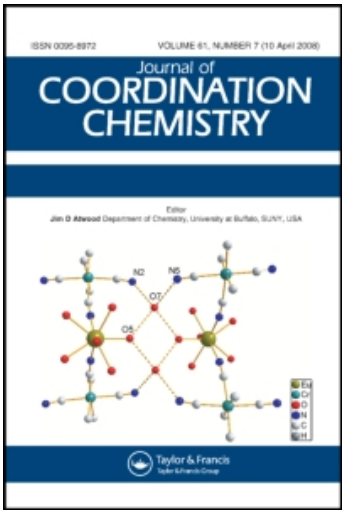

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Chiral Ir(I) and Ir(III) complexes [Ir{(*R*)-binap}(1,2-diamine)]Cl and *trans*-[Ir(H)$_2${(*R*)-binap}(1,2-diamine)]Cl: synthesis and catalytic applications†

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The P_2,N_2-coordinated iridium(I) chelate complexes [Ir{(*R*)-binap}(1,2-diamine)]Cl, where (*R*)-binap = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl and 1,2-diamine = $H_2NCMe_2CMe_2NH_2$ (tmen) (**1**), (1*R*,2*R*)-$H_2NCH(Ph)CH(Ph)NH_2$ [(*R*,*R*)-dpen] (**2**), or *cyclo*-(1*R*,2*R*)-1,2-$(H_2N)_2C_6H_{10}$ [(*R*,*R*)-dach] (**3**), were formed by treating [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] with the respective *N*,*N* ligand in inert solvents at ambient conditions. They reacted with methanol in benzene or toluene at reflux producing dihydridoiridium(III) complexes, *trans*-[Ir(H)$_2${(*R*)-binap}(1,2-diamine)]Cl [1,2-diamine = tmen (**4**), (*R*,*R*)-dpen (**5**), or (*R*,*R*)-dach (**6**)]. Compounds **4**–**6** are base-free (albeit rather slow) catalysts for both the transfer hydrogenation of acetophenone and the hydrogenation of the ketone with molecular hydrogen, giving (*S*)-1-phenylethanol with moderate enantioselectivities (ee_{max}: 74%). A cyclometallated hydridoiridium(III) complex, characterized as (*OC*-6-54)-[Ir(H)(Cl){(*R*,*R*)-binap}{C_6H_4-2-[(*R*,*R*)-$CH(NH_2)CH(Ph)N{=}CMe_2$]-$\kappa C^1,\kappa N^\alpha$}] (**7**) by single-crystal X-ray diffraction, was identified as one of the products formed from [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] and the (*R*,*R*)-dpen ligand in acetone under hydrogen.

Keywords: Iridium; Nitrogen ligands; Phosphorus ligands; Asymmetric catalysis

1. Introduction

In previous work, we isolated the bis(β-aminophosphine)-chelated ionic Ir^{III} complex (*OC*-6-43)-[Ir(H)(Cl)($Ph_2PCH_2CH_2NH_2$)$_2$]Cl (scheme 1: **I**) by combining *trans*-[Ir(Cl)(CO)(PPh_3)$_2$] with the *P*,*N* chelate ligand in refluxing xylenes and obtained the *trans*-dihydride (*OC*-6-22)-[Ir(H)$_2$($Ph_2PCH_2CH_2NH_2$)$_2$]Cl (**II**) upon treatment of **I** with KOH in isopropanol [1]. Despite their structural resemblance to the isoelectronic P_2,N_2-coordinated Ru^{II} compounds (*OC*-6-43)-[Ru(H)(Cl){bis(phosphine)}(1,2-diamine)] and (*OC*-6-22)-[Ru(H)$_2${bis(phosphine)}(1,2-diamine)], which are powerful >C=O

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†Dedicated to Professor Rudi van Eldik on the occasion of his 65th birthday in recognition of his outstanding contributions to the reactivity of inorganic and coordination compounds.

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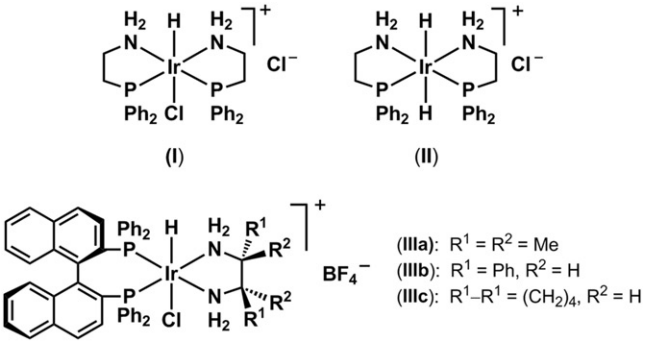


Scheme 1. Complexes **I**–**III**.

hydrogenation (pre)catalysts [2, 3], the two Ir^{III}-centered cations did not parallel their neutral Ru^{II} equivalents in the ability to catalyze the reduction of ketones by molecular hydrogen (referred to as "H_2-hydrogenation" in the following) but only acted as catalysts for transfer hydrogenations of the >C=O function with alcohols as proton/hydride donors. Similar to the Ru^{II}-catalyzed H_2- and transfer hydrogenations, the presence of a strong base was mandatory for chloridohydrido complex **I** to be catalytically active, whereas dihydrido complex **II** maintained catalysis even in the absence of the added base and hence was attributed the role of the actual catalyst [1]. Theoretical calculations which used $H_2PCH_2CH_2NH_2$-coordinated molecules as simplified models showed that both the Ru^{II}- and the Ir^{III}-catalyzed hydrogenations involve weakly solvated amidohydrides *trans*-$[M(H)(solv)(H_2P \cap NH)(H_2P \cap NH_2]^{0/+}$ and aminodihydrides *trans*-$[M(H)_2(H_2P \cap NH_2)_2]^{0/+}$ as key intermediates. The failure of the cationic Ir^{III} system to support H_2-hydrogenations was traced back to that step of the catalytic cycle where the H_2 molecule has to displace the coordinated solvent from the amidohydrides to generate amido(dihydrogen) transients, *trans*-$[M(H)(\eta^2\text{-}H_2)(H_2P \cap NH)(H_2P \cap NH_2]^{0/+}$, which are needed to restore the aminodihydrides *trans*-$[M(H)_2(H_2P \cap NH_2)_2]^{0/+}$ by proton transfer from the H_2 ligand to the amide function; because of the stronger coordination of the solvent molecule to the cationic Ir^{III} complex compared to the neutral Ru^{II} compound, this substitution reaction turned out to be significantly endothermic for $M = Ir^{III}$, but close to thermoneutral for $M = Ru^{II}$ [4].

Chelate ligands of spatial demand greater than that of $Ph_2PCH_2CH_2NH_2$ could facilitate the decoordination of weakly bound molecules from the Ir^{III} center through "steric pressure" [5] and thereby contribute to easier replacement of solvent by H_2 in the iridium-catalyzed H_2-hydrogenations as well. In fact, the chloridohydrido complexes (*OC*-6-43)-[Ir(H)(Cl){(*R*)-binap}(1,2-diamine)]BF_4, where (*R*)-binap = (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl and 1,2-diamine = $H_2NCMe_2CMe_2NH_2$ (tmen), (1*R*,2*R*)-$H_2NCH(Ph)CH(Ph)NH_2$ [(*R*,*R*)-dpen], or *cyclo*-(1*R*,2*R*)-1,2-$(H_2N)_2C_6H_{10}$ [(*R*,*R*)-dach] (scheme 1: **IIIa – IIIc**), were shown to act as catalysts for the H_2-hydrogenation of acetophenone, if activated by a strong base [6]. This raised the question as to whether Ir^{III}-centered cationic dihydrido complexes *trans*-$[Ir(H)_2\{(R)\text{-binap}\}(1,2\text{-diamine})]^+$ would likewise support H_2-hydrogenations of ketones, and whether the close structural relationship of such cations to their catalytically active

neutral Ru^{II} equivalents *trans*-[Ru(H)$_2${(*R*)-binap}(1,2-diamine)] [2, 3] would be favorable for their functioning as >C=O hydrogenation catalysts even in the absence of a base.

In this article, we describe the somewhat elusive synthesis of three ionic *trans*-dihydridoiridium(III) complexes [Ir(H)$_2${(*R*)-binap}(1,2-diamine)]BF_4 and their Ir^I precursors [Ir{(*R*)-binap}(1,2-diamine)]BF_4 containing the diamine ligands tmen, (*R*,*R*)-dpen, and (*R*,*R*)-dach, and also give a first account of the behavior of the *trans*-dihydrides as base-free catalysts for the hydrogenation of acetophenone.

2. Experimental

2.1. *General*

All manipulations were performed under argon using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents prior to use. IR: Mattson Infinity 60 AR. NMR: Bruker DPX 300 (300.1 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P) with $SiMe_4$ as internal or H_3PO_4 as external standards (downfield positive) in CD_2Cl_2 at ambient temperature. Gas chromatography: Shimadzu GC-17A (FID). Silver tetrafluoroborate and the bis(phosphine) and diamine ligands (*R*)-binap, (*R*,*R*)-dpen, and (*R*,*R*)-dach were used as commercially supplied. 1,1′,2,2′-Tetramethylethylenediamine (tmen) [7] and [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] [8] were prepared according to published procedures or slight modifications thereof.

2.2. *Preparation and formation of Ir^I complexes [Ir{(R)-binap}(1,2-diamine)]Cl*

2.2.1. Preparation of [Ir{(R)-binap}(tmen)]Cl (1). A solution of 80 mg (0.05 mmol) of [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] and 44 mg (0.38 mmol) of tmen in 15 mL benzene was stirred at ambient conditions. The mixture gradually changed from dark red to orange red, and the product separated within 6 h as a bright red solid which was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 22 mg (24%). Anal. Calcd for $C_{50}H_{48}ClIrN_2P_2$ (%): C, 62.13; H, 5.01; N, 2.70. Found: C, 62.09; H, 5.07; N, 2.77. ^{1}H NMR: δ 1.17, 1.31 [both s, 6H each, C(CH$_3$)$_2$], 2.19, 4.67 (both br, d, $^2J_{H-H} = 11.8$ Hz each, 2H each, NH$_2$), 6.4–7.8 (m, 32H, aryl H) ppm. ^{31}P{^{1}H} NMR: δ 16.99 (s) ppm.

2.2.2. Formation of [Ir{(*R*)-binap}{(*R*,*R*)-dpen}]Cl (2). Stirring the red suspension of 237 mg (0.14 mmol) of [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] and 135 mg (0.64 mmol) of the diamine in 30 mL of benzene for 30 min at room temperature gave a clear orange solution. An orange solid began to precipitate after an additional 30 min and was collected by filtration after stirring overnight. ^{1}H and ^{31}P{^{1}H} NMR spectroscopy revealed the presence of **2** along with *trans*-[Ir(H)(Cl){(*R*)-binap}{(*R*,*R*)-dpen}]Cl (**2**·HCl) in approximate 4 : 1 stoichiometry. ^{1}H NMR: δ −19.68 (dd, *cis*-$^2J_{P-H} = 15.6$ and 18.4 Hz, IrH of **2**·HCl), 4.32, 4.42 (both br, 2H each, NH$_2$ of **2**), 4.77 (m, 2H, CH of **2**), 6.4–8.2 (m, 42H, aryl H) ppm. ^{31}P{^{1}H} NMR: δ −9.40, 0.05 (both d, *cis*-$^2J_{P-P} = 22.3$ Hz, **2**·HCl), 18.00 (s, **2**) ppm; relative ^{31}P{^{1}H} intensities **2** : **2**·HCl ≅ 4 : 1. Comparative data (CD_2Cl_2) for authentic *trans*-[Ir(H)(Cl){(*R*)-binap}{(*R*,*R*)-dpen}]$^+$ (BF_4^- salt) [6]:

δ_H −19.81 (dd, *cis*-$^2J_{P-H}$ = 15.9 and 18.0 Hz, IrH) ppm; δ_P −9.99, 0.64 (both d, *cis*-$^2J_{P-P}$ = 22.3 Hz) ppm.

2.2.3. Formation of [Ir{(*R*)-binap}{(*R*,*R*)-dach}]Cl (3). [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] (431 mg, 0.25 mmol) and 69 mg (0.60 mmol) of (*R*,*R*)-dach were suspended in 25 mL of toluene. Stirring for 30 min at ambient conditions caused the precipitation of a red solid, the ^{1}H and ^{31}P{^{1}H} NMR spectra of which showed the presence of **3**, again accompanied by *trans*-[Ir(H)(Cl){(*R*)-binap}{(*R*,*R*)-dach}]Cl (**3**·HCl) as well as by an unidentified additional by-product in 3 : 1 : 1 molar ratio. ^{1}H NMR: δ −20.17 (dd, *cis*-$^2J_{P-H}$ = 15.4 and 18.1 Hz, IrH of **3**·HCl), 1.2–1.7 (m, 8H, CH_2), 2.81, 3.33 (both br, 2H each, NH_2 of **3**), 3.52 (m, 2H, CH of **3**), 6.2–8.4 (m, 32H, aryl H) ppm. ^{31}P{^{1}H} NMR: δ −32.16, −31.65 (both d, *cis*-$^2J_{P-P}$ = 20.0 Hz, unidentified), −10.36, −1.06 (both d, *cis*-$^2J_{P-P}$ = 22.0 Hz, **3**·HCl), 16.99 (s, **3**) ppm; relative ^{31}P{^{1}H} intensities **3 : 3**·HCl: "unidentified" ≅ 3 : 1 : 1. Comparative data (CD_2Cl_2) for authentic *trans*-[Ir(H)(Cl){(*R*)-binap}{(*R*,*R*)-dach}]$^+$ (BF_4^- salt) [6]: δ_H −20.35 (dd, *cis*-$^2J_{P-H}$ = 15.5 and 18.2 Hz, IrH) ppm; δ_P −10.69, −1.10 (both d, *cis*-$^2J_{P-P}$ = 22.3 Hz) ppm.

2.3. *Preparation of trans-dihydridoiridium(III) complexes [Ir(H)$_2${(R)-binap}(1,2-diamine)]Cl*

2.3.1. *Trans*-[Ir(H)$_2${(*R*)-binap}(tmen)]Cl (4). A solution of 648 mg (0.38 mmol) of [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] and 122 mg (1.05 mmol) of tmen in 45 mL benzene was stirred at ambient temperature for 90 min to initiate the intermediate formation of [Ir{(*R*)-binap}(tmen)]Cl, which was subsequently treated with 6 mL of methanol. The mixture was refluxed for 40 h and then concentrated to a final volume of 10 mL. Dilution with 120 mL of diethyl ether resulted in the precipitation of the product as a yellow solid which was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 522 mg (71%). Anal. Calcd for $C_{50}H_{50}ClIrN_2P_2$ (%): C, 62.00; H, 5.20; N, 2.89. Found: C, 62.38; H, 5.33; N, 2.59. IR (KBr, cm^{-1}): 1735 (IrH$_2$). ^{1}H NMR: δ −6.40 (t, *cis*-$^2J_{P-H}$ = 13.2 Hz, 2H, IrH$_2$), 1.09, 1.29 [both s, 6H each, C(CH$_3$)$_2$], 1.76, 4.89 (both br, d, $^2J_{H-H}$ = 10.7 Hz each, 2H each, NH_2), 6.4–7.9 (m, 32H, aryl H) ppm. ^{31}P{^{1}H} NMR: δ 17.63 (s) ppm.

2.3.2. *Trans*-[Ir(H)$_2${(*R*)-binap}{(*R*,*R*)-dpen}]Cl (5). [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] (298 mg, 0.17 mmol) and (*R*,*R*)-dpen (81 mg, 0.38 mmol) were suspended in 10 mL of toluene. The mixture was stirred for 3 h at room temperature, then treated with 3 mL of methanol, and heated at reflux for 20 h. Evaporation under vacuum to 2 mL followed by the addition of 60 mL of diethyl ether caused **5** to separate from solution as an off-white solid which was collected, washed with diethyl ether, and dried. Yield: 161 mg (43%). Anal. Calcd for $C_{58}H_{50}ClIrN_2P_2$ (%): C, 65.43; H, 4.73; N, 2.63. Found: C, 65.54; H, 4.81; N, 2.26. IR (KBr, cm^{-1}): 1719 (IrH$_2$). ^{1}H NMR: δ −5.67 (t, *cis*-$^2J_{P-H}$ = 12.6 Hz, 2H, IrH$_2$), 4.18 (br, 4H, NH_2), 4.56 (m, 2H, CH), 6.4–8.0 (m, 42H, aryl H) ppm. ^{31}P{^{1}H} NMR: δ 18.22 (s) ppm.

2.3.3. *Trans*-[Ir(H)$_2${(*R*)-binap}{(*R*,*R*)-dach}]Cl (6). The complex was prepared similar to the procedure outlined for **4** from 497 mg (0.29 mmol) of [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] and 92 mg (0.81 mmol) of the diamine in 35 mL of benzene: Stirring at ambient temperature for 2 h, followed by the addition of 5 mL of methanol and heating under reflux for 40 h gave a dark red solution which was concentrated to 2 mL. The off-white product was isolated by adding diethyl ether (150 mL), then washed with diethyl ether and dried under vacuum. Yield: 273 mg (48%). Anal. Calcd for $C_{50}H_{48}ClIrN_2P_2$ (%): C, 62.13; H, 5.01; N, 2.90. Found: C, 62.23; H, 5.43; N, 3.00. IR (KBr, cm^{-1}): 1722 (IrH$_2$). ^{1}H NMR: δ −6.41 (t, *cis*-$^2J_{P-H}$ = 12.6 Hz, 2H, IrH$_2$), 1.1–1.8 (m, 8H, CH$_2$), 2.58, 3.09 (both br, 2H each, NH$_2$), 3.68 (m, 2H, CH), 6.3–8.0 (m, 32H, aryl H) ppm. ^{31}P{^{1}H} NMR: δ 17.87 (s) ppm.

2.4. *Isolation of (OC-6-54)-[Ir(H)(Cl){(R,R)-binap}{C$_6$H$_4$-2-[(R,R)-CH(NH$_2$)CH(Ph)N=CMe$_2$]-κC^1,κN^α}] (7)*

An acetone solution (15 mL) containing 548 mg (0.32 mmol) of [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] and 144 mg (0.68 mmol) of the diamine was stirred for 20 h at ambient conditions, cooled to −65°C, and exposed to a stream of hydrogen. The mixture was then allowed to warm to room temperature under hydrogen, treated with 2 mL of methanol, and heated under reflux for 2 h. Dilution with 25 mL of diethyl ether resulted in deposition of a pale yellow solid which was washed with diethyl ether and dried under vacuum. ^{31}P{^{1}H} spectroscopy showed predominantly the presence of a species displaying an AB pattern at δ 5.18 and 5.37 ppm ($^2J_{AB}$ = 11.1 Hz), accompanied by minor amounts of *trans*-[Ir(H)(Cl){(*R*)-binap}{(*R*,*R*)-dpen}]Cl (δ −9.41, 0.03; both d, *cis*-$^2J_{P-P}$ = 22.0 Hz; see Section 2.2.2) and traces of additional unidentified side products. Recrystallization from CH_2Cl_2/Et_2O afforded the main product as single crystals, identified by X-ray crystallography (see below) and ^{1}H NMR spectroscopy as (*OC*-6-54)-[Ir(H)(Cl){(*R*,*R*)-binap}{C$_6$H$_4$-2-[(*R*,*R*)-CH(NH$_2$)CH(Ph)N=CMe$_2$]-κC^1,κN^α}] (**7**). ^{1}H NMR: δ −20.53 (dd, *cis*-$^2J_{P-H}$ = 11.6 and 19.2 Hz, 1H, IrH), 1.54, 1.86 (both s, 3H each, CH$_3$), 3.78, 4.76 (both d, $^2J_{H-H}$ = 9.3 Hz, 1H each, CH), 4.06 (br, 2H, NH$_2$), 5.7–8.3 (m, 41H, aryl H) ppm.

2.5. *General procedure for catalytic >C=O hydrogenation*

A Schlenk tube equipped with a small magnetic stirring bar was charged with 0.01–0.02 mmol of the iridium catalysts **4**–**6**, dissolved in 10–20 mL of benzene or in MeOH, EtOH, and *i*-PrOH, respectively. The required amount of acetophenone (table 1) was then added and the mixtures were stirred for 5 min at ambient conditions under argon. In transfer hydrogenations catalyzed by **5** and **6**, stirring was continued for 24 or 36 h at 50°C. In H_2-hydrogenations catalyzed by **4**–**6**, the tube was subsequently inserted into an argon-filled stainless steel autoclave. The autoclave was pressurized and vented several times with H_2 (Messer-Griesheim; 99.999%), and finally pressurized to 25 or 50 bar and kept at 50°C for 24 h.

At the end of all catalytic runs, the residues remaining after evaporation of the solvent were diluted with diethyl ether to precipitate the catalyst as a brownish black solid. The ethereal solutions were decanted and chromatographed on a silica gel column with diethyl ether as the eluent. Volatile material was distilled off and the mixtures of the products were analyzed by ^{1}H NMR spectroscopy. Conversions and product

Table 1. Enantioselective hydrogenation of acetophenone in the presence of **4–6** with $s:c = 1000:1$ at $T = 50°C$ for $t = 24$ h, except otherwise noted.

Number	Catalyst	Solvent	$p(H_2)$ (bar)	% PhCH(OH)Me	TOF (h^{-1})	% *ee* (*S*)
1	**4**	MeOH	25	14	7	46
2	**5**	MeOH	25	18	8	44
3	**5**	CD_3OD	25	22	9	38
4	**5**	*i*-PrOH	50	12	5	43
5	**6**	MeOH	50	35	15	50
6	**6**	EtOH	50	33	14	74
7	**6**	*i*-PrOH	50	58	24	58
8	**6**	C_6H_6	25	7	3	38
9	**5**	*i*-PrOH	– (Ar atm.)	5	2	34
10	**6**[a]	MeOH	– (Ar atm.)	77	8	53
11	**6**[b]	EtOH	– (Ar atm.)	64	13	25
12	**6**[b,c]	*i*-PrOH	– (Ar atm.)	47	7	50

[a] $s:c = 250:1$; [b] $s:c = 500:1$; and [c] $t = 36$ h. TOF, turnover frequency.

compositions were determined on the basis of the integrations of the $PhC(O)CH_3$ and $PhCH(OH)CH_3$ signals. Enantiomeric excesses were measured by GC using a Chrompack Chirasil Dex CB column.

2.6. *X-ray structure determination*

The crystal used for the structure analysis of **7** (size $0.28 \times 0.18 \times 0.08\ mm^3$) was grown from CH_2Cl_2/Et_2O. Diffraction measurements were made at $-123 \pm 2°C$ on a Bruker-Nonius Kappa CCD instrument using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å): orientation matrices and unit cell parameters from the setting angles of 472 centered medium-angle reflections; diffraction data corrected for absorption by empirical methods [9] ($T_{min} = 0.501$, $T_{max} = 0.790$). The structure was solved by direct methods and subsequently refined by full-matrix least-squares on F^2 with allowance for anisotropic thermal motion of all nonhydrogen atoms employing both the SHELXTL NT [10] and the WinGX [11] package with some of the relevant programs (SIR-97 [12], SHELXL-97 [13], Ortep-3 [14]) implemented therein. $C_{61}H_{52}ClIrN_2P_2$ (1102.6); orthorhombic, $P2_12_12_1$, $a = 12.4642(5)$, $b = 17.8904(14)$, $c = 21.2814(9)$ Å, $V = 4767.8(5)$ Å^3, $Z = 4$, $d_{Calcd} = 1.536\ g\,cm^{-3}$, $F(000) = 2224$, $\mu(\text{Mo-K}\alpha) = 2.967\ mm^{-1}$; $3.39° \le \theta \le 27.88°$, 62617 reflections collected ($-16 \le h \le +16$, $-22 \le k \le +23$, $-27 \le l \le +28$), 11347 unique ($R_{int} = 0.049$); $wR_2 = 0.065$ for all data and 606 parameters, $R_1 = 0.0294$ for 10377 structure factors $F_o > 4\sigma(F_o)$; weighting scheme applied: $w = 1/[\sigma^2(F_o) + (0.0107P)^2 + 8.656P]$, where $P = (F_o^2 + 2F_c^2)/3$; absolute structure parameter $x = 0.05(5)$ [15]; largest difference peak and hole: 2.668 and $-1.121\ e\,Å^{-3}$.

3. Results and discussion

3.1. *Complexes*

We recently described several (*R*)-binap-(1,2-diamine)-coordinated complexes of rhodium(I), $[Rh\{(R)\text{-binap}\}\{(R,R)\text{-dpen}\}]BF_4$ and the like, which were obtained

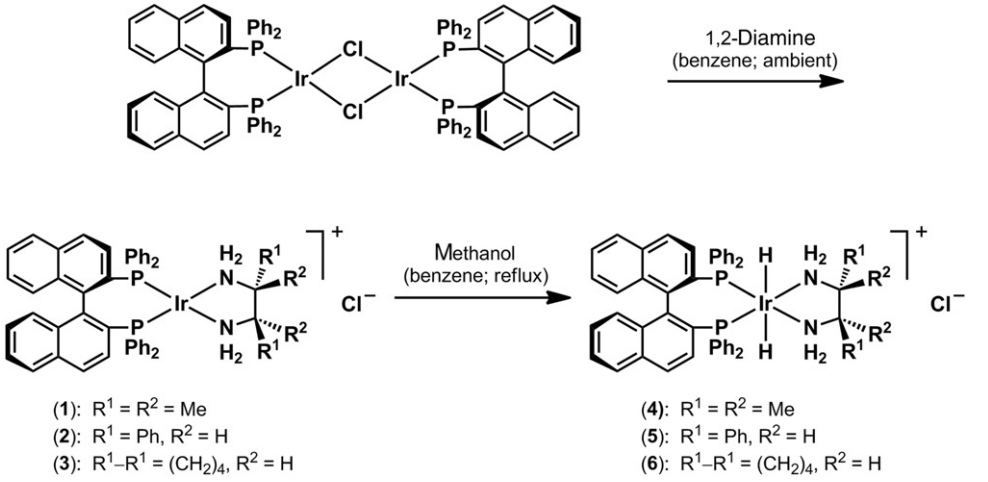
without difficulty by combining the cyclooctadiene precursor [(η^4-1,5-C_8H_{12})Rh{(*R*)-binap}]BF_4 with the required *N*,*N*-chelate ligand under an atmosphere of hydrogen [16]. In view of the pronounced tendency of iridium to form metal-hydride bonds, it was expected that similar hydrogenation of [(η^4-1,5-C_8H_{12})Ir{(*R*)-binap}]BF_4 in the presence of a chelating 1,2-diamine would lead to dihydridoiridium(III) derivatives, [$Ir(H)_2${(*R*)-binap}(1,2-diamine)]BF_4, by oxidative addition of H_2 to the initially formed [Ir{(*R*)-binap}(1,2-diamine)]BF_4 intermediates. However, only mixtures of the products containing various unidentified hydrido species were obtained, from which no well-defined compounds could be isolated [6].

Having shown that nucleophilic cleavage of the triply chlorido-bridged diiridium(III) complex [{(*R*)-binap}$_2Ir_2(H)_2(\mu$-Cl)$_3$]BF_4 by different 1,2-diamines presents a useful method for the preparation of the mixed-ligand bis(chelates) *trans*-[Ir(H)(Cl){(*R*)-binap}(1,2-diamine)]BF_4 (scheme 1: **IIIa–IIIc**) [6], we examined the corresponding reaction between the tmen ligand $H_2NCMe_2CMe_2NH_2$ and the doubly bridged diiridium(I) compound [{(*R*)-binap}$_2Ir_2(\mu$-Cl)$_2$] [8]. In benzene or toluene at room temperature, opening of the chloride bridges by an excess of the diamine nucleophile occurred smoothly to give [Ir{(*R*)-binap}(tmen)]Cl (**1**) which separated directly from solution and was readily isolated in pure state (scheme 2). Because of the C_2 symmetry of the cation, the ^{1}H NMR spectrum of **1** displays the resonances of the four methyl groups as pairs of singlets with equal intensity (δ 1.17 and 1.31 ppm), and the four NH_2 protons likewise show up as two broad doublets centered at δ 2.19 and 4.67 ppm ($^2J_{H-H} = 11.8$ Hz).

As expected, similar treatment of [{(*R*)-binap}$_2Ir_2(\mu$-Cl)$_2$] with (1*R*,2*R*)-1,2-diphenylethylenediamine and (1*R*,2*R*)-1,2-diaminocyclohexane resulted in the formation of two related P_2,N_2-coordinated bis(chelates) of Ir^I, [Ir{(*R*)-binap}{(*R*,*R*)-dpen}]Cl (**2**) and [Ir{(*R*)-binap}{(*R*,*R*)-dach}]Cl (**3**). Unlike **1**, however, these complexes could not be obtained as pure compounds but were invariably contaminated by hydridic species, two of which could be identified as the chloridohydrido products *trans*-[Ir(H)(Cl){(*R*)-binap}(1,2-diamine)]Cl [1,2-diamine = (*R*,*R*)-dpen (**2**·HCl) or (*R*,*R*)-dach (**3**·HCl)] by comparison of their $^{31}P\{^1H\}$ and IrH NMR data with those of the authentic BF_4^- salts **IIIb** and **IIIc** [6] depicted in scheme 1. Competing hydrogen abstraction from the solvent (or from the excess diamine), for which there is ample precedence in literature, presents the most likely pathway to the two hydridoiridium(III) complexes observed as unwanted by-products of these chloride/amine exchange reactions.

Either of the two Ir^I compounds, [{(*R*)-binap}$_2Ir_2(\mu$-Cl)$_2$] and [Ir{(*R*)-binap}(tmen)]Cl (**1**), could be used as the starting material for the synthesis of the *trans*-dihydrido complex [$Ir(H)_2${(*R*)-binap}(tmen)]Cl (**4**) which was obtained (1) upon combination of the chlorido-bridged dimer with the tmen ligand in benzene (to generate **1** as an intermediate) followed by the addition of a few milliliters of methanol and heating at reflux and (2) by direct methanolysis of preformed **1** in boiling benzene or toluene solution. Similar treatment of [{(*R*)-binap}$_2Ir_2(\mu$-Cl)$_2$], first with (*R*,*R*)-dpen or (*R*,*R*)-dach and then with methanol, furnished the *trans*-dihydrides [$Ir(H)_2${(*R*)-binap}{(*R*,*R*)-dpen}]Cl (**5**) and [$Ir(H)_2${(*R*)-binap}{(*R*,*R*)-dach}]Cl (**6**) as two additional target complexes (scheme 2).

The presence, in molecules **4**–**6**, of two metal-bonded hydrides in *trans* positions follows from their spectral data. Thus, the low IR stretching frequencies of the Ir–H bonds (*ca* 1720–1735 cm^{-1}) is highly characteristic of the *trans*-H–M–H fragment and is



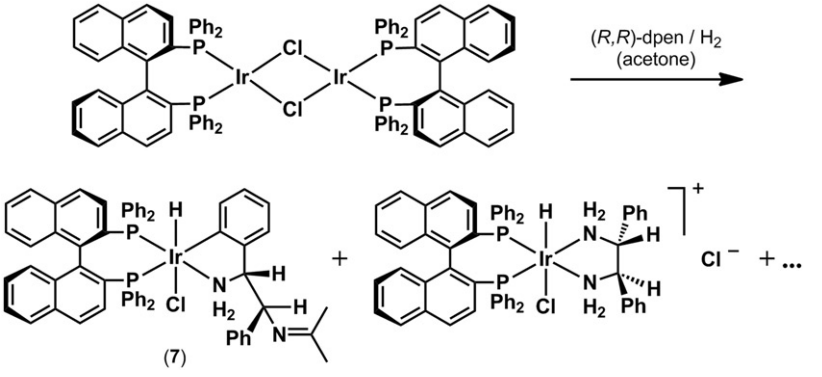
Scheme 2. Preparation of complexes **1**–**6**.

due to the strong mutual *trans* influence of the hydrido ligands [17]. Further confirmation of the C_2-symmetric coordination geometry sketched in scheme 2 arises from $^{31}P\{^1H\}$ singlets (δ *ca* 18 ppm) and, consistently, from the appearance of the IrH_2 ^1H resonances as *cis*-P–H-coupled triplets centered around $\delta -6$ ppm ($^2J_{P-H} \cong 13$ Hz).

Whereas *cis*-dihydrido complexes are numerous, their *trans* counterparts are still rather rare [1, 3h, 18], which is assumed to be a consequence of the high *trans* influence of the hydride ligand rendering the *trans*-H–M–H arrangement less favorable than the *cis*-MH_2 configuration. We do not know the mechanism of formation of the *trans*-dihydrides **4**–**6** from their *in situ* generated or isolated precursors **1**–**3** and methanol, but note that a related *trans*-dihydridoiridium(III) compound, $[Ir(H)_2(C_6H_5)(PMe_3)_3]$, was previously obtained from the action of the alcohol on $[Ir(C_6H_5)(PMe_3)_3]$. In that case, oxidative addition of CH_3OH to the iridium(I) complex was observed to produce the *trans*-hydrido(methoxo) adduct $[Ir(H)(OCH_3)(C_6H_5)(PMe_3)_3]$ as the first-formed intermediate, which cleanly decomposed to the *trans*-dihydrido compound and formaldehyde by an unusual β-hydride elimination process not requiring a vacant site *cis* to the coordinated methoxide [18c].

Obvious attempts at the preparation of P_2,N_2-coordinated dihydridoiridium(III) complexes by oxidative addition of dihydrogen to $[\{(R)\text{-binap}\}_2Ir_2(\mu\text{-Cl})_2]$ in the presence of a chelating diamine remained inconclusive in that mixtures of largely ill-defined or unwanted products were obtained, some of which were already known. Thus, the treatment of the bridged dimer in acetone with (*R*,*R*)-dpen, followed by exposure of the solution to an atmosphere of hydrogen at low temperature, gave *trans*-[Ir(H)(Cl){(*R*)-binap}{(*R*,*R*)-dpen}]Cl, in addition to traces of unidentified materials and a predominantly formed compound displaying an IrH ^1H doublet of doublets centered at δ −20.53 ppm (*cis*-$^2J_{P-H} = 11.6$ and 19.2 Hz) together with two $^{31}P\{^1H\}$ AB multiplets at δ 5.18 and 5.37 ppm ($^2J_{AB} = 11.1$ Hz). Repeated crystallization of the mixture from dichloromethane/diethyl ether allowed the prevailing product to be isolated as single crystals. Subsequent X-ray structure analysis revealed that [Ir(H)(Cl){(*R*,*R*)-binap}{C_6H_4-2-[(*R*,*R*)-CH(NH_2)CH(Ph)N=CMe_2]-κC^1,κN^α}] (**7**) had been formed by partial displacement of (1*R*,2*R*)-H_2NCH(Ph)CH(Ph)NH_2 through

chloride, orthometallation of one phenyl ring of the diamine backbone, and condensation of the dangling amino group with Me_2CO (scheme 3). As shown in figure 1, **7** has (*OC*-6-54) stereochemistry with the metallated phenyl ring and the hydride ligand *cis* and the chloride as the weakest *trans*-bond influencing ligand



Scheme 3. Formation of complex **7**.

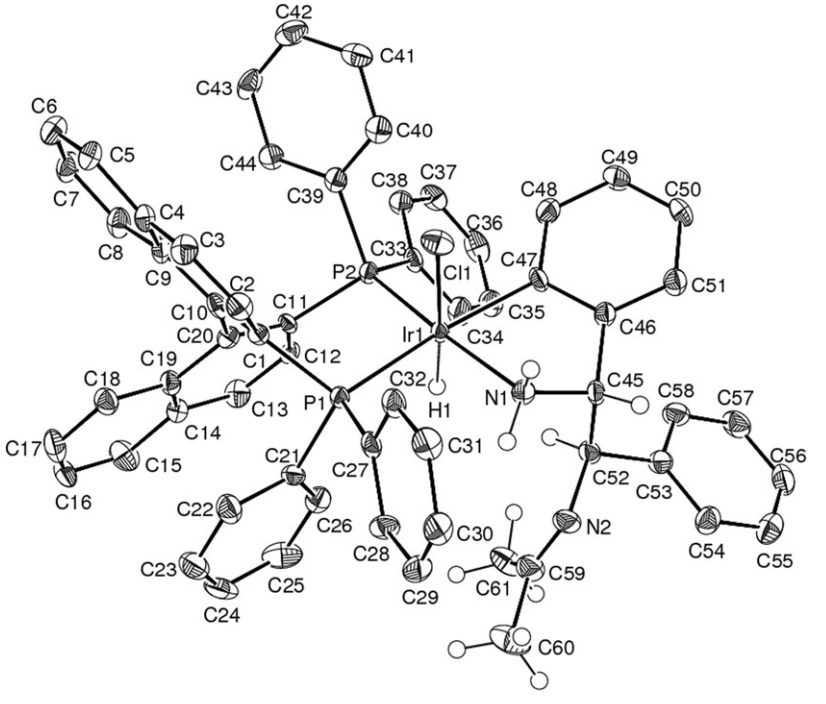


Figure 1. Molecular structure of **7** in the crystal. Selected bond lengths (Å) and angles (°). Ir1–Cl1, 2.481(1); Ir1–P1, 2.336(1); Ir1–P2, 2.241(1); Ir1–N1, 2.148(3); Ir1–C47, 2.099(4); Ir1–H1, 1.695 (unrefined). Cl1–Ir1–P1, 87.40(4); Cl1–Ir1–P2, 101.28(4); Cl1–Ir1–N1, 83.9(1); Cl1–Ir1–C47, 86.7(1); Cl1–Ir1–H1, 176.8; P1–Ir1–P2, 94.32(4); P1–Ir1–N1, 92.01(9); P1–Ir1–C47, 168.6(1); P1–Ir1–H1, 91.5; P2–Ir1–N1, 172.0(1); P2–Ir1–C47, 96.4(1); P2–Ir1–H1, 75.8; N1–Ir1–C47, 77.6(1); N1–Ir1–H1, 99.2; C47–Ir1–H1, 94.8; Ir1–N1–C45, 110.4(2); Ir1–C47–C46, 114.9(3); N1–C45–C46, 105.6(3); C45–C46–C47, 115.6(4).

opposite to the Ir–H. The most prominent structural feature of **7** is the presence of a five-membered Ir–C–C–C–N metalaheterocycle originating from the insertion of iridium into one of the *ortho*-C–H bonds of the phenyl substituent adjacent to the coordinated NH_2 function. The metal-to-carbon distance, 2.099(4) Å, is slightly longer than, but still comparable to, the Ir–C bond length of 2.058(1) Å, previously reported for $[(C_5Me_5)Ir\{C_6H_4\text{-}2\text{-}[CH(NH_2)CH(Ph)N(SO_2C_6H_4Me\text{-}p)]\text{-}\kappa C^1,\kappa N^\alpha\}]$ [19], which represents the only other example of a structurally characterized iridium complex bearing a cyclometallated dpen ligand [20]. The lengths of the two Ir−binap linkages differ significantly: while the Ir–P distance opposite to the Ir–N bond, 2.241(1) Å, compares favorably with the corresponding values of 2.246–2.262 Å measured for other iridium complexes of binap [6, 8, 21], the Ir–P bond *trans* to the metallated carbon atom is long at 2.336(1) Å, which thereby reflects the stronger *trans* influence of the aryl ligand than that of the nitrogen donor.

3.2. *Catalytic hydrogenation of acetophenone*

With the standard test substrate acetophenone at an *s : c* ratio of 1000 : 1, the three dihydrido complexes **4**–**6** were inspected for their ability to catalyze enantioselective >C=O hydrogenations. In fact, all of them act as catalysts for the asymmetric hydrogenation of the ketone at 50°C under 25 or 50 bar of H_2, slowly producing (*S*)-1-phenylethanol with moderate enantioselectivity (ee_{max} : 74%; table 1). Formation of the product alcohol was observed in the absence of any activating basic additive, irrespective of whether the reactions were carried out in alcoholic solution (entries 1–7) or in an aprotic solvent such as benzene (entry 8), which clearly demonstrates that the three-dihydrido complexes operate as active catalysts.

The observation that hydrogenation of the substrate does proceed, albeit with low activity, even in benzene, where no competing transfer of $H^{\delta+}$ and $H^{\delta-}$ equivalents from the solvent to the >C=O dipole can occur, points to a reaction pathway involving slow H_2-hydrogenation rather than transfer hydrogenation of the ketone. On the other hand, acetophenone was also slowly reduced to (*S*)-1-phenylethanol when the reactions were carried out with catalysts **5** and **6** at *s : c* ratios of 250 : 1 or 500 : 1 in alcoholic media in the absence of hydrogen, confirming that transfer hydrogenation is operative under these conditions (table 1, entries 9−12). For an estimation of the extent to which the two alternative pathways are competitive in alcoholic reaction media, a solution of acetophenone in CD_3OD was exposed to 25 bar of H_2 employing **5** as catalyst (entry 3). The product alcohol obtained from this experiment contained the two isotopomers PhC*H*(OD)Me and PhC*D*(OD)Me in an almost 1 : 1 molar ratio as demonstrated by ^1H and ^{13}C NMR. In principle, the formation of the α-deuterated alcohol could be attributed to $D^{\delta-}/D^{\delta+}$ transfer processes to the >C=O dipole from HD or D_2 gas, formed on the H_2-hydrogenation route by accompanying metal-assisted isotopic scrambling according to "$H_2 + CD_3OD = CD_3OH + HD$" and "$HD + CD_3OD = CD_3OH + D_2$", i.e., heterolytic activation of the H_2 molecule [22]. Prior work [6] with the chloridohydrido precatalysts *trans*-[Ir(H)(Cl){(*R*)-binap}(1,2-diamine)]BF_4 (**IIIa**−**IIIc**), all of which must be activated by a strong base and then will exclusively maintain the H_2-hydrogenation of acetophenone, has established, however, that such scrambling of isotopes into the cycle of H_2-hydrogenation will influence the isotopic distribution in the product alcohol only to a minor degree.

From the observed formation of PhC*H*(OD)Me and PhC*D*(OD)Me in approximate 1 : 1 stoichiometry it is, hence, inferred that dihydrido complex **5** supports the H_2-hydrogenation and the transfer hydrogenation of acetophenone, in methanol under H_2, at comparable rates.

4. Conclusions

This work has shown that cationic iridium(I) complexes [Ir{(*R*)-binap}(1,2-diamine)]Cl bearing chelating *N*,*N*-donors tmen, (*R*,*R*)-dpen and (*R*,*R*)-dach together with the (*R*)-binap ligand can be obtained by treatment of [{(*R*)-binap}$_2$Ir$_2$(μ-Cl)$_2$] with the required 1,2-diamine in an inert solvent. They react with methanol in refluxing benzene or toluene to afford *trans*-dihydridoiridium(III) complexes, [Ir(H)$_2$\{(*R*)-binap}(1,2-diamine)]Cl, which work – with moderate enantioselectivity – as base-free, albeit rather slow, catalysts for both the H_2-hydrogenation and the transfer hydrogenation of acetophenone. That the dihydrides described are able to maintain the H_2-hydrogenation pathway in addition to the route of transfer hydrogenation comes up to our expectation that the spatial demand of the coligands can lower the energy required for displacing coordinated solvent by dihydrogen from feasible amidohydrido intermediates, [Ir(H)(solv)\{(*R*)-binap}(HN$\cap$NH$_2$)]$^+$ [4], through steric pressure.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 761553. Copies of this information can be had free of charge from The Director, CCD, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.com.ac.uk or www: http://www.ccdc.com.ac.uk).

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