Preparation of Novel Rhodonocenium Complexes via [2 + 2 + 1] Cyclotrimerization of Terminal Aryl Alkynes

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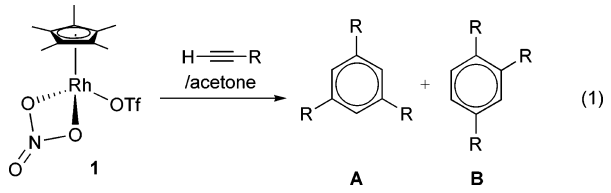
Reactions of [Cp*Rh(η^2-NO_3)(OTf)] (**1**), which bears two labile ligands (NO_3^- and OTf^-), with a terminal aryl alkyne (phenylacetylene (HC≡CPh) or 4-ethynyltoluene (HC≡CC_6H_4-CH_3)) in alcohol (EtOH or *n*-BuOH) gave the substituted-rhodocenium cation [Cp*Rh(η^5-$C_5H_2Ar_2$−CH(Ar)OR)]$^+$($OTf)^-$ (**2a**−**d**: Ar = Ph, *p*-tolyl; R = Et, *n*-Bu). Treatment of **1** with 4-ethynyltoluene in ethanol followed by the addition of a pseudo-halide (HSPh, Me_3SiN_3, or Me_3SiNCS) in dichloromethane also produced the substituted-rhodocenium cation [Cp*Rh-(η^5-C_5H_2(*p*-tolyl)$_2$−CH(*p*-tolyl)Nu)]$^+$($OTf)^-$ (Nu^- = SPh (**3a**), N_3 (**3b**), NCS (**3c**)). All products appeared to have been formed by the formal [2 + 2 + 1] cyclotrimerization of the terminal aryl alkynes and the subsequent nucleophilic addition of the alcohol or pseudo-halide at the exocyclic double bond of a fulvene intermediate. Molecular structures of **2b**,**c** and **3a**,**c** were determined by X-ray diffraction. All complexes are isostructural and show sandwich-type structures composed of one Cp* ligand and one substituted-Cp ligand.

Introduction

The common [2 + 2 + 2] cyclotrimerization of substituted alkynes by transition-metal complexes gives 1,3,5- (**A**) or 1,2,4-trisubstituted (**B**) benzene derivatives.



Various transition-metal complexes have been employed for this reaction, and selectivity control to **A** or **B** is possible to some extent.[1−10] In sharp contrast, there have been only a few reports on the formal [2 + 2 + 1] cyclotrimerization of alkynes to give five-membered rings.[11−20] In addition, although a number of metallocenes and bent metallocenes of rhodium have been known, these do not show reactivity in the [2 + 2 + 1] cyclotrimerization of alkynes.[21−28]

Very recently, we reported on the reactions of [Cp*Rh-(η^2-NO_3)(OTf)] (**1**), which contains two labile ligands (NO_3^- and OTf^-), with terminal alkynyl esters (HC≡CCO_2Me and HC≡CCO_2Et) in acetone. These reactions produced benzene derivatives (1,3,5- and 1,2,4-$C_6H_3R_3$ (R = CO_2Me, CO_2Et)) by the [2 + 2 + 2] cyclotrimer-

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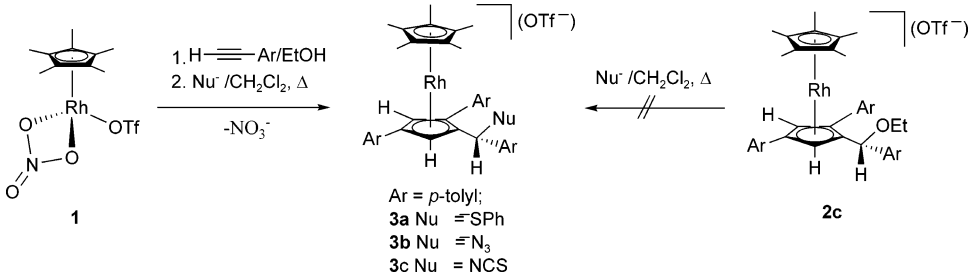
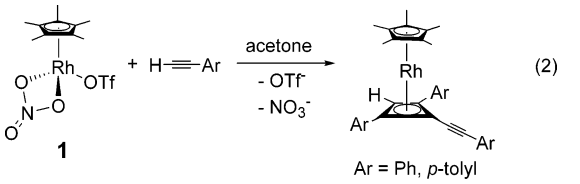
Scheme 1



ization of those esters (eq 1).[29] As a continuation of our work, we examined the reactivity of **1** toward terminal aryl alkynes (HC≡CPh and HC≡$CC_6H_4CH_3$) in alcohol (EtOH or *n*-BuOH). In these reactions, complex **1** unexpectedly mediated the [2 + 2 + 1] cyclotrimerization of those alkynes to give rhodonocene-like complexes containing one Cp* and one substituted Cp, [Cp*Rh(η^5-$C_5H_2Ar_2$−CH(Ar)OR)]$^+$(OTf)$^-$ (Ar = Ph, *p*-tolyl; R = Et, *n*-Bu) (**2a**−**d**). The solvent alcohol turned out to act as both a proton donor and a nucleophile. We also examined the corresponding reactions between **1** and 4-ethynyltoluene (HC≡$CC_6H_4CH_3$) in either dichloromethane or alcohol in the presence of a pseudo-halide (HSPh, Me_3SiN_3, or Me_3SiNCS), a potential nucleophile. Herein, we report the synthesis and structures of cationic rhodium complexes of the type [Cp*Rh(η^5-$C_5H_2Ar_2$−CH(Ar)Nu)]$^+$(OTf)$^-$ (Ar = Ph, *p*-tolyl; Nu = OEt, O-*n*-Bu, SPh, N_3, NCS).

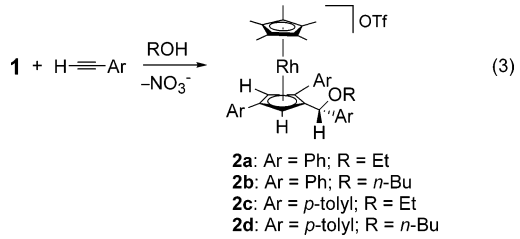
Results and Discussion

We recently observed that [Cp*Rh(η^2-NO_3)(OTf)] (**1**) mediated the [2 + 2] cyclodimerization of some terminal aryl alkynes (HC≡CPh and HC≡$CC_6H_4CH_3$) in acetone to give (η^4-cyclobutadiene)rhodium complexes, [Cp*Rh(η^4-C_4HAr_2−C≡CAr)] (Ar = Ph, *p*-tolyl) (eq 2).[29] In this



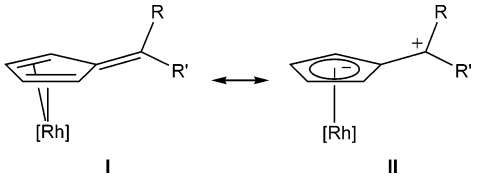
reaction, the terminal alkyne hydrogen serves as a proton donor to the labile ligands (NO_3^- and OTf^-). It should be mentioned that Carmona's group was the first to report this type of cyclotrimerization of aryl alkynes with [Cp*Rh(l-alaninate)Cl].[30]

Considering the higher acidity of an alcohol compared to that of a terminal alkyne, we decided to change the solvent from acetone to alcohol with an attempt to bring about different reactions, in which the alcohol may act as a proton donor to the labile ligands. Consistent with our expectation, the alkyne-cycloaddition reactivity of complex **1** changed from a [2 + 2 + 2] manner in acetone to a [2 + 2 + 1] manner in alcohol. Reactions of complex **1** with aryl alkynes in alcohol (EtOH or *n*-BuOH) in place of acetone produced cationic rhodonocene-like complexes, [Cp*Rh(η^5-$C_5H_2Ar_2$−CH(Ar)OR)]$^+$(OTf)$^-$ (**2a**−**d**: Ar = Ph, *p*-tolyl; R = Et, *n*-Bu) (eq 3). The product



formula tells us that the solvent alcohol acts as a nucleophile as well as a proton donor to the nitrato ligand. We previously observed this type of alcohol acidity in the Pd-mediated cyclotrimerization of phenylacetylene (PhC≡CH) to fulvene[14] and also in the Rh-mediated cyclodimerization of diphenylacetylene (PhC≡CPh) to cyclobutadiene.[29]

In general, structures of fulvene complexes can be described on the basis of two resonance forms (**I** and **II**). Because of the resonance form **II**, in which the exo



carbon has a partial positive character and the Cp fragment has an aromatic character, the exocyclic double bond is susceptible to nucleophilic addition.[31−37] In our reactions, the solvent alcohol (probably in the form of an alkoxide) appears to have undergone nucleophilic attack at the exo carbon of a fulvene intermediate (the resonance form **II**) to give a substituted Cp ring.

We carried out the reactions of **1** with 4-ethynyltoluene in dichloromethane in the presence of a pseudo-halide (HSPh, Me_3SiN_3, or Me_3SiNCS), which is likely to act as a nucleophile, to get more information about the formation of **2a**−**d**. Unexpectedly, these reactions

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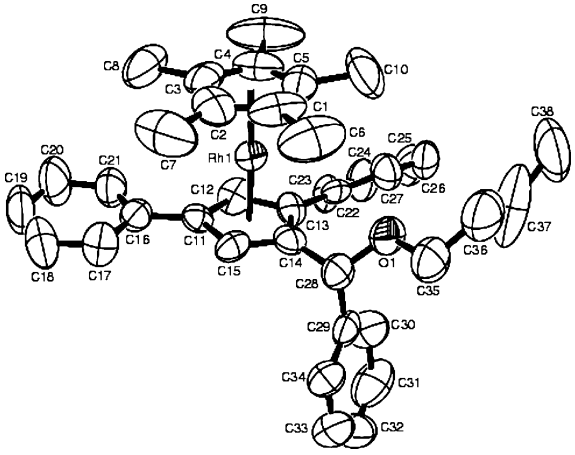

Figure 1. ORTEP drawing of **2b**, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

gave totally different products, the dinuclear rhodium(III) complexes [Cp*Rh(μ-SPh)$_3$RhCp*](OTf),[38] [Cp*Rh(μ-N$_3$)$_2$(H$_2$O)]$_2$,[39] and [Cp*Rh(η^1-SCN)$_2$(HSCN)]$_2$,[39] depending on the added pseudo-halide. These observations indicate that the solvent alcohol plays a fundamental role in this reaction system. Therefore, we tried the corresponding reactions in ethanol in place of dichloromethane. Unfortunately, those reactions give a mixture of **2c** (major) and a dinuclear rhodium(III) complex in a trace amount. These results prompted us to find out more relevant reaction conditions, and we came to the following set.

The novel ionic substituted-Cp rhodium complexes [Cp*Rh(η^5-C$_5$H$_2$(*p*-tolyl)$_2$−CH(*p*-tolyl)Nu)]$^+$(OTf)$^-$ (Nu = SPh (**3a**), N$_3$ (**3b**), NCS (**3c**)) could be prepared by the stepwise additions of two ligands. In the first step, complex **1** was treated with 4-ethynyltoluene in ethanol for 2 h, and then the solvent was removed. In the second step, excess (3 equiv) pseudo-halide in dichloromethane was added, and the resultant solution was refluxed further for 18 h to give **3a**−**c** (Scheme 1). Interestingly, we did not observe any reactivity of **2c** toward these pseudo-halides.

All products are air- and moisture-stable both in solution and in the solid state and were characterized by ^{1}H and ^{13}C{^{1}H} NMR, IR, and elemental analysis. The ^{1}H NMR spectra of **2c** display characteristic resonances at 6.08 (d, $^4J_{H-H}$ = 1.0 Hz, Cp proton), 6.04 (d, $^4J_{H-H}$ = 1.0 Hz, Cp proton), and 5.37 ppm (s, the exocyclic sp^3 carbon proton). In ^{13}C{^{1}H} NMR spectra of **2c**, the *C*H carbons on the Cp ring exhibit doublets at 84.22 ($^1J_{Rh-C}$ = 7.3 Hz) and 84.04 ppm ($^1J_{Rh-C}$ = 6.7 Hz), whereas the *C*C carbons exhibit doublets at 106.09 ($^1J_{Rh-C}$ = 6.2 Hz), 103.45 ($^1J_{Rh-C}$ = 6.7 Hz), and 101.22 ppm ($^1J_{Rh-C}$ = 7.8 Hz). Practically the same NMR spectral patterns are observed for the remaining complexes. In the IR spectra of **3b**,**c**, the strong bands at 2097 and 2102 cm^{-1}, respectively, can be assigned to the N$_3$ and NCS stretching.

The molecular structures of complexes **2b**,**c** and **3a**,**c** are shown in Figures 1−4, respectively. All complexes are isostructural, and therefore we will discuss only complex **2c** in detail. There are two stereoisomers in an asymmetric unit, which are chemically equal on the basis of ^{1}H NMR. The molecular structure of the cationic part of complex **2c** demonstrates a sandwich-type structure based on one Cp* and one substituted Cp (Cp′). The Rh−C$_{Cp*}$ (C$_{Cp*}$ is the centroid of C1−C5; 1.800 Å) and Rh−C$_{Cp'}$ (C$_{Cp'}$ is the a centroid of C11−C15; 1.823 Å) distances and the C$_{Cp*}$−Rh−C$_{Cp'}$ angle (176.87°) are

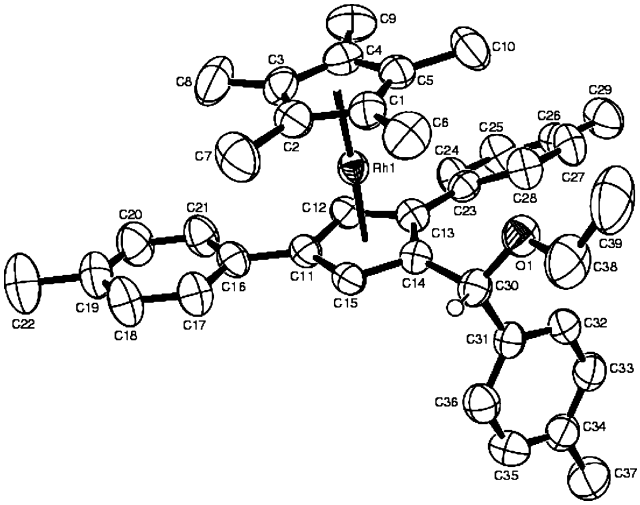

Figure 2. ORTEP drawing of **2c**.

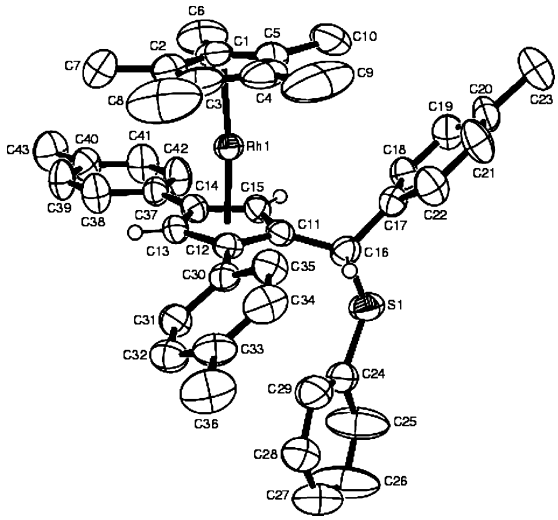

Figure 3. ORTEP drawing of **3a**.

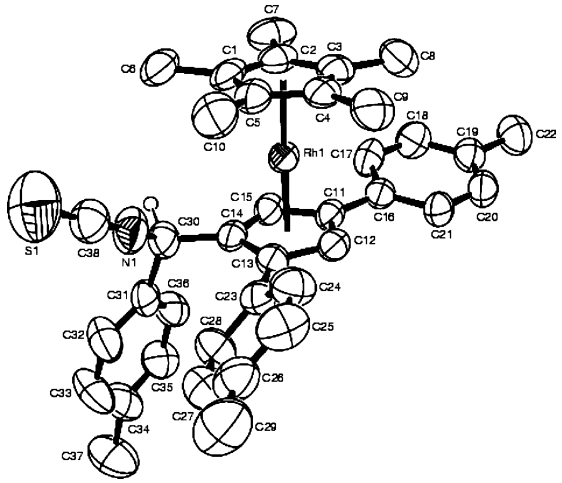

Figure 4. ORTEP drawing of **3c**.

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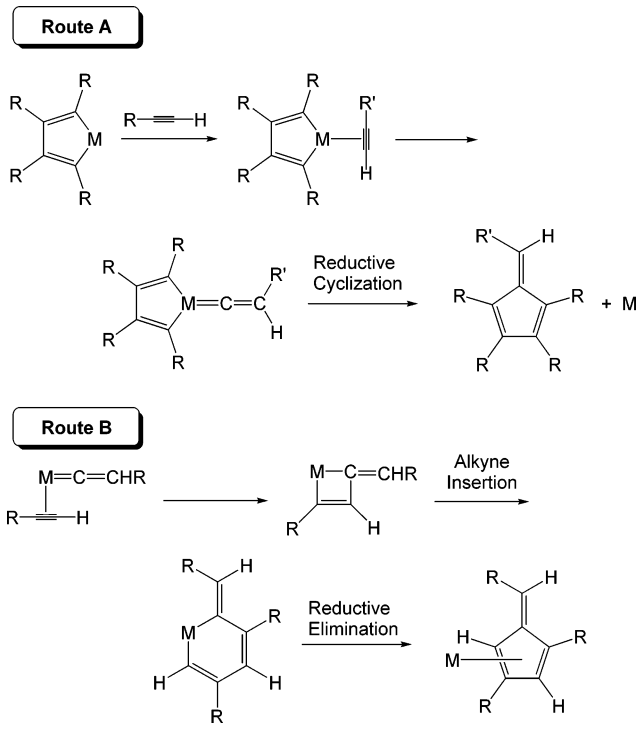
Scheme 2



very close to those of the decamethylrhodocenium cation $[Cp^*_2Rh]^+(PF_6)^-$ [21] and the monophospholyl rhodocenium cation $[Cp^*Rh(\eta^5\text{-}PC_4H_2\text{-}t\text{-}Bu_2)]^+(BPh_4)^-$.[40]

The two parallel five-membered rings in all complexes are twisted away from each other with a dihedral angle of 2.7(13)° (**2b**), 3.9(4)° (**2c**), 7.0(4)° (**3a**), or 4.2(4)° (**3c**). The alkoxy or pseudo-halide substituent at the exocyclic sp^3 carbon of **2b**,**c** and **3c** is endo to the rhodium metal. On the other hand, the SPh substituent of **3a** is exo-oriented, perhaps due to its steric bulk. The isothiocyanato ligand of **3c** is essentially linear with a N−C−S bond angle of 176.5(6)°.

For the [2 + 2 + 1] cyclotrimerization of alkynes, two mechanisms have been proposed so far: a metallacyclopentadiene route (**A**) and a metallacyclohexadiene route (**B**) (Scheme 2).[11−20] O'Conner and co-workers reported the [2 + 2 + 1] alkyne cyclotrimerization to give fulvenes via a metallacyclopentadiene intermediate, using the chloro bis(phosphine) iridacyclopentadiene complex. Their proposed mechanism involves an initial coordination of an alkyne to the Ir metal, rearrangement of the alkynyl ligand to a vinylidene ligand, and reductive cyclization to give the fulvene products by the coupling of the vinylidene ligand and the metallacyclopentadiene ring (**A**).[17] On the other hand, Moran and co-workers reported the trimerization of 3,3-dimethylbut-1-yne, proposing that the reaction proceeds via a metallacyclobutene intermediate that reacts with the alkyne by insertion, followed by reductive elimination from the metallacyclohexadiene to give the final product (**B**).[19] The known mechanism involving a metallacyclohexadiene intermediate seems to be appropriate to our case.

Although the present results do not give any detailed information about how rhodocenium cations have been formed, one of the possible mechanisms is proposed in Scheme 3. The first step involves the formation of the rhodium−vinylidene species **A** by proton transfer of an aryl alkyne and the binding of an alkoxide with the liberation of HNO_3. The next step is the sequential insertions of two aryl alkynes to give the metallacyclohexadiene intermediate **C** via the metallacyclobutene intermediate **B**. The intermediate **C** undergoes reductive elimination to give the fulvene-type species **D**. Finally, the coordinated alkoxide or the external pseudo-halide attacks the exocyclic carbon of the intermediate **D** to give the ultimate product.

There are several observations that indirectly support the proposed mechanism. (1) The terminal alkyne hydrogen has been shown previously to serve as a proton donor to the labile ligands (NO_3^- and OTf^-) in complex **1**.[29] The acidity of the alcohol (EtOH or *n*-BuOH) employed in our system is higher than that of the terminal alkyne, and therefore the alcohol is believed to protonate NO_3^- to release HNO_3. However, the possibility that the alcohol has simply facilitated the dissociation of the anionic ligands cannot be ruled out. (2) From the reaction of complex **1**, 4-ethynyltoluene, and the pseudo-halide in CH_2Cl_2, a mixture of complex **2c** (major) and a dinuclear rhodium(III) complex (a trace amount) is obtained, indicating the solvent alcohol plays a critical role in our system. (3) As mentioned above, complex **2c** does not react with pseudo-halides in CH_2Cl_2 at all, which indicates that the alkoxy substituent at the exo carbon of the fulvene ring in complex **2c** cannot be replaced with the external nucleophile. (4) Finally, we performed NMR characterization of the crude mixture, which is generated in ethanol after 2 h and appears to be a mixture of green powder (major) and some crystalline material (minor), prior to addition of nucleophiles to give the products (**3a**−**c**). The ^1H NMR spectra of the mixture exhibited too many peaks, but we could see two distinct peaks of protons corresponding to the $-OCH_2CH_3$ groups: one set of a triplet (δ 1.09 ppm, OCH_2CH_3) and a quartet of doublets (δ 3.32 ppm, OCH_2CH_3) for **2c** and the other set at slightly higher positions (a triplet at δ 1.21 and a quartet at δ 3.45 ppm). In the $^{13}C\{^1H\}$ NMR spectra, we could also observe two kinds of carbons corresponding to the $-OCH_2CH_3$ groups: one set of two singlets (δ 15.23 and 64.92 ppm) for **2c** and another set of two singlets (δ 15.54 and 64.51 ppm). These NMR data indicate the existence of two distinct ethoxy groups in the crude reaction mixture, which consists of at least two species. In addition, recrystallization of the crude mixture from acetone−hexane for 2 days produced only the crystals of complex **2c**, whose identity was confirmed by NMR and X-ray diffraction. From these aforementioned facts, we believe that the alkoxide remains bound to the Rh metal center during the reaction and that it is weakly nucleophilic as well as labile enough to be replaced by the external nucleophile (the pseudo-halide).

In summary, we prepared several substituted-rhodonocene cations $[Cp^*Rh(\eta^5\text{-}C_5H_2Ar_2\text{−}CH(Ar)Nu)]^+(OTf)^-$ (Ar = Ph, *p*-tolyl; Nu^- = OEt, O-*n*-Bu, SPh, N_3, NCS) by the formal [2 + 2 + 1] cyclotrimerization of terminal aryl alkynes and the subsequent nucleophilic addition of the alcohol or pseudo-halide at the exocyclic double

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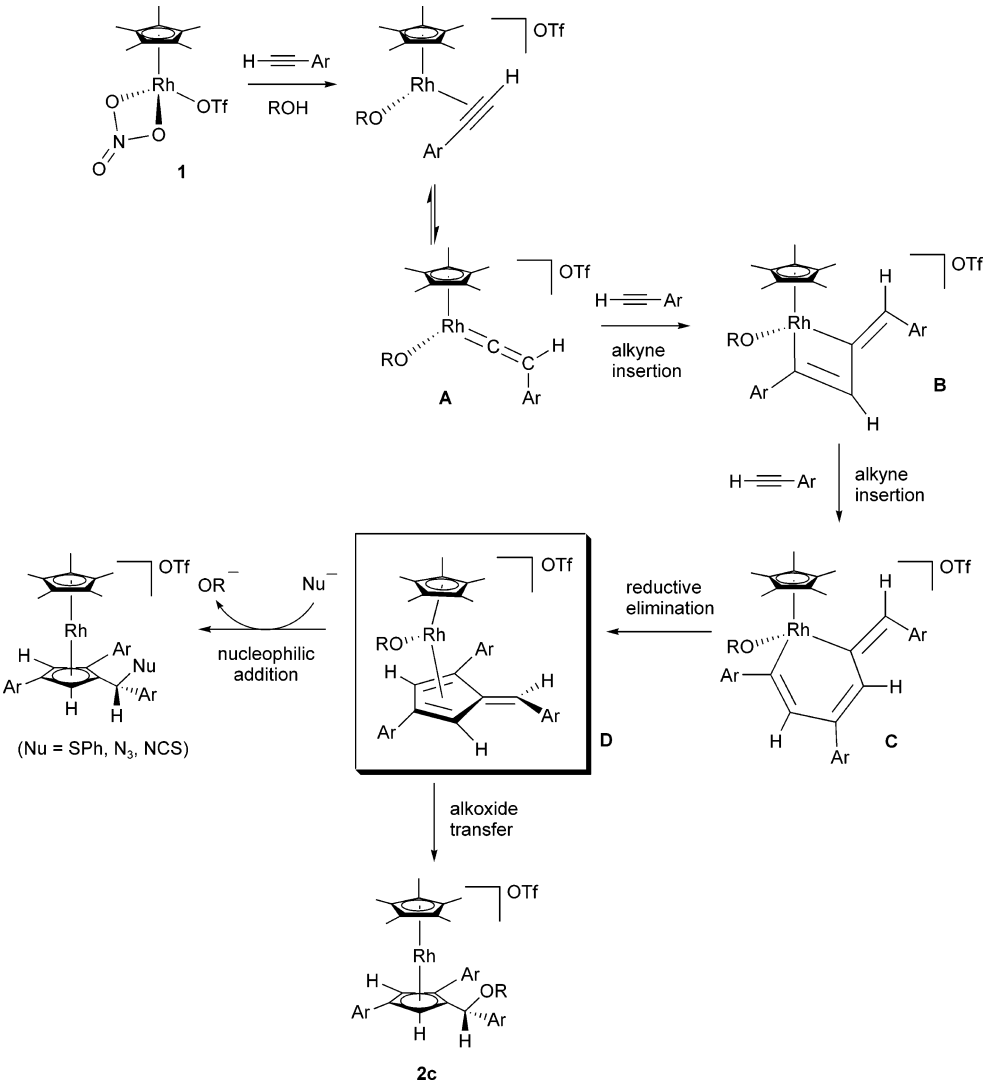
Scheme 3



bond of a fulvene intermediate. The reactivity of these reactions turned out to be essentially solvent-dependent.

Experimental Section

All reactions have been performed with standard Schlenk line and cannula techniques under argon. [Cp*Rh(η^2-NO_3)(OTf)] (**1**) was prepared by the literature method.[41] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer. IR spectra were recorded with a Nicolet Avatar 320 FTIR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Institute.

Preparation of 2a−d. A solution of **1** (100 mg, 0.223 mmol) and phenylacetylene (0.073 mL, 0.669 mmol) in EtOH (30 mL) was stirred for 18 h, and then the solvent was removed under vacuum. The resulting solids were washed with diethyl ether (20 mL × 2) and then recrystallized from acetone−hexane to give yellow crystals of [Cp*Rh(η^5-$C_5H_2Ph_2$−CH(Ph)OEt)]$^+$(OTf)$^-$ (**2a**; 118 mg, 72%). ^{1}H NMR ($CDCl_3$): δ 1.11 (dt, $^2J_{H-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 3H, OCH_2CH_3), 1.66 (s, 15H, $C_5(CH_3)_5$), 3.36 (dq, $^2J_{H-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 2H, OCH_2CH_3), 5.47 (s, 1H, CH(Ph)OEt), 6.09 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, Cp), 6.29 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, Cp), 7.26−7.71 (m, 15H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.46 (s, $C_5(CH_3)_5$), 15.23 (s, OCH_2CH_3), 65.10 (s, OCH_2CH_3), 77.82 (s, CH(Ph)OEt), 84.43 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CH), 84.69 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CH), 84.91 (d, $^1J_{Rh-C}$ = 7.3 Hz, $C_5(CH_3)_5$), 101.46 (d, $^1J_{Rh-C}$ = 7.8 Hz, Cp CC), 103.17 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp CC), 106.29 (d, $^1J_{Rh-C}$ = 6.0 Hz, Cp CC), 126.46−139.31 (m, Ph). Mp: 216 °C. Anal. Calcd for $C_{37}H_{38}F_3O_4SRh$: C, 60.16; H, 5.19; S, 4.34. Found: C, 59.89; H, 5.07; S, 4.21.

Complexes **2b−d** were prepared analogously. Data for **2b** (67%) are as follows. ^{1}H NMR ($CDCl_3$): δ 0.79 (dt, $^2J_{H-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 3H, $OCH_2CH_2CH_2CH_3$), 1.19 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.45 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.65 (s, 15H, $C_5(CH_3)_5$), 3.26 (m, 2H, $OCH_2CH_2CH_2CH_3$), 5.44 (s, 1H, CH(Ph)(O-*n*-Bu)), 6.11 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, Cp), 6.23 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, Cp), 7.26−7.70 (m, 15H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.48 (s, $C_5(CH_3)_5$), 14.03 (s, $OCH_2CH_2CH_2CH_3$), 19.42 (s, $OCH_2CH_2CH_2CH_3$), 31.97 (s, $OCH_2CH_2CH_2CH_3$), 69.60 (s, $OCH_2CH_2CH_2CH_3$), 77.92 (s, CH(Ph)O*n*Bu), 83.78 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp CH), 84.46 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp CH), 84.77 (d, $^1J_{Rh-C}$ = 6.7 Hz, $C_5(CH_3)_5$), 101.47 (d, $^1J_{Rh-C}$ = 7.8 Hz, Cp CC), 106.35 (d, $^1J_{Rh-C}$ = 6.2 Hz, Cp CC), 106.94 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CC), 126.44−139.36 (m, Ph). Mp: 202 °C. Anal. Calcd for $C_{39}H_{42}F_3O_4SRh$: C, 57.96; H, 5.52; S, 4.18. Found: C, 57.77; H, 5.32; S, 4.23.

Data for **2c** (78%) are as follows. ^{1}H NMR ($CDCl_3$): δ 1.09 (dt, $^2J_{H-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 3H, OCH_2CH_3), 1.63 (s, 15H, $C_5(CH_3)_5$), 2.32 (s, 3H, $C_6H_4CH_3$), 2.36 (s, 3H, $C_6H_4CH_3$), 2.43 (s, 3H, $C_6H_4CH_3$), 3.32 (dq, $^2J_{H-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 2H, OCH_2CH_3), 5.37 (s, 1H, CH(*p*-tolyl)OEt), 6.04 (d, $^4J_{H-H}$ = 1.0 Hz, 1H, Cp), 6.08 (d, $^4J_{H-H}$ = 1.0 Hz, 1H, Cp), 7.14−7.58 (m, 15H, $C_6H_4CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.45 (s, C_5-

(41) Han, W. S.; Lee, S. W. *Inorg. Chim. Acta* **2003**, *348*, 15−24.

Table 1. X-ray Data Collection and Structure Refinement Details

	2b	2c	3a	3c
formula	$C_{39}H_{42}F_3O_4SRh$	$C_{40}H_{44}F_3O_4SRh$	$C_{44}H_{44}F_3O_3S_2Rh$	$C_{39}H_{39}F_3NO_3S_2Rh$
fw	766.70	780.72	844.82	793.74
temp, K	293(2)	293(2)	293(2)	293(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	13.277(2)	9.2188(6)	22.908(3)	22.531(3)
b, Å	20.202(4)	19.319(2)	10.666(2)	7.844(2)
c, Å	15.130(4)	21.339(2)	16.549(3)	20.623(3)
β, deg	113.20(2)	98.198(6)	102.90(1)	90.929(9)
V, Å^3	3730(1)	3761.7(6)	3941(1)	3644(1)
Z	4	4	4	4
D_{calcd}, g cm^{-3}	1.365	1.379	1.424	1.447
μ, mm^{-1}	0.566	0.563	0.593	0.636
F(000)	1584	1616	1744	1632
T_{min}	0.5504	0.6623	0.2987	
T_{max}	0.8614	0.9021	0.3424	
2θ range (deg)	3.5−50	3.5−50	3.5−50	3.5−50
no. of rflns measd	6781	6969	7052	6492
no. of unique rflns	6487	6535	6790	6295
no. of rflns with $I > 2\sigma(I)$	2662	4434	4318	4718
no. of params refined	398	459	483	459
max in $\Delta\rho$ (e Å^{-3})	0.960	0.409	0.791	0.678
min in $\Delta\rho$ (e Å^{-3})	−1.000	−0.290	−0.846	−0.534
GOF on F^2	1.025	1.019	1.009	1.023
R1[a]	0.1087	0.0460	0.0593	0.0450
wR2[b]	0.2514	0.0893	0.1428	0.1061

[a] $R1 = \sum||F_o| - |F_c||\sum|F_o|$. [b] $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

(CH_3)$_5$), 15.23 (s, OCH$_2$$CH_3$), 21.39 (s, C$_6H_4$$CH_3$), 21.57 (s, C$_6H_4$$CH_3$), 21.61 (s, C$_6H_4$$CH_3$), 64.92 (s, O$CH_2CH_3$), 77.64 (s, CH(*p*-tolyl)OEt), 84.04 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp CH), 84.22 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CH), 84.69 (d, $^1J_{Rh-C}$ = 7.3 Hz, C_5(CH$_3$)$_5$), 101.22 (d, $^1J_{Rh-C}$ = 7.8 Hz, Cp CC), 103.45 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp CC), 106.09 (d, $^1J_{Rh-C}$ = 6.2 Hz, Cp CC), 124.54−140.69 (m, C_6H$_4$CH$_3$). Mp: 228 °C. Anal. Calcd for $C_{40}H_{44}F_3O_4SRh$: C, 61.54; H, 5.68; S, 4.11. Found: C, 61.65; H, 5.49; S, 4.03.

Data for **2d** (71%) are as follows. ^{1}H NMR (CDCl$_3$): δ 0.78 (dt, $^2J_{H-H}$ = 3.0 Hz, $^3J_{H-H}$ = 7.0 Hz, 3H, OCH$_2$CH$_2$CH$_2$$CH_3$), 1.15 (m, 2H, OCH$_2CH_2$$CH_2CH_3$), 1.40 (m, 2H, OCH$_2$$CH_2CH_2CH_3$), 1. 62 (s, 15H, C$_5$(C$H_3$)$_5$), 2.34 (s, 3H, C$_6H_4CH_3$), 2.37 (s, 3H, C$_6H_4CH_3$), 2.44 (s, 3H, C$_6H_4CH_3$), 3.28 (m, 2H, OC$H_2CH_2CH_2CH_3$), 5.33 (s, 1H, C$H$(*p*-tolyl)(O-*n*-Bu)), 5.99 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, Cp), 6.05 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, Cp), 7.16−7.56 (m, 15H, C$_6$$H_4CH_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.46 (s, C$_5$(CH_3)$_5$), 14.02 (s, OCH$_2$CH$_2$CH$_2$$CH_3$), 19.39 (s, OCH$_2CH_2$$CH_2CH_3$), 21.42 (s, C$_6H_4$$CH_3$), 21.57 (s, C$_6H_4$$CH_3$), 21.61 (s, C$_6H_4$$CH_3$), 31.94 (s, OCH$_2$$CH_2CH_2CH_3$), 69.41 (s, O$CH_2CH_2CH_2CH_3$), 77.67 (s, CH(*p*-tolyl)(O-*n*-Bu)), 83.97 (d, $^1J_{Rh-C}$ = 4.4 Hz, Cp CH), 84.08 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CH), 85.28 (d, $^1J_{Rh-C}$ = 7.3 Hz, C_5(CH$_3$)$_5$), 101.24 (d, $^1J_{Rh-C}$ = 7.8 Hz, Cp CC), 103.43 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp CC), 106.23 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CC), 124.52−140.72 (m, C_6H$_4$CH$_3$). Mp: 190 °C. Anal. Calcd for $C_{42}H_{48}F_3O_4SRh$: C, 62.37; H, 5.98; S, 3.96. Found: C, 61.98; H, 5.79; S, 3.89.

Preparation of 3a−c. A solution of **1** (100 mg, 0.223 mmol) and 4-ethynyltoluene (0.085 mL, 0.669 mmol) in EtOH (30 mL) was stirred for 2 h, and then the solvent was removed under vacuum. Then, to the resulting solids were added sequentially CH_2Cl_2 (30 mL) and thiophenol (0.069 mL, 0.669 mmol). The reaction mixture was refluxed for 18 h, and the solvent was removed. The resulting solids were washed with diethyl ether (20 mL × 2) and then recrystallized from CH_2Cl_2−hexane to give yellow crystals of [Cp*Rh(η^5-C$_5$H$_2$(*p*-tolyl)$_2$−CH(*p*-tolyl)-SPh)]$^+$(OTf)$^-$ (**3a**; 117 mg, 62%). ^{1}H NMR (CDCl$_3$): δ 1.35 (s, 15H, C$_5$(CH_3)$_5$), 2.40 (s, 3H, C$_6$H$_4$CH_3), 2.41 (s, 3H, C$_6$H$_4$CH_3), 2.43 (s, 3H, C$_6$H$_4$CH_3), 5.27 (s, 1H, CH(*p*-tolyl)SPh), 6.07 (d, $^4J_{H-H}$ = 1 Hz, 1H, Cp), 6.90 (d, $^4J_{H-H}$ = 1 Hz, 1H, Cp), 6.90−7.52 (m, 15H, C$_6$$H_4CH_3$ and SC$_6$$H_5$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 9.18 (s, C$_5$(CH_3)$_5$), 21.42 (s, C$_6$H$_4$$CH_3$), 21.59 (s, C$_6H_4$$CH_3$), 21.65 (s, C$_6H_4$$CH_3$), 49.65 (s, CH(*p*-tolyl)SPh), 81.80 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp CH), 82.69 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CH), 83.21 (d, $^1J_{Rh-C}$ = 7.3 Hz, C_5(CH$_3$)$_5$), 101.41 (d, $^1J_{Rh-C}$ = 7.2 Hz, Cp CC), 103.29 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CC), 107.39 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp CC), 124.30−141.03 (m, C_6H$_4$CH$_3$ and SC$_6$H$_5$). Mp: 226 °C. Anal. Calcd for $C_{44}H_{44}F_3O_3S_2Rh$: C, 62.56; H, 5.25; S, 7.59. Found: C, 62.87; H, 5.33; S, 7.62.

Complexes **3b**,**c** were prepared analogously. Data for **3b** (58%) are as follows. IR (KBr): ν(N$_3$) 2097 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.67 (s, 15H, C$_5$(CH_3)$_5$), 2.35 (s, 3H, C$_6$H$_4$CH_3), 2.38

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)

	Complex **2b**		
Rh1−C11	2.20(1)	O1−C28	1.40(2)
Rh1−C14	2.20(1)	Rh1−C13	2.24(2)
O1−C35	1.40(2)	C14−C28	1.53(2)
Rh1−C12	2.23(1)		
Rh1−C15	2.16(1)		
O1−C28−C29	116(1)	C35−O1−C28	111(1)
O1−C28−C14	110(1)	C29−C28−C14	102(1)
	Complex **2c**		
Rh1−C11	2.215(4)	Rh1−C15	2.192(5)
Rh1−C14	2.191(4)	O1−C38	1.440(6)
O1−C30	1.422(5)	Rh1−C13	2.198(4)
Rh1−C12	2.171(4)	C14−C30	1.514(5)
O1−C30−C14	111.6(4)	C30−O1−C38	111.8(4)
O1−C30−C31	113.0(4)	C14−C30−C31	110.1(3)
	Complex **3a**		
Rh1−C11	2.210(5)	Rh1−C15	2.198(6)
Rh1−C14	2.234(6)	C11−C16	1.503(7)
S1−C16	1.850(6)	Rh1−C13	2.216(5)
Rh1−C12	2.177(5)	S1−C24	1.765(7)
C11−C16−S1	110.5(4)	C11−C16−C17	117.3(5)
C17−C16−S1	105.1(4)		
	Complex **3c**		
Rh1−C11	2.198(4)	N1−C30	1.406(7)
Rh1−C14	2.199(4)	Rh1−C13	2.224(5)
N1−C38	1.148(7)	S1−C38	1.574(7)
Rh1−C12	2.189(5)	C14−C30	1.521(6)
Rh1−C15	2.178(4)		
N1−C38−S1	176.5(6)	N1−C30−C14	111.3(4)
C14−C30−C31	111.9(4)	N1−C30−C31	112.6(5)

(s, 3H, $C_6H_4CH_3$), 2.44 (s, 3H, $C_6H_4CH_3$), 5.84 (s, 1H, C*H*(*p*-tolyl)N_3), 6.05 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, Cp), 6.34 (d, $^4J_{H-H}$ = 1.5 Hz, 1H, Cp), 7.21−7.46 (m, 15H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.51 (s, $C_5(CH_3)_5$), 21.42 (s, $C_6H_4CH_3$), 21.58 (s, $C_6H_4CH_3$), 21.63 (s, $C_6H_4CH_3$), 61.66 (s, *C*H(*p*-tolyl)N_3), 82.78 (d, $^1J_{Rh-C}$ = 6.2 Hz, Cp *C*H), 84.51 (d, $^1J_{Rh-C}$ = 3.3 Hz, Cp *C*H), 84.56 (d, $^1J_{Rh-C}$ = 3.9 Hz, $C_5(CH_3)_5$), 101.66 (d, $^1J_{Rh-C}$ = 7.2 Hz, Cp *C*C), 104.07 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp *C*C), 106.59 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp *C*C), 124.15−140.97 (m, $C_6H_4CH_3$). Mp: 224 °C. Anal. Calcd for $C_{38}H_{39}F_3N_3O_3SRh$: C, 58.69; H, 5.05; N, 5.40; S, 4.12. Found: C, 59.12; H, 4.99; N, 5.33; S, 4.21.

Data for **3c** (65%) are as follows. IR (KBr): ν(NCS) 2102 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.79 (s, 15H, $_5(CH_3)_5$), 2.33 (s, 3H, $C_6H_4CH_3$), 2.38 (s, 3H, $C_6H_4CH_3$), 2.41 (s, 3H, $C_6H_4CH_3$), 5.30 (s, 1H, C*H*(*p*-tolyl)NCS), 5.95 (d, $^4J_{H-H}$ = 2.0 Hz, 1H, Cp), 6.40 (d, $^4J_{H-H}$ = 2.0 Hz, 1H, Cp), 7.17−7.50 (m, 15H, $C_6H_4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.60 (s, $C_5(CH_3)_5$), 21.34 (s, $C_6H_4CH_3$), 21.56 (s, $C_6H_4CH_3$), 21.65 (s, $C_6H_4CH_3$), 57.30 (s, *C*H(*p*-tolyl)-NCS), 83.13 (d, $^1J_{Rh-C}$ = 7.3 Hz, Cp *C*H), 84.71 (d, $^1J_{Rh-C}$ = 6.2 Hz, Cp *C*H), 85.52 (d, $^1J_{Rh-C}$ = 7.2 Hz, $C_5(CH_3)_5$), 101.90 (d, $^1J_{Rh-C}$ = 7.8 Hz, Cp *C*C), 103.54 (d, $^1J_{Rh-C}$ = 7.2 Hz, Cp *C*C), 106.36 (d, $^1J_{Rh-C}$ = 6.7 Hz, Cp *C*C), 124.13−141.01 (m, $C_6H_4CH_3$ and N*C*S). Mp: 218 °C. Anal. Calcd for $C_{39}H_{39}F_3NO_3S_2Rh$: C, 59.02; H, 4.95; N, 1.76; S, 8.08. Found: C, 58.68; H, 4.79; N, 1.81; S, 8.21.

Structure Determinations. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube. Details on crystal data and refinement details are given in Table 1. Intensity data were empirically corrected for absorption with ψ-scan data, except for **3c**. All crystal structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically, except the counterion (OTf−) in complex **2b**, which exhibited an extreme structural disorder; therefore, it was refined isotropically. The hydrogen atoms bonded to the fulvene ring and the exo carbon were located and refined isotropically. The remaining hydrogen atoms were generated in ideal positions and refined in a riding model. All calculations were carried out with use of SHELXTL programs.[42] Selected bond lengths and angles are shown in Table 2.

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Supporting Information Available: Crystallographic data of **2b**,**c** and **3a**,**c** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0492404

(42) Sheldrick, G. M. SHELXTL, Structure Determination Software Programs; Bruker Analytical X-ray Instruments Inc., Madison, WI, 1997.