The First Transition Metal Thiosulphinate and Sulphenate Esters: $[Ir(\eta^2\text{-}S_2OMe)(dppe)_2]^{2+}$ and $[Ir(\eta^1\text{-}SOMe)(MeNC)(dppe)_2]^{2+}$ [dppe = 1,2-bis(diphenylphosphino)ethane]

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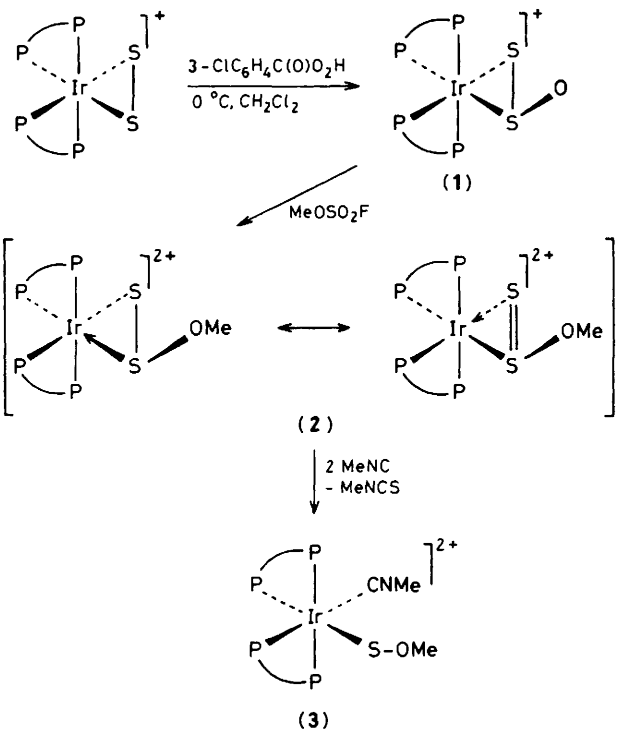
$[Ir(S_2O)(dppe)_2]^+$ reacts with $MeOSO_2F$ giving $[Ir(\eta^2\text{-}S_2OMe)(dppe)_2]^{2+}$ which was characterised by *X*-ray crystallography and can be converted into $[Ir(\eta^1\text{-}SOMe)(MeNC)(dppe)_2]^{2+}$ [dppe = 1,2-bis(diphenylphosphino)ethane].

Sulphenic acids, RSOH, and their esters, RSOR, are classes of metastable compounds which are hybrids between peroxides and disulphides.[1] Alkyl *O*-sulphenic acids (ROSH) and their salts, ROS^-M^+, have not been reported and in the absence of special stabilising effects they may be assumed to be very reactive. The ability of metal ions to stabilise otherwise highly reactive sulphur fragments like SO,[2] S_2,[3] and S_3[4] suggested that a similar strategy should be successful in developing the chemistry of alkyl *O*-sulphenic acid derivatives.

We have found that one equivalent of triphenylphosphine reacts with $[Ir(S_2O)(dppe)_2]^+$ (**1**) [dppe = 1,2-bis(diphenylphosphino)ethane][5] to give Ph_3PS, but very little Ph_3PO and $[Ir(S_2)(dppe)_2]^+$. This indicates that the unsubstituted sulphur is the most electrophilic site on (**1**) and this is consistent with similar results in the $[Ir(\eta^2\text{-}S_2Me)(dppe)_2](PF_6)_2$ system.[6] Complementary to this finding, protonation (CF_3CO_2H) and methylation ($MeOSO_2F$) studies establish that the exocyclic oxygen is the most nucleophilic site on (**1**). Thus, treatment of



Scheme 1. P–P = 1,2-bis(diphenylphosphino)ethane.

(1) with $MeOSO_2F$ (1.1 equiv., CH_2Cl_2 solution, 25 °C, 1 day), followed by anion metathesis afforded $[Ir(S_2OMe)(dppe)_2](PF_6)_2$ (2) in 70% yield as pale yellow crystals from CH_2Cl_2–MeOH (Scheme 1). The 360 MHz ^1H n.m.r. spectrum of (2)† exhibits two pseudotriplets of equal intensity high field of the main phenyl proton resonances; this behaviour is characteristic of a *cis*-$[IrXY(dppe)_2]^{n+}$ species.[7] The lack of observable ^{31}P coupling to the single methyl n.m.r. signal indicated that O-methylation occurred with the formation of only one diastereoisomer.

Crystal data: (2), $C_{53}H_{51}F_{12}IrOP_6S_2$, $M = 1374.1$, monoclinic, space group $P2_1/c$, $a = 12.414(2)$, $b = 23.165(3)$, $c = 23.620(4)$ Å, $\beta = 117.70(1)°$, $U = 6014(2)$ Å^3, $Z = 4$, $D_c = 1.518$ g cm^{-3}; data were collected on a Syntex $P2_1$ automated diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) up to $2\theta = 55°$. The structure was solved by Patterson methods using 10284 independent reflections with $I > 2.56\sigma(I)$. The refinement converged to $R = 0.059$ ($R_w = 0.094$).‡ It is seen that (2) consists of the unprecedented S_2OMe^- moiety co-ordinated in the η^2-fashion to a *cis*-$[Ir(dppe)_2]^{3+}$ fragment (Figure 1). The bond distances and angles within the sulphur chelate are close to those expected for single bonds between sp^3-hybridized S_2OC atoms. The S · · · S bond distance at 2.01 Å is *ca.* 0.03—0.05 Å, shorter than observed in $[Ir(S_2O_2)(dppe)_2]PF_6$[8] and $[Ir(S_2)(dppe)_2]^+$.[9]

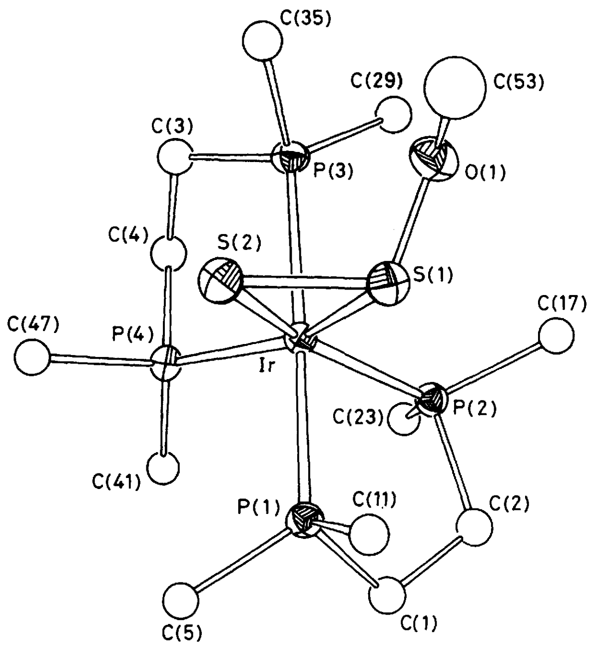


Figure 1. Crystal structure of (2). For clarity, the phenyl substituents and hydrogens on the dppe ligands have been omitted. The PF_6^- counterions have also been excluded. Selected bond distances and angles are: Ir–S(1) 2.368(2), Ir–S(2) 2.431(2), S(1)–S(2) 2.011(3), S(1)–O(1) 1.619(8), O(1)–C(53) 1.46(2), Ir–P(4) 2.372(2), Ir–P(2) 2.359(2), Ir–P(3) 2.435(2), Ir–P(1) 2.404(2) Å: S(1)–Ir–S(2) 49.53(8), Ir–S(1)–S(2) 66.88(10), Ir–S(2)–S(1) 63.6(1), S(2)–S(1)–O(1) 109.6(3), S(1)–O(1)–C(53) 114.8(8), S(1)–Ir–P(3) 91.76(8), S(2)–Ir–P(3) 89.42(8), S(1)–Ir–P(1) 85.40(8), S(2)–Ir–P(1) 86.39(8), S(1)–Ir–P(2) 105.75(8), S(2)–Ir–P(4) 109.03(8), P(2)–Ir–P(4) 95.99(8)°.

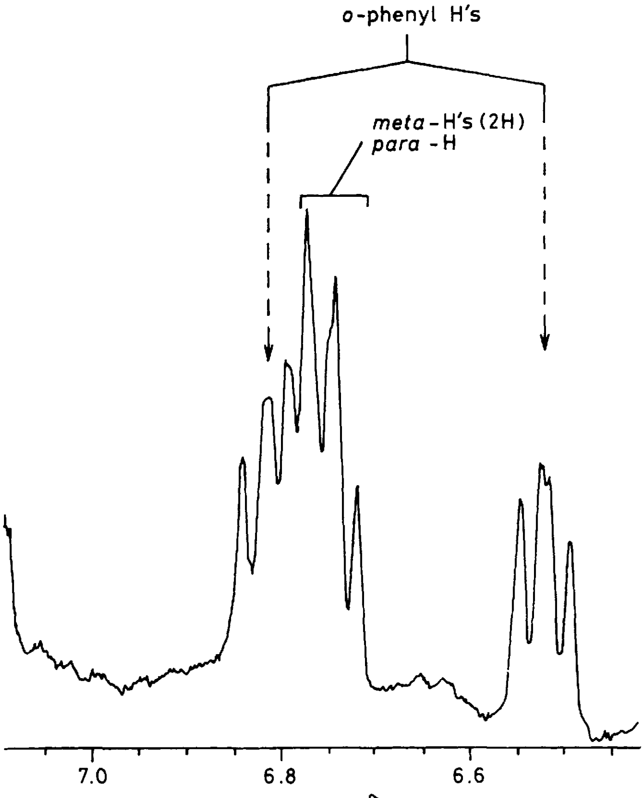


Figure 2. ^1H N.m.r. (360 MHz) of (3) showing high-field shifted aromatic resonances. Phenyl resonances at δ 7.1—8.0 have been omitted for clarity.

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† δ (3 : 1 v/v $CDCl_3$–CD_3NO_2, 20 °C) 6.47 and 6.29 (4H, pseudotriplet, $^3J_{HH}$ approx. = $^3J_{PH}$ 8–9 Hz, high-field *o*-phenyl H's), 3.08 (3H, s, OMe). Satisfactory analytical data were obtained.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23800 (59 pp.) from the British Library Lending Division. For details of how to obtain this material, see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, issue 3, p. xvii.

The results can be accommodated by viewing the S_2OMe ligands as a hybrid of two resonance forms, as shown in Scheme 1. A similar rationale has been applied to η^2-acyl complexes. The orientation of the OMe group in the cleft between the two dppe chelates suggests that steric effects, and the rigidity of the S_2OC subunit, give rise to only one diastereoisomer in contrast to $[Ir(\eta^2\text{-}S_2Me)(dppe)_2]^{2+}$ where a 15:1 equilibrium mixture of diastereoisomers is formed.[6]

Compound (**2**) is a potent sulphur-transfer agent and reacted with 2 equivalents of MeNC ($CDCl_3$–CD_3NO_2 solution, 25 °C, 1 day) to yield MeNCS (*ca.* 1 equiv.) and *cis*-$[Ir(SOMe)(MeNC)(dppe)_2](PF_6)_2 \cdot CHCl_3$, (**3**) isolated in 50% yield (Scheme 1). In comparison, MeNC reacted very slowly with (**1**) at 40 °C and failed to react with elemental sulphur at 80 °C. Satisfactory elemental analyses (C, H, N, P, S, Cl) and spectroscopic evidence confirmed that (**3**) contains the new η^1-SOMe ligand *cis* to the MeNC group. The ^{1}H n.m.r. spectrum revealed two high-field *o*-phenyl resonances (δ 6.81 and 6.52) and two methyl singlets, δ 3.44 (MeNC) and 2.64 (MeOS) (no J_{PH} observed). The i.r. spectrum of (**3**) in $MeNO_2$ solution showed a strong ν_{CN} absorption at 2243 cm^{-1}. The field-desorption mass spectrum (F.D.M.S.) revealed comparably intense sets of signals centred at *m/z* 547 (M^{2+}) and 1238 $[(MPF_6)^+]$ whose intensity distributions were satisfactorily simulated. Although comparably strong dication signals are rare in F.D.M.S., we find that they are a recurring feature in $[IrXY(dppe)_2]^{2+}$ complexes. The ability of (**3**) to desorb at 100 °C with retention of one PF_6^- counterion is striking. Another peculiar spectroscopic feature of (**3**) is that its ^{1}H n.m.r. signals for certain *meta*- and *para*-phenyl protons actually overlap the high-field *ortho*-phenyl resonances (Figure 2). A decoupling experiment showed that the *meta* protons were definitely on a phenyl ring unique from that which bears the high-field *ortho*-phenyl protons. This behaviour indicates unusual shielding interactions in (**3**) which, we suggest, reflect considerable steric crowding.

In summary, we have shown how the reactions of the coordinated S_2O moiety, and in principle related heterocumulenes, can be used to prepare stable derivatives of highly reactive organosulphur compounds.

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