

Hydrolysis and methanolysis of silanes catalyzed by iridium(III) bis-N-heterocyclic carbene complexes: Influence of the wingtip groups.

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Supporting Information Placeholder

ABSTRACT: New $[\text{Ir}(\text{CH}_3\text{CN})_2(\text{I})_2\{\kappa\text{C},\text{C}'\text{-bis}(\text{NHC})\}]\text{BF}_4$ complexes featuring bis-NHC ligands with a methylene bridge and different N-substitution ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $-\text{CH}_2\text{CH}_2\text{OPh}$) were synthesized. NMR studies and X-ray diffraction structures evidenced that the wingtip group $-\text{CH}_2\text{CH}_2\text{OPh}$ presents a hemilabile behavior in solution, with the oxygen atom coordinating and dissociating at room temperature, which contrasts with the strong coordination of the ether functions in complex $[\text{Ir}(\text{I})_2\{\kappa\text{C},\text{C}',\text{O},\text{O}'\text{-bis}(\text{NHCOMe})\}]\text{BF}_4$ (bis(NHCOMe) = methylenebis(N-2-methoxyethyl)imidazole-2-ylidene)), previously reported by us. These complexes proved to be efficient catalysts for the hydrolysis and methanolysis of silanes, affording molecular hydrogen and silyl alcohols or silyl ethers as main reaction products in excellent yields. The hydrogen generation rates were very much dependent on the nature of the hydrosilane and the coordination ability of the wingtip group. The latter also played a key role in the recyclability of the catalytic system.

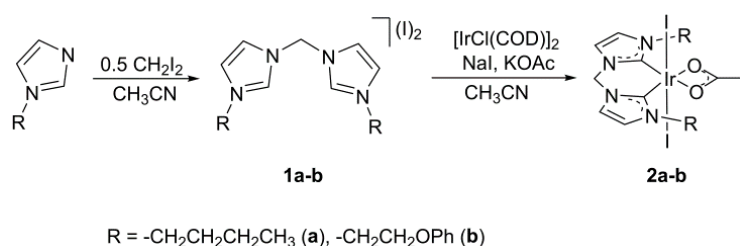
INTRODUCTION

The metal-catalyzed hydrolysis of hydrosilanes is an atom economic route to silanols, which can be prepared selectively under mild conditions as the only reaction product together with molecular hydrogen. The synthetic relevance of silanols as building blocks for a variety of organic transformations, including cross-coupling reactions and production of silicon-based polymeric materials,^[1] illustrates the importance of this reaction. Although the production of silanols and silyl ethers by hydrolysis or the latter by alcoholysis of Si–H bonds have been extensively studied,^[2] the use of organosilanes as potential hydrogen storage agents is relatively unexplored.^[3] A variety of hydrogen storage candidates has been proposed in the literature for the implementation of a hydrogen-based economy.^[4] In the last decades many efforts have focused on the development of fuel cells based on chemical hydrides, ammonia borane and borohydrides being particularly promising due to their stability and efficient hydrogen production under mild conditions.^[5] However, the use of solvents is required in both cases as they are solids at room temperature, which significantly lowers their hydrogen weight percent and hampers their potential use in fuel-cells. Organosilanes on the other hand are usually liquids at room temperature, and their boiling point and hydrogen weight percent

can be easily tuned by modifying their structure, e.g., 1,3,5-trisilacyclohexane is a cyclic organosilane, liquid at room temperature, that contains three SiH₂ units and has a boiling point of 142 °C.[3d] The hydrolysis or alcoholysis of Si–H bonds is a thermodynamically favorable but kinetically slow process; therefore, the use of a catalyst is essential for an efficient release of molecular hydrogen from organosilanes. Iridium complexes have showed good activities in both the hydrolysis and alcoholysis of a range of hydrosilanes under mild conditions.[2d,3a] In this work we have focused on the development of iridium(III) complexes stabilized with chelating bis-N-heterocyclic carbene (NHC) ligands aiming at the preparation of active and robust catalysts for the production of hydrogen from hydrosilanes. The use of NHCs as spectator ligands in homogeneous catalysis has met with great success in the past two decades. The remarkable performance of NHCs as ancillary ligands has generally been attributed to the stability provided by the covalent character of the M–Ccarbene bond and to their electronic and steric capabilities.[6] NHCs are strong σ -donor ligands that render highly electron-rich metal centers.[7] Moreover, the straightforward modification of the N-substituents permits the preparation of NHCs featuring functionalized wingtip groups. Thus, fine tuning of the activity and stability of the catalyst can be achieved by the introduction of wingtip groups with different coordination abilities. Here we report on the catalytic activity of [Ir(CH₃CN)₂(I)₂{ κ -C,C'-bis(NHC)}]BF₄ complexes in the methanolysis and hydrolysis of organosilanes. The methylene bridged bis-NHC ligands feature N-substituents with different coordination ability (-CH₂CH₂CH₂CH₃, -CH₂CH₂OPh and -CH₂CH₂OMe). The coordination behavior of the ligands and the relationship between structure and catalytic activity of the complexes was investigated.

RESULTS AND DISCUSSION

Synthesis and characterization of bis-imidazolium salts. Bis-imidazolium salt 1a was synthesized according to a known literature procedure.⁸ Methylenebis(N-2-phenoxyethyl)imidazolium) iodide (1b) was prepared likewise by reaction of (1-(2-phenoxyethyl)-1H-imidazole) with 0.5 equivalents of diiodomethane in refluxing acetonitrile and isolated as a white solid (Scheme 1) upon precipitation from the reaction mixture using diethyl ether.



Scheme 1. Preparation of bis-imidazolium salts 1a–b and complexes 2a–b.

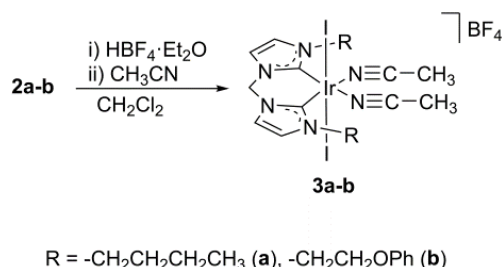
¹H NMR spectra of 1b in acetonitrile-*d*₃ show a resonance corresponding to the NCHN protons at δ 9.69 ppm. The protons corresponding to the imidazole rings (NCHs) appear as apparent triplets at δ 7.94 and 7.58 ppm. The resonance assigned to the protons of the methylene bridge is observed as a singlet at δ 6.81 ppm. The –NCH₂– and –OCH₂– resonances appear as multiplets centered at δ 4.60 and 4.32 ppm, respectively. In the ¹³C{¹H} NMR spectra the most

significant signals are those corresponding to the NCHN and methylene bridge carbons, which appear as singlets at δ 138.8 and 58.5 ppm, respectively.

Synthesis and characterization of complexes 2a–b. The synthesis of complex 2a has been previously described in the literature.[8,9] In a modified procedure, complex $[\text{Ir}(\kappa^2\text{O},\text{O}'\text{-CH}_3\text{COO})(\text{I})_2\{\kappa^2\text{C},\text{C}'\text{-bis}(\text{NHC})\}]$ (bis-NHC = methylenebis(N-2-phenoxyethyl)imidazole-2-ylidene) (2b) was prepared by refluxing 1b with 0.5 equivalents of $[\text{Ir}(\mu\text{-Cl})(\text{cod})]_2$ (cod = 1,5-cyclooctadiene), and an excess of sodium iodide and potassium acetate. The reaction mixture was refluxed for 3 days and monitored by the disappearance of the NCHN peak of the bis(imidazolium salt) in the ^1H NMR. After this period the solvent was evaporated and the residue extracted in dichloromethane. The insoluble inorganic salts were filtered off and the complex was isolated as an air-stable orange solid in 87% yield after evaporation of the solvent.

The ^1H NMR spectra of complex 2b in CD_2Cl_2 show a singlet corresponding to the methylene bridge at δ 6.11 ppm. The protons assigned to the $-\text{CH}_2\text{N}-$ and $-\text{CH}_2\text{O}-$ resonances appear as apparent triplets centered at δ 4.83 and 4.40 ppm, respectively. The coordination of the acetato ligand was confirmed by the presence of a singlet at δ 2.01 ppm that belongs to the methyl group. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra the most prominent resonances are those corresponding to the two carbene carbons, which appear as a singlet at δ 158.9 ppm, and the η^2 -coordinated acetato ligand that shows two peaks at δ 26.6 and 189.8 ppm for the CH_3 and COO carbons, respectively.

Synthesis and characterization of complexes 3a–b. Bis-acetonitrile adducts $[\text{Ir}(\text{CH}_3\text{CN})_2(\text{I})_2\{\kappa^2\text{C},\text{C}'\text{-bis}(\text{NHCBu})\}]\text{BF}_4$ (NHCBu = methylenebis(N-nbutyl)imidazole-2-ylidene) (3a) and $[\text{Ir}(\text{CH}_3\text{CN})_2(\text{I})_2\{\kappa^2\text{C},\text{C}'\text{-bis}(\text{NHCOPh})\}]\text{BF}_4$ (NHCOPh = methylenebis(N-2-phenoxyethyl)imidazole-2-ylidene) (3b) were prepared by reaction of 2a or 2b with 1.1 equivalents of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ in CH_2Cl_2 at 0°C , followed by addition of excess acetonitrile to the reaction mixture. Both complexes were isolated in good yields as air stable orange solids (Scheme 2). A related complex, which features two coordinated R groups $[\text{Ir}(\text{I})_2\{\kappa^4\text{C},\text{C}',\text{O}',\text{O}-(\text{bis-NHCOMe})\}]$ (R = $-\text{CH}_2\text{CH}_2\text{OCH}_3$; bis-NHCOMe = methylenebis(N-2-methoxyethyl)imidazole-2-ylidene). This complex, previously reported by us[9,10] will be named as 3c in this manuscript for comparison purposes.



Scheme 2. Preparation of complexes 3a–b.

The formation of the acetonitrile adducts was confirmed by loss of the bidentate acetato ligand, evidenced by the disappearance of the resonances belonging to the CH₃COO⁻ protons and carbons in ¹H NMR and ¹³C{¹H} NMR, respectively. Moreover, new peaks corresponding to the acetonitrile ligands emerge in the ¹H NMR spectra in deuterated acetone at δ 2.97 and 2.87 ppm for 3a or 3b, respectively. The two carbon peaks assigned to the acetonitrile ligands in the ¹³C{¹H} NMR spectra are observed at 3.4 (–CH₃) and 122.6 (–CN) ppm for 3a, and 3.6 (–CH₃) and 123.2 (–CN) ppm for 3b. ¹⁹F NMR further confirms the formation of cationic species 3a and 3b by the presence of resonances at δ –150.9 and –150.6 ppm, respectively, due to the BF₄⁻ counterions.

Suitable crystals of 3a were grown by slow diffusion of diethyl ether into a saturated acetone solution. The molecular structures obtained by single crystal X-ray diffraction analysis (Figure 1) confirms the coordination of the acetonitrile ligands in the vacant positions left by the acetate ligand, trans to the NHCs. The iridium center adopts a slightly distorted octahedral geometry. At the apical sites, the iodido ligands form an I1–Ir1–I2 angle of 175.65(4)°. The equatorial plane is completed by both acetonitrile units (N51–Ir1–N41, 84.1(4)°) and the chelating bis-NHC ligand (C12–Ir1–C22, 87.4(6)°). Both imidazole rings exhibit an (open-book) dihedral angle of 137.7(7)°, allowing the IrC₃N₂ metallacycle to achieve a boat conformation.

¹H-NMR spectra of 3a in deuterated acetone showed that no apparent exchange between the CH₃CN ligands and the deuterated acetone occurs, as no free acetonitrile was observed, and only one singlet that integrates for six protons was attributed to the methyl protons belonging to the two coordinated acetonitrile ligands. However, it is worth mentioning that the peak corresponding to the coordinated acetonitrile ligands disappears in CD₃CN due to ligand exchange with the solvent.

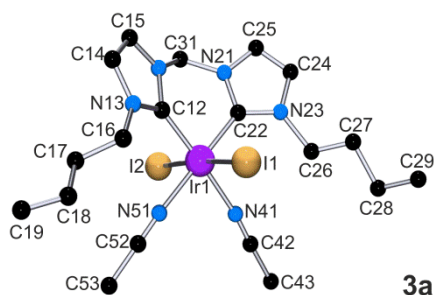


Figure 1. View of cation 3a. Selected distances [Å] and bond angles [°]: Ir1–I1, 2.6805(11); Ir1–I2, 2.6856(11); Ir1–C12, 1.989(15); Ir1–C22, 2.011(13); Ir1–N41, 2.077(13); Ir1–N51, 2.074(10); C12–Ir1–C22, 87.4(6); N41–Ir1–N51, 84.1(4); C12–Ir1–I1, 90.7(4); C22–Ir1–I1, 91.4(4); I1–Ir1–I2, 175.65(4).

In addition, two doublets at δ 7.58 and 7.55 ppm (*J*_{H–H} = 2.2 Hz) and a singlet at δ 6.61 ppm that were assigned to the NCH= protons and the methylene bridge, respectively. The butyl groups on the nitrogen atoms show as most representative peaks those belonging to the NCH₂ and CH₃ protons, which appear as a multiplet and a triplet (*J*_{H–H} = 7.4 Hz) centered at δ 4.47 and 1.01 ppm, respectively. ¹³C{¹H}-NMR spectra in deuterated acetone show a singlet at δ 127.5 ppm corresponding to the carbene carbon and two resonances at δ 122.9 and 122.8

ppm due to the NCH= carbon atoms. The carbon atoms of the methylene bridge appear at δ 64.4 ppm. The acetonitrile ligands give two resonances at δ 122.6 y 3.4 ppm corresponding to the CN and CH₃ carbon atoms.

Attempts to crystallize 3b (κ^2C,C') by slow diffusion of diethyl ether into a saturated acetone solution resulted in loss of one acetonitrile ligand, thus affording suitable crystals of 3b' (κ^3C,C',O). The molecular structure obtained by single crystal X-ray diffraction analysis (Figure 2) show the coordination of one acetonitrile ligand in one of the vacant positions trans to the NHC ligands left by the acetate ligand, while the other is occupied by one of the ether functions of the wingtip groups.

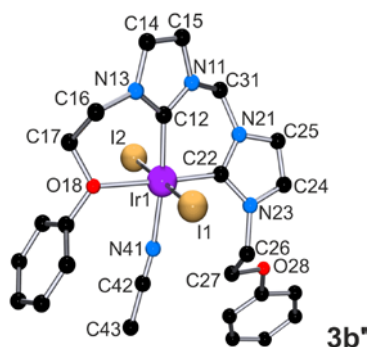


Figure 2. View of cation 3b'. Selection of distances [\AA] and bond angles [$^\circ$] are as follows: Ir1–I1, 2.674(2); Ir1–I2, 2.672(2); Ir1–C12, Ir1–C22, 1.981(5); 1.974(5); Ir1–O18, 2.239(4); Ir1–N41, 2.082(5); C12–Ir1–C22 88.6(2); C12–Ir1–O18, 88.98(19); I1–Ir1–I2, 178.577(13).

The axial positions are occupied by the two iodido ligands (Ir1–I2, 2.674(2) \AA ; Ir1–I3, 2.672(2) \AA ; I1–Ir1–I2, 178.577(13) $^\circ$), while the bis-NHC ligand is located at the equatorial plane with the NHC-rings cis-positioned (Ir1–C12, 1.974(5) \AA ; Ir1–C22, 1.981(5) \AA). One of the wingtip groups of the bis-NHC ligand is coordinated to one of the other two available equatorial positions, resulting in an Ir–O bond distance (Ir1–O18, 2.239(4)) slightly longer than those recently reported by us for [Ir(I)2(κ^4O,C,C',O' -(bis-NHCOMe))]BF₄9 (Ir–O, 2.200(3) and 2.204(3) \AA). The last available equatorial position, cis to the coordinated oxygen atom, is occupied by an acetonitrile ligand (Ir1–N41, 2.082(5)), which leaves one dangling 2-phenoxyethyl substituent. The dihedral angle formed by both imidazole units of 3b (157.7(2) $^\circ$) is considerably wider if compared with 3a (137.7(7) $^\circ$). The boat conformation of the IrC₃N₂ metallacycle is maintained.

Analogously to complex 3a, the 6-membered metallacycle formed by the bis-NHC ligand and the Ir center adopts a boat conformation. However, in this case, the angle between the two planes that contain each N-heterocyclic ring (160 $^\circ$) is closer to planarity than that in 3a, probably due to coordination of one of the wingtip groups by its oxygen in 3b.

¹H-NMR spectra of 3b in deuterated acetone at room temperature suggest a fluxional behavior in solution, which was confirmed by variable temperature ¹H-NMR spectra of 3b in deuterated acetone (Figure 3). This behavior could be attributed to the coordination and

dissociation of the ether functions to give a mixture of species 3b ($\kappa^2\text{C,C}'$), 3b' ($\kappa^3\text{C,C',O}$), and 3b'' ($\kappa^4\text{C,C',O',O}$) (Supporting Information).

An additional proof that supports the above proposed equilibrium is that the addition of excess CH_3CN (30 eq) to a solution of 3b in deuterated acetone affords only one species in the ^1H NMR. The ^1H NMR spectra of 3b in deuterated acetone with 30 equivalents of CH_3CN show two doublets ($J_{\text{H-H}} = 2.0$ Hz) at δ 7.65 and 7.58 ppm corresponding to the NCH= protons of the N-heterocyclic rings. The hydrogen atoms of the methylene bridge appear at δ 6.65 ppm as a singlet, and the two hydrogen atoms of the NCH_2 's and OCH_2 's at the wingtip groups appear as multiplets centered at δ 4.95 and 4.52 ppm, respectively.

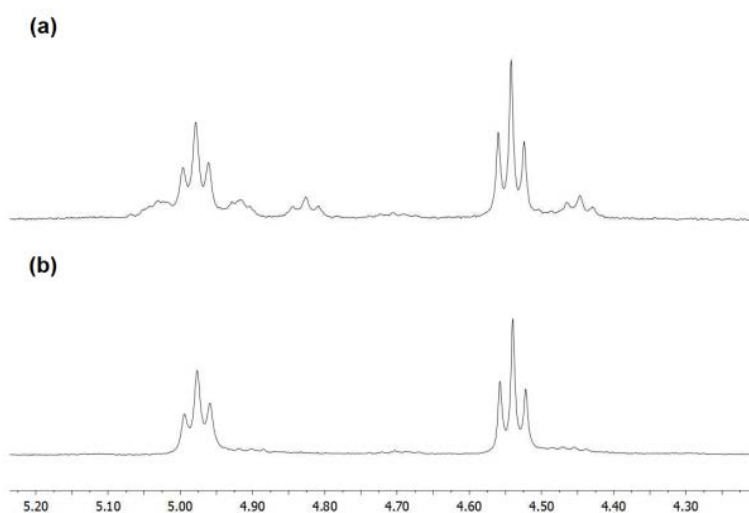


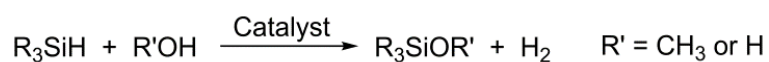
Figure 3. ^1H -NMR spectra of the NCH_2 and OCH_2 region for complex 3b at room temperature with 30 equivalents of CH_3CN (a) and without added CH_3CN (b).

The isolation of the previously suggested tetracoordinated species 3b'' ($\kappa^4\text{C,C',O',O}$) was attempted by avoiding the addition of CH_3CN ; however, the low solubility of the resulting complex in non-coordinating solvents precluded its characterization. ^1H NMR spectra of this complex in acetone show a fluxional behavior that does not resolve at low or high temperatures, which may correspond to a mixture of three species, namely, $[\text{Ir}(\text{CH}_3\text{COCH}_3)_2(\text{I})_2\{\kappa^2\text{C,C}'\text{-bis}(\text{NHCOPh})\}]$, $[\text{Ir}(\text{CH}_3\text{COCH}_3)(\text{I})_2\{\kappa^3\text{C,C',O-bis}(\text{NHCOPh})\}]$ and $[\text{Ir}(\text{I})_2\{\kappa^4\text{C,C',O',O-bis}(\text{NHCOPh})\}]$ (Supporting Information).

The fluxional behavior of 3b sharply contrasts with the strength of the Ir-O bonds displayed by its analogous complex 3c. The latter does not show acetonitrile coordination even in the presence of excess acetonitrile at temperatures as high as 80°C .

$^{13}\text{C}\{^1\text{H}\}$ -MNR spectra of 3b in deuterated acetone show a peak at δ 123.2 ppm for the carbene carbon and two peaks at δ 123.8 and 123.0 ppm corresponding to the NCH= carbon atoms. The carbon atom of the NCH_2N bridge appears at δ 64.5 ppm. The two carbon atoms of the acetonitrile ligands appear at δ 123.2 and 3.60 ppm (CH_3 and CN , respectively).

Catalytic studies on the generation of hydrogen from hydrosilanes. Catalysts 3a and 3b together with 3c were tested as catalyst precursors for the hydrolysis and methanolysis of a range of organosilanes with the aim of using these reactions as a test bench that would allow assessing the activity of the three complexes in generation of hydrogen from silanes (Scheme 3). The three potential catalysts contain bis-NHC ligands that present wingtip groups with different coordination ability. Complex 3a does not contain a coordinating group, while the phenoxy moieties at 3b behave as a hemilabile ligands. On the other hand, the methoxy groups at 3c are strongly coordinated to the iridium center.



Scheme 3. Hydrolysis or methanolysis of silanes.

The rate of hydrogen production, generated by hydrolysis or methanolysis of the silane during the catalytic tests, was monitored by measuring the variation of pressure inside the system throughout the reaction by means of closed reactor flask equipped with a pressure transducer. After the cease of hydrogen evolution, the pressure is released and the resulting solution analyzed by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{29}Si NMR spectroscopy in order to identify the silicon containing reaction products.

Initial tests for the hydrolysis of hydrosilanes were carried out using CH_2Cl_2 as solvent; however, the low solubility of the complex in chlorinated solvents led to low reaction rates ($\text{TOF}_{1/2} = 111 \text{ h}^{-1}$ (3a), 86 h^{-1} (3b) and 35 h^{-1} (3c)). Therefore, acetone was selected as reaction media for the hydrolysis tests due to its capacity to dissolve the complexes 3a-c. For comparison purposes, catalysts 3a, 3b and 3c were tested under analogous reaction conditions. PhMe_2SiH (1 equivalent) was added to a solution of the corresponding catalysts (1 mol%) and 5 equivalents of water in acetone at 298 K. This study revealed that catalyst 3b, which presents two hemilabile functionalities in the wingtip groups, shows a better activity than that of catalyst 3a, which contains two non-coordinating N-substituents. However, the two strongly coordinating wingtip groups at 3c seem to thwart its catalytic activity (Figure 4).

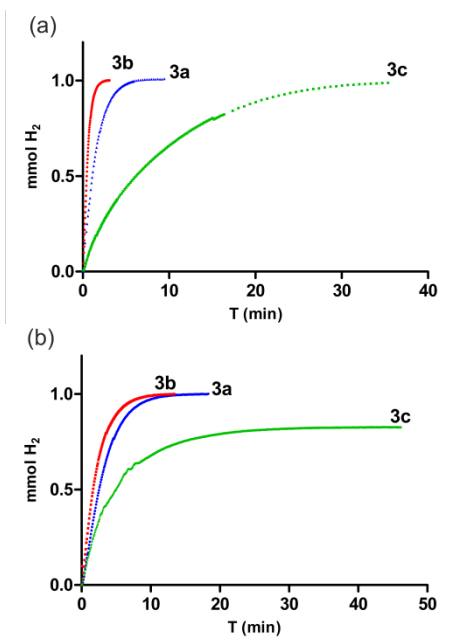


Figure 4. Hydrogen generation [mmol] versus time [min] for the catalytic hydrolysis (a) and methanolysis (b) of PhMe₂SiH using 3a-c (1 mol%) as catalyst and (a) 5.0 equivalents of water in 2 mL of acetone or (b) 2mL of Methanol.

Regarding hydrogen generation, alcoholysis has the advantage that no additional solvent is required as the alcohol acts as solvent and reagent; moreover, the Si-H bond can be easily regenerated from the silyl ether thus obtained.[3d,11]

In order to explore the activity of 3a-c towards silane methanolysis, PhMe₂SiH was added to a solution of the corresponding catalyst in methanol. Remarkably, the reactivity trend described above is maintained for the methanolysis of PhMe₂SiH. However, in this case, the difference in activity between 3a and 3b is less pronounced (Figure 4b). It is worth mentioning that the production of hydrogen noticeably decreases when methanol is employed instead of water for Si-H splitting, e.g., the best TOF_{1/2} obtained for the hydrolysis reaction is 7143 h⁻¹ for 3b with PhMe₂SiH, while for methanolysis the best TOF_{1/2}, also obtained for the same pair catalyst/silane, is 1785 h⁻¹ (Tables 1 and 2, entry 2).

When a more encumbered silane (Et₃SiH) is employed, two different effects can be observed: (i) significantly lower reaction rates and (ii) higher catalytic activity of 3a compared to 3b, i.e. better yields with non-coordinating wingtip groups (Figure 5).

We observe again that the reactions of silane methanolysis afford smaller values of TOF_{1/2} than their hydrolysis analogues (Tables 1 and 2; Entries 4-6). It is remarkable that, in the case of the methanolysis of Et₃SiH, 3c performs significantly better than 3b at short reaction times (Figure 5b). This observation suggests that the steric hindrance generated by the wingtip groups may play an important role in the activity of the catalyst when more encumbered hydrosilanes are employed.

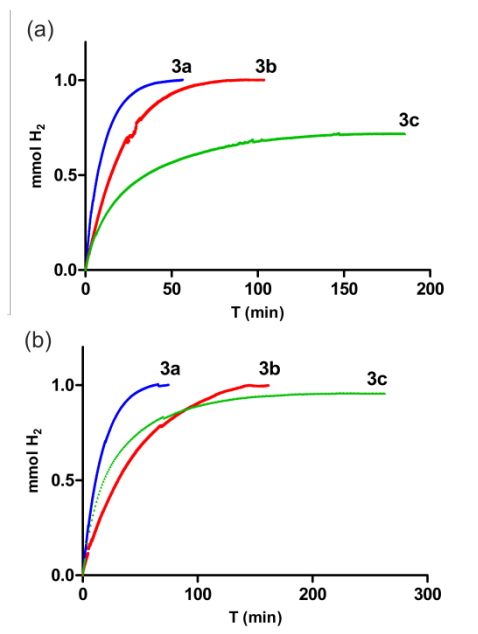


Figure 5. Hydrogen generation [mmol] versus time [min] for the catalytic hydrolysis (a) and methanolysis (b) of Et₃SiH using 3a-c (1 mol%) as catalyst and (a) 5.0 equivalents of water in 2 mL of acetone or (b) 2 mL of Methanol.

Alkoxy silanes were also tested under analogous reaction condition to give low activities and yields even for the most active catalysts (3a and 3b) (Tables 1 and 2; Entries 7 and 8). The solutions obtained after the hydrolysis of silanes were analyzed by ¹H and ²⁹Si NMR. Remarkably, only the formation of silanols (R₃SiOH) was observed with no traces of (R₃Si)₂O.[12] The activities and TOF_{1/2} values here reported compare well with those described in the literature for iridium complexes employing the same hydrosilanes.2d,3a

Table 1. Hydrolysis of silanes catalyzed by **3a-c**.

Entry	Silane	Catalyst	Time [min]	Yield [H ₂ %]	TOF _{1/2} [h ⁻¹]
1	PhMe ₂ SiH	3a	6.4	100	2778
2	PhMe ₂ SiH	3b	3.0	100	7143
3	PhMe ₂ SiH	3c	39.0	99	485
4	Et ₃ SiH	3a	55.4	100	421
5	Et ₃ SiH	3b	88.3	100	202
6	Et ₃ SiH	3c	185.0	72	85.9
7	(MeO) ₃ SiH	3a	94.0	64	402
8	(MeO) ₃ SiH	3b	94.0	70	422

Reaction conditions: Silane (1.0 mmol), water (5 equivalents), acetone (2 mL), catalyst (1

mol%) at RT.

Table 2. Methanolysis of silanes catalyzed by **3a-c**.

Entry	Silane	Catalyst	Time [min]	Yield [H ₂ %]	TOF _{1/2} [h ⁻¹]
1	PhMe ₂ SiH	3a	18.3	100	1190
2	PhMe ₂ SiH	3b	13.4	100	1785
3	PhMe ₂ SiH	3c	46.2	83	610
4	Et ₃ SiH	3a	74.0	100	265
5	Et ₃ SiH	3b	173.3	100	98
6	Et ₃ SiH	3c	268.9	95	163
7	(MeO) ₃ SiH	3a	106.2	89	167
8	(MeO) ₃ SiH	3b	406.0	94	55

Reaction conditions: Silane (1.0 mmol), methanol (2 mL), catalyst (1 mol%) at RT.

In order to explore the effect of the coordination ability of the wingtip groups on the stability of the catalysts, a reusability study with the most active catalysts, **3a** and **3b**, and PhMe₂SiH was undertaken. The catalytic system was reused five times without a significant activity loss of any of the catalysts for the methanolysis reactions. Conversely, for the hydrolysis reaction we observed that the activity of catalyst **3a** gradually decays, becoming especially evident in the fifth cycle. In the next two cycles **3a** completely deactivates, the sixth cycle does not reach a 30% yield, while the seventh cycle shows no conversion whatsoever. This contrasts with the good activities showed by catalyst **3b** throughout the whole process (Figure 6). A plausible explanation for the higher stability showed by catalyst **3b** compared with **3a** may be that the stabilization of the active species by the hemilabile wingtip groups results in a longer catalyst lifetime. Notably, this study represents the first example of a reusable homogeneous catalyst for the hydrolysis and methanolysis of silanes.

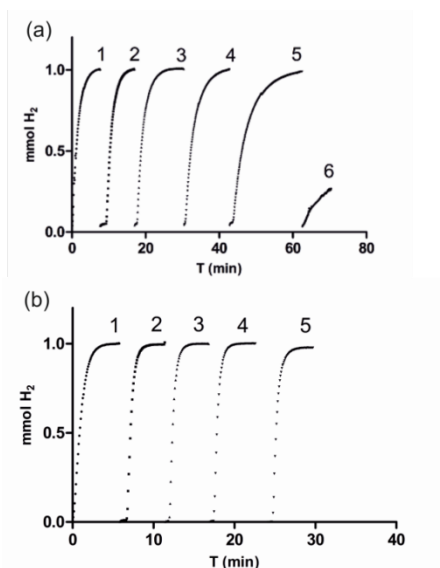


Figure 6. Catalyst recycling experiments 3a (a) vs 3b (b). Hydro-gen generation [mmol] versus time [min] for the catalytic hydrolysis of PhMe₂SiH using 3a (1 mol%) as catalyst and 5.0 equivalents of water in acetone. The cycles are numbered from 1 to 6.

CONCLUSIONS

The new iridium(III) complexes of general formula $[\text{Ir}(\text{CH}_3\text{CN})_2(\text{I})_2\{\kappa^2\text{C},\text{C}'\text{-}(\text{bis-NHC})\}]$ have proved active catalysts for the hydrolysis and methanolysis of a variety of silanes under mild reaction conditions. The activity of the catalyst is significantly influenced by the coordinating ability of the wingtip groups and the nature of the hydrosilane. Less encumbered silanes seem to promote greater reaction rates, while strongly coordinating groups, as a general rule, hamper the activity of the catalyst. Remarkably, the use of weakly coordinating (hemilabile) wingtip groups leads to a manifest improvement of the catalytic activity when less encumbered silanes were employed, but patently hampers the reaction for more sterically hindered silanes.

Catalysts 3a and 3b can be reused without a significant loss of activity in the methanolysis of PhMe₂SiH. However, in the case of the hydrolysis reaction a progressive drop of the reaction rate throughout the recycling steps, and an eventual deactivation of the catalyst was observed for 3a. This effect was not observed for catalyst 3b, which seems to retain its activity after 5 cycles.

In conclusion, the subtle effects of hemilabile functions at the N-substituents of bis-N-heterocyclic carbene ligands, stabilizing or blocking vacant coordination sites, seem to play a key role in the activity of these catalysts towards hydrogen production from hydrosilanes.

EXPERIMENTAL SECTION

General Considerations. All reactions and manipulations were carried out under an argon atmosphere by using Schlenk-type techniques. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a

Solvent Purification System (Innovative Technologies). 1-(2-phenoxyethyl)-1H-imidazole¹³ was prepared according to a literature procedure. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker ARX-300 (300 and 75 MHz respectively) spectrometer using TMS as the internal reference in toluene-d₈ as solvent. All chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hz to apparent peak multiplications. ¹H-¹H-COSY, ¹³C-APT, ¹H-¹³C HSQC and ¹H-¹³C HMBC sequences were used for help in the assignments of the ¹H and ¹³C spectra.

Synthesis of 1b. 1-(2-phenoxyethyl)-1H-imidazole (1.05 mmol, 0.331 g) and CH₂I₂ (0.53 mmoles, 42 μL) were dissolved in CH₃CN (20 mL). The resulting solution was stirred under reflux for 48 h, after which time the solvent was evaporated under reduced pressure to a volume of 5 mL and precipitated with Et₂O. The remaining residue was washed with Et₂O (3 × 20 mL) and dried in vacuo to give 0.224 g of a white solid (0.25 mmol, 48% yield). ¹H NMR (CD₃CN, 300 MHz): δ 9.69 (s, 2H, NCHNim), 7.94 (m, 2H, NCHim), 7.58 (m, 2H, NCHim), 7.31 (m, 4H, 4xCHm), 7.00 (m, 6H, 2xCHp, 4xCHO), 6.81 (s, 2H, CH₂ bridge), 4.60 (m, 4H, NCH₂), 4.32 (m, 4H, OCH₂). ¹³C NMR (CD₃CN, 300 MHz): δ 158.8 (CipsoAr), 138.8 (NCHN), 130.6 (CHm-Ar), 124.9 (NCHim), 123.2 (NCHim), 122.5 (CHp-Ar), 115.6 (CHO-Ar), 66.3 (NCH₂), 58.5 (CH₂ bridge), 50.8 (OCH₂). Anal. Calcd. for C₂₃H₂₆I₂N₄O₂ (644,01): C, 42.86; H, 4.07; N, 8.70. Found: C, 42.76; H, 4.05; N, 8.84.

Synthesis of 2b. [Ir(μ-Cl)(COD)]₂ (0.19 mmol, 0.13 mg) was dissolved in 20 mL of acetonitrile, subsequently 2 equivalents of 1b (0.38 mmol, 0.34 g), 13 equivalents of NaI (2.47 mmol, 0.37 g) and 13 equivalents of KOAc (2.47 mmol, 0.24 g) were added. The resulting suspension was refluxed for 3 days. The volatiles were evaporated under reduced pressure, the residue extracted with CH₂Cl₂ (2 × 25 mL) and the insoluble inorganic salts filtered off. The solution thus obtained was evaporated in vacuo to afford a residue that was washed with Et₂O (3 × 20 mL). The title compound was isolated as an orange solid in 82% yield (0.139 g, 0.16 mmol) ¹H NMR (CD₂Cl₂, 300 MHz): δ 7.34 (d, 2H, J_{H-H} = 2.1 Hz, CHim ext), 7.29 (2H, CHAR-para), 7.26 (4H, CHAR-orto), 6.98 (d, J_{H-H} = 2.1 Hz, CHim int), 6.95 (m, 4H, CHAR-meta), 6.11 (s, 2H, NCH₂N), 4.83 (m, 4H, NCH₂), 4.40 (m, 4H, OCH₂), 2.01 (s, 3H, CH₃COO). ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz): δ 190.4 (COO), 158.9 (Cipso), 130.0, 121.7 y 115.2 (CHAR), 127.9 (NCimN), 124.6 (CHim ext), 119.7 (CHim int), 68.8 (OCH₂), 63.0 (NCH₂N), 50.3 (NCH₂), 26.2 (CH₃COO). Anal. Calcd. for C₂₃H₂₆I₂N₄O₂ (644,01): C, 42.86; H, 4.07; N, 8.70. Found: C, 42.76; H, 4.05; N, 8.84.

Synthesis of complex 3a. The title compound was prepared in 82% yield following a procedure analogous to 3b. ¹H NMR (acetone-d₆, 300 MHz): δ 7.44, 7.41 (d, 2H, J_{H-H} = 2.2 Hz, CHim ext), 6.61 (s, 2H, NCH₂N), 4.47 (m, 4H, NCH₂), 2.97 (s, 6H, CH₃CN), 1.99–1.85 (m, 4H, NCH₂CH₂), 1.51 (m, 4H, NCH₂CH₂CH₂), 1.01 (t, 6H, J_{H-H} = 7.4 Hz, CH₃). ¹³C{¹H} NMR (acetone-d₆, 75.5 MHz): δ 127.5 (NCImN), 122.9 y 122.8 (CHim), 122.6 (CH₃CN), 64.4 (NCH₂N), 52.2 (NCH₂), 33.9 (NCH₂CH₂), 20.6 (NCH₂CH₂CH₂), 14.1 (CH₃ terminal), 3.4 (CH₃CN). ¹⁹F NMR (acetone-d₆, 300 MHz): δ -150.9 ppm. HRMS (ESI) m/z calcd for C₁₇H₂₇I₂IrN₅ (M⁺ - CH₃CN) 747.9980, found

748.0035. Anal. Calcd. for C₁₉H₃₀BF₄I₂IrN₆ (875,32): C, 26.07; H, 3.45; N, 9.60. Found: C, 26.37; H, 3.44; N, 9.34.

Synthesis of complex 3b. Compound 2b (0.15 mmol, 0.14 g) was dissolved in 20 mL of CH₂Cl₂, then HBF₄·Et₂O (0.16 mmol, 22 μ L) was added dropwise at 0 °C. After the addition the reaction mixture was stirred for 1 h at 0 °C. Subsequently, 10 mL of CH₃CN were added and the reaction stirred at room temperature for 1 h. Vacuum evaporation of the volatiles afforded a residue which was washed with Et₂O (3 x 20 mL) and dried under vacuum give the title compound as an orange solid in 87% yield (0.13 mmol, 0.12 g). ¹H NMR (acetone-d₆ with 30 equivalents of CH₃CN, 300 MHz): δ 7.67 (d, 2H, J_{H-H} = 2.0 Hz, CH_{im} ext), 7.58 (d, J_{H-H} = 2.0 Hz, CH_{im} int), 7.31 (m, 4H, CH_{Ar}-meta), 7.06 (d, 4H, J_{H-H} = 8.2 Hz, CH_{Ar}-orto), 6.97 (t, 2H, J_{H-H} = 7.4 Hz, CH_{Ar}-para), 6.65 (s, 2H, NCH₂N), 4.95 (m, 4H, NCH₂), 4.52 (m, 4H, OCH₂), 2.87 (s, 6H, CH₃CN). ¹³C{¹H} NMR (acetone-d₆, 75.5 MHz): δ 159.2 (Cipso), 130.5 (CH_{Ar}-meta), 127.8 (NC_{im}N), 123.8 (CH_{im} ext), 123.2 (CH₃CN), 123.0 (CH_{im} int), 122.2 (CH_{Ar}-para), 115.4 (CH_{Ar}-orto), 68.3 (OCH₂), 64.5 (NCH₂N), 51.7 (NCH₂), 3.6 (CH₃CN). ¹⁹F NMR (acetone-d₆, 300 MHz): δ -150.6 ppm. HRMS (ESI) m/z calcd for C₂₅H₂₇I₂IrN₅O₂ (M⁺ - CH₃CN) 875.9874, found 875.9914.

General procedure for the hydrolysis of silanes. The reactions were performed on a Man on the Moon series X102 kit (www.manonthemoon.com) micro-reactor with a total volume of 14.2 mL placed on an isothermal bath at 298 K.

In a typical procedure, the reactor was charged with a solution of the catalyst (0.01 mmol, 8.8 mg 3a, 9.1 mg 3b or 8.0 mg 3c) and 5 equivalents of distilled water (5 mmol, 90 μ L) in 2 mL of acetone. The reactor was closed and the pressure measurement started. Once the reading of hydrogen pressure stabilized, the corresponding silane (1.0 mmol; 160 μ L PhMe₂SiH, 161 μ L Et₃SiH or 134 μ L (MeO)₃SiH) was added with a syringe in one batch. The amount of H₂ generated during the reaction was calculated by means of the Ideal Gas Law, P·V=n·R·T. At the end of the reaction the reaction mixture was analyzed by ¹H NMR.

General procedure for the methanolysis of silanes. The reactions were performed analogously to the procedure described above for the hydrolysis of silanes, except that in this case the corresponding silane was added to a solution of the catalyst (3a, 3b or 3c) in 2 mL of Methanol.

General procedure for recycling experiments. The reactions were performed analogously to the procedure described above. After every cycle the system was depressurized and a new equivalent of PhMe₂SiH was added. In the case of the hydrolysis experiments one equivalent of water was previously added to maintain the excess of 5 equivalents.

Crystal data for 3a: [C₂₀H₃₁BCl₂F₄I₂IrN₆], monoclinic, P21/c, a = 12.2648(8) Å, b = 9.2929(6) Å, c = 26.5659(17) Å, β = 95.5340(10)°, Z = 4, Mr = 959.22 g mol⁻¹, V = 3013.8(3) Å³, D_{calcd} = 2.114 g cm⁻³, λ(Mo Kα) = 0.71073 Å, T = 100 K, μ = 6.702 mm⁻¹, 25231 reflections collected, 7109 observed (R_{int} = 0.0595), R₁(Fo) = 0.0778 [I > 2σ(I)], wR₂(Fo²) = 0.1772 (all data), GOF = 1.080. CCDC 1034731.

Crystal data for 3b': [C₂₅H₂₇BF₄I₂IrN₅O₂], monoclinic, P21/n, a = 15.841(12) Å, b = 12.668(9) Å, c = 16.196(12) Å, β = 116.078(8)°, Z = 4, Mr = 962.33 g mol⁻¹, V = 2919(4) Å³, D_{calcd} = 2.190 g cm⁻³, λ(Mo Kα) = 0.71073 Å, T = 100 K, μ = 6.747 mm⁻¹, 32539 reflections collected, 6775 unique (R_{int} = 0.0437), 5644 observed, R₁(Fo) = 0.0352 [I > 2σ(I)], wR₂(Fo²) = 0.1055 (all data), GOF = 0.998. CCDC 1034732.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic details and tables and additional NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

Any additional relevant notes should be placed here.

ACKNOWLEDGMENT

This work was supported by the Spanish Ministry of Economy and Competitiveness (MINECO/FEDER) (CONSOLIDER INGENIO CSD2009-0050, CTQ2011-27593 projects, and "Juan de la Cierva" (M.I.) and Ramón y Cajal (P.J.S.M.) programs) and the DGA/FSE-E07. The authors express their appreciation to the support from the Ministry of Higher Education, Saudi Arabia, in establishment of the Center of Research Excellence in Petroleum Refining & Petrochemicals at King Fahd University of Petroleum & Minerals (KFUPM) and the support from KFUPM-University of Zaragoza research agreement.

DEDICATION

Dedicated to the memory of Prof Michael F. Lappert, an outstanding and creative scientist, for his many and diverse contributions to organometallic chemistry.

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