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Reaction of singlet oxygen with Ir(I) and Rh(I) thiolato complexes: oxidative addition *vs.* S-oxidation†

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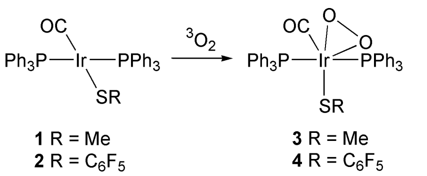
Singlet oxygen reacts with Ir(I) and Rh(I) thiolato complexes to form the corresponding Ir(III) and Rh(III) peroxo thiolato complexes which do not undergo intramolecular oxidation of the thiolate moiety.

There have been a number of reports of reactions of triplet[1,2] and singlet[1f,3,4] dioxygen with a variety of metal thiolate complexes leading to formation of isolable sulfenato and sulfinato complexes. In all cases, the primary site of attack by the dioxygen molecule appears to have been the thiolate moiety rather than the metal atom; no peroxo thiolato complexes have been observed as intermediates. For coordinatively unsaturated thiolato complexes, however, attack at either the metal or the thiolate ligand is *a priori* possible. We reasoned that studying the reactivity of singlet dioxygen with such complexes would be particularly interesting, since singlet oxygen tends to be more reactive both with thiolato ligands[1f,4] and with late transition metal centers such as Rh(I) and Ir(I)[5] than ground state oxygen. We have therefore prepared a number of Rh(I) and Ir(I) thiolato complexes containing electron-rich and electron-poor thiolato ligands, and have studied their reactivity with triplet and singlet dioxygen. Such thiolato complexes are of great interest as their high catalytic activity in hydroformylation is well documented.[6] We now report that oxidative addition of the dioxygen molecule to the metal center of such complexes is generally preferred over S-oxidation, and that the resulting peroxo thiolato complexes are in fact remarkably resistant towards intramolecular oxidation.

The mononuclear Ir(I) thiolato complexes *trans*-Ir(CO)(PPh_3)$_2$(SR) (**1**: R = Me,[7] **2**: R = C_6F_5[8]) react with triplet dioxygen to form stable peroxo thiolato complexes Ir(III)(CO)(PPh_3)$_2$(SR)O_2 (**3**: R = Me, **4**: R = C_6F_5[9]) [eqn. (1)]. No oxidation of the thiolate moiety is observed during the reaction.



(1)

For complex **2**, the same peroxo thiolato complex **4** is cleanly obtained upon reaction with singlet dioxygen; no oxidation at the sulfur is observed. Reaction of complex **1** with singlet dioxygen also leads to some formation of the corresponding peroxo thiolato complex **3**, accompanied by extensive decomposition and formation of triphenylphosphine oxide. Since the peroxo thiolato complex **3** itself is very stable (see below), the decomposition must result from attack of a second singlet oxygen molecule on the thiolate ligand. Since triphenylphosphine oxide is one of the reaction products, we hypothesize that the intermediate persulfoxide formed by attack of $^1O_2$ on the sulfur is trapped intramolecularly by one of the phosphine ligands. Support for this hypothesis is derived from the observation that the peroxo complex **3** itself slowly reacts with singlet oxygen resulting in the same intractable mixture of decomposition products. X-Ray molecular structures have been obtained for both peroxo thiolato complexes, and the ORTEP diagrams of **3** and **4** are shown in Fig. 1.‡ The peroxo complexes **3** and **4** are remarkably stable, and despite the proximity of the peroxo ligand to the sulfur of the thiolato group, no intramolecular attack on the thiolate ligand is observed. Even upon

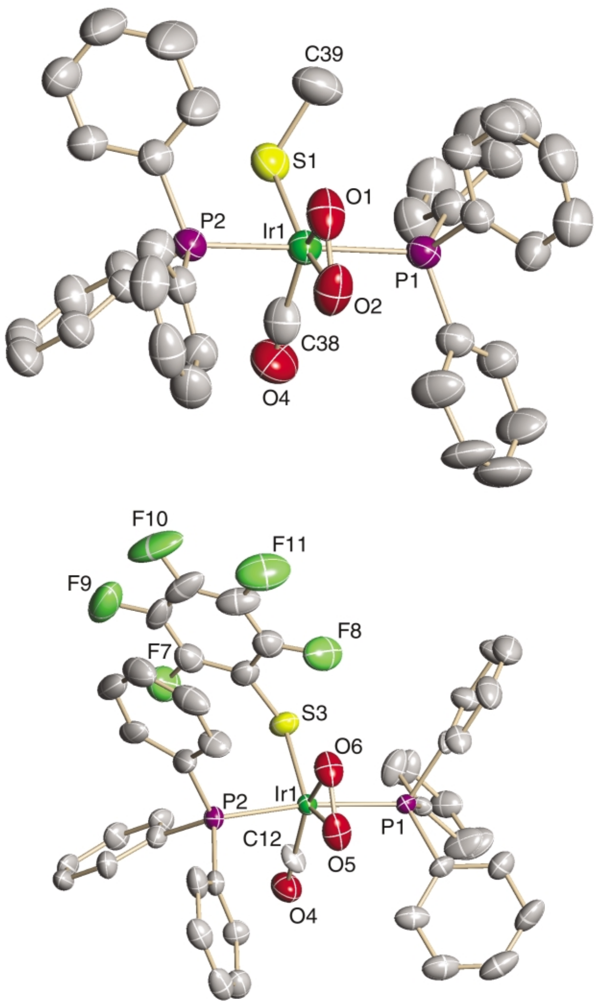


Fig. 1 (Top): ORTEP diagram of the peroxo thiolato complex **3**. Selected bond lengths (Å) and angles (°): O(1)···S(1) 3.69, O(1)–O(2) 1.473(3), Ir(1)–C(38) 1.917(7), Ir(1)–S(1) 2.375(2), Ir(1)–O(1) 2.027(2), Ir(1)–P(1) 2.3575(8), Ir(1)–P(2) 2.3563(8); O(1)–Ir(1)–S(1) 116.70(8), C(38)–Ir(1)–S(1) 92.2(2). (Bottom): ORTEP diagram of peroxo thiolato complex **4**. Selected bond lengths (Å) and angles (°): O(6)···S(3) 3.55, O(5)–O(6) 1.474(9), Ir(1)–C(12) 1.891(9), Ir(1)–S(3) 2.436(3), Ir(1)–O(5) 2.2029(6), Ir(1)–O(6) 2.017(6), Ir(1)–P(1) 2.388(3), Ir(1)–P(2) 2.400(3); O(6)–Ir(1)–S(3) 105.2(3), C(12)–Ir(1)–S(3) 92.4(8).

† Electronic supplementary information (ESI) available: experimental crystallographic details. See http://www.rsc.org/suppdata/cc/b1/b110396m/

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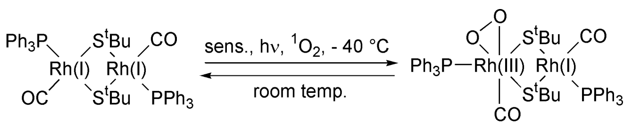
refluxing in benzene under nitrogen or irradiation under nitrogen, complex **4** reductively eliminates dioxygen to re-form complex **1**, rather than attacking the thiolate ligand. Complex **3** is stable in refluxing benzene and under irradiation without significant loss of dioxygen or oxidation of the thiolate ligand!

The related Rh(I) complex *trans*-$Rh(CO)(PPh_3)_2(SR)$ (**5**: R = C_6F_5[8]) also reacts with singlet dioxygen to form the corresponding previously unknown peroxo thiolato complex Rh(III)$(CO)(PPh_3)_2(SC_6F_5)O_2$ (**6**). This complex is unstable at room temperature, and decomposes into a mixture of the starting complex **5** and the dinuclear Rh(I) complex $[Rh(CO)(PPh_3)(SC_6F_5)]_2$. Again, no oxidation of the thiolate ligand is observed. Mononuclear Rh(I) complexes $Rh(CO)(PPh_3)_2(SR)$ bearing more electron-rich thiolate ligands cannot be isolated, as they rapidly dimerize even at very low temperature.[10] Such dimers might react with singlet oxygen by four different pathways, namely (i) oxidative addition at one of the metal centers, leading to a dimer containing one Rh(I) and one Rh(III) center; (ii) oxidative addition at both metal centers; (iii) formation of a μ-peroxo bridged dimer, or (iv) oxidation of the bridging thiolate ligands. We therefore studied the reaction of *trans*-$[Rh(CO)(PPh_3)(S^tBu)]_2$[11] (**7**) with singlet oxygen. At −40 °C, reaction of **7** with $^1O_2$ leads to formation of the remarkable mixed dimer Rh(III)$(O_2)(CO)(PPh_3)(\mu\text{-}S^tBu)_2$Rh(I)$(CO)(PPh_3)$ (**8**)[12] [eqn. (2)]. Formation of this species is



7 **8** (2)

reversible, and warming leads to re-formation of starting material, implying that no oxidation of the bridging thiolato ligand occurs. Singlet oxygen luminescence quenching studies are consistent with this reactivity, as the rate of singlet oxygen removal by **7** is approximately twice that of the mononuclear species **5**, indicating that the quenching of singlet oxygen occurs by a similar mechanism as in the mononuclear complexes (Table 1).

Table 1 Singlet oxygen luminescence quenching constants for Ir(I) and Rh(I) thiolato complexes

Compound	$K_T \times 10^8\ M^{-1}\ s^{-1}$ in $CDCl_3$
$Ir(CO)(PPh_3)_2(SCH_3)$ (**1**)	2.0 ± 0.3
$Ir(CO)(PPh_3)_2(SC_6F_5)$ (**2**)	1.3 ± 0.1
$Rh(CO)(PPh_3)_2(SC_6F_5)$ (**5**)	1.6 ± 0.2
$[Rh(CO)(PPh_3)(S^tBu)]_2$ (**7**)	3.3 ± 0.2

Singlet oxygen luminescence quenching rates by all other complexes have also been obtained and are summarized in Table 1.[14] All complexes remove singlet oxygen with very large rates, comparable with those of Vaska's complex and derivatives,[5] consistent with attack of singlet dioxygen at the metal. The lack of reactivity of the thiolate ligands of the Ir(I) and Rh(I) complexes is in remarkable contrast with that of several Co and Ni complexes.[1,4] The peroxo ligand on group VIII peroxo complexes has often been considered to be nucleophilic. The lack of intramolecular oxidation of both electron-poor and electron-rich thiolate ligands by the peroxo group indicates that this group should at times be considered unreactive rather than nucleophilic.

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Notes and references

‡ *Crystal data* for **3**: $C_{38}H_{33}IrO_3P_2S$, M = 823.84, monoclinic, space group $P2_1/c$ (no. 14), a = 9.7548(8), b = 17.652(1), c = 22.680(2) Å, β = 99.540(1)°, V = 3851.4(5) Å³, Z = 4, D_c = 1.776 g cm⁻³, T = 293(2) K, μ = 4.545 mm⁻¹, 8454 total reflections, 5625 observed reflections, 487 parameters, $R1$ (all data) = 0.0528, $wR2$ (all data) = 0.0769.

For **4**: $C_{43}H_{30}F_5IrO_3P_2S$, M = 975.87, triclinic, space group $P\bar{1}$ (no. 2), a = 9.878(8), b = 11.854(6), c = 18.538(9) Å, α = 99.98(4), β = 101.32(5), γ = 111.39(5)°, V = 1909.2(20) Å³, Z = 2, D_c = 1.698 g cm⁻³, T = 293(2) K, μ = 3.699 mm⁻¹, 4895 total reflections, 4010 observed reflections, 472 parameters, $R1$ (all data) = 0.0699, $wR2$ (all data) = 0.1131.

CCDC reference numbers 179090 and 179091. See http://www.rsc.org/suppdata/cc/b1/b110396m/ for crystallographic data in CIF or other electronic format.

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7 Complex **1** was prepared by treatment of $IrCl(CO)(PPh_3)_2$ with a stoichiometric amount of $AgBF_4$ in CH_3CN followed by addition of ethanolic $NaSCH_3$.

8 This was prepared as previously described: M. H. B Stiddard and R. E. Townsend, *J. Chem. Soc. (A)*, 1970, 2719.

9 Complex **4** has been previously obtained by slow reaction of **2** with ground state dioxygen. However, only IR data have been reported. See ref. 8.

10 Treatment of complexes $[Rh(CO)(PPh_3)_2(NCCH_3)]^+(BF_4)^-$ with ethanolic NaSR (R = Me, ^{t}Bu) should initially lead to formation of the mononuclear species; however, even at −80 °C, only the corresponding dimers were observed.

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12 Complex **8** is easily identified by its ^{31}P NMR spectrum which gives two doublets of doublets [δ 34.34 (dd, 1P, J_{Rh-P} 144 Hz, J_{P-P} 7 Hz); 27.37 (dd, 1P, J_{Rh-P} 102 Hz, J_{P-P} 7 Hz)]. The Rh–P coupling constant of 144 Hz is consistent with a square planar Rh(I) center, whereas the smaller Rh–P coupling constant is consistent with an octahedral Rh(III) center. See ref. 13.

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14 Time-resolved singlet oxygen luminescence quenching experiments were conducted by exciting a solution containing the sensitizer (TPP or methylene blue) and varying amounts of substrate (quencher) with a short (a few ns) laser pulse and monitoring the singlet oxygen luminescence decay at a right angle.