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Preliminary communication

New sulphinate complexes of the Group IB metals and their oxidation by molecular oxygen

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SUMMARY

The preparation of some sulphinate complexes of the Group IB metals is reported, and the reaction of the complexes with molecular oxygen has been studied.

A large number of transition metal sulphinate complexes have been prepared in recent years, primarily as a result of studies on the SO_2 insertion reaction[1,2]. The majority of these complexes contain S-bonded sulphinate ligands, although a number of O-bonded complexes are also known.

We report here the new Group IB sulphinate complexes $(Ph_3P)_2CuO_2SPh$, $(Ph_3P)_2AgO_2SPh$ and Ph_3PAuSO_2Ph. The Cu and Ag complexes may be prepared by the metathetical exchange reaction of Ph_3PMCl with AgO_2SPh in tetrahydrofuran (THF) solution under N_2, followed by addition of a mole of Ph_3P. The gold complex may also be prepared by this metathetical route or, alternatively, by the reaction of Ph_3PAuPh with SO_2. The copper and silver complexes are shown by their infrared spectra[2,3] to be O,O′-bonded while the gold complex is S-bonded (Table 1).

TABLE 1

INFRARED SPECTRA OF NEW COMPLEXES[a]

Compound	*ν(S–O) (cm^{-1})*
$(Ph_3P)_2CuO_2SPh$	1028 (sh), 1020 s, 964 s
$(Ph_3P)_2AgO_2SPh$	1032 (sh), 1024 s, 967 s
Ph_3PAuSO_2Ph	1203 s, 1049 s
$(Ph_3P)_2CuO_3SPh$	1248 s, 1150 s, 1117 s, 1014 vs
$(Ph_3P)_2AuO_3SPh$	1214 s, 1124 m, 1020 m

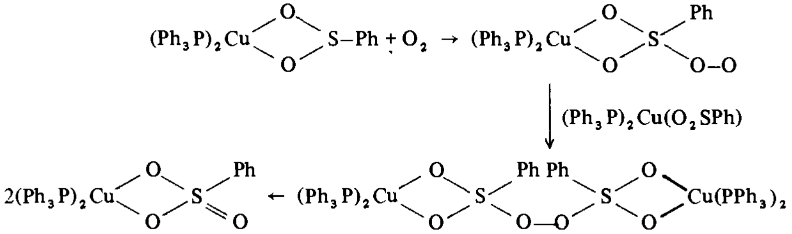
[a] Recorded in nujol mulls All new complexes have been characterised by elemental analysis.

We find that the Cu and Au complexes are readily oxidised to sulphonate complexes by molecular oxygen, a reaction which does not appear to have been reported previously for either transition metal or main group metal sulphinate complexes.

Aerial oxidation of the copper complex is complete after 1½ h in either THF or $CHCl_3$ solution and takes place slowly even in a nujol mull. In contrast the silver and gold sulphinate complexes are entirely unaffected by air either in the solid state or in solution. On addition of 1 mole of Ph_3P to a THF solution of the gold complex, however, oxidation to the sulphonate complex $(Ph_3P)_2AuSO_3Ph$ proceeds smoothly and at approximately the same rate as in the case of the copper complex.

The above data can best be accounted for by a mechanism of oxidation which involves electrophilic attack of oxygen on the sulphur atom of the sulphinate ligand. Such a mechanism (Scheme 1) can only operate for O-bonded complexes since the sulphur atom is coordinatively saturated in S-bonded complexes. A similar mechanism has been proposed to account for the ready oxygenation of $Ni(SO_2)(Bu\text{-}t\text{-}NC)_3$ to $Ni(SO_4)(Bu\text{-}t\text{-}NC)_2$ as compared to the inertness of $Pd_3(SO_2)(Bu\text{-}t\text{-}NC)_5$ towards oxygen[4,5]. The fact that the oxidation of Ph_3PAuSO_2Ph only proceeds in the presence of excess Ph_3P suggests that an equilibrium with an O-bonded isomer of formula $(Ph_3P)_2AuO_2SPh$, analogous to the copper and silver complexes already described, may be established, and that it is this O-bonded isomer which undergoes oxidation. We were, however, unable to detect the presence of such an isomer from solution infrared measurements.

SCHEME 1



The transfer of one oxygen atom to the sulphinate ligand is best explained by the formation of an intermediate dimeric complex similar to that previously postulated to account for the oxidation of Co–NO to Co–NO_2 complexes by molecular oxygen[6]. An alternative possibility is that Ph_3P is concurrently oxidised to Ph_3PO, but the oxidation of $(Ph_3P)_2CuO_2SPh$ is not speeded up by the addition of excess Ph_3P nor is Ph_3PO formed in detectable amounts in the reaction.

The fact that only O-bonded sulphinate complexes can undergo oxidation by the above mechanism explains why the majority of transition metal sulphinate complexes, which are S-bonded, do not undergo this reaction. Not all O-bonded complexes undergo oxidation by aerial oxygen, however, and coordination of the sulphinate ligand to a metal in a low oxidation state, which presumably increases the electron density on the sulphur atom, seems also to be a requirement. However, since neither $(Ph_3P)_2AgO_2SPh$ nor the recently reported iridium complex, $Ir(PPh_3)_2(CO)(OSOC_6H_4Me)$ [7], are oxidised to sulphonate complexes by aerial oxygen other factors must also clearly be involved.

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