and H were taken from ref 17, and the scattering was corrected for the real and imaginary components of anomalous dispersion.[17]

The gadolinium analogue was solved first, and the position of the gadolinium atom was determined from a Patterson map. The remaining non-hydrogen atoms were located from successive difference Fourier maps. These coordinates were used for the solution of the Sm and Tb analogues. Higher than normal thermal motion was observed for carbon atoms C(1), C(2), C(3), C(4), C(5), and C(6). Inspection of a difference Fourier around these atoms revealed what appeared to be a disordered conformation, indicated in Tables V–VII as C(3)′, C(4)′. No other resolvable peaks near C(1), C(2), C(5), or C(6) were observed. Refinement of the occupancy factors for C(3), C(4) and C(3)′, C(4)′ converged at 65%/35% for M = Gd, 50%/50% for M = Sm, and 60%/40% for M = Tb. Due to the disorder, C(3)′ and C(4)′ were only refined isotropically in all three compounds. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.075$ (M = Gd), 0.057 (M = Sm), and 0.089 (M = Tb). The hydrogen atoms of the crown ether were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Due to the proximity of C(3), C(4) and C(3)′, C(4)′, no attempt was made to place hydrogen atoms around these atoms. The hydrogen atoms associated with the water molecules were not located. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.027$ and $R_w = 0.033$ for the Gd analogue. No systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The Sm and Tb analogues were refined similarly. The final values of the positional parameters are given in Table V (M = Sm), Table VI (M = Gd), and Table VII (M = Tb). Due to the limited data resulting from the small crystal size, only the Tb, Cl, and O atoms were refined anisotropically for M = Tb. An investigation of absolute configuration revealed the M = Sm complex to have an absolute configuration opposite to that for the M = Gd or M = Tb complex. R factors for the inverse configurations (from those in Tables V–VII) were 0.038 (M = Gd), 0.044 (M = Sm), and 0.092 (M = Tb). Final values for M = Sm were $R = 0.034$ and $R_w = 0.041$ and for M = Tb $R = 0.088$ and $R_w = 0.090$.

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Supplementary Material Available: Tables SI–SX, listing derived hydrogen positions, thermal parameters, complete bond distances and angles, and least-squares planes results (8 pages); Tables SXI–SXIII, giving observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Contribution from the Laboratoire de Chimie de Coordination du CNRS,
Unitê No. 8241 liêe par convention â l'Universitê Paul Sabatier, 31077 Toulouse Cedex, France

Assembling Potentialities of an Anionic Tripod Ligand: Trirhodium and Triiridium Complexes of 1,1,1-Tris(sulfidomethyl)ethane.[1] Molecular Structure and Crystal Packing of $Ir_3(CH_3C(CH_2S)_3)(CO)_6$

Andrê Maisonnat,[2a] Jean Devillers,*[2b] and Renê Poilblanc[2a]

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Reaction of $CH_3C(CH_2SLi)_3$ with $M_2(\mu\text{-}Cl)_2(C_8H_{12})_2$ gives quantitatively trimetallic complexes, $M_3(CH_3C(CH_2S)_3)(C_8H_{12})_3$ (**1**, M = Rh; **2**, M = Ir). Reaction of **1** and **2** with carbon monoxide gives $M_3(CH_3C(CH_2S)_3)(CO)_6$ derivatives (**3**, M = Rh; **4**, M = Ir). The structure of **4** has been determined by single-crystal X-ray diffraction. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in a unit cell of dimensions $a = 10.304$ (3) Å, $b = 14.712$ (2) Å, $c = 12.270$ (3) Å, and $\beta = 104.17$ (2)° ($V = 1803$ (1) Å^3). Least-squares refinement leads to a value of 0.037 for the conventional R index for 2082 reflections having $I > 3\sigma(I)$. The crystallographic investigation confirms the formulation of **4** as a hexacarbonyl trimetallic species in which the trithiolato group acts as a 12-electron-donor ligand bridging a triangle of three nonbonded iridium atoms (Ir–Ir = 3.315 (1), 3.366 (1), 3.336 (1) Å) giving a trithiatrimetallaadamantane-like structure. Short intermolecular Ir⋯Ir distances (3.471 (1), 3.506 (1), 3.506 (1) Å) lead to a description of the packing of adamantane units as a stacking of bidimensional networks. Spectroscopic investigations of **3** and **4**, i.e. IR ν(CO) absorption and ^{1}H NMR, indicate that the molecular structure of **4** remains unchanged in solution while that of **3** is quite similar to that determined for **4**. Substitution of tertiary phosphine ligands for carbonyl on **3** leads to trisubstituted derivatives, $Rh_3(CH_3C(CH_2S)_3)(CO)_3(PR_3)_3$, of C_3 symmetry (**5**, R = OMe; **6**, R = Ph). Identical complexes may be prepared by reaction of $CH_3C(CH_2SLi)_3$ with $Rh_2(\mu\text{-}Cl_2)(CO)_2(PR_3)_2$. $Rh_3(CH_3C(CH_2S)_3)(P(OMe)_3)_6$ (**7**) has similarly been prepared by the reaction of $CH_3C(CH_2SLi)_3$ with $Rh_2(\mu\text{-}Cl_2)(P(OMe)_3)_4$. Reaction of dimethyl acetylenedicarboxylate with **2** yields quantitatively a 1:1 adduct, $Ir_3(CH_3C(CH_2S)_3)(CO)_6(\mu\text{-}(CH_3COOC)_2)$, in which the added alkyne is assumed to bridge two bonded metallic centers, leading to a formally "d^8, d^7–d^7" derivative.

Introduction

A few years ago, we[3] and others[4] claimed that the synthesis of polymetallic compounds in which the metallic reactive sites are kept close to each other by means of bridging ligands may be used as one of the most convenient experimental approaches to polymetallic activation.

In this context, we extensively studied the reactivity of thiolato-bridged bimetallic complexes, and we have shown that, among these, dirhodium and diiridium complexes exhibit rich stoichiometric reactivity (oxidative addition of a variety of small molecules including molecular hydrogen,[5] iodine,[6] tetracyanoethylene,[7] hexafluoro-2-butyne,[8] dihalomethane,[9] methyl iodide[10]) as well as outstanding catalytic activities (hydrogenation[11] and hydroformylation[12] of alkenes).

Moreover, from a more fundamental point of view, we were able to establish clearly, following the example of bimetallic activation of dihydrogen over diiridium species, a relationship between the reactivity of these complexes and the deformability

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[1] Preliminary communication: Maisonnat, A.; Poilblanc, R. *C. R. Acad. Sci., Ser. 2* **1984**, *298*, 69–71.

[2] (a) Laboratoire de Chimie de Coordination du CNRS. (b) Laboratoire des IMRCP, UA CNRS 470, Universitê Paul Sabatier, 31062 Toulouse Cedex, France.

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of their dimeric geometry due to the particular flexibility of the thiolato bridging ligands.[5,13]

In the course of these studies, we also described the synthesis and the structure of a series of trinuclear "crown-like" metal complexes, $Ir_3(\mu\text{-S-}t\text{-Bu})_3(\mu\text{-A})(CO)_{6-n}L_n$.[8a,14] They exemplify, through different types of intramolecular bonding, the propensity of the flexible triiridatrithiacyclohexane ring to spread the electronic perturbations due to the reaction, e.g. substitution of L, oxidative addition from one metal to the whole molecule.

As an extension of this work, starting from the tripod ligand 1,1,1-tris(sulfidomethyl)ethane, $CH_3C(CH_2S^-)_3$, as a building block, we tailored a new series of trimetallic complexes having the general formula $M_3(CH_3C(CH_2S)_3)L_6$, preserving the trimetallatrithiacyclohexane ring within an "adamantane-like" structure. We wish to report here the synthesis and structural determination of novel trirhodium and triiridium complexes of this family, together with some aspects of their reactivity.

Experimental Section

General Remarks. All reactions and manipulations were routinely performed under a nitrogen or argon atmosphere in Schlenk-type glassware. All solvents were appropriately dried and freed from molecular oxygen prior to use. Microanalyses were performed by the Service de Microanalyses du Laboratoire de Chimie de Coordination du CNRS. Mass spectra were recorded on a Varian MAT 311 A. Infrared spectra were recorded from hexane solutions or cesium bromide dispersions with use of a Perkin-Elmer Model 225 grating spectrometer or a Perkin-Elmer Model 983 grating spectrometer equipped with an IR PE 3600 data station. In the carbonyl stretching region, the spectra were calibrated with water vapor lines. ^1H NMR spectra were obtained at 90 MHz on a Bruker WH 90 FT spectrometer. Chemical shifts were measured with respect to internal tetramethylsilane and are given in parts per million, downfield positive. ^{31}P NMR spectra were obtained at 36.4 MHz on a Bruker WH90 FT spectrometer. Chemical shifts were measured with respect to external H_3PO_4 and are given in parts per million, downfield positive.

Preparation of Compounds. The starting materials, $Rh_2Cl_2(C_8H_{12})_2$,[15] $Rh_2Cl_2(CO)_4$,[16] $Rh_2Cl_2(CO)_2(PR_3)_2$ (R = OMe, Ph),[17] $Rh_2Cl_2(P(OMe)_3)_4$,[17] and $Ir_2Cl_2(C_8H_{12})_2$,[18] were routinely prepared according to published procedures. 1,1,1-Tris(mercaptomethyl)ethane was prepared from 1,1,1-tris(hydroxymethyl)ethane according to the procedure described by Bosnich et al.[19]

Preparation of $Rh_3(CH_3C(CH_2S)_3)(C_8H_{12})_3$ (1). A solution of butyllithium (2.03 mmol) in hexane (1.16 mL of a 112 g·L^{-1} solution) was added dropwise at room temperature to a solution of 1,1,1-tris(mercaptomethyl)ethane (0.098 mL, 0.68 mmol) in toluene (10 mL). The resulting mixture, which appeared as a white suspension of $CH_3C(CH_2SLi)_3$, was slowly added, at room temperature, to a solution of $Rh_2Cl_2(C_8H_{12})_2$ (0.5 g, 1.01 mmol) in toluene (20 mL). The solution immediately turned deep red. After being stirred for 1 h, the solution was filtered and the filtrate was concentrated under reduced pressure to about 10 mL. Slow addition of petroleum ether (20 mL) afforded air-stable orange crystals of the title compound (0.44 g, 82%). Anal. Calcd for $C_{29}H_{45}S_3Rh_3$: C, 43.62; H, 5.69. Found: C, 43.45; H, 5.85.

Preparation of $Rh_3(CH_3C(CH_2S)_3)(CO)_6$ (3). Method A. Carbon monoxide was bubbled through a solution of **1** (0.161 g, 0.202 mmol) in toluene (30 mL) for 15 min, with stirring. The initial deep red solution becomes brown-yellow within a few seconds. Evaporation of the solvents leads to a black solid (0.105 g, 81%). IR (ν(CO) in hexane): 2088 (s), 2061 (vs), 2020 (vs) cm^{-1}. Bright black prismatic crystals may be obtained upon cooling to −20 °C saturated toluene/hexane (1:2) solutions (typically, 30 mL of such solutions leads to 0.123 g of crystals). Anal. Calcd for $C_{11}H_9O_6S_3Rh_3$: C, 20.58; H, 1.42. Found: C, 20.46; H, 1.36. Electron-impact MS (70 eV), *m/e*: 642 (M^+) plus fragment ions corresponding to successive loss of six CO groups.

Method B. To a solution of 1,1,1-tris(mercaptomethyl)ethane (0.131 mL, 0.90 mmol) in toluene (20 mL) was slowly added a solution of butyllithium (2.7 mL) in hexane (1.69 mL of a 103 g·L^{-1} solution). The resulting white suspension was then slowly added, at room temperature, to a solution of $Rh_2Cl_2(CO)_4$ (0.528 g, 1.36 mmol) in toluene (20 mL). The initial yellow solution of $Rh_2Cl_2(CO)_4$ immediately turned brown-yellow. After being stirred for 2 h, the solution was filtered and the solvents were evaporated under reduced pressure, leading to black crystals of the title compound (0.418 g, 72%).

Preparation of $Ir_3(CH_3C(CH_2S)_3)(C_8H_{12})_3$ (2). This complex was prepared from $Ir_2Cl_2(C_8H_{12})_2$ (0.642 g, 0.96 mmol) by the method used for the preparation of **1**. An orange-red solid was obtained (0.575 g, 84%). Anal. Calcd for $C_{29}H_{45}S_3Ir_3$: C, 32.66; H, 4.25. Found: C, 32.74; H, 4.28.

Reaction of 2 with Carbon Monoxide. Preparation of $Ir_3(CH_3C(CH_2S)_3)(CO)_6$ (4) and Identification of $Ir_3(CH_3C(CH_2S)_3)(C_8H_{12})_2(CO)_2$ and $Ir_3(CH_3C(CH_2S)_3)(C_8H_{12})(CO)_4$. Carbon monoxide was bubbled through a solution of **2** (0.575 g, 0.54 mmol) in dichloromethane (12 mL). The initial deep red solution turned brown-yellow within a few seconds. After the mixture was stirred for 15 min, the solvents were evaporated under reduced pressure, affording a black solid (0.420 g, 85%). IR (ν(CO) in hexane): 2084 (s), 2054 (vs), and 2010 (vs) cm^{-1}. The product may be recrystallized from a saturated toluene/hexane (1:1) solution cooled to −20 °C. Prismatic bright black crystals were so obtained. Anal. Calcd for $C_{11}H_9O_6S_3IR_3$: C, 14.52; H, 1.00. Found: C, 14.44; H, 0.91. Electron-impact MS (70 eV), *m/e* (intensity): 906 (1), 908 (6), 910 (12), 912 (8) (principal peaks for the parent ion), and fragment ions corresponding to successive loss of six CO groups. The observed pattern for the parent ion is quite consistent with the presence of three iridium atoms in the molecule.

When carbon monoxide was slowly introduced through a hexane solution of **2** by means of a gas syringe, the successive substitutions of the three cyclooctadiene ligands could be observed by IR and we were able to characterize two intermediates, i.e. $Ir_3(CH_3C(CH_2S)_3)(C_8H_{12})_2(CO)_2$ [IR (ν(CO) in hexane): 2044 (s), 1988 (s) cm^{-1}] and $Ir_3(CH_3C(CH_2S)_3)(C_8H_{12})(CO)_4$ [IR (ν(CO) in hexane): 2066 (s), 2000 (s) cm^{-1}].

Preparation of $Rh_3(CH_3C(CH_2S)_3)(CO)_3(P(OMe)_3)_3$ (5). Method A. To a solution of **3** (0.129 g, 0.20 mmol) in dichloromethane (10 mL) was added 3 equiv amounts of trimethyl phosphite (0.075 mL, 0.60 mmol). The initial brown-yellow solution immediately turned red. The change in the IR spectrum indicated the total conversion of the initial material into a new one having a broad ν(CO) band at 1985 cm^{-1} (in CH_2Cl_2). The solvent was evaporated under reduced pressure, giving an orange-red oil to which methanol (12 mL) was added. Orange prismatic crystals were obtained upon cooling the solution to −20 °C (0.138 g, 74%). Anal. Calcd for $C_{17}H_{36}O_{12}S_3P_3Rh_3$: C, 21.95; H, 3.91. Found: C, 21.57; H, 3.86. These crystals quickly decomposed in the air, giving a brown residue.

Method B. A similar product could be quantitatively obtained starting from $Rh_2Cl_2(CO)_2(P(OMe_3))_2$ (0.118 g, 0.203 mmol) in dichloromethane (10 mL) to which a stoichiometric amount of $CH_3C(CH_2SLi)_3$ (prepared by addition of 0.465 mL of a 112 g·L^{-1} solution of butyllithium in hexane over 0.039 mL of $CH_3C(CH_2SH)_3$ in 5 mL of toluene) was added.

Preparation of $Rh_3(CH_3C(CH_2S)_3)(CO)_3(PPh_3)_3$ (6). To a solution of **3** (0.062 g, 0.096 mmol) in toluene (15 mL) was added triphenylphosphine (0.076 g, 0.29 mmol) in toluene (5 mL). The initital orange solution immediately turned deep red. The solution was then concentrated under reduced pressure until an orange-yellow precipitate appeared. The precipitate was filtered out, washed with hexane, and dried under vacuum (0.100 g, 77%). IR (ν(CO) in CH_2Cl_2): 1966 (br) cm^{-1}. Anal. Calcd for $C_{62}H_{54}O_3P_3S_3Rh_3$: C, 55.36; H, 4.06. Found: C, 55.63; H, 4.16.

Preparation of $Rh_3(CH_3C(CH_2S)_3)(P(OMe)_3)_6$ (7). To a solution of 1,1,1-tris(mercaptomethyl)ethane (0.108 mL, 0.75 mmol) in toluene (10 mL) was added a solution of butyllithium (2.25 mmol) in hexane (1.28 mL of a 112 g·L^{-1} solution). The resulting white suspension was slowly added, at room temperature, to a solution of $Rh_2Cl_2(P(OMe)_3)_4$ (0.862 g, 1.12 mmol) in toluene (15 mL). The initial solution immediately turned red. After being stirred for 1 h, the red solution was filtered and the filtrate concentrated under reduced pressure to about 7 mL. Slow addition of hexane afforded the title compound as an air-sensitive orange-red solid (0.652 g, 72%). Anal. Calcd for $C_{23}H_{63}O_{18}P_6S_3Rh_3$: C, 22.67; H, 5.21. Found: C, 22.91; H, 5.43.

Reaction of 4 with 1 equiv of Dimethyl Acetylenedicarboxylate ($CH_3CO_2C{\equiv}CCO_2CH_3$). Preparation of a 1:1 Alkyne Adduct, $Ir_3(CH_3C(CH_2S)_3)(CO)_6(CH_3CO_2C{\equiv}CCO_2CH_3)$ (8). To a solution of **4** (0.185 g, 0.29 mmol) in hexane (25 mL) was added dimethyl acetylenedicarboxylate (0.030 g, 0.034 mL). The solution was stirred overnight. The IR spectrum of the solution indicated the presence of a new com-

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Table I. Physical and Crystallographic Data for Compound **4** and Experimental Conditions for Crystallographic Measurements

Physical and Crystallographic Data	
formula	$Ir_3(CH_3C(CH_2S)_3)(CO)_6$
mol wt	910.0
cryst syst	monoclinic
space group	C_{2h}^5–$P2_1/c$
a, Å	10.304 (3)
b, Å	14.712 (2)
c, Å	12.270 (3)
β, deg	104.17 (2)
V, Å^3	1803 (1)
Z	4
ρ_{exptl}, g·cm^{-3}	3.33 ± 0.3
ρ_{calcd}, g·cm^{-3}	3.35
μ(λ Mo), cm^{-1}	223.6
F(000)	1608
Data Collection	
temp, °C	20
Mo radiation, Å	0.71069
monochromatization	oriented graphite crystal
cryst–detector dist, mm	208
detector window^a	
height, mm	4
width, mm	4.50 + 0.00 tan θ
takeoff angle, deg	2.75
scan mode	$\theta/2\theta$
max Bragg angle, deg	29.0
values determining scan speed	
first shell	1.0° < θ < 25.0°; SIGPRE^a 0.80, SIGMA^a 0.018, VPRE^a 5.03 min^{-1} for θ; TMAX^a = 90 s
second shell	25.0° < θ < 29.0°; same as for first shell
intensity controls	060, 400, 004; measd every 3600 s of irradn
orientation controls	250, 20$\bar{8}$, 0$\bar{3}\bar{4}$; measd every 500 reflcns
Conditions for Refinement	
no. of reflcns recorded	4769 (unique)
no. of reflcns utilized ($I < 3\sigma(I)$)	2082
reliability factors	
$R = \sum \lvert k\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum k\lvert F_o\rvert$	0.037
$R_w = [\sum w(k\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum wk^2F_o^2]^{1/2}$	0.044
std error in an observn of unit wt	1.40

^{a} Values specified in ref 20.

pound having ν(CO) bands at 2094 (m), 2076 (s), 2059 (s), 2044 (s), 2030 (m), and 2000 (vs) cm^{-1}. Upon crystallization at −40 °C in hexane, air-stable yellow crystals were obtained and dried under vacuum (0.154 g, 72%). Anal. Calcd for $C_{17}H_{15}O_{10}S_3Ir_3$: C, 19.41; H, 1.44. Found: C, 19.78; H, 1.50.

Crystal and Molecular Structure Determination of 4. Black prismatic air-stable crystals were obtained by slow cooling of a saturated toluene/hexane (1:1) solution of **4** to −20 °C.

A suitable crystal was directly mounted on the goniometer head of an automatic Enraf-Nonius CAD4 diffractometer. The setting angles of 25 *hkl* reflections, regularly distributed in the half-sphere, were used in a least-squares calculation that led to a monoclinic cell whose constants are reported in Table I. On the assumption of four formula units per cell, the calculated density, ρ_{calcd} = 3.35 g·cm^{-3}, is in satisfactory agreement with the experimental one, ρ_{exptl} = 3.33 ± 0.3 g·cm^{-3}, measured by flotation in ZnI_2 aqueous solutions.

A preliminary short data collection revealed the systematic absences (0*k*0, *k* = 2*n* + 1; *h*0*l*, *l* = 2*n* + 1) consistent with the $P2_1/c$ space group.

Data Collection. Table I gives pertinent details concerning the experimental data collection conditions. Reflections have been recorded in two shells with the same crystal. Examination of the control reflection intensities, periodically measured, showed no appreciable decrease. So no correction for crystal degradation was applied. Data were then processed in the usual way.[20]

Table II. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å^2 × 100) with Esd's in Parentheses for Compound **4**

atom	*x/a*	*y/b*	*z/c*	U_{eq}/U_{iso}
Ir(1)	0.16144 (6)	0.54331 (4)	0.52759 (6)	5.25 (4)
Ir(2)	0.37702 (7)	0.69130 (5)	0.46857 (7)	6.61 (5)
Ir(3)	0.35614 (7)	0.66811 (5)	0.73419 (6)	5.81 (4)
S(1)	0.1449 (4)	0.6640 (3)	0.3974 (4)	5.6 (3)
S(2)	0.3493 (4)	0.7934 (3)	0.6101 (4)	6.7 (3)
S(3)	0.1251 (4)	0.6370 (3)	0.6751 (4)	5.1 (2)
C(1)	0.195 (2)	0.447 (1)	0.628 (2)	7 (1)
O(1)	0.214 (2)	0.3888 (9)	0.691 (1)	11 (1)
C(2)	0.182 (2)	0.472 (1)	0.409 (2)	7 (1)
O(2)	0.200 (2)	0.429 (1)	0.336 (2)	13 (1)
C(3)	0.417 (2)	0.603 (1)	0.371 (2)	8 (1)
O(3)	0.442 (2)	0.547 (1)	0.317 (2)	12 (1)
C(4)	0.556 (2)	0.716 (2)	0.515 (2)	9 (2)
O(4)	0.666 (2)	0.735 (1)	0.545 (2)	13 (2)
C(5)	0.362 (2)	0.575 (2)	0.835 (2)	8 (1)
O(5)	0.369 (2)	0.517 (1)	0.900 (2)	12 (1)
C(6)	0.540 (2)	0.681 (1)	0.775 (1)	7 (1)
O(6)	0.657 (1)	0.688 (1)	0.801 (1)	11 (1)
C(7)	0.044 (2)	0.758 (1)	0.420 (1)	5 (1)
C(8)	0.191 (2)	0.852 (1)	0.578 (2)	6 (1)
C(9)	0.023 (1)	0.7356 (9)	0.621 (1)	4.6 (9)
C(10)	0.056 (2)	0.8003 (9)	0.535 (1)	4.8 (9)
C(11)	−0.057 (2)	0.875 (1)	0.520 (1)	6 (1)

Absorption corrections have been carried out by using a numerical method.[21] The crystal selected for data collection can be roughly described as a flat needle with nine bounding faces: 100, $1\bar{1}0$, 110, $\bar{1}00$, $\bar{1}10$, $\bar{1}\bar{1}0$ (lateral faces); $0\bar{1}\bar{1}$, $01\bar{1}$ (summit faces); 001 (basal face). Distances of lateral, summit, and basal faces to an internal origin, respectively: 0.035, 0.035, 0.072 mm; 0.0130 mm; 0.098 mm. On the basis of a linear absorption coefficient of 223.6 cm^{-1}, the resultant transmission factors were found to range from 0.088 to 0.332.

Structure Determination. The structure has been solved by using standard Patterson and Fourier method conditions for refinement, and the used agreement indices are listed in Table I. Values of the atomic scattering factors and anomalous terms of common elements were those inherent to the SHELX program.[21] For the iridium atoms, the parameters were taken from usual sources.[22]

From the Patterson function were located the three Ir atoms and the three S atoms. All non-hydrogen atoms were found on a Fourier map subsequent to two cycles of refinement. A further least-squares refinement using isotropic thermal parameters for 23 heavy atoms led to R = 0.16 and R_w = 0.18. At this point, absorption corrections were performed. Subsequent least-squares refinements using anisotropic thermal parameters for Ir and S atoms lowered the R values to 0.043 and 0.046, respectively. A difference Fourier map revealed five among the nine hydrogen atoms. At this point, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms introduced with a fixed isotropic thermal coefficient U = 0.05 Å^2. With the use of "AFIX" instructions (a SHELX facility), H atoms of the CH_2 and CH_3 groups were allowed to move along with the C atom to which they were linked, with preservation of an "ideal" geometry (C–H = 0.95 Å; HCH = 109.5°). Within these conditions, the last refinement cycle led to R = 0.037 and R_w = 0.044 for a weighting term of $1.4075/(\sigma^2(F) + 0.000687F^2)$. A final difference Fourier electron density map revealed six peaks ranging from 1.0 to 1.8 e·Å^{-3} located around the Ir atoms and having no structural significance. They were accordingly attributed to Ir "residues".

Atomic positional parameters with their estimated standard deviations are reported in Table II.

Results and Discussion

Preparation and Molecular Structure of Hexacarbonyl Compounds, $M_3(CH_3C(CH_2S)_3)(CO)_6$ (3, M = Rh; 4, M = Ir). $M_2Cl_2(C_8H_{12})_2$ (M = Rh, Ir) and $Rh_2Cl_2(CO)_4$ react readily and quantitatively at room temperature with stoichiometric amounts

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(20) Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2639–2644.

(21) Calculations have been performed on a VAX 11/730 digital computer using a computer program for crystal structure determination (Sheldrick, G. M. "SHELX-76"; University of Cambridge: Cambridge, England, 1976), with the exception of absorption corrections that have been performed with help of the programs CRYSTL and ABSCOR of the SDP package (Enraf-Nonius) implemented on the VAX computer.

(22) (a) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 99, 149. (b) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

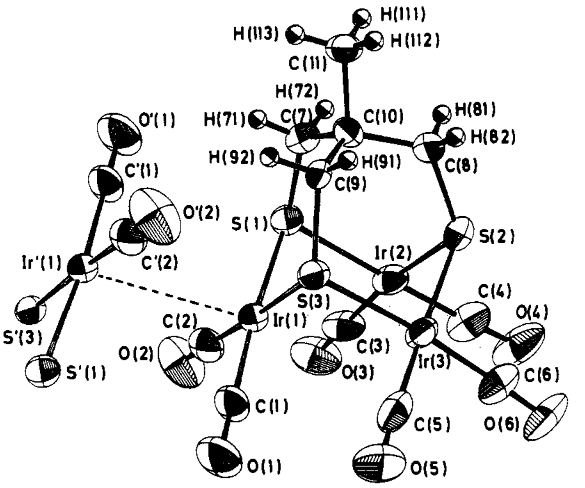

Figure 1. A perspective view of $Ir_3(CH_3C(CH_2S)_3)(CO)_6$ (**4**). The vibrational ellipsoids are drawn at the 35% probability level for the non-hydrogen atoms. One of the three intermolecular interactions of the molecule is represented on the left (see text).

Table III. Bond Lengths (Å) and Angles (deg) for Compound **4**

Ir(1)–S(1)	2.366 (4)	S(1)–C(7)	1.793 (15)
Ir(1)–S(3)	2.376 (4)	S(2)–C(8)	1.797 (16)
Ir(1)–C(1)	1.854 (18)	S(3)–C(9)	1.819 (14)
Ir(1)–C(2)	1.851 (22)	C(1)–O(1)	1.140 (19)
Ir(2)–S(1)	2.371 (4)	C(2)–O(2)	1.148 (21)
Ir(2)–S(2)	2.366 (5)	C(3)–O(3)	1.138 (21)
Ir(2)–C(3)	1.876 (21)	C(4)–O(4)	1.142 (23)
Ir(2)–C(4)	1.826 (22)	C(5)–O(5)	1.156 (24)
Ir(3)–S(2)	2.380 (5)	C(6)–O(6)	1.171 (22)
Ir(3)–S(3)	2.357 (4)	C(7)–C(10)	1.523 (21)
Ir(3)–C(5)	1.840 (25)	C(8)–C(10)	1.554 (21)
Ir(3)–C(6)	1.845 (20)	C(9)–C(10)	1.523 (19)
		C(10)–C(11)	1.577 (19)
S(1)–Ir(1)–S(3)	94.6 (1)	S(3)–Ir(1)–C(1)	88.7 (6)
S(1)–Ir(1)–C(1)	173.2 (6)	S(3)–Ir(1)–C(2)	177.5 (6)
S(1)–Ir(1)–C(2)	84.3 (5)	C(1)–Ir(1)–C(2)	92.7 (8)
S(1)–Ir(2)–S(2)	94.9 (1)	S(2)–Ir(2)–C(3)	172.4 (6)
S(1)–Ir(2)–C(3)	90.3 (6)	S(2)–Ir(2)–C(4)	86.5 (7)
S(1)–Ir(2)–C(4)	176.5 (6)	C(3)–Ir(2)–C(4)	88.5 (9)
S(2)–Ir(3)–S(3)	94.8 (1)	S(3)–Ir(3)–C(5)	85.9 (6)
S(2)–Ir(3)–C(5)	177.6 (6)	S(3)–Ir(3)–C(6)	174.3 (6)
S(2)–Ir(3)–C(6)	87.8 (6)	C(5)–Ir(3)–C(6)	91.8 (8)
Ir(1)–S(1)–Ir(2)	88.8 (1)	Ir(1)–C(1)–O(1)	178.3 (19)
Ir(1)–S(1)–C(7)	115.2 (5)	Ir(1)–C(2)–O(2)	177.0 (17)
Ir(2)–S(1)–C(7)	112.4 (6)	Ir(2)–C(3)–O(3)	176.6 (17)
Ir(2)–S(2)–Ir(3)	89.3 (2)	Ir(2)–C(4)–O(4)	176.9 (21)
Ir(2)–S(2)–C(8)	114.1 (6)	Ir(3)–C(5)–O(5)	178.5 (18)
Ir(3)–S(2)–C(8)	113.0 (6)	Ir(3)–C(6)–O(6)	178.6 (19)
Ir(1)–S(3)–Ir(3)	90.7 (1)	S(1)–C(7)–C(10)	122.6 (11)
Ir(1)–S(3)–C(9)	111.8 (5)	S(2)–C(8)–C(10)	122.1 (11)
Ir(3)–S(3)–C(9)	114.1 (5)	S(3)–C(9)–C(10)	122.8 (10)
C(7)–C(10)–C(11)	106.5 (12)	C(7)–C(10)–C(9)	114.3 (11)
C(8)–C(10)–C(11)	106.1 (11)	C(7)–C(10)–C(8)	111.9 (13)
C(9)–C(10)–C(11)	103.3 (12)	C(8)–C(10)–C(9)	113.7 (13)

Table IV. Selected Nonbonded Distances (Å) and Angles (deg) for Compound **4**[a]

Ir(1)···Ir(2)	3.315 (1)	Ir(1){56602}–Ir(1)–S(1)	103.7 (1)
Ir(1)···Ir(3)	3.366 (1)	Ir(1){56602}–Ir(1)–S(3)	92.3 (1)
Ir(2)···Ir(3)	3.336 (1)	Ir(1){56602}–Ir(1)–C(1)	82.1 (6)
		Ir(1){56602}–Ir(1)–C(2)	85.8 (6)
S(1)···S(2)	3.490 (6)	Ir(3){56404}–Ir(2)–S(1)	86.8 (1)
S(1)···S(3)	3.485 (6)	Ir(3){56404}–Ir(2)–S(2)	103.5 (1)
S(2)···S(3)	3.488 (6)	Ir(3){56404}–Ir(2)–C(3)	82.3 (6)
Ir(1)···Ir(1){56602}	3.471 (1)	Ir(3){56404}–Ir(2)–C(4)	89.8 (7)
Ir(2)···Ir(3){56404}	3.506 (1)	Ir(2){56504}–Ir(3)–S(2)	93.1 (1)
Ir(3)···Ir(2){56504}	3.506 (1)	Ir(2){56504}–Ir(3)–S(3)	102.8 (1)
		Ir(2){56504}–Ir(3)–C(5)	84.5 (7)
		Ir(2){56504}–Ir(3)–C(6)	82.1 (6)

[a] Numbers in braces are atom codes as used in the ORFFE program. When not specified, they are 55501. An increase or decrease by one unit of one or several of the first three digits adds one unit to or subtracts one unit from fractional coordinates whose codes from left to right are attributed to x/a, y/b, z/c. The last two digits concern the symmetry positions, which in this case are as follows: 01 for x, y, z; 02 for $\bar{x}, \bar{y}, \bar{z}$; 03 for $\bar{x}$, $^1/_2 + y$, $^1/_2 - z$; 04 for x, $^1/_2 - y$, $^1/_2 + z$.

of $CH_3C(CH_2SLi)_3$, according to the molar ratio 3:2, to yield trinuclear derivatives, $M_3(CH_3C(CH_2S)_3)(C_8H_{12})_3$ (**1**, M = Rh; **2**, M = Ir) and $Rh_3(CH_3C(CH_2S)_3)(CO)_6$ (**3**), respectively. When CO is bubbled through hexane or dichloromethane solutions of **1** or **2**, substitution of the cyclooctadiene ligands occurs, quantitatively yielding the hexacarbonyl derivatives $M_3(CH_3C(CH_2S)_3)(CO)_6$ (**3**, M = Rh; **4**, M = Ir). Dicarbonyl and tetracarbonyl intermediates, $M_3(CH_3C(CH_2S)_3)(C_8H_{12})_2(CO)_2$ and $M_3(CH_3C(CH_2S)_3)(C_8H_{12})(CO)_4$, may be observed and identified by their IR (ν(CO)) spectra when CO is slowly added.

The hexacarbonyl trinuclear complexes, **3** and **4**, are reasonably stable to air in solution as well as in the solid state. They crystallize from cooled brown-yellow toluene/hexane solutions as black prisms in both cases. The structure of these new compounds has been resolved by elemental analyses, mass spectra, and IR (ν(CO)) and ^{1}H NMR spectra as well as by the X-ray diffraction analysis of **4**.

The presence of three iridium atoms and six carbonyl groups in **4** was fully established by the electron-impact mass spectrometry of black crystals. The mass spectrum of **4** actually exhibits a remarkable isotopic pattern consisting of four principal peaks at *m/e* 906, 908, 910, and 912 for the parent ion—quite consistent with the isotopic abundance of iridium (i.e. 191–37.3% and 193–62.7%) together with typical patterns for fragment ions corresponding to the loss of six carbonyl groups.

IR spectra of **3** and **4** in hexane, which exhibit in both cases three CO stretching bands, indicate highly symmetrical structures and are fully consistent with a C_{3v} symmetry for which three active ν(CO) bands, i.e. 1A$_1$ and 2E, can be predicted.

^{1}H NMR data of **3** and **4** are in agreement with the symmetrical molecular structure predicted from IR experiments. They exhibit resonances for the CH_3 and CH_2 groups of the bridging trithiolato ligand in the expected intensity ratio 3:6. CH_3 protons appear as singlets at 0.06 ppm for **3** and –0.19 ppm for **4**. In compound **3**, CH_2 protons coupled with the Rh atoms form an $[AX_2]_3$ spin system:[23] they appear as a triplet centered at 1.39 ppm, with an apparent J_{H-Rh} coupling of 1.2 Hz. In compound **4**, CH_2 protons appear—as a singlet—at 1.49 ppm.

Crystal Structure of 4. The crystal structure of **4** consists of a packing of four trinuclear molecules per unit cell. A perspective view of the $Ir_3(CH_3C(CH_2S)_3)(CO)_6$ molecule, including the labeling scheme, is shown in Figure 1. Bond lengths and angles are reported in Table III, while Table IV collects nonbonded distances and angles of interest. The easiest way to describe the molecular structure is to consider it as an adamantane-like entity that nearly accepts a C_3 symmetry axis passing through the C(10) and C(11) atoms. Deviation from the symmetry is small enough to be reasonably attributed to packing forces.

Geometry around the Ir atoms is in agreement with the usual square-planar hybridization (Table III). Because of the Ir–S bond length, the triirida trithia ring is of larger size than the corresponding cyclohexane ring. However, the replacement of tetrahedral carbon atoms by square-planar iridium changes the "natural" bond angle S–X–S (X = C or Ir) from 109.5 to 90° and contributes to a drawing-up of the sulfur atoms. The tris-chelating ligand produces a similar effect. On the other hand, the triirida trithia ring causes, due to its size, a distortion of the tris-chelating ligand, so that the observed structure is a compromise between the two tendencies. As expected from energy considerations, the shrinkage of the Ir_3S_3 ring is obtained mostly by dihedral angle changes than by angle changes. Dihedral angles between the [Ir$_i$–S–Ir$_j$] and [Ir$_i$–S–S–Ir$_j$] planes are close to 90°

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(23) Haigh, C. W. *J. Chem. Soc. A* **1970**, 1682–1683.

(24) Similar effects have also been observed in 1,3,5-triphenyl-2,4,6-trithia-1,3,5-tristannaadamantane: Beauchamp, A. L.; Latour, S.; Olivier, M. J.; Wuest, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 7778–7780.

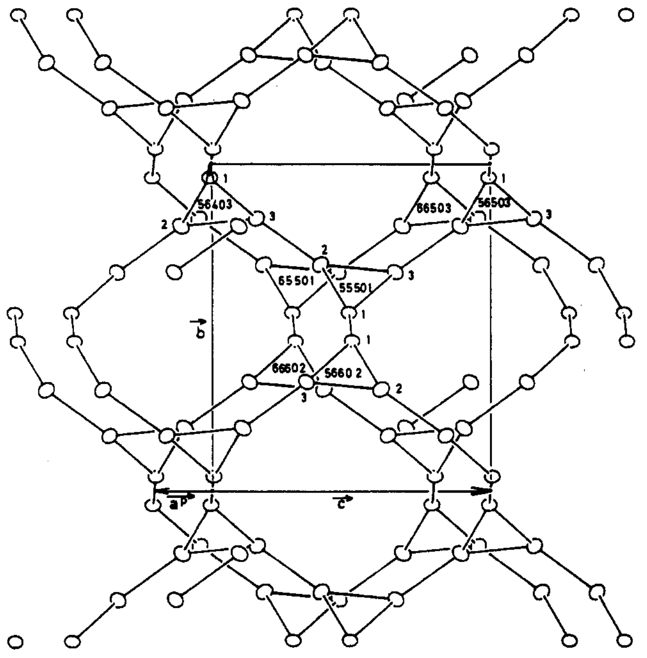


Figure 2. Projection along the axis perpendicular to $\vec{b}$ and $\vec{c}$ of all the Ir atoms contained in a box centered on the $^{1}/_{2}$, $^{1}/_{2}$, $^{1}/_{2}$ position (dimensions 2*a*, 2*b*, 2*c*). Links are not bonds but materialize the Ir···Ir interatomic distances (all close to each other) either within the same molecule (triangles) or between molecules. $\vec{a}^{P}$ is the projection of vector $\vec{a}$ on the $(\vec{b},\vec{c})$ plane. Five-digit numbers are designator codes (see note in Table IV).

(Table SIII, supplementary material), which is much smaller than the value known for cyclohexane (125.25°). While S–Ir–S angles have a mean value of 94.7 (1)°, which is a compromise between 90 and 109.5°, Ir–S–Ir angles range from 88.8 (1) to 90.7 (1)°, which is a consequence of the chelating effect of the $CH_3C(CH_2S)_3$ ligand—the coordination polyhedron of the sulfur atom being very easily distorted, as noticed elsewhere.[14b] Because of the S···S distances (3.485–3.490 Å), the tris-chelating ligand has to increase its bites. The main consequences are that the C(7)–C(8)–C(9)–C(10) pyramid is somewhat flattened (C(11)–C(10)–C angles ranging from 103.3 (12) to 106.5 (12)°) and that the C(10)–C–S angles are increased up to a mean value of 122.5 (11)°.

Intramolecular distances between Ir atoms are in the same range of magnitude as those previously observed in dinuclear Ir(I) complexes[25] and preclude metal–metal bonds (Table IV) so that similar but *intermolecular* distances observed cannot be attributed to an incipient fifth coordination of the Ir atoms, even if the geometry is adequate. However, the relative disposal of the planar entities containing the Ir–S and C–O bonds is not fortuitous, for it has been already shown[25] that it can lead to monodimensional associations, by either pairs or chains of molecules. We thus have here the first example, for this type of compound, of a bidimensional structure composed of "fused rings". Each ring consists of six interacting molecules, each of which is at the junction of three rings (Figure 2).

From Figure 2, it can be seen that all interacting molecules form bidimensional networks whose mean planes are parallel to the $(\vec{b}, \vec{c})$ plane. The networks can be deduced from each other by an $\vec{a}$ translation. In each ring, a molecule is related to the opposite one by a symmetry through a center having 0, $^{1}/_{2}$, 1 coordinates (Figure 3). Thus, the atoms of three molecules in each ring are characterized by the x/a fractional coordinate, while the corresponding atoms of the other three are characterized by $-x/a$. This disposal is repeated all along the $\vec{b}$ direction. Consequently, the network can also be described as chains of molecules aligned in the $\vec{c}$ direction, alternatively characterized by the x/a or $-x/a$ fractional atom coordinates, cross-linked together by interactions between the Ir(1) planar moieties (Figure 3). Figure 3 also clearly shows that the organic ligand is alternatively on one side or the other of the $(\vec{b}, \vec{c})$ plane when one passes from one chain to the next one in the $\vec{b}$ direction. The above described bidimensionality of the packing is to be considered with caution: it is actually the result of the propensity of square-planar moieties to approach each other at rather short distances by taking advantage of a specific steric fitting. But the space between iridium bidimensional networks is filled: there are neither intermolecular spaces nor channels in this structure.

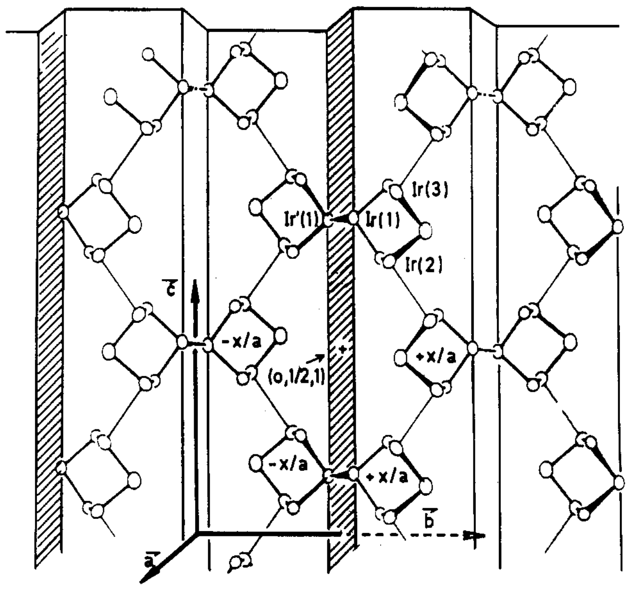
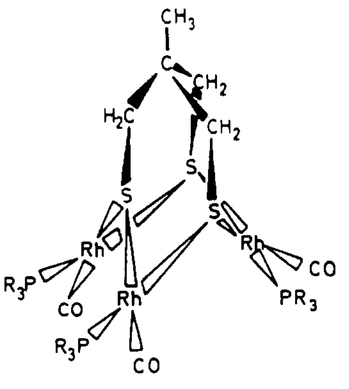


Figure 3. Representation of a bidimensional network for compound **4**. Chains of molecules aligned in the $\vec{c}$ direction are cross-linked through Ir(1) planar moiety interactions (see text).

Preparation and Molecular Structures of $Rh_3(CH_3C(CH_2S)_3)(CO)_3(PR_3)_3$ (5, R = OMe; 6, R = Ph) and $Rh_3(CH_3C(CH_2S)_3)(P(OMe)_3)_6$ (7). Compound **3** reacts readily and quantitatively, in toluene or dichloromethane solutions at room temperature, with 3 equiv of PR_3 (R = OMe, Ph) to yield trisubstituted trinuclear derivatives, $Rh_3(CH_3C(CH_2S)_3)(CO)_3(Pr_3)_3$ (**5**, R = OMe; **6**, R = Ph). Compound **5** was also directly prepared by reaction of toluene solutions of $Rh_2Cl_2(CO)_2(P(OMe)_3)_2$ with $CH_3C(CH_2SLi)_3$ added in the 3:2 molar ratio.



5, R = OMe
6, R = Ph

Compounds **5** and **6**, which were obtained in pure crystalline forms, are unsoluble in petroleum ether, moderately soluble in toluene or benzene, and soluble in methanol or dichloromethane. Their molecular structure has been resolved by elemental analyses and IR and $^{31}P\{^1H\}$ NMR spectra. The IR spectrum of CH_2Cl_2 solutions of **5** and **6** exhibits single broad bands centered at 1992 and 1966 cm^{-1}, respectively. $^{31}P\{^1H\}$ NMR spectra, which reveal

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(25) (a) Bonnet, J.-J.; Galy, J.; de Montauzon, D.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1977**, 47–49. (b) Bonnet, J.-J.; de Montauzon, D.; Poilblanc, R.; Galy, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 832–837. (c) Pince, R.; de Montauzon, D.; Poilblanc, R. *J. Chim. Phys. Phys.-Chim. Biol.* **1981**, *78*, 745–748.

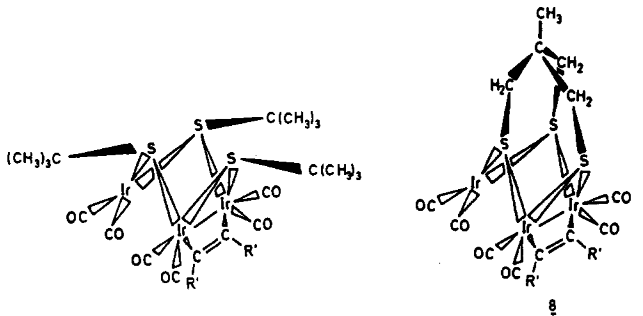

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Figure 4. Proposed structural analogy between compound **8** and the triiridatrithiacyclohexane crown-like compound $Ir_3(\mu\text{-S-}t\text{-Bu})_3(CO)_6(\mu\text{-}\eta^1\text{-}(CH_3COOC)_2)$.

equivalent phosphorus nuclei in both cases [**5** $\delta(^{31}P)$ 139.0 (d) (J_{P-Rh} = 238 Hz) and **6** $\delta(^{31}P)$ 37.95 (d) (J_{P-Rh} = 153 Hz) in CD_2Cl_2], indicate molecular structures in which phosphorus ligands occupy a regular disposition according to a molecular structure of C_3 symmetry.

$Rh_3(CH_3C(CH_2S)_3)(P(OMe)_3)_6$ (**7**) has been quantitatively obtained by reaction of $Rh_2Cl_2(P(OMe)_3)_4$, prepared in situ by addition of 4 equiv of trimethyl phosphite to a toluene solution of $Rh_2Cl_2(C_8H_{12})_2$, with $CH_3C(CH_2SLi)_3$, added in a 3:2 molar ratio. **7** crystallizes from toluene/hexane solutions, upon cooling, as an air-sensitive red-orange solid.

The $^{31}P\{^1H\}$ NMR spectrum of **7** in CD_2Cl_2, which exhibits a single doublet centered at 143.8 ppm (J_{P-Rh} = 262 Hz), reveals a molecular structure of C_{3v} symmetry.

Reaction of 4 with Dimethyl Acetylenedicarboxylate. **4** reacts quantitatively at room temperature with stoichiometric amounts of dimethyl acetylenedicarboxylate to yield a 1:1 adduct, **8**. During the reaction, the three typical ν(CO) bands of the highly symmetrical starting material, **4**, disappear and six new ν(CO) bands appear at 2094 (s), 2076 (vs), 2059 (vs), 2044 (s), 2030 (m), and 2000 (vs) cm^{-1} for the adduct **8** (IR spectrum in hexane). As far as the number and the intensities of the ν(CO) bands are concerned, the IR spectrum of **8** is remarkably similar to that observed, and previously reported,[8a] for $Ir_3(\mu\text{-S-}t\text{-Bu})_3(CO)_6(\mu\text{-}\eta^1\text{-}(CH_3COOC)_2)$, i.e. 2084 (s), 2066 (vs), 2042 (vs), 2033 (s), 2011 (m), and 1977 (vs) cm^{-1}. As in the latter complex, whose crystal structure has been previously described, we assumed the added alkyne in **8** to be $\mu\text{-}\eta^1$ bonded to two of the three iridium atoms, leading to a molecular structure of C_s symmetry, with the two bridged metallic centers mutually bonding (Figure 4).

To our knowledge, the ability of trifunctional ligands to bind together three metallic centers has been recognized so far in cases of ligands with tertiary phosphine or arsine functionalities.[26-29]

The above results clearly show that 1,1,1-tris(sulfidomethyl)ethane can serve as a 12-electron-donor ligand to complex three nonbonded metal atoms, leading to triple-square-planar rhodium(I) and iridium(I) species. Our preliminary observations on the reactivity of these new trimetallic complexes toward electrophilic substrates also indicate that the bridging tripod 1,1,1-tris(sulfidomethyl)ethane is flexible enough to support the geometric deformations induced by the formation of a metal-metal bond.

Supplementary Material Available: Tables SI-SIII, listing final anisotropic thermal parameters for non-hydrogen atoms, hydrogen positional and thermal parameters, and least-squares planes and dihedral angles for **4** (6 pages); tables of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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Novel Polypyrazolylborate Ligands: Coordination Control through 3-Substituents of the Pyrazole Ring

Swiatoslaw Trofimenko, Joseph C. Calabrese, and Jeffery S. Thompson*

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The synthesis, structures and coordination chemistry of a series of polypyrazolylborate ligands, $[H_nB(3\text{-Rpz})_{4-n}]^-$, are presented, where R is a *tert*-butyl or phenyl group. These ligands are made by the reaction of tetrahydridoborate ion with the appropriate pyrazole. A series of transition-metal complexes were prepared and characterized by analytical and spectroscopic data. In addition two complexes were characterized by means of X-ray diffraction techniques. The complex Co(HB(3-*tert*-butylpyrazol-1-yl)$_3$)(NCS) crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules per unit cell of dimensions a = 16.466 (4) Å, b = 16.884 (2) Å, c = 9.635 (2) Å, and β = 95.04 (2)°, at -75 °C. Least-squares refinement of 289 variables led to a value of the conventional R index (on F) of 0.043 and of R_w of 0.042 for 3401 reflections having $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to three pyrazolyl nitrogen atoms and the nitrogen atom of the thiocyanate group, is tetrahedral. The *tert*-butyl group is in the 3-position of the pyrazolyl group. The complex Co(HB(3-phenylpyrazol-1-yl)$_3$)(NCS)(tetrahydrofuran) crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules per unit cell of dimensions a = 18.530 (2) Å, b = 14.177 (2) Å, c = 11.733 (2) Å, and β = 100.34 (1)° at -100 °C. Least-squares refinement of 388 variables led to a value of the conventional R index (on F) of 0.045 and of R_w of 0.043 for 3094 reflections with $I > 3.0\sigma(I)$. The geometry about the Co(II) ion, which is coordinated to three pyrazolyl nitrogen atoms, the nitrogen from the NCS group, and the oxygen atom of a tetrahydrofuran molecule, is trigonal bipyramidal. The phenyl group is in the 3-position of the pyrazolyl ring. The results presented here indicate that appropriate selection of the 3-R group in the $[HB(3\text{-Rpz})_3]^-$ ligand will permit the construction of custom-sized pockets around metal ions, allowing access only to molecules of predetermined size and/or shape.

In this contribution, we present the synthesis and coordination chemistry of a new series of polypyrazolylborate ligands with bulky alkyl and phenyl groups in the 3-position of the pyrazole ring. The polypyrazolylborate ligands have been widely used in inorganic,

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