{31}P NMR. After overnight standing, the sample showed a 1:5 mixture of **10a** and **16a** by ^{31}P NMR. On evaporation and redissolution in C_6D_6, all of **16a** reverted to **10a**. **16a**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −7.95 (ddd, J_{PP} = 29.2, 4.4, J_{RhP} = 146.5, PMe_3), −13.90 (ddd, J_{PP} = 38.0, 4.5, J_{RhP} = 133.6, PMe_3), −21.50 (ddd, J_{PP} = 37.9, 29.2, J_{RhP} = 75.1, PMe_3).

(b) PF_6^- Salt. A solution of **10a** (25 mg, 48 μmol) in acetonitrile (4 mL) was treated with trimethylphosphine (25 μL, 0.24 mmol, 5 equiv), causing the yellow solution to pale slightly. A solution of NH_4PF_6 (49 mg, 0.30 mmol, 6 equiv) in acetonitrile (4 mL) was added and the resulting suspension purged of NH_4Cl by filtration through Celite. The filtrate was evaporated, and the yellow residue was extracted with methylene chloride. The extracts were passed through Celite, concentrated, precipitated with ether, and evaporated to give **16b** as a yellow solid (34 mg, 100%). An analytical sample was recrystallized from methanol. Mp: 115−120 °C, dec. Calcd for $C_{26}H_{41}P_4F_6Rh$: 44.97, C; 5.95, H. Found: 44.81, C; 5.96, H. ^1H NMR (CD_3CN): δ 6.8−7.3 (m, 10 H, Ph), 5.08 (dddd, 1H, J_{HH} = 6.9, J_{HP} = 3.0, 0.9, 0.6, H_3), 4.96 (dtdtd, 1H, J_{HH} = 10.8, 6.9, 6.9, J_{HP} = 3.9, 1.4, 1.4, J_{RhH} = 1.1, H_{cent}), 3.21 (ddddd, 1H, J_{HH} = 6.8, 1.5, J_{HP} = 4.5, 1.8, 0.8, H_{syn}), 2.83 (ddddd, 1H, J_{HH} = 10.7, 1.3, J_{HP} = 5.7, 5.3, 2.5, H_{anti}), 1.23 (dd, 9H, J_{HP} = 9.6, J_{RhH} = 0.9, PMe_3), 1.66 (dd, 9H, J_{HP} = 8.6, J_{RhH} = 0.6, PMe_3), 1.30 (d, 9H, J_{HP} = 7.6, PMe_3). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −6.73 (ddd, 1P, J_{PP} = 29, 4, J_{RhP} = 150, PMe_3), −12.80 (ddd, 1 P, J_{PP} = 38, 4, J_{RhP} = 134, PMe_3), −20.72, (ddd, 1P, J_{PP} = 38, 29, J_{RhP} = 75, PMe_3), −142.9 (sept, 1P, J_{PF} = 707, PF_6). IR (KBr, cm^{-1}): 1437 s, 1428 s, 794 m, 774 m, 731 s.

Complex 19b. (a) By Chloride Abstraction from 17/18. $AgPF_6$ (25 mg, 98 μmol, 1.5 equiv) and **17**/**18** (38 mg, 64 μmol) were suspended in methylene chloride (10 mL) containing trimethylphosphine (20 μL, 0.20 mmol, 3 equiv). The orange suspension was stirred overnight in the dark, then filtered through Celite, and evaporated. The residue was dissolved in acetonitrile (1 mL), allowed to stand overnight, and passed through Celite to remove residual AgCl. Evaporation left an oil, which solidified on the addition of methanol or petroleum ether, to give **19b** as a yellow-orange powder (43 mg, 95%). Mp: 168−170 °C. ^1H NMR (CD_3CN): δ 7.50 (dddd, 1H, J_{HP} = 18.2, 13.1, 1.7, J_{RhH} = 1.1, H_1), 6.94−7.66 (m, 10H, Ph), 5.88 (ddddt, 1H, J_{HH} = 10.3, 7.0, J_{HP} = 2.6, 1.1, 0.7, J_{RhH} = 0.7, $H_{central}$), 2.97 (dddddd, 1H, J_{HH} = 7.4, 1.6, J_{HP} = 5.6, 3.9, 1.0, J_{RhH} = 0.7, H_{syn}), 2.45 (ddddd, 1H, J_{HH} = 10.7, 1.3, J_{HP} = 8.5, 6.6, 3.6, J_{RhH} = 1.8, H_{anti}), 1.63 (dd, 9H, J_{HP} = 10.0, J_{RhH} = 1.3, PMe_3), 1.23 (d, J_{HP} = 7.3, 9H, PMe_3), 1.17 (d, 9H, J_{HP} = 8.3, PMe_3). ^{31}P $\{^1H\}$ NMR (CD_3CN): δ 4.82, (ddd, 1P, J_{PP} = 23, 9, J_{RhP} = 155, PMe_3), −17.73 (ddd, 1P, J_{PP} = 34, 9, J_{RhP} = 127, PMe_3), −21.72 (ddd, 1P, J_{PP} = 34, 23, J_{RhP} = 79, PMe_3), −142.93 (sept, 1P, J_{PF} = 709, PF_6). IR (KBr, cm^{-1}): 1308 m, 964 s, 948 s, 870 s, 841 vs, 557 s. This abstraction may also be performed in benzene or dimethoxyethane with similar results.

The deuterated isotopomer, **19b**-*d* was prepared similarly. ^1H and ^{31}P NMR spectra: identical to those of the protic material except for the absence of the H_1 signal at δ ^1H 7.50. $^2H\{^1H\}$ NMR (MeCN): δ 7.55 (br s, D_1).

(b) By Metathesis of 17/18. A suspension of NH_4PF_6 (73 mg, 0.44 mmol, 5 equiv) in acetonitrile (3 mL) was added to a solution of **17**/**18** (47 mg, 0.080 mmol) in acetonitrile (3 mL). The resulting opaque orange suspension was passed through Celite and evaporated to dryness. Extraction of the residue with methylene chloride (5 × 1 mL), filtration through Celite, concentration to near dryness, and precipitation with petroleum ether gave an orange powder (50.4 mg, 90%) identical to that from the abstraction procedure above.

Attempted deprotonation of 19b. With LDA in THF. Diisopropylamine (0.3 mL, 2 mmol) was treated with *n*-BuLi (0.56 mL, 2.4 M in hexanes, 1.3 mmol) at −78 °C, warmed to room temperature, and diluted to 10 mL. A portion of the resulting LDA solution (1 mL, 0.13 mmol, 1.0 equiv) was added to a solution of **19b** (80 mg, 1.4 mmol) in THF (10 mL) at −78 °C. The mixture was stirred for 1 h at room temperature and then evaporated to an oil, whose proton and phosphorus NMR spectra showed only starting material.

With LDA in Acetonitrile. 19b (241 mg, 0.412 mmol) and LDA (42 mg, 0.39 mmol. 0.965 equiv) were dissolved in acetonitrile (10 1L) at −45 °C. The orange suspension darkened slowly as it warmed to room temperature, although periodic phosphorus NMR spectra showed no change over 3 h. Three additional equivalents of LDA was added over 48 h without significant diminution of the starting material peaks, after which time the mixture smelled strongly of acetamidine.

With KH in Ether. Three doses of potassium hydride (each roughly 22 mg, 0.54 mmol, 6.4 equiv) were added to a suspension of **19b** (50 mg, 0.086 mmol) in ether (10 mL) over 4 h, followed by overnight stirring, without visible changes. Sodium hydride (55 mg, 50% oil dispersion, 1.1 mmol, 13 equiv) was washed with petroleum ether (2 × 1 mL), pumped dry, and added to the reaction mixture. After being stirred for 4.5 h, the mixture was filtered and concentrated to 2 mL. The $^{31}P\{^1H\}$ NMR spectrum of the resulting yellow solution showed primarily starting material and trimethylphosphine oxide.

Crystal Structure Determination of 11a. The parameters used during the collection of diffraction data for **11a** are contained in Table 1. Orange crystals of **11a** were attached to a fine glass fiber using epoxy cement. On the basis of systematic absences in the intensity data, it was determined that **11a** crystallized in one of the rhombohedral space groups $R3$, $R\bar{3}$, $R32$, $R3m$, or $R\bar{3}m$. $R\bar{3}$ was initially chosen on the basis of *E*-statistics and the supposed molecular structure and was subsequently confirmed by the successful solution and well-behaved refinement of the structure. Unit-cell parameters were derived from the least-squares fit of the angular settings of 25 reflections with $20° \le 2\theta \le 26°$. All intensity data were corrected for absorption using an empirical procedure which

uses six parameters to define a pseudoellipsoid. No significant decay occurred in three standard reflections.

The structure was solved using the direct methods program SOLV, which located the Rh atom. Remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and refined anisotropically. Idealized hydrogen atom positions were calculated ($d_{CH} = 0.96$ Å, thermal parameters equal to 1.2 times the isotropic equivalent for the attached carbon). The phenyl rings were fixed to fit rigid hexagons. Final difference Fourier syntheses showed only diffuse backgrounds (maximum 0.57 e/Å^3). All computer programs used in the data collections and refinements are contained in the Nicolet program packages *p*3 and SHELXTL (5.1), Nicolet XRD, Madison, WI. Atomic coordinates for **11a** are contained in the Supporting Information, and bond lengths and angles are in Tables 2 and 3. Additional crystallographic data is available as Supporting Information.

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Supporting Information Available: Atomic coordinates and isotropic thermal parameters, bond distances, bond angles, anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters for **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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