O-Bonded and *S*-Bonded Sulphinate Complexes of Iridium(I) and Iridium(III). Ligand Isomerisation accompanying Change in Co-ordination Number

By C. A. REED and W. R. ROPER*

(*Department of Chemistry, University of Auckland, Auckland, New Zealand*)

Summary The four-co-ordinate iridium(I) compound, $Ir(O_2S\text{-}p\text{-tolyl})(CO)(PPh_3)_2$ has *O*-bonded sulphinate but uptake of carbon monoxide or dioxygen results in isomerisation to *S*-bonded sulphinate while addition of methyl iodide leaves the ligand *O*-bonded.

THE sulphinate ion can co-ordinate to a metal through either sulphur or oxygen, the particular atom being indicative of the bonding character of the co-ordination site. It is generally found[1] that class *a* acceptors bind through oxygen and class *b* acceptors through sulphur and in keeping with this generalisation the known sulphinate derivatives of the platinum metals are all *S*-bonded except for one instance [in $Pt_2(SO_2\text{-}p\text{-tolyl})_2(SnCl_3)_2(PEt_3)_2$[2]] in which it appears that the sulphinate ligand is bridging. $IrCl_2(SO_2\text{-}p\text{-tolyl})(CO)(PPh_3)_2$ is prepared by addition of sulphonyl halide to $IrCl(CO)(PPh_3)_2$ and has the sulphinate *S*-bonded.[3] To investigate further the nature of the bonding site for anionic ligands in four-co-ordinate complexes of the type $IrX(CO)(PPh_3)_2$ we have prepared $Ir(O_2S\text{-}p\text{-tolyl})(CO)$-

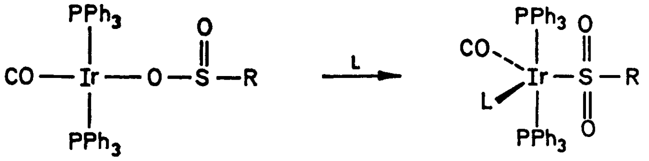
$(PPh_3)_2$ (I), from $[Ir(MeCN)(CO)(PPH_3)_2]ClO_4$[4] and sodium toluene-*p*-sulphinate. The ν(SO) frequencies observed for (I) (see Table) require *O*-bonded sulphinate.[1] The possibility of a bridging situation existing in a dimer or polymer can be discounted in view of the similarity of ν(CO) with that for other $IrX(CO)(PPh_3)_2$ complexes, the compounds normal solubility, and a molecular weight determination in benzene (osmometer; 37 °C, *M*, found 890; calc. 899).

TABLE

I.r. frequencies[a] *for iridium sulphinates*[b] (cm^{-1})

	ν(SO)	ν_{as}(SOIr)	$\nu_{as}(SO_2)$	$\nu_s(SO_2)$	Other bands
$Ir(O_2S$-*p*-tolyl)$(CO)(PPh_3)_2$	1085s	855vs, 840s			1955vs[ν(CO)]
$Ir(SO_2$-*p*-tolyl)$(CO)_2(PPh_3)_2$			1155s, 1140s	1020s, 1010s	1940vs 2000vs[ν(CO)]
$Ir(O_2)(SO_2$-*p*-tolyl)$(CO)(PPh_3)_2$			1210vs, 1190vs	1050s	2025vs[ν(CO)] 835s[ν(IrO_2)]
$Ir(SO_4)(SO_2$-*p*-tolyl)$(CO)(PPh_3)_2$			1240s	1060s	2055vs[ν(CO)] 1300vs, 1190vs 890s, 860s, 660s(SO_4)
$Ir(Me)I(O_2S$-*p*-tolyl)$(CO)(PPh_3)_2$	1075s	870s			2040vs[ν(CO)]

[a] All measured for Nujol mulls. [b] Satisfactory elemental analyses have been obtained for all compounds reported.



L = CO or O_2, R = *p*-tolyl

The unexpected preference of the site *trans* to carbon monoxide in $IrX(CO)(PPh_3)_2$ for 'hard' ligands is shown also by the *N*-bonded selenocyanate complex[5] and the existence of $Ir(OH)(CO)(PPh_3)_2$[4] and $IrF(CO)(PPh_3)_2$.[4] Like other members of this series (I) reacts with CO and O_2 forming the five-co-ordinate complexes $Ir(SO_2$-*p*-tolyl)$(CO)_2(PPh_3)_2$ and $Ir(O_2)(SO_2$-*p*-tolyl)$(CO)(PPh_3)_2$ but in doing so the sulphinate ligand switches from *O*- to *S*-bonded. The CO uptake is easily reversed but the O_2 uptake is irreversible. When $Ir(O_2)(SO_2$-*p*-tolyl)$(CO)(PPh_3)_2$ is converted into the chelated sulphate $Ir(SO_4)(SO_2$-*p*-tolyl)$(CO)(PPh_3)_2$ through reaction with SO_2 the sulphinate remains *S*-bound. The further co-ordination of both CO and O_2 requires electron transfer from iridium to these ligands [it has been estimated that 1·8 electrons transfer from Pt to O_2 in $Pt(O_2)(PPh_3)_2$][6] and since this coincides with a switch from *O*- to *S*-bonded sulphinate it can be concluded that *S*-bonded sulphinate is a good σ-donor. This same conclusion was drawn from a consideration of the strong *trans*-influence of the *S*-bonded sulphinate in platinum compounds[2] but it conflicts with other views.[1]

Oxidation of (I) with methyl iodide produces an iridium (III) compound in which *O*-bonded sulphinate persists (see Table). Steric factors could be influencing the preferred isomer in this case as they can do in sulphoxide complexes.[7]

(*Received, September 20th,* 1971; *Com.* 1649.)

[1] G. Vitzthum and E. Lindner, *Angew. Chem. Internat. Edn.*, 1971, **10**, 315.
[2] J. Chatt and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 1770.
[3] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1966, **88**, 180.
[4] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758.
[5] J. L. Burmeister and N. J. DeStefano, *Chem. Comm.*, 1970, 1698.
[6] C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, 1971, **93**, 1904.
[7] J. H. Price, R. F. Schramm, and B. B. Wayland, *Chem. Comm.*, 1970, 1377.