The Structure of a Bis(dimethyl sulphoxide)iridium(III) Complex containing a Metal–Carbon σ-Bond

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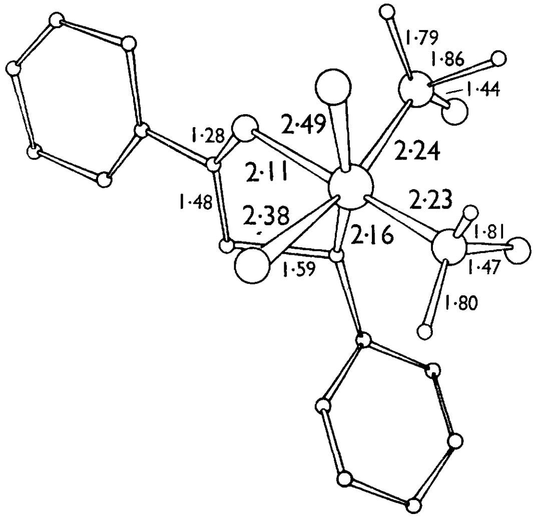
THE catalysis of the reduction of ketones to alcohols and hydrogenation of unsaturated ketones by iridium complexes has been discussed by Henbest and his colleagues.[1,2] An *X*-ray analysis of the iridium(III) complex isolated by Trocha-Grimshaw and Henbest[2] has been completed, the main structural features being shown in the Figure.

The iridium(III) ion has a distorted octahedral co-ordination made up of two dimethyl sulphoxide (Me_2SO) molecules co-ordinated through their sulphur atoms, two chloride ions, and a benzylacetophenone forming a puckered five-membered chelate ring.



FIGURE

The observation of the *cis*-dimethyl sulphoxide ligands co-ordinating through their sulphur atoms is of interest in relation to the structures of palladium– and iron–Me_2SO complexes.[3] While in $[Fe(Me_2SO)_4Cl_2][FeCl_4]$ the Me_2SO is oxygen-bonded, in *trans*-$PdCl_2(Me_2SO)_2$ it is sulphur-bonded. The covalent radius of octahedral iridium(III) may be estimated as 1·38 Å from the *shorter* Ir–Cl bond length of 2·38 Å (*vide infra*) while the covalent radius of sulphur is estimated as 1·05 Å from the mean S–C(H_3) bond length of 1·82 Å. The sum of the Ir^{III}–S covalent radii is therefore 2·43 Å, 0·19 Å ($\sim 35\sigma$) longer than the observed value. Bennett *et al.*,[3] comment on the possibility of $d\pi$–$d\pi$ bonding between the filled *d* orbitals of palladium(II) and empty sulphur *d* orbitals. In the palladium complex, this must, judged from the Pd–S bond length of 2·300 Å, be very small—the palladium(II) radius is estimated as 1·29 Å from the Pd–Cl bond length of 2·288 Å so that the calculated sum of radii is $1{\cdot}29 + 1{\cdot}05 = 2{\cdot}34$ Å, only 0·04 Å greater than the observed value. These calculations must, however, only be taken as indicating a trend among the bond lengths since they suffer from all the defects associated with a 'hard-sphere' approximation.

The iridium–chlorine bond length *trans* to the σ-bonded carbon atom is 0·09 Å (18σ) larger than the *cis*-value. This lengthening is very similar to that found, for example, in the square-planar platinum(II) complex, K $Pt(Acac)_2Cl$,[4] where the two Pt–O bond lengths *cis* and *trans* to the σ-bonded carbon atom differ by 0·12 Å and to the difference of 0·08 Å in the *cis* and *trans* Pt–Br bonds in an octahedral platinum(IV) complex containing a σ-bonded carbon atom.[5]

The geometry of the chelate ring clearly suggests that the formation of the cyclic organoiridium complex described by Trocha-Grimshaw and Henbest[2] occurs through the Markownikoff addition of the iridium hydride across the carbon–carbon double bond of the benzylideneacetophenone. Additions of this type are of interest in connection with suggestions which have been made on the mechanisms of homogeneous isomerisation of olefins[6] since similar mechanisms may be anticipated for the catalytic hydrogenation of unsaturated ketones.

The crystals of $(C_{15}H_{13}O)Cl_2Ir(Me_2SO)_2$ are triclinic with a unit cell $a = 7{\cdot}47$, $b = 11{\cdot}51$, $c = 13{\cdot}61$ Å, $\alpha = 101{\cdot}5°$, $\beta = 108{\cdot}0°$, $\gamma = 90{\cdot}0°$. The integrated intensities of 2309 reflexions with $F_0^2/\sigma F_0^2 \geqslant 2{\cdot}5$ have been measured on a 'Pailred' automatic diffractometer; a least squares refinement of atomic co-ordinates derived by Patterson and Fourier methods has converged the discrepancy index to 0·081 when the average estimated standard deviations are Ir–Cl 0·005 Å, Ir–C 0·015 Å, C–S 0·020 Å, C–O and C–C 0·025 Å.

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