# Cationic Carboxylato Complexes of Dirhodium(II) with Oxo Thioethers: Promising Catalysts with Unusual Coordination Modes

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Removal of an acetato ligand from dirhodium(II) acetato complexes with thioethers of the general structure $[Rh_2(\mu\text{-}OAc)_4(RSCH_2Z)_2]$ yields the cationic complexes $[Rh_2(\mu\text{-}OAc)_3(RSCH_2Z)_2](BF_4)$ (R = Me, Ph; Z = C(O)OEt, $CH_2C(O)OMe$). The methylthio complex with Z = C(O)OEt has been structurally characterized and found to exhibit an unusual bidentate O−S coordination of the oxo thioether ligands. Preliminary tests indicate that the complex is a promising catalyst of the silylformylation or hydrosilylation of 1-hexyne with dimethylphenylsilane.



## Introduction

Functionalized thioethers having C−H acidic groups represent an interesting class of ligands, because in their anionic form they can combine the good coordinating properties of the sulfur atom with those of the carbon or of other donor atoms present in the functional groups. For example, it has recently been shown that palladium acetate reacts with α-substituted thioethers $RSCH_2Z$ (Z = ester, ketone, sulfone) to give trinuclear complexes of the type $[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}RSCHZ)_3]$.[1,2] This metalation reaction results from the ligand exchange process, in which the sulfur ligand, despite its lower acidity ($\Delta pK_a^{DMF} > 10$),[3,4] protonates and substitutes half of the coordinated acetato ligands. As shown by the X-ray structure of the prototype complex $[Pd_3(\mu\text{-}OAc)_3(\mu\text{-}MeSCHC(O)OEt)_3]$, the anionic ligand $MeSCHC(O)OEt^-$ bridges two palladium centers through the sulfur and the methine carbon atoms, without involving the ester group in the coordination. Moreover, in the set of six chiral donor atoms (three C−S couples) which is generated upon coordination, all atoms exhibit the same configuration (*S*,*S*,*S*,*S*,*S*,*S* or *R*,*R*,*R*,*R*,*R*,*R*). Therefore, the behavior of these potentially O−S chelating ligands appears more similar to that of the carbanionic ligands $R'SCHR^-$ (R′ = Me, Ph; R = H, $CH_2C_6F_5$)[5,6] than to that of other related anionic O−O, O−P, and O−N ligands deriving from β-dicarbonyls, β-ketophosphines, or β-ketoamines.[7−9]

There are at least two interesting points in the above reaction: (i) the bidentate coordination of the ligand blocks the configuration of the sulfur atom, which becomes a chiral center, and (ii) the synthetic procedure is very simple, which makes it potentially attractive also for other metal carboxylates.

We report here on the reaction of a series of thioethers with dirhodium(II) acetate, $[Rh_2(\mu\text{-}OAc)_4]$. This choice is based on the importance of rhodium acetate and of related neutral rhodium(II) dimers as catalysts in a very large number of organic reactions involving unstable metal−carbene intermediates (for example, C−C coupling and C−H and C−X insertion)[10] or silanes (for example silylations, hydrosilylations, or silylformylations).[11] The investigated ligands are generally oxo thioethers of the type $RSCH_2Z$ (R = Me, Ph; Z = C(O)OEt, C(O)Me, $CH_2C(O)OMe$), and some of them have already been shown to give carbon metalation in the

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reaction with palladium acetate. On the other hand, Lahuerta has proved in his extensive studies that rhodium acetate itself undergoes easy metalation with arylphosphines, forming $\mu$-P,C-bridged complexes.[12] It can be anticipated that in our case only the simple addition complexes $[Rh_2(\mu\text{-}OAc)_4(RSCH_2Z)_2]$ are obtained with all sulfur-based ligands. However, a bidentate O−S coordination of the oxo thioether can be forced by protonating or alkylating an acetato ligand to give the cationic complexes $[Rh_2(\mu\text{-}OAc)_3(RSCH_2Z)_2](BF_4)$ (R = Me, Ph; Z = C(O)OEt, $CH_2C(O)OMe$). Preliminary tests indicate that the methylthio complex with Z = C(O)OEt is a promising catalyst of the silylformylation or hydrosilylation of 1-hexyne with dimethylphenylsilane.

## Experimental Section

**General Procedures.** The reagents (Aldrich-Chemie) were high-purity products and generally used as received. Solvents were dried before use, and the reaction apparatus was carefully deoxygenated. Reactions were performed under argon, and all operations were carried out under an inert atmosphere. $EtSCH_2C(O)Me$ was synthesized by reaction in ethanol of $ClCH_2C(O)Me$ with EtSNa prepared in situ from EtSH and sodium ethoxide.[13] $PhSCH_2C(O)OEt$ was prepared by reacting $PhSCH_2C(O)OH$ with EtOH at reflux for 3 days after addition of 1 mL of concentrated HCl. Subsequently, the solvent was evaporated under reduced pressure and the final solution distilled to obtain a colorless liquid. Yield: 69%. $^1$H NMR ($CDCl_3$, $\delta$): 1.21 (t, 3H, C*H*$_3$CH$_2$O), 3.62 (s, 2H, SC*H*$_2$), 4.20 (q, 2H, CH$_3$C*H*$_2$O), 7.23−7.45 (m, 5H, Ph). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 13.6 (*C*H$_3$CH$_2$O), 36.1 (*C*H$_2$S), 60.9 (CH$_3$CH$_2$O), 126.4−134.7 (Ar), 169.1 (*C*(O)OEt). IR (KBr, cm$^{-1}$): 3050−2926 ($\nu$(CH), aliphatics and aromatics), 1730 and 1271 ($\nu$(C═O) and $\nu$(C−O), ester), 1581 ($\nu$(CC), aromatic), 1130, 1024, 739, 691. The solution $^1$H and $^{13}$C{$^1$H} NMR spectra were acquired on a Bruker DRX-400 instrument (400.13 MHz for $^1$H and 100.62 MHz for $^{13}$C) at room temperature. The chemical shifts are reported versus tetramethylsilane and were determined by reference to the residual solvent peaks, using tetramethylsilane as internal standard. The FT IR spectra were recorded on a Biorad FT S7 PC spectrophotometer at 2 cm$^{-1}$ resolution in KBr disks.

**Synthesis of the Neutral Complexes $[Rh_2(OAc)_4(RSCH_2Z)_2]$ (1−4).** Complexes **1**−**4** were obtained by reaction of $[Rh_2(OAc)_4]$ with the appropriate thioether in a 1/2 molar ratio, in toluene at room temperature under argon. They are isolated spectroscopically pure by removal of the solvent and treatment of the residue with diethyl ether and can be recrystallized from dichloromethane to give analytically pure samples.

**$[Rh_2(OAc)_4(MeSCH_2C(O)OEt)_2]$ (1).** In this typical reaction, to a suspension of $[Rh_2(OAc)_4]$ (0.30 g, 0.68 mmol) in toluene (25 mL) was added $MeSCH_2C(O)OEt$ (196 $\mu$L, 0.20 g, 1.49 mmol). The reaction mixture was stirred for 3 h, at room temperature, evaporated to small volume under reduced pressure, and treated with diethyl ether to give a purple solid, which was filtered and dried under vacuum. Recrystallization from dichloromethane afforded brilliant purple crystals. Yield: 0.41 g (84%). $^1$H NMR ($CDCl_3$, $\delta$): 1.38 (t, 3H, C*H*$_3$CH$_2$O), 1.86 (s, 6H, C*H*$_3$CO$_2^-$), 2.72 (s, 3H, C*H*$_3$S), 3.80 (s, 2H, SC*H*$_2$), 4.33 (q, 2H, CH$_3$C*H*$_2$O). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 14.1 (*C*H$_3$CH$_2$O), 17.9 (*C*H$_3$S), 23.6 (*C*H$_3$CO$_2^-$), 37.2 (S*C*H$_2$), 61.3 (CH$_3$*C*H$_2$O), 169.4 (*C*(O)OEt), 191.6 (CO$_2^-$). IR (KBr, cm$^{-1}$): 2994−2922 ($\nu$(CH)), 1738 and 1300 ($\nu$(C═O) and $\nu$(C−O), ester), 1584 and 1426 ($\nu$(CO$_2^-$)), 1179, 1024. Anal. Calcd for $C_{18}H_{32}O_{12}Rh_2S_2$: C, 30.43; H, 4.54; S, 9.03. Found: C, 30.28; H, 4.41; S, 8.88.

**$[Rh_2(OAc)_4(PhSCH_2C(O)OEt)_2]$ (2).** This compound was obtained from $[Rh_2(OAc)_4]$ (0.30 g, 0.68 mmol) and $PhSCH_2C(O)OEt$ (0.28 g, 1.42 mmol), as a purple solid from diethyl ether. Yield: 85%. $^1$H NMR ($CDCl_3$, $\delta$): 1.23 (t, 3H, C*H*$_3$CH$_2$O), 1.84 (s, 6H, C*H*$_3$CO$_2^-$), 3.93 (s, 2H, SC*H*$_2$), 4.18 (q, 2H, CH$_3$C*H*$_2$O), 7.35 and 7.70 (m, 5H, Ph). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 14.2 (*C*H$_3$CH$_2$O), 23.9 (*C*H$_3$CO$_2^-$), 38.9 (S*C*H$_2$), 61.5 (CH$_3$*C*H$_2$O), 128.4, 128.9, 129.3, 132.2 (Ph), 168.9 (*C*(O)OEt), 191.7 (*C*O$_2^-$). IR (KBr, cm$^{-1}$): 3053−2928 ($\nu$(CH)), 1721 and 1264 ($\nu$(C═O) and $\nu$(C−O), ester), 1586 and 1437 ($\nu$(CO$_2^-$)), 1140, 1028, 752, 693. Anal. Calcd for $C_{28}H_{36}O_{12}Rh_2S_2$: C, 40.30; H, 4.35; S, 7.68. Found: C, 40.76; H, 4.33; S, 8.06.

**$[Rh_2(OAc)_4(EtSCH_2C(O)Me)_2]$ (3).** This compound was obtained from $[Rh_2(OAc)_4]$ (0.30 g, 0.68 mmol) and $EtSCH_2C(O)Me$ (0.17 g, 1.44 mmol), as purple crystals from dichloromethane. Yield: 74%. $^1$H NMR ($CDCl_3$, $\delta$): 1.49 (t, 3H, C*H*$_3$CH$_2$), 1.86 (s, 6H, C*H*$_3$CO$_2^-$), 2.49 (s, 3H, C*H*$_3$C(O)), 3.12 (q, 2H, CH$_3$C*H*$_2$), 3.79 (s, 2H, SC*H*$_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 13.0 (*C*H$_3$CH$_2$), 23.8 (*C*H$_3$CO$_2^-$), 28.6 (*C*H$_3$C(O)), 29.0 (CH$_3$*C*H$_2$), 43.7 (S*C*H$_2$), 191.7 (*C*O$_2^-$), 204.5 (CH$_3$*C*(O)). IR (KBr, cm$^{-1}$): 2973−2903 ($\nu$(CH)), 1713 ($\nu$(C═O), ketone), 1591 and 1429 ($\nu$(CO$_2^-$)), 1155. Anal. Calcd for $C_{18}H_{32}O_{10}Rh_2S_2$: C, 31.87; H, 4.75; S, 9.45. Found: C, 31.68; H, 4.62; S, 9.35.

**$[Rh_2(OAc)_4(MeSCH_2CH_2C(O)OMe)_2]$ (4).** This compound was obtained from $[Rh_2(OAc)_4]$ (0.30 g, 0.68 mmol) and $MeSCH_2CH_2C(O)OMe$ (0.20 g, 1.49 mmol), as a purple solid from diethyl ether. Yield: 72%. $^1$H NMR ($CDCl_3$, $\delta$): 1.85 (s, 6H, C*H*$_3$CO$_2^-$), 2.60 (s, 3H, C*H*$_3$S), 2.96 (ct, 2H, SCH$_2$C*H*$_2$), 3.33 (ct, 2H, SC*H*$_2$CH$_2$), 3.73 (s, 3H, C*H*$_3$O). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 17.0 (*C*H$_3$S), 23.7 (*C*H$_3$CO$_2^-$), 30.8 (SCH$_2$*C*H$_2$), 32.6 (S*C*H$_2$CH$_2$), 51.8 (*C*H$_3$O), 172.7 (*C*(O)OCH$_3$), 191.7 (*C*O$_2^-$). IR (KBr, cm$^{-1}$): 2997−2922 ($\nu$(CH)), 1732 and 1256 ($\nu$(C═O) and $\nu$(C−O), ester), 1593 and 1437 ($\nu$(CO$_2^-$)), 1346, 1194. Anal. Calcd for $C_{18}H_{32}O_{12}Rh_2S_2$: C, 30.43; H, 4.54; S, 9.03. Found: C, 30.19; H, 4.46; S, 9.21.

**Reaction of the Neutral Complexes $[Rh_2(OAc)_4(RSCH_2Z)_2]$ (1, 2, and 4) with $HBF_4$ or $(Et_3O)BF_4$: Synthesis of the Complexes $[Rh_2(OAc)_3(RSCH_2Z)_2](BF_4)$ (5−7).** Complexes **5**−**7** were obtained by reaction of the appropriate neutral complexes with $HBF_4$ (**5**−**7**) or $(Et_3O)BF_4$ (**5**, **6**) in a 1/2 molar ratio, in anhydrous dichloromethane, at room temperature under argon. The complexes are spectroscopically pure, but their carbon content is always slightly low, even after recrystallization from dichloromethane, probably because of a very limited hydrolysis of the ester group.

**$[Rh_2(OAc)_3(MeSCH_2C(O)OEt)_2](BF_4)$ (5).** $[Rh_2(OAc)_4(MeSCH_2C(O)OEt)_2]$ (**1**; 0.31 g, 0.43 mmol) was dissolved in dichloromethane (25 mL), and to the resulting solution was added 118 $\mu$L of a 54% w/w solution of $HBF_4$ in diethyl ether (0.14 g of $HBF_4$, 0.86 mmol). The reaction mixture was stirred for 3 h, during which time the color changed from purple to green; evaporation to small volume under reduced pressure and treatment with diethyl ether afforded a green compound, which was filtered and dried under vacuum. Yield: 0.26 g (81%). $^1$H NMR ($CDCl_3$, $\delta$): 1.42 (t, 3H, C*H*$_3$CH$_2$), 1.83 (s, 3H, C*H*$_3$CO$_2^-$), 2.14 (s, 3H, C*H*$_3$S), 2.35 (s, 1.5H, C*H*$_3$CO$_2^-$), 3.93 (AB system, 2H, $J$ = 17.4 Hz, SC*H*$_2$), 4.70 (cm, 2H, CH$_3$C*H*$_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 14.0 (*C*H$_3$CH$_2$), 17.7 (*C*H$_3$S), 22.5 and 24.0 (*C*H$_3$CO$_2^-$), 43.2 (S*C*H$_2$), 66.2 (CH$_3$*C*H$_2$), 177.8 (*C*(O)OEt), 187.6 and 193.4 (CO$_2^-$). IR (KBr, cm$^{-1}$): 2986−2934 ($\nu$(CH)), 1730 (w, $\nu$(C═O), ester), 1657, 1570 and 1429 (CO$_2^-$), 1331, 1219, 1061. Anal. Calcd for $C_{16}H_{29}BF_4O_{10}Rh_2S_2$: C, 26.03; H, 3.95; S, 8.69. Found: C, 25.26; H, 3.95; S, 9.17.

The same reaction with $(Et_3O)BF_4$ (1 M solution in dichloromethane), instead of $HBF_4$, leads to the same compound in 71% yield.

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**$[Rh_2(OAc)_3(PhSCH_2C(O)OEt)_2](BF_4)$ (6).** This compound was obtained from $[Rh_2(OAc)_4(PhSCH_2C(O)OMe)_2]$ (**4**; 0.30 g, 0.36 mmol) and $HBF_4$ in diethyl ether (100 $\mu$L, 0.12 g of $HBF_4$, 0.73 mmol), as a green solid. Yield: 75%. $^1$H NMR ($CDCl_3$, $\delta$): 1.34 (s, 3H, C$H_3CO_2^-$), 1.52 (t, 3H, C$H_3$CH$_2$O), 2.41 (s, 1.5H, C$H_3CO_2^-$), 4.21 (AB system, 2H, $J$ = 17.7 Hz, SC$H_2$), 4.82 (bm, 2H, CH$_3$C$H_2$O), 7.54 and 7.85 (m, 5H, Ph). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 14.1 (*C*H$_3$CH$_2$), 22.5 and 23.4 (*C*H$_3$CO$_2^-$), 46.2 (CH$_3$*C*H$_2$), 66.8 (S*C*H$_2$), 125−132 (Ph), 178.6 (*C*(O)OEt), 188.3 and 193.3 (*C*O$_2^-$). IR (KBr, cm$^{-1}$): 3055−2932 ($\nu$(CH)), 1732 ($\nu$(C=O), ester), 1661, 1566 and 1443 ($\nu$(CO$_2^-$)), 1321, 1084, 750, 691. Anal. Calcd for $C_{26}H_{33}BF_4O_{10}Rh_2S_2$: C, 36.21; H, 3.85; S, 7.43. Found: C, 35.63; H, 3.52; S, 7.18.

The same reaction with $(Et_3O)BF_4$ (1 M solution in dichloromethane), instead of $HBF_4$, leads to the same compound in 71% yield.

**$[Rh_2(OAc)_3(MeSCH_2CH_2C(O)OMe)_2](BF_4)$ (7).** This compound was obtained from $[Rh_2(OAc)_4(MeSCH_2CH_2C(O)OMe)_2]$ (**4**; 0.30 g, 0.42 mmol) and $HBF_4$ in diethyl ether (118 $\mu$L, 0.14 g $HBF_4$, 0.86 mmol), as a green solid. Yield: 74%. $^1$H NMR ($CDCl_3$, $\delta$): 1.87 (s, 3H, C$H_3CO_2^-$), 2.11 (s, 3H, C$H_3$S), 2.45 (s, 1.5H, C$H_3CO_2^-$), 2.99 and 3.19 (2 cm, 4H, C$H_2$C$H_2$S), 3.14 (bt, 2H, C$H_2$CH$_2$S, AB system), 4.11 (s, 3H, C$H_3$O). $^{13}$C{$^1$H} NMR ($CDCl_3$, $\delta$): 14.7 (*C*H$_3$S), 22.9 and 24.9 (*C*H$_3$CO$_2^-$), 28.4 (CH$_2$*C*H$_2$S), 29.2 (*C*H$_2$CH$_2$S), 54.5 (*C*H$_3$O), 177.9 (*C*(O)OCH$_3$), 187.4 and 193.1 (*C*O$_2^-$). IR (KBr, cm$^{-1}$): 2953−2924 ($\nu$(CH)), 1734 ($\nu$(C=O), ester), 1688, 1642, 1564 and 1435 ($\nu$(CO$_2^-$)), 1362, 1055, 702. Anal. Calcd for $C_{16}H_{29}BF_4O_{10}Rh_2S_2$: C, 26.03; H, 3.95; S, 8.69. Found: C, 24.22; H, 3.73; S, 8.60.

**Silylformylation and Hydrosilylation Reactions.** The silylformylation reaction was performed in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. $Me_2PhSiH$, (0.31 mL, 2 mmol), 1-hexyne (0.23 mL, 2 mmol), and rhodium catalyst (0.002 mmol) were dissolved in dichloromethane (2 mL) under a CO atmosphere in a Pyrex Schlenk tube. The obtained solution was introduced in the autoclave, previously placed under vacuum (0.1 mmHg), by a steel siphon. The reactor was pressurized with 10 atm of carbon monoxide, and the mixture was stirred at room temperature for 6 h. After removal of excess CO (fume hood), the reaction mixture was diluted with pentane (10 mL), filtered on Celite, and concentrated under vacuum. The composition of the reaction mixture was determined by GLC, GC-MS, and $^1$H NMR analysis.[14] The hydrosilylation reaction was run in a Pyrex Carius tube fitted with a Corning Rotaflo tap. $Me_2PhSiH$ (0.31 mL, 2 mmol) and 1-hexyne (0.92 mL, 8 mmol) were added, under an argon atmosphere via syringe, to the rhodium catalyst (0.002 mmol). The suspension was stirred at 90 °C; after 5 h the GLC analysis showed 62% conversion of the silane. The reaction mixture was filtered on Celite and concentrated under vacuum in order to remove the excess alkyne. The isomeric composition of the reaction products was determined by $^1$H NMR analyses.[15]

**X-ray Crystallography.** Single crystals of compound **1** suitable for X-ray analysis were obtained by concentration of the corresponding solution in DCM/acetone (5/1); slow diffusion over a period of ca. 10 days at room temperature afforded purple transparent crystals. For compound **5** single crystals resulted from slow concentration at room temperature of a solution in acetone/hexane (5/1); the sample consisted of green transparent crystals growing in clumps. Cell constants were determined for both structures by least-squares refinement of 30 independent reflections. Data were measured on a four-circle Philips PW1100 (Febo System) diffractometer equipped with graphite-monochromated Mo K$\alpha$ radiation, following standard procedures. Data were collected at room temperature using the $\theta-2\theta$ scan technique to a maximum $2\theta$ value of 52°. There were no significant fluctuations of intensities, other than those expected from Poisson statistics. The intensity data were corrected for Lorentz−polarization effects and for absorption, as described by North et al.[16]

**Table 1. Summary of X-ray Crystallographic Data for Complexes 1 and 5**

| | **1** | **5** |
|---|---|---|
| empirical formula | $C_{18}H_{32}O_{12}Rh_2S_2$ | $C_{16}H_{29}O_{10}Rh_2S_2 \cdot BF_4 \cdot {}^1/_4H_2O$ |
| fw | 710.38 | 742.65 |
| cryst syst | monoclinic | monoclinic |
| space group | *I*2/*a* | *C*2 |
| *a* (Å) | 17.622(3) | 30.225(5) |
| *b* (Å) | 8.535(2) | 14.103(3) |
| *c* (Å) | 18.667(3) | 13.148(3) |
| $\beta$ (deg) | 106.32(3) | 93.08(3) |
| *V* (Å$^3$) | 2694.5(9) | 5596(2) |
| *Z* | 4 | 8 |
| calcd density (g cm$^{-3}$) | 1.751 | 1.763 |
| *F*(000) | 1432 | 2964 |
| $\lambda$ (Å) | 0.710 73 | 0.710 73 |
| temp (K) | 293(2) | 293(2) |
| abs coeff (mm$^{-1}$) | 1.434 | 1.399 |
| no. of rflns collected | 3717 | 8389 |
| no. of obsd rflns ($I > 2\sigma(I)$) | 2281 | 5351 |
| $R^a$ | 0.030 | 0.048 |
| $R_w{}^b$ | 0.071 | 0.106 |

$^a$ $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b$ $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

The structures were solved by direct methods[17] and were refined by the full-matrix least-squares method with the SHELX-97 program[18] implemented in the WinGX package.[19] All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms were placed in calculated positions with fixed, isotropic thermal parameters ($1.2U_{equiv}$ of the parent carbon atom). Molecular graphics were drawn using the ORTEP-III program program.[20] Other experimental details of crystal structure determinations, including data collection and refinement for compounds **1** and **5**, are reported in Table 1.

## Results and Discussion

The neutral complexes $[Rh_2(\mu\text{-}OAc)_4(RSCH_2Z)_2]$ (**1**, R = Me, Z = C(O)OEt; **2**, R = Ph, Z = C(O)OEt; **3**, R = Et, Z = C(O)Me; **4**, R = Me, Z = $CH_2C(O)OMe$) are obtained by a very straightforward procedure, which consists of the reaction of $Rh_2(\mu\text{-}OAc)_4$ with the proper sulfur ligand (1/1 Rh/$RCH_2Z$ ratio) in toluene. Yields are high (72−85%), and the compounds are stable both in the solid state and in solution.

The spectroscopic data do not require particular comments. The IR spectra are characterized by the presence of a pair of symmetric and asymmetric stretchings of the acetato groups in the ranges 1593−1584 and 1437−1426 cm$^{-1}$; moreover, the $\nu$(C=O) band of the thioether ligand is present at 1738−1713 cm$^{-1}$. These last values are close to those found in the free ligands, thus suggesting the absence of coordination of the oxygen atom.[21] The $^1$H and $^{13}$C NMR spectra show the

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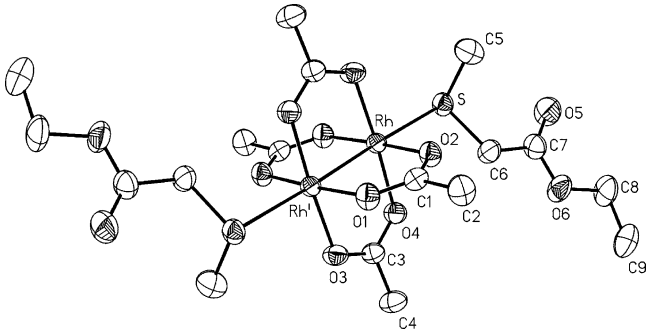


**Figure 1.** ORTEP view of the molecular structure of complex **1**.

**Table 2. Selected Bond Distances and Angles for $[Rh_2(OAc)_4(MeSCH_2C(O)OEt)_2]$ (1)[a]**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Rh−Rh′ | 2.4073(7) | Rh−O(1)′ | 2.042(3) |
| Rh−O(2) | 2.049(3) | Rh−O(3)′ | 2.045(3) |
| Rh−O(4) | 2.039(3) | Rh−S | 2.541(1) |
| S−C(5) | 1.793(6) | S−C(6) | 1.797(5) |
| **Bond Angles (deg)** | | | |
| Rh−Rh′−O(1)′ | 87.7(1) | Rh′−Rh−O(2) | 88.0(1) |
| Rh−Rh′−O(3)′ | 88.5(1) | Rh′−Rh−O(4) | 87.1(1) |
| O(1)′−Rh′−O(3)′ | 88.5(2) | O(1)′−Rh−O(4) | 91.5(2) |
| O(2)−Rh−O(3)′ | 91.5(2) | O(2)−Rh−O(4) | 88.2(2) |
| C(5)−S−C(6) | 101.7(3) | | |

[a] The slanted prime (′) indicates the symmetry transformation $1 - x, -y, 1 - z$.

expected resonances for the functional groups present in the molecule and, in particular, one singlet at 3.79−3.93 ppm of the methylene protons (complexes **1**−**3**). This indicates that the two hydrogen nuclei are magnetically equivalent and suggests that the inversion of configuration of the coordinated sulfur atom is fast at room temperature on the NMR time scale. This process remains fast also at lower temperatures, as suggested, for example, by the $^1$H NMR spectrum of **1** in $CD_2Cl_2$ at 203 K, in which only a slight broadening of the signals can be observed, without any evidence of the appearance of an AB system for the methylene protons.

The molecular structure of the complexes is fully confirmed by a single-crystal X-ray analysis of $[Rh_2(OAc)_4(MeSCH_2C(O)OEt)_2]$ (**1**). Its structure is shown in Figure 1 with the atom-labeling scheme, and Table 2 reports the relevant molecular parameters.

The geometrical features of the $Rh_2(OAc)_4$ core of this complex are virtually identical with those of the other reported neutral carboxylato complexes. For example, in a series of $Rh_2(OAc)_4L_2$ complexes (L = $H_2O$, py, $Me_2SO$, tethrahydrothiophene, $PPh_3$) the Rh−Rh and Rh−S bond distances are in the ranges 2.3855(5)−2.449(2) and 2.451(1)−2.517(1) Å, which compare well with the values found in **1** (2.4073(7) and 2.541(1) Å).[22] The molecular unit lies on inversion centers. The thioether ligand engages the vacant axial coordination site on Rh with a fully extended conformation. The preferred S instead of O bonding was expected in terms of *hardness*−*softness* character of these atoms.[23]

Complexes **1**−**4** are also obtained under more severe conditions, such as with a large excess of thioether and high reaction temperatures (in boiling toluene at reflux). Thus, the behavior exibited by $Rh_2(\mu\text{-}OAc)_4$ is different from that observed with $Pd_3(\mu\text{-}OAc)_6$: i.e., the preliminary $\eta^1$-S bonding of the oxothioether to the metal center is not followed by deprotonation of the methylene group and subsequent $\mu_2$-C,S coordination. Independently of electronic reasons related to the different natures of the metal centers, it appears that the short Rh−Rh bond distance in the rhodium dimer (2.4073(7) Å) (compared with that of Pd−Pd in the trimer, average 3.214 Å)[24] does not allow, because of steric constraints, a proper approach of the methylene carbon atom to the adjacent metal center. A bridging ortho metalation involving the phenyl ring of $PhSCH_2C(O)OEt$ is also not observed, in contrast with the more favorable geometrical parameters for this type of coordination and with the results obtained in the reaction of rhodium acetate with arylphosphines.[12]

However, it is possible to induce a chelate O,S coordination of the oxo thioether ligand by removing an acetato bridging group via its protonation or alkylation. Complexes **1**, **2**, and **4** react at room temperature with $HBF_4$ in dichloromethane−diethyl ether, or with $(Et_3O)BF_4$ in dichloromethane, to give in high yields (74−81%) the monocationic complexes $[Rh_2(OAc)_3(RSCH_2Z)_2](BF_4)$ (**5**, R = Me, Z = C(O)OEt; **6**, R = Ph, Z = C(O)OEt; **7**, R = Me, Z = $CH_2C(O)OMe$) (eq 1). In contrast, complex

$$[Rh_2(OAc)_4(RSCH_2Z)_2] \xrightarrow[+(Et_3O)(BF_4),\ -EtOAc]{+HBF_4,\ -HOAc} [Rh_2(OAc)_3(RSCH_2Z)_2](BF_4) \quad (1)$$

**3** turns out to decompose without yielding a definite cationic product under the reaction conditions employed.

In their $^1$H NMR spectra two distinct sets of signals for the bridging acetato ligands are present in the ranges 1.34−1.87 and 2.35−2.45 ppm with 2/1 intensity ratios. Moreover, the methylene protons show an AB system centered at 3.90 (**5**) or 4.18 (**6**) ppm. These data indicate that one of the three acetato groups occupies a unique position and that the $CH_2$ protons have become diastereotopic.

Decoordination of one acetato group leaves one equatorial coordination site on Rh available for an alternative bonding mode with S. This bond, stronger than that in the axial position (see the involved bond lengths below), is preferred and gives rise to the configurational rearrangement of the thioester ligands as actually observed in the molecular structure of **5**.

The binuclear carboxylato complex $[Rh_2(OAc)_3(MeSCH_2C(O)OEt)_2](BF_4)\cdot{}^1/_4H_2O$ (**5**) crystallizes in the acentric space group *C*2; the crystal structure is characterized by the presence of two subunits (A and B) in the independent asymmetric unit. The subunits with the atom-numbering scheme are shown in Figure 2, suitably oriented in order to make evident their reciprocal relationship. This compound affords an example of rather infrequent binuclear Rh complexes having an odd number of coordinated carboxylato groups and bidentate ligands chelating the metal at nonequivalent coordination sites. Actually, the bidentate thioesters $MeSCH_2C(O)OEt$ are bonded to Rh with S and O in equatorial

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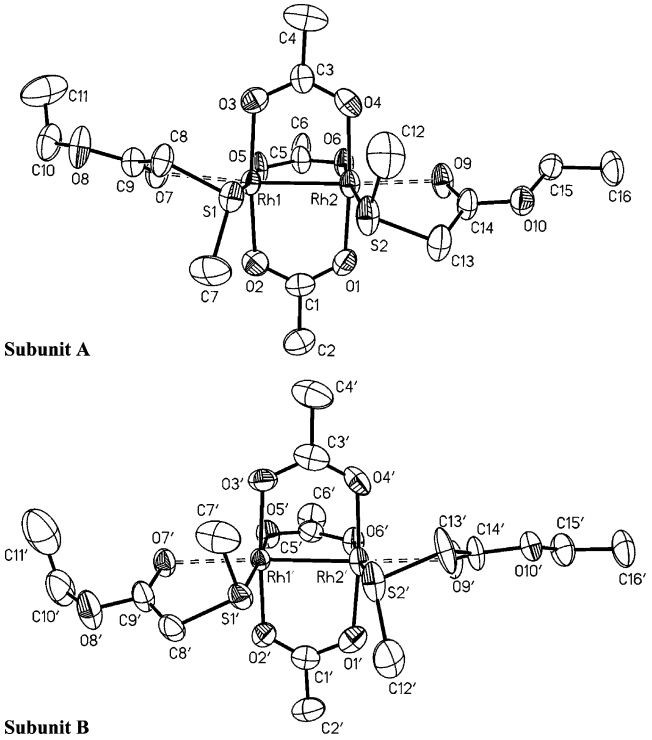


**Figure 2.** ORTEP view of the molecular structure of the subunits A (top) and B (bottom) forming the independent unit of complex **5**. They are suitably oriented to show their reciprocal relationship.

and axial positions, respectively, and the three acetato groups bridge the two Rh atoms, producing a molecular pseudosymmetry of $C_2$ with the binary axis normal to the Rh−Rh bond and passing through C(5) and C(5)′ in A and B, respectively, in agreement with the NMR spectroscopic data. In both the molecular subunits the two sulfur atoms exhibit the same configuration but A and B are mutually enantiomeric.

Table 3 reports the most relevant geometrical parameters of A and B. The conformations of the two subunits are virtually identical, except for the opposite configurations of the sulfur chiral atoms. It is worth noting that opposite configurations of the S atoms in the same subunit would be severely hampered by stereochemical reasons (very short intramolecular contact distances between the S's methyl groups would arise), which also seems to prevent any configurational disorder through a mechanism of *pyramidal inversion* at the S chiral centers.[25] This fact accounts for the presence of the two enantiomeric subunits A and B in the structural unit. In the case of allowable configurational inversion they are expected to be statistically disordered, geometrically identical, and therefore structurally equivalent, as actually found in some complexes containing similar thio derivatives.[26] In both subunits A and B, the Rh atoms are $\sigma$-bonded at the most frequently observed metal−metal distance of 2.439(5) Å,[22] and they show the usual octahedral, almost undistorted coordination; only the angles S−Rh−Rh are markedly larger than 90° (average ca. 99°), due to closure requirements of the five-membered rings involved and for relieving nonbonded

**Table 3. Selected Bond Lengths and Angles for $[Rh_2(OAc)_3(MeSCH_2C(O)OEt)_2](BF_4)$ (5)**

| subunit A | | subunit B | |
|---|---|---|---|
| | Bond Distances (Å) | | |
| Rh(1)−Rh(2) | 2.439(1) | Rh(1)′−Rh(2)′ | 2.436(1) |
| Rh(1)−S(1) | 2.270(3) | Rh(1)′−S(1)′ | 2.279(3) |
| Rh(1)−O(2) | 2.060(9) | Rh(1)′−O(2)′ | 2.011(9) |
| Rh(1)−O(3) | 2.043(9) | Rh(1)′−O(3)′ | 2.023(9) |
| Rh(1)−O(5) | 2.052(8) | Rh(1)′−O(5)′ | 2.039(8) |
| Rh(1)−O(7) | 2.319(9) | Rh(1)′−O(7)′ | 2.358(9) |
| Rh(2)−S(2) | 2.265(3) | Rh(2)′−S(2)′ | 2.276(3) |
| Rh(2)−O(1) | 2.040(9) | Rh(2)′−O(1)′ | 2.047(9) |
| Rh(2)−O(4) | 2.027(9) | Rh(2)′−O(4)′ | 2.025(9) |
| Rh(2)−O(6) | 2.038(8) | Rh(2)′−O(6)′ | 2.069(8) |
| Rh(2)−O(9) | 2.296(9) | Rh(2)′n-O(9)′ | 2.309(9) |
| | Bond Angles (deg) | | |
| Rh(1)−Rh(2)−O(1) | 87.6(3) | Rh(1)′−Rh(2)′−O(1)′ | 86.8(3) |
| Rh(1)−Rh(2)−O(6) | 87.5(3) | Rh(1)′−Rh(2)′−O(6)′ | 86.7(3) |
| Rh(1)−Rh(2)−O(4) | 87.7(3) | Rh(1)′−Rh(2)′−O(4)′ | 87.3(3) |
| Rh(1)−Rh(2)−S(2) | 99.0(1) | Rh(1)′−Rh(2)′−S(2)′ | 97.7(1) |
| Rh(1)−Rh(2)−O(9) | 177.3(3) | Rh(1)′−Rh(2)′−O(9)′ | 177.5(2) |
| Rh(2)−Rh(1)−O(2) | 86.6(3) | Rh(2)′−Rh(1)′−O(2)′ | 87.2(3) |
| Rh(2)−Rh(1)−O(5) | 86.2(2) | Rh(2)′−Rh(1)′−O(5)′ | 87.4(3) |
| Rh(2)−Rh(1)−O(3) | 87.8(3) | Rh(2)′−Rh(1)′−O(3)′ | 88.4(3) |
| Rh(2)−Rh(1)−S(1) | 99.3(3) | Rh(2)′−Rh(1)′−S(1)′ | 98.6(1) |
| Rh(2)−Rh(1)−O(7) | 174.9(2) | Rh(2)′−Rh(1)′−O(7)′ | 176.9(3) |
| O(1)−C(1)−O(2) | 124(1) | O(1)′−C(1)′−O(2)′ | 125(1) |
| O(5)−C(5)−O(6) | 123(1) | O(6)′−C(5)′−O(5)′ | 126(1) |
| O(3)−C(3)−O(4) | 127(1) | O(3)′−C(3)′−O(4)′ | 127(1) |
| Rh(1)−S(1)−C(8) | 99.4(4) | Rh(1)′−S(1)′−C(8)′ | 99.9(5) |
| S(1)−C(8)−C(9) | 112.6(9) | S(1)′−C(8)′−C(9)′ | 112.4(9) |
| C(8)−C(9)−O(7) | 124(1) | C(8)′−C(9)′−O(7)′ | 127(1) |
| C(9)−O(7)−Rh(1) | 114.2(9) | C(9)′−O(7)′−Rh(1)′ | 110.9(9) |
| O(7)−Rh(1)−S(1) | 81.0(2) | O(7)′−Rh(1)′−S(1)′ | 80.5(2) |
| Rh(2)−S(2)−C(13) | 96.8(4) | Rh(2)′−S(2)′−C(13)′ | 98.5(5) |
| S(2)−C(13)−C(14) | 110(1) | S(2)′−C(13)′−C(14)′ | 112.3(1) |
| C(13)−C(14)−O(9) | 123(1) | C(13)′−C(14)′−O(9)′ | 125(1) |
| C(14)−O(9)−Rh(2) | 112.8(9) | C(14)′−O(9)′−Rh(2)′ | 113.0(9) |
| O(9)−Rh(2)−S(2) | 82.3(2) | O(9)′−Rh(2)′−S(2)′ | 81.8(2) |
| | Torsion Angles (deg) | | |
| Rh(2)−Rh(1)−S(1)−C(7) | −102.6(8) | Rh(2)′−Rh(1)′−S(1)′−C(7)′ | 102.3(8) |
| Rh(1)−Rh(2)−S(2)−C(12) | −98.2(9) | Rh(1)′−Rh(2)′−S(2)′−C(12)′ | 100.3(7) |
| C(14)−O(10)−C(15)−C(16) | 178(1) | C(14)′−O(10)′−C(15)′−C(16)′ | −172(1) |
| C(9)−O(8)−C(10)−C(11) | −103(1) | C(9)′−O(8)′−C(10)′−C(11)′ | −84(1) |

interactions between the S's methyl groups. The coordination bond distances are in the norm except for the axial bonds Rh−O in the range of 2.29−2.35 Å. These distances have been generally explained in terms of a trans effect induced by the covalent Rh−Rh $\sigma$-bond.[22] Thus, a weakening of these bonds is expected with a consequent high reactivity of the corresponding coordination site, as confirmed by the catalytic behavior of this complex (see below).

The discrete molecules A and B are weakly held together by hydrogen-bridge interactions of the types C−H····O and C−H····F with H···O and H···F distances in the ranges of 2.50−2.70 and 2.20−2.50 Å, respectively (Table 4).[27] An intricate network of additional *intra*- and *inter*molecular hydrogen-bond interactions also involving the $BF_4^-$ anions cooperates to afford further lattice stability (Table 5).[27] The crystal contains $^1/_2$ mol of hydration water per structural unit; its specific role in the crystal lattice could not be clarified.

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**Scheme 1**

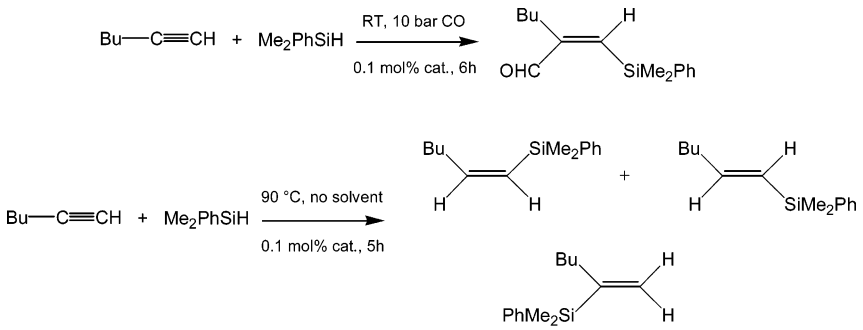


**Table 4. Intramolecular Weak Hydrogen-Bond Interactions**

| C−H···X (X = O, F) | C···X (Å) | H···X (Å) | C−H···X (deg) |
|---|---|---|---|
| C(2)−H(2A)···O(6)′ | 3.51 | 2.87 | 125 |
| C(2)−H(2C)···O(9)′ | 3.50 | 2.58 | 161 |
| C(2)′−H(2A)′···O(10) | 3.38 | 2.71 | 128 |
| C(16)−H(16C)···F(2) | 3.55 | 2.62 | 162. |
| C(16)−H(16B)···F(5) | 3.40 | 2.61 | 140 |
| C(2)′−H(2A)′···F(3) | 3.27 | 2.67 | 120 |
| C(12)′−H(12E)···F(3) | 3.18 | 2.28 | 155 |
| C(8)′−H(8D)···F(4) | 3.18 | 2.35 | 143 |

**Table 5. Possible CH···O and CH···F Intermolecular Hydrogen Bonds**

| C−H···X (X = O, F) | C···X (Å) | H···X (Å) | C−H···X (deg) | equiv position of X |
|---|---|---|---|---|
| C(8)−H(8B)···F(5) | 3.34 | 2.50 | 146 | $x, y-1, z$ |
| C(16)′−H(16E)···F(4) | 3.41 | 2.66 | 135 | $x, y-1, z$ |
| C(4)−H(4A)···F(8) | 3.42 | 2.64 | 140 | $x, y-1, z$ |
| C(7)−H(7A)···F(2) | 3.42 | 2.63 | 140 | $x, y-1, z$ |
| C(8)−H(8A)···F(2) | 3.36 | 2.44 | 159 | $x, y-1, z$ |
| C(6)′−H(6A)′···O(1) | 3.48 | 2.68 | 140 | $-x, y, -z$ |
| C(6)′−H(6A)′···O(6) | 3.45 | 2.66 | 138 | $-x, y, -z$ |
| C(6)−H(6B)···O(6)′ | 3.59 | 2.66 | 163 | $-x, y, -z$ |
| C(10)−H(10A)···O(7)′ | 3.44 | 2.77 | 127 | $-x, y-1, -z$ |
| C(10)−H(10B)···O(5)′ | 3.33 | 2.63 | 129 | $-x, y-1, -z$ |
| C(13)′−H(13A)′···F(7) | 3.24 | 2.57 | 126 | $-x+1/2, y-1/2, -z$ |
| C(12)′−H(12D)···F(1) | 3.39 | 2.57 | 143 | $-x+1/2, y-1/2, -z$ |

The monocationic complex **5** is a good catalyst of the silylformylation or hydrosilylation with dimethylphenylsilane of a model alkyne such as 1-hexyne.

The silylformylation (Scheme 1, top equation) is performed in dichloromethane, at room temperature, under 10 atm of CO, using a 1/1000 catalyst/substrate ratio. After 6 h, the conversion was 98% and the selectivity toward the silylformylation product was 73%, other byproducts stemming almost exclusively from hydrosilylation of the triple bond (25%), which is known to be the main competitive reaction. Only the *Z* isomer of the silylformylated product is observed, which highlights the high regio- and stereoselectivity that can be obtained with this catalyst. Although not optimized, the catalytic performance of **5** compares favorably with that of other rhodium-based catalysts such as dirhodium(II) perfluorobutyrate,[11d,e] $Rh_4(CO)_{12}$,[14,28] or solvated rhodium atoms.[14] It is interesting to note that under the same experimental conditions dirhodium(II) acetate is almost inactive (6% conversion). The high catalytic efficiency of complex **5** appears to be related to the presence of the positive charge on the rhodium dimer, which enhances the acid character of the metal center. On the other hand, the strained coordination of the ester oxygen on the axial position should favor its decoordination in the course of the reaction and consequently the approach of the reagents.

The hydrosilylation (Scheme 1, bottom equation) requires a higher reaction temperature than the silylformylation in order to be performed (90 °C), but it can be run neat using an excess of 1-hexyne as the solvent (catalyst/silane/hexyne ratio 1/1000/4000). The conversion after 5 h is 62%, and (*Z*)-(dimethylphenylsilyl)-1-hexene turns out to be the main product (81% selectivity), other products stemming from the formal cis addition of the silane to the triple bond. These preliminary, not optimized, data point out the good catalytic activity of **5** also in this reaction and, most notably, its unusual selectivity for the less thermodynamically stable *Z* isomer. In fact, cationic rhodium-based catalysts are reported to exhibit a preference for cis hydrosilylation, leading to the *E* isomer.[29] In this case, the control catalytic test performed using simple dirhodium(II) acetate also led to interesting results. In fact, under the same reaction conditions both the conversion (88%) and the selectivity for the *Z* isomer (98%) appear to be significantly higher than with the cationic catalyst. Apparently, the observation of such a high selectivity with dirhodium(II) acetate is unprecedented in the literature. The same reaction was described quite some time ago[30] and was found to reach comparable conversion, but the selectivity for the various isomers was not reported. We are currently engaged in a detailed investigation of these reactions, as well as in the preparation of chiral monocationic complexes related in structure to complex **5**, which appear to be potentially interesting catalysts for enantioselective transformations.

**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of $[Rh_2(OAc)_4(MeSCH_2C(O)OEt)_2]$ and $[Rh_2(OAc)_3(MeSCH_2C(O)OEt)_2](BF_4)\cdot{}^1/_4H_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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