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Preliminary communication

SULFENE-TRANSITION METAL COMPLEXES FROM SO_2 ADDITION TO TERMINAL METHYLENE COMPLEXES OF OSMIUM(0) AND IRIDIUM(I). STRUCTURE OF $\overline{\mathrm{Os(CH_2S[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$

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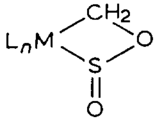
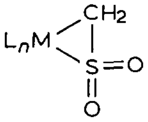
Summary

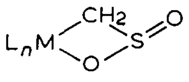
The methylene complexes $\mathrm{Os(=CH_2)Cl(NO)(PPh_3)_2}$ and $\mathrm{Ir(=CH_2)I(CO)(PPh_3)_2}$ form 1/1 adducts with SO_2 and X-ray crystal structure determination of the osmium complex, $\overline{\mathrm{Os(CH_2S[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$, reveals that the sulfene fragment ($\mathrm{CH_2SO_2}$) is C,O-bound forming a non-planar four-membered ring with the S atom having pyramidal geometry.

The osmium—carbon double bond in $\mathrm{Os(=CH_2)Cl(NO)(PPh_3)_2}$ reacts with various electrophiles, e.g., protic acids, halogens, $\mathrm{(AuPPh_3)^+}$ and chalcogens [1]. With CO and CNR coupling reactions occur and C,C-bound ketene and ketenimine complexes result [2]. In a continuing study of the reactions of the $\mathrm{L_nM{=}CH_2}$ functionality with various small molecules we report here that both $\mathrm{Os(=CH_2)Cl(NO)(PPh_3)_2}$ and the related iridium methylene complex $\mathrm{Ir(=CH_2)I(CO)(PPh_3)_2}$ [3] form yellow-orange crystalline 1/1 adducts with SO_2. The structure of these adducts follow from spectroscopic studies and X-ray crystal structure analysis of the osmium compound.

Possible structural arrangements to be considered for these adducts are:


(A)


(B)


(C)

HCl reacts with the two adducts to give complete loss of the sulfene fragment and formation of $\mathrm{OsCl_3(NO)(PPh_3)_2}$ and $\mathrm{IrCl_2I(CO)(PPh_3)_2}$, respectively. This counts against structures A and B since osmium and iridium S-bound fragments

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TABLE 1

IR DATA^a FOR SULFENE AND RELATED COMPOUNDS

Compound^b	ν(SO)	ν(NO) or ν(CO)
$\overline{\mathrm{Os(CH_2S[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$	1120s,1100s,788m	1797vs
$\overline{\mathrm{Ir(CH_2S[O]O}}\mathrm{)I(CO)(PPh_3)_2}$	1105s 800m	2025vs
$\mathrm{Ir(OS[O]R)MeI(CO)(PPh_3)_2}$	1075s 870m	
$\mathrm{Ir(O_2)(SO_2R)(CO)(PPh_3)_2}$	1210s,1190s,1050s	

^{a}cm^{-1} measured as Nujol mulls. ^{b}Both SO_2 adducts have satisfactory elemental analyses.

would be expected to be retained in isolable complexes upon reaction with HCl. Furthermore, the ν(SO) bands observed in the IR spectra (see Table 1) are not similar to other *S*-sulfinato compounds, e.g. $\mathrm{Ir(O_2)(SO_2\text{-}}p\mathrm{\text{-}tolyl)(CO)(PPh_3)_2}$ but more like those of *O*-sulfinato-compounds [4]. Structure C is therefore most likely and since SO_2 forms adducts with Lewis bases, e.g., Me_3N [5] which are S-bound and with Lewis acids, e.g., SbF_5 [6] which are O-bound, it is to be expected in view of other evidence that the carbene centres in these methylene complexes are nucleophilic [1,3]. To confirm this structure an X-ray crystal structure determination of $\overline{\mathrm{Os(CH_2S[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$ was undertaken. Single crystals were grown from CH_2Cl_2/C_6H_{12}. Crystal data: *a* 12.635(2), *b* 13.737(3), *c* 10.224(4) Å, α 90.89(3), β 97.52(2), γ 76.66(2)°. Triclinic, space group $P\bar{1}$, $Z = 2$. $\mu(\text{Mo-}K_\alpha)$ 42.30 cm^{-1}. The structure was solved by the heavy-atom method and refined by a full-matrix least-squares technique to a final *R* of 0.033 for 5612 observed reflections. Anisotropic thermal motion was assumed for all non-hydrogen atoms except those of the phenyl rings. These latter atoms were restrained as rigid groups. Two disordered positions were located for the S and terminal O of the chelate ring. These are not equally weighted at any one crystallographic site (Fig. 1 shows one contributor) although overall the crystal contains equal numbers of two enantiomers. The observed Os—C and C—S bond

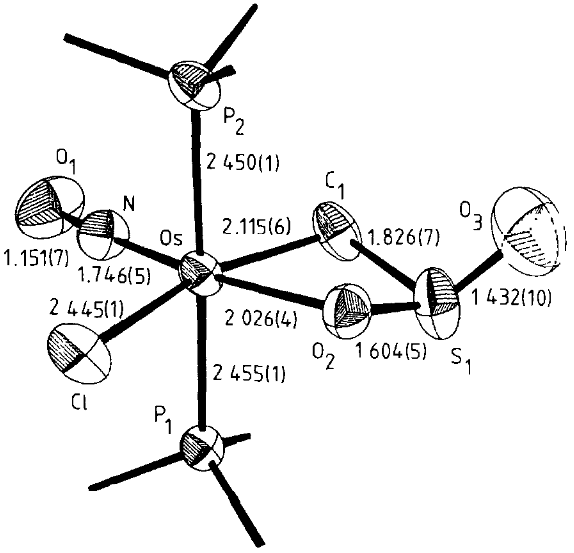
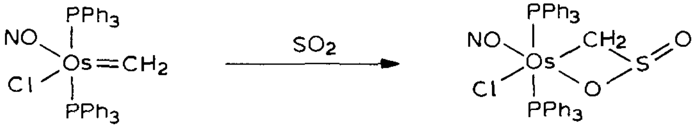


Fig. 1. Molecular structure of $\overline{\mathrm{Os(CH_2S[O]O}}\mathrm{)Cl(NO)(PPh_3)_2}$ with phenyl groups omitted for clarity.

distances are appropriate for single bonds and the reaction forming the SO_2-adduct may be written:



An alternative mode of bonding for the sulfene fragment, μ-C,S has been reported for a bimetallic rhodium complex [7].

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