A New Hydrido-iridium(III) Isomer of $Ir(PPh_3)_2(CO)Cl$

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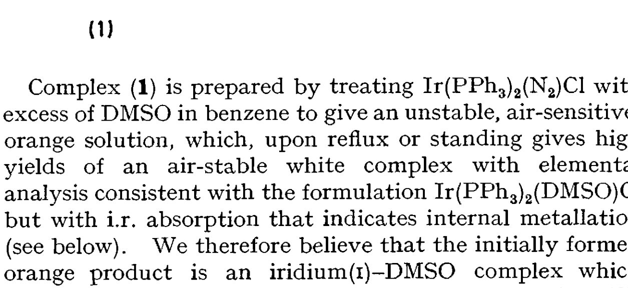
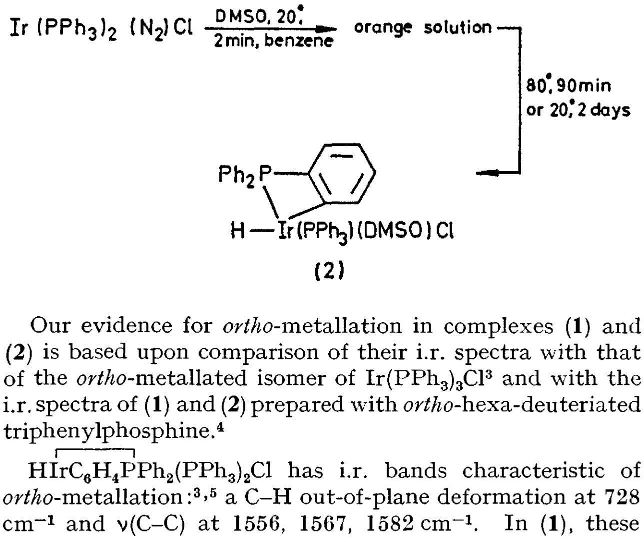
Summary A new internally metallated iridium(III) hydride–DMSO complex has been prepared; it reacts with carbon monoxide to give a hydrido-iridium(III) isomer of $Ir(PPh_3)_2(CO)Cl$.

There has been much recent interest in transition metal triphenylphosphine complexes in which the metal atom has inserted into an *ortho*-phenyl carbon–hydrogen bond.[1,2] We have prepared a new complex of this type, (**1**), which is an isomer of the extensively studied complex $Ir(PPh_3)_2(CO)Cl$ into which it spontaneously reverts.



(**1**)

Complex (**1**) is prepared by treating $Ir(PPh_3)_2(N_2)Cl$ with excess of DMSO in benzene to give an unstable, air-sensitive, orange solution, which, upon reflux or standing gives high yields of an air-stable white complex with elemental analysis consistent with the formulation $Ir(PPh_3)_2(DMSO)Cl$ but with i.r. absorption that indicates internal metallation (see below). We therefore believe that the initially formed orange product is an iridium(I)–DMSO complex which undergoes an internal oxidative-addition to give (**2**). Complex (**1**) is prepared by stirring a suspension of (**2**) in benzene under CO at 1 atm. for 90 min, followed by precipitation of the yellow powder by addition of hexane. Complex (**1**) is thermally unstable at 20 °C in the solid and in solution. It is stable for long periods as a solid at −5 °C.



(**2**)

Our evidence for *ortho*-metallation in complexes (**1**) and (**2**) is based upon comparison of their i.r. spectra with that of the *ortho*-metallated isomer of $Ir(PPh_3)_3Cl$[3] and with the i.r. spectra of (**1**) and (**2**) prepared with *ortho*-hexa-deuteriated triphenylphosphine.[4]

$HIrC_6H_4PPh_2(PPh_3)_2Cl$ has i.r. bands characteristic of *ortho*-metallation:[3,5] a C–H out-of-plane deformation at 728 cm^{-1} and ν(C–C) at 1556, 1567, 1582 cm^{-1}. In (**1**), these bands occur at 733 and 1563 cm^{-1} (KBr) in (**2**), at 721 and 1560 cm^{-1} (KBr). The identification of these complexes as hydrides where the hydride ligand originated on the *ortho*-position of a phenyl ring is verified by the observation of i.r. bands appropriate for iridium(III) hydrides which do not appear in the *ortho*-deuteriated complexes. Thus, i.r. spectra of (**2**) show ν(Ir–H) at 2190 and δ(Ir–H) at 818 cm^{-1} (KBr) which do not appear in the deuteriated complex. Spectra of (**1**) show a mixture of isomers with ν(Ir–H) at 2102 and 2190 cm^{-1} (CH_2Cl_2) and δ(Ir–H) at 815 cm^{-1} (KBr). These bands do not appear in the deuteriated complex and a resonance shift[6] for one of the isomers is observed in the carbonyl region: the carbonyl bands with maxima at 2003 and 2028 cm^{-1} (CH_2Cl_2) in the hydride merges to one band at 2030 cm^{-1} (CH_2Cl_2) in the deuteride. Thus one isomer has the *trans* H–Ir–CO configuration.

Unfortunately, the region where ν(Ir–D) is expected in the deuterides is obscured by other ligand absorption.

I thank the Research Council of Rutgers, the State University for support, Hoffmann-La Roche, for analytical services and Dr. Donald Valentine and Professors Jeffrey Schwartz and Joseph San Filippo for helpful discussions.

(*Received, 25th April* 1973; *Com.* 595.)

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