Oxidation of Substrates by an Iridium Dioxygen Complex: Intramolecular Oxidation of Carbon Monoxide and Activation of a Carbonyl Group by Attack of a Heterocyclic Nitrogen

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The square-planar complex $[Ir(C_7H_4NS_2)(CO)(PPh_3)_2]$ (1) is obtained in high yield from the reaction of lithium benzothiazole-2-thiolate $(LiC_7H_4NS_2)$ with Vaska's complex, $[IrCl-(CO)(PPh_3)_2]$. Coordination of the new ligand in 1 and in the homologous rhodium complex should occur through the sulfur atom, as shown by their protonation reactions with HBF₄, which give the hydridoiridium(III) complex $[IrH(C_7H_4NS_2)(CO)(PPh_3)_2]BF_4$ and the rhodium(I) compound $[Rh(CO)(PPh_3)_2(C_7H_5NS_2)]BF_4$, respectively. The neutral ligand $C_7H_5NS_2$ reacts with 1 to give $[IrH(C_7H_4NS_2)_2(CO)(PPh_3)_2]$ (4). Complex 1 adds dihydrogen, methyl iodide, and dioxygen. The dioxygen complex $[Ir(C_7H_4NS_2)(O_2)(CO)(PPh_3)_2]$ (7) undergoes an intramolecular oxidation of the carbonyl ligand, catalyzed by water, to yield the carbonato complex $[Ir(C_7H_4NS_2)(CO_3)(PPh_3)_2]$ (8). Labeling studies show that the reaction is multistep and oxygen from water is incorporated into the carbonate ligand. Sulfur dioxide is oxidized by complex 7, but in addition, activation of the carbonyl group occurs by attack of the

heterocyclic nitrogen of the benzothiazole-2-thiolate ligand to give $[Ir{C(O)NC(S)SC_6H_4}-(SO_4)(PPh_3)_2]$ (11). In 8 both benzothiazole-2-thiolate and carbonate anions act as N,S- and O,O-chelating ligands. The structure of 11 shows a C,S-chelating ligand, obtained by an unprecedented incorporation of the carbonyl group of 7 into the benzothiazole-2-thiolate through the heterocyclic nitrogen, in addition to a chelating sulfato ligand.

Introduction

The activation of dioxygen by coordination to a transition metal¹ has attracted considerable attention in recent years owing to its importance in biological systems² and in the oxidation of organic³ and inorganic molecules.⁴ Fundamental in these studies is the controlled transfer of oxygen to a molecule of substrate. The most common (radical chain) pathway for oxygen transfer involves transition-metal-promoted autoxidation. More controlled oxidations may be achieved if the metal

center serves for the coordination of both substrate and dioxygen where bond breaking and re-forming steps occur at the metal center. A recent model of this template synthesis is the oxidation of alcohols to carboxylic acids by an iridium dioxygen complex.⁵ In addition, a rare example of a clean O-O bond rupture concurrent with carbon-oxygen bond formation has been reported by Bercaw,⁶ but an understanding of the intimate mechanism of the oxygen atom transfer is still required.

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benzothiazole-2-thiolate

Oxidation of carbon monoxide by a transition metal dioxygen complex has been observed for platinum, iridium, and rhodium compounds,^{4a,b,7} and oxidation of a carbonyl ligand by O_2 in a dinuclear complex has been recently reported.⁸ The kinetics studies^{4b} of the oxidation of carbon monoxide by the dioxygen adduct of [IrR- $(CO)(PR'_3)_2$] (R = alkyl, alkoxy) reveal a reversible cleavage of one of the two Ir-O bonds followed by attack at this oxygen atom by free CO. Furthermore, the presence of the R group gives rise to a chemistry different from that of their halide analogs.^{4c,9} In view of this feature, we have prepared the Vaska type complex $[Ir(C_7H_4NS_2)(CO)(PPh_3)_2]$, which contains an anionic (S or N donor atom) and potentially binucleating or chelating ligand, expecting new chemical properties relative to the above-mentioned systems. In this paper we describe some reactions of this complex and, in particular, those of its dioxygen derivative that lead to the intramolecular oxidation of the carbonyl ligand to carbonate and to the activation of the carbonyl ligand by attack of the heterocyclic nitrogen of the ligand in the oxidation of sulfur dioxide. Part of these results have been previously communicated.¹⁰

Results and Discussion

Synthesis, Structure, and Protonation Reactions of $[Ir(C_7H_4NS_2)(CO)(PPh_3)_2]$ (1). The complex $[IrCl(CO)(PPh_3)_2]$ reacts with the lithium salt of benzothiazole-2-thiolate $(LiC_7H_4NS_2)$ in refluxing tetrahydrofuran to give the yellow complex $[Ir(C_7H_4NS_2)(CO)]$ - $(PPh_3)_2$ (1) in high yield. The reaction stops at the mononuclear complex 1 even if the refluxing is maintained for long periods, as occurs in the reactions of Vaska's complex with alkaline salts of thiolates¹¹ and disubstituted pyrazolates.¹² Thus, elimination of triphenylphosphine in this reaction to give the dinuclear complex $[{Ir(\mu-C_7H_4NS_2)(CO)(PPh_3)}_2]$ does not take place, in contrast with the syntheses of the pyrazolate $(pz)^{13}$ and phosphide¹⁴ complexes of iridium [{Ir(μ -X)- $(CO)(PPh_3)$ ₂] (X = pz, PPh₂) by the same method.

Compound 1 is square-planar, like its homologous rhodium complex¹⁵ [Rh($\overline{C_7}H_4NS_2$)(CO)(PPh₃)₂]. The phosphine ligands are in a trans disposition, in accord

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complexes of iridium and rhodium of this type:¹⁵ they should be at lower frequency for pentacoordinated structures.7b Coordination of benzothiazole-2-thiolate in these complexes is through the S atom, as evidenced by their protonation reactions, which show in addition differences in the reactivities of these compounds (see Scheme 1).

with their equivalency in their ${}^{31}P{}^{1}H$ NMR spectrum. and the coordination mode of the benzothiazole-2thiolate ligand is monodentate. Although this ligand can act as a bidentate group chelating through the sulfur and nitrogen atoms, the positions of $\nu(CO)$ at 1966 cm^{-1} in 1 and 1982 cm^{-1} for the homologous rhodium complex are the usual ones for tetracoordinated

Protonation of the rhodium complex with HBF₄ takes place on the nitrogen in the free arm of the ligand to give the rhodium(I) complex [Rh(CO)(PPh₃)₂(C₇H₅NS₂)]- $BF_4(2)$ quantitatively.¹⁶ In contrast, protonation of the iridium complex occurs on the metal, giving the iridium-(III) hydrido complex [IrH(C₇H₄NS₂)(CO)(PPh₃)₂]BF₄ (3) as a yellow solid in good yield. Oxidation of the iridium center upon reaction is detected by the increase in ν -(CO) (at 2060 cm^{-1} in 3). In addition, benzothiazole-2thiolate should change its coordination mode to act as a bidentate and chelating ligand through the S and N atoms. Complex 3 is octahedral with equivalent trans phosphine ligands, and the hydrido ligand is cis to both phosphorus atoms, which gives rise to a triplet in the ¹H NMR spectrum (${}^{1}J_{HP} = 10.5$ Hz). The chemical shift of the hydride resonance in bis(phosphine)iridium complexes¹⁷ is sensitive to the donor atom *trans* to it, in such a way that electronegative atoms shift this resonance to higher fields. The position found in complex 3 (δ -14.5 ppm) is similar to that found in complexes with hydride *trans* to a thiolate group ($\delta \sim -15$ ppm), suggesting that it is trans to the sulfur atom.

The final result of this reaction could lead one to think that the iridium center is more basic than the uncoordinated nitrogen of the ligand benzothiazole-2-thiolate $(pK_a \text{ of } C_7H_5NS_2 6.9)$.¹⁸ If so, the direct protonation of the metal would leave the hydrido ligand trans to a vacant coordination site, which should then be occupied by the free nitrogen atom of the ligand. Then the hydride would be *trans* to the nitrogen atom, which is not the case. Hence, the result should be due to a different reaction course. Most probably the reaction starts with the protonation of the nitrogen atom, as occurs for its homologous rhodium complex, followed by the oxidative addition of the N-H bond to the metal center to give the complex where the hydrido ligand is trans to the sulfur atom, as found in 3. Oxidativeaddition reactions of N-H bonds to iridium complexes have been reported recently.¹⁹ Further support for this rationalization is the reaction of 2-mercaptobenzothiazole (the neutral form of the ligand) with complex 1 to give the iridium(III) hydrido complex [IrH(C₇H₄NS₂)₂-

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^{*a*} Abbreviations: $P = PPh_3$; NS = benzothiazole-2-thiolate.

 $(CO)(PPh_3)_2$] (4). In complex 4 the hydrido ligand is trans to the carbonyl group, as evidenced by its chemical shift in the ¹H NMR spectrum; both phosphine ligands are equivalent, mutually trans, and are cis to the hydrido group. As the protonation of the coordinated ligand by the free molecule is unlikely, a concerted oxidative addition of either the N-H or S-H bond of one of the tautomeric forms of the ligand to the metal should occur. In this way, the oxidative addition of 2-mercaptobenzothiazole to 1 gives a complex where the carbonyl and hydrido ligands are mutually trans. Complex 4 was reacted with tetrafluoroboric acid to investigate whether the benzothiazole-2-thiolate ligands are coordinated to the iridium through the N or the S atom, as described above. The protonation of one ligand indeed occurs, but whether it takes place at the N or at the S atom is unknown, since this ligand is released as free 2-mercaptobenzothiazole; the other benzothiazole-2-thiolate ligand remaining in the complex becames chelating, and thus, complex 3 is produced quantitatively in this reaction.

Oxidative-Addition Reactions of $[Ir(C_7H_4NS_2)-(CO)(PPh_3)_2]$ (1). Complex 1 differs from Vaska's complex because it contains a potentially binucleating or chelating ligand having an uncoordinated donor atom. The electronic environment on the metal created by benzothiazole-2-thiolate can be compared with that of Vaska's complex through oxidative-addition reactions as shown below, and besides, the possible coordination of the free end of the ligand in these reactions may produce unpredictable consequences.

Methyl iodide reacts with complex 1, giving the already known complex $[IrI_2(Me)(CO)(PPh_3)_2]$, which

does not contain the benzothiazole-2-thiolate ligand. The reaction should be multistep; the first oxidative addition should take place as for Vaska's complex to give [Ir- $(Me)I(C_7H_4NS_2)(CO)(PPh_3)_2]$, which is followed by a reductive elimination of 2-(methylthio)benzothiazole. A further oxidative addition of methyl iodide to the intermediate [IrI(CO)(PPh₃)₂] affords the final product. Hydrogen reacts with complex 1 to give the complex $[IrH_2(C_7H_4NS_2)(CO)(PPh_3)_2]\,({\bf 5})$ as a white solid in good yield. Complex 5 is isolated as a single isomer having two equivalent phosphine ligands trans to each other and two hydrido ligands mutually cis. One of the hydride ligands is *trans* to the carbonyl group and the other trans to the sulfur, in accord with their chemical shifts in the ¹H NMR spectrum. The structure of complex 5, in which the nitrogen atom is uncoordinated, is shown in Scheme 1. Thus, the addition of hydrogen is a concerted process that occurs parallel to the S-Ir-CO axis of the complex. The related cis-dihydrido complex $[IrH_2(C_7H_4NS_2)(PPh_3)_2]$ (6) is obtained by reaction of the solvated species $[IrH_2(PPh_3)_2S_2]^+$ (S = acetone) with $LiC_7H_4NS_2$. A single isomer having the phosphine ligands in trans positions results from this reaction. Interestingly, the chemical shifts of the hydrido ligands in 6, trans to the N and S atoms, are largely shifted to higher field relative to those in the related complexes 3-5.

Oxygen reacts irreversibly with complex 2 in tetrahydrofuran or dichloromethane, giving an orange solution extremely sensitive to traces of water. In these solutions there is a single compound, as observed by ³¹P NMR spectroscopy, characterized as the dioxygen complex $[Ir(C_7H_4NS_2)(O_2)(CO)(PPh_3)_2]$ (7). Attempts to isolate this compound gave slightly impure off-white solids due to its high reactivity. In 7 both phosphine ligands are equivalent and are therefore in a *trans* disposition. Oxidation of the iridium center is detected by an increase in $\nu(CO)$ at 2015 cm⁻¹ and a new IR band at 885 cm⁻¹ ($\nu(O-O)$) characteristic of peroxo or η^2 bonded dioxygen complexes of iridium. The structure of this dioxygen complex is then octahedral, with the dioxygen, carbonyl, and benzothiazole-2-thiolate ligands in the equatorial plane, the last ligand being monodentate and presumably bonded to the metal by the sulfur atom.

Oxidations with $[Ir(C_7H_4NS_2)(O_2)(CO)(PPh_3)_2]$ (7). Addition of water discolors the solutions of complex 7, from which yellow crystals analyzed as $[Ir(C_7H_4NS_2) (CO_3)(PPh_3)_2$ (8) are obtained. Characterization of 8 as a carbonate complex in solution and in the solid state relies on spectroscopic evidence and on an X-ray diffraction study. This yellow compound does not have a carbonyl group but has a strong ν (C=O) band at 1683 cm^{-1} in its IR spectrum. This and a resonance at δ 167 ppm in the ${}^{13}C{}^{1}H$ NMR spectrum of 8, which has no attached protons in the ¹³C APT spectrum, are characteristic of carbonato complexes. Although oxidation of carbon monoxide by dioxygen complexes is known,^{4a,b,7} confirmation of this type of reaction by the presence of the carbonate group and the structure of the complex 8 in the solid state required an X-ray diffraction study (see below). A chemical confirmation of the presence of the carbonato ligand comes from the reaction of complex 8 with strong acids, but the product depends on the anion. Acids such as HCl, having a coordinating anion, protonate the carbonato ligand in complex 8 to give carbon dioxide; the vacant coordination positions are occupied by the anion of the acid, giving $[Ir(C_7H_4 NS_2(Cl)_2(PPh_3)_2$ (9). On the other hand, acids which have poorly coordinating anions such as HBF₄ reacts with complex 8 in a similar fashion but the coordination positions left are occupied by water molecules to give $[Ir(C_7H_4NS_2)(H_2O)_2(PPh_3)_2](BF_4)_2$ (10).

X-ray Crystal Structure of the Carbonato Complex 8. A view of $[Ir(C_7H_4NS_2)(CO_3)(PPh_3)_2]$ (8) is shown in Figure 1 together with the atom-numbering scheme. Selected bond distances and angles are given in Table 1. The Ir atom displays an octahedral coordination with the two apical positions occupied by P atoms from PPh_3 ligands (Ir-P = 2.370(3) and 2.354(3) Å), two *cis*-equatorial sites occupied by O atoms from the chelating carbonato ligand (Ir-O(1) = 2.068(6) Å)and Ir-O(2) = 2.071(6) Å), and the remaining two equatorial sites occupied by the N and S(1) atoms from the chelating benzothiazole-2-thiolate (Ir-S(1) = 2.425)(3) Å and Ir-N = 2.061(7) Å). To the best of our knowledge, this is the first structurally characterized iridium complex in which the carbonate anion acts as a chelating ligand. In the dinuclear complex $[Ir_2(CO)_2 (\mu$ -CO₃) $(\mu$ -dppm)₂] the carbonato ligand bridges two Ir atoms through two oxygen atoms with Ir-O bond distances of 2.08(1) and 2.09(1) Å.20 The four-membered O(1)C(8)O(2)Ir and NC(1)S(1)Ir chelating rings are planar and are characterized by very narrow bite angles $(N-Ir-S(1) = 66.9(2)^{\circ} \text{ and } O(1)-Ir-O(2) = 64.1(3)^{\circ}).$ The complex as a whole has an approximate C_s sym-



Figure 1. View of the molecular structure of the complex $[Ir(C_7H_4NS_2)(CO_3)(PPh_3)_2]$ (8) with the atom-numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

Table 1.	Selected Bond Distances (Å) and Angles
	(deg) for Complex 8

		-	
Ir-S(1)	2.425(3)	Ir-N	2.061(7)
Ir-P(1)	2.370(3)	Ir-P(2)	2.354(3)
Ir - O(1)	2.068(6)	Ir - O(2)	2.071(6)
P(1) - C(9)	1.80(1)	P(2) - C(27)	1.84(1)
P(1) - C(15)	1.83(1)	P(2) - C(33)	1.81(1)
P(1) - C(21)	1.82(1)	P(2) - C(39)	1.83(1)
S(1) - C(1)	1.70(1)	O(1)-C(8)	1.34(1)
S(2) - C(1)	1.74(1)	O(2) - C(8)	1.35(1)
S(2) - C(2)	1.76(1)	O(3) - C(8)	1.21(1)
N-C(1)	1.32(1)	C(3) - C(4)	1.40(2)
N-C(7)	1.39(1)	C(4) - C(5)	1.40(2)
C(2) - C(3)	1.39(2)	C(5) - C(6)	1.43(2)
C(2) - C(7)	1.39(2)	C(6) - C(7)	1.39(2)
O(1)-Ir-O(2)	64.1(3)	O(1)-Ir-N	113.2(3)
P(1)-Ir-N	92.1(2)	P(2)-Ir-N	91.6(2)
P(1) - Ir - O(2)	88.7(2)	P(2) - Ir - O(2)	87.7(2)
P(1) - Ir - O(1)	91.6(2)	P(2) - Ir - O(1)	91.0(2)
S(1)-Ir-N	66.9(2)	S(1) - Ir - O(2)	115.9(2)
S(1) - Ir - P(1)	90.0(1)	S(1) - Ir - P(2)	87.5(1)
Ir - S(1) - C(1)	79.3(3)	C(1)-S(2)-C(2)	89.3(5)
Ir - O(1) - C(8)	93.5(6)	Ir - O(2) - C(8)	93.2(6)
Ir-N-C(7)	142.9(6)	Ir-N-C(1)	103.2(6)
C(1) - N - C(7)	113.9(8)	C(4) - C(5) - C(6)	119.5(13)
S(2)-C(1)-N	113.7(7)	C(5)-C(6)-C(7)	116.4(11)
S(1)-C(1)-N	110.6(7)	N-C(7)-C(6)	126.1(10)
S(1)-C(1)-S(2)	135.4(6)	N-C(7)-C(2)	112.5(9)
S(2)-C(2)-C(7)	110.5(8)	O(2) - C(8) - O(3)	126.0(10)
S(2)-C(2)-C(3)	125.4(9)	O(1) - C(8) - O(3)	124.8(10)
C(2)-C(3)-C(4)	113.9(13)	O(1)-C(8)-O(2)	109.2(8)
C(3) - C(4) - C(5)	124.5(15)		

metry, with the carbonato and benzothiazole-2-thiolato ligands lying on the mirror plane. In the tetranuclear complex $Ir_4(\mu$ -C₇H₄NS₂)₄I₂(CO)₈ two benzothiazole-2thiolates have been found bridging two Ir atoms through the same S and N atoms with slightly shorter Ir-S bond distances (2.382(7) and 2.408(6) Å) and slightly longer Ir-N bond distances (2.09(2) and 2.11(2) Å) than in 8.²¹ Also, in the dinuclear complex $Ir_2(\mu$ -C₅H₄NS)I(CO)₄-(CH₂I), in which two pyridine-2-thiolates form chelating rings comparable to those formed by benzothiazole-2-

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Figure 2. Fine structure of the molecular ion in the mass spectra of the carbonate complex **8** obtained (a) with labeled $H_2^{18}O$ and (b) with unlabeled H_2O .

thiolate, the Ir-S and Ir-N bond distances show the same trend (Ir-S = 2.360(4) and 2.361(4) Å, Ir-N = 2.112(12) and 2.109(11) Å).²²

The action of water is essential to accomplish the oxidation of the carbonyl ligand in the dioxygen complex 7. In fact, the elements for building up the carbonate ligand, i.e., the atoms of oxygen and carbon, are already coordinated as ligands in complex 7 but the reaction does not take place under anhydrous conditions. The need for water is one differential feature in the oxidation of the carbonyl ligand or carbon monoxide in comparison with other systems; the second is that in previous reports one of the reacting molecules, either CO or O₂, is not coordinated to the metal. In view of this novelty, we decided to investigate the reaction further. Chemical evidence for the mechanism and the action of the water were obtained using both labeled water (H₂¹⁸O) and protonation reactions of complex 7.

Incorporation of oxygen from water into the carbonate ligand is revealed by the mass spectrum of the carbonato complex 8 obtained from the reaction of complex 7 with labeled water. The fine structure of the molecular ion is made by overlapping the fine structures of the isotopomers containing from zero up to three ¹⁸O atoms. Figure 2 shows the fine structures of the molecular ions of the normal and labeled carbonato complexes for comparative purposes. The analysis of this structure gives the following proportions of the isotopomers: $C^{16}O_3$, 17%; $C^{18}O^{16}O_2$, 17%; $C^{18}O_2^{16}O$, 53%; $C^{18}O_3$, 13%.

As the carbonate complex 8 does not interchange oxygen with labeled water after 3 days, it is evident that water reacts with complex 7 at the carbonyl ligand. Furthermore, the presence of the isotopomer containing three ¹⁸O atoms in the carbonate shows that the mechanism is multistep and one of the intermediates interchanges oxygen with water. A possible mechanism to account for some of these results, outlined in Scheme 2, starts with a nucleophilic attack of water at the carbonyl ligand. The ability of the carbonyl group to carry out such a nucleophilic attack is increased upon oxidation, as revealed by the $\nu(CO)$ frequency of complex 7 relative to that of the iridium(I) complex 1, and it is a well-documented reaction for the late transition metals.²³ This would give an iridium(III) complex containing a protonated hydrocarbonyl ligand (a), which easily transfers the proton to a close basic center in the molecule, either to the nitrogen or to the dioxygen ligand. In the first instance a further transfer of the proton to the dioxygen ligand occurs which would open the metallacycle to give species b, as observed for the reactions of dioxygen complexes with electrophiles.²⁴ Then benzothiazole-2-thiolate should become a chelating ligand. The attack by an electrophile at the dioxygen ligand enhances the heterolysis of the O-O bond, as pointed out by Bercaw.⁶ In this way, a hydroxy-

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^a The asterisk denotes labeled ¹⁸O.

(hydrogencarbonate)iridium(III) complex results (c), and the reaction ends up with the formation of the carbonate group (d) and elimination of water. The water then acts as a catalyst for the reaction, but unlabeled water results from it. The mechanism relies on the following observations.

Protonation of the dioxygen complex is required for the formation of the carbonate ligand. Thus, addition of an ethereal solution of HBF_4 to the dioxygen complex 7 in the molar ratio 0.25:1 gives the carbonate complex, as observed by ${}^{31}P{}^{1}H$ NMR. The other two phosphoruscontaining species in solution are triphenylphosphine oxide and complex 10, the product from the reaction of the carbonate complex with HBF₄. The protonation occurs at the dioxygen ligand but not at the nitrogen, since two new singlets at δ 5.78 and 5.58 ppm observed in the ¹H NMR spectrum of the reaction mixture should be attributed to hydroxo species, the hydroperoxo ligand²⁵ among them, but resonances at low field due to acidic N-H are not detected. These two resonances disappear when the reaction is completed to give a broad band centered at 5.5 ppm. Besides, an IR band at 860 $\rm cm^{-1}$ observed in the IR spectrum of this mixture evidences the presence of the peroxo group. The action of the acid

is catalytic for the formation of the carbonate complex, but part of it reacts with the product. In fact, complex 10 crystallizes out from this mixture if an excess of acid is used.

Other nucleophiles react similarly to water. Thus, ammonia gas reacts with the dioxygen complex 7, giving the carbonate complex 8. Presumably, an intermediate complex in this reaction contains an amidocarbonate ligand, which should undergo hydrolysis by the water formed in the reaction to give the carbonato complex. On the other hand, methanol reacts with complex 7, giving the dihydride complex 6 in low yield, but the carbonate complex 8 does not result from this reaction.

Aqueous hydrogen peroxide reacts with complex 1 to give triphenylphosphine oxide and some of the carbonate complex. Oxidation of the phosphine ligands is not observed in the reaction of the dioxygen complex 7 with water, which rules out that hydrogen peroxide participates in the reaction.

This simple mechanism explains the presence of the isotopomers $C^{16}O_3$ and $CO_2^{18}O$; the former is due to the formation of normal water in the reaction, but it does not justify the presence of the most abundant isotopomer, containing two ¹⁸O atoms. For that, an exchange of oxygen between labeled water and the hydroxycarbonyl ligand is the most reasonable proposal, as observed in carboxylic acids.²⁶ Furthermore, a fast exchange of both oxygen atoms of the hydroxycarbonyl ligand in $[Ru(bpy)_2(CO)\{C(O)OH\}]^+$ with labeled $H_2^{18}O$ has been reported recently,27 in accord with our proposal. A further exchange of oxygen between an intermediate, for example the hydrogencarbonate ligand (c in Scheme 2), and labeled water should occur to give the isotopomer containing three ¹⁸O atoms in the carbonate ligand.

Sulfur dioxide reacts with the dioxygen complex 7 in tetrahydrofuran at atmospheric pressure to give the sulfate complex 11. The sulfato ligand is coordinated in complex 11 in a bidentate and chelating mode, as deduced from the positions of the fundamental modes of this ligand.²⁸ Oxidation of SO₂ is a common reaction of metal dioxygen complexes. More surprising is that complex 11 does not have a terminal carbonyl ligand but has a $\nu(CO)$ band at 1680 cm⁻¹. Furthermore, the molecular ion in the mass spectrum of 11 corresponds to the formula $[Ir(C_7H_4NS_2)(SO_4)(CO)(PPh_3)_2]$, which shows that an unusual reaction has taken place on the carbonyl group. The X-ray diffraction study of 11 has revealed that the carbonyl group inserts formally into the metal-nitrogen bond. In this way, a new bidentate ligand is formed on incorporation of the carbonyl group into benzothiazole-2-thiolate between the heterocyclic nitrogen and the metal. Complex 11 should be then

reformulated as $[Ir{C(O)NC(S)SC_6H_4)}(SO_4)(PPh_3)_2]$.

X-ray Crystal Structure of the Sulfato Complex 11. In the crystals of 11 two crystallographically independent, but very similar, $[Ir{C(O)NC(S)SC_6H_4}]$ -

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Figure 3. View of the molecular structure of one of the two independent complexes $[Ir\{C(O)NC(S)SC_6H_4\}(SO_4)-(PPh_3)_2]$ (11) with the atom-numbering scheme. The thermal ellipsoids are drawn at the 30% probability level.

 $(SO_4)(PPh_3)_2$ complexes are present. The structure of one of them is shown in Figure 3 together with the atomnumbering scheme. Selected bond distances and angles are given in Table 2. In the octahedral coordination around the Ir atom the two axial positions are occupied by P atoms from PPh₃ groups, whereas two cis-equatorial sites are occupied by O atoms from the chelating sulfato ligand and the remaining two by the C(8) and S(1) atoms of the new chelating ligand, obtained by an unprecedented incorporation of the carbonyl group of 7 into benzothiazole-2-thiolate through the heterocyclic nitrogen. The Ir-P bond distances, 2.368(4) and 2.386-(5) Å [2.376(4)] and 2.367(4) Å; hereafter the values in brackets refer to the second independent complex] are comparable to those found in 8. The two Ir-O bond distances, 2.154(9) and 2.067(8) Å [2.187(9) and 2.123-(8) Å], are significantly different, probably because of the different trans effects of the S and C atoms. The O(1)S(3)O(2)Ir four-membered chelating ring is planar, with a bite angle of $66.4(4)^{\circ}$ [65.2(4)°]. The Ir-S(1) and Ir-C(8) bond distances are 2.323(4) Å [2.293(4) Å] and 1.96(1) Å [1.93(1) Å], respectively. Also, the S(1)C(1)N-(1)C(8)Ir five-membered chelating ring, with a bite angle of $86.1(5)^{\circ}$ [87.3(4)°], is planar with the O(5) atom lying in the same plane. The new ligand has preserved its planarity after insertion of the adjacent CO ligand. The values of the N(1)-C(8)(1.51(2) Å [1.49(2) Å]) and C(8)-O(5) (1.20(2) Å [1.21(2) Å]) bond distances are in accordance with a slight delocalization of the double bond, as shown by the resonance structures in Scheme 3. The weakness of the N-C bond is revealed also by the mass spectrum of 11, which shows the sequential loss of the sulfato and then the carbonyl group from the molecular ion. In contrast, the carbonyl group is not observed in the fragmentation of formamides. Furthermore, this bond should be similar to that in N-acyl derivatives of pyridine, which are proposed intermediates in acylation reactions of organic substrates where 4-(dimethylamino)pyridine is added to promote the reaction.⁴ The N-acyl derivative easily transfers the

Table 2. Selected Bond Distances (Å) and Angles(deg) for Complex 11

	9, <u>F</u>	-
	complex 1	complex 2
Ir-S(1)	2.323(4)	2.292(4)
Ir - P(1)	2.368(4)	2.376(4)
Ir-P(2)	2.386(5)	2.367(4)
Ir-O(1)	2.154(9)	2.187(9)
Ir-O(2)	2.067(8)	2.123(8)
Ir-C(8)	1.96(1)	1.93(1)
S(1) - C(1)	1.71(1)	1.67(1)
S(2) - C(1)	1.69(2)	1.73(2)
S(2) - C(2)	1.71(1)	1.79(2)
S(3) - O(1)	1.51(1)	1.53(1)
S(3) = O(2)	1.53(1)	1.50(1)
S(3) = O(3) S(3) = O(4)	1.44(1) 1 $44(1)$	1.43(1) 1 45(1)
P(1) = C(0)	1.44(1) 1.78(9)	1.40(1)
P(1) = C(15)	1.(0(2)	1.00(2)
P(1) - C(21)	1.83(2) 1.82(1)	1.83(2)
P(2) - C(27)	1.02(1) 1.86(2)	1.85(2)
P(2) - C(33)	1.86(2)	1.00(2) 1.79(2)
P(2) - C(39)	1.82(2)	1.84(2)
O(5) - C(8)	1.20(2)	1.21(2)
N(1) - C(1)	1.33(2)	1.35(2)
N(1) - C(3)	1.44(2)	1.42(2)
N(1) - C(8)	1.51(2)	1.49(2)
C(2)-C(3)	1.38(2)	1.40(2)
C(2) - C(7)	1.41(2)	1.36(2)
C(3) - C(4)	1.36(2)	1.40(2)
C(4) - C(5)	1.40(2)	1.38(2)
C(5)-C(6)	1.40(3)	1.40(2)
C(6) - C(7)	1.35(2)	1.38(2)
O(2) - Ir - C(8)	102.0(5)	101.8(5)
O(1) - Ir - O(2)	66.4 (4)	65.2 (4)
P(2)-Ir-C(8)	89.6(5)	87.7(5)
P(2)-Ir-O(2)	89.8(3)	89.1(3)
P(2)-Ir-O(1)	90.1(3)	94.3(3)
P(1) - Ir - C(8)	89.3(5)	90.3(5)
P(1) - Ir - O(2)	91.2(3)	92.1(3)
P(1) = Ir = O(1)	91.1(3)	87.8(3)
S(1) = Ir = C(0) S(1) = Ir = O(1)	00.1(0) 105 4(9)	07.3(4) 105 7(9)
S(1) - Ir - O(1) S(1) - Ir - P(2)	100.4(0)	100.7(3) QA A(2)
S(1) - Ir - P(1)	90.1(1)	89 1(2)
Ir - S(1) - C(1)	98.2(5)	97.1(6)
C(1)-S(2)-C(2)	90.1(8)	90.9(8)
O(3) - S(3) - O(4)	114.9(7)	112.0(7)
O(2) - S(3) - O(4)	109.4(6)	112.8(7)
O(2) - S(3) - O(3)	110.4(6)	108.8(6)
O(1) - S(3) - O(4)	112.6(7)	112.3(7)
O(1) - S(3) - O(3)	109.5(6)	110.1(7)
O(1) - S(3) - O(2)	98.9(5)	100.2(5)
Ir - O(1) - S(3)	95.7(6)	95.4(5)
$\frac{\mathrm{Ir}-\mathrm{O}(2)-\mathrm{S}(3)}{\mathrm{O}(2)}$	98.9(4)	98.9(4)
U(3) = N(1) = U(8) O(1) = N(1) = O(8)	129.6(12)	129.7(11)
C(1) = N(1) = C(8) C(1) = N(1) = C(8)	111 5(12)	112 9(12)
$O(1) = I_{N}(1) = O(3)$ O(5) = C(8) = N(1)	111.0(12) 114.1(12)	113.2(13) 119.6(19)
Ir - C(8) - N(1)	116 0(10)	116 1(Q)
Ir - C(8) - O(5)	129.9(13)	130.2(11)

acyl group because of the instability associated with the weak N-C(O) bond.

The reactions described here involve the dioxygen ligand as a central place of reactivity of complex 7. In fact, all require an electrophile (H^+ and SO_2 respectively) to start a further reaction. This electrophile is directly added or generated in the reaction and then selectively attacks at the dioxygen ligand, opening the dioxo metallacycle. In other words, the Lewis acids bind to a dipolar intermediate (M^+-O-O^-) through the free oxygen atom as the first step in these reactions. The second step involves the breaking of the O-O bond to give the hydrogencarbonate or the sulfate ligand. A further reaction takes place then in the formation of complex 11. As benzothiazole-2-thiolate still has a free Scheme 3



Scheme 4. Possible Pathways Leading to the Formation of Complex 11



arm, there are two different but indistinguishable possibilities depending on the donor atom (S or N) bonded to the iridium atom (Scheme 4). The first alternative implies that the carbonyl group inserts into the N-Ir bond while the sulfur atom covers the vacant coordination position. In the second case, the uncoordinated nitrogen adds to the carbonyl group to straightforwardly give the new organic ligand. Both possibilities have been proposed in the reactions of carbon monoxide with amido and imido complexes of rhodium.²⁹ Molecular models suggest that the S-coordination of benzothiazole-2-thiolate is preferred for steric reasons and that the second alternative is the most probable. Then the carbonyl group simply undergoes a nucleophilic attack by the aromatic nitrogen of benzothiazole-2-thiolate. On the other hand, this reaction is quite uncommon for tertiary amines and heterocyclic compounds due to their reluctance to give formyl derivatives. In fact, homogeneous catalysis of the water-gas shift reaction and related reactions in organic basic solvents, in which nucleophilic attack at carbonyl groups is involved, is carried out in pyridine and tertiary amines to avoid side reactions.²³ In this case, the reaction involves the unprecedented attack of a heterocycle at coordinated carbon monoxide, resulting in the carbonylation of the nitrogen to give a new organic ligand without loss of the aromaticity of this ring.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen atmosphere using Schlenk techniques, but isolations of most of the compounds were performed in air. Solvents were dried by refluxing over Na/benzophenone ketyl or CaH₂ and distilled under nitrogen immediately before use. ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectra were recorded on a Varian XL-200 operating at 200.057, 80.984, and 50.309 MHz respectively; chemical shifts are reported relative to tetramethylsilane and phosphoric acid as external references. IR spectra (range 4000-200 cm⁻¹) were recorded on a Perkin-Elmer 783 spectrometer as Nujol mulls between polyethylene sheets or in solution in NaCl windows. Elemental analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Molecular weights were determined with a Knauer osmometer using chloroform solutions of the complexes. Mass spectra were recorded with a VG Autospec apparatus using the FAB method. O_2 and H_2 were used as received. SO_2 was prepared according to a reported method and dried through H₂SO₄. $H_2^{18}O(99\%)$ was purchased from Aldrich and used as received, and HBF4 OEt2 (54% solution in diethyl ether) was purchased from Merck. $[IrCl(CO)(PPh_3)_2]^{30}$ and $[IrH_2(Me_2CO)_2(PPh_3)_2]$ - $[PF_6]^{31}$ were prepared by literature procedures.

Preparation of the Compounds. [Ir($C_7H_4NS_2$)(CO)-(**PPh**₃)₂] (1). A solution of 2-mercaptobenzothiazole (0.033 g, 0.20 mmol) in tetrahydrofuran (10 mL) was added to a solution of *n*-butyllithium (0.12 mL, 1.64 mol L⁻¹, 0.20 mmol) in hexane.

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After the mixture was stirred for 10 min, solid [IrCl(CO)-(PPh₃)₂] (0.156 g, 0.20 mmol) was added and the mixture refluxed for 1 h to give a bright red solution. Concentration of this solution to ca. 1 mL and slow addition of diethyl ether rendered complex 1 as a yellow microcrystalline solid which was filtered, washed with methanol, and dried under vacuum (yield 0.154 g, 85%). Anal. Calcd for C₄₄H₃₄IrNOP₂S₂: C, 58.00; H, 3.76; N, 1.53. Found: C, 57.76; H, 4.01; N, 1.40. Molecular weight: calcd, 911; found, 738. IR (cm⁻¹, CH₂Cl₂): ν (CO) 1966 s. ³¹P{¹H} NMR (δ , CDCl₃, 293 K): 26.6 (s).

[IrH(C₇H₄NS₂)(CO)(PPh₃)₂]BF₄ (3). Tetrafluoroboric acid in diethyl ether (17 μL, 0.12 mmol) was added to a solution of the complex [Ir(C₇H₄NS₂)(CO)(PPh₃)₂] (1; 0.12 mmol) in a mixture of tetrahydrofuran and diethyl ether (1:5; 10 mL). The yellow solid immediately formed was filtered, washed with diethyl ether, and vacuum dried (yield 90%). Anal. Calcd for C₄₄H₃₅BF₄IrNOP₂S₂: C, 52.90; H, 3.53; N, 1.40. Found: C, 52.45; H, 3.72; N, 1.37. Molar conductivity, Λ_M (S cm² mol⁻¹, acetone): 128. IR (cm⁻¹): ν(Ir-H) (Nujol) 2185 m; ν(CO) (CH₂-Cl₂) 2060 s. ¹H NMR (δ, CDCl₃, 293 K): 7.44-7.29 (m, 32H, PPh₃ and C₇H₄NS₂); 7.00 (dd, 1H, C₇H₄NS₂); 6.78 (d, 1H, C₇H₄-NS₂); -14.51 (t, J_{H-P} = 10 Hz, 1H, Ir-H). ³¹P{¹H} NMR (δ, CDCl₃, 293 K): 10.5 (s).

[IrH(C₇H₄NS₂)₂(CO)(PPh₃)₂] (4). Solid 2-mercaptobenzothiazole (0.019 g, 0.11 mmol) was added to a solution of the complex 1 (0.100 g, 0.11 mmol) in tetrahydrofuran (10 mL). The mixture was refluxed for 2 h to give a colorless solution. Evaporation under vacuum to 1 mL and slow addition of diethyl ether gave white crystals of the complex, which were filtered, washed with diethyl ether, and dried under vacuum (yield 0.093 g, 65%). Anal. Calcd for C₅₁H₃₉IrN₂OP₂S₄: C, 56.81; H, 3.64; N, 2.59. Found: C, 56.45; H, 4.05; N, 2.17. IR (cm⁻¹): ν (Ir-H) (Nujol) 2165 m; ν (CO) (CH₂Cl₂) 2030 s. ¹H NMR (δ , CDCl₃, 293 K): 7.64 (m, 16H) and 7.10 (m, 22H) PPh₃ and C₇H₄NS₂ ligand; -11.67 (t, J_{H-P} = 11 Hz, 1H, Ir-H). ³¹P-{¹H} NMR (δ , CDCl₃, 293 K): 1.8 (s).

Reaction of $[IrH(C_7H_4NS_2)_2(CO)(PPh_3)_2]$ (4) with HBF₄. EtO₂. Tetrafluoroboric acid in diethyl ether (7.6 μ L, 0.05 mmol) was added to a stirred solution of the complex 4 (0.060 g, 0.05 mmol) in dichloromethane (3 mL). The mixture was stirred for 30 min, and then diethyl ether (15 mL) was added. A yellow microcrystalline solid was immediately formed, which was filtered, washed with diethyl ether, and vacuum-dried. The compound was identified as the complex 3 (0.050 g, 90%) by comparison of its spectroscopic properties.

[IrH₂(C₇H₄NS₂)(CO)(PPh₃)₂] (5). Hydrogen was bubbled through a solution of complex 1 (0.091 g, 0.10 mmol) in tetrahydrofuran (5 mL) for 10 min, and then the solution was stirred under a hydrogen atmosphere for 4 h. Concentration of the resulting yellow solution to ca. 1 mL and addition of diethyl ether gave the complex as a white microcrystalline solid which was isolated by filtration (yield 0.073 g, 80%). Anal. Calcd for C₄₄H₃₆IrNOP₂S₂: C, 57.88; H, 3.97; N, 1.53. Found: C, 58.38; H, 4.85; N, 1.44. Molecular weight: calcd, 913; found, 931. IR (cm⁻¹, Nujol): ν(Ir-H) + ν(CO) 2120, 2090, 1988. ¹H NMR (δ, CDCl₃, 293 K): 7.44 (m, 12H, PPh₃); 7.40 (m, 1H, C₇H₄NS₂); 7.25 (m, 1H, C₇H₄NS₂); 7.16 (m, 18H, PPh₃); 7.10 (m, 1H), 7.00 (m, 1H) (C₇H₄NS₂); -9.25 (td, J_{H-P} = 18 Hz, J_{H-H} = 4 Hz, 1H, Ir-H); -14.77 (td, J_{H-P} = 15 Hz, J_{H-H} = 4 Hz, 1H, Ir-H). ³¹P{¹H} NMR (δ, CDCl₃, 293 K): 11.0 (s).

 $[IrH_2(C_7H_4NS_2)(PPh_3)_2]$ (6). Solid $[IrH_2(Me_2CO)_2(PPh_3)_2]$ -PF₆ (0.150 g, 0.15 mmol) was added to a solution of LiC₇H₄-NS₂ in tetrahydrofuran (10 mL) prepared by reaction of 2-mercaptobenzothiazole (0.025 g, 0.15 mmol) with butyllithium (0.10 mL, 1.54 mol L⁻¹, 0.15 mmol) in hexane. The mixture was reacted for 30 min to give a yellow solution, which was concentrated to ca. 1 mL under vacuum. Addition of methanol to the concentrate gave the complex as a white solid which was separated by filtration, washed with methanol, and vacuum-dried (yield 0.088 g, 65%). Anal. Calcd for C₄₃H₃₆IrNP₂S₂: C, 58.31; H, 4.06; N, 1.58. Found: C, 58.67; H, 4.52; N, 1.58. Molecular weight: calcd, 884; found, 874.

Table 3. Experimental Data for the X-rayDiffraction Studies of Compounds 8 and 11

	8	11
formula	C44H34IrNO3P2S2	C44H34IrNO5P2S3
mol wt	943.04	1007.10
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1$
radiation (λ, \mathbf{A})	graphite monochromated	nickel filtered
	(Mo Ka, 0.710 73)	(Cu Ka, 1.541 78)
a, Å	15.626(6)	14.414(8)
b, Å	20.568(8)	20.220(6)
c, Å	11.996(5)	14.800(5)
β , deg	93.52(2)	107.41(2)
V, Å ³	3848(3)	4116(3)
Ζ	4	4
$D_{ m calcd},{ m g}~{ m cm}^{-3}$	1.628	1.625
F(000)	1872	2000
cryst size, mm	0.15 imes 0.24 imes 0.35	0.10 imes 0.22 imes 0.30
μ , cm ⁻¹	36.82 (Mo Ka)	86.92 (Cu Ka)
diffractometer	Philips PW 1100	Siemens AED
scan type	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	3 - 12	3-12
θ range, deg	3-23	3 - 70
std rfln	one measd after	100 reflctns
rflns measd	hkl	hkl
no. of unique data total	5520	8374
no. of unique data obsd $(I > 2\sigma(I))$	3643	5324
R^{a}	0.0344	0.0423
$R_{\mathrm{w}}{}^{b}$	0.0441	0.0526

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|$, ${}^{b}R_{w} = [\sum w(|F_{o}| - |F_{c}|)^{2} / \sum w(F_{o})^{2}]^{1/2}$.

IR (cm⁻¹, Nujol): ν (Ir-H) 2150 m, 2110 m. ¹H NMR (δ , CDCl₃, 293 K): 7.65 (m, 12H, PPh₃); 7.52 (m, 1H, C₇H₄NS₂); 7.13 (m, 18H, PPh₃); 7.07 (m, 1H), 6.78 (t, 1H), 6.75 (d, 1H) (C₇H₄NS₂); -21.23 (td, $J_{H-P} = 16$ Hz, $J_{H-H} = 7$ Hz, 1H, Ir-H); -22.68 (td, $J_{H-P} = 16$ Hz, $J_{H-H} = 7$ Hz, 1H, Ir-H). ³¹P{¹H} NMR (δ , CDCl₃, 293 K): 22.8 (s).

[Ir(C₇H₄NS₂)(O₂)(CO)(PPh₃)₂] (7). Oxygen was bubbled though a solution of complex 1 (0.100 g, 0.11 mmol) in dichloromethane (5 mL) for 10 min. The solution was stirred under an oxygen atmosphere for 30 min and then concentrated under vacuum to ca. 1 mL. Addition of hexane gave the complex as an off-white solid, which was washed several times with hexane and then vacuum-dried (yield 0.077 g, 75%). Anal. Calcd for C₄₄H₃₄IrNO₃P₂S₂: C, 56.04; H, 3.63; N, 1.48. Found: C, 54.98; H, 3.52; N, 1.38. IR (cm⁻¹): ν (CO) (CH₂Cl₂) 2015 s; ν (O–O) (Nujol) 885 s. ³¹P{¹H} NMR (δ , CDCl₃, 293 K): 6.1 (s).

 $[Ir(C_7H_4NS_2)(CO_3)(PPh_3)_2]$ (8). An orange solution of the complex 1 (0.150 g, 0.16 mmol) in tetrahydrofuran (15 mL) and distilled water (3 mL) was stirred under an oxygen atmosphere for 2 h to give a yellow solution. The solvents were removed under vacuum, and the residue was extracted with dichloromethane. The extract was dried over MgSO₄ and concentrated to ca. 1 mL. Addition of diethyl ether gave yellow crystals of complex 8, which were filtered, washed with diethyl ether, and vacuum-dried (yield 0.120 g, 78%). Anal. Calcd for C44H34IrNO3P2S2: C, 56.04; H, 3.63; N, 1.48. Found: C, 55.90; H, 3.86; N, 1.35. Molecular weight: calcd, 943; found, 966. IR (cm⁻¹, Nujol): ν (CO) 1683 s. ¹³C{¹H} NMR (δ , CDCl₃, 293 K): 181.6 (CS), 125.2, 122.3, 119.5, 114.5 (CH), 145.1, and 128.9 (C₇H₄NS₂ ligand); 133, 129.3, 127.0, 126.2 (PPh₃ ligands); 167.1 (CO₃). ${}^{31}P{}^{1}H$ NMR (δ , CDCl₃, 293 K): -3.8 (s). MS (FAB): $m/e 944(M^+ + H, 45\%), 882(M^+ - HCO_3, 100\%)$. Good quality crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in dichloromethane.

 $[Ir(C_7H_4NS_2)Cl_2(PPh_3)_2]$ (9). A solution of HCl (0.8 mL, 0.21 mol L⁻¹, 0.17 mmol) in acetone was added to a solution of complex 8 (0.080 g, 0.08 mmol) in dichloromethane (10 mL)

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent^a Isotropic Thermal Parameters (Å² $\times 10^4$) for the Non-Hydrogen Atoms of Complex 8

atom	x/a	y/b	z/c	$U_{ m eq}$	atom	x/a	y/b	z/c	$U_{ m eq}$
Ir	2570.6(2)	667.4(2)	754.8(3)	312(1)	C(19)	4322(8)	1752(6)	3827(9)	663(48)
S(1)	4083(2)	397(1)	819(2)	405(8)	C(20)	3655(7)	1448(5)	3191(8)	540(39)
S(2)	4029(2)	-1107(1)	209(2)	544(10)	C(21)	1595(6)	682(5)	3387(7)	374(31)
P (1)	2539(2)	425(1)	2683(2)	338(8)	C(22)	1676(7)	943(5)	4479 (8)	546(39)
P(2)	2699(2)	994 (1)	-1109(2)	358(8)	C(23)	937(9)	1044(6)	5048(9)	694(49)
O(1)	1282(4)	906(4)	656(5)	440(24)	C(24)	125(9)	900(6)	4589(11)	718(51)
O (2)	2282(4)	1624(3)	1117(5)	415(22)	C(25)	36(7)	640(6)	3494(10)	640(43)
O(3)	878(5)	1933(4)	1044(7)	658(30)	C(26)	788(6)	545(5)	2868(9)	522(39)
Ν	2798(5)	-290(4)	360(6)	355(27)	C(27)	2929(6)	330(5)	-2081(7)	377(32)
C(1)	3642(6)	-329(5)	433 (7)	399(33)	C(28)	2264(7)	43(6)	-2730(9)	666(45)
C(2)	2967(7)	-1387(5)	3(8)	550(41)	C(29)	2479(9)	-507(7)	-3379(11)	861(58)
C(3)	2725(10)	-2030(6)	-193(10)	804(55)	C(30)	3316(8)	-741(6)	-3384(9)	614(44)
C(4)	1842(12)	-2119(8)	-362(12)	1035(69)	C(31)	3956(7)	-434(6)	-2769(8)	579(41)
C(5)	1231(9)	-1626(8)	-267(10)	822(56)	C(32)	3766(7)	99 (5)	-2107(8)	484(37)
C(6)	1509(7)	-973(6)	-49(9)	618(43)	C(33)	3551(6)	1577(5)	-1285(8)	426(34)
C(7)	2390(7)	-877(5)	107(8)	498(39)	C(34)	3853(7)	1957(5)	-354(8)	496(37)
C(8)	1428(7)	1527(5)	959(8)	453(39)	C(35)	4477(7)	2427(5)	-522(9)	597(43)
C(9)	2613(7)	-422(5)	3065(7)	439(35)	C(36)	4805(7)	2530(5)	-1587(9)	580(43)
C(10)	3393(7)	-774(5)	2893(8)	505(39)	C(37)	4482(7)	2161(5)	-2496(8)	523(39)
C(11)	3436(8)	-1436(5)	3109(8)	579(43)	C(38)	3871(7)	1684(5)	-2352(8)	556(40)
C(12)	2753(9)	-1762(5)	3550(10)	688(51)	C(39)	1730(6)	1385(5)	-1715(7)	460(37)
C(13)	2008(8)	-1429(5)	3759(11)	751(52)	C(40)	945(7)	1055(6)	-1692(7)	537(41)
C(14)	1930(7)	-751(6)	3510(10)	620(44)	C(41)	179(7)	1340(7)	-2127(8)	674(49)
C(15)	3425(6)	822(5)	3486(7)	417(35)	C(42)	229(9)	1985(8)	-2578(9)	810(59)
C(16)	3845(7)	509(5)	4415(8)	521(39)	C(43)	983(10)	2320(7)	-2587(9)	836(57)
C(17)	4507(7)	848(7)	5016(9)	647(47)	C(44)	1765(7)	2032(6)	-2152(8)	602(43)
C(18)	4750(7)	1459(6)	4712(9)	596(44)					

^a Equivalent isotropic U, defined as one-third of the trace of the orthogonalized \mathbf{U}_{ij} tensor.

slowly to give a yellow-green solution in 10 min. This solution was dried over MgSO₄ and then filtered. Concentration of the filtrate to ca. 1 mL and addition of diethyl ether rendered yellow crystals of the complex, which were isolated by filtration, washed with diethyl ether, and vacuum-dried (yield 0.056 g, 70%). Anal. Calcd for C₄₃H₃₄Cl₂IrNP₂S₂: C, 54.14; H, 3.95; N, 1.46. Found: C, 53.84; H, 4.34; N, 1.37. Molecular weight: calcd, 954; found, 990. ³¹P{¹H} NMR (δ , CDCl₃, 293 K): -9.8 (s).

Reaction of [Ir(C₇H₄NS₂)(O₂)(CO)(PPh₃)₂] (7) with NH₃. A solution of the dioxygen complex 7 (prepared as described above; 0.16 mmol) in dichloromethane (10 mL) was stirred under an NH₃ atmosphere for 48 h. Concentration of the orange solution to 2 mL and addition of diethyl ether gave a yellow solid, which was filtered, washed with diethyl ether, and vacuum-dried. The compound was identified as the carbonate complex 8 (yield 0.120 g, 80%) by comparison of the IR and NMR spectra with those obtained from a pure sample. When the reaction time is reduced to 12 h and the mixture worked up as above, pale yellow solids containing mixtures of the carbonate complex and the starting material are obtained.

Reaction of $[Ir(C_7H_4NS_2)(O_2)(CO)(PPh_3)_2]$ (7) with HBF₄·EtO₂. Method A. NMR-Monitored Experiment. A 5 mm NMR tube was charged with 0.5 mL of a CDCl₃ solution (0.06 mol L⁻¹) of the dioxygen complex 7 (0.03 mmol) and HBF₄·EtO₂ (7 μ L, 0.05 mmol) to give a yellow solution. The reaction was periodically monitored by ¹H NMR spectroscopy. After 30 min a yellow microcrystalline solid precipitated off.

Method B. Preparative-Scale Experiment. HBF_4EtO_2 (42 μ L, 0.30 mmol) was added to a solution of the dioxygen complex 7 (0.15 mmol) in dichloromethane (10 mL; prepared as described above). The color of the solution changed from red to orange-yellow, and a pale yellow solid precipitated off. The suspension was stirred for 2 h and then concentrated to 2 mL. Addition of diethyl ether (15 mL) gave [Ir(C₇H₄NS₂)-(H₂O)₂(PPh₃)₂](BF₄)₂ (10) as a yellow solid, which was recrystallized from acetone/diethyl ether (yield 0.125 g, 76%). Anal. Calcd for C₄₃H₃₈B₂F₈IrNO₂P₂S₂: C, 47.26; H, 3.50; N, 1.28. Found: C, 47.01; H, 3.47; N, 1.15. IR (cm⁻¹, Nujol): 3350, 1650 (H₂O); 1080 (BF₄). [Ir{C(O)NC(S)SC₆H₄}(SO₄)(PPh₃)₂] (11). Oxygen was bubbled through a solution of complex 1 (0.170 g, 0.18 mmol) in tetrahydrofuran (10 mL) for 30 min to give a solution of complex 7. Then, SO₂ was bubbled for 10 min to give a pale yellow solution which was stirred under a SO₂ atmosphere for 2 h to render a yellow solid, which was filtered, washed with tetrahydrofuran, and vacuum-dried (yield 0.125 g, 68%). Anal. Calcd for C₄₃H₃₄IrNO₄P₂S₃: C, 52.76; H, 3.50; N, 1.43. Found: C, 52.79; H, 3.71; N, 1.25. IR (cm⁻¹, Nujol): 1680 ν -(C=O); 1257, 1155, 927, 890, 690, 650 (SO₄). MS (FAB): *m/e* 1007 (M⁺ - H, 45%), 911 (M⁺ - SO₄, 28%), 882 (M⁺ - HSO₄ - CO, 100%). ³¹P{¹H} NMR (δ , CDCl₃, 293 K): -6.0 (s). Good quality crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the complex in dichloromethane.

X-ray Data Collection, Structure Determination, and Refinement for Compounds 8 and 11. The crystallographic data for both compounds are summarized in Table 3. Data were collected at room temperature (22 °C) on a Philips PW 1100 (8) and on a Siemens AED diffractometer (11), using graphite-monochromated Mo Ka (8) and nickel-filtered Cu Ka radiation (11) and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of $3-12^{\circ}$ min⁻¹ for both compounds and a scan width (deg) of 1.30 \pm 0.346 tan θ (8) and $1.30 + 0.142 \tan \theta$ (11). One standard reflection was monitored every 75 measurements; no significant decay was noticed over the time of data collection. The individual profiles have been analyzed by following the method of Lehmann and Larsen.³² Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied (maximum and minimum values for the transmission factors were 1.09 and 0.94 (8), 1.174 and 0.889 (11)).³³ Only the observed reflections were used in the structure solutions and refinements.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, first with isotropic thermal parameters and then with anisotropic ther-

⁽³²⁾ Lehmann, M. S.; Larsen, F. K. Acta Crystallogr., Sect. A 1974, 30, 580.

 ⁽³³⁾ Walker, N.; Stuart, D. Acta Crystallogr., Sect. A 1983, 39, 158.
 Ugozzoli, F. Comput. Chem. 1987, 11, 109.

Table 5.	Atomic Coordinates ($\times 10^4$) and Equivalent ^a Isotropic Thermal Parameters (Å ² $\times 10^4$) for t	he						
Non-Hydrogen Atoms of Complex 11								

			• •			A			
atom	x/a	y/b	z/c	U	atom	x/a	y/b	z/c	U
Ir(1)	81.7(5)	2500	4627.8(5)	347(2) ^a	Ir(2)	5418.9 (5)	1986.1(4)	-56.0(5)	$368(2)^a$
S(11)	-99(3)	3624(2)	4300(3)	$408(14)^{a}$	S(12)	5633(3)	873(2)	224(3)	$480(14)^{a}$
S(21)	1138(3)	4708(2)	5428(3)	$449(14)^a$	S(22)	4390(3)	-201(2)	-936(3)	$574(16)^{a}$
S(31)	-802(3)	1328(2)	3896(3)	401(13) ^a	S(32)	6255(3)	3171(2)	746(3)	$436(14)^{a}$
P(11)	-939(2)	2590(2)	5614(2)	310(11) ^a	P(12)	6456(3)	1925(2)	-1036(2)	418(13) ^a
$\mathbf{P}(21)$	1133(3)	2431(3)	3655(3)	419(13) ^a	P(22)	4344(2)	2022(2)	879(2)	342(11)ª
O(11)	-1060(6)	2026(6)	3538(6)	437(34) ^a	O(12)	6614(7)	2466(6)	1012(6)	474(34) ^a
O(21)	92(7)	1481(4)	4735(6)	$225(30)^{a}$	O(22)	5398(6)	3036(4)	-104(6)	209(25) ^a
O(31)	-1573(7)	1061(5)	4225(8)	496(43) ^a	O(32)	5913(8)	3453(6)	1474(8)	555(44)ª
O(41)	-519(8)	918(6)	3225(7)	567(46) ^a	O(42)	6984(8)	3582(6)	528(9)	589(48)ª
O(51)	1732(7)	2410(6)	6300(8)	$551(45)^{a}$	O(52)	3777(7)	2117(5)	-1706(8)	$542(43)^{a}$
N(11)	1416(8)	3479(6)	5828(8)	380(45) ^a	N(12)	4109(9)	1045(6)	-1291(8)	410(45) ^a
C(11)	842(11)	3902(7)	5223(12)	432(59) ^a	C(12)	4698(11)	620(9)	-684(11)	$512(61)^{a}$
C(21)	2078(11)	4495(8)	6397(10)	435(59) ^a	C(22)	3377(11)	34(8)	-1918(12)	491(61) ^a
C(31)	2175(10)	3818(7)	6538(10)	$362(50)^{a}$	C(32)	3358(11)	727(7)	-2000(10)	$425(52)^{a}$
C(41)	2876(10)	3524(8)	7255(10)	$448(59)^{a}$	C(42)	2622(10)	1029(9)	-2715(10)	464(58) ^a
C(51)	3522(11)	3939(9)	7904(14)	$622(72)^{a}$	C(52)	1955(12)	613(7)	-3314(12)	508(61) ^a
C(61)	3492(15)	4623(11)	7750(13)	$722(85)^{a}$	C(62)	1991(13)	-74(9)	-3199(14)	663(75) ^a
C(71)	2774(11)	4891(9)	7037(13)	663(77) ^a	C(72)	2720(12)	-379(9)	-2497(12)	603(69) ^a
C(81)	1197(11)	2749(8)	5708(12)	$465(62)^a$	C(82)	4315(11)	1764(6)	-1120(10)	357(52) ^a
C(91)	-1144(10)	1841(7)	6151(10)	418(37)	C(92)	3266(11)	1488(8)	416(11)	464(37)
C(101)	-347(13)	1436(10)	6558(12)	590(48)	C(102)	3358(13)	820(9)	612(13)	594(46)
C(111)	-467(14)	823(10)	6924(13)	668(52)	C(112)	2591(15)	389(11)	180(15)	779(59)
C(121)	-1408(13)	601(9)	6852(13)	646(49)	C(122)	1750(16)	657(12)	-445(16)	860(65)
C(131)	-2201(14)	986(10)	6454(13)	667(52)	C(132)	1666(15)	1303(11)	-668(15)	764(57)
C(141)	-2055(12)	1606(8)	6096(12)	578(45)	C(142)	2414(13)	1734(10)	-253(13)	650(51)
C(151)	-410(11)	3170(8)	6640(11)	427(37)	C(152)	4820(12)	1760(8)	2087(12)	528(42)
C(161)	178(11)	2928(8)	7515(11)	484(40)	C(162)	5786(12)	1715(8)	2534(13)	597(45)
C(171)	633(13)	3372(10)	8213(14)	649(51)	C(172)	6181(14)	1499(9)	3470(13)	600(48)
C(181)	532(12)	4043(9)	8065(12)	542(43)	C(182)	5519 (15)	1349(11)	3934(16)	853(61)
C(191)	-48(13)	4284(10)	7198(13)	642(52)	C(192)	4488(15)	1360(11)	3541(15)	801(62)
C(201)	-510(11)	3857(8)	6507(12)	507(40)	C(202)	4164(16)	1598(10)	2603(15)	803(62)
C(211)	-2143(10)	2951(7)	5105(10)	372(33)	C(212)	3819(11)	2844(8)	951(11)	502(39)
C(221)	-2554(11)	2993(8)	4133(11)	504(42)	C(222)	3453(12)	3209(9)	121(13)	595(48)
C(231)	-3467(12)	3255(9)	3727(12)	568(45)	C(232)	3048(15)	3856(11)	143(15)	770(58)
C(241)	-3941(13)	3515(10)	4333(13)	648(52)	C(242)	3001(15)	4096(12)	983(15)	864(65)
C(251)	-3580(14)	3458(10)	5337(14)	784(58)	C(252)	3386(15)	3756(11)	1799(15)	822(59)
C(261)	-2641(13)	3211(9)	5675(14)	667(52)	C(262)	3778(14)	3104(11)	1816(15)	769(57)
C(271)	1620(12)	1583(9)	3639(13)	561(45)	C(272)	5942 (11)	1422(8)	-2114(11)	469 (38)
C(281)	1989(12)	1239(9)	4438(12)	511(44)	C(282)	5411(14)	1735(11)	-2945(14)	809(59)
C(291)	2358(14)	605(11)	4461(16)	773(60)	C(292)	4964(13)	1325(11)	-3739(15)	678(53)
C(301)	2256(15)	337(12)	3591(16)	940(69)	C(302)	4961(15)	670(11)	-3666(15)	803(58)
C(311)	1935(14)	649 (10)	2776(15)	791(60)	C(312)	5472(11)	373(9)	-2838(12)	566(42)
C(321)	1557(12)	1299(10)	2759(13)	627(49)	C(322)	5950 (14)	770(10)	-2065(14)	651(50)
C(331)	2223(11)	2966(8)	4099(11)	466(39)	C(332)	7612(12)	1526(9)	-471(12)	536(42)
C(341)	3055(11)	2732(9)	4744(11)	552(44)	C(342)	7972(12)	1473(9)	508(12)	548(42)
C(351)	3801(15)	3155(11)	5144(15)	794(60)	C(352)	8883(15)	1159(11)	885(16)	822(62)
C(361)	3728(13)	3828(9)	4948(12)	575(47)	C(362)	9398 (18)	902(13)	359(18)	920(75)
C(371)	2894(12)	4074(10)	4307(12)	601(48)	C(372)	9054(18)	961(12)	-642(18)	945(74)
C(381)	2175(13)	3624(9)	3881(12)	549(44)	C(382)	8188(13)	1288(10)	-1040(15)	695(53)
C(391)	667(11)	2736(8)	2444(11)	471(41)	C(392)	6711(11)	2734(8)	-1458(11)	487(38)
C(401)	-339(13)	2827(9)	2039(13)	660(50)	C(402)	7676(14)	2936(10)	-1385(14)	691(53)
C(411)	-684(17)	3088(12)	1148(16)	995(71)	C(412)	7734(16)	3594(11)	-1753(15)	849(64)
C(421)	-35(18)	3162(14)	584(19)	1134(84)	C(422)	6983(16)	3979(12)	-2069(15)	876(67)
C(431)	932(15)	3014(11)	963(15)	844(65)	C(432)	6058(18)	3812(12)	-2175(17)	876(72)
C(441)	1263(12)	2839(8)	1901(12)	558(43)	C(442)	5919(14)	3157(10)	-1864(13)	614(50)

^a Equivalent isotropic U, defined as one-third of the trace of the orthogonalized \mathbf{U}_{ij} tensor.

mal parameters for the non-hydrogen atoms, except for the carbon atoms of the phenyl rings of 11. Since the space group $P2_1$ leads to a chiral configuration in the structure of 11, a refinement of the non-hydrogen atoms with anisotropic thermal parameters was carried out using the coordinates -x, -y, -z; a slight decrease in the R and R_w values was obtained $(R(x,y,z) = 0.0462, R_w(x,y,z) = 0.0555; R(-x,-y,-z) = 0.0449,$ $R_{\rm w}(-x,-y,-z) = 0.0538$). The latter model was selected, and the reported data refer to this model. All hydrogen atoms were placed at their geometrically calculated positions and refined "riding" on the corresponding carbon atoms (with isotropic thermal parameters). The final cycles of refinement were carried out on the basis of 512 (8) and 665 (11) variables; after the last cycles, no parameters shifted by more than 0.81 (8) and 0.97 (11) esd. The highest remaining peak in the final difference map was equivalent to about 0.94 (8) and 0.98 (11)

e/Å³. In the final cycles of refinement the weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence the K and g values were 0.570 and 0.0047 (8) and 0.643 and 0.0029 (11), respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref 34. All calculations were carried out on the Gould Powernode 6040 and Encore 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, Italy, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.³⁵ The final atomic coordinates for the non-hydrogen atoms are given in Tables 4 (8) and 5 (11). The atomic coordinates of the hydrogen atoms are given in Tables SI (8) and SII (11) and

⁽³⁴⁾ International Tables for X-Ray Crystallography; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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the thermal parameters in Tables SIII (8) and SIV (11) (supporting information).

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Supporting Information Available: Atomic coordinates of the hydrogen atoms (Tables SI (8) and SII (11)), thermal parameters (Tables SIII (8) and SIV (11)), and all bond distances and angles (Tables SV (8) and SVI (11)) (18 pages). Ordering information is given on any current masthead page.

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