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Binuclear Complexes of Rhodium and Iridium Bridged by Some New Bifunctional Anionic Ligands

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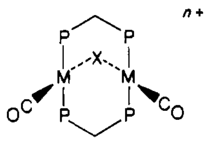
Reaction of the binuclear complexes $[M(\mu\text{-Cl})(COD)]_2$ (M = Rh, Ir) with the bifunctional anionic 2-hydroxypyridinate, 2-mercaptopyridinate, and 2-mercaptothiazolinate groups yields the binuclear complexes $[M(\mu\text{-XY})(COD)]_2$, where XY^- are the anionic groups listed. The structures of the 2-mercaptothiazolinate-bridged rhodium (**3a**) and iridium (**3b**) complexes have been determined. Compound **3a** crystallizes with 1 molar equiv of CH_2Cl_2 in the triclinic space group $P\bar{1}$ with a = 10.555 (3) Å, b = 10.664 (3) Å, c = 12.691 (3) Å, α = 91.54 (2)°, β = 97.05 (2)°, γ = 102.02 (2)°, and Z = 2, whereas **3b** crystallizes in the monoclinic space group $P2_1/c$ with a = 9.995 (1) Å, b = 24.327 (4) Å, c = 10.823 (1) Å, β = 106.054 (7)°, and Z = 4. In both complexes the bridging 2-mercaptothiazolinate ligands are bound to the adjacent metals via the nitrogen and mercapto sulfur atoms. The square-planar coordination planes of the adjacent metals in the two complexes are inclined to each other by approximately 54.3 (2)° (**3a**) and 55.2 (2)° (**3b**), and the metals are separated by 3.7154 (5) and 3.5434 (4) Å, respectively. In addition, the square planes are staggered with respect to each other by approximately 39.1° (**3a**) and 37.3° (**3b**).

Introduction

Interest in binuclear complexes, in which the two metal centers are held in close proximity, has arisen primarily due to the possibility that the metals may act in a cooperative manner and by so doing may display chemistry which differs from that of the mononuclear counterparts. With complexes involving the group 8 metals two principal strategies have been used to ensure that the metals remain together during reactions of interest. The first involves the use of diphosphine[1] or related ligands[2] to bridge the two metal centers, as shown in **1** for $[M_2(CO)_2(\mu\text{-X})(DPM)_2]^{n+}$ (M = Rh, Ir; DPM = $Ph_2PCH_2PPh_2$; X = anionic group), and the second utilizes anionic ligands as the bridging groups,[3-9] as shown in **2** for $[Rh(\mu\text{-Cl})(PPh_3)_2]_2$.



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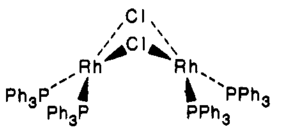

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Although the structural types **1** and **2** appear rather different, they are in fact quite analogous; both are square-planar d^8–d^8 complexes in which the metals are in close proximity, and both have a vacant coordination site between the two metals. Furthermore, as pointed out by Hoffman and Hoffmann, the valence orbitals of the two types are also very similar.[10]

In complexes of type **2** the most common bridging anionic ligands utilized have been halide,[3] thiolato,[4] phosphido,[5] and pyrazolyl[6,7] groups. Our interest in complexes of this type was prompted by two different aspects of their chemistry. The first relates to the possible involvement of the bridging anionic ligand in reactions of the complexes. Poilblanc and co-workers had shown that reactivity of some thiolato-bridged complexes involved movement of one of the bridging thiolato groups to a terminal position,[4d] and it was proposed that such a transformation could be important in catalysis by such complexes.[11] We had also postulated a similar "windshield-wiper" movement of a bridged anionic group to explain the reactivity of "A-frame" complexes with H_2 and alkynes.[12] It was felt that such a bridge-to-terminal transformation could be significantly influenced by utilizing bridging groups having two different atom types to bind to the two metals, so we set out to synthesize binuclear complexes of Rh and Ir bridged by such groups. Our initial chemistry in this area has focussed on the anionic ligands shown below. The hydroxypyridinate group has been frequently used as a bridging group,[13] and one complex of the type we describe herein was previously reported.[14] In addition, while this work was in progress, some preliminary studies on the complexes $[Ir(\mu\text{-SC}_5H_4N)(COD)]_2$ (COD = 1,5-cyclooctadiene) and $[Ir(\mu\text{-SC}_5H_4N)(CO)_2]_2$, having bridging 2-mercaptopyridinate groups, were communicated.[15]

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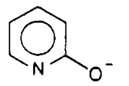

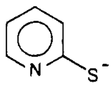

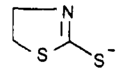

The second aspect of interest relates to the photochemical activation of these binuclear d^8–d^8 complexes. It had been shown that a very similar pyrazolyl-bridged system underwent photoinduced, two-center oxidative addition reactions,[16] and we were interested in the influence of the bridging groups shown above on the photochemistry. It was our feeling that with the above groups, which would contain three atoms in the bridge, the geometry of the complex would differ from the pyrazolyl complexes, containing two atoms in the bridge, or the pseudohalide complexes which contain only one-atom bridges and that this difference could influence metal–metal interactions and therefore the photochemistry.[17] Preliminary studies on the hydroxypyridinate complexes had already shown some difference,[14] and investigations of the mercaptopyridinate-bridged carbonyl complex showed facile, photoinduced oxidative addition reactions.[15]

Experimental Section

General Comments. All solvents were appropriately dried and degassed prior to use under an atmosphere of dinitrogen, and all operations were routinely carried out under Schlenk conditions utilizing a dinitrogen atmosphere. The compounds 2-mercaptothiazoline, 2-mercaptopyridine, 2-hydroxypyridine, and COD (1,5-cyclooctadiene) were obtained from Aldrich, hydrated rhodium trichloride was purchased from Johnson Matthey, and hydrated iridium trichloride was received from Engelhard. Sodium hydride as a 60% oil emulsion was obtained from Aldrich and was stored under dinitrogen; before use it was washed with toluene and hexanes to remove the oil. The complexes $[Rh(\mu\text{-}Cl)(COD)]_2$[18] and $[Ir(\mu\text{-}Cl)(COD)]_2$[19] were prepared by the reported procedures. IR spectra were recorded on a Nicolet 7199 Fourier transform spectrometer with use of Nujol mulls on KBr plates. ^1H NMR spectra were run on either a Bruker WP200 or a Bruker WP400 instrument. Elemental analyses were performed within the department.

Preparation of Complexes. (a) $[Rh(\mu\text{-}OC_5H_4N)(COD)]_2$ (1a). A solution of sodium 2-hydroxypyridinate in THF (10 mL), prepared by stirring 113 mg (1.19 mmol) of 2-hydroxypyridine and 28.5 mg (1.19 mmol) of NaH for 1 h at ambient temperature, was added slowly to a yellow solution of 280 mg (0.57 mmol) of $[Rh(\mu\text{-}Cl)(COD)]_2$ in THF (10 mL). An orange color developed within 2 h, and the reaction mixture was stirred overnight to complete the reaction. Filtration was followed by concentration to 7 mL, after which diethyl ether (15 mL) was slowly layered on top. Refrigeration afforded the compound as orange-yellow crystals, yield 175 mg (50%). Anal. Calcd for $C_{26}H_{32}N_2O_2Rh_2$: C, 51.16; H, 5.29; N, 4.59. Found: C, 51.02, H, 5.27; N, 4.46. ^1H NMR (200 MHz, $CDCl_3$, −40 °C): OC_5H_4N ring δ 7.94 (d, 2 H), 6.93 (m, 2 H), 6.17 (d, 2 H), and 6.08 (t, 2 H); COD olefinic δ 4.76 (br, 4 H), 3.68 (br, 2 H), and 3.12 (br, 2 H); COD methylene δ 2.76 (m, 6 H), 2.25 (br, 2 H), and 1.73 (m, 8 H).

(b) $[Rh(\mu\text{-}SC_5H_4N)(COD)]_2$ (2a). A yellow solution of sodium 2-mercaptopyridinate in THF (10 mL), prepared by stirring 140 mg (1.26 mmol) of 2-mercaptopyridine and 30.3 mg (1.26 mmol) of NaH for 1 h at room temperature, was slowly added to a solution of 300 mg (0.61 mmol) of $[Rh(\mu\text{-}Cl)(COD)]_2$ in THF (10 mL). A red-orange color developed within a few minutes. The reaction mixture was allowed to stir for 4 h, and the resulting red-brown solution was filtered and concentrated to 7 mL, and 10 mL of diethyl ether was slowly layered on top affording yellow-orange crystals after refrigeration; yield 165 mg (42%). Anal. Calcd for $C_{26}H_{32}N_2Rh_2S_2$: C, 48.60; H, 5.02; N, 4.36. Found: C, 47.99; H, 4.96; N, 4.19. ^1H NMR (200 MHz, $CDCl_3$, −65 °C): SC_5H_4N *ring* δ 7.98 (br, 2 H), 7.34 (d, 2 H), 6.85 (t, 2 H), and 6.49 (t, 2 H); COD olefinic δ 4.83 (br, 2 H), 4.37 (br, 2 H), 4.05 (br, 2 H), and 3.86 (br, 2 H); COD methylene δ 2.48 (br, 8 H), and 1.90 (br, 8 H).

(c) $[Rh(\mu\text{-}S_2NC_3H_4)(COD)]_2$ (3a). A solution of sodium 2-mercaptothiazolinate in THF (10 mL), prepared by stirring 150 mg (1.26 mmol) of 2-mercaptothiazoline and 30.5 mg (1.27 mmol) of NaH for 1 h at room temperature, was slowly added to a solution of 300 mg (0.61 mmol) of $[Rh(\mu\text{-}Cl)(COD)]_2$ in THF (10 mL). An orange color developed within 1 h, and the reaction mixture was stirred overnight to ensure completion of the reaction. Filtration was followed by concentration to 7 mL, after which 10 mL of diethyl ether was slowly layered on top. Refrigeration afforded the product as orange-crystals, yield 265 mg (66%). Anal. Calcd for $C_{22}H_{32}N_2Rh_2S_4$: C, 40.12; H, 4.90; N, 4.25. Found: C, 41.01; H, 4.94; N, 4.13. ^1H NMR (200 MHz, $CDCl_3$, −40 °C): $S_2NC_3H_4$ ring δ 3.92 (m, 4 H) and 3.28 (m, 4 H); COD olefinic δ 4.57 (m, 4 H), 4.33 (m, 2 H) and 3.66 (m, 2 H); COD methylene δ 2.60 (m, 6 H), 2.21 (m, 2 H), 1.92 (m, 6 H), and 1.66 (m, 2 H).

(d) $[Ir(\mu\text{-}S_2NC_3H_4)(COD)]_2$ (3b). A solution of $[S_2NC_3H_4]Na$ in THF (10 mL), prepared by stirring 90 mg (0.75 mmol) of 2-mercaptothiazoline and 18 mg (0.75 mmol) of NaH for 1 h at ambient temperature, was added slowly to a light red solution *of 250 mg (0.37 mmol) of $[Ir(\mu\text{-}Cl)(COD)]_2$ in THF (10 mL).* The color of the reaction mixture immediately changed to dark red. This mixture was allowed to stir for 2 h to ensure complete reaction. Filtration was followed by concentration to a small volume (ca. 5 mL), after which diethyl ether (10 mL) was slowly layered in to form an upper layer. Refrigeration afforded the compound as deep red crystals; yield 170 mg (55%). Anal. Calcd for $C_{22}H_{32}Ir_2N_2S_4$: C, 31.56; H, 3.85; N, 3.35. Found: C, 31.33; H, 3.80; N, 3.35. ^1H NMR (400 MHz, $CDCl_3$, −40 °C): $C_3H_4NS_2$ ring δ 4.28 (m, 2 H), 4.13 (m, 2 H), 3.63 (m, 2 H), and 3.15 (m, 2 H); COD olefinic δ 4.43 (m, 2 H), 3.98 (m, 2 H), and 3.35 (m, 4 H); COD methylene δ 2.45 (m, 4 H), 2.15 (m, 2 H), 2.00 (m, 2 H), 1.65 (m, 6 H), and 1.33 (m, 2 H).

The preparations noted above yielded well-formed single crystals of the products, which were of high purity, albeit in moderate yield. Higher isolated yields were obtained in all cases when the compounds were isolated as powders by reducing the volume of THF, after filtration, to ca. 2 mL and adding ca. 15 mL of hexanes, followed by cooling. In any case the preparations appeared to be essentially quantitative, as determined by ^1H NMR spectroscopy, so in subsequent reactions of these species the COD complexes (1–3) were not isolated but were reacted in situ.

Compounds $[Ir(\mu\text{-}OC_5H_4N)(COD)]_2$ (**1b**) and $[Ir(\mu\text{-}SC_5H_4N)(CO)]_2$ (**2b**) were also prepared and characterized as described above for the other complexes. However these preparations were reported previously[14,15] so are not described in this paper.

X-ray Data Collection. Crystals suitable for X-ray diffraction studies were obtained by the slow diffusion of Et_2O into saturated CH_2Cl_2 solutions of compounds **3a** and **3b**. Data were collected on an Enraf-Nonius CAD4 diffractometer at 22 °C using graphite-monochromated Mo Kα radiation. The automatic peak search and reflection indexing programs, in conjunction with a cell reduction program, established the crystal systems. For compound **3a** the triclinic system and lack of systematic absences indicated that the space group was $P1$ or $P\bar{1}$; the latter was chosen and later verified by the successful refinement of the structure. The systematic absences for compound **3b** together with the monoclinic cell unambiguously established $P2_1/c$ as the space group. Cell constants for both compounds were obtained from a least-squares refinement of the setting angles (centered in both positive and negative theta) of 25 reflections having 2θ between 18.92° and 25.68° for compound **3a** and between 21.96° and 27.42° for compound **3b**.

The intensity data were collected by using a $\theta/2\theta$ scan with variable scan speeds chosen to give $\sigma(I)/I \leq 0.03$ within a time limit of 50 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the α_1–α_2 wavelength dispersion, and backgrounds for the peaks were

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Table I. Crystal Data and Details of Intensity Collection

	$[Rh(S_2NC_3H_4)(COD)]_2 \cdot CH_2Cl_2$ (**3a**)	$[Ir(S_2NC_3H_4)(COD)]_2$ (**3b**)
mol formula	$C_{23}H_{34}Cl_2N_2Rh_2S_4$	$C_{22}H_{32}Ir_2N_2S_4$
fw	743.51	837.17
cryst shape	triclinic prism	monoclinic prism
cryst size, mm	0.24 × 0.24 × 0.17	0.41 × 0.15 × 0.23
systematic absences	none	*h0l*, *l* odd, *0k0*, *k* odd
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
temp, °C	22	22
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
unit cell parameters		
a, Å	10.555 (3)	9.995 (1)
b, Å	10.664 (3)	24.327 (4)
c, Å	12.691 (3)	10.823 (1)
α, deg	91.54 (2)	
β, deg	97.05 (2)	106.054 (7)
γ, deg	102.02 (2)	
V, Å^3	1384.6	2529.0
Z	2	4
ρ_{calcd}, g cm^{-3}	1.783	2.199
linear absorp coeff, μ, cm^{-1}	16.76	108.06
max 2θ, deg	52.00	55.00
takeoff angle, deg	3.00	3.00
detector aperture, mm	3.00 + (tan θ) wide × 4.00 high	3.00 + (tan θ) wide × 4.00 high
cryst to detector dist, mm	173	173
scan type	θ/2θ	θ/2θ
scan rate, deg min^{-1}	variable between 1.25 and 6.67	variable between 1.11 and 6.67
scan width, deg	(0.80 + 0.347 tan θ)	(0.60 + 0.347 tan θ)
total no. of reflectns collected	5728 ($h,\pm k,\pm l$)	6248 ($h,k,\pm l$)
no. of indep reflectns	5417	5921
no. of obserns (NO) ($I > 3\sigma(I)$)	3852	3836
no. of variables (NV)	298	271
R^a	0.037	0.029
$R_w{}^a$	0.047	0.037
GOF^a	1.547	1.160

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

measured by extending the scan 25% on either side of the calculated range. Three reflections were chosen as standard reflections and were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection. For compound **3a** a 5.1% decrease in the intensity of these standards was corrected assuming linear decay; for compound **3b** the mean drop in intensity was only 2.8% but was not uniform over the three standards, so no correction was applied. See Table I for crystal data and details of intensity collection. The data were corrected for Lorenz and polarization effects and for absorption using the method of Walker and Stuart.[20] Data were reduced in the usual manner by using a value of $p = 0.04$ to downweight intense reflections.[21]

Structure Solution and Refinement. Both structures were solved by using Patterson techniques to locate the metals and subsequent least-squares and difference Fourier calculations to obtain the other atom positions. All hydrogen atoms were located but were input in their idealized positions by using C–H distances of 0.95 Å; their thermal parameters were fixed at 1.2 times that of their attached carbon atom.

Refinement was carried out by full-matrix least-squares techniques[22] minimizing the function $\sum w(|F_o| - |F_c|)^2$, with $w = 4F_o{}^2/\sigma^2(F_o{}^2)$. The neutral atom scattering factors[23,24] and anomalous dispersion terms[25] for the atoms were obtained from the usual sources. The parameters for the hydrogen atoms were not refined, but these atoms were allowed to "ride" on their attached carbon. Analyses of F_o vs F_c for both structures showed no unusual trends. The highest peak in the final difference Fourier map was 0.72 e Å^{-3} for compound **3a** and 0.63 e Å^{-3} for compound **3b**.

Table II. Positional and Equivalent Isotropic Thermal Parameters for $[Rh(\mu\text{-}S_2NC_3H_4)(COD)]_2 \cdot CH_2Cl_2$ (3a)

atom	*x*	*y*	*z*	*B*,^{a} Å^2
Rh(1)	0.25028 (4)	0.23203 (4)	0.14236 (4)	3.18 (1)
Rh(2)	0.11336 (5)	0.30100 (4)	0.38837 (4)	3.09 (1)
Cl(1)^b	0.4103 (2)	0.7930 (3)	0.2484 (2)	7.11 (6)
Cl(2)^b	0.3394 (3)	0.8500 (4)	0.4541 (2)	10.87 (9)
S(1)	0.1286 (2)	0.0420 (2)	0.2028 (2)	4.15 (4)
S(2)	−0.1635 (2)	−0.0275 (2)	0.1746 (2)	5.54 (5)
S(3)	0.0890 (2)	0.4543 (2)	0.2612 (1)	4.01 (4)
S(4)	−0.1243 (2)	0.3986 (2)	0.0772 (2)	5.21 (4)
N(1)	−0.0302 (5)	0.1633 (5)	0.2980 (4)	3.3 (1)
N(2)	0.0765 (5)	0.2924 (5)	0.0916 (4)	3.2 (1)
C(1)	−0.0173 (6)	0.0723 (6)	0.2348 (5)	3.3 (1)
C(2)	−0.2582 (7)	0.0518 (8)	0.2553 (8)	6.3 (2)
C(3)	−0.1702 (6)	0.1695 (8)	0.3037 (6)	4.8 (2)
C(4)	0.0255 (6)	0.3712 (6)	0.1403 (5)	3.3 (1)
C(5)	−0.1205 (8)	0.2912 (8)	−0.0344 (6)	5.8 (2)
C(6)	−0.0004 (8)	0.2347 (8)	−0.0081 (5)	5.1 (2)
C(7)	0.4313 (6)	0.2041 (7)	0.2241 (6)	4.1 (1)
C(8)	0.4015 (6)	0.1293 (7)	0.1286 (6)	4.5 (2)
C(9)	0.4609 (8)	0.1609 (8)	0.0254 (7)	5.8 (2)
C(10)	0.4536 (8)	0.2929 (8)	−0.0126 (7)	6.2 (2)
C(11)	0.3473 (7)	0.3498 (7)	0.0299 (6)	4.5 (2)
C(12)	0.3661 (7)	0.4195 (6)	0.1274 (6)	4.1 (1)
C(13)	0.4901 (8)	0.4438 (8)	0.2052 (7)	5.6 (2)
C(14)	0.5375 (7)	0.3273 (8)	0.2403 (6)	5.0 (2)
C(15)	0.0702 (7)	0.1968 (7)	0.5259 (5)	4.4 (2)
C(16)	0.1776 (7)	0.1617 (6)	0.4881 (5)	4.1 (1)
C(17)	0.3176 (8)	0.2082 (8)	0.5434 (7)	6.1 (2)
C(18)	0.3838 (7)	0.3356 (8)	0.5069 (6)	5.3 (2)
C(19)	0.2932 (7)	0.4194 (7)	0.4586 (5)	4.2 (2)
C(20)	0.1943 (7)	0.4540 (6)	0.5081 (6)	4.3 (2)
C(21)	0.1690 (8)	0.4159 (8)	0.6186 (6)	5.9 (2)
C(22)	0.0684 (9)	0.2891 (9)	0.6180 (6)	6.3 (2)
C(23)^b	0.2831 (8)	0.7898 (9)	0.3250 (7)	6.4 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] Atoms Cl(1), Cl(2), and C(23) belong to the CH_2Cl_2 molecule of crystallization.

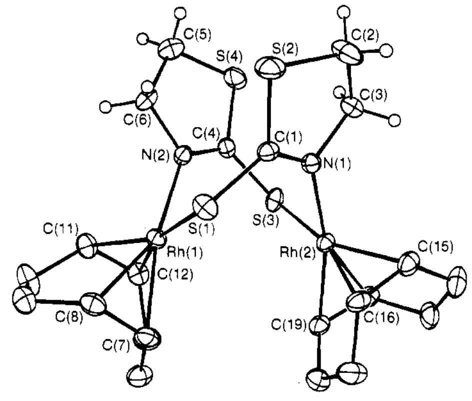

Figure 1. A perspective view of $[Rh(\mu\text{-}S_2NC_3H_4)(COD)]_2$ (**3a**) showing the numbering scheme. Thermal parameters are shown at the 20% level except for hydrogens that are drawn artificially small. Hydrogen atoms on the COD ligands are omitted for clarity.

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Table III. Positional and Equivalent Isotropic Thermal Parameters for $[Ir(\mu\text{-}S_2NC_3H_4)(COD)]_2$ (3b)

atom	x	y	z	B^a Å^2
Ir(1)	0.47131 (3)	0.11652 (1)	0.31439 (2)	2.987 (5)
Ir(2)	0.13892 (3)	0.12245 (1)	0.08811 (2)	3.016 (5)
S(1)	0.3093 (2)	0.10412 (8)	0.4317 (2)	3.68 (4)
S(2)	0.1292 (2)	0.0061 (1)	0.4260 (2)	4.72 (5)
S(3)	0.2760 (2)	0.06649 (8)	−0.0021 (2)	3.34 (4)
S(4)	0.3715 (2)	−0.04657 (8)	0.0830 (2)	4.46 (5)
N(1)	0.1239 (5)	0.0626 (2)	0.2218 (5)	3.1 (1)
N(2)	0.4350 (5)	0.0378 (2)	0.2330 (5)	2.9 (1)
C(1)	0.1831 (6)	0.0599 (3)	0.3430 (6)	3.1 (1)
C(2)	−0.0128 (8)	−0.0100 (4)	0.2876 (7)	5.2 (2)
C(3)	0.0286 (7)	0.0158 (4)	0.1750 (7)	4.1 (2)
C(4)	0.3679 (6)	0.0236 (3)	0.1185 (6)	2.9 (1)
C(5)	0.501 (1)	−0.0592 (4)	0.2327 (9)	5.8 (2)
C(6)	0.4903 (7)	−0.0099 (3)	0.3173 (7)	3.8 (2)
C(7)	0.6713 (7)	0.1130 (4)	0.2841 (8)	4.8 (2)
C(8)	0.5839 (7)	0.1414 (4)	0.1837 (7)	4.1 (2)
C(9)	0.585 (1)	0.2032 (4)	0.1661 (8)	6.2 (2)
C(10)	0.554 (1)	0.2358 (4)	0.274 (1)	7.4 (3)
C(11)	0.4920 (9)	0.2010 (3)	0.3633 (7)	4.8 (2)
C(12)	0.5732 (8)	0.1700 (4)	0.4630 (7)	4.6 (2)
C(13)	0.729 (1)	0.1623 (5)	0.496 (1)	7.9 (3)
C(14)	0.7798 (9)	0.1412 (5)	0.391 (1)	6.8 (3)
C(15)	0.1757 (9)	0.1920 (3)	−0.0153 (8)	5.1 (2)
C(16)	0.0700 (8)	0.1588 (4)	−0.0940 (7)	4.6 (2)
C(17)	−0.087 (1)	0.1712 (5)	−0.1323 (9)	7.6 (3)
C(18)	−0.1451 (8)	0.1771 (4)	−0.0189 (8)	5.0 (2)
C(19)	−0.0509 (8)	0.1549 (4)	0.1074 (8)	5.3 (2)
C(20)	0.0568 (8)	0.1833 (4)	0.1862 (7)	4.9 (2)
C(21)	0.105 (1)	0.2416 (4)	0.160 (1)	6.2 (2)
C(22)	0.145 (1)	0.2472 (4)	0.040 (1)	7.9 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

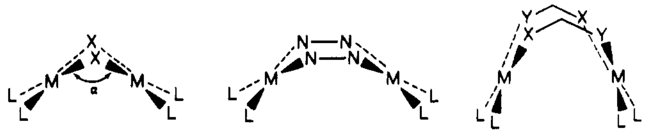
The positional and isotropic thermal parameters for the two structures are given in Tables II and III. Additional information is presented as supplementary material.

Results and Discussion

(a) Description of Structures. (i) $[Rh(\mu\text{-}S_2NC_3H_4)(COD)]_2\cdot CH_2Cl_2$ (3a). The unit cell contains two molecules of the complex and two methylene chloride molecules of crystallization, the latter of which are well-behaved and having the expected geometry. There are no unusual nonbonded contacts between adjacent molecules of complex or solvent. The complex molecule has essentially the expected overall geometry, shown in Figure 1, in which the two metal coordination planes are inclined to each other, bridged by the bifunctional mercaptothiazolinate groups in a head-to-tail arrangement. Although the bridging ligands could in principle be S,N- or S,S-bound, this structure determination clearly shows that they are bound to one Rh by the ring nitrogen and to the other Rh by the exocyclic sulfur atom of the mercapto group. The coordination planes of the two metals are staggered with respect to each other by between 38.6° and 40.0°, presumably in order to minimize nonbonded contacts between the COD hydrogens on the halves of the two ligands facing each other (see Figure 1), although the existing contacts are all greater than 2.40 Å and as such are unexceptional.

The geometries of the COD ligands are quite normal and compare well with other determinations.[3a,b,5a,6] The olefinic C–C bonds (Table IV) range from 1.389 (7) to 1.398 (7) Å, falling between the limits for normal single and double bond distances[26] of 1.54 and 1.34 Å, respectively. By comparison, the other C–C distances within the saturated part of the COD ligands range from 1.492 (8) to 1.537 (8) Å. All distances of the olefinic carbons to the Rh atoms (average 2.140 (4) Å) are also typical, as are the angles within the COD ligand (Table V). Within the mercaptothiazolinate ligands the parameters are also not unexpected. The N(1)–C(1) and N(2)–C(4) distances of 1.283 (5) and 1.272 (5) Å, respectively, are typical for C=N double bonds[26] and are much shorter than the N(1)–C(3) and N(2)–C(6) single-bonded values (1.504 (6), 1.463 (6) Å). Both C(1)–S(1) and C(4)–S(3) distances involving the exocyclic sulfurs (1.731 (4) and 1.737 (4) Å) are slightly shorter than the endocyclic bonds, C(1)–S(2) and C(4)–S(4) (1.756 (4) and 1.767 (4) Å), suggesting somewhat greater multiple-bond character in the exocyclic C–S bonds (vide infra). All of these above C–S distances are significantly shorter than the C(2)–S(2) and C(5)–S(4) distances of 1.822 (6) and 1.807 (6) Å; this lengthening is clearly a consequence of the different hybridization involving C(1), C(4) (sp^2) and C(2), C(5) (sp^3).[27] Nevertheless all C–S distances are within the normal range for such bonds.[26] Within the five-membered thiazolinate rings the angles at the carbon and nitrogen atoms are consistent with the appropriate hybridization, while those at the sulfur atoms (average 91.2 (2)°) are acute due to its large covalent radius and resulting strain within the small ring. By contrast, the Rh–S–C angles at the exocyclic sulfurs are normal (average 108.0 (1)°), showing the lack of strain at these atoms. The Rh–S distances (2.363 (1), 2.358 (1) Å) are close to those in a related thiolato-bridged complex[4b] and the Rh–N distances (2.102 (3), 2.079 (3) Å) compare closely to the related distances (between 2.08 (1) and 2.11 (1) Å) in two pyrazolyl-bridged rhodium compounds.[7] All angles about both Rh(1) and Rh(2) are close to the values expected for idealized square-planar coordination.

As noted, the coordination planes of the two metals are inclined rather markedly with respect to each other, such that the angle between them is 54.3 (2)°. This angle incorporates both a folding of the two coordination planes about the bridging groups and a twisting of these planes about the Rh–Rh axis in order to stagger the COD ligands. So although we have no exact measure of folding, the above dihedral angle clearly indicates that at, ca. 54.3°, the complex is folded much more than the halide, or thiolato-bridged analogues, in which these dihedral angles were about 120° in most cases. (In fact in a few cases, planar structures were observed.[3a,5e]) Furthermore, the folding is significantly greater than in the pyrazolyl-bridged complexes (ca. 79°).[6,7] It seems clear that the increased folding (decreased dihedral angle) is related to the constraints of the one-, two-, or three-atom bridging units as sketched.



In order to maintain normal, unstrained angles at the bridging atoms, and therefore optimal orbital overlap, it is necessary for the complex to fold more. This fold is not accompanied by a compression of the metal–metal distance; on the contrary, the Rh–Rh separation, at 3.7154 (5) Å is longer than any of which we are aware in related species. In one of the pyrazolyl-bridged Rh_2 complexes a Rh–Rh separation of 3.568 Å has been reported[7a] and a Pt–Cr separation of 3.686 (3) Å was observed in

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(26) *International Tables for X-ray Crystallography*; Macgilvray, C. H., Rieck, G. D., Eds.; Kynoch: Birmingham, England, 1974; Vol. III, Table 4.2.

(27) The covalent radii for sp^3 and sp^2 carbons are 0.77 and 0.74Å, respectively.

Table IV. Selected Distances (Å) for $[Rh(\mu\text{-}S_2NC_3H_4)(COD)]_2 \bullet CH_2Cl_2$ (3a)

Rh(1)–S(1)	2.363 (1)[a]	S(1)–C(1)	1.731 (4)	C(8)–C(9)	1.537 (8)
Rh(1)–N(2)	2.102 (3)	S(2)–C(1)	1.756 (4)	C(9)–C(10)	1.514 (8)
Rh(1)–C(7)	2.140 (4)	S(2)–C(2)	1.822 (6)	C(10)–C(11)	1.527 (7)
Rh(1)–C(8)	2.136 (4)	S(3)–C(4)	1.737 (4)	C(11)–C(12)	1.396 (7)
Rh(1)–C(11)	2.141 (5)	S(4)–C(4)	1.767 (4)	C(12)–C(13)	1.511 (7)
Rh(1)–C(12)	2.141 (5)	S(4)–C(5)	1.807 (6)	C(13)–C(14)	1.492 (8)
Rh(2)–S(3)	2.358 (1)	N(1)–C(1)	1.283 (5)	C(15)–C(16)	1.398 (7)
Rh(2)–N(1)	2.079 (3)	N(1)–C(3)	1.504 (6)	C(15)–C(22)	1.513 (7)
Rh(2)–C(15)	2.140 (5)	N(2)–C(4)	1.272 (5)	C(16)–C(17)	1.531 (7)
Rh(2)–C(16)	2.139 (4)	N(2)–C(6)	1.463 (6)	C(17)–C(18)	1.506 (8)
Rh(2)–C(19)	2.125 (4)	C(2)–C(3)	1.466 (7)	C(18)–C(19)	1.529 (7)
Rh(2)–C(20)	2.161 (4)	C(5)–C(6)	1.519 (8)	C(19)–C(20)	1.389 (7)
Cl(1)–C(23)	1.748 (6)[b]	C(7)–C(8)	1.398 (7)	C(20)–C(21)	1.510 (7)
Cl(2)–C(23)	1.731 (7)[b]	C(7)–C(14)	1.530 (7)	C(21)–C(22)	1.535 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Atoms Cl(1), Cl(2), and C(23) are from the methylene chloride of crystallization.

Table V. Selected Angles (deg) for $[Rh(\mu\text{-}S_2NC_3H_4)(COD]_2 \bullet CH_2Cl_2$ (3a)

S(1)–Rh(1)–N(2)	90.3 (1)[a]	C(16)–Rh(2)–C(20)	91.8 (2)	C(8)–C(9)–C(10)	114.3 (4)
S(1)–Rh(1)–C(7)	93.3 (1)	C(19)–Rh(2)–C(20)	37.9 (2)	C(9)–C(10)–C(11)	114.1 (5)
S(1)–Rh(1)–C(8)	87.1 (1)	Rh(1)–S(1)–C(1)	108.5 (1)	Rh(1)–C(11)–C(10)	112.6 (3)
S(1)–Rh(1)–C(11)	155.7 (1)	C(1)–S(2)–C(2)	91.0 (2)	Rh(1)–C(11)–C(12)	71.0 (3)
S(1)–Rth(1)–C(12)	166.1 (1)	Rh(2)–S(3)–C(4)	107.4 (1)	C(10)–C(11)–C(12)	123.3 (5)
N(2)–Rh(1)–C(7)	166.4 (2)	C(4)–S(4)–C(5)	91.3 (2)	Rh(1)–C(12)–C(13)	70.9 (3)
N(2)–Rh(1)–C(8)	155.4 (2)	Rh(2)–N(1)–C(1)	129.1 (3)	Rh(1)–C(12)–C(11)	110.8 (3)
N(2)–Rh(1)–C(11)	90.1 (2)	Rh(2)–N(1)–C(3)	117.4 (3)	C(11)–C(12)–C(13)	125.0 (5)
N(2)–Rh(1)–C(12)	91.8 (2)	C(1)–N(1)–C(3)	113.5 (4)	C(12)–C(13)–C(14)	115.8 (4)
C(7)–Rh(1)–C(8)	38.1 (2)	Rh(1)–N(2)–C(4)	127.4 (3)	C(7)–C(14)–C(13)	113.4 (4)
C(7)–Rh(1)–C(11)	92.2 (2)	Rh(1)–N(2)–C(6)	118.0 (3)	Rh(2)–C(15)–C(16)	71.0 (3)
C(7)–Rh(1)–C(12)	81.8 (2)	C(4)–N(2)–C(6)	114.5 (4)	Rh(2)–C(15)–C(22)	109.9 (3)
C(8)–Rh(1)–C(11)	82.6 (2)	S(1)–C(1)–S(2)	118.2 (2)	C(16)–C(15)–C(22)	128.8 (5)
C(8)–Rh(1)–C(12)	96.6 (2)	S(1)–C(1)–N(1)	126.3 (3)	Rh(2)–C(16)–C(15)	71.0 (3)
C(11)–Rh(1)–C(12)	38.1 (2)	S(2)–C(1)–N(1)	115.6 (3)	Rh(2)–C(16)–C(17)	112.7 (3)
S(3)–Rh(2)–N(1)	90.9 (1)	S(2)–C(2)–C(3)	106.7 (4)	C(15)–C(16)–C(17)	122.6 (5)
S(3)–Rh(2)–C(15)	115.3 (2)	N(1)–C(3)–C(2)	110.5 (4)	C(16)–C(17)–C(18)	112.8 (4)
S(3)–Rh(2)–C(16)	166.3 (1)	S(3)–C(4)–S(4)	117.4 (2)	C(17)–C(18)–C(19)	115.8 (4)
S(3)–Rh(2)–C(19)	90.2 (1)	S(3)–C(4)–N(2)	126.5 (3)	Rh(2)–C(19)–C(18)	109.6 (3)
S(3)–Rh(2)–C(20)	89.8 (1)	S(4)–C(4)–N(2)	116.2 (3)	Rh(2)–C(19)–C(20)	72.5 (3)
N(1)–Rh(2)–C(15)	88.4 (2)	S(4)–C(5)–C(6)	106.6 (3)	C(18)–C(19)–C(20)	124.3 (4)
N(1)–Rh(2)–C(16)	92.9 (2)	N(2)–C(6)–C(5)	111.2 (4)	Rh(2)–C(20)–C(19)	69.7 (3)
N(1)–Rh(2)–C(19)	165.0 (2)	Rh(1)–C(7)–C(8)	70.8 (3)	Rh(2)–C(20)–C(21)	112.8 (4)
N(1)–Rh(2)–C(20)	157.3 (2)	Rh(1)–C(7)–C(14)	113.1 (3)	C(19)–C(20)–C(21)	122.8 (5)
C(15)–Rh(2)–C(16)	38.1 (2)	C(8)–C(7)–C(14)	122.7 (5)	C(20)–C(21)–C(22)	112.6 (4)
C(15)–Rh(2)–C(19)	96.9 (2)	Rh(1)–C(8)–C(7)	71.1 (3)	C(15)–C(22)–C(21)	113.1 (4)
C(15)–Rh(2)–C(20)	81.6 (2)	Rh(1)–C(8)–C(9)	110.1 (3)	Cl(1)–C(23)–Cl(2)[b]	112.1 (4)
C(16)–Rh(2)–C(19)	82.8 (2)	C(7)–C(8)–C(9)	126.4 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] CH_2Cl_2 of crystallization.

Table VI. Selected Distances (Å) for $[Ir(\mu\text{-}S_2NC_3H_4)(COD)]_2$ (3b)

Ir(1)–S(1)	2.337 (2)[a]	S(2)–C(2)	1.799 (8)	C(9)–C(10)	1.52 (1)
Ir(1)–N(2)	2.096 (5)	S(3)–C(4)	1.723 (7)	C(10)–C(11)	1.53 (1)
Ir(1)–C(7)	2.115 (7)	S(4)–C(4)	1.753 (7)	C(11)–C(12)	1.38 (1)
Ir(1)–C(8)	2.125 (7)	S(4)–C(5)	1.80 (1)	C(12)–C(13)	1.52 (1)
Ir(1)–C(11)	2.117 (7)	N(1)–C(1)	1.283 (8)	C(13)–C(14)	1.46 (1)
Ir(1)–C(12)	2.100 (7)	N(1)–C(3)	1.482 (9)	C(15)–C(16)	1.41 (1)
Ir(2)–S(3)	2.329 (2)	N(2)–C(4)	1.282 (8)	C(15)–C(22)	1.53 (1)
Ir(2)–N(1)	2.087 (5)	N(2)–C(6)	1.486 (8)	C(16)–C(17)	1.53 (1)
Ir(2)–C(15)	2.117 (8)	C(2)–C(3)	1.53 (1)	C(17)–C(18)	1.51 (1)
Ir(2)–C(16)	2.095 (7)	C(5)–C(6)	1.53 (1)	C(18)–C(19)	1.53 (1)
Ir(2)–C(19)	2.118 (7)	C(7)–C(8)	1.38 (1)	C(19)–C(20)	1.36 (1)
Ir(2)–C(20)	2.116 (7)	C(7)–C(14)	1.51 (1)	C(20)–C(21)	1.55 (1)
S(1)–C(1)	1.733 (7)	C(8)–C(9)	1.51 (1)	C(21)–C(22)	1.47 (1)
S(2)–C(1)	1.755 (7)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

$(Et_3P)_2Pt(\mu\text{-}pz)_2Cr(CO)_4$.[28] In one isomer of the phosphido-bridged species, $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ a very long Rh–Rh distance of 3.717 (1) Å was observed;[5e] however this compound had a planar Rh_2P_2 framework.

(ii) $[Ir(\mu\text{-}S_2NC_3H_4)(COD)]_2$ (3b). The molecular structure of the diiridium species, shown in Figure 2, is almost identical with that of the dirhodium analogue (**3a**). Again the bifunctional bridging ligands bind in a head-to-tail manner to the two metals via the mercapto sulfur atom and the ring nitrogen. All parameters within the COD ligands and 2-mercaptothiazolinate groups are in excellent agreement with those of **3a**, so no further discussion of these parameters seems necessary. Similarly, all angles and bond lengths at the metals are like those of **3a**. The Ir–N distances (2.096 (5), 2.087 (5) Å) are com-

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[28] Stobart, S. R.; Dixon, K. R.; Eadie, D. T.; Atwood, J. L.; Zawarotko, M. J. *Angew. Chem., Int. Ed. Engl.* 1980, *19*, 931.

Table VII. Selected Angles (deg) for [Ir(μ-$S_2NC_3H_4$)(COD)]$_2$ (3b)

S(1)-Ir(1)-N(2)[a]	92.6 (1)	C(16)-Ir(2)-C(20)	96.0 (3)	C(7)-C(8)-C(9)	124.9 (8)
S(1)-Ir(1)-C(7)	154.9 (3)	C(19)-Ir(2)-C(20)	37.6 (3)	C(8)-C(9)-C(10)	114.4 (7)
S(1)-Ir(1)-C(8)	166.5 (2)	Ir(1)-S(1)-C(1)	106.7 (2)	C(9)-C(10)-C(11)	113.5 (7)
S(1)-Ir(1)-C(11)	91.4 (2)	C(1)-S(2)-C(2)	91.1 (3)	Ir(1)-C(11)-C(10)	114.1 (6)
S(1)-Ir(1)-C(12)	85.8 (2)	Ir(2)-S(3)-C(4)	106.7 (2)	Ir(1)-C(11)-C(12)	70.2 (4)
N(2)-Ir(1)-C(7)	87.7 (3)	C(4)-S(4)-C(5)	91.3 (3)	C(10)-C(11)-C(12)	122.7 (9)
N(2)-Ir(1)-C(8)	92.4 (3)	Ir(2)-N(1)-C(1)	130.1 (5)	Ir(1)-C(12)-C(11)	71.6 (4)
N(2)-Ir(1)-C(11)	169.9 (3)	Ir(2)-N(1)-C(3)	117.5 (4)	Ir(1)-C(12)-C(13)	110.8 (6)
N(2)-Ir(1)-C(12)	151.5 (3)	C(1)-N(1)-C(3)	112.4 (6)	C(11)-C(12)-C(13)	126.7 (9)
C(7)-Ir(1)-C(8)	37.9 (3)	Ir(1)-N(2)-C(4)	129.5 (5)	C(12)-C(13)-C(14)	114.6 (8)
C(7)-Ir(1)-C(11)	92.8 (3)	Ir(1)-N(2)-C(6)	117.6 (4)	C(7)-C(14)-C(13)	115.1 (8)
C(7)-Ir(1)-C(12)	82.2 (3)	C(4)-N(2)-C(6)	112.9 (5)	Ir(2)-C(15)-C(16)	69.6 (4)
C(8)-Ir(1)-C(11)	81.8 (3)	S(1)-C(1)-S(2)	117.4 (4)	Ir(2)-C(15)-C(22)	114.2 (6)
C(8)-Ir(1)-C(12)	95.8 (3)	S(1)-C(1)-N(1)	126.4 (5)	C(16)-C(15)-C(22)	122.5 (9)
C(11)-Ir(1)-C(12)	38.2 (3)	S(2)-C(1)-N(1)	116.2 (5)	Ir(2)-C(16)-C(15)	71.2 (4)
S(3)-Ir(2)-N(1)	92.7 (2)	S(2)-C(2)-C(3)	104.6 (5)	Ir(2)-C(16)-C(17)	112.6 (5)
S(3)-Ir(2)-C(15)	92.1 (2)	N(1)-C(3)-C(2)	109.5 (6)	C(15)-C(16)-C(17)	126.0 (8)
S(3)-Ir(2)-C(16)	86.1 (2)	S(3)-C(4)-S(4)	117.5 (4)	C(16)-C(17)-C(18)	113.3 (7)
S(3)-Ir(2)-C(19)	155.0 (3)	S(3)-C(4)-N(2)	126.6 (5)	C(17)-C(18)-C(19)	114.4 (7)
S(3)-Ir(2)-C(20)	167.0 (3)	S(4)-C(4)-N(2)	115.9 (5)	Ir(2)-C(19)-C(18)	113.1 (5)
N(1)-Ir(2)-C(15)	168.7 (3)	S(4)-C(5)-C(6)	104.5 (6)	Ir(2)-C(19)-C(20)	71.1 (4)
N(1)-Ir(2)-C(16)	151.5 (3)	N(2)-C(6)-C(5)	108.7 (6)	C(18)-C(19)-C(20)	124.5 (9)
N(1)-Ir(2)-C(19)	87.4 (3)	Ir(1)-C(7)-C(8)	71.4 (4)	Ir(2)-C(20)-C(19)	71.3 (5)
N(1)-Ir(2)-C(20)	91.6 (3)	Ir(1)-C(7)-C(14)	111.8 (6)	Ir(2)-C(20)-C(21)	111.5 (5)
C(15)-Ir(2)-C(16)	39.2 (3)	C(8)-C(7)-C(14)	122.6 (8)	C(19)-C(20)-C(21)	125.7 (8)
C(15)-Ir(2)-C(19)	92.6 (3)	Ir(1)-C(8)-C(7)	70.6 (4)	C(20)-C(21)-C(22)	114.8 (9)
C(15)-Ir(2)-C(20)	81.6 (3)	Ir(1)-C(8)-C(9)	112.9 (5)	C(15)-C(22)-C(21)	113.5 (8)
C(16)-Ir(2)-C(19)	82.2 (3)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

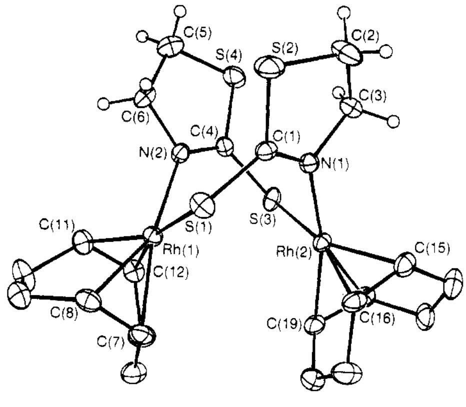

Figure 2. A perspective view of [Ir(μ-$S_2NC_3H_4$)(COD)]$_2$ (**3b**) showing the numbering scheme. Thermal parameters are as for Figure 1.

parable to those of the pyrazolyl-bridged complexes,[6] and the Ir–S (2.337 (2), 2.329 (2) Å) distances are like those of the thiolato-bridged systems.[4] In addition, the complex is twisted about the Ir–Ir vector by ca. 37.3°, much as was observed for **3a**, and the folding of the complex is also similar to that of **3a**, at 55.2 (2)°. The only significant difference in the two structures is in the metal–metal separation; in **3b** this distance (3.5434 (4) Å), is ca. 0.17 Å less than in **3a**. We attach no chemical significance to this difference since the metals are presumably too far apart to be interacting appreciably. This difference is most likely due to differences in packing; we have previously noted a significant influence of packing on metal–metal separation in one example in which a marked difference in Rh–Rh separation between the solvated species [RhCl(CO)(DAM)]$_2$·CH_2Cl_2 (3.236 (2) Å)[29] and the unsolvated complex (3.396 (1) Å)[30] was observed. Both structures **3a** and **3b** bear a strong resemblance to the 6-methyl-2-hydroxypyridinate-bridged species [Ir(μ-mhp)(COD)]$_2$.[14] Although the numerical values for the fold and twist angles are not given in the preliminary communication, it appears that the values are comparable to our compounds. In this, N,O-bound species the Ir–Ir separation is 3.242 (1) Å, which is much shorter than in **3a** or **3b**. This shortening is due in part to the covalent radius difference (ca. 0.29 Å)[31] between sulfur and oxygen but is probably also a consequence of packing. Certainly the 2-mercaptothiazolinate ligands are capable of spanning much shorter distances than those described in this paper; in principle, as long as the ligands opposite the bridging groups do not give rise to unfavourable nonbonded contacts, metal–metal separations approaching the intraligand separation between the mercapto sulfur and nitrogen (average 2.69 Å) should be possible. Consistent with these ideas we have observed a Rh–Rh separation of 3.052 Å in the formally non-metal–metal bonded species, [Rh(μ-$S_2NC_3H_4$)(CO)(PMe_3)]$_2$,[32] and an Ir–Ir separation of 2.695 (2) Å has been reported in a metal–metal bonded complex bridged by similar mercaptopyridinate groups.[15]

(b) Discussion. The complexes [M(μ-XY)(COD)]$_2$, where M = Rh or Ir and XY represents the bifunctional anionic groups referred to earlier, are readily prepared by exchange of the bridging chloride ligands in [M(μ-Cl)(COD)]$_2$ by the appropriate anionic groups as shown in eq 1. In the case of the 2-hydroxy- and 2-mercaptopyridinate

$$M_2(\mu\text{-}Cl)_2(COD)_2 + 2Na^+XY^- \xrightarrow{THF} M_2(\mu\text{-}XY)_2(COD)_2 + 2NaCl \quad (1)$$

$$M = Rh, Ir$$

complexes the binding sites are unambiguous, being at the pyridine nitrogen and the hydroxy or mercapto oxygen or sulfur atoms, as shown clearly in the structures of the 6-methyl-2-hydroxypyridinate-bridged and 2-mercapto-

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(29) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1981**, *20*, 1534.

(30) Mague, J. T. *Inorg. Chem.* **1969**, *8*, 1975.

(31) The covalent radii are 0.73 Å for O and 1.02 Å for S. See: Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row; New York, 1983; pp 258–259.

(32) Sielisch, T.; Cowie, M., manuscript in prepration.

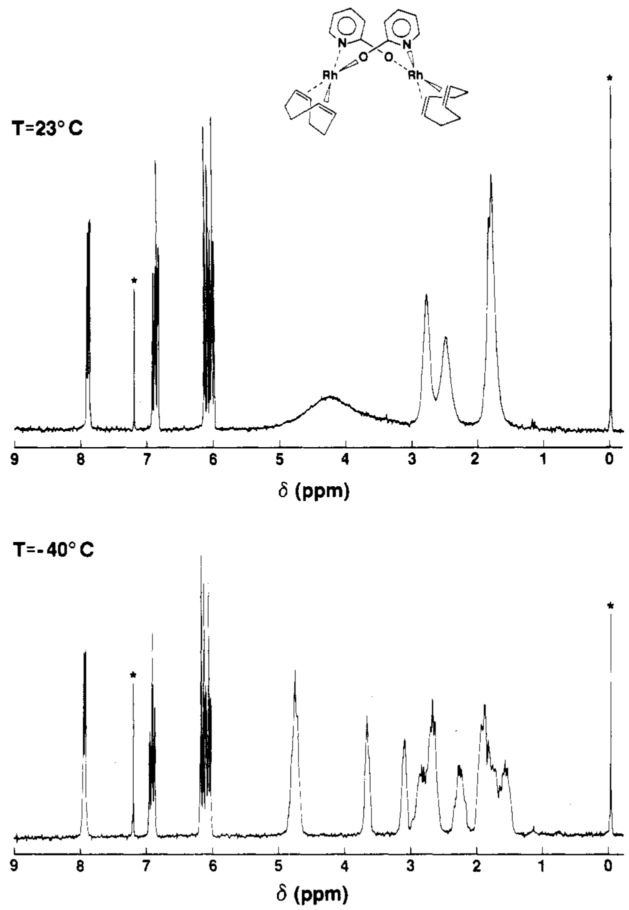
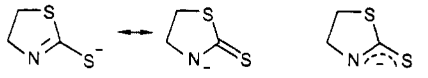


Figure 3. ^1H NMR spectra for $[Rh(\mu\text{-}OC_5H_4N)(COD)]_2$ (**1a**) at +23 and −40 °C.

pyridinate-bridged diiridium complexes noted.[14,15] For the 2-mercaptothiazolinate anion, however, two binding modes appear possible: either through both sulfur atoms or through the mercapto sulfur and the nitrogen atom. As described, both **3a** and **3b** display the latter binding mode; even the softer iridium atom does not favor binding via the softer sulfur atom instead of nitrogen. A consideration of the two most favorable resonance structures shown suggests that the mercapto sulfur and the nitrogen atoms will be most nucleophilic, so it is not surprising that these atoms coordinate.



Infrared spectroscopy does not prove to be particularly useful in characterizing these complexes (although all show bands due to the coordinated olefins in the 1500–1550 cm^{-1} region), but ^1H NMR spectroscopy is helpful. The rhodium complexes are found to be fluxional as shown in the ^1H NMR spectra of **1a**, shown in Figure 3. At ambient temperature only four broad resonances for the COD ligands are observed between 1.5 and 4.5 ppm, with relative intensities 2:1:1:2, corresponding to two sets of methylene and olefin protons. In fact, however, all protons on each COD ligand are inequivalent, owing to the low idealized symmetry (C_2) of the molecule, so cooling the sample to −40 °C yields a much more complex spectrum, which is more typical for such a low-symmetry species. The hydroxypyridine resonances remain unchanged at between 6.0 and 8.0 ppm. Similar results were obtained with the other Rh species. It appears that the fluxionality results from facile rotation of the COD ligand about the metal–COD axis. The iridium complexes, on the other hand, do not appear to be fluxional, even at ambient temperature.

One aspect of structural interest in these complexes concerns the effects of using anionic ligands, which incorporate three atoms in the bridge, on the tilt of the two coordination planes. The mercaptopyridine and mercaptothiazoline ligands are not unlike the 2-(diphenylphosphino)pyridine group used by Balch and co-workers,[2] so in principle it should be possible to achieve almost parallel square planes as has been observed for this latter bridging group and it may also be possible to do so with the bridging groups in a trans arrangement, analogous to DPM[1] and related groups.[2] This of course will not be possible with bulky groups such as COD, but it may be with small ligands; studies into this are underway and will be the topic of future reports. The effect of this larger tilt on the subsequent chemistry of these complexes with small molecules also remains to be determined. It appears that such a tilt could hinder access by substrate molecules to the bridging site between the metals and may therefore be a detriment to the chemistry. However, it must be noted that it is not clear whether such initial attack between the metals is important in the chemistry of binuclear compounds. It may be that attack is at the vacant coordination site on the "outside" of the complex with subsequent rearrangement. From this point of view it will be of interest to determine what effect the differing labilities of the two ends of these bifunctional ligands will have on the chemistry, keeping in mind the bridge-breaking mechanism proposed by Poilblanc[4d] for the thiolato-bridged complexes.

It is also of interest to determine what effect (if any) the tilt of the coordination planes has on the photochemistry of these complexes. The closely related species, $[Ir(\mu\text{-}SC_5H_4N)(CO)_2]_2$ and $[Ir(\mu\text{-}OC_5H_4N)(COD)]_2$, for example, displayed rather different photochemical behaviors. The former species reacted under photochemical conditions with I_2, MeI, and CH_2I_2 yielding metal–metal bonded Ir(II)–Ir(II) species in which the X and Y groups (X, Y = I, Me, CH_2I) were trans to the Ir–Ir bond.[15] This is much as was observed in the pyrazolyl-bridged complex, $[Ir(\mu\text{-}pz)(COD)]_2$,[16] in which the coordination planes are presumably less tilted. In contrast to this, the photochemical reaction of the above hydroxypyridinate-bridged dimer with Cl_2 yielded a mononuclear Ir(III) complex.[14] We are currently investigating the photochemistry of our COD dimers and their derivatives[32] in order to gain a better understanding of the influence of these bridging groups.

In binuclear complexes metal–metal bond making and breaking are almost essential to the chemistry, and the related thiolato-, phosphido-, and pyrazolyl-bridged complexes have displayed a wealth of chemistry in which the making or breaking of metal–metal bonds accompanied ligand gain or loss.[32] In one remarkable case involving a phosphido-bridged species, an equilibrium was observed between two isomers, one with and the other without a Rh–Rh bond.[5e] It remains to be seen whether these COD-containing complexes reported herein are capable of bond making, since it is unclear whether the acute angle between the two metal coordination planes and the bulky COD groups will allow close enough approach. In compound **3a**, for example, a contraction in Rh–Rh distance of almost 1 Å would be required. However, without the constraints imposed by bulky terminal ligands there appears to be no geometrical restriction involving the bridging groups themselves that should destabilize metal–metal bonding. Clearly the example cited earlier,[32] of the PMe_3 complex in which the formally nonbonded metals are only 3.052 Å apart, indicates that metal–metal bonding in this species should be possible, and the structural characterization[15] of the metal-metal bonded species $[Ir_2(CO)_4(I)(CH_2I)(\mu\text{-}SC_5H_4N)_2]$ offers unambiguous proof that metal-metal bond formation is possible, at least with small carbonyl groups as the terminal ligands. The feasibility of metal-metal bond making in our complexes is currently under investigation.

Acknowledgment. We thank the University of Alberta and The Natural Sciences and Engineering Research Council of Canada (NSERC) for support of this research and NSERC for partial funding of the diffractometer.

Registry No. **1a**, 112021-29-1; **2a**, 112041-51-7; **3a**, 112041-53-9; **3b**, 112021-30-4; $[Rh(\mu\text{-}Cl)(COD)]_2$, 12092-47-6; $[Ir(\mu\text{-}Cl)(COD)]_2$, 12112-67-3; sodium 2-hydroxypyridinate, 930-70-1; sodium 2-mercaptopyridinate, 13327-62-3; sodium 2-mercaptothiazolinate, 40003-49-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen parameters, and least-squares planes for compounds **3a** and **3b** (11 pages); listings of structure factor amplitudes for compounds **3a** and **3b** (40 pages). Ordering information is given on any current masthead page.

Michael-Type Addition Reactions of Bis(phenylphosphido)bis(tricarbonyliron) with Acetylenic α,β-Unsaturated Carbonyl Compounds: Multiple Reaction Pathways

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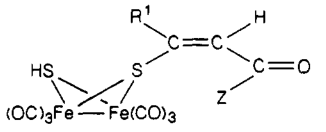
The piperidine-catalyzed addition of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ to acetylenic α,β-unsaturated esters and ketones has been studied. The type of product obtained depended on the organic substrate used. Of special interest were those products in which addition of both P-H bonds to the substrate gave complexes with a one-, two-, or three-carbon bridge between the PhP units.

Introduction

In earlier work, we investigated base-catalyzed Michael-type addition reactions of $(\mu\text{-}HS)_2Fe_2(CO)_6$ with acetylenic α,β-unsaturated carbonyl compounds.[1] In all cases, the initial 1:1 adduct, 1, underwent intramolecular SH addition to the C═C bond of the alkenethiolate ligand to give products of type **2** when R^1 was H or alkyl. When R^1 was CO_2CH_3 and Z = OCH_3 (i.e., when dimethyl acetylenedicarboxylate was used), addition to either carbon atom of the C═C bond was activated by an ester function and the less strained **3** was formed.



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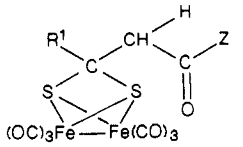

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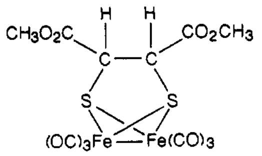

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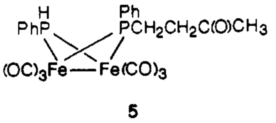
We have also been studying the chemical reactivity of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ (**4**) and during the course of this work have examined its base-catalyzed addition reactions with olefinic α,β-unsaturated carbonyl compounds.[2c] A comparison with the reactions of $(\mu\text{-}HS)_2Fe_2(CO)_6$ with the same α,β-unsaturated substrates showed some interesting differences, and, for this reason, we have investigated base-catalyzed reactions of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ with acetylenic α,β-unsaturated carbonyl compounds.

In comparison to olefinic α,β-unsaturated carbonyl compounds, the acetylenic analogs present a somewhat more complicated and perhaps, therefore, more interesting problem in terms of reaction mechanism than do the olefins. In the olefin case, essentially only two different types of products, the unbridged and the three-carbon-bridged compounds, are possible, and this makes structural assignments fairly straightfoward. Such products are, for instance, in the case of the 1:1 piperidine-catalyzed reaction of $(\mu\text{-}PhPH)_2Fe_2(CO)_6$ with methyl vinyl ketone, the complexes **5** and **6**.



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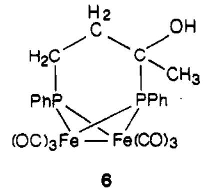

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With the acetylene reactions, however, four distinct reaction pathways are possible, leading to products **7**, **8**, **9**, and **10**. First, the trivial unbridged product, **7**, which

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(1) Seyferth, D.; Womack, G. B.; Henderson, R. S.; Cowie, M.; Hames, B. W. *Organometallics* **1986**, *5*, 1568.

(2) (a) Seyferth, D.; Wood, T. G.; Henderson, R. S. *J. Organomet. Chem.*, **1987**, *336*, 163. (b) Seyferth, D.; Henderson, R. S.; Wood, T. G. *Recl. J. R. Neth. Chem. Soc.*, in press. (c) Seyferth, D.; Wood, T. G., in press.

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