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Syntheses and Structures of Bis(thioether)-Bridged Rhodium Complexes and Their Catalytic Reactions with Alkynes

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The reaction of bis(ethylthio)methane (ETM) with $Rh_2Cl_2(CO)_4$ results in the formation of $Rh_2Cl_2(CO)_2(ETM)_2$, I, which has been characterized by an X-ray diffraction study. Complex I crystallizes in space group $C2/c$ with $a = 17.224$ (5) Å, $b = 7.699$ (2) Å, $c = 16.296$ (5) Å, and $\beta = 104.79$ (2)°. The bis(thioether) ligands bridge the two rhodium ions which display square-planar coordination geometries. The reaction of I with triethylamine *N*-oxide results in the formation of $Rh_2Cl_2(\mu\text{-}CO)(ETM)_2$, II. Complex II crystallizes in space group $P2_12_12_1$ with $a = 9.777$ (2) Å, $b = 13.710$ (2) Å, and $c = 14.695$ (2) Å. The complex displays an A-frame structure with a Rh–Rh distance of 2.647 (1) Å. Complex I forms adducts with certain alkynes and carbon monoxide in which the coordination spheres of the metal ions are expanded. Complexes I and II serve as catalyst precursors for the cyclotrimerization of terminal alkynes. Under a mixture of carbon monoxide and acetylene (1–2 atm) at 60–70 °C in wet acetonitrile, complex I produces hydroquinone. The structures and reactivities of the bis(thioether) complexes I and II are compared and contrasted with those of the analogous bis(diphenylphosphino)methane derivatives of rhodium.

Introduction

Relatively few complexes of the group 8–10 metals with thioether ligands display catalytic activity in reactions with hydrogen. This is in sharp contrast to the extensive number of phosphine complexes of the iron, cobalt, and nickel triads which are known to function as homogeneous hydrogenation catalysts.[1] Investigations of the ligating ability of thioether complexes have led to the conclusion that these sulfur ligands are, in general, only moderate σ donors. In addition there is little evidence for strong π accepting ability by the monodentate donors.[2,3] As a result, in catalytic applications the thioether ligands appear to be more prone to dissociation from the metal ion than phosphines, and they are less effective in stabilizing low metal ion oxidation states which may be formed in hydrogenation cycles.[4-8] In several cases, thioether complexes have been found to form elemental metal in the presence of hydrogen.[4,7,8] Very little work has been done to determine whether complexes with neutral sulfur ligands might be active in nonreductive catalytic cycles, despite the fact that ease of ligand dissociation may be an advantage in these cases. We report here the syntheses and structural characterizations of rhodium dimers bridged by bis(thioether) ligands and a study of their catalytic activity in alkyne trimerization.

In previous work, a mercaptal of the formula $PhSCH_2SPh$ has been investigated briefly as a ligand in the synthesis of a dinuclear A-frame complex of rhodium,[7] which was analogous to the extensively studied bis(diphenylphosphino)methane (DPM) derivatives, $Rh_2(DPM)_2(\mu\text{-}CO)X_2$.[9] The sulfur-coordinated rhodium A-frame complex was found to be less stable under oxidative and hydrolytic conditions and less effective as a hydrogenation catalyst than the DPM analogues.[7] Since bis(alkylthio)methanes have been reported to be better donor ligands than the aryl derivative,[10] it seemed likely that this ligand type would contribute to the stability of the metal complexes. In our initial studies we learned that deriva-

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[1] Alyea, E. C., Meek, D. W., Ed. *Catalytic Aspects of Metal Phosphine Complexes*; Advances in Chemistry 196; American Chemical Society Washington, DC, 1982.

[2] Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

[3] In a recent study, electrochemical data suggest that polydentate thioether ligands function as effective π acceptors in Co(II) complexes: Hartman, J. R.; Hintsa, E. J.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1208.

[4] James, B. R.; Ng, F. T. T. *J. Chem. Soc. Dalton Trans.* **1972**, 355.

[5] James, B. R.; Ng, F. T. T. *J. Chem. Soc. Dalton Trans.* **1972**, 1321.

[6] Chatt, J.; Leigh, G. J.; Storace, A. P. *J. Chem. Soc. A* **1971**, 1380.

[7] (a) Sanger, A. R.; Lobe, C. G.; Weiner-Fedorak, J. E. *Inorg. Chim. Acta* **1981**, *53*, L123. (b) Sanger, A. R. *Can. J. Chem.* **1982**, *60*, 1363.

[8] (a) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 849. (b) *J. Chem. Soc., Dalton. Trans.* **1978**, 857.

[9] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2508.

[10] Murray, S. G.; Levason, W.; Tuttlebee, H. E. *Inorg. Chim. Acta* **1981**, *51*, 185.

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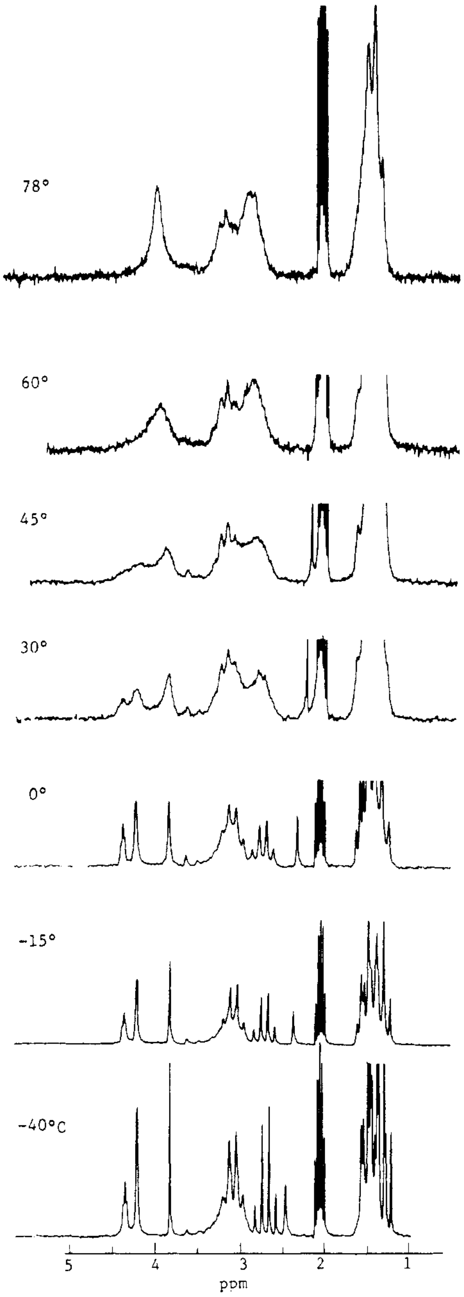

Figure 1. 90-MHz ^1H NMR spectra of $[RhCl(CO)(ETM)]_2$, I, and ca. $^1/_2$ equiv of $CH_3CH_2SCH_2SCH_2CH_3$, ETM, in CD_3CN. Resonances of the free ligand in the low-temperature spectrum occur at δ 3.80 (s, S_2CH_2), 2.68 (q, SCH_2Me); 1.3 (t, CH_3). Resonances of coordinated ETM at −40 °C occur at δ 4.33, 4.20 (S_2CH_2), 3.06 (SCH_2Me), 1.4 (CH_3). The resonances at δ 2 are from the proton impurity in CD_3CN and the singlet near δ 2.5 is a solvent impurity, probably water.

tives of bis(ethylthio)methane (ETM) have significantly better solubility characteristics than the methylthio analogues, and this paper concerns the complexes of this ligand.

Results and Discussion

Synthesis and Characterization of $[RhCl(CO)(ETM)]_2$, I. The reaction of bis(ethylthio)methane with $Rh_2Cl_2(CO)_4$ resulted in the formation of a red crystalline, slightly air-sensitive complex that was formulated as *trans*-$[RhCl(CO)(ETM)]_2$ on the basis of elemental analyses and infrared spectroscopy. The IR spectrum of I showed a single strong carbonyl stretch at 1965 cm^{-1}. The ^1H NMR spectrum of I confirmed the presence of the ETM ligand, but the resonances were broad and poorly defined. Factors that could contribute to the broadness of the spectrum include the number of different sulfur invertomers that are possible and/or the possibility of dithio ligand dissociation from the dimer. The ^1H NMR spectrum of I in the presence of ca. $^1/_2$ equiv of free ETM was recorded over a temperature range of −40 to +78 °C. At the low temperature limit, relatively sharp resonances are observed for both coordinated and free ETM protons. As the temperature is increased, both sets of resonances broaden, and at 60 °C coalescence of the resonances assigned to the free and coordinated S_2CH_2 groups is observed (Figure 1). Although the methylene resonances of the ethyl groups have not completely coalesced,[11] the data suggest that a ligand exchange process is occurring.

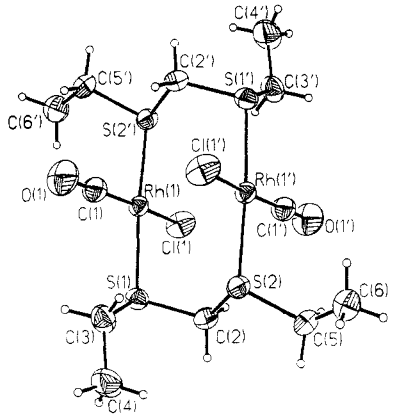

Figure 2. Perspective drawing and numbering scheme for $[RhCl(CO)(ETM)]_2$, I. Thermal ellipsoids are shown at the 50% probability level.

Table I. Bond Lengths (Å) and Bond Angles (deg) for $[RhCl(CO)(ETM)]_2$, I

	Bond Lengths		
Rh(1)–Cl(1)	2.373 (1)	Rh(1)–S(1)	2.331 (1)
Rh(1)–C(1)	1.813 (2)	Rh(1)–Rh(1A)	3.067 (1)
Rh(1)–S(2A)	2.307 (1)	S(1)–C(2)	1.809 (2)
S(1)–C(3)	1.816 (2)	S(2)–C(2)	1.819 (2)
S(2)–C(5)	1.825 (2)	S(2)–Rh(1A)	2.307 (1)
O(1)–C(1)	1.142 (3)		
C(5)–C(6)	1.512 (3)		
	Bond Angles		
Cl(1)–Rh(1)–S(1)	86.0 (1)	Cl(1)–Rh(1)–C(1)	172.1 (1)
S(1)–Rh(1)–C(1)	94.9 (1)	Cl(1)–Rh(1)–Rh(1A)	93.3 (1)
S(1)–Rh(1)–Rh(1A)	92.4 (1)	C(1)–Rh(1)–Rh(1A)	94.5 (1)
Cl(1)–Rh(1)–S(2A)	87.8 (1)	S(1)–Rh(1)–S(2A)	173.7 (1)
C(1)–Rh(1)–S(2A)	91.3 (1)	Rh(1A)–Rh(1)–S(2A)	86.4 (1)
Rh(1)–S(1)–C(2)	105.2 (1)	Rh(1)–S(1)–C(3)	110.0 (1)
C(2)–S(1)–C(3)	102.3 (1)	C(2)–S(2)–C(5)	98.3 (1)
C(2)–S(2)–Rh(1A)	108.1 (1)	C(5)–S(2)–Rh(1A)	111.6 (1)
Rh(1)–C(1)–O(1)	176.0 (2)	S(1)–C(2)–S(2)	113.4 (1)
S(1)–C(2)–H(2A)	108.5 (1)	S(2)–C(2)–H(2A)	108.5 (1)
S(1)–C(2)–H(2B)	108.5 (1)	S(2)–C(2)–H(2B)	108.5 (1)
H(2A)–C(2)–H(2B)	109.5 (1)	S(1)–C(3)–H(3A)	108.3 (1)
S(1)–C(3)–H(3B)	108.3 (1)	H(3A)–C(3)–H(3B)	109.5 (1)
S(1)–C(3)–C(4)	114.0 (2)	H(3A)–C(3)–C(4)	108.4 (1)
H(3B)–C(3)–C(4)	108.3 (1)	C(3)–C(4)–H(4A)	106.4 (1)
C(3)–C(4)–H(4B)	112.2 (1)	C(3)–C(4)–H(4C)	109.7 (1)
S(2)–C(5)–H(5A)	109.5 (1)	S(2)–C(5)–H(5B)	109.5 (1)
H(5A)–C(5)–H(5B)	109.5 (1)	S(2)–C(5)–C(6)	109.3 (1)
H(5A)–C(5)–C(6)	109.5 (1)	H(5B)–C(5)–C(6)	109.5 (1)
C(5)–C(6)–H(6A)	102.9 (1)	C(5)–C(6)–H(6B)	113.6 (1)
C(5)–C(6)–H(6C)	111.6 (1)		

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[11] Coalescence is not observed for resonances of free and coordinated SCH_2CH_3 protons, even though the chemical shift difference is similar to that observed between free and coordinated S_2CH_2 resonances. The lack of coalescence may be due to a temperature-dependent chemical shift for a set of methylene resonances.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[RhCl(CO)(ETM)]_2$, I

	x	y	z	U^a
Rh(1)	1699 (1)	2273 (1)	−667 (1)	28 (1)
Cl(1)	2120 (1)	−306 (1)	−1224 (1)	51 (1)
S(1)	1192 (1)	451 (1)	214 (1)	34 (1)
S(2)	2723 (1)	1185 (1)	1572 (1)	34 (1)
O(1)	949 (1)	5473 (2)	−227 (1)	68 (1)
C(1)	1256 (1)	4235 (2)	−368 (1)	41 (1)
C(2)	2065 (1)	−452 (2)	952 (1)	40 (1)
C(3)	739 (1)	1734 (3)	904 (1)	44 (1)
C(4)	500 (1)	687 (4)	1587 (2)	64 (1)
C(5)	3445 (1)	−270 (3)	2254 (1)	44 (1)
C(6)	4064 (1)	794 (3)	2877 (2)	57 (1)

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

Table III. Bond Lengths (Å) and Bond Angles (deg) for $[Rh_2Cl_2(\mu\text{-}CO)(ETM)_2]$, II

Bond Lengths			
Rh(1)–Rh(2)	2.647 (1)	Rh(1)–Cl(1)	2.374 (3)
Rh(1)–S(1)	2.295 (3)	Rh(1)–S(3)	2.323 (3)
Rh(1)–C(1)	1.916 (11)	Rh(2)–Cl(2)	2.382 (3)
Rh(2)–S(2)	2.308 (3)	Rh(2)–S(4)	2.294 (3)
Rh(2)–C(1)	1.960 (10)	S(1)–C(2)	1.838 (12)
S(1)–C(3)	1.813 (12)	S(2)–C(2)	1.790 (11)
S(2)–C(5)	1.847 (11)	S(3)–C(7)	1.808 (10)
S(3)–C(8)	1.866 (12)	S(4)–C(7)	1.834 (10)
S(4)–C(10)	1.836 (11)	O(1)–C(1)	1.200 (14)
C(3)–C(4)	1.516 (20)	C(5)–C(6)	1.535 (16)
C(8)–C(9)	1.530 (17)	C(10)–C(11)	1.531 (15)
Bond Angles			
Rh(2)–Rh(1)–Cl(1)	160.2 (1)	Rh(2)–Rh(1)–S(1)	90.8 (1)
Cl(1)–Rh(1)–S(1)	86.2 (1)	Rh(2)–Rh(1)–S(3)	95.8 (1)
Cl(1)–Rh(1)–S(3)	86.5 (1)	S(1)–Rh(1)–S(3)	172.7 (1)
Rh(2)–Rh(1)–C(1)	47.6 (3)	Cl(1)–Rh(1)–C(1)	152.1 (3)
S(1)–Rh(1)–C(1)	94.2 (3)	S(3)–Rh(1)–C(1)	92.6 (3)
Rh(1)–Rh(2)–Cl(2)	156.3 (1)	Rh(1)–Rh(2)–S(2)	96.7 (1)
Cl(2)–Rh(2)–S(2)	84.7 (1)	Rh(1)–Rh(2)–S(4)	91.7 (1)
Cl(2)–Rh(2)–S(4)	86.7 (1)	S(2)–Rh(2)–S(4)	171.3 (1)
Rh(1)–Rh(2)–C(1)	46.2 (3)	Cl(2)–Rh(2)–C(1)	157.5 (3)
S(2)–Rh(2)–C(1)	91.5 (3)	S(4)–Rh(2)–C(1)	96.0 (3)
Rh(1)–S(1)–C(2)	109.6 (4)	Rh(1)–S(1)–C(3)	109.7 (4)
C(2)–S(1)–C(3)	99.9 (6)	Rh(2)–S(2)–C(2)	108.8 (4)
Rh(2)–S(2)–C(5)	109.4 (3)	C(2)–S(2)–C(5)	100.9 (5)
Rh(1)–S(3)–C(7)	108.5 (3)	Rh(1)–S(3)–C(8)	107.7 (4)
C(7)–S(3)–C(8)	100.9 (5)	Rh(2)–S(4)–C(7)	108.9 (3)
Rh(2)–S(4)–C(10)	106.2 (4)	C(7)–S(4)–C(10)	99.9 (5)
Rh(1)–C(1)–Rh(2)	86.2 (5)	Rh(1)–C(1)–O(1)	138.8 (8)
Rh(2)–C(1)–O(1)	135.0 (8)	S(1)–C(2)–S(2)	109.9 (6)
S(1)–C(3)–C(4)	117.2 (9)	S(2)–C(5)–C(6)	110.9 (8)
S(3)–C(7)–S(4)	109.3 (5)	S(3)–C(8)–C(9)	110.4 (8)
S(4)–C(10)–C(11)	111.8 (8)		

The dimeric nature of I was confirmed by an X-ray diffraction study. Single crystals of I were grown from acetonitrile solution. The complex crystallized in the centrosymmetric space group $C2/c$ with four molecules in a unit cell. A perspective view of the molecule is shown in Figure 2. Selected bond distances and angles are presented in Table I, and positional and thermal parameters are given in Table II. The coordination geometry about each rhodium(I) is a slight tetrahedral distortion of a square plane with trans geometry about each metal. In addition, the chloride and carbonyl ligands are mutually trans on adjacent rhodium ions. The two square planes are bridged by dithiomethane ligands in which the methylene groups are folded in a trans configuration. The square plane of ligands are parallel to each other and are close to perpendicular to the Rh–Rh vector. The Rh–Rh separation of 3.067 Å is much greater than normal two-electron Rh–Rh bonds, which range from 2.617 (3) to 2.796 (8) Å.[12] However, the distance is consistent with a weak metal–metal interaction.[13] The parameters involving the chloride and carbonyl ligands appear normal.

Two different rhodium–sulfur distances are observed in complex I. Few rhodium(I) thioether complexes have been prepared previously,[14-18] and few structural data are available for comparison. The square-pyramidal complex $[Rh(NBD)_2SEt_2]ClO_4$ (NBD = norbornadiene) contains the thioether in the apical position with a rather long Rh–S distance of 2.500 (4) Å.[17] The planar rhodium(I) complexes of the formulas $Rh(CO)(PPh_3)(Et\text{-}mnt)$ and $Rh(COD)(Me\text{-}mnt)$ (R-mnt = S-alkylated maleonitriledithiolate) involve both thioether and thiolate type donors.[18] The Rh–S bond distances in these complexes, which range from 2.290 (2) to 2.3214 (13) Å, display values similar to those observed for complex I.[18]

The structural features of complex I can be compared to those reported previously for the closely related bis(diphenylphosphino)methane and bis(diphenylarsino)methane derivatives, $Rh_2Cl_2(CO)_2(DPM)_2$[19] and $Rh_2Cl_2(CO)_2(DAM)_2$.[20] Similar tetrahedral distortions of the square-planar geometries are observed at the metal ions in these dimers. A further distortion is observed in the latter derivatives. For example, in the DPM complex the coordination planes are inclined toward the Rh–Rh vector by 75.9° with the chloride ligands folded in toward the bridging sites between the two metal ions. The skewed planes were believed to result from a minimizing of the nonbonded contacts between the equatorial chloride and carbonyl ligands and the phenyl rings of the chelated phosphine. In contrast, the sulfur ligand of complex I is much less sterically demanding. The dihedral angle between the plane of ligands around rhodium and the plane defined by the two rhodium and four sulfur atoms is 91°.[21]

The rhodium–rhodium distances in the phosphine- and arsine-bonded complexes, 3.2386 (5) and 3.396 (1) Å, respectively, are significantly longer than the metal–metal distance in complex I. The difference may be an additional consequence of the lower steric requirements of the bis(thioether) ligands. The structural differences observed in this series suggest that the chemical properties of the rhodium dimer I may also be significantly altered from those of the phosphine and arsine complexes.

Synthesis and Characterization of $[Rh_2Cl_2(\mu\text{-}CO)(ETM)_2]$. Complex I was quite stable thermally and did not lose significant amounts of carbon monoxide when refluxed in toluene or photolyzed in acetonitrile. However, the addition of 1 equiv of $(CH_3)_3NO$ to an acetonitrile solution of complex I at room temperature resulted in a color change from red to green. The resulting green complex isolated from this solution was formulated as $Rh_2Cl_2(\mu\text{-}CO)(ETM)_2$, II. The elemental analyses and the infrared spectrum, which showed a strong absorbance at

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[12] Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628 and references therein.

[13] Bonnet, J. J.; Kalck, P.; Poiblanc, R. *Inorg. Chem.* **1977**, *16*, 1514.

[14] Faraone, F.; Pretropaolo, R.; Sergi, S. *J. Organomet. Chem.* **1970**, *24*, 797.

[15] Busello, L.; Carturan, G.; Palazzi, A.; Belluco, U. *J. Chem. Soc. A* **1970**, 474.

[16] Chatt, J.; Leigh, G. J.; Storace, A. P.; Squire, D. A.; Starkey, B. J. *J. Chem. Soc. A* **1971**, 899.

[17] Tiripicchio, A.; Tiripicchio-Camellini, M.; Claver, C.; Ruiz, A.; Oro, L. A. *J. Organomet. Chem.* **1983**, *241*, 77.

[18] (a) Eisenberg, R.; Cheng, C. H. *Inorg. Chem.* **1979**, *18*, 2438. (b) Eisenberg, R.; VanDerveer, D. *J. Am. Chem. Soc.* **1974**, *96*, 4994.

[19] Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 2500.

[20] Mague, J. T. *Inorg. Chem.* **1969**, *8*, 1975.

[21] Plane 1 for Rh1, Cl1, S1, O1, C1, S2′: $0.8366x + 0.1178y + 0.5349z = 1.5149$. Plane 2 for Rh1, Rh1′, S1, S1′, S2, S2′: $-0.3979x + 0.8188y + 0.4138z = -0.5354$.

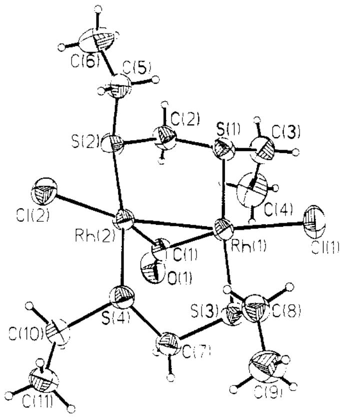

Figure 3. Perspective drawing and numbering scheme for $Rh_2Cl_2(\mu\text{-}CO)(ETM)_2$, II. Thermal ellipsoids are shown at the 50% probability level.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Rh_2Cl_2(\mu\text{-}CO)(ETM)_2]$, II

	x	*y*	*z*	U^a
Rh(1)	2912 (1)	2096 (1)	2745 (1)	32 (1)
Rh(2)	3279 (1)	3220 (1)	4189 (1)	32 (1)
Cl(1)	1789 (4)	1235 (2)	1559 (2)	57 (1)
Cl(2)	2611 (3)	4233 (2)	5429 (2)	49 (1)
S(1)	2739 (3)	3444 (2)	1825 (2)	38 (1)
S(2)	3525 (3)	4670 (2)	3407 (2)	39 (1)
S(3)	2916 (3)	631 (2)	3539 (2)	37 (1)
S(4)	2988 (3)	1925 (2)	5159 (2)	37 (1)
O(1)	5744 (8)	2502 (6)	3269 (6)	58 (3)
C(1)	4525 (12)	2551 (7)	3352 (7)	34 (4)
C(2)	3894 (12)	4404 (8)	2240 (7)	47 (4)
C(3)	3521 (15)	3192 (8)	732 (7)	65 (5)
C(4)	4978 (14)	2812 (11)	736 (9)	78 (5)
C(5)	1842 (12)	5270 (7)	3300 (8)	45 (4)
C(6)	2009 (14)	6364 (9)	3110 (9)	69 (5)
C(7)	3715 (11)	829 (7)	4632 (6)	34 (3)
C(8)	1119 (11)	369 (9)	3890 (8)	54 (4)
C(9)	1031 (14)	-627 (9)	4356 (10)	67 (5)
C(10)	4211 (12)	2106 (8)	6091 (7)	44 (4)
C(11)	3932 (14)	1416 (8)	6889 (8)	55 (4)

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

1805 cm^{-1}, were consistent with this formulation.

Single crystals of II were isolated from an acetonitrile solution and characterized by an X-ray diffraction study. The complex crystallized in the chiral space group $P2_12_12_1$. A perspective drawing of the molecule is shown in Figure 3, and bond distances and angles are given in Table III. Positional and thermal parameters are presented in Table IV. The structure verifies that the complex consists of two rhodium chloride centers bridged by two ETM ligands and a carbonyl ligand. The equatorial plane containing the carbonyl and chloride ligands is approximately perpendicular to the Rh_2S_2 plane. The overall geometry establishes that this complex has an A-frame structure. Angles about each rhodium in the equatorial plane are similar to those observed for previously characterized A-frame complexes $Rh_2Cl_2(\mu\text{-}CO)(DPM)_2{\cdot}2C_6H_6$[22] and $Rh_2Br_2(\mu\text{-}CO)(DPM)_2$.[9]

In contrast to *trans*-$[RhCl(CO)(ETM)]_2$ the methylene linkages of the ETM ligands in II are folded on the same side as the bridging carbonyl ligand. This is also observed in $Rh_2Cl_2(\mu\text{-}CO)(DPM)_2{\cdot}2C_6H_6$ and $Rh_2Br_2(\mu\text{-}CO)(DPM)_2$.[9,22] This configuration minimizes the steric effects involving the ethyl groups in the ETM ligand and the carbonyl and chloride ligands. The Rh–Cl bond distances of 2.374 (3) and 2.382 (3) Å are in the range of normal terminal Rh–Cl distances (2.34–2.39 Å). The Rh–S distances (2.294–2.323 Å) are similar to those in *trans*-$[RhCl(CO)(ETM)]_2$. The carbonyl ligand bridges the Rh–Rh bond quite symmetrically as shown by the Rh–C distances of 1.960 (10) and 1.916 (11) Å. These distances are comparable to those of Rh_2Cl_2 $(\mu\text{-}CO)(DPM)_2{\cdot}2C_6H_6$ (1.90 (3) Å) and $[Rh_2Br_2(\mu\text{-}CO)(DPM)_2]$ (1.961 (8) Å). The Rh–Rh distance of 2.647 (1) Å is considerably shorter than those observed in $Rh_2Cl_2(\mu\text{-}CO)(DPM)_2{\cdot}2C_6H_6$ (2.726 (3) Å) and $Rh_2Br_2(\mu\text{-}CO)(DPM)_2$ (2.7566 (8) Å) but well within the range of two-electron Rh–Rh bonds.[12]

Reactions of I and II with Alkynes. Complex I acts as a catalyst precursor for the cyclotrimerization of acetylene and terminal alkynes in acetonitrile solution at room temperature. The reactions proceed slowly under these conditions (see Experimental Section). In the cyclotrimerization of terminal alkynes, the 1,2,4-substituted benzenes are the dominant products; in both the propyne and 1-butyne systems, the ratio of this product isomer to the 1,3,5-isomer is 5:1 or greater. Internal alkynes are not readily trimerized. For example, the reaction of I with diphenylacetylene at 70 °C gives only a trace of hexaphenylbenzene, and no trimerized product was observed with 2-butyne or with dimethyl acetylenedicarboxylate (DMA). We did not observe evidence for pyridine products that would result from cotrimerization of alkyne and solvent.[23] Complex II also catalyzes alkyne trimerization reactions, but it is much less soluble than I, and its reactivity has not been investigated in detail.

The nature of the active catalyst in these trimerization reactions has not been identified. No free dithiomethane ligand was recovered by vacuum distillation of the product solution. The rhodium species that has been isolated after the catalytic reaction with acetylene was found to have a new high-frequency carbonyl stretch in the infrared spectrum near 2100 cm^{-1} as well as an absorption at 1990 cm^{-1}. A new band was also observed at 1650 cm^{-1}, which is the frequency assigned for a perturbed acetylene stretching vibration. When the complex was redissolved in acetonitrile under acetylene, the cyclotrimerization reaction was again observed. However, we were unable to obtain elemental analysis data for this intermediate consistent with the formulation of a single complex.

Complex I reacts with dimethylacetylenedicarboxylate (DMA) to form a stable adduct, III, which may be related to the possible intermediate discussed above. Elemental analyses are consistent with the formulation $Rh_2Cl_2(CO)_2(ETM)_2(DMA)$ for III. Conductivity studies indicate that the product is a nonelectrolyte in acetone solution. The infrared spectrum of III shows two carbonyl stretches at 2070 and 1995 cm^{-1} and a weak band at 1590 cm^{-1} which is attributed to $\nu_{C{=}C}$ of the coordinated alkyne. The frequency of the acetylenic stretch has been used as an indication of the bonding mode of this ligand. The cis-dimetalated olefin generally has a higher stretching frequency (>1600 cm^{-1}) than the η^2-bridging ligand which is perpedicular to the metal-metal vector (<1600 cm^{-1}).[24] For example the cis-metalated ligand in $Rh_2Cl_2(\mu\text{-}DMA)(DPM)_2$ shows a band in the IR spectrum at 1615 cm^{-1}.[25] However, the nature of the metal ion as well as

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(22) Gelmini, L.; Stephan, D. W.; Loeb, S. J. *Inorg. Chim. Acta* **1985**, *98*, L3.

(23) (a) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1973**, 280. (b) Bonnemann, H.; Brinkman, R.; Schenkluhn, H. *Synthesis* **1974**, 575.

(24) Sutherland, B. R.; Cowie, M. *Organometallics* **1984**, *3*, 1869 and references therein.

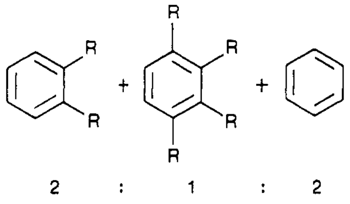
(25) Cowie, M.; Dickson, R. S.; Hames, B. W. *Organometallics* **1984**, *3*, 1879.

that of the other ligands can shift this acetylene frequency. In the iridium complex $Ir_2Cl_2(CO)_2(\mu\text{-DMA})(DPM)_2\cdot 2CH_2Cl_2$, which also contains a cis-dimetalated olefin, the acetylene vibration occurs at 1549 cm^{-1}.[24] An X-ray diffraction study will be necessary to definitely establish the bonding mode of the DMA molecule in III.

As discussed above, DMA is not cyclotrimerized to hexamethyl mellitate by I or II or by the adduct III. However, the DMA adduct III does react with acetylene (ca. 3 equiv) to form cocyclotrimerized products dimethyl phthalate and 1,2,3,4-benzenetetracarboxylic acid tetramethyl ester as well as benzene (reaction 1). These observations of cocyclotrimerizations involving both one and two DMA molecules suggest that the coordinated DMA may be displaced by acetylene during the trimerization process. The same products are observed when I is reacted with a mixture of DMA and acetylene.

$Rh_2Cl_2(CO)_2(ETM)_2DMA + HC{\equiv}CH \longrightarrow$

III



(1)

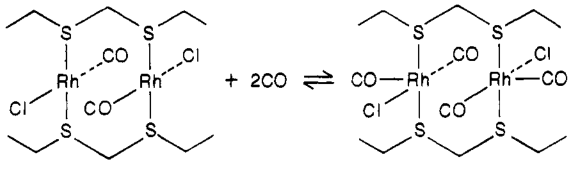
R = CO_2Me

The ability of metal complexes of the cobalt triad to promote the trimerization of alkynes is well-established. Synthetic applications of monomeric cyclopentadienyl derivatives of cobalt have been developed extensively by Vollhardt and co-workers.[26] Related monomeric derivatives of cobalt, rhodium, and iridium have also been studied.[27-29] The simple dimeric rhodium complex $Rh_2(CO)_4Cl_2$ has been found to trimerize internal alkynes. Benzoquinones and cyclopentadienones were also formed.[30] A possible intermediate in the trimerization process has been characterized by X-ray diffraction and found to be a tetrameric complex $[C_4R_4Rh(CO)(\mu\text{-}Cl)_2Rh]_2$, in which two metallocyclopentadiene units are stabilized by η^2,π-bonding to neighboring rhodium ions.[31] In the context of these studies the alkyne trimerizations by I and II are logical extensions of the reactivity of rhodium(I) derivatives. However the reactivity of the thioether bridged derivatives presents an interesting contrast to that of the phosphine coordinated analogues. Several important differences are apparent, and these may help in assessing the relative roles of the phosphorous- and sulfur-donor ligands in controlling reactivity at a metal ion.

Both *trans*$[RhCl(CO)(DPM)]_2$ and $Rh_2Cl_2(\mu\text{-CO})(DPM)_2$ react with activated alkynes to form $Rh_2Cl_2(\mu\text{-CO})(\mu\text{-alkyne})(DPM)_2$.[32] The loss of CO from the former reactant is proposed to proceed by a rather complex mechanism involving Cl^- dissocation. In contrast, the reaction of $[RhCl(CO)(ETM)]_2$ with an activated alkyne results in the addition of the acetylene to the rhodium coordination sphere to form III. The results seem consistent with the greater steric accessibility of the metal ions in the bis(thioether) derivatives compared to the phosphine analogues, as indicated by the X-ray diffraction studies.

The facile dissociation of bis(thioether) ligands from I as well as the ability of the Rh ions in I to expand their coordination spheres may be important factors in the different catalytic reaction chemistry observed for I compared to that of the phosphine analogues. While the alkyne adduct of the thioether complex, III, undergoes a further reaction with acetylene to form trimerization products, the phosphine-coordinated adduct $Rh_2Cl_2(\mu\text{-CO})(DPM)_2DMA$ does not react with additional DMA. This is somewhat surprising since the parent complex $[Rh_2Cl_2(\mu\text{-CO})(DPM)_2]$ does catalyze the cyclotrimerization of this alkyne. The formation of the DMA adduct in the phosphine system appears to inhibit the trimerization process, which is proposed to proceed by initial insertion of the alkyne into the Rh–Cl bond.[32] Nonactivated alkynes are not trimerized by the phosphine system. The mechanistic features of the alkyne trimerization by the thioether systems are of interest, and further attempts to characterize the nature of the interaction of alkynes with I and II are in progress.

Reaction of I with Carbon Monoxide. Complex I undergoes a color change from red to yellow under an atmosphere of carbon monoxide. The infrared spectrum of a $CHCl_3$ solution of I under CO shows new stretches at 2090 and 2015 cm^{-1}. The spectral changes are largely reversed after the solution is purged with nitrogen and evacuated. Reaction of I with ^{13}CO results in the formation of the completely exchanged ^{13}CO adduct with IR bands at 2050 and 1978 cm^{-1}. Purging this solution leads to the formation of I with ^{13}CO incorporation (ν_{CO}, 1940 cm^{-1}). The yellow carbon monoxide adduct was found to be a nonconductor in acetone. The data suggest that carbon monoxide reversibly adds to the coordinatively unsaturated metal centers in I to form $Rh_2Cl_2(CO)_4(ETM)_2$ (eq 1). The ^{13}C NMR spectrum of I in deuterioacetone under an atmosphere of ^{13}CO at room temperature shows a single sharp resonance for the CO adduct at 182 ppm (no Rh–C coupling), consistent with the occurrence of a rapid CO exchange process. At −90 °C this resonance broadens, but we were unable to reach a temperature at which inequivalent CO resonances were resolved. Spectroscopic evidence for displacement of the bis(thioether) ligands during the course of reaction 2 to form $Rh_2(CO)_4(\mu\text{-}Cl)_2$[33] was not observed.



(2)

The reaction of I with CO contrasts with the behavior of the phosphine analogues. $[RhCl(CO)(DPM)]_2$ does not react with carbon monoxide, while in the reaction of $Rh_2Cl_2(\mu\text{-CO})(DPM)_2$, halide loss occurs to form the cationic derivative $[Rh_2(CO)_2(\mu\text{-}Cl)(\mu\text{-CO})(DPM)_2]^+$.[19]

The ability of complex I to add CO leads to further synthetic applications in the trimerization reactions. Under an atmosphere of an acetylene/carbon monoxide mixture (approximately 1:1), complex I does not produce

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(26) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. Hillard, R. L.; Vollhardt, K. P. C. *Tetrahedron* **1980**, *36*, 2435. Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41.

(27) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123. Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 169.

(28) Abdulla, K.; Booth, B. L.; Stacey, C. *J. Organomet. Chem.* **1985**, *293*, 103 and references within.

(29) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. P. *Inorg. Chem.* **1968**, *7*, 1298.

(30) (a) Maitlis, P. M.; McVey, S. *J. Organomet. Chem.* **1965**, *4*, 254. (b) Maitlis, P. M.; McVey, S. *J. Organomet. Chem.* **1969**, *19*, 169. (c) Kang, J. W.; McVey, S.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3189.

(31) Bateman, L. R.; Maitlis, P. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 7292.

(32) (a) Cowie, M.; Southern, T. G. *J. Organomet. Chem.* **1980**, *193*, C46. (b) Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246.

(33) McCleverty, J. A.; Wilkinson, G. *Inorg. Syn.* **1966**, *8*, 211.

benzene at room temperature. However, when the reaction mixture is heated to 60–70 °C in wet acetonitrile, a new product is observed that has been identified as *p*-hydroquinone. The reaction of 1-butyne and CO with I under similar conditions resulted in the formation of diethyl-substituted *p*-hydroquinones. Integration of the NMR spectrum of the products indicates that the reactions are stoichiometric under these mild conditions. Approximately 1 equiv of hydroquinone is produced per mole of complex I. The catalytic synthesis of hydroquinone from acetylene, carbon monoxide, and water has been effected previously under much more rigorous conditions (>100 atm, 200 °C) by catalysts derived from $Ru_3(CO)_{12}$,[34] from $Fe(CO)_5$,[35] and from $[Rh(CO)Cl]_2$.[34]

The effect of varying the nature of the hydrogen donor in the rhodium thioether systems has been investigated briefly. Water may participate in the hydroquinone formation in several ways. For example, we have verified in separate experiments that benzoquinone is reduced to hydroquinone by complex I in wet acetonitrile. However, when the reaction of I with alkyne and carbon monoxide is carried out under anhyhdrous conditions, no benzoquinone products are observed. It therefore appears that water plays a role at an earlier stage of the cyclocondensation reaction. The reaction of water with carbon monoxide to form hydrogen and carbon dioxide is catalyzed by many group 8–10 complexes, and this water gas shift reaction has been proposed previously as a step in catalytic hydroquinone syntheses.[35] However the reaction of I and acetylene with a CO/H_2 mixture (~1 atm) in dry acetonitrile produced only trace amounts of hydroquinone, which may be a result of a residual water impurity. Studies of the reactivity of I in the water gas shift reaction will be necessary in order to further evaluate the respective roles of water and hydrogen in this hydroquinone synthesis.

Experimental Section

$Rh_2Cl_2(CO)_4$ was purchased from Aldrich. Most alkynes and carbon monoxide were purchased from commercial suppliers and used without purification. Propyne was purified by two distillations through a −131 °C trap to remove the acetylene contaminant. All solvents were degassed prior to use, and the synthetic reactions were carried out under a nitrogen atmosphere in standard Schlenkware. Proton NMR spectra were recorded at 90 MHz on a Varian 390 spectrometer or a JOEL FX-90Q spectrometer. Chemical shifts are referenced to CD_2HCN (δ 1.93). ^{13}C NMR spectra were recorded at 22.6 MHz on the JEOL instrument or at 62.9 MHz on a Bruker WM250 spectrometer. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer by using Nujol mulls on KBr plates or chloroform solutions in 0.12-mm NaCl cells. Conductivities were measured with a Serfass conductivity bridge Model RC M15 and a Yellow Springs Instruments platinized conductivity cell Model 3403. The conductivity data were obtained at sample concentrations of 10^{-3} M in acetone. A 0.010 M potassium iodide solution were measured as a standard 1:1 electrolyte. Mass spectra were obtained on a VG Analytical 7070 EQ-HF double quadrupole mass spectrometer. GC/MS analyses were carried out by using a Hewlett-Packard 5790A gas chromatograph and the VG Analytical mass spectrometer. A Hewlett-Packard HP-1 cross-linked methylsilicone gum capillary column was used. Elemental analyses were provided by Spang Laboratory.

X-ray Diffraction Studies. Crystals of complexes I and II grown from acetonitrile were selected and mounted on glass fibers by using epoxy resin. Axial photographs indicated that I had monoclinic and II had orthorhombic symmetry. This was confirmed by analysis and averaging of equivalent reflections. Space groups were determined from systematic absences. Because of the low values of μ and the uniform shape of the crystals, no absorption corrections were applied. For both molecules, all non-hydrogen atoms were refined anisotropically. For complex I the hydrogen atoms were located and included in idealized positions riding on the atoms to which they were attached (d(C–H) = 0.96 Å). The methyl hydrogens were treated as rigid groups allowed to rotate about the C(6)–C(5) bond. All hydrogens were given fixed isotropic thermal parameters equal to 1.2 times the thermal parameter of the atom to which they were attached. For II, the correct enantiomer was determined[36] and is reported in this paper. Details of the crystal data, experimental conditions, and a summary of solution and refinement details for the structural studies of complexes I and II are given in Table V.

Preparation of $CH_3CH_2SCH_2SCH_2CH_3$ (ETM). The synthesis of this compound was carried out according to a published procedure for $CH_3SCH_2SCH_3$[37] by substituting ethanethiol for methanethiol. ^1H NMR (CD_3CN): δ 1.23 (t, 6 H), 2.64 (q, 4 H), 3.76 (s, 2 H).

Preparation of *trans*-$Rh_2Cl_2(CO)_2(ETM)_2$ (I). $[Rh_2Cl_2(CO)_4]$ (0.11 g, 0.28 mmol) was added to ca. 25 mL of hexane in a 100-mL Schlenk flask, and the solution was heated at 50 °C. ETM (8 μL, ca. 0.5 mmol) in 5 mL of benzene was syringed into the solution, and the solution was stirred for 2 h. The solvent was then removed under vacuum, and the product was washed with hexane to remove unreacted $Rh_2Cl_2(CO)_4$ and ETM. The resulting red solid product was obtained in approximately 80% yield. ^1H NMR (CD_3CN): δ 1.43 (t, 12 H), 3.05 (q, br, 8 H), 4.28 (s, br, 4 H). ^{13}C NMR (CD_3CN): δ 182.0 (J_{C-Rh} = 71 Hz). IR (Nujol): ν_{CO} 1965 cm^{-1}. Anal. Calcd for $C_{12}H_{24}Rh_2Cl_2O_2S_4$: C, 23.81; H, 4.00; Cl, 11.71; S, 21.19. Found: C, 23.85; H, 4.01; Cl, 11.78, S, 20.85.

Preparation of $[Rh_2Cl_2(\mu\text{-}CO)(ETM)_2]$ (II). $[RhCl(CO)(ETM)]_2$ (0.15 g, 0.24 mmol) was added to ca. 25 mL of acetonitrile in a 100-mL Schlenk flask, and 5 mL of acetonitrile solution of $(CH_3)_3NO{\cdot}2H_2O$ (0.0300 g, 0.27 mmol) was introduced. The initial red solution turned green in a few minutes. The solution was stirred for 10 min. The volume of the solution was reduced in vacuo to approximately 5 mL to precipitate a green solid. The solution was filtered through a medium porosity frit, and the product was washed with diethyl ether. Yield: 70%. ^1H NMR (CD_3CN): δ 1.44 (t, 12 H), 3.10 (q, 8 H), 3.40–3.75 (m, 4 H). IR (Nujol): ν_{CO} 1805 cm^{-1}. Anal. Calcd for $C_{11}H_{24}Rh_2Cl_2OS_4$: C, 22.88; H, 4.20; Cl, 12.28; S, 22.21. Found: C, 22.74; H, 4.34; Cl, 12.35; S, 22.02.

Preparation of $Rh_2Cl_2(CO)_2(ETM)_2(CH_3O_2CC{\equiv}CCO_2CH_3)$ (III). Complex I (30 mg, 0.050 mmol) was dissolved in ca. 15 mL of acetonitrile in a 100-mL Schlenk flask. About 3 equiv of dimethyl acetylenedicarboxylate (DMA) in 5 mL acetonitrile was added. The solution was stirred for 5 min. The red product was precipitated out of solution by diffusion of diethyl ether. (At longer reaction times additional products were observed; these have not been completely characterized.) ^1H NMR (CD_3CN): δ 1.30 (m, 12 H), 2.97 (m, 8 H), 3.65 (m, 6 H), 3.92 (m, 4 H). IR (Nujol): ν_{CO} 2070, 1995 cm^{-1}; ν_{CO_2} 1700 cm^{-1}; $\nu_{C{=}C}$ 1590 cm^{-1}. Λ_m (10^{-3} M in acetone) = 8.75 Ω^{-1} cm^2 mol^{-1}.[38] Anal. Calcd for $C_{18}H_{30}Rh_2Cl_2S_4O_6$: C, 28.92, H, 4.05, Cl, 9.49; S, 17.16. Found: C, 28.73; H, 4.17; Cl, 9.38; S, 17.02. No cyclotrimerized product was observed in an NMR tube experiment monitored by ^1H NMR spectroscopy.

Cyclotrimerization Reactions. The cyclotrimerization of $RC{\equiv}CH$ (R=H, CH_3, CH_2CH_3, Ph, $CO_2CH_2CH_3$) was carried out in a sealed NMR tube. Complex I (ca. 15 mg) was dissolved in ca. 0.5 mL of CD_3CN. The solution was twice freeze–pump–thaw degassed. Excess alkyne was then introduced at room temperature. The reactions were carried out at room temperature except that of R=$CO_2CH_2CH_3$, which required a reaction temperature of 60 °C. Reactions were monitored by ^1H NMR spectroscopy.

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[34] Pino, P.; Braca, G. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1977; Vol. 2, p 419.

[35] Reppe, W.; Von Kutepow, N.; Magin, A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 727.

[36] Rogers, D. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, 734.

[37] Brandsma, L.; Vermer, P.; Kooijman, J. G. A.; Boelens, H.; Malssen, J. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 730.

[38] Typically a 1:1 electrolyte in acetone gives a value between 100 and 140 Ω^{-1} cm^2 mol^{-1}: Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table V. Crystal Data and Details of the Structure Determination for [RhCl(CO)(ETM)]$_2$, I, and [Rh$_2$Cl$_2$(μ-CO)(ETM)$_2$], II

	I	II
	Crystal Data	
formula	$C_{12}H_{24}O_2Cl_2S_4Rh_2$	$C_{11}H_{24}OCl_2S_4Rh_2$
mol. wt.	605.294	577.284
space group[a]	*C*2/*c*	*P*2$_1$2$_1$2$_1$
cryst syst	monoclinic	orthorhombic
a,[b] Å	17.224 (5)	9.777 (2)
b, Å	7.699 (2)	13.710 (2)
c, Å	16.296 (5)	14.695 (2)
α, deg	90	90
β, deg	104.79 (2)	90
γ, deg	90	90
V, Å^3	2089.5 (6)	1969.7 (6)
Z	4	4
d (calcd), g/cm^3	1.92	1.95
F(000)	1199.9	1143.94
μ, cm-1	21.72	22.96
	Data Collection and Reduction	
diffractometer	Syntex P3/F	Syntex P3/F
radiatn, Å	Mo Kα (0.71069)	Mo Kα (0.71069)
takeoff angle for graphite monochromator, deg	4.0	4.0
temp, K	295–298	295–298
cryst habit (needles, plates, etc.)	parallepiped	parallepiped
cryst color	red	green
cryst dimens, mm	0.3 × 0.3 × 0.35	0.3 × 0.25 × 0.28
scan technique	θ–2θ	θ–2θ
2θ, min, max, deg	3.0, 58.0	3, 58
hkl values scanned	$\pm h,\pm k,\pm l$	$\pm h,\pm k,\pm l$
scan speed, deg/min	3.9–59	3.9–59
scan range, deg below $K\alpha_1$ and above $K\alpha_2$	1.0, 1.0	1.0, 1.0
background	stationary crystal–stationary counter background time = 0.50 scan time	
check reflcns	4	4
freq	every 96 measurements	
variatn	random, net 0% decay	
no. of reflcns measd	13475	12978
no. of unique reflcns	3071	1838
agreement factor during averaging[c]	0.01	0.04
no. of obsd reflcns	2823	1796
σ criterion	$F > 6\sigma(F)$	$F > 6\sigma(F)$
absorption correcn	None	None
transmissn factors	0.89, 0.99	0.89, 0.99
	Structure Determination and Refinement	
method of phase determination	direct methods	direct methods
programs	SHELXTL[d]	SHELXTL[d]
scattering factors	neutral atoms[e]	neutral atoms[e]
R and *wR*[f] for obsd data	0.019, 0.024	0.0434, 0.0607
for all data	0.022, 0.025	0.0465, 0.0767
weight	$1.0/(\sigma^2(F) + 0.00007FF)$	$1.0/(\sigma^2(F) + 0.002FF)$
no. of parameters	107	182
ratio of observns to parameters	28/1	9.9/1
esd of observn of unit weight	1.662	1.271
av shift/error	0.002	0.002
max shift/error	0.011	–0.008
obsd for	*Z*/*c* of C5	U_{22} of C10
residual electron dens *e*/Å^3	0.5, 0.8 Å from Rh1	1, 1.21 Å from Rh1 and 1.09 Å from S4 along the Rh2–S4 bond

[a] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1965; Vol. 1. [b] Cell dimensions were determined by least-squares fit of the setting angles of 25 reflections with 2θ in the range 32.0–39.0. [c] $R_{\text{merge}} = SQRT[\sum N(\sum[w(F_{\text{mean}} - F)^2])/\sum((N-1)\sum[wF^2])]$ [d] G. M. Sheldrick, SHELXTL, A Program For Crystal Structure Determination, Version 5.1, 1985, Nicolet Analytical Instruments; Madison, WI. [e] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4. [f] The quantity minimized in the least-squares procedures is $\sum[w(|F_o| - |F_c|)^2]$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, and $R_2 = \sum[w(|F_o| - |F_c|)^2]/\sum[w(F_o)^2]$

When 3–6 equiv of alkyne were used, reaction times of 1–5 days were required for complete trimerization. The products were extracted with diethyl ether and characterized by ^{1}H NMR, MS, and GC/MS spectroscopic data. (i) Trimethylbenzene from HC≡CCH$_3$: ^{1}H NMR (CD$_3$CN) δ 7.06 (m), 2.21 (s), for 1,2,4-trimethylbenzene; δ 6.88 (s), 2.21 (s) for 1,3,5-trimethylbenzene; the ratio of 1,2,4- to 1,3,5-trimethyl benzene is 4.7:1; MS, *m*/*e* 120 (P), 105 (P – CH$_3$). (ii) Triethylbenzene from HC≡CCH$_2$CH$_3$: ^{1}H NMR δ 7.1 (m), 2.6 (q), 1.17 (m); MS, *m*/*e* 162 (P), 147 (P – CH$_3$), 133 (P – CH$_2$CH$_3$); ratio of 1,2,4- to 1,3,5-isomer is 7.7 to 1, determined by GC/MS. (iii) Triphenylbenzene from HC≡CPh: ^{1}H δ 7.3–7.8 (m); MS, *m*/*e*, 306 (P). (iv) 1,3,5- and 1,2,4-triethylbenzene carboxylate from HC≡CCO$_2$Et: ^{1}H NMR (CD$_3$CN) of 8.77 (s), 4.42 (q), 1.40 (b); MS *m*/*e* 294 (P), 249 (P – OCH$_2$CH$_3$), 221 (P – CO$_2$CH$_2$CH$_3$).

Reactions with the Mixture of CH$_3$O$_2$CC≡CCO$_2$CH$_3$ (DMA) and HC≡CH. Complex I or II (ca. 10 mg) was dissolved in ca. 0.5 mL of CD$_3$CN in an NMR tube, and 3 equiv of DMA were added. The solution was twice freeze–pump thaw degassed. Acetylene (0.5 atm) was introduced at room temperature, and the tube was sealed at –196 °C. The reaction was monitored by ^{1}H NMR spectroscopy. The cocyclotrimerized products were isolated by removing solvent and extracting with diethyl ether and were characterized by ^{1}H NMR spectroscopy and mass spectroscopy.

The products were identified as dimethyl phthalate and 1,2,3,4-benzenetetracarboxylic acid tetramethyl ester (ca. 2:1 ratio). A small amount of benzene was also formed. ^{1}H NMR (CD_3CN): δ 7.74 (m), 3.85 (s) for dimethyl phthalate; δ 8.13 (s), 3.85 (s) for the 1,2,3,4-tetramethyl ester. MS: Dimethyl phthalate, *m/e* 194 (P), 163 (P − OCH_3) 1,2,3,4-tetramethyl ester, *m/e* 310 (P), 279 (P − OCH_3). $Rh_2Cl_2(CO)_2(ETM)_2(DMA)$, III, also reacted with acetylene (0.5 atm) to give the same products. In this case, the ratio of dimethyl phthalate to 1,2,3,4-tetramethyl ester to benzene was 2:1:2.

Reactions of I and II with Carbon Monoxide (i) Complex I (10 mg, 0.016 mmol) was dissolved in ca. 1 mL of $CHCl_3$, and CO was bubbled into the solution. The color of the solution changed immediately from red to yellow. The IR spectrum of this solution showed two carbonyl stretches at 2100 and 2020 cm^{-1}. When ^{13}CO was used in the place of CO, bands for the ^{13}CO exchanged product were observed at 2050 and 1978 cm^{-1}. This complex is assigned as $Rh_2Cl_2(CO)_4(ETM)_2$. Λ_M (10^{-3} M in acetone): 8.86 Ω^{-1} cm^2 mol^{-1}. ^{13}C NMR (acetone-d_6): 182 ppm. The tetracarbonyl complex is largely converted back to I upon bubbling N_2 through the solution. The IR spectrum of complex I in $CHCl_3$ showed a band at 1985 cm^{-1}. The ^{13}CO-exchanged product of complex I in $CHCl_3$ showed an IR band at 1940 cm^{-1}. (ii) Complex II (10 mg, 0.017 mmol) was dissolved in ca. 1 mL of $CHCl_3$, and CO was introduced a bubble at a time until the color of the solution changed from green to red. The IR analysis of this solution showed bands for both $Rh_2Cl_2(CO)_4(ETM)_2$ (2100, 2020 cm^{-1}) and complex I (1985 cm^{-1}). Then, excess CO was bubbled into the solution, and the color of the solution became yellow. The IR spectrum showed CO stretches only at 2100 and 2020 cm^{-1}.

Reaction of I with the Mixture of $HC\equiv CH$ and CO. Complex I (25 mg, 0.041 mmol) was dissolved in ca. 0.5 mL of *wet* CD_3CN in an NMR tube. The solution was twice freeze–pump–thaw degassed. Then, 0.5 atm of acetylene and 0.5 atm of CO were introduced at room temperature and at −196 °C, respectively. The NMR tube was sealed, and the reaction was monitored by ^{1}H NMR spectroscopy. At room temperature, a singlet at 7.32 ppm was observed. When the solution was heated at 60 °C, for 1 day, resonances at 6.67 and 6.36 ppm appeared and the color of the solution changed from yellow to red. The product with proton resonances at 6.67 and 6.36 ppm was characterized as *p*-hydroquinone. Yield: 0.9 mol/mol of I. Addition of an authentic sample of *p*-hydroquinone to the product solution showed an increase in the assigned resonances. In a separate experiment, the *p*-hydroquinone was isolated and analyzed by MS: *m/e* 110 (P), 81 (P − COH), 55 (P − C_2H_2COH). The other products were not completely characterized.

Reaction of I with the Mixture of $HC\equiv CCH_2CH_3$ and CO. Complex I (10 mg, 0.016 mmol) was dissolved in ca. 0.5 mL of CD_3CN in NMR tube, and ca. 2 equiv of $HC\equiv CCH_2CH_3$ were syringed into the solution. The solution was twice freeze–pump–thaw degassed. Then, 0.5 atm of CO was introduced at −196 °C, and the NMR tube was sealed. The ^{1}H NMR spectrum showed no reaction had occurred at room temperature. The solution was heated at 70 °C. Proton resonances were observed at 7.07 (m), 2.5 (doublets), and 1.1 (t) ppm. The product was characterized as 2,5- or 2,6-diethyl-*p*-hydroquinone. Yield: 0.8 mol/mol I. MS: *m/e* 166 (P), 149 (P − OH). The rhodium-containing product was not completely characterized.

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Registry No. I, 109391-65-3; II, 109391-66-4; III, 109391-67-5; $Rh_2Cl_2(CO)_2$, 14523-22-9; $HC\equiv CH$, 74-86-2; $CH_3C\equiv CH$, 74-99-7; $CH_3CH_2C\equiv CH$, 107-00-6; $PhC\equiv CH$, 536-74-3; $CH_3CH_2CO_2C\equiv CH$, 623-47-2; $Rh_2Cl_2(CO)_4(ETM)_2$, 109391-68-6; DMA, 762-42-5; *p*-hydroquinone, 123-31-9; 2,5- or 2,6-diethyl-*p*-hydroquinone, 109391-69-7; 1,3,5-trimethylbenzene, 108-67-8; 1,2,4-trimethylbenzene, 95-63-6; 1,2,4-triethylbenzene, 877-44-1; 1,3,5-triethylbenzene, 102-25-0; 1,3,5-triethylbenzene carboxylate, 4105-92-4; 1,2,4-triethylbenzene carboxylate, 14230-18-3; dimethyl phthalate, 131-11-3; tetramethyl 1,2,3,4-benzenetetracarboxylate, 3451-02-3; triphenylbenzene, 32718-86-8; Rh, 7440-16-6.

Supplementary Material Available: A table of hydrogen atom coordinates and isotropic thermal parameters for $[RhCl(CO)(ETM)]_2$, I, and tables of anisotropic thermal parameters for the structures of I and $Rh_2Cl_2(\mu\text{-}CO)(ETM)_2$, II (3 pages); tables of observed and calculated structure factors for I and II (30 pages). Ordering information is given on any current masthead page.