Reactions of (η^5-C_5Me_5)Ir(PMe_3)$(SH)_2$ and (η^5-C_5Me_5)Ir(PMe_3)(SH)(H) with Thionylaniline (PhNSO) to Give Novel Iridium S_3O and S_2O Complexes

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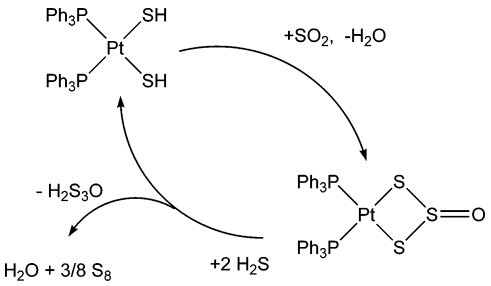
Treatment of Cp*Ir(PMe_3)$(SH)_2$ (**1**), where Cp* = η^5-C_5Me_5, with thionylaniline (PhNSO), CS_2, and *p*-tolylisothiocyanate (*p*-tolNCS) gave Cp*Ir(PMe_3)(S_3O) (**3**), Cp*Ir(PMe_3)(S_2CS) (**4**), and Cp*Ir(PMe_3)-(SH)(SC(S)HN-*p*-tol) (**5**), respectively. Treatment of Cp*Ir(PMe_2R)(H)(SH) (**2a**,**b**), where R = Me (**2a**), Ph (**2b**), with PhNSO gave Cp*Ir(PMe_2R)(S_2O) (**6a**,**b**) as mixtures of interconvertible conformational isomers. Treatment of **2a** with *p*-tolNCS gave Cp*Ir(PMe_3)(H)(SC(S)NH-*p*-tol) (**7**). The crystal structures of **3**−**5**, **6b**, and **7** are reported.

Introduction

Transition-metal complexes containing polysulfur oxide ligands have been implicated in biological[1] and industrial[2] processes. Studies of this class of compounds can be powerful tools for understanding reaction mechanisms of important heterogeneously catalyzed processes such as the Claus process.[3] This process is widely used to convert H_2S, obtained from the hydrodesulfurization (HDS) of petroleum, to sulfur and water ($2H_2S + SO_2 \rightarrow {}^3/_8S_8 + 2H_2O$). This reaction requires somewhat drastic conditions (200−300 °C) over an alumina catalyst. The reaction of a M−SH species with SO_2 models the attack of SO_2 on chemisorbed H_2S. For example, we have shown[4] that *cis*-(Ph_3P)$_2$Pt$(SH)_2$ is the first homogeneous catalyst for the Claus reaction at room temperature. Interestingly, the trans isomer does not catalyze the reaction. The presence of the cis-SH groups leads to the formation of the reactive intermediate (Ph_3P)$_2$PtS_3O, which was isolated from the reaction and which catalyzes the Claus reaction. We proposed the mechanism given in Scheme 1 for this reaction. This led us to investigate[5] to investigate the reaction of SO_2 with a similar iridium dithiolo complex.

Cp*Ir(PMe_3)$(SH)_2$, (**1**)[6] reacted instantaneously with SO_2 under mild conditions to give the tetrasulfido complex Cp*Ir-(PMe_3)S_4, rather than a S_3O complex analogous to the platinum species, and **1** did not catalyze the Claus reaction. This contrasting behavior prompted us to extend our studies to insertion reactions of **1** and an even more interesting Claus chemistry model, Cp*Ir(PMe_3)(H)(SH), (**2**),[6] with PhNSO, CS_2, and *p*-tolNCS. In this paper, we report the synthesis and the characterization of several new iridium complexes via direct insertion reactions of these electrophiles into Ir−SH and Ir−H bonds.

Scheme 1



Results and Discussion

Reaction of Cp*Ir(PMe_3)$(SH)_2$ with PhNSO. Treatment of **1** with PhNSO in benzene or toluene at room temperature gave, after workup, Cp*Ir(PMe_3)S_3O (**3**). No intermediate species were observed. The observation (NMR) of aniline at the end of the reaction is consistent with the reaction shown in eq 1.

$$\underset{\mathbf{1}}{\text{Cp*Ir(PMe}_3\text{)(SH)}_2} + \text{PhNSO} \rightarrow \underset{\mathbf{3}}{\text{Cp*Ir(PMe}_3\text{)(S}_3\text{O)}} + \text{PhNH}_2 \quad (1)$$

Similar reactions[7] occur with CpRu(PPh_3)$_2$SH and *cis*-(Ph_3P)$_2$-Pt$(SH)_2$. The ruthenium complex reacted with PhNSO to give the unstable compound CpRu(PPh_3)$_2$SS(O)NHPh, which is the

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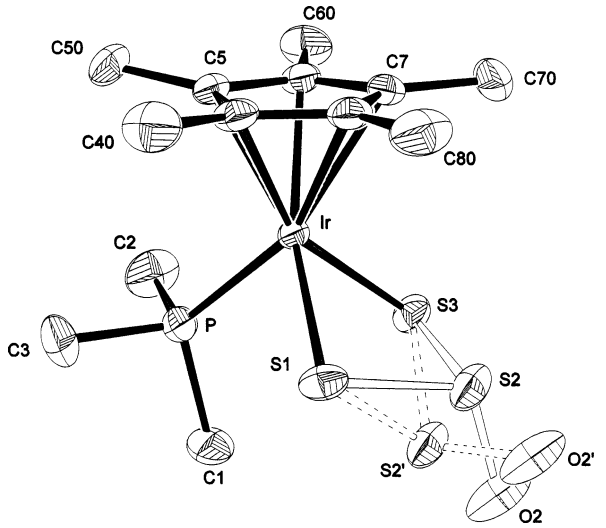

Figure 1. ORTEP view of **3**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Ir−P, 2.274(2); Ir−S(1) 2.364(1); Ir−S(3), 2.357(2); S(1)−S(2), 2.121(3); S(2)−S(3), 2.112(3); S(2)−O, 1.474(7); P−Ir−S(1), 87.6(1); P−Ir−S(3), 88.6(1); S(1)−Ir−S(3), 80.6(6); S(1)−S(2)−S(3), 92.3(1); Ir−S(1)−S(2), 87.2(1); Ir−S(3)−S(2), 87.6(1).

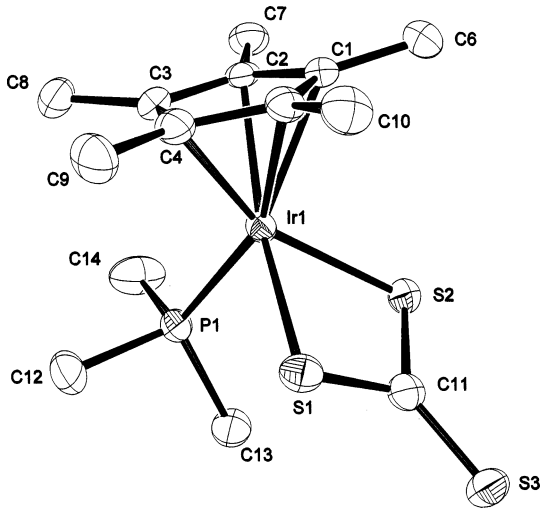

Figure 2. ORTEP view of **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Ir(1)−P(1), 2.279(1); Ir(1)−S(1), 2.371(1); Ir(1)−S(2), 2.376(1); S(1)−C(11), 1.730(5); S(2)−C(11), 1.747(5); S(3)−C(11), 1.655(5); S(1)−Ir(1)−S(2), 71.6(1); S(1)−C(11)−S(2), 106.0(3); Ir(1)−S(1)-C(11), 91.5(2); Ir(1)−S(2)−C(11), 90.9(2).

product of insertion of PhNSO into the S−H bond. With *cis*-$(Ph_3P)_2Pt(SH)_2$ cyclization with elimination of aniline occurred quickly to give the four-membered-ring structure $(Ph_3P)_2PtS_3O$ shown above. The infrared spectrum of **3** exhibits a strong band at 1085 cm^{-1} for ν(S═O), which is very close to that observed for the platinum complex (ν(S═O) 1065 cm^{-1}). Thus, while **1** and *cis*-$(Ph_3P)_2Pt(SH)_2$ react quite differently with SO_2, their reactions with PhNSO, a SO_2 analogue, are identical. Interestingly, neither **3** nor Cp*Ir$(PMe_3)S_4$, the product of **1** and SO_2, is converted back to **1** by H_2S at room temperature in benzene and chloroform, whereas $(PPh_3)_2Pt(S_3O)$ is readily converted back to *cis*-$(Ph_3P)_2Pt(SH)_2$. This difference in reactivity may explain why the latter is a Claus catalyst but **1** is not.

The structure of **3** is shown in Figure 1. Two superimposed conformers, endo (16%) and exo (84%), were observed, due to the nonplanarity of the four-membered $IrS_3(O)$ ring. Separate peaks due to these two conformers were not observed in the NMR spectrum, probably due to their rapid interconversion on the NMR time scale. The four-membered $IrS_3(O)$ ring is structurally very similar to that of its platinum analogue $(PPh_3)_2PtS_3O$.[4] The Ir−S bond lengths are similar to those of other iridium complexes: **1**,[6] Cp*Ir$(PMe_3)S_4$,[5] Cp*Ir$(PMe_3)S_6$,[8] and [Cp*Ir$(SH)]_2(SH)_2$.[9] The S═O bond length is similar to those in $(PPh_3)_2PtS_3O$, Cp_2MoS_4O,[10] and ferrocenylene trisulfane oxide.[11]

Reaction of Cp*Ir$(PMe_3)(SH)_2$ with CS_2. Treatment of **1** with a slight excess of CS_2 in benzene slowly (3 weeks at room temperature or 2 days at 40 °C) gave the trithiocarbonato complex **4**, presumably with loss of H_2S as in eq 2. No evidence

$$\underset{\mathbf{1}}{\text{Cp*Ir(PMe}_3\text{)(SH)}_2} + \text{CS}_2 \rightarrow \underset{\mathbf{4}}{\text{Cp*Ir(PMe}_3\text{)S}_2\text{CS}} + \text{H}_2\text{S} \quad (2)$$

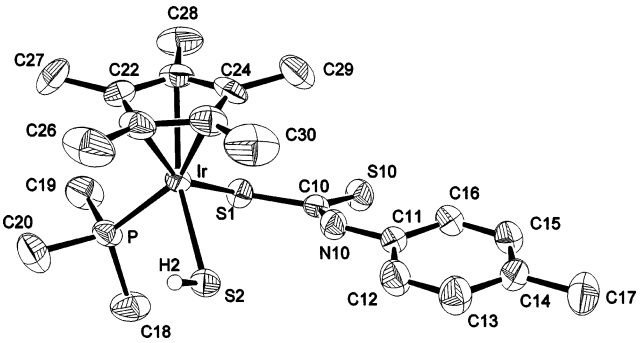

Figure 3. ORTEP view of **5**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity, except for H2. Selected bond distances (Å) and angles (deg) are as follows: Ir−P, 2.277(1); Ir−S(1), 2.369(1); Ir−S(2), 2.392(1); S(1)−C(10), 1.744(4); S(10)−C(10), 1.681(4); N(10)−C(10), 1.335(5); S(1)−Ir−S(2), 95.9(1); S(10)−C(10)−S(1), 115.9(2); N(10)−C(10)−S(1), 117.1(3); N(10)−C(10)−S(10), 127.0(3).

for any intermediate species was detected when the reaction was monitored in benzene-d_6 by ^1H and ^{31}P NMR spectroscopy. This reaction is also analogous to that of *cis*-$(Ph_3P)_2Pt(SH)_2$ with CS_2, which gave $(Ph_3P)_2Pt(S_2CS)$.[12] The structure of **4** is shown in Figure 2.

Unlike the case for **3**, the metallacycle in **4** is planar, as observed for $(PPh_3)_2Pt(CS_3)$,[12] $Cl_2Au(CS_3)$,[13] and $[Mo(CS_3)_4]^{3-}$.[14] The S1−Ir−S2 angle in **4** (71.63°) is smaller than the analogous angle in **3** (80.61°), while the opposite angle in **4** (S1−C11−S2 = 106.0°) is larger than the analogous angle in **3**.

Reaction of Cp*Ir$(PMe_3)(SH)_2$ with *p*-tolNCS. Treatment of **1** with 2 equiv of *p*-tolNCS in toluene at room temperature gave, after 16 h, Cp*Ir(PMe_3)(SH)(SC(S)NH-*p*-tol) (**5**), wherein *p*-tolNCS inserted into only one of the S−H bonds, as shown in eq 3 and Figure 3.

$$\underset{\mathbf{1}}{\text{Cp*Ir(PMe}_3\text{)(SH)}_2} + p\text{-tolNCS} \rightarrow \underset{\mathbf{5}}{\text{Cp*Ir(PMe}_3\text{)(SH)(SC(S)NH-}p\text{-tol)}} \quad (3)$$

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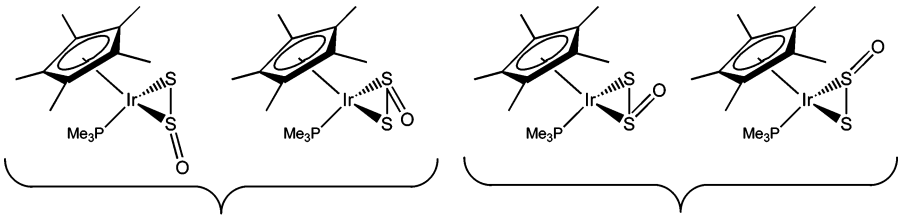
Chart 1



Other complexes such as $CpNi(PBu_3)(SH)$,[15] $[W(CO)_5SH]^-$,[16] and $CpRu(PPh_3)_2(SH)$[17] react with isothiocyanates to give the corresponding dithiocarbamates. Monodentate coordination is relatively rare, and to our knowledge, **5** is the first X-ray-characterized example of a monodentate dithiocarbamate ligand. It is interesting that the reaction stops with insertion into only one of the eligible S−H bonds, even in the presence of a large excess of *p*-tolNCS. Perhaps the increased steric hindrance in **5** prevents further reaction. There also appears to be an interaction between the proton on the nitrogen atom and S2 in **5**, which may reduce its reactivity with *p*-tolNCS.

Reactivity of Cp*Ir(PMe$_2$R)(H)(SH) with PhNSO. Treatment of complexes **2a**,**b**, where R = Me (**2a**), Ph (**2b**), with PhNSO in toluene at room temperature rapidly gave Cp*Ir(PMe$_2$R)S_2O (**6a**,**b**) as 1:1 mixtures of exo and endo isomers with respect to the relative arrangements of the Cp* group and the oxygen atom (eq 4).

$$\underset{\textbf{2a,b}}{Cp^*Ir(PMe_2R)(H)(SH)} + PhNSO \rightarrow \underset{\textbf{6a,b}}{Cp^*Ir(PMe_2R)S_2O} + PhNH_2 \quad (4)$$

There are two chiral centers in **6a**,**b**: (1) around the Ir atom and (2) around the S(O) group (Chart 1). Peaks due to the diastereomers of **6a** are observed in its ^{1}H and ^{31}P NMR spectra. Peaks for all four stereoisomers are observed in the ^{1}H NMR spectrum upon addition of 6 equiv of Pirkle's alcohol. After a few hours in a C_6D_6 solution, peaks due to one diastereomer of **6a** increased in intensity at the expense of the other; presumably via slow inversion about the S(O) group. This is assumed to be due to the conversion of the endo isomer into the less sterically hindered exo isomer. Similar behavior is observed for the isomers of **6b**. The diastereotopic methyl groups on **6b** permit all four diastereomers to be observed in the ^{1}H NMR spectrum.

The first step in the reaction could be insertion of PhNSO either into the S−H bond, as observed above and in the literature, or into the Ir−H bond (Scheme 2). No intermediates were detected when the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy, and it has not been possible to rule out either as the first step.

Three routes to MS_2O moieties have been reported: (1) use of an organic S_2O source,[18] (2) nucleophillic attack[19] of a metal−PhNSO complex with H_2S, and (3) oxidation of a S_2 ligand to S_2O, which has been applied to several systems.[20] The syntheses of **6a**,**b** from **2a**,**b** and PhNSO is an interesting example of a new route to MS_2O moieties.

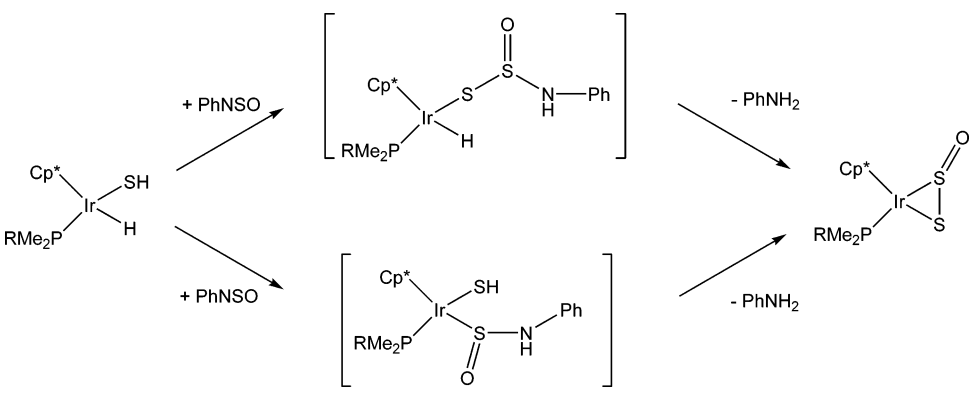
The crystal structure of **6b** is shown in Figure 4. The exo and endo isomers are superimposed, with the exo isomer being present at 64% versus 36% for the endo isomer. The Ir−S bond distances in the exo isomer are statistically equal (Ir−S1 = 2.382(6) Å, Ir−S2 = 2.344(6) Å), while they are quite different in the more hindered endo isomer (Ir−S10 = 2.410(12) Å, Ir−S20 = 2.264(11) Å). All these bond lengths are shorter than those in $[(dppe)_2Ir(S_2O_2)]^+$ [21] (Ir−S1 = 2.413 Å, Ir−S2 = 2.401 Å). The S−S bond distances do not appear to differ between the two geometries (S1−S2 = 2.087(6) Å, S10−S20 = 2.087(12) Å). These are slightly longer than those in $[(dppe)_2Ir(S_2O_2)]^+$ (2.041 Å), Cp*Mo(O)S_2O, (2.050 Å[20c]), and Cp*Mn(CO)$_2S_2O$ (2.013 Å[20e]). The S=O bond lengths for the two isomers are similar (S1−O1 = 1.162(9) Å, S10−O10 = 1.123(14) Å), but they are much shorter than those in other MS_2O complexes[19−21] or in other organic molecules.[22] For example, the S=O bond length in $[(dppe)_2Ir(S_2O_2)]^+$ is 1.213 Å.

Reaction of Cp*Ir(PMe$_3$)(H)(SH) with *p*-tolNCS. Treatment of **2a** with *p*-tolNCS in toluene at room temperature for 4 h gave Cp*Ir(PMe$_3$)(H)(SC(S)N(H)-*p*-tol (**7**), as shown in eq 5. The structure of **7** is very similar to that of **5** and is shown in Figure 5.

$$\underset{\textbf{2a}}{Cp^*Ir(PMe_3)(H)(SH)} + p\text{-tolNCS} \rightarrow \underset{\textbf{7}}{Cp^*Ir(PMe_3)(H)(SC(S)N(H)\text{-}p\text{-tol})} \quad (5)$$

When the reaction was monitored by ^{1}H NMR spectroscopy, the resonance due to the S−H proton gradually decreased in intensity, while a new doublet assigned to the Ir−H proton

Scheme 2



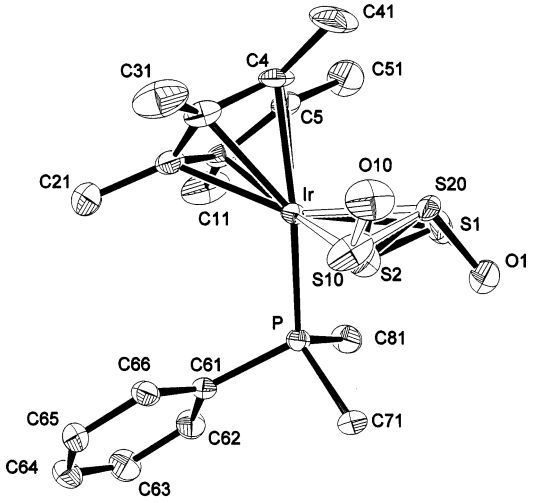


Figure 4. ORTEP view of **6b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg) of **6b-*exo*** are as follows: Ir−P, 2.273(1); Ir−S(1), 2.382(6); Ir−S(2), 2.344(6); S(1)−O(1), 1.162(9); S(1)−S(2), 2.087(6); S(2)−Ir−S(1), 52.4(2); S(2)−S(1)−Ir, 62.9(2); S(1)−S(2)−Ir, 64.7(2).

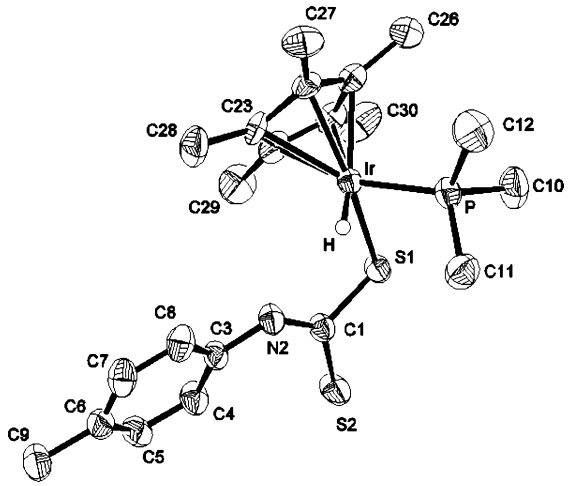


Figure 5. ORTEP view of **7**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity, except for the hydride H. Selected bond distances (Å) and angles (deg) are as follows: Ir−P, 2.251(2); Ir−H, 1.04(8); Ir−S(1), 2.355(2); Ir−C(22), 2.203(6); Ir−C(21), 2.258(7); C(1)−S(1), 1.747(7); C(1)−S(2), 1.683(7); C(1)−N(2), 1.336(9); P−Ir−S(1), 86.3(1); P−Ir−H, 81(4); S(1)-Ir−H, 62(4); N(2)−C(1)−S(2), 125.4(5); N(2)−C(1)−S(1), 116.4(5); S(2)−C(1)−S(1), 118.2(4).

resonance of **7** (δ −15.88 ppm, J_{PH} = 34.8 Hz) and a new peak assigned to the N−H proton resonance of **7** (δ 10.84 ppm) appeared. Thus, only the S−H function reacted with *p*-tolNCS, even in the presence of a large excess of the latter. No trace of a Ir−H insertion product was detected. Compound **7** is an analogue of Cp*Ir(PMe$_3$)(H)(SC(S)NHPh), which has been reported as the product of insertion of CS_2 into the Ir−N bond in Cp*Ir(PMe$_3$)(H)(NHPh).[23]

Experimental Section

All manipulations were performed under argon or nitrogen using standard Schlenk techniques. Solvents were distilled and degassed according to literature procedures. The compounds $IrCl_3 \cdot 3H_2O$, C_5Me_5H, and PMe_2Ph were purchased from Strem Chemical. The compounds PMe_3, PhNSO, and *p*-tolNCS were purchased from Aldrich, while SO_2, H_2S, and CS_2 were obtained from Matheson. All of the chemicals were used as received. Complexes **1** and **2** were prepared according to literature[6] methods and were used without further purification.

Caution! The preparation of **1** and **2a,b** involves the use of H_2S, which is very toxic. Extreme care must be exercised. Every effort must be made to ensure containment of the gas within a specially dedicated H_2S manifold[24] in a well-ventilated, properly functioning fume hood.

Nuclear magnetic resonance (NMR) spectra were recorded on Varian XL-200, XL-300, and XL-400 and JEOL CPF 270 spectrometers. IR spectra were recorded on a Bruker IFS 48 spectrometer. FAB mass spectra were recorded on a MS25RFA instrument, and electrospray mass spectra were recorded on a Thermoquest Finnigan LCQDUO. Elemental analyses were performed by the Laboratoire d'analyze élémentaire at the University of Montreal. X-ray structures were carried out by the Laboratoire de christallographie at the University of Montreal and at the X-ray laboratory of the University of Toronto. Crystal data and details of the structure refinement are given in Table 1.

Preparation of 3. Compound **1** (52 mg, 0.11 mmol) in toluene (2 mL) was treated with thionylaniline (14 μL, 0.122 mmol). The yellow solution turned red-orange after a few minutes, and crystals of **3** suitable for X-ray analysis formed after standing overnight at −20 °C. The ^{1}H NMR spectrum of the crude residue of a small sample of the reaction solution showed total conversion of the starting material after 1 h. The solvent was removed with a syringe, and crystals were dried under vacuum to give **3** (43 mg, 76%). ^{1}H NMR ($CDCl_3$): δ 1.71 (d, J_{PH} = 10.4 Hz, 9H), 1.87 (d, J_{PH} = 2.4 Hz, 15H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.0 (C_{MeCp}), 15.6 (d, J_{CP} = 43 Hz, C_{Me_3P}), 95.9 (C_{Cp}). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −32.03. IR (KBr): ν_{C-H} 2986, ν_{C-H} 2908, $\nu_{S=O}$ 1075 cm^{-1}. Mp: 154−156 °C. Mass spectrum: *m*/*e* 517 [M + H$^+$]. Anal. Calcd for $C_{13}H_{24}IrS_3OP \cdot 0.25C_7H_8$: C, 31.61; H, 4.78; S, 18.25. Found: C, 31.80; H, 4.71; S, 17.96.

Preparation of 4. Compound **1** (190 mg, 0.4 mmol) in benzene (20 mL) was treated with an excess (0.5 mL) of CS_2, and the solution was allowed to stand for 3 weeks at room temperature, whereupon orange crystals formed. These were collected by filtration to give **4** (162 mg, 77%). ^{1}H NMR (C_6D_6): δ 1.11 (d, J_{PH} = 10.4 Hz, 9H), 1.36 (d, J_{PH} = 2 Hz, 15H). ^{13}C{^{1}H} NMR (C_6D_6): δ 9.2 (C_{MeCp}), 14.6 (d, J_{CP} = 40 Hz, C_{MeP}), 94.0 (d, J_{CP} = 3.7 Hz, C_{Cp}), 249.7 (CS). ^{31}P{^{1}H} NMR (C_6D_6): δ −34.5. IR (C_6D_6): ν_{C-S} 1077, ν_{C-S} 897. Mass spectrum: *m*/*e* 511−513 [M

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Table 1. Crystallographic Data and Structure Refinement Details for 3−5, 6b, and 7

	3	4	5	6b	7
formula	$C_{13}H_{24}IrOPS_3$	$C_{14}H_{24}IrPS_3 + C_6H_6$	$C_{21}H_{33}IrNPS_3 + CH_2Cl_2$	$C_{18}H_{26}IrOPS_2$	$C_{21}H_{33}IrNPS_2$
fw	515.672	589.79	703.76	545.68	586.77
temp (K)	293(2)	150(1)	220(2)	220(2)	220(2)
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Cu Kα, 1.541 78	Cu Kα, 1.541 78	Cu Kα, 1.541 78
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	triclinic
space group	$P2_1/c$	$P2_1/n$	P-1	$Pbca$	P-1
a (Å)	12.5674(14)	12.4173(2)	8.8659(8)	15.9591(1)	8.2770(1)
b (Å)	8.5789(10)	13.3048(2)	12.3044(10)	15.3955(1)	10.0979(2)
c (Å)	16.8698(18)	14.1418(2)	13.2239(11)	16.1920(2)	14.5981(2)
α (deg)	90	90	79.312(5)	90	77.063(1)
β (deg)	99.724(11)	103.355 (7)	83.152(6)	90	80.045(1)
γ (deg)	90	90	81.035(6)	90	82.608(1)
V (Å^3)	1792.7(3)	2273.18(6)	1394.2(2)	3978.35(6)	1166.09(3)
Z	4	4	2	8	2
calcd density (Mg/m^3)	1.9106	1.723	1.676	1.822	1.671
μ (mm^{-1})	7.877	6.221	13.749	15.717	13.430
size (mm)	0.38 × 0.36 × 0.07	0.24 × 0.22 × 0.14	0.31 × 0.11 × 0.08	0.55 × 0.11 × 0.08	0.20 × 0.16 × 0.08
no. of rflns collected	13 598	18 493	16 762	22 749	13 992
no. of indep rflns (R_{int})	3527	5188	5311	3774	4434 (0.044)
GOF	1.125	1.067	1.069	1.087	1.095
R ($F^2 > 2\sigma(F^2)$)	0.0285	0.0272	0.0282	0.0305	0.0418
R_w (F^2)	0.0597	0.0566	0.0784	0.0821	0.1069

+ H$^+$]. Anal. Calcd for $C_{14}H_{24}IrS_3P$: C, 32.86; H, 4.73; S, 18.80. Found: C, 32.73; H, 4.77; S, 17.77.

Preparation of 5. Compound **1** (46 mg, 0.1 mmol) in toluene (1.0 mL) was treated with *p*-tolNCS (29 mg, 0.2 mmol), the resulting solution was left at room temperature for 16 h, and then the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2 and applied to SiO_2 chromatography. Elution with CH_2Cl_2/EtOH (95/5) gave a yellow band, which was evaporated to dryness to give **5** as a pale yellow solid (39 mg, 64%). ^{1}H NMR ($CDCl_3$): δ −1.78 (d, J_{PH} = 1.6 Hz, 1H), 1.60 (d, J_{PH} = 10.4 Hz, 9H), 1.74 (d, J_{PH} = 2.4 Hz, 15H), 2.30 (s, 3H), 7.10 (d, J_{PH} = 8.8 Hz, 2H), 7.73 (d, J_{PH} = 8.8 Hz, 2H), 10.95 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$: δ 9.0 (C_{MeCp}), 14.4 (d, J_{CP} = 42 Hz, C_{MeP}), 95.2 (C_{Cp}, d, J_{CP} = 2.3 Hz), 122.6 (C_{ar}), 129.2 (C_{ar}), 134.6 (C_{ar}), 138.5 (C_{ar}), 155.3 (C_{ar}); C_{CS} was not detected. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −37.7. IR (KBr): ν_{N-H} 3164, ν_{C-H} 2969, ν_{C-N} 1511 cm^{-1}, $\nu_{C=S}$ 956 cm^{-1}. Mp: 174−176 °C. Mass spectrum: *m*/*e* 435−437 ([M − S(CS)NHtol]$^+$, 100%), 540−542 ([M − Me_3P], 22%),640−642 ([M + Na], 12%). Anal. Calcd for $C_{21}H_{33}IrS_3NP\cdot0.4CH_2Cl_2$: C, 39.37; H, 5.22; N, 2.15; S, 14.73. Found: C, 39.53; H, 5.26; N, 2.16; S, 14.21.

Preparation of 6a. Compound **2a**, prepared from Cp*Ir(PMe_3)Cl_2 (100 mg, 0.2 mmol) and used without further purification, in toluene (10 mL) was treated with PhNSO (14 μL, 0.12 mmol), and the resulting solution was left standing for 30 min at room temperature. The solvent was removed under vacuum, and the residue was dissolved in CH_2Cl_2 and applied to a SiO_2 chromatography column. Elution with CH_2Cl_2/Et_3N (98/3) gave **6a** (35 mg, 34% based on the dichloride). Spectroscopic data for **6a-*exo*** are as follows. ^{1}H NMR (C_6D_6): δ 1.25 (d, J_{PH} = 10.8 Hz, 9H), 1.46 (d, J_{PH} = 1.6 Hz, 15H). ^{13}C{^{1}H} NMR (C_6D_6): δ 8.7 (d, C_{MeCp}, J_{PC} = 1 Hz), 15.7−16.5 (d, C_{MeP}, J_{PC} = 54 Hz), 93.0 (d, C_{Cp}, J_{PC} = 3.1 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −35.6. Spectroscopic data for **6a-*endo*** are as follows. ^{1}H NMR (C_6D_6): δ 0.77 (d, J_{PH} = 9.6 Hz, 9H), 1.69 (d, J_{PH} = 2 Hz, 15H). ^{13}C{^{1}H} NMR (C_6D_6): δ 8.7 (d, C_{MeCp}, J_{PC} = 1 Hz), 15.7−16.5 (d, C_{MeP}, J_{PC} = 54 Hz), 93.0 (d, C_{Cp}, J_{PC} = 3.1 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −40.4. Other data for **6a** are as follows. IR (KBr): ν_{C-H} 2970, ν_{S-O} 1070, ν_{S-O} 1024, ν_{C-N} 1511 cm^{-1}. Mp: 156−158 °C. Mass spectrum: *m*/*e* 449−451 ([M + H$^+$ − S], 12%), 481−483 ([M + H$^+$], 2%). Anal. Calcd for $C_{13}H_{24}IrS_2OP$: C, 32.28; H, 5.00; S, 13.26. Found: C, 32.33; H, 5.03; S, 13.36.

Preparation of 6b. As for **6a**, compound **2b** in toluene (8 mL), prepared from Cp*Ir(PMe_2Ph)Cl_2 (135 mg, 0.25 mmol) and used without further purification, was treated with PhNSO (17 μL, 0.15 mmol). Elution with CH_2Cl_2/Et_2O (8/2) gave **6b** (44 mg, 32% based on the dichloride). Spectroscopic data for **6b-*exo*** are as follows. ^{1}H NMR (C_6D_6): δ 1.40−1.42 (d, J_{PH} = 10.0 Hz, 3H), 1.48−1.51 (d, J_{PH} = 9.6 Hz, 3H), 1.71 (d, J_{PH} = 2 Hz, 15H), 7.35−7.40 (m, 3H), 7.50−7.55 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6): δ −24.9. Spectroscopic data for **6b-*endo*** are as follows. ^{1}H NMR (C_6D_6): δ 1.64−1.67 (d, J_{PH} = 11.2 Hz, 3H), 1.71−1.74 (d, J_{PH} = 11.6 Hz, 3H), 1.58 (d, J_{PH} = 1.6 Hz, 15H), 7.35−7.40 (m, 3H), 7.50−7.55 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6): δ −20.6. Spectroscopic data for **6b** are as follows. ^{13}C{^{1}H} NMR (C_6D_6): δ 9.0 and 9.2 (d, C_{MeCp}), 12.8, 12.8, 13.2, 13.6, 17.2, 17.6 (C_{MeP}), 94.2 and 95.9 (d, C_{Cp}), 128.3 and 128.4 (CH_{ar}), 130.5 and 130.7 (CH_{ar}). Mp: 140 °C dec. Mass spectrum: *m*/*e* 569.1−567.1 ([M + Na$^+$, 100%), 431.0−429.1 ([M + Na$^+$ − Me_2PhP], 20%). Anal. Calcd for $C_{18}H_{26}IrS_2OP$: C, 39.62; H, 4.80; S, 11.75. Found: C, 39.75; H, 5.15; S, 11.40. High-resolution mass spectrum: *m*/*e* calcd for $C_{18}H_{26}IrS_2OP$, 546.079 21; found, *m*/*e* 546.080 74.

Preparation of 7. Compound **2a**, prepared from Cp*Ir(PMe_3)Cl_2 (108 mg, 0.23 mmol) and used without further purification, in toluene (10 mL) was treated with *p*-tolNCS (68 mg, 0.46 mmol) in toluene (1 mL), and the resulting solution was allowed to stand for 2 h at room temperature. The solvent was removed under vacuum, and the residue was purified on a SiO_2 chromatography column. Elution with CH_2Cl_2/Et_2O (98/1.5) gave **7** (71 mg, 49%, based on the dichloride). ^{1}H NMR ($CDCl_3$): δ −15.80 (d, J_{PH} = 34.8 Hz, 1H), 1.60 (d, J_{PH} = 10.4 Hz, 9H), 1.97 (d, J_{PH} = 2 Hz, 15H), 2.32 (s, 3H), 7.14 (d, J_{PH} = 8.4 Hz, 2H), 7.71 (d, J_{PH} = 8.4 Hz, 2H), 10.84 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5 (C_{MeCp}), 19.1 (d, J_{CP} = 41 Hz, C_{MeP}), 94.5 (C_{Cp}, d, J_{CP} = 2.6 Hz), 121.4 (C_{ar}), 129.3 (C_{ar}), 134.4 (C_{ar}), 138.4 (C_{ar}); C_{CS} was not detected. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −37.7. IR (KBr): ν_{N-H} 3154, ν_{C-H} 2979, ν_{Ir-H} 2069 ν_{C-N} 1512, $\nu_{C=S}$ 957 cm^{-1}. Mp: 176−178 °C. Mass spectrun: *m*/*e* 610−608 ([M + Na$^+$], 100%). Anal. Calcd for $C_{21}H_{32}S_2NPIr\cdot0.25CH_2Cl_2$: C, 41.97; H, 5.55; N, 2.30; S, 10.55. Found: C, 42.25; H, 5.67; N, 2.26; S, 10.34.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **3**−**5**, **6b**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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