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NHC Complexes

Dinuclear Di(N-heterocyclic carbene) Iridium(III) Complexes as Catalysts in Transfer Hydrogenation

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Abstract: Two novel di(N-heterocyclic carbene) complexes of formula (μ-PyrIm-CH_2-ImPyr)$[IrCp^*Cl]_2(PF_6)_2$ (**1**) and μ-MeIm-CH_2(p-C_6H_2)CH_2-ImMe$[IrCp^*Cl]_2$ (**2**) (Im = imidazol-2-ylidene) have been synthesised by transmetallation of the dicarbene ligand from the corresponding dicarbene silver complex, using $[IrCp^*(\mu\text{-}Cl)Cl]_2$ as an iridium precursor. The structure of complex **2** has been determined by X-ray diffraction and is characterized by a double *ortho*-metallation of the *p*-xylylene bridge between the carbene units. Both complexes show good activity in the transfer hydrogenation of ketones to alcohols in 2-propanol.

Introduction

N-Heterocyclic carbenes (NHCs) have emerged in the last two decades as a new class of σ-donor ligands, alternative or complementary to the classical ones based on phosphorus or nitrogen donor atoms. The applications of metal N-heterocyclic carbene complexes span from catalysis[1,2] to bioinorganic chemistry[3] and material science.[4] With regard to the first topic, several NHC–metal complexes have been synthesized and effectively employed as catalysts for example in olefin metathesis (Ru complexes)[5] and C–C coupling (Pd complexes).[6] Moreover, ruthenium(II),[7–10] iridium(I)[11] and Cp* iridium(III)[12,13] complexes bearing NHC ligands have also been successfully employed in the transfer hydrogenation reaction of carbonyl compounds.[14] Most of the examples reported in the literature are complexes with carbene ligands bearing a second donating group, such as pyridine,[12e,7] or phosphine.[8] The stability of the complexes can be enhanced by using poly-NHC ligands, as we have already demonstrated for palladium(II), copper(I) and iridium(III) complexes in C–C coupling, nitrene transfer and water oxidation reactions, respectively.[15–17] In this work we describe the synthesis and catalytic application in transfer hydrogenation of two new iridium(III) dinuclear complexes bearing a bridging dicarbene ligand.

Results and Discussion

Reaction of $[IrCp^*(\mu\text{-}Cl)Cl]_2$ with the silver dicarbene complexes **1a**[18] or **2a**[19] (Ir/diNHC 2:1 ratio) in acetonitrile or MeOH/DCM at room temperature affords the novel dinuclear (diNHC)iridium(III) complexes **1** and **2** (Scheme 1). In both complexes the dicarbene ligand is coordinated in a bridging fashion between the two metal fragments IrCp*Cl. In the case of the cationic complex **1**, the iridium coordination sphere is completed by the nitrogen atom of the (imidazol-2-ylidene)-pyridine substituent, while complex **2** is neutral on account of the double metallation of the phenylene ring, which acts as a linker between the two NHC moieties.

Complexes **1** and **2** were characterized by ^1H NMR and ^{13}C NMR spectroscopy, elemental analysis and positive mass spectrometry. The ^1H NMR spectrum of **1** in [D$_3$]acetonitrile shows a singlet for the methylene protons of the dicarbene, suggesting a bridging coordination of the diNHC ligand. The ^1H NMR spectroscopic data of **1** are consistent with the proposed structure, whereas the ^{31}P NMR spectrum shows the typical heptet for the PF_6^- counterion. Finally, the positive ESI mass spectra present two peaks relative to the fragments $[M - PF_6]^+$ (m/z = 1173) and $[M - 2PF_6]^{2+}$ (m/z = 514), confirming both the dicationic and dinuclear nature of the compound. No suitable crystals for an X-ray study were obtained. The ^1H NMR spectrum of **2** is consistent with the formation of a dinuclear species, characterized by the double *ortho*-metallation of the phenylene ring of the bridge connecting the two carbene units and affording an AB system for the methylene hydrogens. Conversely, in the dinuclear dicarbene silver precursor **2a** the methylene hydrogens give rise to a singlet, on account of the less strained and fluxional behaviour of the silver complex. The MALDI mass spectra present a peak relative to the fragment $[M - Cl]^+$ (m/z = 956). It is worth pointing out that the formation of **2** does not require the addition of an external base (i.e. potassium acetate or cesium carbonate), indicating that metallation is a straight-

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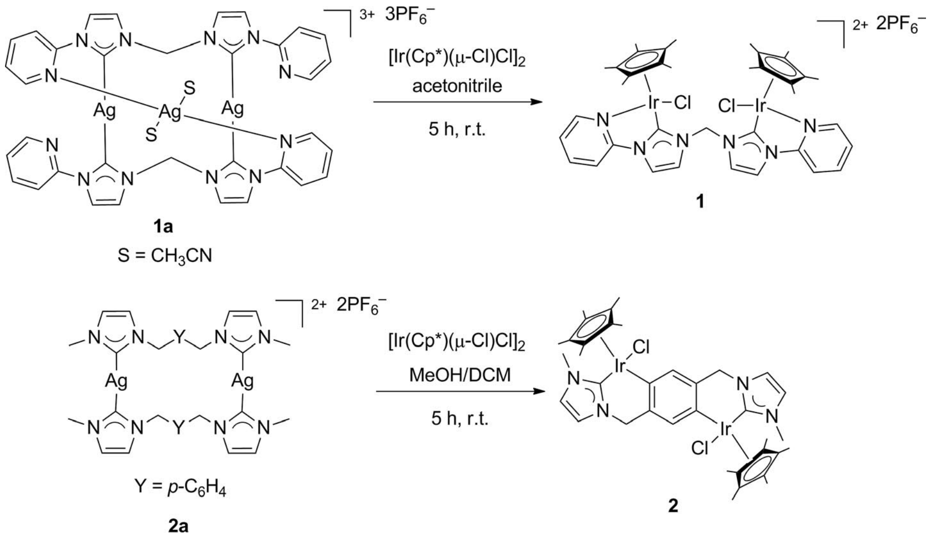


Scheme 1. Synthesis of complexes **1** and **2**.

forward process.[20] The ^{13}C NMR spectra of both complexes **1** and **2** show a unique signal for the carbene carbons at δ = 172.0 and 157.6, in the typical range of carbene carbons coordinated to an iridium(III) center,[13,21] upfield shifted with respect to the corresponding silver complexes ($\delta \approx$ 180 ppm).

The molecular structure of compound **2** was established by an X-ray diffraction study performed on a crystal obtained by the diffusion of *n*-hexane into a dichloromethane solution of **2** (Figure 1). The structure is centrosymmetric, with the inversion centre located in the middle of the phenylene ring. The coordination around the metal centre is described as a three-legged piano stool, where the three legs are the chlorine atom and the carbon atoms of the imidazol-2-ylidene and the metallated phenylene units. The centroid (CT) of the pentamethylcyclopentadienyl ligand completes the coordination at the metal. The Ir–C1 and Ir–C8 bond lengths are 1.998(3) and 2.073(3) Å, respectively, in good agreement with those found in the dinuclear Ir^{III} complex containing a NHC donor and an *ortho*-metallated phenylene ligand [1.987(4) and 1.989(4), 2.089(3) and 2.091(3) Å, respectively].[20a] The bite angle C1–Ir–C8 is 84.65(11)° and falls in the range [83.2–87.2°], which is observed for C$_{NHC}$–Ir–C$_{Ph}$ angles in iridium complexes containing a six-member chelate ring.[22] The six-membered ring, formed by Ir1, C1, N2, C5, C6 and C8 atoms, is in a boat conformation. The Ir–Cl and the Ir–CT bond lengths [2.4254(7) and 1.903(3) Å, respectively] fall in the typical range for similar chloride cyclopentadienyl iridium(III) compounds.

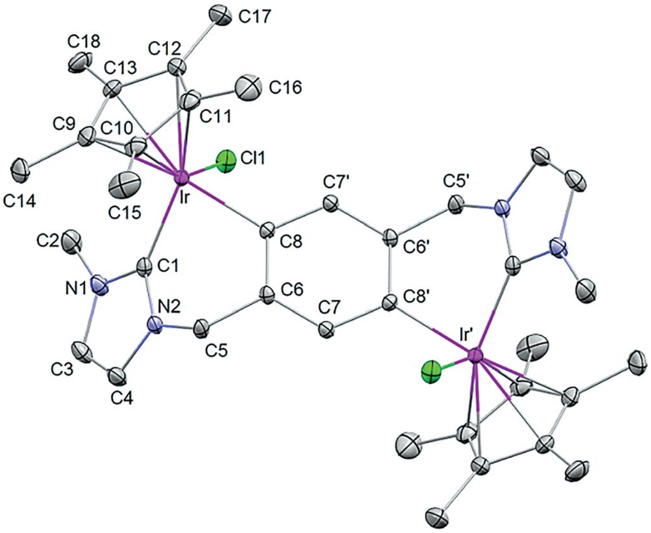
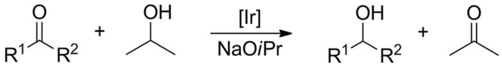


Figure 1. ORTEP diagram of complex **2**. Ellipsoids are drawn at their 30 % probability level. Hydrogen atoms and crystallization solvent (dichloromethane) have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–Ir 1.998(3), C8–Ir 2.073(3), Cl1–Ir 2.4254(7), CT–Ir 1.903(3); C8–Ir–Cl1 89.03(8), C1–Ir–Cl1 92.69(9), CT–Ir–Cl1 120.57(10), CT–Ir–C1 128.40(12), CT–Ir–C8 129.53(12), C1–Ir–C8 84.65(11). Symmetry code ′: 1 – *x*, –*y*, 1 – *z*.

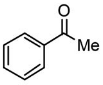
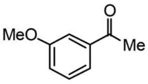
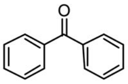
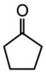
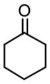
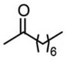
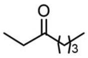
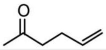
The iridium complexes **1** and **2** display catalytic activity in the transfer hydrogenation (TH) of ketones in 2-propanol under basic conditions (Scheme 2), using acetophenone as a model substrate. The cationic pyridine-based complex **1** (0.5 mol-%) catalyses the reduction of acetophenone to 1-phenylethanol (97 % after 4 h) under reflux conditions and in the presence of NaO*i*Pr (3 mol-%) with a TOF of 38 h^{-1} (Table 1), while with the *ortho*-metallated complex **2** only 57 % conversion was attained in 14 h with a reduced rate (TOF = 6 h^{-1}).



Scheme 2. TH of ketones catalysed by complexes **1** and **2**.

Complexes **1** and **2** were tested in the TH of alkyl aryl, diaryl, dialkyl and cyclic ketones. With catalyst **1**, 3-methoxyacetophenone is quantitatively transformed into the corresponding alcohol (99 %) in 4 h with a TOF of 30 h^{-1}, whereas complex **2** shows a higher rate at 50 % conversion (TOF = 50 h^{-1}), but a lower conversion (86 %) is achieved after 5 h (Table 1). A higher rate for the methoxy derivative with respect to acetophenone has also been found with some ruthenium complexes.[23] Benzophenone is reduced to benzhydrol in 12 h (catalyst **1**, 95 %) and in 16 h (catalyst **2**, 99 %) with comparable TOF values (16 and 13 h^{-1}, respectively), showing a lower activity with re-

Table 1. Catalytic TH of ketones with complexes **1** and **2** (0.5 mol-%) in the presence of NaO*i*Pr (3 mol-%).

Ketone	Catalyst	Time [h]	Conv. [%]	TOF [h^{-1}][a]
	**1**	4	97	38
	2	14	57	6
	**1**	4	99	30
	2	5	86	50
	**1**	12	95	16
	2	16	99	13
	**1**	3	98	50
	2	8	99	9
	**1**	0.67	100	170
	2	4	99	61
	**1**	12	99	25
	2	12	22	–
	**1**	12	98	13
	2	8	5	–
	**1**	6	96	40
	2	10	86	17

[a] The conversion and TOF (mol of ketone converted into alcohol per mol of catalyst per hour at 50 % conversion) were determined by GC analysis. Conditions: T = 82 °C, substrate 0.1 M in 2-propanol.

spect to the acetophenone substrates. Complete conversion of cyclopentanone into cyclopentanol has been observed with **1** in 3 h (98 %, TOF = 50 h^{-1}) and with **2** in 8 h (99 %, TOF = 9 h^{-1}). Interestingly, complex **1** catalyses the quantitative reduction of cyclohexanone to cyclohexanol (100 %) in 40 min with a TOF of 170 h^{-1}, while **2** takes a longer time (4 h) to achieve complete conversion (99 %, TOF = 61 h^{-1}). Using complex **1**, the aliphatic ketones 2-nonanone and also 3-heptanone afford the corresponding alcohols in 12 h (99 and 98 %, respectively), whereas **2** leads to poor conversion. The unsaturated ketone 5-hexen-2-one was chemoselectively transformed into 5-hexen-2-ol in 6 h with catalyst **1** (96 %, TOF = 40 h^{-1}) and in 10 h with complex **2**, the latter reaching a lower conversion (86 %) with a lower rate (TOF = 17 h^{-1}).

In the absence of base complexes **1** and **2** are not catalytically active, suggesting that NaO*i*Pr is crucial for the formation of an Ir hydride species.[24] A possible mechanism of the TH with complexes **1** and **2** involves the formation of the Ir isopropoxide species, by substitution of the chloride, and successive β-hydrogen elimination, leading to the Ir hydride complex. Insertion of the ketone substrate into the Ir–H bond affords the Ir alkoxide, which reacts with 2-propanol giving the alcohol and the Ir isopropoxide that closes the catalytic cycle. The higher activity of **1**, with respect to **2**, is likely due to the generation of a *cis* vacant site by displacement of the pyridine ligand, allowing an inner-sphere mechanism.[25] Although a direct hydrogen transfer[12a] and an inner-sphere mechanism through ring slippage or ring displacement have been postulated for Cp*Ir systems,[12c,14a] it is worth noting that 18-electron alkoxide Ir^{III} complexes may also undergo β-hydrogen elimination in the presence of additional alcohol, as described by Milstein.[26] The rate of the transfer hydrogenation of **1** and of the Cp*Ir(NHC) catalysts reported in the literature[12,13] is in the range 10^1–10^2 h^{-1}. However, a direct comparison is not possible since different catalytic conditions were employed (i.e. temperature, base concentration, presence of silver salts).

Conclusions

In conclusion, we have reported the synthesis of two novel dinuclear iridium(III) complexes, both having a bridging di(N-heterocyclic carbene) ligand. In particular complex **2** displays a structurally interesting double *ortho*-metallated phenylene bridge, as proven by an X-ray crystal structure determination. These complexes catalyse the TH of carbonyl compounds, where the cationic complex **1** is more active than the neutral *ortho*-metallated complex **2**. Further studies are underway to extend this synthetic route to other iridium carbene complexes and to characterize the species involved in the catalytic TH process.

Experimental Section

General: All manipulations were carried out using standard Schlenk techniques under an atmosphere of argon. The reagents were purchased as high-purity products and generally used as received. The silver complexes **1a** and **2a** were prepared according to literature procedures.[18,19] The NMR spectra were recorded with a Bruker Avance 300 MHz instrument, chemical shifts are in ppm and are relative to the residual solvent signal or H_3PO_4 (85 % in D_2O). The GC analyses were performed with a Varian GP-3380 gas chromatograph.

Synthesis of Complex 1: A solution of $[IrCp^*Cl_2]_2$ (80 mg, 0.10 mmol) in acetonitrile (15 mL) was added to a solution of the silver(I) complex **1a** (73 mg, 0.05 mmol) in acetonitrile (15 mL) and the suspension was stirred at room temperature in the dark for 4 h. The mixture was then filtered through Celite and the filtrate was concentrated under reduced pressure to about 2–3 mL. Addition of diethyl ether (10 mL) afforded the product as a pale yellow solid, which was filtered off, washed with diethyl ether (2 × 5 mL) and dried under vacuum; yield 58 %. $C_{37}H_{44}Cl_2F_{12}Ir_2N_6P_2$ (1318.1): calcd. C 33.78, H 3.36, N 6.37; found C 33.57, H 3.69, N 5.96. ^{1}H NMR (300 MHz, CD_3CN): δ = 1.85 (s, 30 H, CH_3Cp^*), 6.57 (s, 2 H, CH_2), 7.60 (t, J = 6 Hz, 2 H, H_{pyr}), 7.92–8.00 (m, 6 H, H_{im} and H_{pyr}), 8.21 (t, J = 6 Hz, 2 H, H_{pyr}), 8.69 (d, J = 6 Hz, 2 H, H_{pyr}) ppm. ^{1}H NMR (300 MHz, $[D_6]$DMSO): δ = 1.87 (s, 30 H, CH_3Cp^*), 6.54 (s, 2 H, CH_2), 7.67 (t, J = 6 Hz, 2 H, H_{pyr}), 7.87 (d, 2 H, H_{im}), 8.30–8.35 (m, 4 H, H_{pyr}), 8.58 (d, 2 H, H_{im}), 8.83 (d, J = 6 Hz, 2 H, H_{pyr}) ppm. ^{1}H NMR (300 MHz, D_2O): δ = 1.71 (s, 30 H, CH_3Cp^*), 6.58 (s, 2 H, CH_2), 7.49 (t, J = 6 Hz, 2 H, H_{pyr}), 7.60 (d, 2 H, H_{im}), 7.85 (m, 2 H, H_{pyr}), 7.93 (d, 2 H, H_{im}), 8.08 (t, J = 6 Hz, 2 H, H_{pyr}), 8.63 (d, J = 6 Hz, 2 H, H_{pyr}) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ = 9.0 (CH_3Cp^*), 64.0 (CH_2), 94.8 (CCp*), 112.5 (C_{im}), 120.0 (C_{im}), 123.5 (C_{pyr}), 125.1 (C_{pyr}), 142.9 (C_{pyr}), 152.0 (C_{pyr}), 152.9 (C_{pyr}), 172.0 (C-Ir) ppm. $^{13}C^1$H NMR (75 MHz, DMSO): δ = 9.0 (CH_3Cp^*), 93.2 (CCp*), 112.8 (C_{im}), 119.9 (C_{im}), 122.7 (C_{pyr}), 125.4 (C_{pyr}), 142.8 (C_{pyr}), 151.5 (C_{pyr}), 152.4 (C_{pyr}), 168.9 (C-Ir) ppm. The CH_2 signal was not detected. ^{31}P NMR (121 MHz, CD_3CN): δ = –144.1 (heptet, PF_6) ppm. ESI-MS (CH_3CN): m/z (%) = 1173 $[M - PF_6]^+$, 514 $[M - 2PF_6]^{2+}$.

Synthesis of Complex 2: The same procedure as described for complex **1**, but using a solution of $[IrCp^*Cl_2]_2$ (80 mg, 0.10 mmol) in dichloromethane (8 mL) and a solution of the silver(I) complex **2a** (52 mg, 0.05 mmol) in MeOH/dichloromethane (1:1) (15 mL); yield 64 %. $C_{36}H_{44}Cl_2Ir_2N_4$ (988.1): calcd. C 42.71, H 4.48, N 5.67; found C 42.74, H 4.50, N 5.49. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 30 H, CH_3Cp^*), 3.97 (s, 6 H, CH_3), 4.71 (AB system, 4 H, CH_2), 6.92 (s, 2 H, H_{im}), 6.95 (s, 2 H, H_{im}), 7.10 (s, 2 H, CH_{xylyl}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.3 (CH_3Cp^*), 37.0 (NCH_3), 56.7 (CH_2), 89.8 (CCp^*), 120.6 (CH), 121.2 (CH), 133.2 (C), 137.0 (CH), 138.0 (C), 157.6 (NCN) ppm. MALDI ($CHCl_3$; sinapinic acid in 75 % MeCN, 0.1 % TFA): m/z (%) = 955.9 $[M - Cl]^+$.

Typical Procedure for the Catalytic Transfer Hydrogenation of Ketones: The iridium complex (2.5 µmol) was introduced into an oven-dried Schlenk flask and the ketone (0.5 mmol) and 2-propanol were added under argon (total volume 4.85 mL). The yellow mixture was refluxed (90 °C bath temperature) under argon for 5 min and a solution of NaO*i*Pr (150 µL, 0.1 M, 0.015 mmol) in 2-propanol was added. The reaction started and the mixture changed its colour. With complex **1** the solution gradually turned into deep red, whereas with **2** it became deep yellow. The reaction was sampled by removing an aliquot of the reaction mixture and diethyl ether was added (1:1 in volume). The solution was filtered through a short silica pad and the conversion was determined by GC analysis (ketone 0.1 M, Ir 0.5 mol-%, NaO*i*Pr 3 mol-%).

Solid-State Structure Determination of Compound 2: Data for compound **2** were collected at 203 K with a Bruker APEX II single-crystal diffractometer, using Mo-K_α graphite-monochromated radiation (λ = 0.71073 Å) and equipped with an area detector.[27] Compound **2** crystallizes in the monoclinic system, space group $P2_1/c$, with a = 11.2125(6) Å, b = 14.7547(8) Å, c = 13.6141(7) Å, β = 111.2420(10)°, V = 2099.25(19) Å^3, Z = 2, μ = 6.747 mm^{-1}, ρ = 1.835 g cm^{-3}. Unique reflections: 6173, (R_{int} = 0.0468), final R = 0.0245, Rw = 0.0557, GOF = 1.039. The structure was solved by direct methods with SHELXS-97 and refined against F^2 with SHELXL-97, with anisotropic thermal parameters for all non-hydrogen atoms.[28] The hydrogen atoms were placed in the ideal geometrical positions.

CCDC-999051 contains the supplementary crystallographic data for compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR spectroscopic data for complexes **1** and **2**.

Acknowledgments

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Keywords: Iridium · Di(NHC) complexes · Hydrogenation · Metalation · Dinuclear complexes

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