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Preliminary communication

A TRIPLY BRIDGED DIMERIC IRIDIUM(III) HYDRIDE: μ-CHLORODI-μ-(PHENYLTHIO)DI{HYDRIDOBIS(TRIPHENYLPHOSPHINE)IRIDIUM(III)} PERCHLORATE, $[(Ph_3P)_2(H)Ir(SPh)_2ClIr(H)(PPh_3)_2]ClO_4 \cdot 3(CH_3)_2CO$

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Summary

The dimeric iridium(III) hydride, $[IrHCl(SPh)(PPh_3)_2]_2$ has been shown to react with silver perchlorate in acetone to produce the triply bridged dimeric species, $[(Ph_3P)_2(H)Ir(SPh)_2ClIr(H)(PPh_3)_2]ClO_4 \cdot 3(CH_3)_2CO$, whose structure has been determined by single-crystal X-ray crystallography.

It is generally recognized that transition metal hydride complexes may undergo a halogenation reaction with halogenated hydrocarbons to produce a metal halide complex [1, 2]. We have observed that the dimeric iridium(III) hydride complex, $[IrHCl(SPh)(PPh_3)_2]_2$ [3], will slowly dissolve in $CHCl_3$ or CH_2ClCH_2Cl with reaction to form a clear yellow solution from which an off-white solid (I) can be precipitated by the addition of petroleum ether (b.p. 63-75 °C). It was not possible to arrive at a satisfactory formulation for I using standard analytical and spectroscopic techniques although the presence of a metal—hydrogen bond was implied by a weak band at 2275 cm^{-1} in the infrared (Nujol) together with a poorly resolved high field signal at ca. 23 ppm in the ^1H NMR (acetone-d_6 or $CDCl_3$).

These unusual observations prompted us to react $[IrHCl(SPh)(PPh_3)_2]_2$ with silver perchlorate. Consequently, when $[IrHCl(SPh)(PPh_3)_2]_2$ is allowed to react with one mole of $AgClO_4$ under reflux in acetone, AgCl is formed and pale yellow crystals of a perchlorate salt are obtained which are solvated with acetone (ν(CO) 1714 cm^{-1}; $\delta(CH_3)$ 2.18 ppm ($CDCl_3$)). A single crystal X-ray analysis of this solvate unambiguously established it to be $[(Ph_3P)_2(H)Ir(SPh)_2ClIr(H)(PPh_3)_2]$-$ClO_4 \cdot 3(CH_3)_2CO$ (II).

The pale yellow crystals are monoclinic, space group $P2_1$ with two formula units of $[C_{84}H_{72}ClIr_2P_4S_2]^+ClO_4^- \cdot 3C_3H_6O$ per cell of dimensions a = 15.013(3), b = 12.918(1), c = 22.044(4) Å, β = 91.94(1)°. The structure was solved by Patterson and Fourier methods using 3726 observed reflexions [$I > 3\sigma(I)$, $\theta < 20°$] measured on a diffractometer with Mo-K_α radiation. Refinement by full-matrix

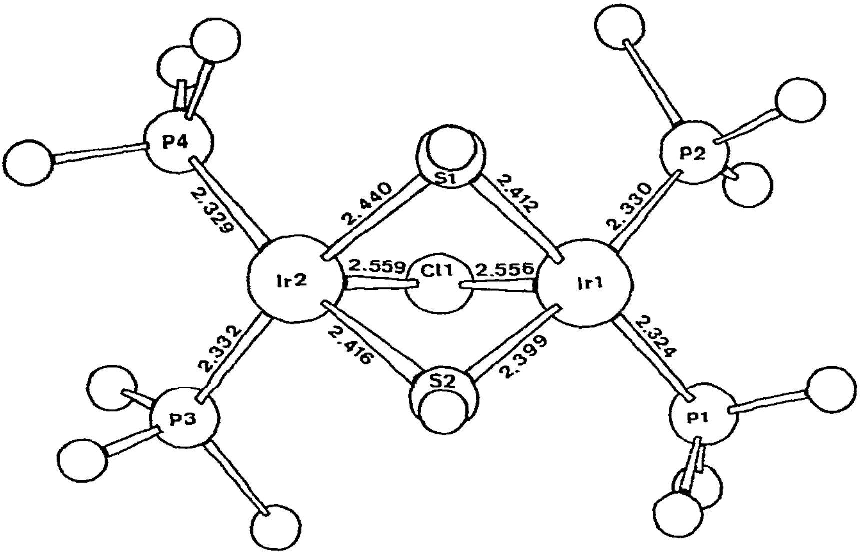

Fig. 1. The structure of the μ-chloro-di-μ-(phenylthio)di {hydridobis(triphenylphosphine)iridium(III)} cation. For clarity, the phenyl rings are represented by the ring atom bonded directly to the phosphorus or sulphur. Standard deviations for Ir—Cl, Ir—P and Ir—S are in the range 0.004-0.006 Å.

least squares calculations with the heavy atoms allowed anisotropic motion and the phenyl rings treated as groups for computing convenience lowered R to its present value of 0.047 over the observed data. Allowance was made for anomalous dispersion of iridium [4] and the structure shown in Fig. 1 represents the correct choice in polar space group $P2_1$ [5] as determined by the measurements of the intensities of 15 Friedel pairs of reflexions.

The Ir—Ir distance is 3.377(1) Å, precluding any metal—metal interaction. The complex can be thought of as consisting of two octahedra sharing a face whose apices are occupied by a chlorine atom and the two sulphur atoms of the phenylthio ligands. The three other coordination sites for each iridium atom are occupied by two triphenylphosphine ligands (*trans* to the sulphurs) and a hydrogen (*trans* to the chlorine).

The hydride hydrogens in II were not located by the X-ray study but the presence of Ir—H bonds is supported by the presence of ν(Ir—H) at 2278 cm^{-1} (Nujol) in the infrared and a poorly resolved ^1H NMR signal at 23.36 ppm upfield from TMS in $CDCl_3$.

In view of these results, I may be formulated as $[(Ph_3P)_2(H)Ir(SPh)_2ClIr(H)(PPh_3)_2]Cl \cdot 2H_2O$*. The singlet observed at 2.78 ppm in acetone-d_6 integrates for four protons relative to the 70 phenyl protons. Presumably, the water of solvation comes from the trace amounts of water present in the reagent-grade solvents used. The ionic chloride in I can be exchanged for tetraphenylborate in methanol to form $[(Ph_3P)_2(H)Ir(SPh)_2ClIr(H)(PPh_3)_2]BPh_4$ which does not contain any water of solvation (ν(Ir—H) 2278 cm^{-1} (Nujol); Λ_M 96.8 ohm^{-1} $mole^{-1}$ cm^2 for a 3.89×10^{-4} M solution in acetone).

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[*] Satisfactory elemental analyses were obtained for all complexes reported herein.

The dimeric hydride complexes reported herein represent the first examples of well defined triply bridged dimers of iridium(III) having terminal metal—hydrogen bonds. The tendency for iridium(III) to be six coordinated appears to be the driving force leading to the formation of these triply bridging species since II is also produced when $[IrHCl(SPh)(PPh_3)_2]_2$ is mixed with two or more moles of $AgClO_4$ under reflux in acetone. Apparently, once one Cl is eliminated by Ag^+, the rate of bridge formation is very much greater than the rate of displacement by Ag^+ of the remaining Cl ligand bonded to iridium.

It may also be noted that the presence of phenylthio bridging ligands in II lends support to the previously proposed structure of $[IrHCl(SPh)(PPh_3)_2]_2$ [3].

Acknowledgments

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