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PREPARATION OF IrH(diene)L_2 COMPOUNDS VIA METHOXYIRIDIUM COMPLEXES: CATALYSTS FOR HYDROGEN TRANSFER REACTIONS

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Summary

Hydrido-diene complexes of general formula IrH(diene)L_2 (diene = tetrafluorobenzobarrelene (TFB), 1,5-cyclooctadiene (COD); L = PPh_3; L_2 = bis(1,2-diphenylphosphino)ethane (dppe), bis(1,3-diphenylphosphino)propane (dppp)) have been obtained by decomposition of methoxyiridium complexes. The related IrH(diene)$(AsPh_3)_2$ complexes have been prepared from iridium chloro-diene compounds. The catalytic activity of IrH(COD)L_2 complexes in hydrogen transfer reactions from alcohols to cyclohexanone is described.

Introduction

Whereas alkoxy derivatives of transition metals have been extensively studied, the chemistry of methoxy compounds of platinum metals has been only briefly explored [1], even though a number of important reactions with methanol may involve methoxy complexes. Among the important reactions are those involving the use of ruthenium, rhodium, or iridium catalysts in the carbonylation of methanol [2] or in the catalytic hydrogen transfer from methanol to unsaturated organic substrates [3,4].

$[M(\mu\text{-OMe})(COD)]_2$ (M = Rh, Ir) complexes [5] have been used as intermediates for synthetic purposes [6–12], and as homogeneous catalyst precursors [13–16]. Our high yield synthesis of $[Ir(\mu\text{-OMe})(COD)]_2$ [17] made possible further studies on the chemistry and reactivity of this interesting starting material.

We have recently reported the preparation and properties of pentamethylcyclopentadienylrhodium(III) or -iridium(III) complexes containing methoxy bridging groups [18]. Such alkoxy derivatives have been invoked as probable intermediates in the preparation of various hydrido-bridged compounds [19]. Very recently Atwood and co-workers have reported that alkoxy Ir(OR)(CO)$(PPh_3)_2$ complexes containing β-hydrogens decompose in the presence of triphenylphosphine to give IrH(CO)-

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$(PPh_3)_3$ [20]. We report here the preparation of $IrH(diene)L_2$ complexes via decomposition of methoxyiridium complexes, and their catalytic activity in hydrogen transfer from alcohols to cyclohexanone.

Results and discussion

Preparation of the $IrH(diene)L_2$ complexes

Treatment of $[Ir(\mu\text{-OMe})(diene)]_2$ (diene = 1,5-cyclooctadiene (COD) or 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (TFB) with phosphorus ligands in methanol gives red solutions from which $IrH(diene)L_2$ complexes separate as white solids, according to eq. 1:

$$\tfrac{1}{2}[Ir(\mu\text{-OMe})(diene)]_2 + 2L \text{ or } L_2 \xrightarrow{MeOH} IrH(diene)L_2 \quad (1)$$

($L = PPh_3$, L_2 = dppe or dppp)

Reaction of the cationic red complex $[Ir(COD)(PPh_3)_2]ClO_4$ with an equimolar amount of MeO^- in methanol likewise leads to the formation of $IrH(COD)(PPh_3)_2$. Cationic iridium complexes have been suggested to act in some cases as Lewis acids [21]. Thus, the cationic $[Ir(COD)(PPh_3)_2]^+$ species probably undergoes nucleophilic attack by the methoxide group at the metal and this is followed by a β-hydrogen elimination. The formation of $IrH(diene)L_2$ by reaction of $[Ir(\mu\text{-OMe})(diene)]_2$ with phosphorus ligands probably involves the intermediacy of $[Ir(diene)L_2]^+$ species. Analysis of the organic products was carried out for the reaction of the ethoxy complex $[Ir(\mu\text{-OEt})(COD)]_2$ with PPh_3 in ethanol, and acetaldehyde was detected by GLC: the overall reaction is shown in eq. 2.

$$\tfrac{1}{2}[Ir(\mu\text{-OCH}_2CH_3)(COD)]_2 + 2PPh_3 \xrightarrow{CH_3CH_2OH} IrH(COD)(PPh_3)_2 + CH_3CHO \quad (2)$$

This result supports the formation of the hydride by decomposition of the alkoxy complex by β-hydrogen elimination, as proposed for $Ir(OR)(CO)(PPh_3)_2$ [20]. The $IrH(COD)(PPh_3)_2$ complex was previously prepared by other methods [22,23].

Related hydride complexes with $AsPh_3$ cannot be prepared by direct reaction of this ligand with $[Ir(\mu\text{-OMe})(diene)]_2$, the methoxy dimers remaining unchanged on such treatment. In contrast, halogen-bridge cleavage occurs when $[Ir(\mu\text{-Cl})(COD)]_2$ is treated with $AsPh_3$ [24]. Addition of an equimolecular amount of MeO^- to a mixture of $[Ir(\mu\text{-Cl})(COD)]_2$ and $AsPh_3$ leads to the formation of $IrH(COD)(AsPh_3)_2$ (eq. 3):

$$[Ir(\mu\text{-Cl})(COD)]_2 \xrightarrow{AsPh_3, MeO^-/MeOH} IrH(COD)(AsPh_3)_2 \quad (3)$$

$$\updownarrow AsPh_3, \uparrow MeOH$$

$$[Ir(\mu\text{-OMe})(COD)]_2$$

The $IrH(TFB)(AsPh_3)_2$ complex can be prepared by the same method from $IrCl(TFB)(AsPh_3)_2$. It is noteworthy that the yields in the preparation of the complexes with $AsPh_3$ are increased by using an excess of the ligand (Ir/L = 1/4), probably owing to decomposition of the complexes in the basic solution via dissociation of the labile $AsPh_3$ ligand.

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR THE COMPLEXES

Compound	Analysis (Found (calcd.) (%))		Yield (%)	ν(Ir–H) (cm^{-1})
	C	H		
$IrH(TFB)(PPh_3)_2$	61.3 (61.1)	4.1 (4.0)	95	2116
$IrH(COD)(AsPh_3)_2$	57.6 (57.8)	4.6 (4.7)	79	2030
$IrH(TFB)(AsPh_3)_2$	55.5 (55.9)	3.6 (3.6)	60	2030
IrH(COD)(dppe)	59.0 (58.4)	5.3 (5.3)	69	2065
IrH(TFB)(dppe)	56.0 (55.8)	3.9 (3.8)	70	2070
IrH(COD)(dppp)	58.4 (58.9)	5.7 (5.5)	30	2096
IrH(TFB)(dppp)	55.9 (56.3)	3.7 (4.0)	30	2170

Table 1 lists the analytical and IR data (ν(Ir–H)) for the isolated complexes. The ^1H NMR spectra (see Experimental) of $IrH(diene)L_2$ (diene = COD, L_2 = dppe, L = $AsPh_3$; diene = TFB, L = PPh_3) complexes show olefinic proton resonances of the coordinated diene ligands and high-field signals (−13 to −18 ppm) which confirm the presence of a metal hydride bond. For the complexes with phosphorus donor ligands the hydride resonance appears as a triplet (J(P–H) 21–23 Hz). In contrast, the ^1H NMR spectrum of $IrH(TFB)(AsPh_3)_2$ in $CDCl_3$ at 20°C shows characteristic aliphatic resonances (4.88 (br, 1H), 4.41 ppm (br, 1H)), a vinyl resonance (2.61 ppm, 2H) and broad signals (2.5–0.5 ppm, 3H), but there is no high-field signal. However, addition of methanol to the solution recovered from ^1H NMR measurements caused precipitation of a white solid of formula $IrH(TFB)(AsPh_3)_2$, the ν(Ir–H) band present in the initial IR spectrum. This result may be tentatively accounted for by assuming that in solution the hydride proton can attack at a double-bound of the coordinated TFB ligand, but the hydrido complex $IrH(TFB)(AsPh_3)_2$ complex was recovered in the solid state. Precedents for such a process has been reported for $IrH(diene)_2$ [25] and $[Ru(\eta^3\text{-}C_8H_{13})L_3]^+$ [26].

Catalytic activity of $IrH(COD)L_2$ complexes

The observed formation of hydrido complexes in the reaction of $[Ir(\mu\text{-}OMe)(diene)]_2$ with phosphorus ligands in methanol prompted us to explore the catalytic activity of the $IrH(COD)L_2$ (L = PPh_3, $AsPh_3$; L_2 = dppe, dppp) complexes in hydrogen transfer reactions from alcohols to cyclohexanone. Isopropanol, ethanol and methanol were used as hydrogen donors and the reactions were carried out at 60°C. The results are listed in Table 2.

The complexes with phosphorus donor-ligands are reasonably active, particularly the IrH(COD)(dppp) compound for transfer reactions from isopropanol. Previous studies from this laboratory with $[Ir(TFB)L_2]^+$ compounds as precursor catalysts

TABLE 2

HYDROGEN TRANSFER FROM ALCOHOLS TO CYCLOHEXANONE CATALYSED BY $IrH(COD)L_2$ COMPLEXES [a]

Complex	Alcohol	Reaction time (h)	Conversion (%)
$IrH(COD)(AsPh_3)_2$	isopropanol	3	0
		24	5
$IrH(COD)(PPh_3)_2$	isopropanol	3	43
		24	62
IrH(COD)(dppe)	isopropanol	3	45
		24	58
IrH(COD)(dppp)	isopropanol	3	55
		24	97
$IrH(COD)(PPh_3)_2$	ethanol	3	1
		24	3
IrH(COD)(dppe)	ethanol	3	14
		24	24
IrH(COD)(dppp)	ethanol	3	12
		24	25
$IrH(COD)(PPh_3)_2$	methanol	3	2
		24	9
IrH(COD)(dppe)	methanol	3	1
		24	3
IrH(COD)(dppp)	methanol	3	0
		24	3

[a] Reaction conditions: cyclohexanone (2 mmol), $IrH(COD)L_2$ (0.02 mmol), alcohol (8 ml), T 60°C.

for hydrogen transfer from isopropanol to acetophenone have shown that the dppp complex gives more active systems than dppe or PPh_3 complexes [27]. For the latter the presence of potassium hydroxide was necessary for the formation of coordinated isopropoxide groups that can lead to the formation of intermediate hydrides by a β-elimination reaction [27,28]. In contrast with the hydride complexes reported in this paper the presence of KOH or other cocatalysts was not necessary.

The rates of the catalytic reactions depend on the nature of the hydrogen source. In general, the sequence of rates is isopropanol > ethanol > methanol, except in the case of $IrH(COD)(PPh_3)_2$ which gives a higher conversion in methanol than in ethanol. The decrease in the catalytic activity from isopropanol to methanol is consistent with that observed for other catalysts [3b,4].

It is worth noting that the initial $IrH(COD)L_2$ complexes are coordinatively saturated, and so activation is needed to initiate the catalytic reaction. This activation could involve an isomerization or hydrogenation of the coordinated 1,5-cyclooctadiene. In this connection, in a separate experiment we added 0.5 mmol of 1,5-cyclooctadiene to a mixture of IrH(COD)(dppe), isopropanol and cyclohexanone, under conditions similar to those used in the catalytic reactions. The 1,5-cyclooctadiene was isomerized, in 90% yield, to 1,3-cyclooctadiene in 1 h, and only traces of cyclooctene were detected. Thus, the diene probably separates from the iridium centre after an isomerization to 1,3-cyclooctadiene, leaving unsaturated $IrHL_2$ species which then can coordinate the alcohol and ketone, and initiate the catalytic reaction.

Experimental

All reactions were carried out under N_2 and in N_2-saturated solvents. ^1H NMR spectra were recorded in $CDCl_3$ solutions on a Varian XL 200 Spectrometer and IR spectra on a Perkin–Elmer 599 spectrophotometer in the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets; calibration was with polyethylene. The C, H, analyses were carried out with a Perkin–Elmer 240 microanalyzer. The GC analyses were performed on a Perkin–Elmer 3920 B chromatograph connected to a Perkin–Elmer M-2 integrator. The starting materials, $[Ir(\mu\text{-OMe})(COD)]_2$ [17], $[Ir(\mu\text{-Cl})(COD)]_2$ [29], $[Ir(COD)(PPh_3)_2]ClO_4$ [30], $[Ir(\mu\text{-OMe})(TFB)]_2$ [31] and $IrCl(TFB)(AsPh_3)_2$ [32] were prepared by published methods.

Preparation of $IrH(COD)(PPh_3)_2$ (I)

This was obtained by three methods:

(*i*) A suspension of $[Ir(\mu\text{-OMe})(COD)]_2$ (78.3 mg, 0.12 mmol) in 25 ml of methanol was treated with PPh_3 (124.0 mg, 0.50 mmol), and the mixture was kept for 3 h at room temperature. The resulting white precipitate was filtered off, washed with methanol, and vacuum-dried. Yield: 110 mg (85%).

(*ii*) A suspension of $[Ir(COD)(PPh_3)_2]ClO_4$ (110.9 mg, 0.12 mmol) in 20 ml of methanol was treated with 1.2 ml of a methanolic solution of potassium hydroxide (0.10 *N*, 0.12 mmol), and the mixture was kept for 1 h at room temperature. The resulting white precipitate was filtered off, washed with methanol, and vacuum-dried. Yield: 44.7 mg (45%).

(*iii*) A suspension of $[Ir(\mu\text{-Cl})(COD)]_2$ (97.2 mg, 0.14 mmol) in 20 ml of methanol was treated with PPh_3 (147.0 mg, 0.56 mmol) and 2.8 ml of a methanolic solution of potassium hydroxide (0.10 *N*, 0.28 mmol) and the mixture was kept for 3 h at room temperature. The resulting white precipitate was filtered off, washed with methanol, and vacuum-dried. Yield: 186.5 mg (78%). ^1H NMR (ppm): δ 7.2 (phenyl, m); 3.8, 3.4 (=CH,br); 1.8, 1.5 (-CH_2,br); −13.97 (IrH,t; J(PH) 22 Hz).

Preparation of $IrH(TFB)(PPh_3)_2$ (II)

The procedure (i) described for preparation of I was used but starting from $[Ir(\mu\text{-OMe})(TFB)]_2$ (100 mg, 0.11 mmol) and PPh_3 (116.7 mg, 0.44 mmol). This gave a white microcrystalline solid; Yield: 187 mg (90%). ^1H NMR (ppm): δ 7.2 (phenyl,m); 4.13 (-CH,br); 2.61 (=CH,br); −17.34 (IrH,t; J(PH) 22.5 Hz).

Preparation of $IrH(COD)(AsPh_3)_2$ (III)

The procedure (iii) described for preparation of I was used, but starting from $[Ir(\mu\text{-Cl})(COD)]_2$ (109.9 mg, 0.16 mmol) and $AsPh_3$ (400 mg, 1.30 mmol), gave a white microcrystalline solid. Yield: 236 mg (79%). ^1H NMR (ppm): δ 7.4 (phenyl, m), 3.95, 3.50 (=CH,br); 1.80, 1.45 (-CH_2,br); −13.84 (IrH, s).

Preparation of $IrH(TFB)(AsPh_3)_2$ (IV)

A solution of $IrCl(TFB)(AsPh_3)_2$ (106.6 mg, 0.10 mmol) in 20 ml of methanol was treated with 1.0 ml of a methanolic solution of potassium hydroxide (0.10 *N*, 0.10 mmol) and the mixture was kept for 96 h at room temperture. The resulting white precipitate was filtered off, washed with methanol, and vacuum-dried. Yield: 62 mg (60%). ^1H NMR (ppm): δ 7.4 (phenyl,m); 4.88, 4.41 (-CH,br); 2.61 (=CH,br); 2.5–0.5 (not assigned).

Preparation of IrH(COD)(dppe) (V)

The usual procedure (i), but starting from $[Ir(\mu\text{-OMe})(COD)]_2$ (66.1 mg, 0.10 mmol) and dppe (79.3 mg, 0.20 mmol) gave a white microcrystalline solid. Yield: 96.5 mg (69%). ^1H NMR (ppm): δ 7.3 (phenyl,m); 2.05 ($P(CH_2)_2P$, m); −14.00 (IrH,t; J(PH) 21.5 Hz). Some decomposition of the compound was observed in $CDCl_3$ solution, and this prevented the assignments of the COD resonances.

Preparation of IrH(TFB)(dppe) (VI)

The procedure (i) described for preparation of I was used, but starting from $[Ir(\mu\text{-OMe})(TFB)]_2$ (100 mg, 0.11 mmol) and dppe (87.6 mg, 0.22 mmol). This gave a white microcrystalline solid. Yield: 127 mg (70%) *.

Preparation of IrH(COD)(dppp) (VII)

The usual procedure (i), but starting from $[Ir(\mu\text{-OMe})(COD)]_2$ (54.0 mg, 0.081 mmol) and dppp (67.1 mg, 0.16 mmol), gave a white microcrystalline solid. Yield: 57.4 mg (30%) *.

Preparation of IrH(TFB)(dppp) (VIII)

The usual procedure (i), but starting from $[Ir(OMe)(TFB)]_2$ (119.7 mg, 0.13 mmol) and dppp (109.8 mg, 0.26 mmol), gave a white microcrystalline solid. Yield: 50.9 mg (23%) *.

Catalytic hydrogen transfer reactions

The catalytic reactions were performed in a two-necked flask, equipped with a condenser and magnetic stirring bar. In a typical procedure, the $IrH(COD)L_2$ complex (0.02 mmol), cyclohexanone (2 mmol) and alcohol (8 ml) were placed in the flask, which was then immersed in a bath at 60°C. Reactions were followed by GLC using FFAP on Chromosorb GHP 80/100 mesh (3.6 m × 1/8 in) at 110°C.

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