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Dichloro(pentafluorophenylperthiolato)carbonylbis(triphenylphosphine)iridium(III): an Example of a Ligated Organoperthio Group

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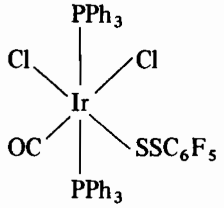
There are many well characterized examples of the following sulfur-containing moieties coordinated to a metal center: S^{2-}= [1], RS^- [2], RSR [3], R_2S^+ [4], S_2 [5], and RSSR [6] where R = an alkyl or aryl group. We now wish to report that the organoperthio group, RSS^- may now be added to this list.

We have found that C_6F_5SSCl [7] will oxidatively add to *trans*-$IrCl(CO)(PPh_3)_2$ to form $IrCl_2(SSC_6F_5)(CO)(PPh_3)_2$, *I*, by analogy to the oxidative addition of RSH [8], RSSR [9] and RSCl [10] to square planar iridium(I) substrates.

Although iridium(III) derivatives containing a coordinated organoperoxo group are known [11], to the best of our knowledge, *I* represents the first reported example of a transition metal complex containing a monodentate organoperthio group. Related perthiocarboxylato groups, $R((S)CSS^-$ are also known to coordinate to various metal centers in a bidentate fashion [12].

Complex *I* is precipitated as a yellow solid from a benzene solution of $IrCl(CO)(PPh_3)_2$ and C_6F_5SSCl by the addition of ligroin. The ^{31}P nmr [^1H] spectrum of *I* in benzene containing 10% C_6D_6 shows a single resonance at 16.8 ppm downfield from 85% H_3PO_4. In the infrared spectrum of *I*, the sharp single absorption band 2052 cm^{-1} and the weak absorption bands at 314 and 275 cm^{-1} have been assigned to the ν(CO) and ν(Ir–Cl) vibrations respectively. Unfortunately, it was not possible to unequivocally assign any absorption band to the ν(S–S) vibration in *I* by a careful comparison of its spectrum with that of the related complex, $IrHCl(SC_6F_5)(CO)(PPh_3)_2$ [13] between 900–350 cm^{-1}. However, these spectral data together with the elemental analysis for *I* are consistent with the following stereochemistry for *I*. The results form a formal *trans*-oxidative addition of C_6F_5SSCl to the Ir(I) substrate and parallel the previously observed stereochemistry when a sulfenylhalide is the incoming group [10].



I

Experimental

Literature methods were used to prepare chloro(pentafluorophenyl)disulfane, C_6F_5SSCl [7] and *trans*-$IrCl(CO)(PPh_3)_2$ [14]. Infrared spectra were recorded on a Beckman IR-12 or a Perkin-Elmer 180 spectrophotometer as Nujol mulls between KBr or CsI discs. $^{31}P[^1H]$ nmr spectra were recorded on a Bruker DP60 spectrometer in the FT mode using 85% H_3PO_4 as external reference. All other chemicals used were reagent grade or better. Microanalyses were carried out by MHW Laboratories, Phoenix, Arizona.

Dichloro(pentafluorophenylperthiolato)carbonylbis(triphenylphosphine)iridium(III), $IrCl_2(SSC_6F_5(CO)(PPh_3)_2$

The following operations were carried out under an atmosphere of dry N_2.

To a sample of $IrCl(CO)(PPh_3)_2$ (0.39, 0.50 mmol) in benzene (20 ml) was added C_6F_5SSCl (0.14 g, 0.50 mmol) and the resulting solution was stirred at room temperature for about 15 min whereupon 80–100 ml of ligroin (bp 63–75 °C) were added to precipitate the product as a yellow crystalline solid. This was collected by filtration, washed with ligroin and dried *in vacuo* at room temperature. Mp. 196 °C (uncorrected). *Anal.* Calcd for C, 49.34; H, 2.89; Cl, 6.75; S, 6.13. Found: C, 49.59; H, 3.17; Cl, 6.96; S, 5.87.

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