similarly upon reaction with LiBr.

Conclusion

The trinuclear carbonyl anions are found to be relatively weakly paired to unipositive cations; the dissociation constants observed in THF are 1–2 orders of magnitude larger than those determined by conductivity measurements for the mononuclear anions $[CpMo(CO)_3]^-$ and $[Mn(CO)_5]^-$.[3]

Experimental Section

Tetrahydrofuran (THF), *p*-dioxane and diethyl ether (Mallinckrodt), 2,5-Me_2 THF and 2,2,5,5-Me_4 THF (Aldrich), 1,2-dimethoxyethane (DME; Matheson Coleman and Bell (MCB)) were freshly distilled from sodium/benzophenone under prepurified dinitrogen. Dichloromethane was distilled from P_2O_5. Tetrahydrofuran-d_8 (Aldrich) was degassed and used without further purification. All procedures were performed under dinitrogen in standard Schlenk-type glassware.[13] Lithium bromide (MCB) was dried at 130 °C under vacuum for a minimum of 24 h. All syringes and the IR cells (CaF_2, 0.1 mm; KCl, 0.5 mm) were flushed with dinitrogen prior to use. All infrared spectra were recorded for solutions under an atmosphere of dinitrogen on a Nicolet MX-1 FT-IR spectrometer. Data were transferred to a VAX computer through an interface developed by B. S. Seiler in these laboratories. THF solutions of $LiBEt_3H$ and $LiB(s\text{-}Bu)_3H$ (Aldrich) were used as received, as were the salts $LiBH_4$ (Aldrich) and $LiOH\cdot H_2O$ (MCB). $Ru_3(CO)_{12}$ was used as purchased (Strem). Literature procedures were used to prepare the Na^+, NEt_4^+, and PPN^+ salts of $[Ru_3H(CO)_{11}]^-$ (**1b**$^-$)[5] and $[PPN][Fe_3H(CO)_{11}]$ ([PPN][**1a**]).[14] $[NEt_3H]$[**1a**] and $[NEt_4]$[**1a**] were prepared by adaptation from the preparation of [PPN][**1a**].

Data Acquisition and Handling. Infrared spectra were obtained on a Nicolet MX-1 FT-IR spectrometer and transferred to an LSI (DEC) microprocessor. For the representation of IR bands we chose the "restricted" Cauchy–Gauss sum function described by R. N. Jones[15] and obtained very satisfactory fits by keeping the half-bandwidths of the two functions equal. For minimization of the sum of weighted least-squares we used the subroutine CURFIT.[16]

Attempted Preparations of Pure [Li][1b]. In a typical experiment $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) is dissolved in 5–10 mL of THF. A THF or Et_2O solution of $LiBR_3H$ (1–10 equiv) is then added by syringe (R = H, 25 °C; R = Et, 0 °C; R = *s*-Bu, −78 °C). The initially orange solution turns deep red with stirring. Reaction progress is followed by infrared spectroscopy. Attempts to isolate solids by solvent removal lead to unidentified decomposition products.

In a second attempt, a flask containing a solution of $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol) in 5 mL of THF is flushed with CO. A solution of $LiOH\cdot H_2O$ (0.02 g, 0.42 mmol) in 1 mL of distilled, degassed H_2O is then added by syringe. The system is flushed with CO again and stirred at room temperature for 1 h. The solvents are stripped off under vacuum; the residue is dried under vacuum and then redissolved in THF. IR spectra confirm the presence of [Li][**1b**]; however, any further experimental manipulations lead to decomposition.

Dilution Studies. For $[NEt_3H]$[**1a**] and $[NEt_4]$[**1a**], THF solutions at the varying concentrations shown in Table II (supplemental) were made by adding successive increments of the salt to an initial dilute solution. For $[NEt_4]$[**1b**] a 30 mg/mL stock solution was prepared in THF. Solutions of lower concentration (see Table II (supplemental)) were prepared by successive dilutions of the initial stock solution.

Competition Study between $[NEt_4][Ru_3H(CO)_{11}]$ and LiBr in THF. A stock solution of $[NEt_4][Ru_3H(CO)_{11}]$ and a stock solution of LiBr (1 mg/mL) were prepared as described above. Infrared spectra were obtained of solutions containing the lithium salts and the ruthenium anion as shown in Table IV (supplemental).

Acknowledgment. Partial support of this work from NSF Grant CHE 81-11332 to H.D.K. and discussions with Dr. Joel S. Miller of Occidental Research Corp. are gratefully acknowledged.

Registry No. $[NEt_4^+]$[**1a**], 55976-22-2; $[Na^+]$[**1a**], 87145-37-7; $[Li^+]$[**1a**], 87145-36-6; $[PPN^+]$[**1a**], 23254-21-9; $[NEt_3H^+]$[**1a**], 56048-18-1; $[NEt_4^+]$[**1b**], 12693-45-7; $[Na^+]$[**1b**], 71936-71-5; $[PPN^+]$[**1b**], 85781-92-6; $[PPN^+]$[**1b**], 71936-70-4; ^{13}C, 14762-74-4; LiBr, 7550-35-8.

Supplementary Material Available: Figures 2 and 3 (IR spectra), Figure 5 (a Lambert–Beer plot), Table II (data for concentration studies), and Table IV (data for competition studies) (4 pages). Ordering information is given on any current masthead page.

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Iridium Complexes of (Diphenylphosphino)ethanethiol. Crystal and Molecular Structure of $[IrH(SCH_2CH_2PPh_2)(HSCH_2CH_2PPh_2)(CO)]^+Cl^-$: A New and Novel Example of Thiol Coordination

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Transition-metal complexes of thiolates and thioethers have received considerable attention because of their involvement in both enzymatic[1] and nonbiological catalytic processes.[2,3] The chemistry of phosphine complexes, on the other hand, forms the basis for a variety of catalytic reactions.[4,5] The development of these two fields of research led to the recent interest in mixed-donor phosphorus–sulfur ligands. Phosphine–thioether chelates have been studied by the research groups of Meek,[6,7] Clark,[8] Roundhill,[9] Sanger,[10] and others.[11-14] The chemistry of phosphine–thiol ligands has received lesser attention.[15-18] In this paper we report our initial investigations of the chemistry of one such phosphine–thiol chelate, (diphenylphosphino)ethanethiol, $Ph_2PCH_2CH_2SH$ (PSH). The reactions of PSH with *trans*-$Ir(PPh_3)_2(CO)Cl$ (**1**) are described. The resulting new Ir(III) and Ir(I) species are characterized. An X-ray crystallographic investigation reveals that reaction of **1** with excess ligand yields a new and novel complex in which thiol and thiolate coordination occurs. The results and implications of this chemistry are discussed below.

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Table I. Spectroscopic Data[a]

compd	^{31}P NMR		^{1}H NMR		IR, cm^{-1}		
	δ	J_{P-P}, Hz	δ	J_{P-H}, Hz	ν_{CO}	ν_{Ir-H}	ν_{S-H}
PSH	−17.8		0.75 (t)[b]				2560 (w)[c]
1	23.4				1961[d]		
2	42.2, 31.4	313			1942		
3	43.0, −0.8	335	−17.1 (dd)[e]	11.7	2018	2252	
4	42.4, 27.3	298	−11.7 (dd)[e]	11.7	2042	2142	

[a] All spectral data were recorded of $CDCl_3$ solutions; IR spectra of Nujol mulls of **2** and **4** were identical to solution spectra. [b] S–H proton resonance. [c] Neat oil. [d] See ref 34. [e] Hydride resonance.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free, N_2. ^{1}H NMR spectra were recorded on Bruker CXP-80 and CXP-100 spectrometers using $Si(CH_3)_4$ as the reference. ^{31}P NMR spectra were recorded on a Bruker CXP-100 spectrometer operating at 36.5 MHz with broad-band proton decoupling. Samples were sealed in 5-mm tubes under a N_2 atmosphere. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. Infrared data were recorded employing a Beckman IR-12 spectrometer. Melting points were recorded on a Fisher stage melting point apparatus and were not corrected. Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario. *trans*-$Ir(PPh_3)_2(CO)Cl$ (**1**) and Ph_2PH were purchased from Strem Chemical Co. Ethylene sulfide and the ligand (diphenylphosphino)ethanethiol, PSH, were prepared by literature methods.[16]

Preparation of $Ir(PPh_3)(PS)(CO)$ (2). **1** (200 mg, 0.26 mmol) was dissolved in 25 mL of freshly distilled, degassed CH_2Cl_2. Separately PSH (63 mg, 0.26 mmol) was dissolved in methanol containing 1 equiv of $NaOCH_3$, thus generating the sodium thiolate. The methanol solution was slowly added to the CH_2Cl_2. The solution became bright yellow in a matter of minutes. Stirring for 1 h was followed by concentration to 5–10 mL and addition of 30 mL of methanol. Precipitation of a bright yellow solid resulted. The product (**2**) was isolated by filtration; 105 mg (54%). Anal. Calcd for $C_{33}H_{29}OP_2SIr$: C, 54.46; H, 4.02. Found: C, 54.27; H, 4.05.

Reaction of $Ir(PPh_3)_2(CO)Cl$ with PSH. **1** (50 mg 0.065 mmol) was dissolved in 1 mL of $CDCl_3$. PSH (16 mg, 0.065 mmol) was added. The reaction was monitored by ^{31}P NMR and IR spectroscopy. The data were consistent with the existence of two species in solution, namely $Ir(PPh_3)(PS)(CO)$ (**2**) and $IrH(PPh_3)(PS)(CO)Cl$ (**3**). The relative abundances of these species were approximately 50:50, as determined by integration of the ^{31}P NMR spectrum.

Preparation of $[IrH(PS)(PSH)(CO)]^+Cl^-$ (4). **1** (200 mg, 0.26 mmol) was dissolved in 30 mL of degassed CH_2Cl_2. PSH (126 mg, 0.52 mmol) was added dropwise with stirring. The mixture lightened in color. It was stirred for 2 h and concentrated to 15 mL, and degassed hexane (10 mL) was slowly added. Clear colorless crystals formed on standing. The crystals were isolated by decantation: yield 50 mg (26%); (mp 165 °C dec. Anal. Calcd for $C_{29}H_{30}OP_2S_2IrCl$: C, 46.55; H, 4.04. Found: C, 46.66; H, 4.35.

X-ray Data Collection and Reduction. Colorless blocks of **4** were obtained by crystallization from a CH_2Cl_2/hexane solution. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. A total of 15 high-angle reflections ($20 < 2\theta < 33°$) were located from a rapid-scan data collection. These high-angle data were used to determine that the crystal system was triclinic. Partial rotation photographs around each axis showed no symmetry. The 15 high-angle reflections were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table II. The observed extinctions were consistent with the space groups $P1$ or $P\bar{1}$. $P\bar{1}$ was confirmed by solution and refinement of the structure. $+h,\pm k,\pm l$ data were collected in two shells (4.5–35 and 35–50°). Three standard reflections were recorded every 197 reflections. Their intensities show no statistically significant change over the duration of data collection. The data were processed by using the SHELX-76 program package on the computing facilities at the University of Windsor. A total of 4393 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the tabulation of Cromer and Waber,[19] while those for hydrogen were from Stewart, Davidson, and Simpson.[20]

Table II. Summary of Crystal Data, Intensity Collection, and Structure Solution

formula	$IrS_2P_2OC_{29}H_{30}Cl$
cryst color, form	colorless, blocks
a, Å	10.261 (3)
b, Å	11.269 (3)
c, Å	14.506 (5)
α, deg	85.20 (3)
β, deg	73.02 (3)
γ, deg	111.69 (2)
cryst syst	triclinic
space group	$P\bar{1}$
V, Å^3	1455.6 (8)
d_{calcd}, g/cm^3	1.71
Z	2
cryst dimens, mm	0.11 × 0.38 × 0.42
cryst faces	(100) (−1,0,0) (011) (0,−1,−1) (−1,1,−1) (1,−1,1)
abs coeff (μ), cm^{-1}	47.43
radiation (λ, Å)	Mo Kα (0.710 69) (graphite monochromator)
temp, °C	24
scan speed, deg/min	2.0–5.0 ($\theta/2\theta$ scan)
scan range, deg	1.0° below Kα, 1.1° above Kα
bkgd/scan time ratio	0.5
data collcd	2θ of 4.5–50.0 ($+h, \pm k, \pm l$)
total no. of data collcd	5197
no. of unique data ($F_o^2 > 3\sigma F_o^2$)	4393
no. of variables	325 (2 blocks)
R, %	2.37
R_w, %	2.53

The Ir position was determined from a Patterson map synthesis. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Full-matrix least-squares refinement, in which all non-hydrogen atoms were assigned isotropic temperature factors gave $R = 13.19\%$. Hydrogen atom contributions for the phenyl and alkyl hydrogens were included. C–H bond distances of 1.08 Å were assumed, and hydrogen atom temperature factors were fixed at 0.066. An analytical absorption correction was applied.[21] The average correction was 2.204. Least-squares refinement following the absorption correction gave $R = 3.36\%$. A difference Fourier calculation revealed a peak of electron density for H(S2) at 1.35 Å from S2. Ir–H bond lengths are expected to be 1.85 Å.[22] No such peak could be located. Refinement of the calculated or located hydrogen atom positions was not performed.

In the final cycles of blocked-diagonal refinement in which all hydrogen atom contributions were included and all non-hydrogen atoms were assigned anisotropic temperature factors, $R = 2.37\%$ and $R_w = 2.53\%$ were obtained. The maximum shift/σ on any of the parameters in the final cycles was 0.017. A final difference Fourier calculation showed no peaks of chemical significance. The largest

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Table III. Positional Parameters[a]

atom	*x*	*y*	*z*
Ir	4872 (1)	2009 (1)	1990 (1)
S2	5848 (1)	4258 (1)	2244 (1)
S1	3165 (1)	2611 (1)	1428 (1)
P1	2930 (1)	1176 (1)	3509 (1)
P2	6611 (1)	2906 (1)	378 (1)
O	6655 (4)	869 (3)	2783 (2)
C1	6050 (5)	1347 (4)	2463 (3)
C2	1284 (5)	1256 (5)	3303 (3)
C3	1801 (5)	2533 (5)	2582 (3)
C4	7641 (5)	4642 (4)	310 (3)
C5	6651 (5)	5186 (4)	977 (3)
C11	2351 (4)	−526 (4)	4080 (3)
C12	1905 (5)	−1484 (4)	3547 (3)
C13	1390 (6)	−2787 (5)	3969 (4)
C14	1333 (6)	−3146 (5)	4928 (4)
C15	1796 (5)	−2218 (5)	5448 (4)
C16	2310 (5)	−905 (4)	5032 (3)
C21	3242 (5)	2091 (4)	4460 (3)
C22	2142 (6)	2418 (5)	5053 (3)
C23	2422 (7)	3091 (6)	5781 (4)
C24	3869 (7)	3477 (5)	5886 (4)
C25	4895 (7)	3174 (6)	5301 (4)
C26	4611 (6)	2487 (5)	4588 (3)
C31	5812 (4)	2720 (4)	−593 (3)
C32	4599 (5)	1548 (4)	−471 (3)
C33	4051 (5)	1283 (5)	−1231 (3)
C34	4676 (6)	2200 (5)	−2102 (3)
C35	5880 (6)	3375 (5)	−2227 (3)
C36	6439 (5)	3628 (4)	−1473 (3)
C41	8064 (4)	2307 (4)	−18 (3)
C42	9023 (5)	2414 (4)	523 (3)
C43	10136 (5)	1972 (5)	238 (4)
C44	10319 (5)	1425 (5)	−583 (4)
C45	9394 (6)	1332 (5)	−1117 (4)
C46	8249 (5)	1762 (4)	−832 (3)
Cl	10799 (2)	5393 (1)	7611 (1)
H(S2)	7072	4247	2416

[a] Parameters given $\times 10^4$.

Table IV. Selected Bond Distances (Å) and Angles (deg)

Distances			
Ir–S1	2.411 (1)	P1–C11	1.822 (4)
Ir–S2	2.462 (1)	P1–C21	1.822 (4)
Ir–P1	2.327 (1)	P1–C2	1.831 (6)
Ir–P2	2.348 (1)	P2–C31	1.815 (5)
Ir–C1	1.885 (5)	P2–C41	1.821 (5)
C1–O	1.125 (7)	P2–C4	1.826 (4)
S1–C3	1.813 (5)	C2–C3	1.519 (7)
S2–C5	1.819 (4)	C4–C5	1.526 (7)
S2–H(S2)	1.354 (10)		

Angles			
S1–Ir–S2	85.4 (1)	C5–S2–H(S2)	101.9 (2)
S1–Ir–P1	85.0 (1)	Ir–S2–H(S2)	97.0 (2)
S1–Ir–P2	87.6 (1)	Ir–C1–O	174.7 (3)
S1–Ir–C1	173.7 (1)	Ir–S1–C3	101.9 (2)
S2–Ir–P1	94.8 (1)	S1–C3–C2	110.4 (4)
S2–Ir–P2	85.2 (1)	C3–C2–P1	107.9 (3)
S2–Ir–C1	100.3 (1)	Ir–S2–C5	100.7 (1)
P1–Ir–P2	172.6 (1)	S2–C5–C4	111.1 (3)
P1–Ir–C1	91.8 (1)	C5–C4–P2	111.2 (2)
P2–Ir–C1	95.5 (1)	C4–P2–C31	109.5 (2)
C2–P1–C11	105.6 (2)	C4–P2–C41	104.1 (2)
C2–P1–C21	106.5 (2)	C31–P2–C41	103.1 (2)
C11–P1–C21	106.5 (2)	Ir–P1–C31	115.1 (1)
Ir–P1–C11	116.8 (1)	Ir–P1–C41	117.5 (1)
Ir–P1–C21	115.0 (1)	Ir–P2–C4	106.9 (1)
Ir–P1–C2	106.8 (1)		

peak was 1.2 electrons and was associated with the Ir–S2 bond. The following data are tabulated: positional parameters (Table III); interatomic distances and angles (Table IV). Temperature factors (Table S-I), Hydrogen atom parameters (Table S-II), angles and distances associated with phenyl rings (Table S-III), and values of $10|F_o|$ and $10|F_c|$ (Table S-IV) have been deposited as supplementary material.

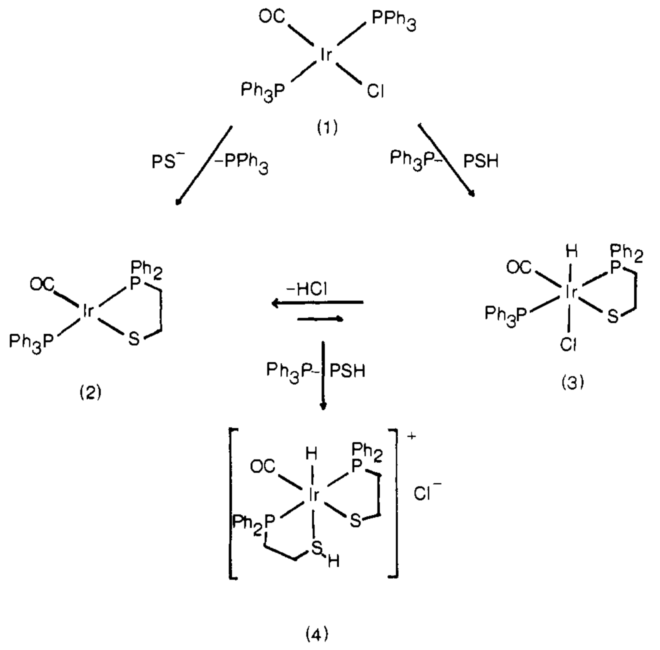

Figure 1. Reaction scheme of PSH with *trans*-Ir(PPh$_3$)$_2$(CO)Cl.

Results and Discussion

The reaction of **1** with the thiolate form of PSH (i.e., PS$^-$) was performed in a methanol/methylene chloride mixture (Figure 1). After workup, a bright yellow solid was isolated in reasonable yield. The ^{31}P NMR spectrum of this compound contained two doublets, consistent with two inequivalent P atoms. The magnitude of the phosphorus coupling constant $^2J_{P-P}$ was consistent with a trans orientation of these P atoms.[23] The IR spectrum contained a strong absorbance at 1942 cm^{-1}. This value was very similar to that previously assigned to ν_{CO} in *trans*-Ir(PPh$_3$)$_2$(CO)(SEt).[25] Our compound was thus formulated as *trans*-Ir(PPh$_3$)(PS)(CO) (**2**). Analytical data were consistent with this formulation. Nucleophilic displacement of Cl$^-$ from Ir by thiolate species has been studied by Roundhill.[25] We presume that such displacement is an initial step in the reaction of PS$^-$ with **1**. This would be followed by the displacement of PPh$_3$ by the P atom of the PS chelating ligand. Although this order of reaction is consistent with chemical intuition, the relative rates of phosphine exchange and thiolate displacement of chloride from Ir have not been studied. Thus, precise comments regarding the mechanism await kinetic studies.

The reaction of **1** with the phosphine–thiol ligand PSH was performed in CDCl$_3$ and monitored by NMR and IR spectroscopy. The ^{31}P NMR spectrum of a 1:1 mixture of PSH and **1** contained two pairs of doublets with approximately equal integrations. In addition, a singlet with the chemical shift of free PPh$_3$ was also observed. These observations are consistent with the presence of two Ir species, each containing two inequivalent trans P atoms. On the basis of chemical shift and $^2J_{P-P}$ values, one of the species was identified as **2**. The IR spectrum of the solution showed the expected ν_{CO} for this species. In addition, absorbances at 2018 and 2252 cm^{-1} were observed. These were assigned to ν_{CO} and ν_{Ir-H}. The ^{1}H NMR spectrum contained a doublet of doublets at −17.1 ppm, consistent with an Ir–H species. The IR frequencies for ν_{CO} and ν_{Ir-H} were similar to those reported for the products of oxidative addition of thiols to **1**.[24] Thus, the second Ir species in the reaction mixture was assigned the structural formula IrH-

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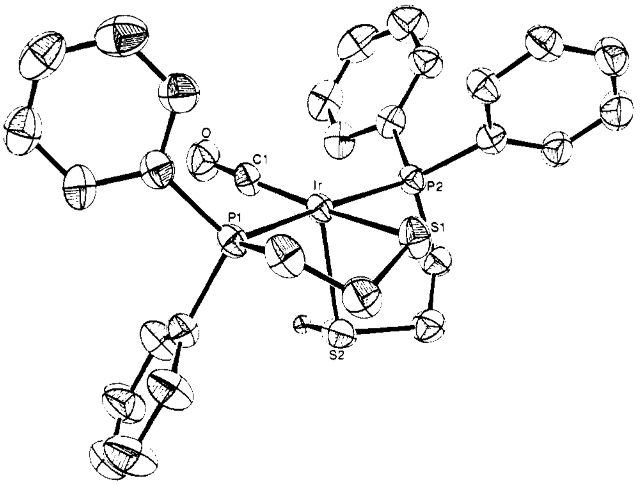

Figure 2. ORTEP view of the cation $[IrH(PS)(PSH)(CO)]^+$. 50% probability thermal ellipsoids are drawn.

$(PPh_3)(PS)(CO)Cl$ (**3**). This Ir(III) species arises from a reaction involving oxidative addition of thiol to Ir(I) and substitution of the more basic phosphine in PSH for PPh_3. In similar reactions involving phosphine–acid or phosphine–aldehyde chelates, Rauchfuss[26] showed that phosphine replacement following chelate-assisted oxidative addition was the reaction sequence leading to the P–O chelate analogues of **3**.

Ir(III) species containing hydride and thiolate ligands are known to be unstable,[25] readily undergoing reductive elimination of HCl, generating an Ir(I) product. We conclude that reductive elimination of HCl from **3** generates the observed equilibrium concentration of the Ir(I) species (**2**) in our reaction mixture.

Reaction of **1** with more than 1 equiv of PSH was performed in CH_2Cl_2. On slow addition of hexane, colorless crystalline blocks of **4** formed. The ^{31}P NMR spectrum of a solution of this compound contained two doublets with chemical shift values distinct from those corresponding to **1**, **2**, or **3**. This is consistent with a new Ir species with two inequivalent P atoms. The $^2J_{P-P}$ value is consistent with a trans arrangement of the P atoms. ^1H NMR data showed a doublet of doublets at −11.7 ppm, consistent with an Ir–H species. IR data contained an absorbance at 2142 cm^{-1}, which was assigned to ν_{Ir-H}. An absorbance assigned to ν_{CO} was observed at 2042 cm^{-1}. The integration of the ^1H NMR signals revealed the presence of an additional H signal masked by the methylene envelope. In addition to these spectroscopic data the combustion analysis was consistent with our formulation of **4** as $[IrH(PS)(PSH)(CO)]^+Cl^-$.

Confirmation of the formulation of **4** was obtained from an X-ray crystallographic investigation. The study clearly showed that the crystal is built from unit cells each containing discrete cations and anions, as is evident from the $Ir\cdots Cl$ distance of 4.562 Å. The closest nonbonded contact between cation and anion is $Cl\cdots H(S2)$, 2.056 Å. This interaction is consistent with hydrogen bonding between the coordinated thiol and the anion. Selected interatomic dimensions are given in Table IV. An ORTEP drawing of the cation is shown in Figure 2. The geometry of Ir as determined from the X-ray experiment is best described as a distorted square-based pyramid, with a coordination sphere consisting of the ligands CO, PS, and PSH. The hydride hydrogen atom was not located; however, the geometry at Ir is consistent with spectroscopic evidence for an Ir–H species. The hydride ligand completes the octahedral coordination of Ir(III) in **4**. The coordination of the thiol group of PSH suggested from the formulation of **4** as an Ir(III) species is confirmed by the location of the thiol hydrogen atom H(S2). The S2–H(S2) distance, 1.35 Å, is consistent with that expected for a S–H bond.[27] The P atoms of the PS and PSH ligands are in a trans orientation, while the thiolate sulfur of PS is trans to CO and the thiol sulfur of PSH is trans to hydride. The bite angles of the two P–S chelates are similar, averaging 85.1°, typically of five-membered chelate rings.[28] Ir–P, Ir–S, and Ir–C bond distances are typical of those observed in other systems.[29] The difference in the Ir–S bond distances (2.411 (1) vs. 2.462 (1) Å) reflects the difference of thiolate vs. thiol coordination as well as the trans influence of CO vs. H. Consequently, direct comparison of Ir–SR and Ir–HSR bond distances cannot be made.

The mechanism of formation of species **4** is a subject for speculation. An obvious route to this compound would involve a phosphine exchange reaction of PSH with **3**, displacing PPh_3. The chelate effect of PSH together with the strong trans effect of hydride could then result in displacement of chloride, yielding **4**.

The species **4** represents the first organometallic species in which thiol coordination has been observed. Other species in which M–HSR coordination have been fully documented are limited to porphyrin complexes of Ru,[30] Fe,[31] and Zn.[32] Clearly, the chelating nature of the mixed phosphorus–sulfur ligand (PSH) assists in stabilizing the novel thiol coordination described herein. Other aspects of the chemistry of mixed-donor ligands are currently under examination and will be reported in due course.[33]

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Supplementary Material Available: Tables S-I–S-IV, listing temperature factors, hydrogen atom parameters, angles and distances associated with phenyl rings, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Mechanistic Organometallic Photochemistry: Observation of Metastable Ruthenocenium in Photolysis of Ruthenocene

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The photochemistry of ruthenocene, $Ru(cp)_2$,[1] in halogenated hydrocarbons has been investigated by several groups, which agreed on the redox nature of the photochemical processes.[2,3] Unfortunately, doubts on the assignments of the

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(1) Throughout this work the symbol Cp stands for η-C_5H_5.

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