Journal of Organometallic Chemistry, 272 (1984) C67—C69
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

DIHYDROIRIDIUM DIOLEFIN COMPLEXES WITH SULFUR LIGANDS

J.C. RODRIGUEZ, C. CLAVER and A. RUIZ

Universidad de Barcelona, Departamento de Quimica Inorgánica, Facultad de Quimica, Pl. Imperial Tarraco s/n, Tarragona (Spain)

(Received April 3rd, 1984)

Summary

Novel dihydroiridium(III) complexes containing mono- and bi-dentate sulfur ligands have been isolated. The cationic complexes $[Ir(COD)L_2]ClO_4$ (COD = 1,5-cyclooctadiene, L = tetrahydrothiophene (tht) or trimethylene sulfide (tms); L_2 = $(CH_3S)_2(CH_2)_3$ (dth)), $[Ir(COD)(L—L)]_2(ClO_4)_2$ (L—L = 1,4-dithiacyclohexane (dt) or $(t\text{-}BuS)_2(CH_2)_2$ (tmdto)) and $[Ir(CO)_2(tmdto)]_2(ClO_4)_2$ react with H_2 to give the corresponding iridium(III) dihydrides: $[IrH_2(COD)L_2]ClO_4$ (Ia: L = tht, Ib: L = tms, Ic: L_2 = dth), $[IrH_2(COD)(L—L)]_2(ClO_4)_2$ (IIa: L—L = tmdto, IIb: L—L = dt) and $[IrH_2(CO)_2(tmdto)]_2(ClO_4)_2$ (III). The ^1H NMR chemical shifts and ν(Ir—H) data are discussed.

Dihydro-olefin complexes $[IrH_2(COD)L_2]^+$ (L = P-coordinated ligand have been described and studied as intermediates in the homogeneous hydrogenation of olefins [1]. Hydrogenation of $[Ir(CO)_3L_2]BPh_4$ L = $P(p\text{-}CH_3C_6H_4)_3$ results in the formation of $[IrH_2(CO)_2L_2]BPh_4$ [2]. The *trans* influences of various anionic and neutral ligands on the hydride ligand have been analysed for octahedral, neutral and cationic hydridoiridium(III) complexes of the basis of ^1H NMR chemical shifts and ν(Ir—H) data [3].

In continuation of our investigations on the chemistry of cationic iridium(I) complexes containing S-donor ligands [4] we have studied the reactions with H_2 of diolefin and carbonyl cationic iridium(I) complexes previously reported [4a,4c].

When H_2 is bubbled for 3 min at room temperature through dichloromethane solutions of the iridium(I) complexes $[Ir(COD)L_2]ClO_4$ (L = tht or tms, L_2 = dth), $[Ir(COD)(L—L)]_2(ClO_4)_2$ (L_2 = dt, tmdto) and $[Ir(CO)_2(tmdto)]_2(ClO_4)_2$, previously isolated or prepared "in situ" [4a,4c], the solutions become lighter in colour and the corresponding dihydridoiridium(III) complexes, can be isolated by addition of diethyl ether (yield 80—90%). The resulting

0022-328X/84/$03.00

solids are relatively air-stables except for III, and they are soluble in the usual organic solvents except for Ib and IIb, which are almost insoluble. All the complexes have been characterized by elemental analyses, infrared spectra, conductance studies and ^{1}H NMR.

The same products can also be obtained by keeping the dichloromethane solutions stirred under hydrogen at room temperature for a few minutes.

It is noteworthy that the complexes can be prepared under normal conditions (of pressure and temperature), whereas some other P-donor complexes had to be isolated at —80°C, and decomposed at about 0°C on warning [1b].

The IR spectra of all isolated complexes show bands due to the coordinated sulfur ligands together with those due to the uncoordinated perchlorate anion and to the Ir—H stretching frequencies.

The infrared spectrum (Nujol mull) of Ia and IIa show two sharp bands (Ia: 2085ms and 2125m cm^{-1}, Ib: 2095ms and 2185m cm^{-1}), suggesting that the two hydrogens occupy *cis* positions [5]. In contrast, for $[IrH_2(COD)(dth)]ClO_4$ the IR spectrum shows only one sharp band at 2020s cm^{-1} implying a *trans* arrangement of the hydrogens. In the case of IIa, there are two bands (2115ms and 2185m cm^{-1}) consistent with a *cis* dispositions for the hydrogens and suggesting that the two iridium(I) atoms are in similar environments.

The IR spectrum of IIb initially show two ν(Ir—H) bands at 2120ms and 2155m cm^{-1}, characteristic of a *cis* disposition of the hydrogens, but this complex is sensitive to light in air and isomerizes rapidly to a *trans* isomer, with the appearance of an infrared band at 2020 cm^{-1} and after a few minutes only a single sharp band Ir—H (2020vs cm^{-1}) is present.

The IR spectrum $[IrH_2(CO)_2(tmdto)]_2(ClO_4)_2$ shows two Ir—H stretching frequencies (2140ms and 2175m cm^{-1}). This compound loses H_2 progressively, to regenerate the original $[Ir(CO)_2(tmdto)]_2(ClO_4)_2$.

As expected [6], the bands from the stretching frequencies of the coordinated carbon monoxide ligands are shifted to higher frequencies in the dihydrido complex.

In the ^{1}H NMR spectrum of Ia two metal-hydride signals can be distinguished, one at δ —13.07 ppm and the other at δ —13.56 ppm. However only single signals from COD and tht are observed. This, together with the IR data, suggest a structure in which the two *cis*-hydride ligands are practically equivalent.

In the case of IIa two different ^{1}H NMR chemical shifts of the hydride ligands are observed, one at δ —12.30 ppm and the other at δ —14.32 ppm, suggesting that there are two different atoms *trans* to the hydride ligands [7]. Splitting of the ^{1}H NMR signals from the COD and tmdto ligands confirm this.

Complex III shows also two different chemical shifts for the hydrido ligands, one at δ —10.14 ppm and the other at δ —13.08 ppm. As expected, the signals from the tmdto ligand are split. The signal at δ —10.14 ppm may be tentatively assigned to a hydride *trans* to a carbonyl group [8].

Studies of hydride mixed complexes with Group Vb ligands are in progress in our laboratory.

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