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# Spontaneous and Induced Carbonylation of $(C_5Me_4Et)_2Ru_2S_4$

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*Summary:* $Cp^*{}_2Ru_2S_4$ ($Cp^* = C_5Me_4Et$, **1**) reacts with CO to give $Cp^*{}_2Ru_2S_4(CO)_x$ ($x$ = 1, 2), the first example of metal-centered addition to a cyclopentadienylmetal sulfide. **1** can be carbonylated under ambient conditions in the presence of $PBu_3$, as a sulfur-abstracting agent, to give $Cp^*{}_2Ru_2S_2(CO)_2$. Sequential addition of $PBu_3$ and CO to a solution of **1** fails to give any carbonylated products. A variety of new $Cp^*{}_2Ru_2S_x(CO)_y$ compounds are formed in the thermal as well as the photochemical reactions of $Cp^*{}_2Ru_2(CO)_4$ and elemental sulfur.

Organometallic sulfides of the type $Cp_2M_2S_4$ have elicited considerable attention in the area of small molecule activation and cluster synthesis.[1-3] All known addition reactions of dimeric cyclopentadienylmetal sulfides result in the binding of the addend to the sulfur atoms. On the basis of our studies on the insertion reactions of $Cp_2TiS_5$ we have suggested that many *apparent* additions to the sulfur centers may in fact result from the facile migration of substrates from the metal to the coordinated sulfide.[4] This suggestion is now supported by our finding that carbon monoxide adds to the metal centers in $Cp^*{}_2Ru_2S_4$ to give a series of dimeric ruthenium carbonyl sulfides.

Toluene solutions of $Cp^*{}_2Ru_2S_4$ ($Cp^* = C_5Me_4Et$, 1) react completely with carbon monoxide (≥4 atm) at 60 °C. No reaction occurs at room temperature under the same conditions. The progress of the carbonylation can be easily monitored by reverse-phase HPLC[5] (Figure 1). The principal product is $Cp^*{}_2Ru_2S_4(CO)_2$ [$1(CO)_2$] which can be isolated as dark blue-green microcrystals after flash chromatography (66% yield). $1(CO)_2$ was characterized by elemental analysis and spectroscopic methods.[6] The formulation is further supported by FD mass spectrometry which shows a molecular ion peak at $m/z$ 686. The 300-MHz $^1H$ NMR spectrum features a quartet, two singlets, and a triplet in a 2:6:6:3 ratio, indicating that the Cp* groups are equivalent and that they are bisected by a time-averaged plane of symmetry. The observation of a single $\nu_{co}$ band in the IR spectrum (1958 $cm^{-1}$, hexane) indicates that $1(CO)_2$ possesses an inversion center consistent with the structure *trans*-1,4-$[Cp^*Ru(CO)]_2S_4$. The crystallographic characterization of the analogous *trans*-1,4-$[(MeCp)Ru(PPh_3)]_2S_4$ was described by us last year.[7]

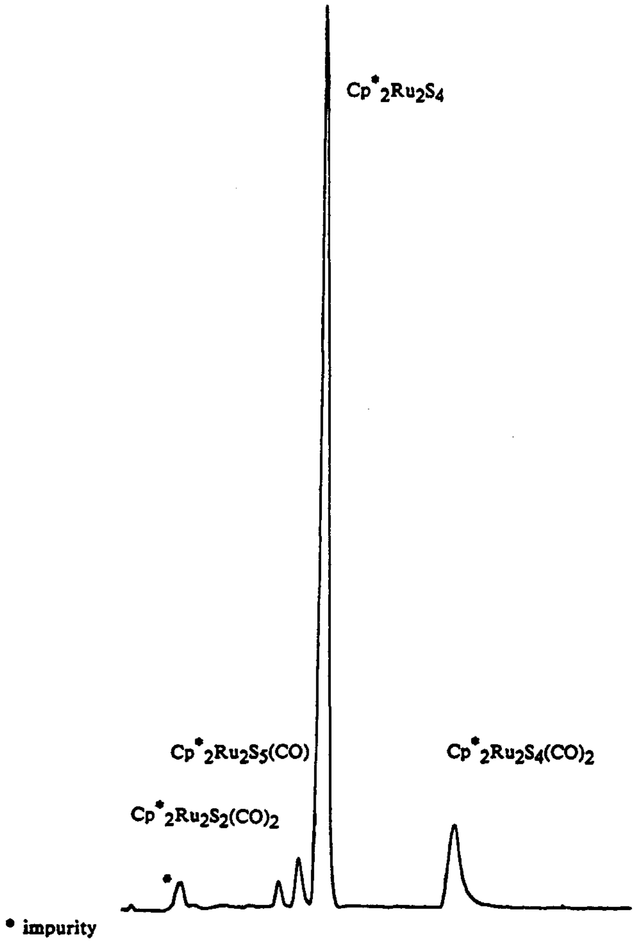

**Figure 1.** HPLC trace from an early stage in the carbonylation of 1 to $1(CO)_2$.

Solutions of $1(CO)_2$ undergo decarbonylation (80 °C, toluene) to give the air-sensitive pine-green monocarbonyl $Cp^*{}_2Ru_2S_4(CO)$ [$1(CO)$] in 90% yield.[8] This monocarbonyl may be converted to the dicarbonyl $1(CO)_2$ upon treatment with CO (30 atm) at 60 °C (eq 1). The $^1H$ NMR spectrum of 1(CO) shows a multiplet ($CH_2CH_3$), four singlets ($CH_3$), and another multiplet ($CH_2CH_3$), indicating that the Cp* groups are nonequivalent but that both are bisected by a plane of symmetry. The IR spectrum shows two $\nu_{co}$ bands at 1970 and 1932 $cm^{-1}$ (hexane). The low frequency of the $\nu_{co}$ band indicates the presence of a relatively electron-rich metal center.[9] The analogous $(C_5H_4Me)_2Fe_2S_4(CO)$ exists as both trans (1950 $cm^{-1}$) and cis (1985 $cm^{-1}$, $C_6H_{12}$ solution) isomers in solution. The structure of the latter compound features nonequivalent CpFe centers bridged by a pair of $\eta^1,\eta^2$-$S_2$ moieties.[10]

While solutions of 1 are unreactive toward CO at room temperature, a rapid reaction ensues when the sulfur abstracting agent $(n\text{-}Bu)_3P$ is added. In a typical experiment,

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[1] Weberg, R. T.; Haltiwanger, R. C.; Laurie, J. C. V.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242 and references within. Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6138.

[2] Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114.

[3] Darkwa, J.; Lockemeyer, J. R.; Boyd, P. D. W.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 141. Bolinger, C. M.; Weatherill, T. D.; Rauchfuss, T. B.; Rheingold, A. L.; Day, C. M.; Wilson, S. R. *Inorg. Chem.* **1986**, *25*, 634. Curtis, M. D.; Williams, P. D. *Inorg. Chem.* **1983**, *22*, 2661. Cowans, B. A.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1987**, *6*, 995. Wachter, J. *J. Coord. Chem.* **1987**, *15*, 219.

[4] Giolando, D. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 6455. Giolando, D. M.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1987**, *6*, 667.

[5] The HPLC setup consists of a Varian 2510 pump, Varian 2550 variable wavelength detector, and a Spectraphysics integrator. Samples were analyzed at 580 nm by using HPLC grade acetonitrile as the mobile phase and a reverse-phase phenyl-capped C10 column (15 cm, 0.5 μm packing) as the stationary phase. The flow rate was 1 mL/min.

[6] Anal. Calcd: C, 42.06; H, 5.00. Found: C, 42.47; H, 5.12. FDMS ($m/z$, $^{102}Ru$): 686 ($P^+$), 658 ($P^+ - CO$). $^1H$ NMR ($C_6D_6$): $\delta$ 2.17 (q, 4 H), 1.62 (s, 12 H), 1.42 (s, 12 H), 0.90 (t, 6 H). IR (hexane): 1958 $cm^{-1}$.

[7] Amarasekera, J.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 2017.

[8] FDMS ($m/z$, $^{102}Ru$): 658 ($P^+$), 690 ($P^+ + S$), 630 ($P^+ - CO$). $^1H$ NMR ($C_6D_6$): $\delta$ 2.09 (m, 4 M), 1.64 (s, 6 H), 1.62 (s, 6 H), 1.44 (s, 6 H), 1.43 (s, 6 H), 0.81 (m, 6 H). IR (hexane): 1970, 1932 $cm^{-1}$.

[9] Ru(S-2,3,5,6-$Me_4CH)_4$(CO) $\nu_{co}$ ($CHCl_3$) 2040 $cm^{-1}$: Millar, M. M.; O'Sullivan, T.; de Vries, N.; Koch, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3714. $(C_5Me_4Et)Ru(CO)Br$ $\nu_{co}$ ($CH_2Cl_2$) 2050 $cm^{-1}$: Nowell, I. W.; Tabatabaian, K.; White, C. *J. Chem. Soc., Chem. Commun.* **1979**, 547.

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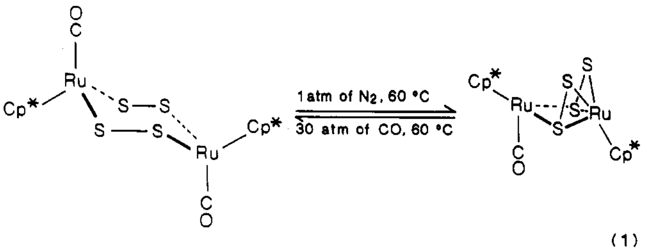
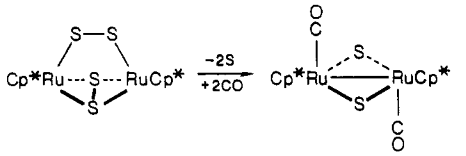


(1)

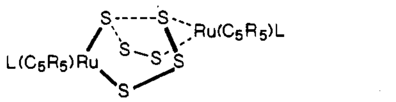
a solution of 21.3 $\mu$L of $(n\text{-Bu})_3P$ (2.3 equiv) in 10 mL of CO-saturated toluene was slowly added dropwise to a solution of 24.4 mg of 1 in 25 mL of CO-saturated toluene. The phosphine discharges the intense blue color characteristic of 1 resulting in a pale yellow solution. After several hours, the golden brown product was purified by filtration through silica gel and recrystallization from $CH_2Cl_2$/hexane. Elemental analysis and FDMS indicate the formulation $Cp*_2Ru_2S_2(CO)_2$ (yield 60%).[11] $^1H$ NMR and IR spectroscopy indicate a centrosymmetric molecule which suggests the following structure (eq 2).[11] We note



(2)

that this $S_2(CO)_2$ compound would have the same number of valence electrons as Roussin's red anion $Fe_2S_2(NO)_4^{2-}$. The latter has a planar $M_2S_2$ core with a short Fe···Fe contact.[12] So far we have been unsuccessful in obtaining X-ray-quality single crystals of the dicarbonyl. Obviously the phosphine-induced carbonylation of 1 follows a different pathway than the thermal process. When 1 is treated with the phosphine in the absence of CO, a red compound is formed which is itself unreactive toward CO. These results parallel our study of the phosphine-induced reaction of 1 and acetylenes that leads to the formation of dithiolene complexes $Cp*_2Ru_2S_2C_2R_2$.[2]

Several of the compounds described above are also formed in variable yields in both the photochemical and thermal (60 °C) syntheses of 1 from $Cp*_2Ru_2(CO)_4$ and 0.5–1 equiv of $S_8$ (toluene solvent). We observed the following new compounds after standard chromatographic workup:[13] red $Cp*_2Ru_2S_5(CO)$[14] (13% yield), black-green $Cp*_2Ru_2S_6(CO)_2$[15] (variable amounts), and traces of a turquoise isomer of $Cp*_2Ru_2S_2(CO)_2$.[16] On the basis of the $^1H$ NMR spectra, the penta- and hexasulfides are chiral; the latter possesses equivalent Cp* ligands while the former has no symmetry (eight methyl singlets). Both species can be quantitatively converted to 1 by photolysis in toluene. The spectroscopic data indicate that the hexasulfide is structurally analogous to 1,5-[(MeCp)Ru(PPh$_3$)]$_2$S$_6$.[8]



1,5-[(C$_5$R$_5$)RuL]$_2$S$_6$ (L = CO, PPh$_3$; R$_5$ = H$_5$ or Me$_4$Et)

In summary, the carbonylation of 1 represents the first example of a metal-centered ligand addition to a cyclopentadienyl metal sulfide. The metal centers in $1(CO)_x$ are good $\pi$ donors and therefore provide the driving force for the carbonylation of 1 despite the relatively high formal oxidation state of Ru(III). The carbonylation of 1 involves the stepwise unfolding of the $M_2S_4$ core and demonstrates the facultative nature of the $\mu$-$S_2$ ligand. Lastly, desulfurization reagents permit the carbonylation of 1 to proceed under very mild conditions. This pattern is reminiscent of the proposed role of anion vacancies in heterogeneous metal sulfide catalysis.[17]

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**Registry No.** 1, 101953-49-5; *trans*-1(CO)$_2$, 115226-90-9; *trans*-1(CO), 115226-91-0; *cis*-1(CO), 115268-39-8; $Cp*_2Ru_2S_2(CO)_2$, 115226-92-1; $Cp*_2Ru_2(CO)_4$, 115226-93-2; $Cp*_2Ru_2(CO)_2$, 115226-94-3.

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(10) Chanaud, H.; Ducourant, A. M.; Gianotti, C. *J. Organomet. Chem.* **1980**, *190*, 201. For an update on this chemistry see: Weberg, R.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 1315. Brunner, H.; Janietz, N.; Meier, W.; Sergeson, G.; Wachter, J.; Zahn, T.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1060.

(11) Anal. Calcd: C, 46.41; H, 5.52. Found: C, 46.18; H, 5.44. FDMS ($m/z$, $^{102}$Ru): 622 ($P^+$). $^1H$ NMR ($C_6D_6$): $\delta$ 2.24 (q, 4 H), 1.69 (s, 12 H), 1.56 (s, 12 H), 0.74 (t, 6 H). IR ($CH_2Cl_2$): 1941 cm$^{-1}$.

(12) Lin, X.; Huang, J.; Lu, J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1981**, *A37*, C232.

(13) Flash chromatography was carried out by using 32–63-$\mu$m Merck silica gel eluting with toluene.

(14) Anal. Calcd: C, 40.07; H, 4.98. Found: C, 40.60; H, 5.19. FDMS ($m/z$, $^{102}$Ru): 690 ($P^+$), 658 ($P^+ - S$), 722 ($P^+ + S$), 630 ($P^+ - COS$). $^1H$ NMR ($C_6D_6$): $\delta$ 2.05 (q, 2 H), 1.86 (q, 2 H), 1.62 (s, 3 H), 1.60 (s, 3 H), 1.58 (s, 3 H), 1.56 (s, 3 H), 1.43 (s, 3 H), 1.40 (s, 3 H), 1.37 (s, 3 H), 1.33 (s, 3 H), 0.85 (t, 3 H), 0.71 (t, 3 H). IR ($CH_2Cl_2$): 1970 (sh), 1945 cm$^{-1}$. The ($C_5Me_5$) derivative of this compound has been isolated by J. Wachter and his group in Regensburg.

(15) FDMS ($m/z$, $^{102}$Ru): 750 ($P^+$), 690 ($P^+ - COS$), 658 ($P^+ - COS_2$). $^1H$ NMR ($C_6D_6$): $\delta$ 2.09 (q, 4 H), 1.61 (s, 6 H), 1.59 (s, 6 H), 1.54 (s, 6 H), 1.51 (s, 6 H), 0.75 (t, 6 H). IR ($CH_2Cl_2$): 1963 cm$^{-1}$.

(16) FDMS ($m/z$, $^{102}$Ru): 622 ($P^+$), 594 ($P^+ - CO$). $^1H$ NMR ($C_6D_6$): $\delta$ 2.31 (q, 4 H), 1.79 (s, 12 H), 1.72 (s, 12 H), 0.88 (q, 6 H).

(17) Gellman, A. J.; Bussell, M. E.; Somorjai, G. A. *J. Catal.* **1987**, *107*, 103 and references therein.

(18) **Note added in proof**: The structure of *trans*-1,4-[Cp*Ru(CO)]$_2$S$_4$ has been confirmed by single-crystal X-ray diffraction. The molecule very closely resembles *trans*-1,4-[(MeCp)Ru(PPh$_3$)]$_2$S$_4$.

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# An Appraisal of the Steric versus Electronic Requirements of Gold(I) Phosphine Substituents in Clusters: The Crystal Structure of [HFe$_4$(CO)$_{12}${AuPEt$_3$}$_2$B]

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*Summary:* The elucidation of the crystal structure of one isomer of the mixed metal boride [HFe$_4$(CO)$_{12}${AuPEt$_3$}$_2$B] illustrates that the geometry of the hexametal atom core and the location of the endo-hydrogen atom depend upon the steric, rather than electronic, requirements of the gold(I) phosphine substituents. Electronic effects, however, are responsible for the AuPR$_3$ fragment interacting with Fe–B rather than Fe–Fe bonds of the core cluster.

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