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IRIDIUM COMPLEXES WITH α-DIIMINES: CATALYTIC HYDROGEN TRANSFER FROM ISOPROPANOL TO CYCLOHEXANONE

MOHAMMED BIKRANI, LUZ FIDALGO and MARÍA A. GARRALDA*

Facultad de Química de San Sebastián, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain

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Abstract— $[Ir(COD)Cl]_2(COD = 1.5$ -cyclooctadiene) reacted with α -diimines (LL) derived from glyoxal (GLL) or biacetyl (BLL) giving different types of compounds depending on the ligand and on the stoichiometric ratios employed, i.e. $[Ir_2(COD)_2Cl_2(GLL)]$ when $[Ir(COD)Cl]_2/GLL = 1:1$ or IrCl(COD)(LL) when $[Ir(COD)Cl]_2/LL = 1:2$. Solutions of $[Ir_2(COD)_2Cl_2(GLL)]$ contain ionic $[Ir(COD)(GLL)]^+[Ir(COD)Cl_2]^-$ species and dimeric $[Ir(COD)Cl]_2(\mu$ -GLL) species with bridging LL groups in equilibrium. IrCl(COD)(LL)compounds are pentacoordinated in the solid state and undergo rearrangements in solution. In the presence of bulky anions, cationic [Ir(COD)(LL)]A species were formed. When the reactions were performed in the presence of $SnCl_2$, pentacoordinated $Ir(SnCl_3)(COD)(LL)$ compounds were obtained, which in solution showed static or dynamic behaviour depending on the ligand. The different compounds are active catalysts in the homogeneous hydrogen transfer from isopropanol to cyclohexanone. The cationic species show higher activity and the most active cation is the compound containing biacetyloximehydrazone.

 α -Diimines, RN: C(R')C(R'): NR (LL), have shown a versatile coordination chemistry.¹ Their reactivity with diolefinic rhodium halocompounds has been studied extensively,²⁻⁶ giving different types of product, depending on the stoichiometric ratios employed and/or the nature of the ligands, while their reactivity with iridium has been scarcely investigated.⁷ Transition metal halocomplexes react with tin(II) halides to give most frequently trihalostannato compounds.8 Several iridium complexes containing phosphine ligands and the trichlorostannato group bonded through the tin atom have been described,9 though unusual compounds containing the SnCl₃ moiety bonded through chlorine atoms have also been reported.¹⁰ Metallomacrocycles such as $Ir_2(CO)_2Cl_2(\mu-LL)_2$ containing diphosphines as bridging ligands react with SnCl₂ to give compounds containing SnCl¹¹ or

(GLL) or biacetyl (BLL) in the presence or absence of $SnCl_2$. The catalytic activity of the species obtained in the hydrogen transfer reaction from isopropanol to cyclohexanone is also reported.

SnCl₂¹² bridging groups. Iridium compounds con-

taining trichlorostannato groups and nitrogen-

donor ligands have been scarcely studied¹³ and the

reported compounds contain tin-bonded groups.

Iridium(I) complexes with bidentate nitrogen-

donor ligands are very active in hydrogen transfer

reactions from alcohols to several unsaturated organic substrates,¹⁴ and iridium(I) compounds

containing trichlorostannato groups have shown

catalytic activity in hydrogenation¹⁵ and hydrogen

transfer¹⁶ processes. Recently, we have reported on

the reactions of rhodium halocomplexes with α -

diimines and their reactions with SnCl₂^{17,18} on

account of the potential catalytic activity of tran-

sition metal complexes containing covalently

bonded tin compounds in organic trans-

formations.⁸ We now report on the reactions of

 $[Ir(COD)Cl]_2$ with α -dimines derived from glyoxal

^{*}Author to whom correspondence should be addressed.

EXPERIMENTAL

The preparation of the metal complexes was carried out at room temperature under nitrogen using standard Schlenk techniques. [Ir(COD)Cl]₂¹⁹ and the α -diimines²⁰ were prepared as reported previously. Microanalysis was carried out with a Perkin-Elmer 240C microanalyser. Conductivities were measured in acetone or methanol solution with a Metrohm E 518 conductimeter. IR spectra were recorded with a Nicolet FTIR 740 in the range 4000-50 cm⁻¹ using Nujol mulls between polyethylene sheets or KBr pellets. NMR spectra were recorded with an XL-300 Varian spectrometer; ¹H (TMS internal standard) spectra were measured in $CDCl_3$ or acetone- d_6 solutions at variable temperature in 5-mm tubes. ¹¹⁹Sn (SnMe₄ external standard) spectra were measured in acetone-acetone- d_6 (1:1) solutions at variable temperature in 10-mm tubes. The analyses of the catalytic reactions were carried out with a Shimadzu GC-14A chromatograph, connected to a Shimadzu C-R6A calculation integrator.

Preparation of [Ir₂(COD)₂Cl₂(LL)] complexes

To a CH_2Cl_2 (LL = GCH (glyoxal-bis(cyclohexylimine)) or GAA (glyoxal-bis(4-dimethylaminophenylimine))) or acetone solution (LL = GHA (glyoxal-bis(4-hydroxyphenylimine))) of [Ir(COD)Cl]₂ (0.06 mmol) was added an equimolar amount (0.06 mmol) of the corresponding ligand upon which solutions or a suspension (LL = GHA) were obtained. Addition of hexane gave the precipitates that were filtered off, washed with the corresponding solvent and vacuum dried. Yields: 45–81%.

Preparation of [IrCl(COD)(LL)] complexes

To a CH₂Cl₂ solution of $[Ir(COD)Cl]_2$ (0.06 mmol) was added twice the amount (0.12 mmol) of GCH, GHA, BDH (Biacetyldihydrazone) or BOH (Biacetyl-oxime-hydrazone), or excess of BDA (Biacetyldanyl) (0.15 mmol) or BDNH (Biacetyl-bis(dimethylhydrazone)) (0.24 mmol). Addition of hexane or diethyl ether gave precipitates. The compounds obtained were filtered off, washed with the corresponding solvent and vacuum dried. Yields: 43–90%.

Preparation of Ir(SnCl₃)(COD)(LL) complexes

To a CH_2Cl_2 solution of $[Ir(COD)Cl]_2$ (0.06 mmol) was added twice the amount (0.12 mmol) of the corresponding ligand. Addition of a methanol

solution of $SnCl_2$ (0.12 mmol) led, after elimination of CH_2Cl_2 , to the precipitation of the complexes, which were filtered off, washed with MeOH and vacuum dried. Yields : 50–85%.

Preparation of [Ir(COD)(LL)]PF₆ complexes

To a CH_2Cl_2 or acetone (LL = BMG (dimethylglyoxime)) solution or MeOH suspension (LL = BDH) of [Ir(COD)Cl]₂ (0.06 mmol) was added twice the amount (0.12 mmol) of the corresponding ligand and double the amount of NH_4PF_6 (0.12 mmol). After filtration of the NH_4Cl formed and addition of hexane or diethyl ether (LL = BDH, BMG) to the clear solution thus obtained, dark coloured solids precipitated which were filtered off, washed with the corresponding solvent and vacuum dried. Yields: 47–65%.

Preparation of [Ir(COD)(GHA)]BF₄

To a CH_2Cl_2 solution of $[Ir(COD)Cl]_2$ (0.06 mmol) was added twice the amount of GHA (0.12 mmol) and double the amount of AgBF₄ (0.12 mmol). After filtration of the AgCl formed and addition of hexane to the clear solution, a brown solid was obtained and then filtered off, washed with hexane and vacuum dried. Yield: 90%.

Catalytic reactions

The transfer hydrogenation reactions were carried out under nitrogen in refluxing isopropanol at 83°C with magnetic stirring. The equipment consisted of a 100 cm³ round-bottomed flask, fitted with a condenser and provided with a serum cap. The catalysts were prepared by adding 0.2 mmol of potassium hydroxide in 10 cm³ of isopropanol to solutions (20 cm³) of: (a) 0.02 mmol of [Ir(CO-D)(LL)]A; (b) 0.01 mmol of $[Ir(COD)Cl]_2$ and 0.02 mmol of LL, i.e. $[Ir(COD)Cl]_2/LL = 1:2;$ (c) 0.01 mmol of [Ir(COD)Cl]₂, 0.02 mmol of LL and 0.02 mmol of $SnCl_2$, i.e. $[Ir(COD)Cl]_2/LL/SnCl_2 =$ 1:2:2; or (d) 0.01 mmol of [Ir(COD)Cl]₂, 0.02 mmol of LL and 0.04 mmol of SnCl₂, i.e. [Ir(COD) $Cl_2/LL/SnCl_2 = 1:2:4$. The resulting solutions were refluxed for 30 min and 4 mmol of the substrate in 10 cm³ of isopropanol were injected.

RESULTS AND DISCUSSION

[Ir(COD)Cl]₂ reacts with α -dimines (LL, RN:C(R')C(R'):NR") derived from glyoxal (GLL, R' = H) abbreviated as GCH (R = R" = cyclohexyl), GAA (R = R" = 4-dimethylaminophenyl) or GHA (R = R" = 4-hydroxyphenyl), and derived from biacetyl (BLL, $R' = CH_3$), abbreviated as BDA (R = R'' = phenyl), BDH ($R = R'' = NH_2$), BOH ($R = NH_2$, R'' = OH) and BDNH [$R = R'' = N(CH_3)_2$] to afford different types of compounds depending on the type of ligand and on the stoichiometric ratios employed in the reaction as indicated in Scheme 1.

When using glyoxal derivatives, GLL and Ir/GLL = 2:1 ratios, $[Ir_2(COD)_2Cl_2(LL)]$ species are obtained (Table 1). The solid compounds show the expected IR bands due to imine coordinated ligands, along with signals due to v(Rh-Cl). Reddish-brown $[Ir_2(COD)_2Cl_2(GCH)]$ is unstable in solution and instantly gives violet solutions, which according to the ¹H NMR spectra at different temperatures, contain mainly IrCl(COD)(GCH) (see below) and [Ir(COD)Cl]2. GHA and GAA compounds show low conductivities in acetone solution, suggesting non-electrolyte behaviour due to dimeric $[Ir_2(COD)_2Cl_2(\mu-GLL)]$ compounds containing bridging diimine groups. The ¹H NMR spectrum of the slightly soluble $[Ir_2(COD)_2]$ $Cl_2(GAA)$] shows, at room temperature (Table 2), one resonance at 8.83 ppm for both imine protons, which indicates chelation of the diimine and two signals for the olefinic protons at 4.38 and 4.23 ppm, respectively, that could correspond to ionic $[Ir(COD)(GAA)]^+[Ir(COD)Cl_2]^-$ species.²¹ Nevertheless, the presence of a weak resonance at 10.24 ppm suggests the existence of a small amount of a dimeric species with a bridging diimine group,^{2,4,5,18} thus indicating an equilibrium between ionic and neutral species that could be responsible for the low conductivity data. The low solubility of this compound precluded low temperature measurements. These results indicate that the tendency to form dimeric species is lower for iridium than for rhodium.¹⁸ When using the biacetyl derivatives, BLL and Ir/BLL = 2:1 ratios, undefined mixtures of products were obtained. A lower tendency of dimines derived from biacetyl to behave as bridging ligands has been reported.¹

When using Ir/LL = 1:1 stoichiometric ratios, pentacoordinated IrCl(COD)(LL) compounds are obtained. They show the expected IR bands due to imine group coordination in all cases, along with signals due to v(Rh-Cl) stretching. In acetone solution these complexes behave as non-electrolytes, while in methanol solution some chloride dissociation occurs (Table 1). ¹H NMR spectra of the compounds containing GCH or BDA show dynamic behaviour in chloroform solution (Table 2). In both cases the olefinic protons show only one resonance at room temperature, which broadens and collapses on lowering the temperature. By -60° C, the expected two resonances of pentacoordinated compounds are observed. The process responsible for the equilibration of the olefinic protons in this pentacoordinated species could be a Berry pseudo-rotation or a dissociation process.

Reaction of IrCl(COD)(LL) with $SnCl_2$ gives neutral pentacoordinated trichlorostannato com-



(i) Ir/GLL=2/1; (ii) LL=GCH; (iii) Ir/LL=1/1; (iv) Ir/LL/SnCl₂=1/1/1; (v) Ir/LL/A^{*}=1/1/1 Scheme 1.

Table 1. Analytical and physical data for the complexes

$\Delta_{\rm M}$							
Compound	C	H	N	mol^{-1}	(cm^{-1})	(cm^{-1})	Colour
$lr_2(COD)_2Cl_2(GCH)$	40.2	5.2	2.9		1650(w)	327(m);	reddish brown
	(40.4)	(5.4)	(3.1)			305(m)	
$Ir_2(COD)_2Cl_2(GAA)$	42.7	3.6	5.9	27 ;" 24 ^b	1602(s);	324(m);	brown
	(42.8)	(4.8)	(5.8)		1558(w); 1515(s)	319(m)	
$Ir_2(COD)_2Cl_2(GHA)$	39.0	3.6	3.2	19 ; ^a 48 ^b	1605(s)	317(m)	brown
	(39.3)	(4.0)	(5.1)	15.4 500	1647()	215 (hread)	wielet
	40.7	0.5	4.0	15, 50	1047(w)	515 (bibad)	violet
	(47.5)	(0.5)	(3.0)	20.4 200	1605(m)	217()	hrown
	40.0	4.2	3.5 (4.0)	20; 20	1003(III)	517(W)	brown
	(43.9)	(4.2)	(4.9)	A .a 20b	1596(a)	226(m)	dant htvo
IICI(COD)(BDA)	50.4	4.4	4.7	4; 50	1360(8)	250(m)	dark blue
	(50.4)	(4.9)	(4.9)	9.a 7ch	15(0()	210()	h
IFCI(COD)(BDH)	32.8	4.9	(12.4)	8;* 30*	1500(m)	319(W)	brown
	(32.0)	(4.9)	(12.4)	5 .a 3 Ab	1555 (21(()	
IfCI(COD)(BOH)	31.2	4.3	9.4	5;* 24*	1555(m)	310(m)	yenow
	(32.0)	(4./)	(9.3)	7.4.100	1(00()	294()	
IrCI(COD)(BDNH)	38.2	5.7	10.7	7;**12*	1600(m)	284(m)	orange
	(38.0)	(6.0)	(11.1)	10.4.00	1(40()	222()	
$Ir(SnCl_3)(COD)(GCH)$	34.9	4.8	3.7	10;* 60*	1049(w)	322(m);	violet
	(35.4)	(4.9)	(3.8)			316(m);	
	20.2	4.2		0 a 5 2 h	1(0)	305(m)	
$Ir(SnCl_3)(COD)(GAA)$	38.2	4.2	0.0	8;" 53"	1602(s);	324(m), $212(m)$	violet
	(38.1)	(4.2)	(6.8)		1557(W);	313(m);	
	24.4	2.2	27	77 .a A 7 b	1512(s)	300(m) 228()	h
$Ir(SnCl_3)(COD)(GHA)$	34.4	3.3	3.0	27;* 47*	1603(m)	328(W);	brown
	(34.5)	(3.2)	(3.7)	0.4.224	1500(323(m)	douls blue
$Ir(SnCl_3)(COD)(BDA)$	38.5	3.7	3.5	9;* 22*	1588(m)	300(s);	dark blue
	(37.8)	(3.7)	(3.7)	7.a Ach	1540(320(8)	hau
Ir(SnCl ₃)(COD)(BDH)	22.3	3.4	8.5	/;* 40*	1549(m)	310(s);	red
	(22.3)	(3.5)	(0.0)	12 .a c Ab	1619()	290(s) 228(m) :	minte
Ir(SnCl ₃)(COD)(BOH)	(22.1)	(2, 2)	3.8 (6.6)	12;" 04"	1018(W)	328(m);	ріпк
$I_{\sigma}(\mathbf{S}_{\sigma},\mathbf{C}^{\dagger})(\mathbf{C},\mathbf{O},\mathbf{D})(\mathbf{D},\mathbf{D},\mathbf{M})$	(22.5)	(3.3)	(0.0)	21,4 600	1625(m)	319(III) 200(a) :	dark blue
$Ir(SIICI_3)(COD)(DDNH)$	20.0	3.9 (4.2)	0.0 (9.0)	21, 60	1023(III)	300(s);	dark blue
	(27.0)	(4.5)	(0.0)	1224	1655(m)	510(8)	violat
	(20.7)	5.0	(4.2)	155	1055(m)		violet
	(39.7)	(3.4)	(4.2)	1144	1600(m)		dark blue
$[II(COD)(GAA)]FF_6$	45.7	4.5	0.0 (7.6)	114	1000(w)		uark blue
	(42.2)	(4.0)	(7.0)	1174	1605(a)		brown
	40.0	(2,0)	4.2	117	1005(8)		UIOWII
	(42.1)	(3.9)	(4.3) 0 7	1154	1622(m);		aroon
	(25.8)	(2,7)	0.7	115	1023(m), $1508(m)$		green
	(23.8)	(5.7)	(10.0)	504	1570(m)		aroon
	(25.7)	5.5 (3.7)	(7.5)	50	1370(W)		green
[Ir(COD)(BMG)]PF (27.0	35	47	714	1626(m)		brown
	(25.0)	3.5 (3.6)	ч./ (Д 3)	/ 1	1020(111)		UTOWII
[Ir(COD)(BDA)]PF	43.0	37	30	5 4 a	1591(m)		brown
	(42.3)	(4.1)	(4.1)	57	1371(111)		010 WII
	(72.3)	(4.1)	(7.1)				

Conductivity measurements have being carried out in acetone^{*a*} or methanol^{*b*} solutions, $ca 2.5 \times 10^{-4}$ M.

^c **BMG** = dimethylglyoxime.

	Temp.						
Compound	(°C)	Solvent	H—C==N	C_6H_4	CH ₃	HC=	$\delta_{{ m Sn}}{}^a$
$Ir_2(COD)_2Cl_2(GAA)$	20	CDCl ₃	8.83(s)	7.47(d);	2.98(s)	4.38(s);	
				6.67(d)		4.23(s)	
IrCl(COD)(GCH)	20	CDCl ₃	8.95(s)			4.41(s)	
	-60	CDCl ₃	9.02(s)			5.15(s),	
						3.62(s)	
IrCl(COD)(BDA)	20	$CDCl_3$		7.40(m)	1.20(s)	3.90(s)	
	-60	CDCl ₃		7.40(m)	1.20(s)	4.47(s),	
		-			.,	3.20(s)	
[Ir(COD)(GCH)]PF ₆	20	CDCl ₃	8.87(s)			4.39(s)	
[Ir(COD)(GAA)]PF ₆	20	CDCl ₃	8.82(s)	7.46(d);	2.98(s)	4.37(s)	
				6.65(d)			
Ir(SnCl ₃)(COD)(GCH)	20	CDCl ₃	8.42(s)	()		4.72(s),	97
						3.77(s)	
Ir(SnCl ₃)(COD)(BDA)	20	CDCl ₃		7.40(m)	1.70(s)	4.05(s),	164
		2			(-)	3.27(s)	
$Ir(SnCl_3)(COD)(GAA)$	20	CDCl ₃	8.33(s)	7.19(d);	2.99(s)		
		5		6.68(d)	(-)		
	-40	CDCl ₃	8.34(s)	7.20(s):	3.02(s)	4.18(s):	
			(-)	6.69(d)		3.83(s)	
Ir(SnCl ₃)(COD)(GHA)	20	Acetone-d ₆	8.6(s)	7.24(d):			
				6.93(d)			
	40	Acetone-d.	8.74(s)	7.20(d):		4.15(s).	
				6.83(d)		3.85(s)	
Ir(SnCl ₂)(COD)(BDH)	20	Acetone-d ₄		()	2.22(s)	4.12(s)	
	-60	Acetone-d			2.19(s)	4 59(s).	98
	00				2(0)	3 63(s)	,,,
						2.05(5)	

Table 2. Selected NMR data

"In acetone-acetone- d_6 (1:1).

pounds (Table 1). Their IR spectra show bands due to LL coordinated through the imine nitrogens, and v(Sn-Cl) bands indicate that the $SnCl_3^-$ group is bonded to iridium.²² These compounds behave as non-electrolytes in acetone solution, and with the exception of the BDA compound behave almost as 1: 1 electrolytes in methanol solution. The ¹H NMR spectra (Table 2) of the GCH and BDA compounds show the expected signals, two resonances for the olefinic protons in CDCl₃ solution, and the ¹¹⁹Sn NMR spectra show singlets for the trichlorostannato group in acetone- d_6 solution. These spectra remain constant down to -60° C, suggesting a static structure at room temperature. On the other hand, the GAA, GHA and BDH complexes are dynamic. At room temperature the ¹H NMR spectra of the GAA and GHA compounds show no resonances for the olefinic protons, while the BDH compound shows only one resonance for all the olefinic protons at 4.12 ppm, which disappears by -40° C. On further lowering the temperature, two signals analogous to those of the GCH and BDA complexes appear in all cases. Furthermore, the tin resonance for the BDH compound is clearly observed only at -60° C. This suggests dissociation of SnCl₃ at room temperature. The pentacoordinated compounds containing diimines derived from glyoxal show the imine protons corresponding to the σ, σ' -N,N'-chelate form. Reaction of IrCl(COD)(LL) with salts of bulky anions gives the expected cationic [Ir(COD)(LL)]A complexes that behave as 1:1 electrolytes in acetone solution and show the expected signals in their IR (Table 1) and ¹H NMR (Table 2) spectra.

We have investigated the activity of cationic [Ir(COD)(LL)]A complexes and of IrCl(COD) (LL) or $Ir(SnCl_3)(COD)(LL)$ species prepared *in situ* in the homogeneous hydrogen transfer from isopropanol to cyclohexanone; the results obtained are collected in Table 3. In all cases the most efficient catalysts are the cationic compounds, especially those containing hydroxy or amino substituents in the imino nitrogens, i.e. BOH, BDH or BMG (dimethylglyoxime). The most active species

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Catalyst	Reaction time (min)	Conversion (%)
[Ir(COD)(BOH)]PF ₆	14	90
$[Ir(COD)Cl]_2 + 2BOH$	224	90
$[Ir(COD)Cl]_2 + 2BOH + 2SnCl_2$	144	90
$[Ir(COD)Cl]_2 + 2BOH + 4SnCl_2$	181	42
$[Ir(COD)(BDH)]PF_6$	36	90
$[Ir(COD)Cl]_2 + 2BDH$	98	90
$[Ir(COD)Cl]_2 + 2BDH + 2SnCl_2$	167	90
$[Ir(COD)Cl]_2 + 2BDH + 4SnCl_2$	164	90
[Ir(COD)BMG]PF ₆ ^b	55	90
[Ir(COD)BDA]PF ₆	156	90
$[Ir(COD)Cl]_2 + 2BDA$	355	50
$[Ir(COD)Cl]_2 + 2BDA + 2SnCl_2$	359	90
$[Ir(COD)Cl]_2 + 2BDA + 4SnCl_2$	273	90
[Ir(COD)(GCH)]PF ₆	85	90
$[Ir(COD)Cl]_2 + 2GCH$	124	90
$[Ir(COD)Cl]_2 + 2GCH + 2SnCl_2$	210	90
$[Ir(COD)Cl]_2 + 2GCH + 4SnCl_2$	180	52
$[lr(COD)(GAA)]PF_6$	90	90
$[lr(COD)Cl]_2 + 2GAA$	180	56
$[Ir(COD)Cl]_2 + 2GAA + 2SnCl_2$	180	90
$[Ir(COD)Cl]_2 + 2GAA + 4SnCl_2$	180	66
[Ir(COD)(GHA)]BF ₄	210	90
$[Ir(COD)Cl]_2 + 2GHA$	350	75
$[Ir(COD)Cl]_2 + 2GHA + 2SnCl_2$	380	90
$[Ir(COD)Cl]_2 + 2GHA + 4SnCl_2$	335	30

^{*a*} Reaction conditions: $[Ir] = 5 \times 10^{-4} M$; [substrate]/[Ir] = 200; [KOH]/[Ir] = 10;

solvent PrⁱOH (40 cm³); $T = 83^{\circ}$ C; activation time = 30 min.

^b BMG = dimethylglyoxime.

is the BOH compound, containing one OH and one NH₂ substituent, though it is less active than complexes containing Me₄phen-type ligands.²³ The pentacoordinated complexes IrX(COD)(LL) $(X = Cl \text{ or } SnCl_3)$ are coordinatively saturated and their catalytic activation probably involves ligand dissociation, which most likely is an ionic dissociation. Chloro compounds are less active than cationic species and the more active catalysts are those showing the highest conductivity values in methanol, i.e. the BDH and GCH compounds. The presence of SnCl₃ groups enhances the activity in those cases where the trichlorostannato compounds are better conductors in methanol than the corresponding chlorocomplexes, i.e. the BOH, GAA and GHA compounds, and in these cases the excess of SnCl₂ lowers the activity. The presence of trichlorostannato groups seems to provide a higher extent of ionic dissociation, which is inhibited in the presence of excess of SnCl₂.

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REFERENCES

- G. van Koten and K. Vrieze, Adv. Organomet. Chem. 1982, 21, 151.
- H. tom Dieck and J. Klaus, J. Organomet. Chem. 1983, 246, 301.
- 3. H. van der Poel, G. van Koten and K. Vrieze, J. Organomet. Chem. 1977, 135, C63.
- 4. H. van der Poel, G. van Koten and K. Vrieze, *Inorg. Chim. Acta* 1981, **51**, 253.
- B. Crociani, F. di Bianca, M. Faci and T. Boschi, Inorg. Chim. Acta 1988, 145, 253.
- (a) G. Clauti, G. Zassinovich and G. Mestroni, Inorg. Chim. Acta 1986, 112, 103; (b) V. García, M. A. Garralda and L. Ibarlucea, Transition Met. Chem. 1985, 10, 288; (c) E. Delgado-Laita and E. Sánchez-Muñoyerro, Polyhedron 1984, 3, 799; (d) J. Kopf, J. Klaus and H. tom Dieck, Cryst. Struct. Commun. 1980, 9, 783; (e) H. van der Poel, G. van Koten and K. Vrieze, Inorg. Chim. Acta 1981, 51, 241; (f) M. Iglesias, C. del Pino and J. L. Nieto, Inorg. Chim.

Acta 1986, **119**, 7; (g) A. J. Deeming, I. P. Rothwell, M. B. Hursthouse and K. M. A. Malik, J. Chem. Soc., Dalton Trans. 1979, 1899; (h) M. Brockman, H. tom Dieck and J. Klaus, J. Organomet. Chem. 1986, **301**, 209; (i) M. Onishi and I. Kakuzo, Inorg. Chim. Acta 1991, **179**, 155.

- 7. G. Mestroni, G. Zassinovich and A. Camus, J. Organomet. Chem. 1977, 140, 63.
- M. S. Holt, W. L. Wilson and J. H. Nelson, *Chem. Rev.* 1989, 89, 11.
- (a) M. Camia, M. P. Lachi, L. Benzoni, C. Zangottera and M. Tacchi Venturi, *Inorg. Chem.* 1970,
 9, 25; (b) M. R. Chruchill and K. G. Lin, J. Am. Chem. Soc. 1974, 96, 76; (c) M. Kretschmer, P. S. Pregosin, A. Albinati and A. Togni, J. Organomet. Chem. 1985, 281, 365; (d) M. Kretschmer, P. S. Pregosin, P. Favre and C. W. Schlaepfer, J. Organomet. Chem. 1983, 253, 17; (e) M. Kretschmer, P. S. Pregosin and M. A. Garralda, J. Organomet. Chem. 1983, 244, 175; (f) R. Usón, L. A. Oro, M. J. Fernández and M. T. Pinillos, Inorg. Chim. Acta 1980, 39, 57.
- 10. M. Kretschmer and P. S. Pregosin, *Inorg. Chim. Acta* 1982, **61**, 247.
- A. L. Balch, M. M. Olmstead, D. E. Oram, Ph. E. Reedy Jr and S. H. Reimer, *J. Am. Chem. Soc.* 1989, 111, 4021.
- A. L. Balch, B. J. Davis and M. M. Olmstead, *Inorg. Chem.* 1990, **29**, 3068.
- (a) R. Usón, L. A. Oro, M. A. Ciriano and R. Gonzalez, J. Organomet. Chem. 1981, 205, 259; (b) R: Usón, L. A. Oro, D. Carmona and M. A. Esteruelas,

J. Organomet. Chem. 1984, 263, 109; (c) M. T. Pinillos, A. Elduque, J. A. López, F. J. Lahoz, L. A. Oro and B. E. Mann, J. Chem. Soc., Dalton Trans. 1992, 2389.

- (a) G. Zassinovich, G. Mestroni and S. Gladiali, *Chem. Rev.* 1992, 92, 1051; (b) M. A. Esteruelas, M. P. García, M. Marín and L. A. Oro, *J. Molec. Catal.* 1994, 87, 151 and refs therein.
- R. Usón, L. A. Oro, M. J. Fernández and M. T. Pinillos, *Inorg. Chim. Acta* 1980, **39**, 57.
- 16. J. Kaspar, R. Spogliarich and M. Graziani, J. Organomet. Chem. 1982, 231, 71.
- 17. L. Fidalgo, M. A. Garralda, R. Hernández and L. Ibarlucea, *Inorg. Chim. Acta* 1993, 207, 121.
- M. Bikrani, M. A. Garralda, L. Ibarlucea and E. Pinilla, J. Organomet. Chem. 1995, 489, 93.
- 19. J. L. Herde, J. C. Lambert and C. V. Senoff, *Inorg.* Synth. 1974, 15, 18.
- 20. (a) Bock and H. tom Dieck, *Chem. Ber.* 1967, 100, 228; (b) H. tom Dieck and I. W. Renk, *Chem. Ber.* 1971, 104, 92.
- (a) M. A. Esteruelas, L. A. Oro, R. M. Claramunt, C. López, J. L. Lavandera and J. Elguero, J. Organomet. Chem. 1989, 366, 245; (b) P. Imhoff, R. van Asselt, C. J. Elsevier, M. C. Zoutberg and C. H. Stam, Inorg. Chim. Acta 1991, 184, 73.
- D. F. Shriver and M. P. Johnson, *Inorg. Chem.* 1967, 6, 1265.
- (a) A. Camus, G. Mestroni and G. Zassinovich, J. Molec. Catal. 1979, 6, 231; (b) G. Mestroni, G. Zassinovich, A. Camus and F. Martinelli, J. Organomet. Chem. 1980, 198, 87.