acentric space group $P12_11$; the unit cell parameters found were a = 5.279 (2) Å, b = 10.222 (2), Å, c = 11.990 (2) Å, β = 100.11 (2)°, V = 367.0 (2) Å^3, and Z = 2. The structure found, portrayed in Figure 1, establishes the R absolute stereochemistry for the (methylenecyclopropyl)acetyl moiety in this amide.

Hydrolysis of this amide in dioxane/aqueous sulfuric acid, followed by purification of the acid through preparative GC, gave (*R*)-(−)-MCPA, $[\alpha]_D$−8° (c = 0.32, $CDCl_3$), while the second amide was similarly converted to (*S*)-(+)-MCPA, $[\alpha]_D$+9° (c = 0.56, $CDCl_3$). The two antipodes of MCPA and racemic MCPA were each converted by way of the corresponding *N*-hydroxysuccinimide esters to the respective coenzyme A esters, which were each purified by HPLC using 20 mM ammonium formate pH 5.5 buffer and a methanol gradient (20–35% over 30 min) on a C_{18} μBondapak column; after concentration under vacuum, HPLC analysis (20 mM KH_2PO_4 with 0.3 mM EDTA pH 6.0 buffer and the methanol gradient) was used to derive each CoA ester concentration from an established linear correlation of known MCPA-CoA concentration[13] with the integrated HPLC detector response at 254 nm. The concentration of the thoroughly purified GAD[14] was established through standard activity assays before and after each set of kinetic runs.[15]

Reactions of (−)-MCPA-CoA, (+)-MCPA-CoA, and (±)-MCPA-CoA with GAD at various initial substrate:enzyme ratios were monitored by following the diminution of absorbance at 446 nm and through activity assays.[15] The data thus secured establish several points: Inactivation reactions employing (*R*)-(−)-MCPA-CoA are appreciably faster than reactions utilizing (*S*)-(+)-MCPA-CoA (Figure 2). Inactivations of GAD by (*R*)-(−)-MCPA-CoA and (*S*)-(+)-MCPA-CoA are thus stereospecific, the stereospecificity[16] being manifest in different rates for inactivation of GAD by the two diastereomers. Racemic MCPA-CoA inactivates GAD at an intermediate rate. After reaction times of approximately 25 min, all three stereoisomeric forms of MCPA-CoA inactivated the enzyme to comparable extents and formed comparable product mixtures, as judged by HPLC analyses of those mixtures after gentle SDS denaturation. Reactions involving (*R*)-(−)- or (±)-MCPA-CoA as functions of time and initial concentrations may be modeled satisfactorily by using a minimal kinetic scheme for suicide inactivation,[17-19] but reactions of (*S*)-(+)-MCPA-CoA may not, indicating that a more complex kinetic situation is involved.

One possible explanation for the latter result, rate-limiting enzyme-catalyzed isomerization of (+)-MCPA-CoA to (−)-MCPA-CoA by way of a (2-methylenecyclopropylidene)acetyl-CoA, is now being tested through additional kinetic experiments with isotopically labeled and structurally related (methylenecyclopropyl)acetyl thioesters. This possibility may have a bearing as well on the biphasic kinetic behavior of the inactivation process:[7] enzyme-mediated interconversion of (−)-MCPA-CoA and (+)-MCPA-CoA in competition with inactivation could leave the slower reacting isomer to give further inactivation after the faster (*R*)-(−)-MCPA-CoA ester had been consumed.

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(12) Data collected at 23 °C by using pyrolyzed graphite monochromated Mo Kα X-radiation. A total of 4303 reflections including Bijvoet pairs were collected, with 1938 reflections having $I > 3\sigma I$. Full-matrix least-squares refinement of 221 variables gave R = 0.0398 and R_w = 0.0403 with a goodness of fit of 1.19. A check of the Fourier difference map showed that the largest peak was 0.17 e/Å^3.

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Synthesis and Reactivity of (Pentamethylcyclopentadienyl)iridium Bis(thiolate) and Thiolate Hydride Complexes

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Because metal–sulfur bonds are relatively strong, sulfur ligands are frequently used to hold metal centers together in di- and polynuclear complexes, catalysts, biological systems, and solid-state materials.[1-3] In such environments, the sulfur ligands are often relatively inert.[4] Recently, there has been growing interest in preparing mononuclear complexes with simple thiolate (M–SR) and hydrosulfido (M–SH) groups, because of the increased reactivity such ligands might exhibit toward organic substrates.[5] We report that pentamethylcyclopentadienyl–iridium complexes provide a useful system for preparing and studying such mononuclear metal–sulfur complexes. Replacement of halides and alkoxides at iridium by sulfur nucleophiles occurs in a straightforward way, leading to a series of simple, mononuclear iridium bis(thiolates), bis(hydrosulfides), and hydrido thiolates in which the structure and behavior of these ligands can be studied at a single metal center. We have completed the structural characterization of several of these materials and offer a preliminary account of their reactivity.

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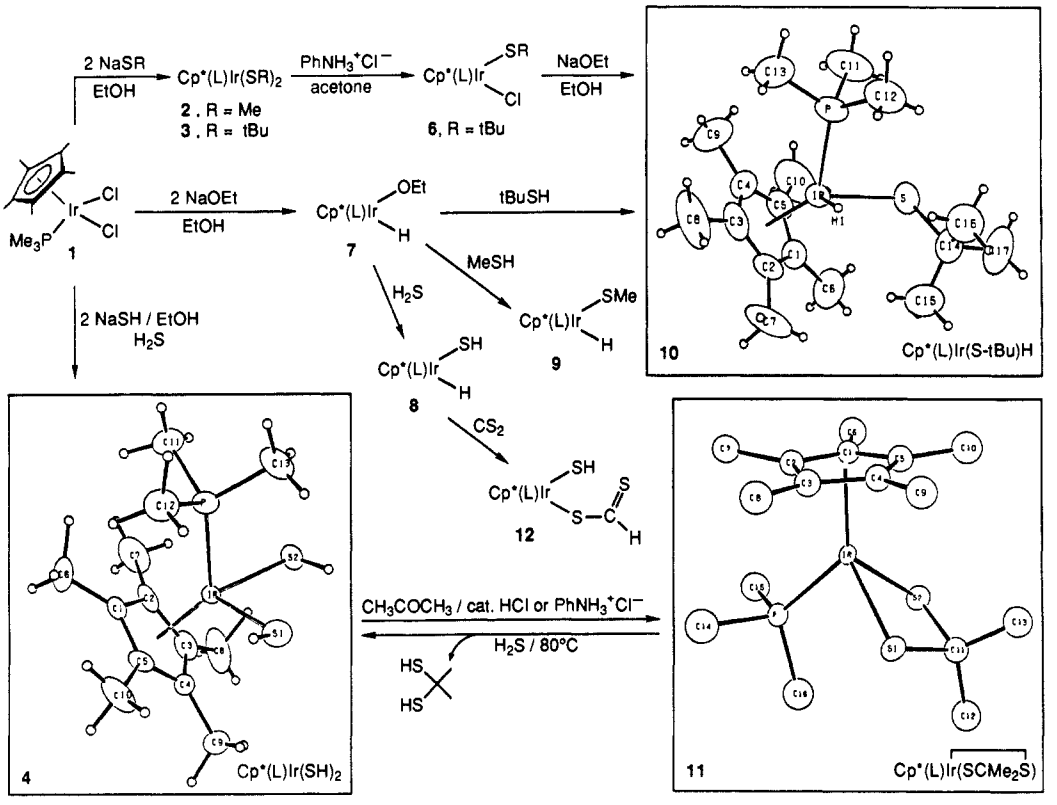
Scheme I



The chemistry described here, summarized in Scheme I, originates with the dichloride $Cp^*(PMe_3)IrCl_2$ (**1**).[6] Reaction with sulfur nucleophiles leads to replacement of the chloride ligands in **1** with thiol and thioalkoxide ligands. Thus, addition of dry ethanol to a mixture of the dichloride and slightly more than 2 equiv of either sodium methanethiolate or sodium 1,1-dimethylethanethiolate[7] leads to the iridium bis(thiolates) $Cp^*(PMe_3)Ir(SMe)_2$ (**2**) and $Cp^*(PMe_3)Ir(S\text{-}tBu)_2$ (**3**) in excellent isolated yield. Both complexes are air-stable orange solids that can be purified by chromatography on alumina III and have been fully characterized by standard spectroscopic and analytical techniques.

Treatment of the dichloride **1** with excess sodium hydrogen sulfide (NaSH) in ethanol also leads to a successful substitution reaction. After workup (removal of ethanol, chromatography on alumina III), two products are isolated. One is the expected iridium dithiol $Cp^*(PMe_3)Ir(SH)_2$ (**4**). In addition, an intensely green complex is obtained. On the basis of spectroscopic data, we formulate this species as the unsymmetrical dimer $Cp^*(PMe_3)Ir(\mu\text{-}S)_2IrCp^*$ (**5**).[8] The mechanism by which this dimer forms is unclear, but may involve deprotonation of $Cp^*(PMe_3)Ir(SH)_2$. Formation of **5** can be suppressed by the addition of excess hydrogen sulfide (H_2S) to the reaction mixture; under these conditions, **4** is isolated in 92% yield.

Besides the expected resonances for the coordinated Cp^* and PMe_3 ligands, the ^1H NMR spectrum of **4** exhibits a doublet for the thiol protons at δ −1.93 ppm (J_{P-H} = 4.5 Hz). The infrared spectrum shows weak S–H stretches at 2521 and 2496 cm^{-1}. Because of the paucity of metalla dithiol complexes,[9] we undertook a single-crystal X-ray diffraction study of **4**; an ORTEP diagram is included in Scheme I. The iridium–sulfur bond lengths are 2.370 (2) and 2.380 (2) Å, and the S_1–Ir–S_2 angle is 88.74 (7)°. The thiol hydrogens were located and refined; however, motion and/or disorder gave large thermal parameters for these atoms. It appears that the "inside" hydrogen, on the basis of its location[10] and an S–H distance of 1.25 (18) Å (compared with the "outside" S–H at 1.02 (14) Å), may be hydrogen bonded to the neighboring sulfur atom, although the error in the structural values does not allow us to state this assertion with great confidence.

The bis(1,1-dimethylethanethiolate) **3** also serves as a precursor to a novel thiolate hydride. Reaction of **3** with aniline hydrochloride gives $Cp^*(PMe_3)Ir(S\text{-}tBu)Cl$ (**6**) in 45% isolated yield. Upon treatment with sodium ethoxide in ethanol, this material is converted to the thiolate hydride **10** in 88% isolated yield. The structure of the 1,1-dimethylethanethiolate hydride complex **10** has been determined by X-ray diffraction, and an ORTEP diagram is included in Scheme I. Synthesis of this and other iridium thiolate hydrides has also been accomplished by an exchange route. Treatment of dichloride **1** with 2 equiv of sodium ethoxide in ethanol gives the iridium ethoxy hydride $Cp^*(PMe_3)Ir(OEt)H$ (**7**).[11] Unlike its PPh_3-substituted analogue, which can be purified, we have been unable to separate this complex from small amounts of hydrido chloride $Cp^*(PMe_3)Ir(H)(Cl)$[4] and/or dihydride $Cp^*(PMe_3)IrH_2$[4,12] that also form in the reaction. However, treatment of crude ethoxy hydride **7** with H_2S, methanethiol, or 1,1-dimethylethanethiol in benzene leads to the rapid formation

(6) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003.

(7) Sodium alkanethiolates were prepared by the reaction of a slight excess (1.1 equiv) of the appropriate thiol with sodium ethoxide in ethanol.

(8) **Note Added in Proof**: The structure of **5** has recently been confirmed by X-ray diffraction; details will be reported in a full paper. An oxygen-containing complex similar to this dimer, but containing one rather than two bridging atoms ($Cp^*(PMe_3)Ir(\mu\text{-}O)IrCp^*$) is also intensely green. Its spectral characteristics (^1H and $^{13}C\{^1H\}$ NMR, IR, and UV–vis) are very similar to those of the dimer **5**. McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543.

(9) Other structurally characterized neutral metalla dithiols include the following: (a) Briant, C. E.; Hughes, G. R.; Minshall, P. C.; Mingos, D. M. P. *J. Organomet. Chem.* **1980**, *202*, C18. (b) Ghilardi, C. A.; Midollini, S.; Nuzzi, F.; Orlandini, A. *Transition Met. Chem. (Weinheim, Ger.)* **1983**, *8*, 73. (c) Bottomley, F.; Drummond, D. F.; Egharevba, G. O.; White, P. S. *Organometallics* **1986**, *5*, 1620.

(10) The iridium atom, both sulfur atoms, and H2 lie in approximately the same plane. The H2–S1 distance is 2.68 (16) Å.

(11) The PPh_3-substituted analogue, synthesized in this manner, has been reported. Newman, L. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 5314.

(12) (a) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

of $Cp^*(PMe_3)Ir(SH)H$ (**8**), $Cp^*(PMe_3)Ir(SMe)H$ (**9**), and $Cp^*(PMe_3)Ir(S\text{-}tBu)H$ (**10**), respectively. All three complexes can be isolated in pure form and fully characterized and show characteristic hydride doublets at high field in the ^1H NMR spectrum and iridium hydride stretches in the infrared spectrum.[13] The thiol hydride **8** also shows a doublet of doublets at δ -2.18 ppm (J_{P-H} = 4.6 Hz, J_{H-H} = 1.8 Hz) for the thiol proton in the ^1H NMR spectrum and a weak S-H stretch at 2524 cm^{-1} in the infrared spectrum.

Preliminary reactivity studies on some of these complexes have established that reactions with small molecules may take place at either the S-H bond or the metal center, depending on the structure of the complex and reagent. For example, metalla dithiol **4** reacts with solvent acetone in the presence of catalytic acid (HCl or aniline hydrochloride) to give a single new complex that exhibits inequivalent methyl groups at δ 2.02 and 1.81 ppm in the ^1H NMR spectrum. This, in addition to other spectroscopic and analytical data, led us to assign the structure of this product as $Cp^*(PMe_3)Ir(SCMe_2S)$ (**11**), to our knowledge the first 2,4-dithiametallacyclobutane complex.[14] An X-ray diffraction study confirms this assignment; once again, an ORTEP diagram is included in Scheme I. Treatment of **11** with H_2S at 80 °C for 24 h quantitatively regenerates the dithiol **4** and gives 2,2-propanedithiol[15] in 25% yield (^1H NMR).

In reactivity studies on thiol hydride complex **8**, insertion of carbon disulfide (CS_2) has been found to take place into the metal-hydrogen bond, rather than the metal-heteroatom bond as occurs in the PPh_3-substituted analogue of the ethoxy hydride **7**.[11] Thus, **8** reacts with 1 equiv of CS_2 in benzene to give the dithioformate complex **12** as the only product (^1H NMR).[16] In addition to the resonances attributable to the Cp^* and PMe_3 ligands, a new thiol doublet (δ -2.01, J_{P-H} = 4.8 Hz) and a singlet integrating as one proton (δ 11.97) are seen in the ^1H NMR spectrum. Complex **12** is unstable and slowly decomposes to an as yet uncharacterized species.

In summary, mononuclear iridium complexes containing M-S bonds (some of which also possess other potentially reactive σ-bound ligands, such as hydrides) can be prepared in a straightforward way. These complexes are very robust, although they exhibit at least some reactivity toward small organic molecules; reaction may take place at either the metal or sulfur atom, depending on the structure of the molecule involved. Further investigations are under way aimed at understanding the physical principles that guide this choice.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **2-12** and details of the structure determinations for complexes **4**, **10**, and **11**, including experimental description, ORTEP drawings showing full atomic numbering, crystal and data collection parameters, general temperature factor expressions (B's), root-mean-square amplitudes, positional parameters and their estimated standard deviations, and intramolecular distances and angles (37 pages); tables of observed and calculated structure factors for **4** and **10** (31 pages). Ordering information is given on any current masthead page.

(13) Complex **8**: ^1H NMR (C_6D_6) δ_{Ir-H} -16.01 (dd, J = 36.7, 1.8 Hz, 1 H); IR (KBr pellet) ν_{Ir-H} 2093 cm^{-1}. Complex **9**: ^1H NMR (C_6D_6) δ_{Ir-H} -16.58 (d, J = 36.4 Hz, 1 H); IR (KBr pellet) ν_{Ir-H} 2114 cm^{-1}. Complex **10**: ^1H NMR (C_6D_6) δ_{Ir-H} -16.47 (d, J = 35.1 Hz, 1 H); IR (KBr pellet) ν_{Ir-H} 2096 cm^{-1}.

(14) The pentasulfide Cp_2TiS_5 reacts with acetone to give a complex containing an $M[(S_2)CR_2]$ six-membered ring: (a) Giolando, D. M.; Rauchfuss, T. B. *Organometallics* **1984**, *3*, 487. We are grateful to a referee for calling this paper to our attention. For other metal-sulfur compounds that react with acetone to form new C-S bonds, see: (b) Angelici, R. J.; Gingerich, R. G. W. *Organometallics* **1983**, *2*, 89. (c) Mueting, A. M.; Boyle, P. D.; Wagner, R.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 271.

(15) The first synthesis of 2,2-propanedithiol was accomplished by treating H_2S with acetone at 7500-8500 atm. (a) Cairns, T. L.; Evans, G. L.; Larchar, A. W.; McKusick, B. C. *J. Am. Chem. Soc.* **1952**, *74*, 3982. Other routes have since been developed. See: (b) Demuynck, M.; Vialle, J. *Bull. Soc. Chim. Fr.* **1967**, 1213. (c) Adolfsson, L.; Andersson, R.; Olsson, K. *Chem. Scr.* **1980**, *16*, 122.

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Rhodium(II) Complex with a Highly Reactive Rhodium-Rhodium Bond: Insertion of Dioxygen and Nitrosobenzene

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We report the synthesis and some preliminary reaction chemistry of $[Cp^*Rh(\mu\text{-}Cl)]_2$ (**1**) ($Cp^* = C_5Me_5$), a Rh(II) dimer with a reactive Rh-Rh bond.[1] While many Rh(II) complexes containing Rh-Rh bonds have been reported in the literature,[2] including several analogues of **1**,[3] the high reactivity of the Rh-Rh bond in **1** is remarkable and has allowed us to prepare several unusual products. The observed chemistry is outlined in Scheme I.

Complex **1** is produced by the reduction of $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$[4] in CH_2Cl_2 with excess Na/Hg (0.4%).[5] Blue-black crystals of **1** are isolated in yields ranging from 65 to 75% by the addition of hexane to the filtered and reduced solutions and by cooling to -40 °C. An ORTEP diagram[6] of **1** is included in Scheme I. Complex **1** is soluble in aromatic solvents and slightly soluble in saturated hydrocarbons and Et_2O. Solubility is high in CH_2Cl_2; however, there is a slow reaction at ambient temperatures, and after solutions stand for 12 h, the starting complex, $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$, is cleanly produced. A more rapid reaction occurs in $CHCl_3$, again producing mostly $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$. Solutions are highly air sensitive, and the reaction of **1** with dry O_2 was investigated.

(1) Presented at the 196th National Meeting of the American Chemical Society, Los Angeles, CA, Sept 1988; Inorganic Abstract 159.

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(4) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(5) ^1H NMR (C_6D_6, 90 MHz, 25 °C): 1.59 ppm.

(6) Crystal data for **1**, $C_{20}H_{30}Cl_2Rh_2$ (FW = 547.18): monoclinic ($C2/c$), a = 33.068 (8) Å, b = 13.173 (3) Å, c = 16.810 (4) Å, β = 117.77 (2)°, V = 6479.4 Å^3, Z = 12. Data (Mo Kα) were collected on a CAD4 diffractometer. The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares refinement (SDP) to R = 0.040 and R_w = 0.047 for 2326 absorption-corrected observations with $F_o^2 > 2\sigma(F_o^2)$ and 325 variables. Two independent molecules are present, one on a 2-fold site and the other on a general position (molecule shown in Scheme I). Selected bond distances and angles (2-fold site molecule in parentheses): Rh-Rh, 2.617 (1) (2.628 (1)); Rh-Cl, 2.411 (4) and 2.408 (3) (2.392 (3) and 2.393 (5)); Rh-Cl-Rh, 65.74 (8) and 65.92 (9) (66.6 (1)). Details will be provided in a forthcoming full paper.

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