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Syntheses, Structures, and Reactivities of Mono- and Dinuclear Iridium Thiolato Complexes Containing Nitrosyl Ligands

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Reactions of the iridium(III) nitrosyl complex $[\mathrm{Ir(NO)Cl_2(PPh_3)_2}]$ (**1**) with hydrosulfide and arenethiolate anions afforded the square-pyramidal iridium(III) complex $[\mathrm{Ir(NO)(SH)_2(PPh_3)_2}]$ (**2**) with a bent nitrosyl ligand and a series of the square-planar iridium(I) complexes $[\mathrm{Ir(NO)(SAr)_2(PPh_3)}]$ (**3a**, Ar = $\mathrm{C_6H_2Me_3}$-2,4,6 (Mes); **3b**, Ar = $\mathrm{C_6H_3Me_2}$-2,6 (Xy); **3c**, Ar = $\mathrm{C_6H_2Pr^i_3}$-2,4,6) containing a linear nitrosyl ligand, respectively. Complex **1** also reacted with alkanethiolate anions or alkanethiols to give the thiolato-bridged diiridium complexes $[\mathrm{Ir(NO)(\mu\text{-}SPr^i)(SPr^i)(PPh_3)}]_2$ (**4**) and $[\mathrm{Ir(NO)(\mu\text{-}SBu^t)(PPh_3)}]_2$ (**5**). Complex **4** contains two square-pyramidal iridium(III) centers with a bent nitrosyl ligand, whereas **5** contains two tetrahedral iridium(0) centers with a linear nitrosyl ligand and has an Ir−Ir bond. Upon treatment with benzoyl chloride, **3a** and **3b** were converted into the (diaryl disulfide)- and thiolato-bridged dichlorodiiridium(III) complexes $[\{\overline{\mathrm{IrCl}(\mu\text{-}\mathrm{SC_6H}_n\mathrm{Me}_{4-n}\mathrm{CH_2})}(\mathrm{PPh_3})\}_2(\mu\text{-}\mathrm{ArSSAr})]$ (**6a**, Ar = Mes, $n = 2$; **6b**, Ar = Xy, $n = 3$) accompanied by a loss of the nitrosyl ligands and cleavage of a C−H bond in an ortho methyl group of the thiolato ligands. Similar treatment of **4** gave the dichlorodiiridium complex $[\mathrm{Ir(NO)(PPh_3)(\mu\text{-}SPr^i)_3IrCl_2(PPh_3)}]$ (**7**), which has an octahedral dichloroiridium(III) center and a distorted trigonal-bipyramidal Ir(I) atom with a linear nitrosyl ligand. The detailed structures of **3a**, **4**, **5**, **6a**, and **7** have been determined by X-ray crystallography.

Introduction

Transition metal nitrosyl complexes have been the subject of much attention.[1−5] An intriguing feature of the nitrosyl ligand is the ability to change its coordination mode from linear 3e donor to bent 1e donor, which tunes the formal oxidation state of the metals and provides a vacant site for incoming ligands.[6,7] Such latent vacancy is expected to play a key role in the stoichiometric and catalytic reactions promoted by nitrosyl complexes.[8,9]

We have continuously been interested in the preparation and reactivities of dinuclear noble metal thiolato complexes containing Cp* (Cp* = η^5-$\mathrm{C_5Me_5}$) ligands such as $[\mathrm{Cp^*RuCl(\mu\text{-}SPr^i)_2Ru(H_2O)Cp^*}][\mathrm{OTf}]$ and $[\mathrm{Cp^*Ir(\mu\text{-}H)(\mu\text{-}SPr^i)_2IrCp^*}][\mathrm{OTf}]$ (OTf = $\mathrm{OSO_2CF_3}$).[10−15] Notably, various unique transformations of substrates such as alkynes take place on these dinuclear centers supported by bridging thiolato ligands.[16−18] To explore further reactivities on the thiolato-bridged multimetallic centers, we have recently extended our investigation to the ruthenium thiolato complexes containing indenyl[19] and hydrotris(pyrazolyl)borato[20] ligands in place of Cp* ligands. In this context, nitric oxide (NO) seems to be an attractive candidate for ancillary ligands owing to its linear−bent conversion.

Another aspect of the chemistry of the nitrosyl−thiolato complexes is their possible relevance to the physiological role of NO exemplified by the regulation of enzyme activity in nitrile hydratase, a metalloenzyme containing an Fe−thiolato bond.[21,22] Thus, the chemistry of nitrosyl−thiolato complexes has mainly

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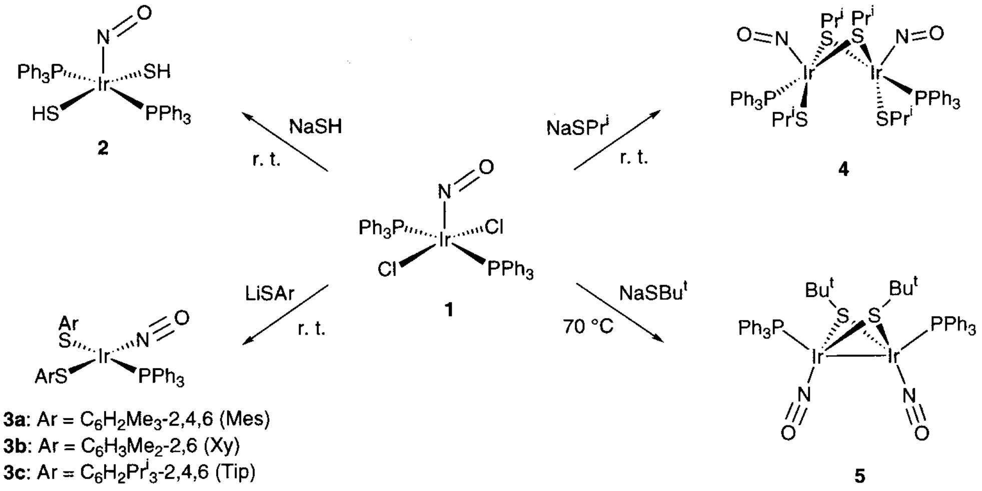
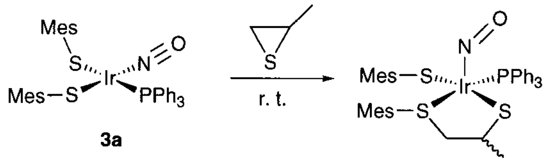
Scheme 1



3a: Ar = $C_6H_2Me_3$-2,4,6 (Mes)
3b: Ar = $C_6H_3Me_2$-2,6 (Xy)
3c: Ar = $C_6H_2Pr^i_3$-2,4,6 (Tip)

been focused on biologically important iron and its congener ruthenium,[3,23−25] and the corresponding chemistry of iridium remains undeveloped. With such a consideration in mind, we embarked on a study of the syntheses and reactivities of iridium thiolato complexes containing nitrosyl ligands. Our initial success was the isolation of the iridium arenethiolato complex [Ir(NO)(SMes)$_2$(PPh$_3$)] (**3a**; Mes = $C_6H_2Me_3$-2,4,6) from [Ir(NO)Cl$_2$(PPh$_3$)$_2$] (**1**).[26] Upon treatment with propylene sulfide, **3a** is further converted into the (mesitylthio)propanethiolato complex [Ir(NO)(SMes)(SCHMeCH$_2$SMes)(PPh$_3$)] accompanied by the transformation of the linear nitrosyl ligand in **3a** to a bent form to accommodate the incoming sulfur atom in the propylene sulfide (eq 1).[26] Now we have extended our investigation to alkanethiolato− and hydrosulfido−nitrosyl complexes of iridium and succeeded in the isolation of mono- and dinuclear nitrosyl−thiolato complexes with diverse structures and oxidation states of the metals depending upon the substituents of the thiolato ligands. In this paper we describe the details of preparation and the structures of these nitrosyl−thiolato complexes as well as their reactions with benzoyl chloride.



(1)

Results and Discussion

Preparation of Mononuclear Hydrosulfido−Nitrosyl Complex 2. Hydrosulfido complexes may be regarded as the smallest constituent of thiolato complexes. When **1** was allowed to react with anhydrous sodium hydrosulfide, the mononuclear bis(hydrosulfido)iridium(III) complex [Ir(NO)(SH)$_2$(PPh$_3$)$_2$] (**2**) was obtained in good yield (Scheme 1). Complex **2** has already been prepared through a different synthetic method.[27] In agreement with the formulation, the IR spectrum of **2** displays a weak band at 2544 cm^{-1} characteristic of ν(SH) as well as the strong band ascribed to the stretching of the bent nitrosyl ligand at 1518 cm^{-1}. The ^{1}H NMR spectrum in CDCl$_3$ exhibits the resonance for the hydrosulfido protons at −1.05 ppm as a triplet because of the coupling with the two phosphorus nuclei bound to the iridium center.

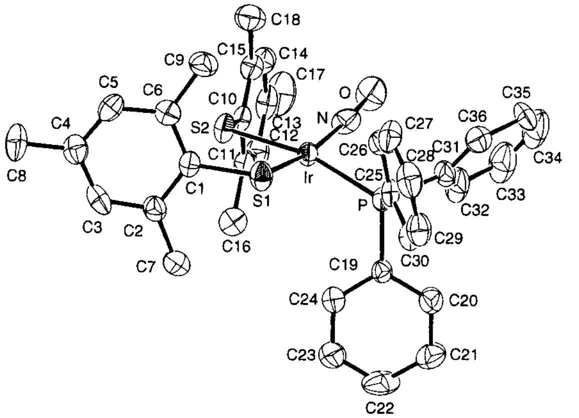


Figure 1. Molecular structure of **3a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **3a**

Ir−S(1)	2.286(3)	Ir−P	2.342(2)
Ir−S(2)	2.358(3)	N−O	1.144(9)
Ir−N	1.759(9)		
Ir−N−O	169.3(9)	N−Ir−P	95.3(3)
S(1)−Ir−S(2)	89.38(9)	P−Ir−S(1)	85.85(9)
S(2)−Ir−N	92.4(3)		

Preparation and Structure of Mononuclear Arenethiolato−Nitrosyl Complexes 3. In contrast to the simple ligand substitution by hydrosulfide anion, the square-planar iridium(I) complexes [Ir(NO)(SAr)$_2$(PPh$_3$)] (**3a**, Ar = Mes; **3b**, Ar = $C_6H_3Me_2$-2,6 (Xy); **3c**, Ar = $C_6H_2Pr^i_3$-2,4,6 (Tip)) were obtained with concurrent liberation of one of the PPh$_3$ ligands in **1** when **1** was treated with sterically hindered arenethiolate anions (Scheme 1). The IR spectra of **3** exhibit the absorption assignable to ν(NO) at 1802−1825 cm^{-1}, suggesting that the nitrosyl ligand has turned linear in **3**. Furthermore, an X-ray analysis of **3a** confirmed the square-planar structure of **3**; the molecular structure of **3a** is depicted in Figure 1, whereas selected bond distances and angles are listed in Table 1. The iridium(I) center in **3a** is bound to a linear nitrosyl ligand with

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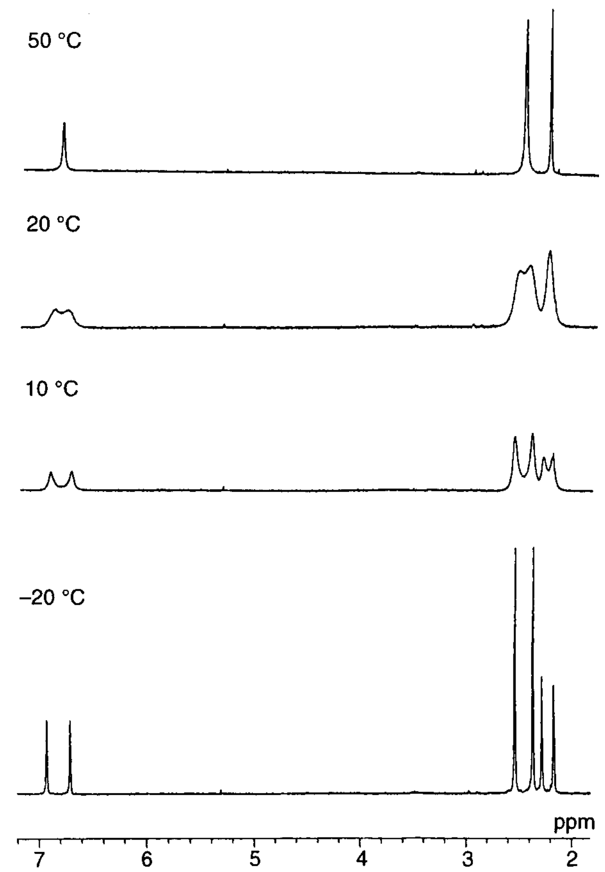
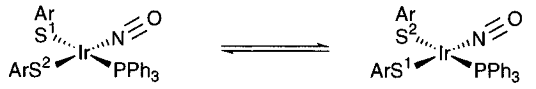


Figure 2. Variable-temperature 270 MHz ^{1}H NMR spectra of **3a**.

an Ir−N−O angle of 169.3(9)°. The mesityl groups in the mutually cis-oriented thiolato ligands are located to avoid steric congestion with the PPh$_3$ ligand. The Ir−S(1) distance trans to the nitrosyl ligand (2.286(3) Å) is shorter than the Ir−S(2) distance (2.358(3) Å), indicating a lower trans influence of the nitrosyl ligand.

Variable-temperature ^{1}H NMR measurements demonstrated the fluxional behavior of the arenethiolato ligands of **3a** and **3b** in solution. For example, the ^{1}H NMR spectrum of **3a** exhibits only broad signals at room temperature (Figure 2). These peaks are averaged at 50 °C, whereas the resonances for two mesityl groups are well resolved at the low-temperature limit (−20 °C) in agreement with the solid state structure of **3a**. These observations suggest the presence of the exchange process of the two arenethiolato ligands as shown in eq 2. The



(2)

value of the free enthalpy of activation $\Delta G^{\ddagger}$, estimated from the separation of the two resonances for the *p*-methyl protons at −55 °C and coalescence temperature of these resonances, is 65 kJ/mol (23 °C). Related isomerization of square-planar complexes has been reviewed.[28] On the other hand, the resonances for the two bulkier arenethiolato ligands in **3c** appear inequivalent at room temperature and start to be broadened at a more elevated temperature (40 °C).

The presence of ortho substituents in arenethiolato ligands seems essential to the successful isolation of **3** because we could not obtain any characterizable products from the reactions of arenethiolate anions without ortho substituents, e.g., benzenethiolate anion.

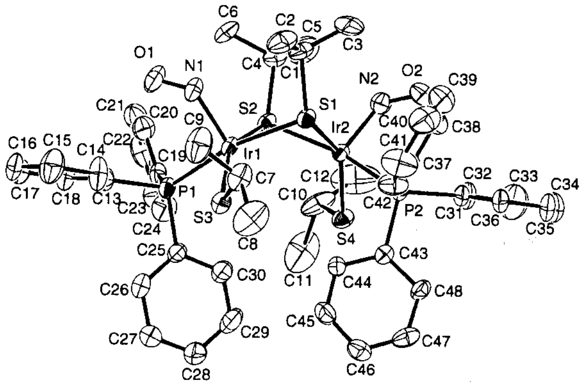


Figure 3. Molecular structure of **4**.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **4**

Ir(1)−Ir(2)	3.221(1)	Ir(1)−P(1)	2.307(3)
Ir(1)−S(1)	2.433(3)	Ir(2)−P(2)	2.304(3)
Ir(1)−S(2)	2.389(3)	Ir(1)−N(1)	1.914(9)
Ir(1)−S(3)	2.328(3)	Ir(2)−N(2)	1.86(1)
Ir(2)−S(1)	2.386(3)	O(1)−N(1)	1.17(1)
Ir(2)−S(2)	2.430(3)	O(2)−N(2)	1.20(1)
Ir(2)−S(4)	2.328(3)		
Ir(1)−S(1)−Ir(2)	83.88(8)	Ir(1)−N(1)−O(1)	127.0(8)
Ir(1)−S(2)−Ir(2)	83.87(8)	Ir(2)−N(2)−O(2)	127.3(9)

Preparation and Structure of 2-Propanethiolato-Bridged Diiridium Nitrosyl Complex 4. We next examined the reactions of **1** with alkanethiolate anions. Like the reaction with arenethiolate anions, treatment of **1** with NaSPr^i at room temperature resulted in a loss of one of the PPh$_3$ ligands of **1**. Isolated from the reaction mixture was, however, the thiolato-bridged diiridium(III) complex [Ir(NO)(μ-SPr^i)(SPr^i)(PPh$_3$)]$_2$ (**4**; Scheme 1). Complex **4** can also be obtained by the reaction of **1** with Pr^{i}SH in the presence of triethylamine in better yield. The dinuclear structure of **4** has unambiguously been determined by X-ray crystallography (Figure 3); selected interatomic distances and angles are listed in Table 2. The molecule has an idealized C_2 axis bisecting the Ir−Ir vector. Each iridium center has a square-pyramidal environment with sharing an edge in the basal plane. The nitrosyl ligand at the apical position is bent toward the PPh$_3$ ligand (Ir−N−O: 127° (mean)) as in the parent complex **1**. It is to be noted that only a few polynuclear complexes with bent nitrosyl ligands have been reported so far.[29,30] The Ir(III)−Ir(III) distance of 3.221(1) Å suggests the absence of a bonding interaction between these metal atoms. The Ir$_2$S$_2$ four-membered ring is puckered with a dihedral angle of 127.4° along with the Ir−Ir vector. The two Pr^i groups in the bridging thiolato ligands lie in syn-axial positions with respect to the Ir$_2$S$_2$ face.

The ^{1}H NMR spectrum of **4** shows the presence of two kinds of SPr^i groups, suggesting that the dinuclear structure is preserved even in the solution. The resonances for two of the four kinds of diastereotopic methyl groups in SPr^i ligands overlap accidentally with each other. The syn−anti isomerism of the bridging thiolato ligands in the solution is not observed at room temperature. The IR spectrum of **4** exhibits a ν(NO) band at 1538 cm^{-1}, which is consistent with the bent nature of the nitrosyl ligands.

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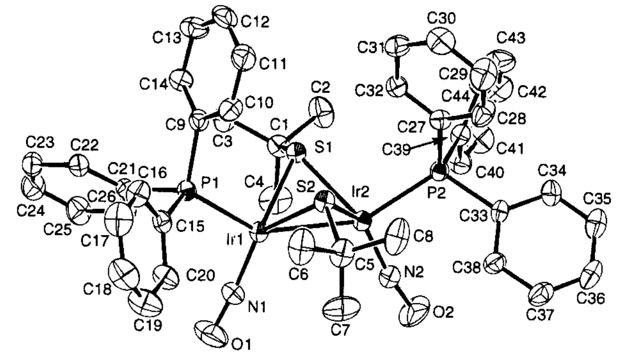

Figure 4. Molecular structure of $\mathbf{5}\cdot\mathrm{CH_2Cl_2}$. Solvating $\mathrm{CH_2Cl_2}$ is omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $\mathbf{5}\cdot\mathrm{CH_2Cl_2}$

Ir(1)−Ir(2)	2.6653(6)	Ir(1)−P(1)	2.305(2)
Ir(1)−S(1)	2.398(2)	Ir(2)−N(2)	1.738(8)
Ir(1)−S(2)	2.383(2)	Ir(2)−P(2)	2.301(2)
Ir(2)−S(1)	2.414(2)	N(1)−O(1)	1.194(10)
Ir(2)−S(2)	2.385(2)	N(2)−O(2)	1.198(9)
Ir(1)−N(1)	1.739(8)		
Ir(1)−S(1)−Ir(2)	67.27(6)	Ir(1)−N(1)−O(1)	174.7(8)
Ir(1)−S(2)−Ir(2)	67.97(6)	Ir(2)-N(2)−O(2)	172.1(8)

Preparation and Structure of *tert*-Butanethiolato-Bridged Diiridium Nitrosyl Complex 5. Our attempts to prepare the *tert*-butanethiolato complex corresponding to **4** have failed. However, **1** reacted with *tert*-butanethiolate anion under more forcing conditions to afford the thiolato-bridged diiridium(0) complex $[\mathrm{Ir(NO)}(\mu\text{-SBu}^t)(\mathrm{PPh_3})]_2$ (**5**) in low yield (Scheme 1). Concurrently a small amount of the iridium(−I) complex $[\mathrm{Ir(NO)(PPh_3)_3}]$[31] was also produced. The ^{1}H NMR spectrum of **5** indicates the presence of only one $\mathrm{SBu^t}$ group per $\mathrm{PPh_3}$ ligand unlike the 2-propanethiolato complex **4**. The ν(NO) bands observed at 1646 and 1676 $\mathrm{cm^{-1}}$ in the IR spectrum of **5** are consistent with the linear nitrosyl ligands bound to the low-valent Ir(0) centers.

The molecular structure of **5** determined by an X-ray analysis is depicted in Figure 4, and selected bond distances and angles are listed in Table 3. The molecule has an approximate C_{2v} symmetry with a 2-fold axis bisecting the Ir−Ir vector. The short Ir−Ir distance (2.6653(6) Å) and the small Ir−S−Ir angles (67.6° (mean)) as well as the diamagnetic nature of **5** suggest the presence of an Ir−Ir single bond. If this Ir−Ir bond is disregarded, each iridium(0) center has a distorted tetrahedral geometry with a linear nitrosyl ligand (Ir−N−O: 173° (mean)); these nitrosyl ligands lie in mutually cis positions with respect to the $\mathrm{Ir_2S_2}$ face. The $\mathrm{Ir_2S_2}$ face is folded with a dihedral angle of 93.7° along with the Ir−Ir bond. Related core structures are observed in some phosphido-bridged dinuclear complexes such as $[\mathrm{Ir}(\mu\text{-PPh}_2)(\mathrm{CO})(\mathrm{PPh_3})]_2$[32] and $[\mathrm{Ru(NO)}(\mu\text{-PPh}_2)(\mathrm{PMePh_2})]_2$.[33] However, these complexes have a metal−metal double bond, and the carbonyl or nitrosyl ligands are mutually trans-oriented with respect to the planar $\mathrm{M_2P_2}$ four-membered ring.

In contrast to the formation of 2-propanethiolato diiridium(III) complex **4**, reduction of iridium centers by butanethiolate anion occurred in the present reaction. Indeed, formation of $\mathrm{Bu^tSSBu^t}$ was confirmed by the ^{1}H NMR spectrum of the reaction mixture. We have already encountered similar dependence of the oxidation state of the product upon the substituent of the thiolato ligands. Thus, the diruthenium(III) complex $[\mathrm{Cp^*Ru}(\mu\text{-Cl})\mathrm{Cl}]_2$ reacts with $\mathrm{NaSBu^t}$ to afford the thiolato-bridged diruthenium(II) complex $[\mathrm{Cp^*Ru}(\mu\text{-SBu}^t)]_2$, whereas the corresponding reaction with $\mathrm{NaSPr^i}$ gives the paramagnetic Ru(II)/Ru(III) complex $[\mathrm{Cp^*_2Ru_2}(\mu\text{-SPr}^i)_3]$.[34,35] Such a difference of the products is probably ascribed to the electron-donating nature and bulkiness of the *tert*-butyl group. It may be also worth mentioning that the reaction of **4** with an excess of $\mathrm{Bu^tSH}$ did not proceed even at 60 °C. Attempts to isolate EtS− or $\mathrm{PhCH_2S}$− alkanethiolato complexes corresponding to **4** and **5** have also failed.

As summarized in Scheme 1, we have thus obtained nitrosyl−thiolato iridium complexes with a variety of structures and formal oxidation states of iridium centers from the reactions of **1** with thiolato anions or thiols. In the reaction with hydrosulfide anion, simple ligand substitution takes place to give the mononuclear bis(hydrosulfido)iridium(III) complex **2**, whereas employment of thiolato ligands causes a loss of one of the $\mathrm{PPh_3}$ ligands in **1**. Structural dependence of the products upon the substituents of the thiolato ligands may be explained as follows. In alkanethiolato complexes, the vacant site generated by the dissociation of the $\mathrm{PPh_3}$ ligand is occupied by the bridging thiolato ligand to form the dinuclear complexes **4** and **5**. In the *tert*-butanethiolato complex **5**, the presence of the bulkier and more electron-donating *tert*-butyl group leads to the reductive elimination of $\mathrm{Bu^tSSBu^t}$, which results in the formation of the diiridium(0) complex **5**. By contrast, arenethiolato ligands with bulky ortho substituents no longer allow the dinuclear structures and cause the formation of mononuclear complexes **3**. In the resultant thiolato complexes, the nitrosyl ligands behave as a linear 3e donor or a bent 1e donor to complete the 16e square-pyramidal (in **2** and **4**), 16e square-planar (in **3**), or 18e tetrahedral (in **5**) iridium centers.

Reaction of Diiridium(0) Complex 5 with Iodine. We have already demonstrated that the oxidative addition of $\mathrm{H_2}$ and alkyl halides to the coordinatively unsaturated diruthenium(II) center in $[\mathrm{Cp^*Ru}(\mu\text{-SPr}^i)]_2$ affords the diruthenium(III) complexes $[\mathrm{Cp^*RuH}(\mu\text{-SPr}^i)_2\mathrm{RuHCp^*}]$ and $[\mathrm{Cp^*RuR}(\mu\text{-SPr}^i)_2\mathrm{RuXCp^*}]$ (R = $\mathrm{PhCH_2}$ or $\mathrm{PhCH_2CH_2}$, X = Br; R = Me or Et, X = I).[34] Although each Ir atom in **5** has an 18e configuration and is coordinatively saturated, the linear−bent isomerization of the nitrosyl ligands might lead to the generation of coordinatively unsaturated 16e iridium(II) centers. Oxidative addition by $\mathrm{H_2}$,[36,37] halogens,[38−40] and dihalomethanes[41] to the related thiolato-bridged 16e iridium(I) centers in $[\mathrm{Ir}(\mu\text{-SR})\mathrm{L_2}]_2$ (R = $\mathrm{Bu^t}$, Ph; L = CO, $\mathrm{PR'_3}$, $^1/_2\mathrm{C_8H_{12}}$) is also well-documented. In order to compare the reactivity of **5** with those of the related thiolato-bridged complexes, we have inspected the reaction of **5** with iodine. No reaction occurred when **5** and an equimolar amount of iodine were stirred at room temperature. However, treatment of **5** with 2 equiv of iodine at 55 °C for 2 days afforded the

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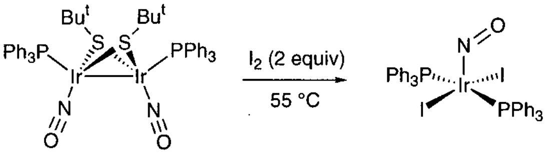
mononuclear diiodo complex [Ir(NO)I_2(PPh_3)$_2$] in 17% yield (eq 3). The fragmentation of the thiolato-bridged diiridium core

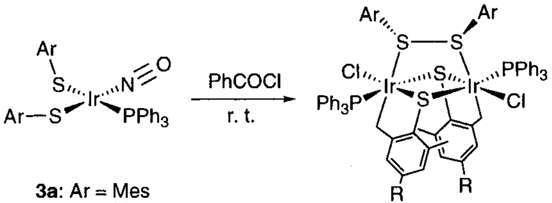


5

(3)

in the nitrosyl complex **5** sharply contrasts with the dinuclear oxidative addition of iodine across the diiridium centers with CO, phosphines, and olefinic coligands.[38−40] It is to be noted that the oxo-bridged complex [{Ir(NO)(PPh_3)}$_2$(μ-O)] containing 16e iridium(0) centers reacts with $HgCl_2$ to afford the dichlororodiiridium(I) complex [{Ir(NO)Cl(PPh_3)}$_2$(μ-O)].[42,43] The oxidative addition of Pr^{i}SH to the diiridium center in **5**, which may lead to the formation of **4**, was also attempted; however, no reaction was observed at room temperature.

Reaction of 3 with Benzoyl Chloride To Give the (Diaryl disulfide)-Bridged Diiridium Complex 6. Acyl chlorides have been recognized as useful reagents for replacement of thiolato ligands by chloro ligands.[44,45] In order to introduce synthetically versatile chloro ligands into the nitrosyl complexes obtained in the present study, we have investigated the reactions of the nitrosyl−thiolato complexes with benzoyl chloride. When the mononuclear bis(arenethiolato)iridium complexes **3a** and **3b** were allowed to react with an equimolar amount of benzoyl chloride, the (diaryl disulfide)- and thiolato-bridged dichlorodiiridium(III) complexes [{IrCl(μ-$SC_6H_nMe_{4-n}CH_2$)(PPh_3)}$_2$(μ-ArSSAr)] (**6a**, Ar = Mes, n = 2; **6b**, Ar = Xy, n = 3) were obtained in low yield (eq 4). On the other hand, isolation of



(4)

3a: Ar = Mes
3b: Ar = Xy

6a: Ar = Mes, R = Me
6b: Ar = Xy, R = H

the corresponding diaryl disulfide complex from the more sterically hindered thiolato complex **3c** was unsuccessful. The molecular structure of **6a** determined by X-ray analysis is shown in Figure 5, and selected interatomic distances and angles are listed in Table 4. The molecule has an approximate C_2 axis bisecting the Ir(1)−Ir(2) and S(3)−S(4) vectors. In the two bridging thiolato ligands a C−H bond in an ortho methyl group is cleaved and this carbon atom is bound to the Ir atom to form a thiairidaindan skeleton. The Ir−S(thiolato) distances in this thiairidaindan ring (2.319 Å (mean)) are considerably shorter than those out of this ring (2.443 Å (mean)). A similar cyclometalated structure is observed in [Bu$^n_4$N][{Ru(NO)(μ-$SC_6HMe_3CH_2$)(SC_6HMe_4)}$_2$(μ-SC_6HMe_4)].[23] In addition, a dimesityl disulfide ligand formed by coupling of the mesitylenethiolato ligands in **3a** bridges the two Ir atoms and completes the octahedral environment of the iridium(III) centers in **6a**. The dimesityl disulfide ligand is twisted with a C(19)−S(3)−S(4)−C(28) dihedral angle of 76.1(5)°. The S(3)−S(4) distance of 2.109(3) Å is comparable to those found in μ-dialkyl disulfide complexes reported so far (2.04(2)−2.161(7) Å).[46−49] The long Ir−Ir distance (3.524(1) Å) precludes the presence of a metal−metal bond.

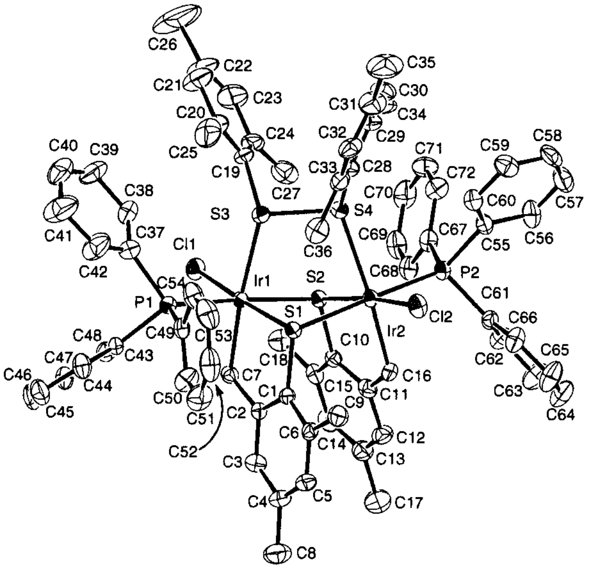


Figure 5. Molecular structure of **6a**.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for **6a**

Ir(1)−Ir(2)	3.524(1)	Ir(2)−Cl(2)	2.394(2)
Ir(1)−Cl(1)	2.412(2)	Ir(2)−S(1)	2.459(2)
Ir(1)−S(1)	2.322(2)	Ir(2)−S(2)	2.316(2)
Ir(1)−S(2)	2.427(2)	Ir(2)−S(4)	2.498(2)
Ir(1)−S(3)	2.484(2)	Ir(2)−P(2)	2.318(2)
Ir(1)−P(1)	2.319(2)	Ir(2)−C(16)	2.094(9)
Ir(1)−C(7)	2.097(9)	S(3)−S(4)	2.109(3)
S(3)−Ir(1)−C(7)	172.1(2)	S(4)−Ir(2)−C(16)	171.2(2)

The ^{1}H NMR spectrum of **6a** exhibits five resonances for methyl protons with the same intensity. The inequivalence of the ortho methyl groups in the dimesityl disulfide ligand suggests that the rotation of the S−C bonds in this ligand is inhibited even in the solution presumably because of the bulkiness of the mesityl groups. The chemically inequivalent methylene protons in the thiairidaindan skeleton give rise to two signals coupled with each other with a geminal coupling constant of 15.1 Hz; one of these signals is further split by the phosphorus nucleus attached to the Ir atom. The ν(NO) band is no longer observed in the IR spectrum of **6a**. These spectroscopic characteristics of **6a** are common to those of the corresponding xylyl complex **6b**.

Formal replacement of the nitrosyl ligands by chloro ligands and C−H bond cleavage in a methyl group of the thiolato ligands take place in the present reaction. However, attempts to clarify the fate of the nitrosyl ligands and hydrogen atoms have failed: neither NO nor H_2 gas has been detected by a GLC

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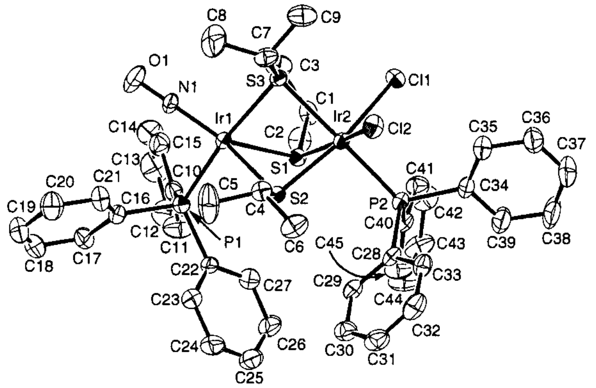
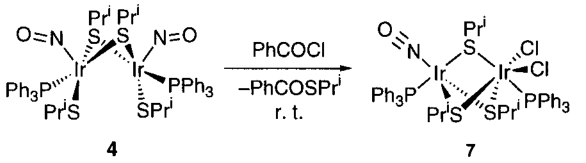


Figure 6. Molecular structure of $7 \cdot CH_2Cl_2 \cdot MeOH$. Solvating CH_2Cl_2 and MeOH are omitted for clarity.

analysis, and a GC−MS analysis of the reaction mixture could not confirm the formation of any products containing an NO moiety.

In addition, the bridging diaryl disulfide ligand is generated in this reaction. Oxidative coupling of the thiolato ligands on metal centers to form a bridging dialkyl disulfide or diaryl disulfide ligand has some precedent.[49−51] For example, the iridium(III) thiolato complex [Ir(aet)$_3$] (aet = $SCH_2CH_2NH_2$) is oxidized with nitric acid to give the disulfide-bridged complex $[\{Ir(aet)_2\}_2(\mu\text{-}NH_2CH_2CH_2SSCH_2CH_2NH_2)]^{2+}$.[49]

Reaction of 4 with Benzoyl Chloride To Give the Dichlorodiiridium Complex 7 with Three Bridging Thiolato Ligands. When the 2-propanethiolato-bridged diiridium complex **4** was allowed to react with an excess of benzoyl chloride at room temperature, the dichlorodiiridium complex [Ir(NO)(PPh$_3$)(μ-SPr^i)$_3$IrCl$_2$(PPh$_3$)] (**7**) with three bridging thiolato ligands was obtained as shown in eq 5. As in the reactions of the arenethiolato complexes **3a** and **3b** (eq 4), one of the two nitrosyl ligands in **4** has been replaced by a chloro ligand; furthermore, one of the four thiolato ligands in **4** has also been substituted by a chloro ligand. Indeed, concurrent formation of PhCOSPr^i has been confirmed by a GC−MS analysis of the reaction mixture, whereas the fate of the lost nitrosyl ligand again remains obscure.



(5)

An X-ray analysis has been carried out to clarify the detailed structure of **7** (Figure 6). The two Ir atoms bridged by three thiolato ligands have very different coordination geometries. The geometry around the Ir(1) atom is distorted trigonal bipyramidal with the P(1) and S(3) atoms in two apical positions; the P(1)−Ir(1)−S(3) angle is 169.02(6)°, and the Ir(1) atom lies apart from the least-squares plane containing the S(1), S(2), N(1), and O(1) atoms by only 0.11 Å, although the S(1)−Ir(1)−S(2) angle is severely acute (71.24(5)°). By contrast, the Ir(2) atom has an octahedral environment. Both iridium centers have an 18e configuration; however, the former iridium center with a linear nitrosyl ligand is formally iridium(I) and the latter is iridium(III). The Ir−Ir distance of 3.273(1) Å suggests the absence of an Ir−Ir bonding interaction. Other bond distances are unexceptional as shown in Table 5. The Ir(1), Ir(2), S(3), P(1), P(2), N(1), and O(1) atoms lie on an approximate mirror plane of the $Ir_2S_3P_2$(NO) core, although the Pr^i group attached to the S(3) atom breaks the pseudo-C_s symmetry in **7**. As a consequence of the lowered symmetry, three methine and six methyl resonances for the SPr^i groups are observed in the ^{1}H NMR spectrum of **7**. The ν(NO) band for the linear nitrosyl ligand in **7** appears at 1725 cm^{-1} in the IR spectrum.

Table 5. Selected Interatomic Distances (Å) and Angles (deg) for $7 \cdot CH_2Cl_2 \cdot MeOH$

Ir(1)−Ir(2)	3.273(1)	Ir(1)−N(1)	1.757(6)
Ir(1)−S(1)	2.451(2)	Ir(1)−P(1)	2.342(2)
Ir(1)−S(2)	2.440(2)	Ir(2)−Cl(1)	2.399(2)
Ir(1)−S(3)	2.390(2)	Ir(2)−Cl(2)	2.388(2)
Ir(2)−S(1)	2.347(2)	Ir(2)−P(2)	2.306(2)
Ir(2)−S(2)	2.360(2)	N(1)−O(1)	1.170(8)
Ir(2)−S(3)	2.417(2)		
Ir(1)−N(1)−O(1)	179.5(6)	S(3)−Ir(1)−P(1)	169.02(6)
S(1)−Ir(1)−S(2)	71.24(5)	S(3)−Ir(2)−P(2)	174.78(6)

Thus we have demonstrated that the nitrosyl−thiolato complexes **3a**, **3b**, and **4** reacted with benzoyl chloride to afford the dichlorodiiridium complexes **6a**, **6b**, and **7**, respectively. Interestingly, these reactions involve formal replacement of nitrosyl ligands by chloro ligands. This is in marked contrast with the reactions of thiolato complexes with acyl chlorides reported so far,[44,45] which result in the liberation of thioester. On the other hand, no reaction occurred when *tert*-butanethiolato complex **5** was treated with benzoyl chloride even under more forcing conditions (50 °C, 2 days). The corresponding reaction of the hydrosulfido complex **2** at 60 °C for 2 days gave a complex mixture containing the chloro complex **1**.

Experimental Section

General Consideration. All manipulations were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. Solvents were dried by common procedures and degassed before use. Benzoyl chloride and triethylamine were distilled and degassed before use. Complex **1**,[52] 2,4,6-trimethylbenzenethiol,[53] and 2,4,6-triisopropylbenzenethiol[53] were prepared according to the literature. Sodium hydrosulfide (Strem) and 2,6-dimethylbenzenethiol (Aldrich) were used as received. Sodium thiolates were synthesized by the reactions of the corresponding thiols with NaH in THF,[54] whereas lithium thiolates were prepared by addition of Bu^{n}Li in hexane to the hexane solution of the corresponding thiols.[55] ^{1}H (270 or 400 MHz) and ^{31}P{^{1}H} (109 or 162 MHz) NMR spectra were recorded in $CDCl_3$ on a JEOL EX-270 or a JEOL LA-400 spectrometer, while IR spectra were recorded on a Shimadzu 8100 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer (for C, H, and N) or at Elemental Analysis Laboratory, Department of Chemistry, School of Science, The University of Tokyo (for Cl). GLC and GC−MS analyses were carried out on a Shimadzu GC-8A and a Shimadzu GCMS-QP5000 instrument, respectively.

Synthesis of [Ir(NO)(SH)$_2$(PPh$_3$)$_2$] (2). To a suspension of **1** (539 mg, 0.659 mmol) in CH_2Cl_2 (10 mL) was added a solution of anhydrous NaSH (94.9 mg, 1.69 mmol) in MeOH (3.5 mL), and the mixture was stirred at room temperature for 8 h. After removal of the solvent in vacuo, the resultant orange powder was washed with MeOH (5 mL, 2 mL × 2) and dried in vacuo. Yield: 505 mg (0.621 mmol, 94%). ^{31}P{^{1}H} NMR: δ 14.6 (s). ^{1}H NMR: δ 7.3−7.7 (m, 30H, PPh$_3$), −1.05

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Table 6. X-ray Crystallographic Data for **3a**, **4**, **5**·CH_2Cl_2, **6a**, and **7**·CH_2Cl_2·MeOH

	3a	**4**	**5**·CH_2Cl_2	**6a**	**7**·CH_2Cl_2·MeOH
formula	$C_{36}H_{37}IrNOPS_2$	$C_{48}H_{58}Ir_2N_2O_2P_2S_4$	$C_{45}H_{50}Cl_2Ir_2N_2O_2P_2S_2$	$C_{72}H_{72}Cl_2Ir_2P_2S_4$	$C_{47}H_{57}Cl_4Ir_2NO_2P_2S_3$
fw	787.01	1269.63	1232.32	1582.89	1352.35
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	10.865(2)	10.217(1)	12.538(3)	23.296(2)	12.710(3)
b, Å	17.006(2)	11.448(2)	24.206(2)	14.912(2)	13.838(3)
c, Å	18.572(2)	23.810(4)	15.678(3)	19.719(2)	16.732(2)
α, deg	90	87.36(1)	90	90	93.18(1)
β, deg	100.44(1)	87.84(1)	93.64(2)	101.492(9)	91.66(1)
γ, deg	90	74.79(1)	90	90	117.33(1)
V, Å^3	3374.6(7)	2683.7(7)	4748(1)	6712(1)	2605.2(9)
Z	4	2	4	4	2
ρ_{calc}, g cm^{-3}	1.549	1.571	1.724	1.566	1.724
μ(Mo Kα), cm^{-1}	41.67	52.18	59.20	42.64	55.40
R_{int}	0.040	0.037	0.038	0.052	0.027
R^a	0.037	0.047	0.046	0.040	0.032
$R_w{}^b$	0.037	0.043	0.046	0.044	0.034

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$, $w = [\sigma_c{}^2(F_o) + p^2F_o{}^2/4]^{-1}$ (p = 0.007 (**3a**), 0.015 (**4**), 0.020 (**5**·CH_2Cl_2 and **6a**), 0.010 (**7**·CH_2Cl_2·MeOH)) with $\sigma_c(F_o)$ from counting statistics.

(t, 2H, SH, J_{PH} = 12.7 Hz). IR (KBr): 2544 cm^{-1} (ν_{SH}), 1518 cm^{-1} (ν_{NO}); the literature values are 2550 and 1510 cm^{-1} (in Nujol), respectively.[27]

Synthesis of [Ir(NO)(SMes)$_2$(PPh$_3$)] (3a). A mixture of **1** (898 mg, 1.10 mmol) and LiSMes (502 mg, 3.17 mmol) in THF (30 mL) was stirred for 8 h at room temperature. The resultant dark brown solution was evaporated to dryness in vacuo and extracted with CH_2Cl_2 (15 mL). Addition of MeOH to the concentrated extract afforded **3a** as black crystals (811 mg, 1.03 mmol, 94%). $^{31}P\{^1H\}$ NMR (23 °C): δ 11.5 (s). ^1H NMR (−20 °C): δ 7.9−7.4 (m, 15H, PPh$_3$), 6.93, 6.71 (s, 2H each, SC$_6$*H*$_2$Me$_3$), 2.54, 2.37 (s, 6H each, *o*-SC$_6$H$_2$*Me*$_2$Me), 2.28, 2.17 (s, 3H each, *p*-SC$_6$H$_2$Me$_2$*Me*). IR (KBr): 1802 cm^{-1} (ν_{NO}). Anal. Calcd for $C_{36}H_{37}IrNOPS_2$: C, 54.94; H, 4.74; N, 1.78. Found: C, 54.86; H, 4.91; N, 2.03. The Xy and Tip analogues, [Ir(NO)(SXy)$_2$(PPh$_3$)] (**3b**) and [Ir(NO)(STip)$_2$(PPh$_3$)] (**3c**), were prepared in a similar manner. **3b**: 85% yield by recrystallization from CH_2Cl_2−MeOH. $^{31}P\{^1H\}$ NMR (20 °C): δ 11.8 (s). ^1H NMR (20 °C): δ 7.9−7.4 (m, 15H, PPh$_3$), 7.4−6.6 (br, 6H, SC$_6$*H*$_3$Me$_2$), 2.60, 2.46 (br s, 6H each, SC$_6$H$_3$*Me*$_2$). IR (KBr): 1817 cm^{-1} (ν_{NO}). Anal. Calcd for $C_{34}H_{33}IrNOPS_2$: C, 53.81; H, 4.38; N, 1.85. Found: C, 54.00; H, 4.37; N, 1.70. **3c**: 79% yield by recrystallization from THF−MeOH. $^{31}P\{^1H\}$ NMR (20 °C): δ 11.7 (s). ^1H NMR (20 °C): δ 7.9−7.4 (m, 15H, PPh$_3$), 6.96, 6.79 (s, 2H each, SC$_6$*H*$_2$Pr$^i{}_3$), 4.43, 3.59 (sep, 2H each, *o*-C*H*Me$_2$), 2.86, 2.76 (sept, 1H each, *p*-C*H*Me$_2$), 1.45 (d, 6H, CH*Me*$_2$), 1.21−1.12 (m, 24H, CH*Me*$_2$), 0.95 (d, 6H, CH*Me*$_2$). IR (KBr): 1825 cm^{-1} (ν_{NO}). Anal. Calcd for $C_{48}H_{61}IrNOPS_2$: C, 60.35; H, 6.44; N, 1.47. Found: C, 60.09; H, 6.43; N, 1.33.

Synthesis of [Ir(NO)(μ-SPr^i)(SPr^i)(PPh$_3$)]$_2$ (4). (a) To a slurry of **1** (1.50 g, 1.83 mmol) in CH_2Cl_2 (30 mL) was added a solution of NaSPr^i (638 mg, 6.5 mmol) in MeOH (10 mL). The mixture was stirred at room temperature for 12 h, and the resultant dark red solution was evaporated to dryness in vacuo. The residue was dissolved in CH_2Cl_2 and chromatographed on alumina. Recrystallization of the dark red band eluted with CH_2Cl_2−hexane (2:1) from CH_2Cl_2−MeOH (6 mL/30 mL) afforded **4** as dark red crystals (575 mg, 0.453 mmol, 50%).

(b) A mixture of **1** (1.00 g, 1.22 mmol), Pr^{i}SH (0.38 mL, 4.06 mmol), and Et$_3$N (0.5 mL, 3.61 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 5 h. After removal of the solvent in vacuo, the residue was extracted with benzene (15 mL). Recrystallization of the extract from CH_2Cl_2−MeOH (10 mL/35 mL) afforded **4** in 92% yield. $^{31}P\{^1H\}$ NMR: δ 8.4 (s). ^1H NMR: δ 6.9−8.4 (br, 30H, PPh$_3$), 3.95 (sep, 2H, SC*H*Me$_2$), 2.86 (m, 2H, SC*H*Me$_2$), 1.14, 0.55 (d, 6H each, SCH*Me*$_2$), 1.03 (d, 12H, SCH*Me*$_2$). IR (KBr): 1538 cm^{-1} (ν_{NO}). Anal. Calcd for $C_{48}H_{58}Ir_2N_2O_2P_2S_4$: C, 45.41; H, 4.60; N, 2.21. Found: C, 45.46; H, 4.81; N, 2.16.

Synthesis of [Ir(NO)(μ-SBu^t)(PPh$_3$)]$_2$·CH$_2$Cl$_2$ (5·CH$_2$Cl$_2$). To a suspension of **1** (710 mg, 0.868 mmol) in 1,2-dichloroethane (20 mL) was added a solution of NaSBu^t (292 mg, 2.60 mmol) in EtOH (10 mL), and the mixture was stirred at 70 °C for 2 days. The resultant dark brown solution was evaporated to dryness in vacuo, and the residue was dissolved in benzene and chromatographed on alumina. The first green band eluted with benzene−hexane (3:1) was discarded, and the second brown band was collected. Recrystallization from CH_2Cl_2−MeOH afforded dark brown crystals of **5**·CH_2Cl_2 along with a small amount of red crystals, [Ir(NO)(PPh$_3$)$_3$],[31] which was removed manually. Yield: 151 mg (0.123 mmol, 28%). $^{31}P\{^1H\}$ NMR: δ −8.7 (s). ^1H NMR: δ 7.5−7.3 (m, 30H, PPh$_3$), 0.86 (s, 18H, SBu^t). IR (KBr): 1646, 1676 cm^{-1} (ν_{NO}). Anal. Calcd for $C_{45}H_{50}Cl_2Ir_2N_2O_2P_2S_2$: C, 43.86; H, 4.09; N, 2.27. Found: C, 43.96; H, 4.00; N, 2.42.

Synthesis of $[\{\overline{\mathrm{IrCl}(\mu\text{-}\mathrm{SC_6H_2Me_2C}}\mathrm{H_2})(\mathrm{PPh_3})\}_2(\mu\text{-}\mathrm{MesSSMes})]$ (6a). To a solution of **3a** (375 mg, 0.476 mmol) in CH_2Cl_2 (10 mL) was added benzoyl chloride (56 μL, 0.484 mmol), and the mixture was stirred for 3 days at room temperature. The resultant solution was concentrated and diluted with MeOH (13 mL). The brown precipitate that formed was collected by filtration and washed with THF (2.5 mL) and MeOH (2.5 mL). Recrystallization from CH_2Cl_2−MeOH (7.5 mL/30 mL) afforded **6a** as orange crystals (43 mg, 0.0272 mmol, 11%). $^{31}P\{^1H\}$ NMR: δ −7.7 (s). ^1H NMR: δ 7.6−6.8 (m, 32H, aryl), 6.45, 6.42, 6.08 (s, 2H each, aryl), 4.15 (d, 2H, IrC*H*H, $^2J_{HH}$ = 15.1 Hz), 3.76 (pseudo t, 2H, IrCH*H*), 3.06, 2.29, 2.20, 2.00, 0.87 (s, 6H each, Me). Anal. Calcd for $C_{72}H_{72}Cl_2Ir_2P_2S_4$: C, 54.63; H, 4.58. Found: C, 54.38; H, 4.53. The Xy analogue $[\{\overline{\mathrm{IrCl}(\mu\text{-}\mathrm{SC_6H_3MeC}}\mathrm{H_2})(\mathrm{PPh_3})\}_2(\mu\text{-}\mathrm{XySSXy})]\cdot 2CH_2Cl_2$ (**6b**·2CH_2Cl_2) was prepared in a similar manner. Yield: 8%. The presence of the solvating CH_2Cl_2 has been confirmed by ^1H NMR spectroscopy as well as elemental analyses. $^{31}P\{^1H\}$ NMR: δ −8.0 (s). ^1H NMR: δ 7.1−6.3 (m, 36H, aryl), 4.26 (d, 2H, IrC*H*H, $^2J_{HH}$ = 14.2 Hz), 3.87 (pseudo t, 2H, IrCH*H*), 3.20, 2.24, 0.89 (s, 6H each, Me). Anal. Calcd for $C_{70}H_{68}Cl_6Ir_2P_2S_4$: C, 49.55; H, 4.04; Cl, 12.54. Found: C, 49.11; H, 4.11; Cl, 12.19.

Synthesis of [Ir(NO)(PPh$_3$)(μ-SPr^i)$_3$IrCl$_2$(PPh$_3$)] (7). A mixture of **4** (598 mg, 0.471 mmol) and benzoyl chloride (0.4 mL, 3.5 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 2 days. After removal of the solvent, the resultant oil was washed with hexane (7 mL) and recrystallized from CH_2Cl_2−MeOH. The dark brown crystals that formed were filtered off and dried in vacuo (506 mg, 0.401 mmol, 85%). $^{31}P\{^1H\}$ NMR: δ 9.4, −21.2 (d, 1P each, $^4J_{PP}$ = 8.1 Hz). ^1H NMR: δ 7.7−7.0 (m, 30H, PPh$_3$), 3.77, 3.30, 3.16 (m, 1H each, SC*H*Me$_2$), 1.84, 1.57, 1.36, 1.33, 0.41, 0.16 (d, 3H each, SCH*Me*$_2$). IR (KBr): 1725 cm^{-1} (ν_{NO}). As confirmed by the X-ray analysis, crystals of **7** obtained from CH_2Cl_2−MeOH contain solvating CH_2Cl_2 and MeOH molecules. However, once dried in vacuo, these crystals turned to a brown powder, whose ^1H NMR spectrum showed the absence of these solvating molecules. Therefore, the calculated values in elemental analysis are based on the formula without these solvating molecules. Anal. Calcd for $C_{45}H_{51}Cl_2Ir_2NOP_2S_3$: C, 43.75; H, 4.16; N, 1.13. Found: C, 43.61; H, 4.36; N, 1.52.

X-ray Diffraction Studies. Single crystals of **3a**, **4**, **5**·CH_2Cl_2, **6a**, and **7**·CH_2Cl_2·MeOH were sealed in argon atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC7R four-circle automated diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,69$ Å) at room temperature using the ω scan (for **5**·CH_2Cl_2) or the $\omega-2\theta$ scan (except for **5**·CH_2Cl_2) technique at a rate of 32° min^{-1} to a maximum 2θ value of 50° (for **3a** and **7**·CH_2Cl_2·MeOH) or 55° (for **4**, **5**·CH_2Cl_2, and **6a**). Intensity data were corrected for Lorentz−polarization effects and for absorption (Ψ scans). Details of crystals and data collection parameters are summarized in Table 6. Structure solution and refinements were carried out by using the teXsan program package.[56] The heavy atom positions were determined by the Patterson methods program (DIRDIF-PATTY94),[57] and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques for **3a**, **4**, **5**·CH_2Cl_2, and **6a**, and all hydrogen atoms were placed at calculated positions and included in the final stages of refinements with fixed parameters. For **7**·CH_2Cl_2·MeOH, the carbon and oxygen atoms in the solvating MeOH molecule were refined isotropically. The hydroxy hydrogen atom in this molecule was not located.

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Supporting Information Available: X-ray crystallographic files in CIF format (for **3a**, **4**, **5**·CH_2Cl_2, **6a**, and **7**·CH_2Cl_2·MeOH). This material is available free of charge via the Internet at http://pubs.acs.org.

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