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Synthesis of Thiolate-Bridged Ruthenium(I) Complexes. The Crystal Structure of $[Ru_2(\mu\text{-}S_2(CH_2)_3)(CO)_4(PPh_3)_2]$

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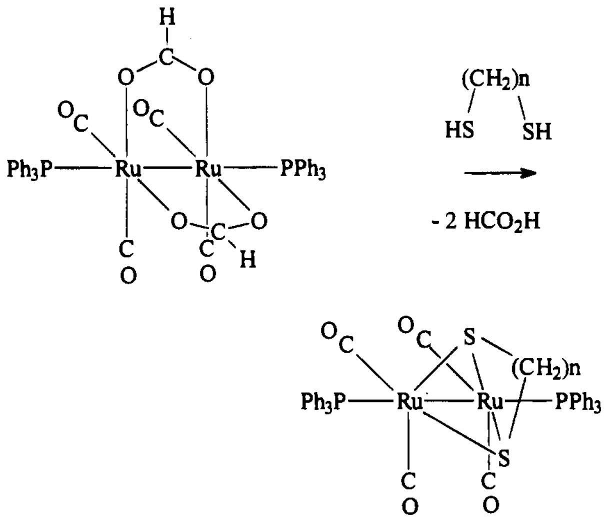
Although the chemistry of thiolate-bridged carbonyl and phosphine-substituted iron complexes $Fe_2(\mu\text{-}SR)_2(CO)_{6-n}L_n$ has been known for many years,[1] the study of the analogous ruthenium complexes $Ru_2(\mu\text{-}SR)_2(CO)_{6-n}L_n$ is still unknown. This fact probably arises from the lack of available synthetic methods and from the poor yields found in the syntheses of some thiolate-bridged carbonyl ruthenium(I) dimers which were obtained from mixtures of polynuclear compounds. The first starting material used was $Ru_3(CO)_{12}$, which reacted with thiols under vigorous conditions to form $Ru_2(\mu\text{-}SR)_2(CO)_6$ with other thiolate compounds.[2] Alkyl and aryl disulfides also gave mixtures of thiolate compounds including $Ru_2(\mu\text{-}SR)_2(CO)_6$.[3] Bruce et al. reported the preparation of dinuclear thiolato-bridged ruthenium(II) complexes containing the phenylazophenyl group.[4] Recently, Cabeza et al. published a new method of synthesis of $Ru_2(\mu\text{-}L)_2(CO)_4(PPh_3)_2$, where L is a three-electron bridging ligand, with good yields.[5] Following this method they presented the formation of the thiolate dinuclear complex $Ru_2(\mu\text{-}S^tBu)_2(CO)_4(PPh_3)_2$.[5] The same authors reported the preparation and the structure of the related compound $Ru_2(\mu\text{-}SePh)_2(CO)_6$,[6] following re-examination of the reaction of $Ru_3(CO)_{12}$ with diphenyl diselenide.[7] It is interesting to note that Cowie et al. suggested a convenient general route of synthesis of binuclear ruthenium(I) complexes $Ru_2(\mu\text{-}L)_2(CO)_4(PPh_3)_2$ from the reaction of the acetate-bridged complex $Ru_2(\mu\text{-}O_2CCH_3)(CO)_4(PPh_3)_2$ with the sodium salts of three-electron ligands HL, but this method was applied only to O and N donor ligands.[8] Apart from these previous results, our knowledge of thiolate- and selenolate-bridged ruthenium complexes is restricted to C_5Me_5 ruthenium(II) and -(III) complexes[9] and to the ruthenium(II) $[Ru_2(\mu\text{-}SPh)_2(S_2CNMe_2)_2(CO)_2(PPh_3)_2]^+$ compound, recently published.[10] This binuclear ruthenium(II) complex is electron-rich and exhibits an unusual one-step four-electron oxidation reaction, with concomitant metal−metal bond formation. This unusual behavior is an example of the great electrochemical potential of the thiolate-bridged ruthenium complexes. The X-ray structure of a new dithiolate dinuclear ruthenium(I) compound was reported while this manuscript was being prepared.[11]

Following our investigations with ruthenium carboxylate complexes,[12] we found that thiolate ligands could replace the carboxylate-bridging ligands in the binuclear ruthenium(I) compounds $Ru_2(\mu\text{-}O_2CCR)_2(CO)_4(PPh_3)_2$ when they reacted with thiols and dithiols. These results provided the first available general route of preparation of thiolate-bridged ruthenium(I) complexes $Ru_2(\mu\text{-}SR)_2(CO)_4(PPh_3)_2$ with R = Bz (**1**), *p*-Tol(**2**), and ^{t}Bu(**3**) and $Ru_2(\mu\text{-}S_2\,(CH_2)_n)(CO)_4(PPh_3)_2$ with $n = 2$ (**4**) and 3 (**5**), which we now report here.

The reaction of $Ru_2(\mu\text{-}O_2CH)_2(CO)_4(PPh_3)_2$ with an excess of a thiol or a dithiol in refluxing toluene gave the dinuclear thiolate-bridged ruthenium(I) compounds $Ru_2(\mu\text{-}SR)_2(CO)_4(PPh_3)_2$ (**1**−**3**) and $Ru_2(\mu\text{-}S_2(CH_2)_n)(CO)_4(PPh_3)_2$ ($n = 2$, **4**, and $n = 3$, **5**) (eq 1). These compounds were isolated as yellow solids and were identified analytically and spectroscopically (analyses agree with one molecule of dichloromethane of solvatation, which was also confirmed by the X-ray diffraction study of **5**). The reactions with *p*-TolSH (**2**) and dithiolates (**4**



(1)

n = 2 (**4**) and 3 (**5**)

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(1) (a) Fehlhammer, W. P.; Stolzenberg H. *Comprehensive Organometallic Chemistry*; Wilkinson, G. W., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 4, Chapter 31, p 513. (b) Hawker, P. H.; Twigg, M. V. *Comprehensive Coordination Chemistry*; Wilkinson, G. W., Gillard, R. D., Eds.; Pergamon: Oxford, England, 1987; Vol. 4, Chapter 44.1, p 1179.

(2) (a) Johnson, B. F. G.; Johnson, R. D.; Josty, P. L.; Lewis, J.; Williams, I. G. *Nature* **1967**, *4*, 901. (b) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G. *J. Chem. Soc. A* **1969**, 797.

(3) (a) Sappa, E.; Gambino, O.; Cetini, G. *J. Organomet. Chem.* **1971**, *30*, 67. (b) Cetini, G.; Gambino, O.; Sappa, E.; Valle, M. *J. Organomet. Chem.* **1972**, *35*, 375.

(4) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2820.

(5) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Robert, F.; Jeannin, Y. *J. Organomet. Chem.* **1989**, *372*, C15.

(6) Andreu, P. L.; Cabeza, J. A.; Miguel, D.; Riera, V.; Villa, M. A.; Garcia-Granda, S. *J. Chem. Soc., Dalton. Trans.* **1991**, 533.

(7) Schermer, E. D.; Baddley, W. H. *J. Organomet. Chem.* **1971**, *30*, 67.

(8) Sherlock, S. J.; Cowie, M.; Singleton, M.; Stein, M. M. de V. *J. Organomet. Chem.* **1989**, *361*, 353.

(9) (a) Hidai, M.; Mizobe, Y.; Matsuzaka, H. *J. Organomet. Chem.* **1994**, *473*, 1. (b) Hidai, M.; Imagawa, K.; Cheng, G.; Mizobe, Y.; Wakatsuki, Y.; Yamazaki, H. *Chem. Lett.* **1986**, 1299. (c) Tanase, T.; Imagawa, K.; Dev, S.; Mizobe, Y.; Yano, S.; Idai, M. *New. J. Chem.* **1988**, *12*, 697. (d) Dev, S.; Imagawa, K.; Mizobe, Y.; Cheng, G.; Wakatsuki, H.; Idai, H. *Organometallics* **1989**, *8*, 1232. (e) Matsuzaka, H.; Ogino, T.; Nishio, M.; Nishibayashi, Y.; Uemura, S. *J. Chem. Soc. Chem. Commun.* **1994**, 223.

(10) Kawano, M.; Uemura, H.; Watanabe, H.; Matsumoto, K. *J. Am. Chem. Soc.* **1993**, *115*, 2068.

(11) Shiu, K. B.; Li, Ch.H.; Chan, T. J.; Peng, S. M.; Cheng, M. Ch.; Wang, S. L.; Liao, F. L. *Organometallics* **1995**, *14*, 524.

(12) (a) Torres, M. R.; Perales, A.; Loumrhari, H.; Ros, J. *J. Organomet. Chem.* **1990**, *385*, 379. (b) Loumrhari, H.; Ros, J.; Torres, M. R.; Perales, A. *J. Organomet. Chem.* **1991**, *403*, 373. (c) Loumrhari, H.; Ros, J.; Torres, M. R.; Perales, A. *Polyhedron* **1990**, *7*, 907. (d) Santos, A.; Lopez, J.; Matas, Ll.; Ros, J.; Galan, A.; Echavarren, A. M. *Organometallics* **1993**, *12*, 4215.

0020-1669/95/1334-6211$09.00/0

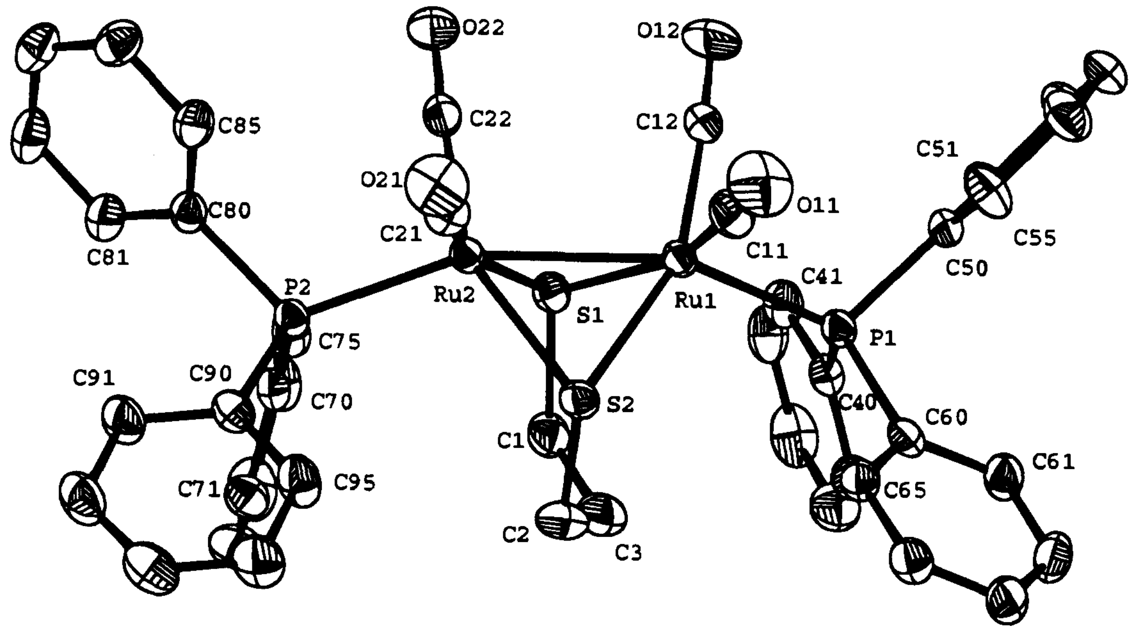

Figure 1. ORTEP drawing of complex $[Ru_2(\mu\text{-}S_2(CH_2)_3)(CO)_4(PPh_3)_2]$ (**5**).

Table 1. Crystal Data and Structure Refinement for **5**

empirical formula	$C_{44}H_{38}Cl_2O_4P_2S_2Ru_2$
M_r	1029.83
cryst system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell params at 298 K	
a, Å	$a = 9.242(2)$ Å
b, Å	$b = 12.379(3)$ Å
c, Å	$c = 20.563(6)$ Å
α, deg	$\alpha = 106.50(2)^\circ$
β, deg	$\beta = 98.29(2)^\circ$
γ, deg	$\gamma = 100.11(2)^\circ$
V, Å^2	$V = 2173.2(9)$ Å^3
Z	2
D_{calcd}, g cm^{-3}	1.574
λ, Å	0.70926
abs coeff, mm^{-1}	1.029
no. of reflcns collcd	7626
no. of indep reflcns	7626 [R(int) = 0.0000]
goodness-of-fit on F^2	0.998^c
final R indexes $[I > 2\sigma(I)]$	$R^a = 0.0376$, $R_w{}^b = 0.0986$
largest diff peak and hole, e Å^{-3}	0.810 and −0.771

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [c] $\mathrm{GOF} = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.069p)^2]$, where $p = [F_o^2 + 2F_c^2]/3$.

and **5**) gave only one product whereas the reactions with BzSH (**1**) and ^{t}BuSH (**3**) gave mixtures of isomers (Chart 1). Except for the Bz derivatives these were cleanly separated in columns of silica using dichloromethane/hexane mixtures as eluants.

The ^{1}H NMR spectra of compounds **1**–**5** show signals of the PPh_3 and SR protons. In the case of the reaction with BzSH the corresponding spectrum of the crude product displays different methylenic signals, suggesting the presence of isomers. These signals agree with the presence of three structural isomers of **1**, two of which display singlets (**1a** and **1b**) and the third of which displays two singlets (**1c**). Three signals in the $\{^1H\}^{31}P$ NMR spectrum of **1** support this hypothesis. Although the ^{1}H NMR spectrum of the product of the reaction with ^{t}BuSH shows one signal corresponding to the methyl hydrogens, its $\{^1H\}^{31}P$ NMR spectrum reveals that two isomers were formed (**3a** and **3b**). These two structural isomers are present in the ^{13}C NMR spectrum of **3** as two signals at 33.6 and 46.4 ppm. These compounds have different patterns of the IR spectra in the carbonyl region measured in dichloromethane solution, which suggests an *anti* configuration for **3a** and a *syn* configuration for **3b**.The same spectra of complexes **4** and **5** display three bands with the pattern expected for the $Ru_2(CO)_4$ fragment, with C_{2v} symmetry and which agrees with a *syn*-type structure as well as in iron complexes.[13] The only product of the reaction with *p*-TolSH (**2**) has a four-IR band pattern in the carbonyl stretching region, which agrees with a lower symmetry (probably C_s) expected for an *anti*-type structure. This isomer is also predominant in the mixture of isomers of the complex $Ru_2(\mu\text{-}SePh)_2(CO)_4(PPh_3)_2$.[6] The three isomers of compound **1**, which were separated with difficulty on a silica column, show diverse IR patterns suggesting different structures: C_{2v} symmetry for **1a** and a lower symmetry (probably C_s) for **1b** and **1c**. The $\{^1H\}^{31}P$ NMR spectra of isomers **1a**, **1b** and **1c** show only a singlet, in accordance with the PPh_3 ligands bonded to ruthenium atoms in a *trans* arrangement, as is usual in dinuclear diphosphine ruthenium complexes. From the ν(CO) frequencies of compounds, it can be seen that *syn* complexes have the higher band at 2000–2012 cm^{-1}, but in *anti* isomers this band appears at 2033–2045 cm^{-1}. For this reason, although complex **1b** has a different ν(CO) pattern of the *syn* isomers (2008 *s*, 1985 *m*, and 1943 *m*) we assign a *syn* structure to it. The rotation around the S–CH_2 bond can allow different arrangements of the two Bz groups; thus it is reasonable to suggest that whereas **1b** has a *syn* structure, the possible nonequivalence of phenyls may cause a decrease in the symmetry of the molecule, changing the ν(CO) set of bands.

The molecular structure of the dimer $Ru_2(\mu\text{-}S_2(CH_2)_3)(CO)_4(PPh_3)_2$ (**5**) consists of dinuclear units in which the two ruthenium atoms are bridged by a propanedithiolate ligand. The sulfur atoms are symmetrically bonded to metals with bond lengths averaging 2.40 Å. The angles Ru(1)–S(1)–Ru(2) and Ru(1)–S(2)–Ru(2) are of 67.8(1) and 68.1(1)° respectively. These values are smaller than those found in compound $[Ru_2(\mu\text{-}SPh)(S_2CNMe_2)(CO)(PPh_3)]_2{}^{4+}$, in which the angle was of 75.17(8)°[10] and the ruthenium–ruthenium distance was 2.876(2) Å, but are bigger than in compound $Ru_2(\mu_2\text{-}S_2C_6H_4)(CO)_4(PPh_3)_2$[11] (67.06(3)°) . The metal–metal bond length of 2.690(1) Å in **5** is consistent with a ruthenium–ruthenium bond.[14] This length is shorter than other found in related ruthenium(I) compounds: the nonbridged triazolylborato Ru-

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(13) King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1584.

Table 2. Atomic Coordinates ($\times 10^{-4}$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^{-3}$) for **5**

	x	*y*	*z*	*U*(eq)[a]
Ru(1)	4690(1)	7292(1)	1894(1)	35(1)
Ru(2)	3754(1)	6932(1)	3010(1)	34(1)
S(1)	2145(1)	6381(1)	1888(1)	43(1)
C(1)	830(5)	7324(5)	1858(3)	65(1)
C(2)	1476(6)	8511(5)	1906(3)	69(2)
C(3)	2553(5)	9266(4)	2566(2)	54(1)
S(2)	4253(1)	8786(1)	2825(1)	39(1)
C(11)	4992(6)	5840(4)	1419(3)	58(1)
O(11)	5199(6)	4957(4)	1164(3)	101(2)
C(12)	6757(5)	7876(4)	2240(2)	51(1)
O(12)	8009(4)	8262(4)	2459(2)	94(1)
C(21)	3678(5)	5366(4)	2904(2)	52(1)
O(21)	3675(5)	4428(3)	2838(2)	85(1)
C(22)	5634(5)	7388(4)	3613(2)	46(1)
O(22)	6815(4)	7649(4)	3949(2)	73(1)
P(1)	4723(1)	8117(1)	993(1)	37(1)
C(40)	4595(5)	9638(4)	1257(2)	41(1)
C(41)	5603(5)	10399(4)	1846(2)	49(1)
C(42)	5538(6)	11532(4)	2088(3)	60(1)
C(43)	4463(7)	11943(4)	1762(3)	71(2)
C(44)	3450(6)	11206(5)	1189(3)	67(1)
C(45)	3508(5)	10063(4)	931(2)	53(1)
C(50)	6471(4)	8156(4)	667(2)	41(1)
C(51)	7537(5)	9161(4)	772(2)	52(1)
C(52)	8864(5)	9112(5)	526(3)	65(1)
C(53)	9121(5)	8070(5)	171(3)	64(1)
C(54)	8065(6)	7081(5)	58(3)	69(2)
C(55)	6758(5)	7119(4)	304(3)	60(1)
C(6O)	3331(4)	7408(4)	181(2)	41(1)
C(61)	3353(5)	7788(4)	−388(2)	53(1)
C(62)	2318(6)	7235(5)	−989(2)	63(1)
C(63)	1246(5)	6276(5)	−1045(2)	61(1)
C(64)	1221(5)	5862(4)	−497(2)	54(1)
C(65)	2253(5)	6432(4)	120(2)	45(1)
P(2)	2329(1)	7220(1)	3881(1)	36(1)
C(70)	1806(4)	8608(3)	4086(2)	38(1)
C(71)	345(5)	8724(4)	3974(2)	50(1)
C(72)	27(6)	9807(4)	4124(3)	66(1)
C(73)	1170(7)	10781(5)	4395(3)	73(2)
C(74)	2640(6)	10688(4)	4505(3)	60(1)
C(75)	2957(5)	9619(4)	4345(2)	49(1)
C(80)	3307(4)	7259(3)	4741(2)	40(1)
C(81)	3165(5)	8031(4)	5346(2)	53(1)
C(82)	3938(6)	8041(5)	5982(2)	62(1)
C(83)	4842(6)	7286(4)	6018(2)	57(1)
C(84)	4966(6)	6518(4)	5420(3)	58(1)
C(85)	4215(5)	6489(4)	4783(2)	49(1)
C(90)	532(5)	6207(4)	3749(2)	45(1)
C(91)	−86(5)	6028(4)	4293(3)	59(1)
C(92)	−1510(6)	5325(5)	4163(3)	69(2)
C(93)	−2313(6)	4821(5)	3499(3)	71(2)
C(94)	−1733(6)	4991(5)	2961(3)	72(2)
C(95)	−299(5)	5666(4)	3085(3)	61(1)
C(10)	1134(12)	2145(10)	3031(5)	189(5)
Cl(11)	368(7)	1815(5)	2167(3)	147(1)
Cl(12)	−715(13)	2211(11)	3386(6)	147(1)
Cl(13)	55(15)	2923(11)	3544(5)	147(1)
Cl(21)	987(7)	3280(5)	3676(3)	147(1)
Cl(22)	−466(13)	1234(9)	2599(6)	147(1)
Cl(23)	−136(14)	1355(10)	2318(6)	147(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond lengths (Å) and Angles (deg) for **5**

Ru(1)−C(12)	1.874(5)	Ru(1)−C(11)	1.876(5)
Ru(1)−P(1)	2.3579(13)	Ru(1)−S(2)	2.3925(12)
Ru(1)−S(1)	2.4198(12)	Ru(1)−Ru(2)	2.6887(8)
Ru(2)−C(22)	1.873(5)	Ru(2)−C(21)	1.876(5)
Ru(2)−P(2)	2.3570(12)	Ru(2)−S(1)	2.3999(13)
Ru(2)−S(2)	2.4079(12)	S(1)−C(1)	1.834(5)
C(1)−C(2)	1.455(7)	C(2)−C(3)	1.507(7)
C(3)−S(2)	1.836(4)	C(11)−O(11)	1.133(6)
C(12)−O(12)	1.141(5)	C(21)−O(21)	1.130(6)
C(22)−O(22)	1.143(5)	P(1)−C(50)	1.834(4)
P(1)−C(6O)	1.835(4)	P(1)−C(40)	1.836(4)
P(2)−C(70)	1.818(4)	P(2)−C(90)	1.830(4)
P(2)−C(80)	1.850(4)		

C(12)−Ru(1)−C(11)	91.5(2)	C(12)−Ru(1)−P(1)	92.4(2)
C(11)−Ru(1)−P(1)	98.3(2)	C(12)−Ru(1)−S(2)	88.6(2)
C(11)−Ru(1)−S(2)	158.3(2)	P(1)−Ru(1)−S(2)	103.39(4)
C(12)−Ru(1)−S(1)	156.73(14)	C(11)−Ru(1)−S(1)	89.4(2)
P(1)−Ru(1)−S(1)	110.45(4)	S(2)−Ru(1)−S(1)	82.14(4)
C(12)−Ru(1)−Ru(2)	101.51(14)	C(11)−Ru(1)−Ru(2)	102.6(2)
P(1)−Ru(1)−Ru(2)	154.41(3)	S(2)−Ru(1)−Ru(2)	56.21(3)
S(1)−Ru(1)−Ru(2)	55.74(3)	C(22)−Ru(2)−C(21)	91.7(2)
C(22)−Ru(2)−P(2)	96.13(13)	C(21)−Ru(2)−P(2)	95.8(2)
C(22)−Ru(2)−S(1)	153.35(13)	C(21)−Ru(2)−S(1)	89.6(2)
P(2)−Ru(2)−S(1)	110.22(4)	C(22)−Ru(2)−S(2)	88.14(14)
C(21)−Ru(2)−S(2)	161.0(2)	P(2)−Ru(2)−S(2)	103.14(4)
S(1)−Ru(2)−S(2)	82.23(4)	C(22)−Ru(2)−Ru(1)	97.76(13)
C(21)−Ru(2)−Ru(1)	105.6(2)	P(2)−Ru(2)−Ru(1)	154.02(3)
S(1)−Ru(2)−Ru(1)	56.45(3)	S(2)−Ru(2)−Ru(1)	55.66(3)
C(1)−S(1)−Ru(2)	112.0(2)	C(1)−S(1)−Ru(1)	113.1(2)
Ru(2)−S(1)−Ru(1)	67.81(4)	C(2)−C(1)−S(1)	116.5(4)
C(1)−C(2)−C(3)	117.8(5)	C(2)−C(3)−S(2)	117.6(3)
C(3)−S(2)−Ru(1)	111.7(2)	C(3)−S(2)−Ru(2)	113.8(2)
Ru(1)−S(2)−Ru(2)	68.12(4)	O(11)−C(11)−Ru(1)	176.4(5)
O(12)−C(12)−Ru(1)	178.0(5)	O(21)−C(21)−Ru(2)	177.9(5)
O(22)−C(22)−Ru(2)	176.2(4)		

(I) compound $[Ru\{\eta^3\text{-}HB(tz)_3\}(CO)_2]_2$ (2.870(1) Å),[15] a carboxylate-bridged compound $Ru_2(\mu\text{-}O_2CC_3H_7)(CO)_4(P^tBu_3)_2$ (2.728(1) Å),[16] and pyrazolate and oxypyridinate $Ru_2(\mu\text{-}X)_2(CO)_4(PPh_3)_2$ complexes.[8] The same distance is quite similar to that found in the selenide compound $Ru_2(\mu\text{-}SePh)(CO)_6$ (2.70 Å)[6] and in the dithiolate complex $Ru_2(\mu_2\text{-}S_2C_6H_4)(CO)_4(PPh_3)_2$[11] (2.68 Å), but it is longer than in the 1,8-diaminonaphthalene $Ru_2(\mu\text{-}C_{10}H_8N_2)(CO)_4\{P(OPh)_3\}_2$ compound (2.571(1) Å).[17] The Ru_2S_2 framework has a butterfly arrangement showing a torsion angle S(2)−Ru(1)−Ru(2)−S(1) of 104.9°. The two phosphine ligands are pseudo-trans to the metal−metal bond with P(1)−Ru(1)−Ru(2) and P(2)−Ru(2)−Ru(1) of 154.4(1) and 154.0(1)°, respectively. These values are in the expected range of metal−metal−phosphine angles in iron[18] and ruthenium derivatives.[11,17] The small Ru−S−Ru angle and the bending of the Ru−Ru−P angles cause an important distortion of the octahedral geometry of the metal atoms. As in related heteroatom-bridged ruthenium(I) compounds of the type $Ru_2(\mu\text{-}X)_2(CO)_4(PR_3)_2$ the CO ligands are nearly *trans* to the Ru−S bonds, displaying C−O bond lengths averaging 1.13−1.14 Å. These bond lengths are slightly shorter than those found in complexes in which X contain a σ,π-donor heteroatom of the second period (N or O),[8] which suggests that the electronic density at metal centers is lower in μ-thiolate complexes. Although the $(CH_2)_3$ fragment in the crystal structure does not occupy an equidistant position with respect to the Ru−Ru bond, the spectroscopic data of **5** measured in solution agree with a C_{2v} symmetry. This observation suggests that the hydrocarbon fragment is fluxional at room temperature.

Experimental Section

All operations were performed under a nitrogen atmosphere using the Schlenk techniques. All the solvents were distilled and dried before use. NMR spectra were obtained on a Bruker AC-250 (^1H, 250 MHz;

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(14) Sherlock, S. J.; Cowie, M.; Singleton, E.; Steyn, M. M. de V. *Organometallics* **1988,** *7,* 1663.

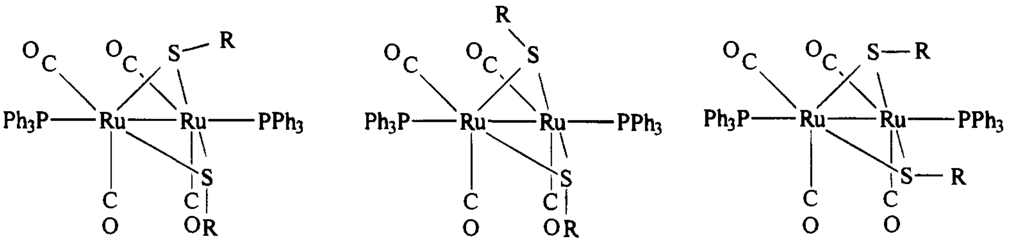
(15) Shiu, K. B.; Guo, W. N.; Peng, S. M.; Cheng, M. C. *Inorg. Chem.* **1994**, *33*, 3010.

(16) Schumann, H.; Opitz, J.; Pickardt, J. *J. Organomet. Chem.* **1977**, *128*, 253.

(17) Cabeza, J. A.; Fernández-Colinas, J. M.; Riera, V.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 371.

(18) Le Borgne, G.; Grandjean, D.; Mathieu, R.; Poilblanc, R. *J. Organomet. Chem.* **1977**, *131*, 429.

Chart 1



anti

R = Bz (**1c**)
R = p-Tol (**2**)
R = t-Bu (**3a**)

syn-endo

R = Bz (**1a**, **1b**)
R = t-Bu (**3b**)

syn-exo

R, R = $(CH_2)_2$ (**4**)
R, R = $(CH_2)_3$ (**5**)

^{13}C, 62 MHz; ^{31}P, 102 MHz) spectrometer in $CDCl_3$ solutions. The IR spectra were recorded on a Perkin-Elmer FT 1710 spectrophotometer with CH_2Cl_2 solutions. Elemental analyses were obtained by the staff of the Chemical Analysis Service at the Department of Chemistry of the Universitat Autònoma de Barcelona.

The compound $[Ru_2(\mu\text{-}O_2CH)_2(CO)_4(PPh_3)_2]$ was prepared by using a previously published procedure.[19]

Preparation of Compounds 1–5. A solution of $[Ru_2(\mu\text{-}O_2CH)_2(CO)_4(PPh_3)_2]$ (0.1 g, 0.11 mmol) and an 8-fold excess (0.88 mmol) of a thiol (RSH, R = Bz, *p*-Tol and ^tBu) or a dithiol ($HS(CH_2)_nSH$, n = 2 and 3) in toluene (20 mL) was heated under reflux (20 h for thiols and 2 h for dithiols). The solvent, the formic acid and the excess of the thiol or the dithiol were evaporated to dryness *in vacuo*. The yellow residue was dissolved in a minimum of CH_2Cl_2 and precipitated with hexane. The products of the reaction were purified and separated by chromatography on a silica column eluted with CH_2Cl_2/hexane mixtures. Monocrystals of **5** were grown from a CH_2Cl_2/hexane mixture.

Reaction with BzSH. **1** (mixture of isomers): Anal. Calcd for $C_{55}H_{46}Cl_2O_4P_2S_2Ru_2$: C, 56.41; H, 3.96; S, 5.47. Found: C, 55.81; H, 4.11; S, 5.18.

1a: 23.4% yield. IR (CH_2Cl_2): ν(CO) 2009 s, 1974 w, 1943 s cm^{-1}. ^1H NMR (298 K, $CDCl_3$): δ 3.5 (s, 4 H), 7.7.8 (m, 35H). $\{^1H\}^{31}P$ NMR (298 K, $CDCl_3$): δ 30.8 (s).

1b: 30.6% yield. IR (CH_2Cl_2): ν(CO) 2008 s, 1985 m, 1943 m cm^{-1}. ^1H NMR (298 K, $CDCl_3$): δ 3.7 (s, 4 H), 7–7.8 (m, 35H). $\{^1H\}^{31}P$ NMR (298 K, $CDCl_3$): δ 26.0 (s).

1c: 19.0% yield. IR (CH_2Cl_2): ν(CO) 2033 s, 1976 s, 1942 w cm^{-1}. ^1H NMR (298 K, $CDCl_3$): δ 3.19 (s, 2H), 3.70 (s, 2H), 7–7.8 (m, 35 H). $\{^1H\}^{31}P$ NMR (298 K, $CDCl_3$): δ 39.8 (s).

Reaction with *p*-TolSH. **2:** 80% yield. Anal. Calcd for $C_{55}H_{46}Cl_2O_4P_2S_2Ru_2$: C, 56.41; H, 3.96; S, 5.47. Found: C, 56.81; H, 4.21; S, 5.09. IR (CH_2Cl_2): ν(CO) 2045 s, 1988 s, 1954 m cm^{-1}. ^1H NMR (298 K, $CDCl_3$): δ 2.3 (s, 6H), 7.0–7.7 (m, 38H). $\{^1H\}^{31}P$ NMR (298 K, $CDCl_3$): δ 24.0 (s).

Reaction with ^{t}BuSH. **3** (mixture of isomers): Anal. Calcd for $C_{46}H_{41}Cl_2O_4P_2S_2Ru_2$: C, 52.23; H, 3.91; S, 6.05. Found: C, 51.80; H, 4.27; S, 5.99. $\{^1H\}^{13}C$ NMR (298 K, $CDCl_3$) of **3** (mixture of isomers): δ 33.6, 46.4, 127.7, 127.8, 127.9, 128.1, 128.3, 128.5, 128.9, 129.3, 131.8, 131.9, 132.1, 133.8, 138.9, 134.0, 136.3, 136.6, 136.9, 205.6.

3a: 70.3% yield. IR (CH_2Cl_2): ν(CO) 2001 s, 1965 m, 1930 s cm^{-1}. ^1H NMR (298 K, $CDCl_3$): δ 0.18 (s, 18H), 7.3–7.8 (m, 30H). $\{^1H\}^{31}P$ NMR (298 K, $CDCl_3$): δ 39.5 (s).

3b: 8.7% yield. IR (CH_2Cl_2): ν(CO) 2033 s, 1964 m, 1930 s cm^{-1}. ^1H NMR (298 K, $CDCl_3$): δ 0.18 (s, 18H), 7.3–7.8 (m, 30H). $\{^1H\}^{31}P$ NMR (298 K, $CDCl_3$): δ 45.3 (s).

Reaction with $(CH_2)_2S_2H_2$. **4:** 83% yield. Anal. Calcd for $C_{42}H_{36}Cl_2O_4P_2S_2Ru_2$: C, 50.79; H, 3.57; S, 6.29. Found: C, 50.61; H, 4.05; S, 5.79. IR (CH_2Cl_2): ν(CO) 2012 s, 1977 m, 1946 s cm^{-1}. ^1H NMR (298 K, $CDCl_3$): δ 0.89 (s, 4H), 7.3–7.7 (m, 30H). $\{^1H\}^{13}C$ NMR (298 K, $CDCl_3$): δ 31.8, 128.3, 129.7, 131.9, 132.3, 133.1, 136.7, 137.2, 203.4. $\{^1H\}^{31}P$ NMR (298 K, $CDCl_3$): δ 36.5 (s).

Reaction with $(CH_2)_3S_2H_2$. **5:** 76% yield. Anal. Calcd for $C_{48}H_{38}Cl_2O_4P_2S_2Ru_2$: C, 51.27; H, 3.72; S, 6.21. Found: C, 51.52; H, 3.70; S, 5.73. IR (CH_2Cl_2): ν(CO) 2011 s, 1977 m, 1946 s cm^{-1}. ^1H NMR (298 K, $CDCl_3$): δ 1.2–3.0 (m, 6H), 7.2–8.0 (m, 30H). $\{^1H\}^{13}C$ NMR (298 K, $CDCl_3$): δ 19.3, 34.0, 128.3, 129.7, 132.1, 133.4, 136.8, 202.0. $\{^1H\}^{31}P$ NMR (298 K, $CDCl_3$): δ 36.5 (s).

X-ray Diffraction Study of 5. Crystal data for **5**: $C_{43}H_{36}O_4P_2Ru_2S_2{\cdot}CH_2Cl_2$, M_r = 1029.83, triclinic, space group $P\bar{1}$ (No. 2), a = 9.242(2) Å, b = 12.379(3) Å, c = 20.563(6) Å, α = 106.50(2)°, β = 98.29(2)°, γ = 100.11(2)°, V = 2173.2 Å^3, Z = 2, D_c = 1.574 g cm^{-3}, μ = 10.29 cm^{-1}. Measurements: Enraf-Nonius CAD4; radiation: graphite monochromated Mo Kα (λ = 0.710 69 Å), T = 293 K, data collection range $2 < 2\theta < 50°$, $\omega-2\theta$ scan, absorption correction based on ψ-scan measurements. Solution: SHELXS-86 program, refinement on F^2 for all reflections; SHELXL-93 program, 7626 unique reflections, 502 variables, hydrogen atoms fixed at calculated positions, two overall isotropic temperature factors used for them (one for phenyl hydrogens and another one for methylene hydrogens). $R(F)$ = 0.0376, $R_w(F^2)$ = 0.0986 for 5713 reflections with $I > 2\sigma(I)$.

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Supporting Information Available: Text giving the structure determination and tables of atomic coordinates and isotropic displacement parameters for hydrogen atoms, anisotropic displacement parameters for non-hydrogen atoms, and complete bond lengths and angles for **5** (9 pages). Ordering information is given on any current masthead page.

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(19) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G.; Gamblen, J. *J. Chem. Soc. A* **1969**, 2761.