Journal of Organometallic Chemistry, 140 (1977) 63—72

COMPLEXES OF RHODIUM(I) AND IRIDIUM(I) WITH 2,2'-BIPYRIDINE AND SIMILAR LIGANDS AS HYDROGENATION CATALYSTS

G. MESTRONI, G. ZASSINOVICH and A. CAMUS
Istituto di Chimica dell'Università di Trieste, 34127 Trieste (Italy)
(Received May 23rd, 1977)

Summary

Complexes of the type [Rh(Chel)ED]PF_6 (Chel = 2,2-bipyridine; 1,10-phenanthroline; methyl substituted phenanthrolines; ED = 1,5-hexadiene; X^- = PF_6^-; $B(Ph)_4$) have been synthesized. They are good catalysts for hydrogenation of ketones in an alkaline medium even at atmospheric pressure and room temperature. In the presence of an excess of Chel (Chel : Rh = 2), they also catalyse the selective reduction of C=O groups in the presence of C=C bonds.

Introduction

In recent years several complexes of rhodium(I), iridium(I), ruthenium(II) and other transition metals proved to be very active as catalysts for hydrogenation of multiple carbon—carbon bonds [1]. Cationic rhodium(I) complexes are useful also for hydrogenation of C=O bonds. An important feature is the possibility of performing asymmetric hydrogenations by using optically active catalysts [2,3]. In general the supporting ligands are tertiary phosphines or chelating diphosphines, in different metal : ligand ratios [3—5]. The only example of nitrogen-containing complexes was the [$RhCl_2$(py)(dmf)]BH_4 (py = pyridine; dmf = dimethylformamide) [6] until Pasternak et al. reported that allyl rhodium derivatives readily catalyse hydrogenation of cyclohexene in the presence of phenanthroline [7]. In this paper we describe the catalytic activity of some rhodium and iridium hexadiene complexes with nitrogen-containing chelating ligands, especially in hydrogenation of ketones. Preliminary results [8,9] have shown that such $[M(Chel)ED]^+$ complexes are able to hydrogenate olefins in a neutral medium (M = Rh, Ir) and olefins and ketones in an alkaline medium (M = Rh).

Results and discussion

Synthesis and reactions of the catalysts precursors

Complexes of the type [Rh(Chel)ED]X (Chel = 2,2'-bipyridine (Bipy); 1,10-

phenanthroline (Phen); 5,6-Me_2-Phen; 4,7-Me_2-Phen; 3,4,7,8-Me_4-Phen; Ed = 1,5-hexadiene; $X^- = PF_6^-$; $B(Ph)_4^-$) (I) can be obtained in high yield by treatment of $[Rh(COT)_2Cl]_2$ (COT = cyclooctene) with an excess of 1,5-hexadiene and then addition of the nitrogen-containing ligand. The resulting methanol solutions give complexes I as microcrystalline solids on addition of the appropriate anion. The iridium complexes $[Ir(Chel)Ed]PF_6$ (II) are obtained analogously, via the corresponding chloro-derivatives, which are then converted into the cationic species. The complex $[Ir(bAdH)COD]B(Ph)_4$ (bAdH = biacetyldihydrazone; COD = *cis,cis*-1,5-cyclooctadiene (III) was also isolated. The analytical data for the new complexes are shown in Table 1.

Complexes I react with molecular hydrogen at room temperature and atmospheric pressure in common solvents, such as acetone, methanol and dimethylformamide. The analogous COD and NBD (norbornadiene) derivatives do not

TABLE I

ANALYTICAL DATA FOR THE COMPLEXES ISOLATED

No.	Complex	Colour	Analyses Found (calcd.) (%)		
			C	H	N
I	$[Rh(Bipy)ED]PF_6$	red	39.3 (39.52)	3.47 (3.73)	5.83 (5.76)
II	$[Rh(Phen)ED]PF_6$	red	42.6 (42.37)	3.74 (3.55)	5.83 (5.49)
III	$[Rh(4,7\text{-}Me_2\text{-}Phen)ED]PG_6$	orange-red	44.7 (44.63)	3.97 (4.12)	5.22 (5.20)
IV	$[Rh(5,6\text{-}Me_2\text{-}Phen)ED]PF_6$	orange	43.8 (44.63)	3.91 (4.12)	5.03 (5.20)
V	$[Rh(3,4,7,8\text{-}Me_4\text{-}Phen)ED]PF_6$	yellow-orange	47.2 (46.66)	4.15 (4.63)	5.10 (4.96)
VI	$[Rh(Bipy)ED]B(Ph)_4$	orange	71.4 (72.96)	5.23 (5.90)	4.44 (4.31)
VII	$[Rh(Phen)ED]B(Ph)_4$	orange-red	73.5 (74.88)	5.04 (5.68)	4.40 (4.16)
VIII	$[Rh(5,6\text{-}Me_2\text{-}Phen)ED]B(Ph)_4$	red	72.7 (75.31)	5.73 (6.03)	4.28 (3.99)
IX	$[Rh(Phen)B(Ph)_4]$	blue-violet	71.8 (71.78)	5.30 (4.69)	4.19 (4.65)
X	$[Rh(Phen)_2PF_6]$	violet	46.7 (47.39)	2.68 (2.65)	9.04 (9.21)
XI	[Ir(Bipy)(ED)Cl]	violet	43.2 (41.34)	3.85 (3.89)	5.88 (6.01)
XII	[Ir(Phen)(ED)Cl]	violet	46.3 (44.12)	3.75 (3.70)	5.69 (5.72)
XIII	$[Ir(Bipy)ED]PF_6$	green	35.01 (33.39)	3.20 (3.15)	4.75 (4.87)
XIV	$[Ir(Phen)ED]PF_6$	green	34.9 (36.60)	2.61 (3.03)	4.32 (4.67)
XV	$[Ir(bipy)ED]B(Ph)_4$	green	62.5 (65.02)	4.87 (5.18)	3.96 (3.79)
XVI	$[Ir(Phen)ED]B(Ph)_4$	green	63.5 (65.26)	4.78 (4.95)	3.80 (3.62)
XVII	[Ir(bAdH)(COD)Cl]	red-violet	32.9 (32.17)	4.85 (4.50)	11.92 (12.50)
XVIII	$[Ir(bAdH)(COD)]B(Ph)_4$	violet	58.2 (59.09)	5.49 (5.51)	7.80 (7.66)

react under these conditions although the corresponding triphenylphosphine complexes do undergo hydrogenation [10].

This differing reactivities of isostructural and isoelectronic complexes may be attributed mainly to a higher *trans* effect and a larger *trans* influence of the P atom with respect to the N atom.

The reactivity of the $[Rh(Chel)ED]^+$ derivatives in comparison with the complexes with other diolefins is attributed to the higher lability and lower stability of the π-olefinic bond, which is associated with the flexibility of 1,5-hexadiene. In agreement with this hypothesis, only the ED-complexes lose the diolefin in methyl cyanide solution, to give, in the presence of an excess of Chel, violet microcrystals of $[Rh(Chel)_2]^+$. Furthermore the COD rapidly replaces the coordinated ED with quantitative formation of $[Rh(Chel)COD]^+$ species. Finally, while the $[Rh(Chel)(L—L)]^+$ (L—L = COD, NBD) complexes react reversibly with carbon monoxide to give the corresponding dicarbonyl derivatives [11], this reaction is irreversible in the case of the ED derivatives.

With iridium only the $[Ir(Chel)ED]^+$ complexes react readily with molecular hydrogen. A rapid and quantitative reaction is observed for the COD derivatives only when the chelating ligand is bAdH or dimethylglyoxime, proving that a lower delocalization of the π-system of the ligand favours the oxidative addition of molecular hydrogen.

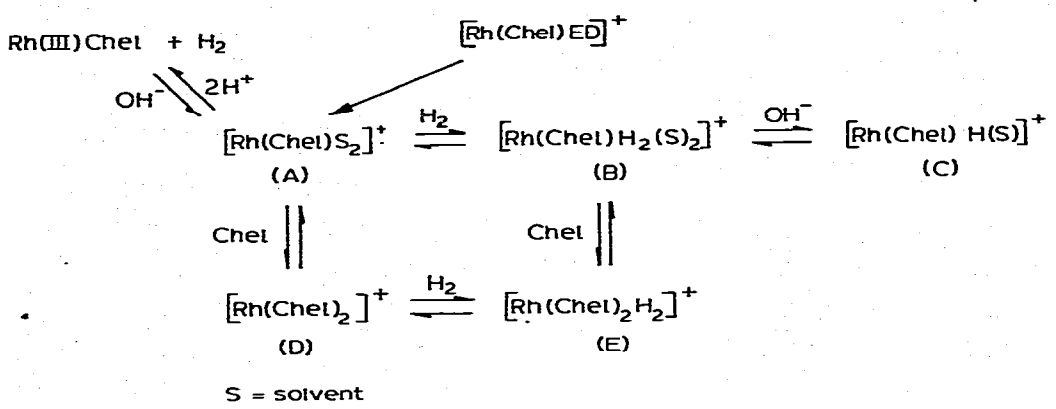
Complexes $[Rh(Chel)ED]PF_6$ react with molecular hydrogen in alkaline methanol to give violet solutions characteristic of $[Rh(I)(Chel)S_2]^+$ species (S = solvent). They are extremely oxygen-sensitive, and react reversibly with hydrogen to become brown-black. $[Rh(Chel)_2]PF_6$ complexes are isolable in the presence of excess of free Chel.

In a neutral medium the same complexes give yellow-brown solutions, from which it is possible to isolate solid compounds of the same colour. They seem not to be hydridic derivatives, since no bands attributable to ν(Rh—H) are present in their infrared spectra. Probably under these conditions, as suggested by Martin et al. [12], the $[Rh(I)(Chel)S_2]^+$ derivatives formed after hydrogenation of the coordinated diolefin react with the protic medium to give Rh(III) complexes with hydrogen evolution. These Rh(III) complexes react rapidly with molecular hydrogen in an alkaline medium, forming $[Rh(I)(Chel)L(S)]$ complexes.

Scheme 1 outlines the suggested equilibria for the system in methanol, in both a neutral and an alkaline medium. The reversible addition of molecular hydrogen to A and D derivatives was previously postulated [13,14]. Some analogous complexes of $[Rh(Chel)L(S)]^+$ and $[Rh(Chel)_2L]^+$ (L = CO, fumaronitrile) have also been isolated [15]. The hydridic forms B and C are probably catalytically active, while E, which is coordinatively saturated, should be inactive.

A blue complex of analytical composition $[Rh(Chel)B(Ph)_4]$ was isolated in the reaction of $[Rh(Chel)ED]^+$ with molecular hydrogen, when the anion is tetraphenylborate. Like the corresponding complexes with phosphines [16] this compound probably has a structure with a phenyl group of the anion π-bonded to the rhodium atom.

As for iridium, the reaction of complexes II with molecular hydrogen in acetone allowed the isolation of hydridic orange solids. The presence in their infrared spectra of a unique hydridic absorption band at 2187 cm^{-1} rules out



SCHEME 1

the formation of *cis*-dihydridic derivatives, suggesting instead the presence of an $[Ir_2H_2(\mu H_3)(Chel)_2]PF_6$ compound with a triple hydridic bridge, as in the corresponding phosphine complexes (ν(Ir—H) = 2200 cm^{-1}) [17].

Hydrogenation of ketones

Only the rhodium complexes I seem to be suitable for hydrogenation of ketones in a basic medium. The reactions were performed at 25°C, with an overall pressure of 1 atm., with acetone, cyclohexanone, and prochiral ketones (methylethyl ketone, methyl-*iso*-butyl ketone, acetophenone and propriophenone) as substrates.

The rates of hydrogenation of acetone with different $[Rh(Chel)ED]PF_6$ complexes are listed in Table 2. The most active species is the 4,7-Me_2-Phen derivative. It is noteworthy that on increasing the Chel : Rh ratio the rate of reaction increases until a maximum is reached, then decreases slowly to zero. In the case of the 4,7-Me_2-Phen the colour of the solution fades as the Chel : Rh ratio increases, to become practically colourless for a Chel : Rh ratio = 8. When the hydrogen is removed, the solution becomes deep violet but becomes colourless again if the hydrogen atmosphere is restored.

Except in the case of acetone, it is necessary to hydrogenate the system before adding the substrate, otherwise variable induction periods and lower reaction rates are observed. In some cases the initial presence of substrates can even inhibit the reaction completely, indicating that the catalytic precursor reacts with the ketone to give inactive species.

High reaction rates in the presence of substrate can be obtained when the hydrogenation of the precursor is carried out in a neutral medium, before the addition of a solution of the required amount of NaOH in water or in alcohol (Table 3). Under similar conditions complexes $[Rh(P(Ph)_3)_2NBD]ClO_4$ and $[Rh(PC_6H_5(CH_3)_2NBD]ClO_4$ are less active than the corresponding complexes with Bipy.

The catalytic activity observed for a Chel : Rh ratio = 1 can be attributed to species B and C (Scheme 1). High Chel : Rh ratios favour the D → E reaction, with formation of inactive E species. Besides B and C species, other active com-

TABLE 2

HYDROGEN UPTAKE FOR ACETONE WITH DIFFERENT [Rh(Chel)ED]PF_6 COMPLEXES

Complex	Moles of catalyst	S[a]/catalyst	Hydrogen uptake (ml min^{-1})	Colour of the solutions
[Rh(Bipy)ED]PF_6	1×10^{-4}	4×10^{-3}	3,1	violet black
[Rh(Bipy)ED]PF_6 + Bipy	1×10^{-4}	4×10^{-3}	3,9	deep-violet
[Rh(Bipy)ED]PF_6 + 2Bipy	1×10^{-4}	4×10^{-3}	4,52	deep-violet
[Rh(Bipy)ED]PF_5 + 4Bipy	1×10^{-4}	4×10^{-3}	3,1	deep-violet
[Rh(Bipy)ED]PF_6 + 15Bipy	1×10^{-4}	4×10^{-3}	0,2	light violet
[Rh(Phen)ED]PF_6	5×10^{-5}	8×10^{-3}	1,5	black
[Rh(5,6-Me_2-Phen)ED]PF_6	5×10^{-5}	8×10^{-3}	2,4	black
[Rh(4,7-Me_2-Phen)ED]PF_6	5×10^{-5}	8×10^{-3}	6,5	violet-black
[Rh(4,7-Me_2-(Phen)ED]PF_6 + 0,3(4,7-Me_2-Phen)	5×10^{-5}	8×10^{-3}	10	deep-violet
[Rh(4,7-Me_2-(Phen)ED]PF_6 + 4,7-Me_2-Phen)	5×10^{-5}	8×10^{-3}	5	violet
[Rh(4,7-Me_2-(Phen)ED]PF_6 + 3(4,7-Me_2-Phen)	5×10^{-5}	8×10^{-3}	1,4	light-violet
[Rh(4,7-Me_2-(Phen)ED]PF_6 + 7(4,7-Me_2-Phen)	5×10^{-5}	8×10^{-3}	0,44	colourless

[a] Acetone in 20 ml MeOH 0,3 *M*, in NaOH.

TABLE 3

RATES OF HYDROGENATION OF ACETONE (Complex: 1×10^{-4} moles; NaOH: 5×10^{-4} moles; total volume = 50 ml)

Complex	Solvent	Hydrogen uptake ($ml \cdot min^{-1}$)
$[Rh(Bipy)ED]PF_6$	MeOH 5 ml	3.2
$[Rh(Bipy)ED]PF_6$ + Bipy	MeOH 5 ml	10.9
$[Rh(Bipy)ED]PF_6$	MeOH 15 ml	5
$[Rh(Bipy)ED]PF_6$	EtOH 15 ml	4.5
$[Rh(Bipy)ED]PF_6$	*iso*-PrOH 15 ml	3.3
$[Rh(P(Ph)_3)_2NBD]PF_6$	MeOH 5 ml	0.9
$[Rh(PPh(Me)_2)_2NBD]PF_6$	MeOH 5 ml	0.8

plexes, having a second bidentate ligand coordinated to rhodium through only one of its nitrogen atoms, could be present at intermediate ratios.

Similar catalytic behaviour is observed in alkaline methanol by using $[Rh(ED)Cl]_2$ or $[Rh(COT)_2Cl]_2$ and the chelating ligand in suitable ratios when the system is pre-hydrogenated for 30—45 min. Thus it is not necessary to isolate the corresponding complexes I.

The results obtained for the various ketones with Bipy complexes are collected in Table 4. Reaction rates are high except for methyl-*iso*-butyl ketone which possibly causes steric hindrance. Under the conditions specified in the table, practically 100% conversion can be reached in a few hours.

As reported, the above complexes are also active in an alkaline medium in the presence of excess Chel. This suggested the possibility of using the *cis*-$[Rh(Bipy)_2Cl_2]Cl \cdot 2H_2O$ complex as an alternative precursor for the catalytic system [8,18]. It is known that this complex reacts with molecular hydrogen at 60°C in alkaline aqueous alcohol to give $[Rh(Bipy)_2]^+$ as the final product [14]. After an induction period, the reaction is autocatalytic, and also takes place in alkaline methanol at room temperature. As expected, the reduced system is active for the catalytic hydrogenation of ketones (Table 3). The ketone is added to the basic methanolic system after hydrogenation period of 45—60 min, and as previously reported [14], induction times depend upon the product purity, Insufficient pre-hydrogenation (i.e. only partial formation of the $[Rh(Bipy)_2]^+$ species) gives

TABLE 4

HYDROGEN UPTAKE ($ml\ min^{-1}$) AT 25°C AND ATMOSPHERIC PRESSURE FOR SEVERAL KETONES AND COMPLEXES (5 ml of ketone in 20 ml MeOH, 0.3 *M* in NaOH)

Substrate	$[Rh(Bipy)ED]PF_6$ (1×10^{-4} mol)	[Rh(ED)Cl] (2×10^{-4} mol) + Bipy	[Rh(ED)Cl] (2×10^{-4} mol) + 2Bipy	[Rh(ED)Cl] (2×10^{-4} mol) + 3Bipy
Acetone	4.2	9.2	10	5
Cyclohexanone	6	9.9	11.4	
Methylethyl ketone	3		7	
Methyl-*iso*-butyl ketone	1		2.4	
Acetophenone	4.5	8	9.4	0.24
Propiophenone	2.6		6	

TABLE 5

HYDROGEN UPTAKE AT VARIOUS TEMPERATURES AND ATMOSPHERIC PRESSURE FOR SOME KETONES WITH $[Rh(Bipy)_2Cl_2]Cl \cdot 2H_2O$ (1×10^{-4} mol in 20 ml MeOH, 0.3 *M*, in NaOH)

Substrate	Temperature (°C)				Substrate catalyst
	25	30	35	40	
Acetone	6	11.6	13.1	11.4	680
Cyclohexanone	8.5	12.1			482
Methylethyl ketone	3.8	8.3			558
Acetophenone	8.9	12.9	12.5	11.6	428
Propiophenone	2.5	4.0			376

reaction rates lower than usual [8]. The effect of the temperature on the rates is shown in Table 5. The best rates are obtained between 30 and 35°C.

One of the most important properties of these complexes is that they also act as hydrogenolysis catalysts for molecular oxygen [19]. Thus the $[Rh(Bipy)_2]^+$ system reacts very rapidly with molecular oxygen giving brown solutions of Rh(III) complexes [18], which in turn react immediately with molecular hydrogen to reform the Rh(I) species. This behaviour is observed also in the presence of the substrate, so that molecular oxygen even when present in large amounts does not deactivate the catalytic system.

Hydrogenation of olefins

$[M(Chel)ED]PF_6$ complexes (M = Rh, Ir) are not very useful for hydrogenation in a neutral medium under our conditions. From the data reported in Table 6 it follows, therefore, that iridium complexes are more active than those of rhodium and that the best chelating ligand is always 4,7-Me_2-Phen. In alkaline methanol the rhodium complexes of Bipy are active when the Chel : Rh ratio = 1, but, unlike the behaviour in hydrogenation of ketones, their activity decreases for Chel : Rh ratios $\gg$ 2, in particular in the case of cyclohexane (Table 5).

The different trend between reaction rates and Chel : Rh ratios for olefins and ketones suggests the possibility of selective hydrogenation of C=O groups in the presence of C=C bonds. The $[Rh(Bipy)_2]^+$ system does, in fact, rapidly hydrogenate ketones in the presence of equimolar amounts of cyclohexene. The results of hydrogenation of mixtures of cyclohexene and ketones confirm the high selectivity of this system.

TABLE 6

HYDROGEN UPTAKE AT 25°C AND ATMOSPHERIC PRESSURE FOR 1-HEXENE (5 ml) WITH $[M(Chel)ED]PF_6$ (4×10^{-4} mol) IN 80 ml DRY ACETONE

Chel	M = Rh	M = Ir
Bipy	2	3
Phen	2.5	3.5
4,7-Me_2-Phen	3.4	
3,4,7,8-Me_4-Phen	2.5	

acetone + cyclohexene → *iso*-propanol (100%) + cyclohexane (10%)

cyclohexanone + cyclohexene → cyclohexanol (91.9%) + cyclohexane (5.1%)

acetophenone + cyclohexene → 1-phenylethanol (95%) + cyclohexane (10%)

This selectivity is not observed with the $[Rh(Bipy)ED]^+$ system:

acetophenone + cyclohexene → *iso*-propanol (66%) + cyclohexane (100%)

Finally the $[Rh(Bipy)_2]^+$ system is very active in the hydrogenation of diolefins and 2-alkynes (e.g. norbornadiene 11 ml min^{-1}; 2-hexine 13.5 ml min^{-1} with 2×10^{-4} mol catalyst). Given the low hydrogenation rate of monoenes under such conditions, the system can probably act also as selective catalyst for the hydrogenation of dienes and alkynes to alkenes.

In all these hydrogenation reactions neither formation of metallic rhodium nor hydrogenation of Chel has been observed, although these reactions occur when pyridine is employed as ligand under the same conditions.

On the basis of the aforesaid results, the rhodium complexes with bidentate nitrogen-containing chelating ligands must be regarded as useful hydrogenation catalysts. At least for hydrogenation of ketones, they are more active than the corresponding phosphine complexes. A more detailed study is needed to establish the reaction mechanism. The catalytic activity could probably be further improved by the use of substituted bipyridine or phenanthrolines. Furthermore, use of optically active Chel should permit asymmetric catalyses, and we are preparing complexes of Rh(I) and Ir(I) in which the chelating ligand is the Schiff base between pyridinaldehyde and (+) or (—) α-phenylethylamine [11].

Experimental

The complexes $[M(COT)_2Cl]_2$ (M = Rh, Ir) and $[Rh(Bipy)_2Cl_2]Cl \cdot 2H_2O$ were made by published methods [20,21,14].

$[Rh(Chel)ED]X$ ($X = PF_6$; Chel = Bipy (I); Phen (II); 5,6-Me_2-Phen (III); 4,7-Me_2-Phen (IV); 3,4,7,8-Me_4-Phen (V); $X = B(Ph)_4$; Chel = Bipy (VI); Phen (VII); 5,6-Me_2-Phen (VIII).

A suspension of 0.35 g (0.5 mmol) of $[Rh(COT)_2Cl]_2$: in MeOH (15 ml) is treated with an excess of ED (24 mmol) and allowed to react until the starting complex disappears (1 h). $[Rh(ED)Cl]_2$ separates as yellow crystals. These are treated with a slight excess of the chelating ligand to give orange or red solutions, which are filtered under nitrogen and treated with NH_4PF_6 or $NaB(Ph)_4$ to give the desired complex. The compounds are filtered off, washed with water, and dried in vacuo at room temperature.

$[Rh(Phen)B(Ph)_4]$ (IX)

0.23 g (0.3 mmol) of VII are partially dissolved in THF (20 ml) and treated with molecular hydrogen. After ca. 1 h water (10 ml) is added to the resulting solution, and the THF removed under vacuum, leaving microcrystals of the complex.

[Rh(Phen)$_2$]PF$_6$ (X)

0.23 g (0.3 mmol) of VII are added to a methyl cyanide (10 ml) solution of Phen (0.4 mmol) and the mixture allowed to react for 20 min. The microcrystalline precipitate must be filtered under nitrogen, since it is very sensitive to oxygen.

Derivatives of other Chel are obtained analogously.

[Ir(Chel)(ED)Cl] (Chel = Bipy (XI); Phen (XII))

A suspension of 0.89 g (1 mmol) of [Ir(COT)$_2$Cl]$_2$ in benzene (50 ml) is treated with large excess of ED (5 ml) to give a turbid ochre-yellow solution, which is filtered under nitrogen. This solution is treated with a slight excess of Chel; it immediately turns violet, and a violet solid separated. The complex is filtered off and washed with ether.

[Ir(Chel)ED]X (X = PF$_6$, Chel = Bipy (XIII); Phen (XIV); X = B(Ph)$_4$, Chel = Bipy (XV); Phen (XVI).

A solution of 1 mmol of 9 or 10 in MeOH (35 ml) is treated with an excess of NH_4PF_6 or NaB(Ph)$_4$. The precipitate is filtered off and washed with water.

[Ir(bAdH)(COD)Cl] (XVII)

A suspension of 1 mmol of [Ir(COT)$_2$Cl]$_2$ in methylene chloride (60 ml) is treated initially with an excess of COD (4 ml) and then, after 5 min, with a slight excess of bAdH. The precipitate is filtered off and washed with water.

[Ir(bAdH)COD]B(Ph)$_4$ (XVIII)

A solution of 1 mmol of XVII in MeOH (40 ml) is treated with solid NaB(Ph)$_4$. The complex precipitates as crystals, which are filtered off, washed with ethanol, and dried in vacuo at room temperature.

Acknowledgement

Financial support from CNR (Rome) is gratefully acknowledged. Microanalyses were carried out by Dr. E. Cebulec.

References

1 R.E. Harmon, S.K. Gupta and D.J. Brown, Chem. Rev., 73 (1973) 21.
2 L. Markò and B. Heil, Catalysis Rev., 8 (1973) 269.
3 H.B. Kagan, Pure Appl. Chem., 43 (1975) 401.
4 R.R. Schrock and J.A. Osborn, Chem. Commun., (1970) 567.
5 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711.
6 P. Abley, J. Jardine and F.J. McQuillin, J. Chem. Soc. C, (1971) 840.
7 H. Pasternak and F. Pruchnik, Inorg. Nucl. Chem. Letters, 12 (1976) 591; H. Pasternak, T. Glowiak and F. Prucknik, Inorg. Chim. Acta, 19 (1976) 11.
8 G. Zassinovich, G. Mestroni and A. Camus, Inorg. Nucl. Chem. Letters, 12 (1976) 865.
9 G. Zassinovich, G. Mestroni and A. Camus, J. Molecular Catalysis, 2 (1977) 63.
10 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 98 (1976) 2134; 2143; 4450.
11 G. Zassinovich, A. Camus and G. Mestroni, J. Organometal. Chem., 133 (1977) 377.
12 B. Martin, W.R. McWhinnie and G.M. Waind, J. Inorg. Nucl. Chem., 23 (1961) 207.
13 I.I. Bhayat and W.R. McWhinnie, J. Organometal. Chem., 46 (1972) 159.
14 J.P. Miller and F.D. Oliver, J. Chem. Soc. Dalton, (1972) 2473.

15 G.Mestroni, A. Camus and G. Zassinovich, J. Organometal. Chem., 65 (1974) 119.
16 P.R. Brookes, J. Organometal. Chem., 43 (1972) 415 and references therein.
17 R.H. Crabtree, H. Felkin, G.E. Morris, T.J. King and J.A. Richards, J. Organometal. Chem., 113 (1976) C7.
18 R.D. Gillard, J.A. Osborn and G. Wilkinson, J. Chem. Soc., (1965) 1951.
19 A.S. Berenblyum, L.I. Lakhman, L.K. Ronzhin and M.L. Khidekel, Bull. Acad. Sci. USSR Div. Chem. Sci., 22 (1973) 483.
20 G. Allegra, A. Immirzi, A. Lionetti and L. Porri, Chem. Commun., (1965) 336.
21 J.L. Herdé and C.V. Senoff, Inorg. Nucl. Chem. Letters, 7 (1971) 1029.