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Functional phosphines. Part XIV. Cationic $(P,N)_2$-coordinated hydrides of iridium(III): catalysts for $\succ$C=O hydrogenation or transfer hydrogenation? ☆

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Abstract

Treatment of *trans*-[IrCl(CO)(PPh_3)$_2$] with $Ph_2PCH_2CH_2NH_2$ in refluxing *para*-xylene gave (OC-6-43)-[Ir(H)(Cl)($Ph_2PCH_2CH_2NH_2$)$_2$]Cl (**1**) which interacted with K[BH(*s*-Bu_3)] to produce a mixture of (OC-6-22)-[IrH_2($Ph_2PCH_2CH_2NH_2$)$_2$]Cl (**2a**) and (OC-6-32)-[Ir(H)(Cl)($Ph_2PCH_2CH_2NH_2$)$_2$]Cl (**2b**). The *trans*-dihydride **2a** was isolated in pure form from the reaction between **1** and KOH/*i*-PrOH. Different from its isoelectronic $(P,N)_2$-coordinated Ru^{II} analogues, the cationic chloro hydrido complex **1** does not act as a catalyst for the direct hydrogenation of acetophenone by molecular H_2, if activated by strong alkoxide base, but rather catalyzes the transfer hydrogenation of the $\succ$C=O bond with methanol or isopropanol as proton/hydride sources. Dihydrido complex **2a** is ascribed the role of the actual catalyst as it supports the transfer hydrogenation reaction even in the absence of base. The crystal structure of the addition compound **1** · 2EtOH has been determined.

Keywords: Iridium; Hydrido complexes; Aminophosphine ligands; Transfer hydrogenation; X-ray structure analysis

1. Introduction

Metal complexes containing both *P* and *N* donor ligands have been dominating the field of homogeneous hydrogenation of organic carbonyl compounds for several years. Noyori's ruthenium complexes [$RuCl_2$ {bis(phosphine)}(1,2-diamine)] in particular have been found to be excellent catalysts for the reduction of simple ketones by H_2, if activated by an excess of strong base in isopropanol solution. These compounds give consistently high enantioselectivities if appropriate chiral bis(phosphines) and diamines – especially the enantiomers of the BINAP ligand in combination with optically active 1,2-diphenylethylenediamine – are used as steering ligands [2]. Seminal work of the Morris group with two [RuH(Cl)(P∩P)(H_2N∩NH_2)]/base/H_2 catalyst systems (P∩P = (*R*)-BINAP or 2 PPh_3; H_2N∩NH_2 = $H_2NCMe_2CMe_2NH_2$; base = KOBu-*t* or K[BH(*s*-$Bu)_3$]) [3] has provided convincing evidence that the addition of dihydrogen to the vacant coordination site of initially formed amine–amido hydrido complexes, [RuH(□)(P∩P)(HN∩NH_2)], with subsequent rate-determining deprotonation of the η^2-H_2 ligand by the amide nitrogen atom is the turn-over limiting step of the catalysis. From the resulting diamine dihydrides, [RuH_2(P∩P)(H_2N∩NH_2)], $H^{\delta+}/H^{\delta-}$ equivalents are rapidly transferred to the ketonic substrate, once the carbonyl group has come into close contact with the second coordination sphere of the catalyst through an unconventional Ru–$H^{\delta-}\cdots\succ C^{\delta+}$=$O^{\delta-}\cdots H^{\delta+}$–N "metal–ligand bifunctional" interaction [3–8]. Hartmann and Chen have shown that the activation of the Ru(II) precursor [$RuCl_2${(*S*)-BINAP}{(*S*,*S*)-H_2NCH(Ph)CH(Ph)NH_2}] for catalytic $\succ$C=O hydrogenation not only needs a strong base for dehydrohalogenation but also requires the presence of alkali metal cations, K^+ being particularly efficacious. They postulated that

☆ Part XIII: [1].

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the role of the Lewis acidic potassium ion is to coordinate to the amido nitrogen atom, thereby making the (η^2-H_2)–Ru-amide intermediates cationic, i.e., sufficiently electron-poor for enhanced heterolysis of the dihydrogen ligand. As a result, the rate-determining cleavage of H_2 into H^+ and H^- is accelerated to such a degree that transfer hydrogenation from the solvent is no longer competitive [9].

Against this background, it seemed worthwhile investigating whether Ir^{III} complexes with *P*,*N*-dominated coordination environments, which a priori are cationic by themselves, would act as catalysts for the direct hydrogenation of ketones by molecular H_2 or would rather catalyze the >C=O hydrogenation by transfer of H^+ and H^-equivalents from the solvent.

2. Experimental

2.1. General remarks

All manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. IR: Mattson Polaris. NMR: Bruker DPX 300 (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P) at 20 ± 2 °C with $SiMe_4$ (or the solvent) as internal or H_3PO_4 as external standards (downfield positive; "m": deceptively simple multiplets). (2-Aminoethyl)diphenylphosphine was used as obtained commercially from Fluka. *Trans*-[IrCl(CO)(PPh_3)$_2$] was prepared as previously described [10].

2.2. Metal complexes

2.2.1. *(OC-6-43)-[Ir(H)(Cl)($Ph_2PCH_2CH_2NH_2$)$_2$]Cl (**1**)*

A solution of 2.214 g (2.84 mmol) of *trans*-[IrCl(CO)(PPh_3)$_2$] and 1.366 g (5.96 mmol) of (2-aminoethyl)diphenylphosphine in *para*-xylene (50 mL) was heated at reflux temperature for 3 h. The pale yellow solid which precipitated from solution was collected by filtration, washed with diethyl ether, and dried under vacuum; yield 830 mg (41%). IR (KBr): 3435 (NH), 2202 (IrH) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = -21.79$ (t, *cis*-^2J(P,H) = 16.66 Hz, 1H, IrH), 2.53, 2.72, 3.43, 3.55 (all m; 4, 2, 1, 1H; all CH_2), 4.11 [s (br), 2H, NH], 7.0–7.5 (m, 20 H, C_6H_5), 7.77 [s (br), 2 H, NH···Cl]. ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 35.26$ ("filled-in AA′*X*-d″, ΣJ(P,C) = 38.51 Hz, PCH_2), 44.75 (s, NCH_2), 127.8–134.5 (C_6H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 18.99$. *Anal.* Calc. for $C_{28}H_{33}Cl_2IrN_2P_2$(722.7): C, 46.54; H, 4.60; N, 3.88. Found: C, 46.22; H, 4.87; N, 3.60%.

2.2.2. *(OC-6-22)-[IrH_2($Ph_2PCH_2CH_2NH_2$)$_2$]Cl (**2a**) and (OC-6-32)-[IrH_2($Ph_2PCH_2CH_2NH_2$)$_2$]Cl (**2b**)*

A solution of 614 mg (0.85 mmol) of the chloro hydrido complex **1** in 20 mL of isopropanol was treated with 50 mg (0.89 mmol) of KOH powder. The mixture was stirred for 1 h at ambient conditions and then evaporated to dryness. Crystallization of the residue from diethyl ether gave 540 mg (92%) of **2a** as a bright yellow solid. ^{1}H NMR ([D$_8$]THF): $\delta = -8.03$ (t, *cis*-^2J(P,H) = 13.75 Hz, 2H, IrH_2), 2.52, 2.94, 3.01, (all m; 4, 2, 2H; all CH_2), 6.52 [s (br), 4H, NH_2], 7.1–7.4 (m, 20 H, C_6H_5). ^{13}C{^{1}H} NMR ([D$_4$]methanol): $\delta = 38.09$ ("filled-in AA′*X*-d″, ΣJ(P,C) = 38.51 Hz, PCH_2), 47.92 (s, NCH_2), 128.6–134.5 (C_6H_5). ^{31}P{^{1}H} NMR ([D$_8$]THF): $\delta = 30.56$. *Anal.* Calc. for $C_{28}H_{34}ClIrN_2P_2$ (688.2): C, 48.87; H, 4.98; N, 4.07. Found: C, 48.75; H, 4.78; N, 3.95%.

Combination of **1** (340 mg, 0.47 mmol) with K[BH(*s*-Bu)$_3$] (0.70 mL of a 1 M THF solution) in THF (20 mL) for 2 h at room temperature, followed by removal of all volatile material and crystallization of the remaining solid from diethyl ether, gave the cationic dihydro complex **2** as 3:1 mixture of its OC-6-22 and OC-6-32 stereoisomers, **2a** and **2b**, respectively. ^{1}H NMR ([D$_8$]THF): $\delta = -18.78$ ("t", Σ*cis*-^2J(P,H) = 28.54 Hz; **2b**: IrH *trans*-N), −9.34 (ddd, *trans*-^2J(P,H) = 147.06, *cis*-^2J (P,H) = 20.32, *cis*-^2J (H,H) ≅ 3 Hz; **2b**: IrH *trans*-P), 8.03 (t, *cis*-^2J(P,H) = 13.75 Hz; **2a**: IrH_2). ^{1}H{^{31}P} NMR ([D$_8$]THF): $\delta = -18.78$ (d, *cis*-^2J(H,H) = 2.52 Hz), −9.34 (d), −8.03 (s). ^{31}P{^{1}H} NMR ([D$_8$]THF): $\delta = 23.13$, 31.89 (both d, *cis*-^2J(P,P) = 5.5 Hz each; **2b**), 30.56 (s; **2a**).

2.3. X-ray structure determination

Single crystals of the addition compound **1** · 2EtOH (size $0.49 \times 0.21 \times 0.04$ mm) were grown from ethanol. Diffraction measurements were made at -80 ± 2 °C on an Enraf-Nonius CAD-4 MACH 3 diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å): orientation matrices and unit cell parameters from the setting angles of 25 centered medium-angle reflections; collection of the diffraction intensities by ω scans (data corrected for absorption empirically by ψ scans [11]; $T_{min} = 0.366$, $T_{max} = 0.841$). The structure was solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing the WinGX package [12a] with the relevant programs (SIR 97 [13], SHELXL 97 [14], ORTEP 3 [12b]) implemented therein. $C_{28}H_{33}ClIrN_2P_2$, Cl, 2(C_2H_6O) (814.7); triclinic, $P\bar{1}$, $a = 9.706(2)$ Å, $b = 12.982(5)$ Å, $c = 15.103(5)$Å, $\alpha = 102.90(2)°$, $\beta = 94.96(2)°$, $\gamma = 111.72°$, $V = 1693.0(9)$ Å^3, $Z = 2$, $d_{calc} = 1.598$g cm^{-3}, μ(Mo Kα) = 4.226 mm^{-1}; $2.27° \leqslant \Theta \leqslant 25.07°$, 6263 reflections collected ($-11 \leqslant h \leqslant +11$, $-15 \leqslant k \leqslant +15$,

Table 1
Homogeneous hydrogenation of acetophenone catalyzed by base-modified hydrido chloro complex **1** or by dihydride **2a**[a]

No.	Complex/base (equivalent relative to c_{Ir})	Solvent	$p(H_2)$ (bar)	T (°C)	t (h)	Conversion (%)	~TON[b]
	$[Ir(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]^+$ (**1**)						
1	**1**/none	MeOH	25	25	17		
2	**1**/KOH (5)	THF	25	25	17		
3	**1**/KOH (5)	MeOH	25	25	17	36	20
4	**1**/KOH (5)	MeOH		25	17	37	20
5	**1**/KOBu-*t* (5)	*i*-PrOH		25	3	55	180
6	**1**/KOBu-*t* (5)	*i*-PrOH	100	25	3	45	150
	$[IrH_2(Ph_2PCH_2CH_2NH_2)_2]^+$ (**2a**)			25			
7	**2a**/none	*i*-PrOH		25	3	55	180
8	**2a**/none	*i*-PrOH		50	3	75	250

[a] 20.0 mmol of acetophenone together with 0.02 mmol of **1** (plus added base) or **2a** in 20 mL of solvent.
[b] mol Ph(Me)CHOH mol^{-1}[Ir] h^{-1}.

$0 \leqslant l \leqslant +17$), 6015 unique; $wR = 0.1040$ for all data and 487 parameters, $R = 0.0395$ for 5375 structure factors $F_o > 4\sigma F_o$.

2.4. General procedures for catalytic $\geq C{=}O$ hydrogenation

A Schlenk tube equipped with a small magnetic stirring bar was charged with 20 mmol of acetophenone and 0.02 mmol of catalyst complex **1** or **2a** dissolved in methanol or isopropanol (typically 20 mL). Transfer hydrogenations catalyzed by **2a** were carried out in the absence of base under nitrogen at 25 or 50 °C for 3 h. In hydrogenations catalyzed by **1**, the required equivalent of activating base (cf. Table 1) was added, the mixtures were stirred for 10 min at ambient conditions, and the tube was inserted into an argon-filled stainless steel autoclave. In reactions run under hydrogen, the autoclave was pressurized and vented several times with H_2 (Messer–Griesheim; 99.999%), and finally pressurized to 25 or 100 bar and kept at 25 °C for the times indicated in Table 1.

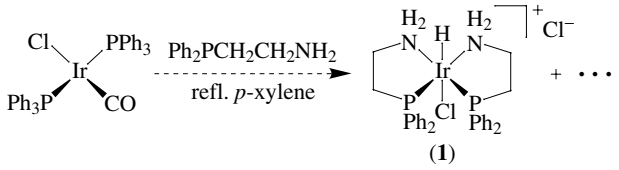
At the end of all catalytic runs, the residues remaining after evaporation of the solvent were diluted with *n*-pentane to precipitate the catalyst as a red oil. The pentane solutions were decanted and chromatographed on a silical gel column using diethyl ether/*n*-pentane (1:1) as the eluent. Volatile material was distilled off and the mixtures of products were analyzed by ^{1}H NMR. Conversions and product compositions were determined on the basis of the integrations of the $PhC(O)CH_3$ and $PhCH(OH)CH_3$ signals. Entries in Table 1 represent the average values of, at least, duplicate runs.

3. Results and discussion

In view of the large number of well-characterized $(P,N)_2$-coordinated ruthenium(II) complexes $[Ru(X)(Y)(P,N)_2]$ (X, Y: halide or hydride) bearing either a bis(phosphine) $R_2P{\cap}PR_2$ ligand in addition to a chelating diamine $H_2N{\cap}NH_2$ [2,3] or, less frequently, two aminophosphines $R_2P{\cap}NH_2$ [15,16], it was surprising to see that a search of the CAS databases [17] gave no indication of the existence of any isostructural cationic iridium(III) complex $[IrX_2(R_2P{\cap}PR_2)(H_2N{\cap}NH_2)]^+$. Moreover, only two dichloro species, (OC-6-13)-$[IrCl_2(Me_2PCH_2CH_2NH_2)_2]^+$ and (OC-6-13)-$[IrCl_2(Ph_2PCH_2CH_2NH_2)_2]^+$, were retrieved as examples of previously described $[IrX_2(R_2P{\cap}NH_2)_2]^+$ cations. Using PF_6^- as the counter-ion, the former was isolated in poor yield (5–9%) from the mixture of products formed upon treatment of $K_3[IrCl_6]$ with an excess of the aminophosphine. Moderate yields of the latter (<50%) were recovered from the reaction between $[Ir_2(\mu\text{-}Cl_2)(\eta^2\text{-}C_8H_{14})_4]$ and $Ph_2CH_2CH_2NH_2$, followed by chlorination of the initially produced iridium(I) intermediates *cis*- and *trans*-$[Ir(Ph_2CH_2CH_2NH_2)_2]Cl$ and separation of the desired complex from the oxidation products as a BF_4^- salt [18].

In a less systematic but – from a preparative point of view – more straightforward way, we obtained the closely related chloro hydrido compound (OC-6-43)-$[Ir(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]Cl$ (**1**) by combining *trans*-$[IrCl(CO)(PPh_3)_2]$ with slightly more than two equivalents of the *P*,*N* chelate ligand in refluxing *para*-xylene for several hours (Scheme 1). The complex separated directly from solution and was readily isolated on a multi-100mg scale. Hydrogen abstraction from the solvent (or from the excess aminophosphine) presents the most likely pathway for the formation of the Ir–H bond, which has much precedence in the literature and is even observed as a competing side reaction in the synthesis of the Vaska complex *trans*-$[IrCl(CO)(PPh_3)_2]$ itself [10a].

Crystallization of **1** from ethanol furnished the addition compound **1**·2EtOH as single crystals, the triclinic unit cell of which contains two formula units connected to a centrosymmetric dimer by multiple NH···Cl, OH···N, and NH···Cl···HO hydrogen bonding (Fig. 1). In the cation itself, the two *P*,*N* ligands span the four equatorial sites of a distorted octahedron such that the phosphino and amino residues are in mutual *trans*-position. The two



(**1**)

Scheme 1. Formation of chloro hydrido complex **1**.

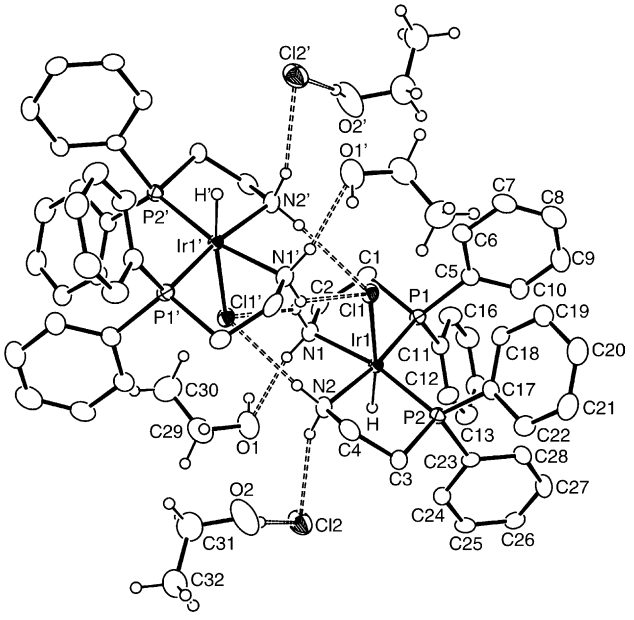
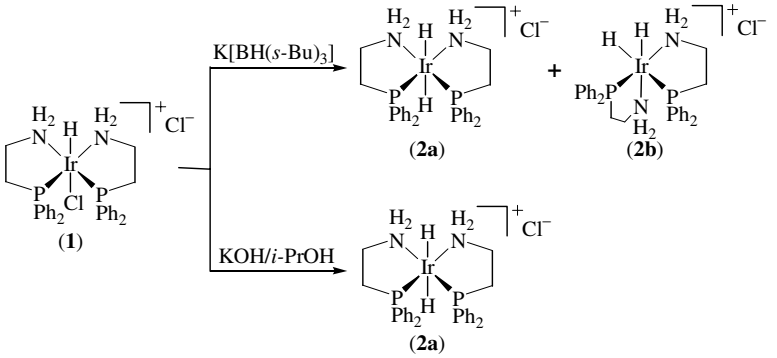


Fig. 1. Perspective view of the multiply hydrogen-bridged centrosymmetric dimer of $[Ir(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]Cl{\cdot}2EtOH$; selected bond lengths [Å] and angles [°]: Ir1–Cl1, 2.5048(17); Ir1–P1, 2.2717(17); Ir1–P2, 2.2632(18); Ir1–N1, 2.136(5); Ir1–N2, 2.138(5); Ir1–H, 1.59(2); N1–H···Cl1′, 3.421(6); N1–H···O1, 2.992(9); N2–H···Cl1′, 3.419(6); N2–H···Cl2, 3.425(6); O2–H···Cl2, 3.098(7). Cl1Ir1–P1, 94.14(6); Cl1–Ir1–P2, 99.44(6); Cl1–Ir1–N1, 85.96(16); Cl1–Ir1–N2, 85.24(16); Cl1–Ir1–H 173(3); P1–Ir1–P2, 105.25(6); P1–Ir1–N1, 84.17(16); P1–Ir1–N2, 170.96(15); P1–Ir1–H, 88(3); P2–Ir1–N1, 168.64(16); P2Ir1–N2, 83.74(16); P2–Ir1–H, 87(3); N1–Ir–N2, 86.8(2); N1–Ir1–H, 87(3); N2–Ir1–H, 92(3); N1–H···Cl1′, 134.5; N1H···O1, 166.3; N2–H···Cl1′, 169.4; N2–H···Cl2, 159.1.

Ir–N bond lengths average out at 2.137(5) Å, which differs only slightly from the mean metal-amine distance of 2.147(6) Å that was previously determined for (OC-6-13)-$[IrCl_2(Ph_2PCH_2CH_2NH_2)_2]$ BF_4 [18]. In contrast, the average value of the Ir–P separations measured as 2.268(2)Å for **1** is considerably below the 2.303(1) Å found in the dichloro complex. As expected, the length of the Ir–Cl linkage opposite the strong *trans*-bond-weakening hydride ligand, 2.505(2) Å, is much longer than the two *trans*-located Ir–Cl bonds of the $[IrCl_2(Ph_2PCH_2CH_2NH_2)_2]^+$ cation (2.365(1) Å [18]).

Combination of the cationic chloro hydrido complex **1** with K[BH(*s*-Bu)$_3$] in THF cleanly produced the dihydride $[IrH_2(Ph_2PCH_2CH_2NH_2)_2]Cl$ as a 3:1 mixture of its OC-6-22 and OC-6-32 stereoisomers, **2a** and **2b**, respectively. Coordination geometries and product compositions were readily inferred from ^1H NMR spectroscopy (Section 2). Potassium isopropoxide (KOH/*i*-PrOH) interacted with **1** to selectively form the *trans*-dihydride **2a** (Scheme 2). This latter transformation resembles the base-induced conversion of the d^6 low-spin and, hence, substitutionally inert Noyori-type precatalysts [Ru(Cl)(X){bis(phosphine)}(1,2-diamine)] (X = H, Cl) into the actually active dihydrido species $[RuH_2\{bis(phosphine)\}(1,2\text{-diamine})]$ [3c,3d,19] and prompted us to examine whether the cationic bis(aminophosphine)iridium(III) complex **2a** parallels its isoelectronic {bis(phosphine)(1,2-diamine)} ruthenium(II) analogues in the ability to catalyze the hydrogenation of ketones.

For that purpose, both the chloro hydrido compound **1** and the *trans*-dihydride **2a** were probed for their behavior as >C=O hydrogenation catalysts under the conditions summarized in Table 1. Using acetophenone as a standard test substrate, virtually no conversion to 1-phenylethanol was observed under 25 bar of H_2 on attempted catalysis by **1** in the absence of an activating base in a protic solvent such as methanol or, vice versa, in an aprotic THF medium containing such a basic additive (entries 1 and 2). Only if combined with po-



Scheme 2. Syntheses of *P*,*N*-coordinated dihydrido complexes **2a** and **2b**.

tassium hydroxide (5 equiv.) in methanol, complex **1** was seen to act as a (slow) catalyst for the hydrogenation of the ketone – in fact, irrespective of whether the reaction was carried out under H_2 pressure or under an inert atmosphere of nitrogen or argon (entries 3 and 4). These observations clearly demonstrate (i) that the chloro hydrido species **1** as such does not behave as a catalyst for homogeneous >C=O reduction and (ii) that the combined catalytic system **1**–KOH/MeOH facilitates the transfer of H^+ and H^- equivalents from the solvent relative to the direct addition of dihydrogen to the substrate.

As anticipated [20], a marked acceleration of the reaction was noted if precatalyst **1** was activated by strong base in isopropanol which, as a secondary alcohol, is a better hydrogen donor than methanol and, hence, is the reducing agent of choice employed for transfer hydrogenations. Thus, acetophenone was converted to 1-phenylethanol in 55% yield, if kept in Me_2CHOH under argon at 25 °C for 3 h in the presence of 0.1 mol% of added **1**–KOBu-*t* (1:5); entry 5. If such reaction mixtures were pressurized to 100 bar of H_2, the degree of substrate transformation dropped to only 45%, showing that the catalytic system looses part of its hydrogenation activity in the presence of hydrogen gas (entry 6).

Hydrogen transfer from the solvent to the substrate in the presence of 0.1 mol% of dihydrido complex **2a** occurs even in the absence of base, giving the alcohol in exactly the same yield as produced in reactions that were carried out under equal conditions with **1**–KOBu-*t* (1:5) as hydrogenation catalyst (entry 7). Raising the temperature from 25 to 50 °C resulted in an increased conversion of the substrate as expected (entry 8). Since the *trans*-dihydride **2a** is the sole product formed in the reaction of the precursor chloro hydrido complex **1** with alkoxide base in isopropyl alcohol, it is evident that **2a** also operates as the true catalyst of the transfer hydrogenations supported by the combined system **1**-KOBu-*t*.

4. Concluding remarks

Although the use of Ir^I and Ir^{III} complexes as transfer hydrogenation catalysts is well documented [20,21], we are not aware of any previously employed cationic iridium(III) compound bearing a direct resemblance to the famous Noyori-Morris [Ru(X)(Y){bis(phosphine)}(1,2-diamine)] hydrogenation catalysts (X, Y = H,Cl). The exactly matching Ru^{II} analogue of the $[Ir(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]^+$ cation, $[Ru(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]$, has recently been described in a patent application [16]. That ruthenium complex differs from its isoelectronic iridium congener reported in this communication in that it efficiently catalyzes the direct addition of H_2 to the >C=O bond if activated by KOPr-*i* (3–10 equiv.) and combined with ketones (neat or dissolved in C_6D_6) at substrate-to-catalyst ratios between 400:1 and 2500:1 at ambient conditions under an atmosphere of hydrogen gas (~3.5 bar). In isopropanol at elevated temperature and H_2 pressure (60 °C, 40 bar), in the presence of a large excess of KOBu-*t* (>1000 equiv.), the bis(aminophosphine) ruthenium complex even displays the extraordinarily high hydrogenation activity characteristic of all [Ru(X)(Y){bis(phosphine)}(1,2-diamine)] catalysts, quantitatively transforming the substrate within a few hours at s/c ratios exceeding 100 000:1. As a further difference between cationic $[Ir(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]^+$ and neutral $[Ru(H)(Cl)(Ph_2PCH_2CH_2NH_2)_2]$, we note that the latter quite surprisingly also behaves as a rather efficient hydrogenation catalyst in the absence of any promoting base [16]. No such catalytic behavior is exhibited by the chloro hydrido species **1**, which requires transformation into dihydride **2a** in order to become catalytically active. In this respect, the iridium(III) precatalyst **1** is more closely akin to, e.g., the chloro hydrido complexes $[Ru(H)(Cl)(PPh_3)_2\{(R,R)\text{-}1,2\text{-}(H_2N)_2C_6H_{10}\}]$ and $[Ru(H)(Cl)\{(R)\text{-BINAP}\}(H_2NCMe_2CMe_2NH_2)\}]$ which likewise do not act as >C=O hydrogenation catalysts unless converted into the corresponding dihydrido derivatives [3]. These dihydrides of Ru^{II}, $[RuH_2(PPh_3)_2\{(R,R)\text{-}1,2\text{-}(H_2N)_2C_6H_{10}\}]$ and $[RuH_2\{(R\text{-BINAP})(H_2NCMe_2CMe_2NH_2)\}]$, then behave as active catalysts for *direct* hydrogenations of ketones in the absence of extra base as does iridium(III) dihydride **2a** for >C=O *transfer* hydrogenations.

Both the observation that the addition of excess potassium *tert*-butoxide to cationic complex **1** does not favor direct over transfer hydrogenation and the finding that the catalysis is even slowed down under H_2 pressure show that there is neither a "potassium effect" [9] nor a beneficial influence of positive charge in the cases studied in this work. This could be due to a mechanism which does not occur via a concerted hydrogen transfer with no direct metal–ketone binding along the pathway as observed for ruthenium(II). The catalytic activity of the coordinatively saturated dihydride **2a**, which as low-spin d^6 system should be quite substitutionally inert, does however suggest that such an unconventional $Ir\text{–}H^{\delta-}\cdots>C^{\delta+}=O^{\delta-}\cdots H^{\delta+}-N$ "metal–ligand bifunctional" interaction is actually operative along the reaction path. It has been proposed by others that the role of K^+ ions in Noyori–Morris systems could merely be to precipitate chloride during catalyst activation rather than act as a Lewis acid which accelerates H–H cleavage at a metal–amide bond bearing a partial positive charge [3d]. Further work aiming at the use of other diamine-bis(phosphine) complexes of Ir^{III} and Rh^{III} as catalysts for the homogeneous reduction of organic carbonyl compounds by direct or transfer hydrogenation is underway.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC-215606. Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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