cis-Butadiene Framework Formation from a Unique Coupling of Two μ-CH_2 Ligands with Activated Alkyne on $[(RhCp^*)_2(\mu\text{-}CH_2)_2\{\mu\text{-}SC(COOMe)=CH(COOMe)\}]^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$) Derived from the Corresponding μ-SH Complex: Effect of the Substituted Ethenethiolate Ligand on the Coupling

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Summary: The reaction of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)](BPh_4)$ (**1**(BPh_4); $Cp^* = \eta^5\text{-}C_5Me_5$) *with 1 equiv of dimethyl acetylenedicarboxylate gives the substituted ethenethiolate complex* $[(RhCp^*)_2(\mu\text{-}CH_2)_2\{\mu\text{-}SC(COOMe)=CH(COOMe)\}](BPh_4)$ (**2**(BPh_4)). *Complex* **2** *reacts further with another alkyne to form the butadiene complex* $[(RhCp^*)_2\{\eta^2{:}\eta^2\text{-}\mu\text{-}CH_2=C(COOMe)C(COOMe)=CH_2\}\{\mu\text{-}SC(COOMe)=CH(COOMe)\}](BPh_4)$ (**3**·BPh_4)), *which results from the C−C bond formation using two* μ-CH_2 *groups and the alkyne.*

The study of C−C bond formation using μ_2-CH_2 ligands in dinuclear complexes has been investigated extensively in connection with surface-catalyzed transformations of CO[1] and the development of a new methodology for organic synthesis.[2] Some of the μ-CH_2 groups react with alkynes to achieve regioselective C−C bond formation.[3] In the course of our study of the application of (μ-methylene)bis((pentamethylcyclopentadienyl)rhodium) complexes[4,5] for organic synthesis and catalytic oligomerization of unsaturated hydrocarbons,[6] we have found that the disubstituted ethenethiolate complex $[(RhCp^*)_2(\mu\text{-}CH_2)_2\{\mu\text{-}SC(COOMe)=CH(COOMe)\}](BPh_4)$ (**2**(BPh_4); $Cp^* = \eta^5\text{-}C_5Me_5$), which is derived from the bridging thiol complex $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SH)](BPh_4)$ (**1**(BPh_4)),[7] shows an intriguing coupling of two μ-CH_2 ligands with dimethyl acetylenedicarboxylate to form the substituted butadiene complex $[(RhCp^*)_2\{\eta^2{:}\eta^2\text{-}\mu\text{-}CH_2=C(COOMe)C(COOMe)=CH_2\}\{\mu\text{-}SC(COOMe)=CH(COOMe)\}](BPh_4)$ (**3**(BPh_4)).

1(BPh_4) reacted smoothly with 1 equiv of dimethyl acetylenedicarboxylate within a few minutes in a mixed solvent (5/1 CH_2Cl_2/MeOH) at 25 °C to form **2**(BPh_4) in 89% yield.[8] The structure of **2** determined by single-crystal X-ray crystallography is shown in Figure 1.[9] The newly formed disubstituted ethenethiolate ligand in **2**(BPh_4) has an *E* configuration resulting from the *syn* addition of the bridging thiol ligand to the alkyne.[10] The Rh−S bond distance (2.428(1) Å) is longer than those of the μ-SH complex of **1**(BPh_4) (2.400(4) Å)[7] and bridging thiolate complexes of $[(RhCp^*)_2(\mu\text{-}SMe)_2Cl_2]$ (2.381(2) Å)[11] and $[Rh_2\{\mu\text{-}S(CH_2)_2S\}Cl_2(CO)_2(PPh_3)_2]$ (2.328(3) Å).[12] Other characteristic features of the structure of **2** are that the S, C(23), C(24), C(27), and O(4) atoms are nearly coplanar and the S−C(23) bond length, 1.775(4) Å, is considerably shorter than that of

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(8) Characterization of **2**(BPh_4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H, μ-CH_2), 8.05 (s, 1H, μ-CH_2), 7.97 (s, 1H, μ-CH_2), 7.60 (s, 1H, μ-CH_2), 7.42−7.40 (m, 8H, ortho protons of BPh_4), 7.02 (t, $J_{H-H} = 7.3$ Hz, 8H, meta protons of BPh_4), 6.87 (t, $J_{H-H} = 7.3$ Hz, 4H, para protons of BPh_4), 5.74 (s, 1H, olefinic), 3.79 (s, 3H, COO*Me*), 3.75 (s, 3H, COO*Me*), 1.71 (s, 30H, Cp*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6 (t, $J_{Rh-C} = 24$ Hz, μ-CH_2), 166.3 (t, $J_{Rh-C} = 24$ Hz, μ-CH_2), 165.9 (carboxyl), 164.2 (q, $J_{B-C} = 50$ Hz, B−*C*), 163.3 (carboxyl), 144.3 (olefinic), 136.3 (Ph), 127.9 (olefinic), 125.4 (Ph), 121.6 (Ph), 103.2 (C_5Me_5), 53.1 (COO*Me*), 52.4 (COO*Me*), 10.2 (C_5Me_5); FAB mass spectrum *m*/*z* (%) 679 (100) $C_{28}H_{41}O_4Rh_2S$ ($M - BPh_4$)$^+$. Anal. Calcd for $C_{52}H_{61}BO_4Rh_2S$: C, 62.54; H, 6.16. Found: C, 62.20; H, 6.16.

(9) Crystal data for **2**(BPh_4): $C_{52}H_{61}BO_4Rh_2S$, $M_r = 998.73$, triclinic, $P\bar{1}$, $a = 12.509(3)$ Å, $b = 11.813(3)$ Å, $c = 11.902(3)$ Å, $\alpha = 94.32(2)°$, $\beta = 108.05(2)°$, $\gamma = 70.28(1)°$, $V = 2372(1)$ Å^3, $D_{calcd} = 1.398$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 7.68 cm^{-1}, 9855 reflections with $|F_o| > 3\sigma(|F_o|)$, $R = 0.045$, $R_w = 0.052$, GOF = 1.50.

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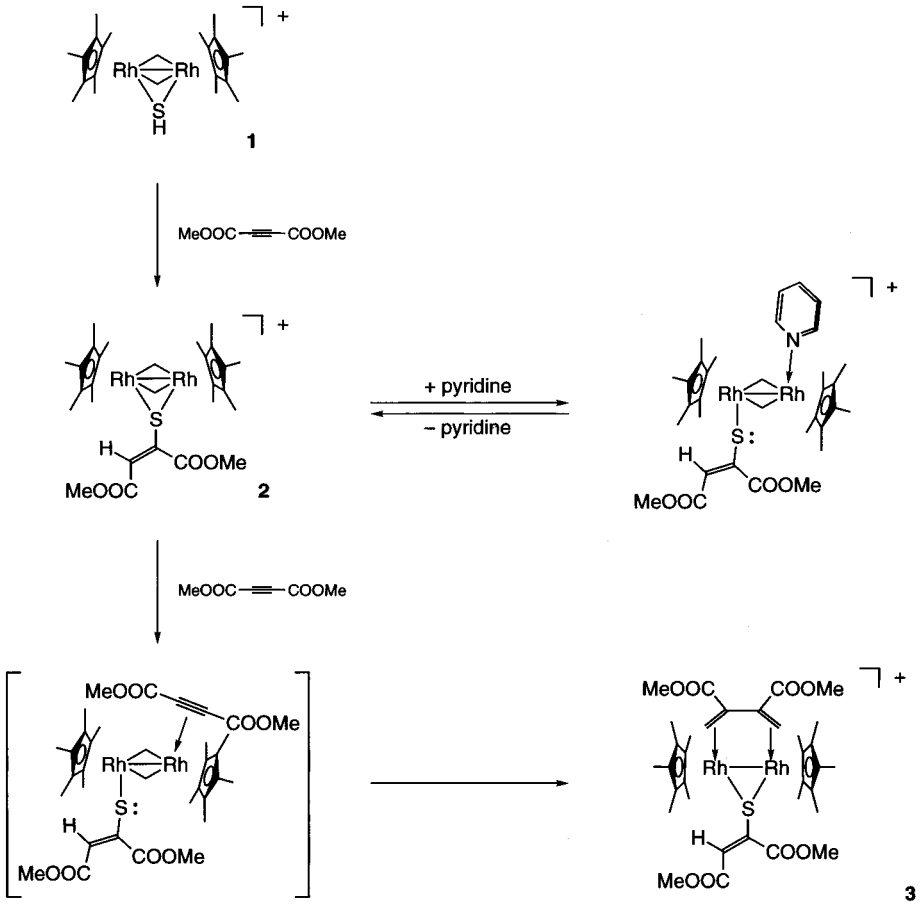
Scheme 1



the bridging methanethiolate ligand in $[(RhCp^*)_2(\mu\text{-}SMe)_2Cl_2]$ (1.828(7) Å).[11] Furthermore, the C(24)−C(27) bond distance (1.468(6) Å) is relatively shorter than the common C−C single-bond distance. This suggests that the disubstituted ethenethiolate ligand has a long electronic conjugate system through the five atoms from S to O(4) in **2**. This conjugate system affects the reactivity of **2**(BPh_4) toward pyridine and dimethyl acetylenedicarboxylate, as described below.

Complex **2** reversibly forms a 1:1 adduct with pyridine in $CDCl_3$. The equilibrium constant, *K*, of the adduct formation is estimated as ca. 40 at 25 °C. The ^{1}H NMR spectrum of the adduct species showed two Cp* signals at δ 1.36 and 1.40 and two μ-CH_2 signals at δ 9.86 and 10.07, indicating that both the thiolate and pyridine act as terminal ligands coordinating to different Rh atoms to produce the species $[(RhCp^*)_2(\mu\text{-}CH_2)_2\{SC(COOMe)=CH(COOMe)\}(py)](BPh_4)$ (Scheme 1).[13] In contrast with **2**(BPh_4), alkane- or benzenethiolate analogues of $[(RhCp^*)_2(\mu\text{-}CH_2)_2(\mu\text{-}SR)]^+$ (R = Me, *t*-Bu, Ph) did not produce adducts with pyridine, even when R was a bulky alkyl group, in the solution. This therefore suggests that the ethenethiolate ligand stabilizes the free lone pair electrons on the S atom and weakens the Rh−S bonds due to the long conjugate system with the electron-withdrawing, bulky ester groups. The disubstituted ethenethiolate ligand induces the intriguing coupling reaction of two μ-CH_2 ligands on **2**(BPh_4) with dimethyl acetylenedicarboxylate to form the substituted butadiene complex $[(RhCp^*)_2\{\eta^2\text{:}\eta^2\text{-}\mu\text{-}CH_2{=}C(COOMe)C(COOMe){=}CH_2\}\{\mu\text{-}SC(COOMe){=}CH(COOMe)\}](BPh_4)$ (**3**(BPh_4)).

When **2**(BPh_4) was treated with 5 equiv of dimethyl acetylenedicarboxylate in CH_2Cl_2 at 25 °C, the reaction proceeded slowly and was almost complete after 2 days. The crude product was purified by silica gel column chromatography to give the pure product **3**(BPh_4) in 76% yield.[14] The structure of **3** confirmed by X-ray analysis is shown in Figure 2.[15] Complex **3** has an *s-cis*-η^2:η^2-μ-butadiene ligand which is formed by incorporation of

(13) The equilibrium constant, *K*, was estimated by the changes in intensities of the CH_3 proton NMR signals for Cp* groups of **2** and the adduct with the concentration of pyridine. The reaction process, of course, is slow enough on the NMR time scale to determine the ratio of **2** and the adduct. For example, a mixture of **2**(BPh_4) (10 mM) and pyridine (47 mM) in $CDCl_3$ led to the formation of the 1:1 adduct in 62% yield at 25 °C. Characterization of $[(RhCp^*)_2(\mu\text{-}CH_2)_2\{SC(COOMe){=}CH(COOMe)\}(py)](BPh_4)$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (br s, 2H, μ-CH_2), 9.85 (br s, 2H, μ-CH_2), 7.62 (d, J = 7.5 Hz, 2H, ortho protons of py), 7.46−7.40 (m, 8H, ortho protons of BPh_4), 7.24 (t, J = 7.5 Hz, 1H, para proton of py), 7.04 (t, J = 7.3 Hz, 8H, meta protons of BPh_4), 6.90 (t, J = 7.3 Hz, 4H, para protons of BPh_4), 6.74 (t, J = 7.5 Hz, 2H, meta protons of py), 5.50 (s, 1H, olefinic), 3.82 (s, 3H, COO*Me*), 3.71 (s, 3H, COO*Me*), 1.40 (s, 15H, Cp*), 1.36 (s, 15H, Cp*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4 (t, J = 29 Hz, μ-CH_2), 168.6 (carboxyl), 165.1 (carboxyl), 164.1 (q, J = 50 Hz, B−*C*), 160.6 (olefinic), 152.5 (py), 140.0 (olefinic), 136.3 (Ph), 127.8 (py), 125.6 (Ph), 121.7 (Ph), 110.8 (py), 105.2 (C_5Me_5), 104.7 (C_5Me_5), 52.7 (COO*Me*), 51.3 (COO*Me*), 9.5 (C_5Me_5), 9.3 (C_5Me_5).

(14) Characterization of **3**(BPh_4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.39 (m, 8H, ortho protons of BPh_4), 7.00 (t, J_{H-H} = 7.3 Hz, 8H, meta protons of BPh_4), 6.86 (t, J_{H-H} = 7.3 Hz, 4H, para protons of BPh_4), 5.41 (s, 1H, olefinic), 3.81 (s, 3H, COO*Me*), 3.71 (s, 6H, COO*Me*), 3.68 (s, 3H, COO*Me*), 3.18 (br s, 2H, butadiene), 1.67 (s, 30H, Cp*), 0.57 (br s, 2H, butadiene); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0 (carboxyl), 164.6 (carboxyl), 164.2 (q, J_{B-C} = 50 Hz, B−*C*), 162.3 (carboxyl), 147.7 (olefinic), 136.3 (Ph), 126.3 (olefinic), 125.4 (Ph), 121.6 (Ph), 105.1 (d, J_{Rh-C} = 3 Hz, C_5Me_5), 67.8 (br, butadiene), 53.4 (COO*Me*), 53.1 (COO*Me*), 52.4 (COO*Me*), 47.5 (br, butadiene), 9.9 (C_5Me_5). Anal. Calcd for $C_{58}H_{67}BO_8Rh_2S$: C, 61.06; H, 5.92. Found: C, 60.89; H, 6.02.

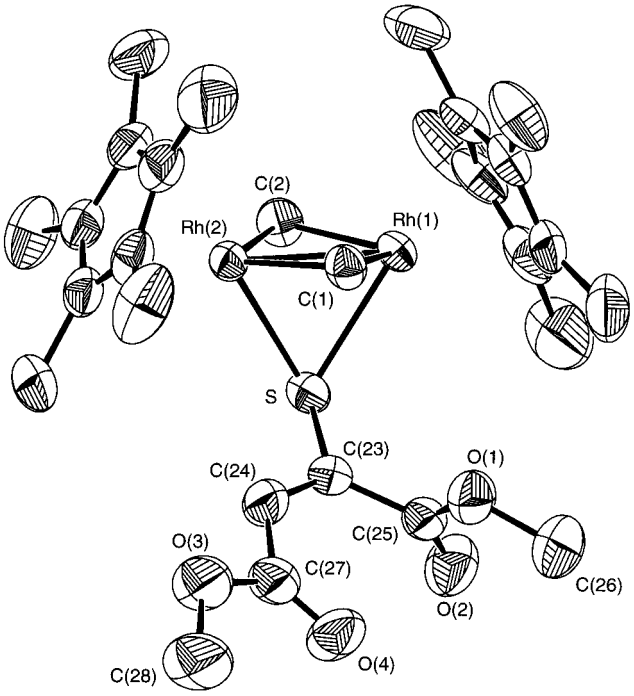


Figure 1. ORTEP drawing for the cationic part of 2(BPh_4). The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Rh(1)−Rh(2), 2.5535(7); Rh(1)−S, 2.428(1); Rh(1)−C(1), 2.037(3); Rh(1)−C(2), 2.052(5); Rh(2)−S, 2.423(1); Rh(2)−C(1), 2.055(4); Rh(2)−C(2), 2.039(3); S−C(23), 1.775(4); C(23)−C(24), 1.321(5); C(23)−C(25), 1.502(6); C(24)−C(27), 1.468(6); Rh(2)−Rh(1)−S, 58.14(3); Rh(2)−Rh(1)−C(1), 51.7(1); Rh(2)−Rh(1)−C(2) 51.14(8); Rh(1)−Rh(2)−S, 58.33(3); Rh(1)−Rh(2)−C(1), 51.07(8); Rh(1)−Rh(2)−C(2), 51.6(1); Rh(1)−S−Rh(2), 63.53(3); Rh(1)−S−C(23), 114.4(1); Rh(2)−S−C(23), 110.0(1).

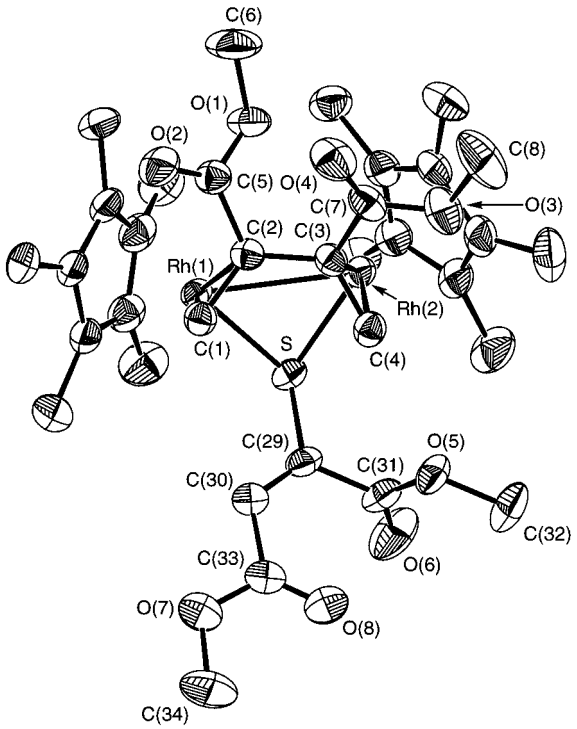


Figure 2. ORTEP drawing for the cationic part of **3**(BPh_4). The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Rh(1)−Rh(2), 2.9012(4); Rh(1)−S, 2.291(1); Rh(1)−C(1), 2.127(3); Rh(1)−C(2), 2.308(3); Rh(2)−S, 2.320(1); Rh(2)−C(3), 2.186(3); Rh(2)−C(4), 2.148(3); S−C(29), 1.780(3); C(1)−C(2), 1.404(5); C(2)−C(3), 1.481(5); C(3)−C(4), 1.414(5); C(29)−C(30), 1.325(5); C(29)−C(31), 1.522(5); C(30)−C(33), 1.489(4); Rh(2)−Rh(1)−S, 51.46(2); Rh(2)−Rh(1)−C(1), 88.9(1); Rh(2)−Rh(1)−C(2), 64.17(9); Rh(1)−Rh(2)−S, 50.56(2); Rh(1)−Rh(2)−C(3), 78.19(9); Rh(1)−Rh(2)−C(4), 91.81(9); Rh(1)−S−Rh(2), 77.98(3); Rh(1)−S−C(29), 119.2(1); Rh(2)−S−C(29), 115.6(1).

one alkyne molecule into two μ-CH_2 groups of **2**. Knox and co-workers have investigated the coupling of one μ-CH_2 group on a diruthenium complex with acetylene, which afforded a σ,π-allyl complex due to the formation of one C−C bond.[3] The present study is the first example of a butadiene framework being constructed through the coupling of two μ-CH_2 groups on the dirhodium with alkyne to simultaneously form two C−C bonds. The above-mentioned alkane- or benzenethiolate analogues did not form the corresponding butadiene complexes. The starting complexes were recovered unchanged under the same reaction conditions.

The reaction sequence is summarized in Scheme 1. The first step is the rapid stereoselective addition of the thiol group of **1** to the alkyne to give the ethenethiolate complex **2**. The next step is the C−C bond formation achieved by the insertion of the second alkyne into two μ-CH_2 groups to give the butadiene complex **3** through an intermediary π-alkyne complex. From the results described above, the disubstituted ethenethiolate ligand in **2** should play an important role in the formation of the π-alkyne complex that leads to the unprecedented alkyne insertion reaction: the terminal thiolate is stabilized by the vinyl substituent, and the alkyne can coordinate to the Rh atom in a manner similar to that for pyridine (Scheme 1). We were not able to detect the π-alkyne complex spectroscopically. This, as well as the dependence of the formation rate of complex **3** on the concentration of the alkyne, suggests that the formation of the π-alkyne complex is a rate-determining step for the formation of **3**. Theoretical and experimental studies of **2**(BPh_4) aimed at the elucidation of the reaction with unsaturated hydrocarbons and its application to the catalytic process are now in progress.

Supporting Information Available: Text giving a description of experimental details and tables of crystal data, bond lengths and angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom locations for **2**·BPh_4 and **3**·BPh_4 (32 pages). Ordering information is given on any current masthead page.

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(15) Crystal data for **3**(BPh_4): $C_{58}H_{67}BO_8Rh_2S$, M_r = 1140.84, triclinic, $P\bar{1}$, a = 14.345(2) Å, b = 17.700(2) Å, c = 11.856(2) Å, α = 102.89(1)°, β = 107.45(1)°, γ = 101.46(1)°, V = 2682.8(7) Å^3, D_{calcd} = 1.412 g cm^{-3}, Z = 2, μ(Mo Kα) = 6.93 cm^{-1}, 9621 reflections with $|F_o| > 3\sigma(|F_o|)$, R = 0.036, R_w = 0.042, GOF = 1.58.