

Synthesis, structure and catalytic activity of the first iridium(I) siloxide *versus* chloride complexes with 1,3-mesitylimidazolin-2-ylidene ligand

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Abstract

The first iridium(I) complex containing siloxyl and N-heterocyclic carbene ligand such as $[\text{Ir}(\text{cod})(\text{IMes})(\text{OSiMe}_3)]$ (**1**) and $[\text{Ir}(\text{CO})_2(\text{IMes})(\text{OSiMe}_3)]$ (**3**) have been synthesized and their structures solved by spectroscopy and X-ray methods as well as catalytic properties in selected hydrogenation reactions have been presented in comparison to their chloride analogues, i.e. $[\text{Ir}(\text{Cl})(\text{cod})(\text{IMes})]$ (**2**) and $[\text{Ir}(\text{Cl})(\text{CO})_2(\text{IMes})]$ (**4**). The attempts at synthesis of iridium(I) complex with *tert*-butoxyl ligand has failed as leading instead to the iridium hydroxide complex $[\text{Ir}(\text{cod})(\text{OH})(\text{IMes})]$ (**5**) whose X-ray structure has also been solved. All complexes (**1**)–(**5**) show square planar geometry typical of the four-coordinated iridium complexes. Catalytic activity of complexes **1** and **2** was tested in transfer hydrogenation of acetophenone and hydrogenation of olefins.

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1. Introduction

N-heterocyclic carbenes have recently attracted considerable attention in homogeneous catalysis because they can be used instead of sterically demanding tertiary phosphine ligands [1] which control the reactivity and selectivity of transition metal complexes as reaction catalysts [2,3]. The phosphorus based ligands are air sensitive and at high temperatures the P–C bond in these ligands undergoes degradation [2b]. On the other hand, strongly nucleophilic (electron-rich) bulky ligands and resistant to oxidation agents such as carbenes, formed from N and C substituted imidazolium salts, can be considered as alternatives to phosphines [4]. The complexes with stable carbenes are known to be formed by almost all metals of the periodic table. Synthetic methods and properties of various carbenes and their TM-complexes (where TM = transition metal) have been recently described in a number of reviews

and papers [5]. In the last decade, numerous reports on synthesis of neutral and cationic iridium complexes with various monodentate and polydentate carbene ligands have been published [6]. Iridium-carbene complexes have been proved very attractive and efficient catalysts of organic transformations including: hydrogenation [6j,6w,7], transfer hydrogenation [6h,6l,8], hydroamination [6r], Oppenauer-type oxidation [6s], hydrosilylation of olefins [6k] and ketones [6o]. Molecular compounds containing a TM–O–Si moiety are regarded as models of metal complexes immobilized on silica and silicate surfaces known to catalyze a variety of organic transformations [9–11]. Since 1982 more than 100 new TM–siloxide complexes including terminal and/or also bridging siloxy ligands have been synthesized and characterized by X-ray and spectroscopic methods to determine their molecular structure (for a review see [9a,9b] and references therein). The properties of siloxide as an ancillary ligand in the system TM–O–SiR₃ have been effectively utilized in molecular catalysis but predominantly by early transition metal complexes. We have reported previously the synthetic methods and crystal structures of binuclear and

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phosphine-containing mononuclear rhodium(I) [12] and iridium(I) [13] siloxide complexes, as well as the application of those complexes in catalytic transformations of organosilicon compounds, i.e. silylative coupling of olefins with vinylsilanes [13a,14], curing of polysiloxanes *via* hydrosilylation [15] as well as hydroformylation [16] and silylcarbonylation [17] of vinylsilanes.

In this paper, we present the synthesis of the first iridium(I) complexes containing siloxyl and carbene ligands as well as their structure and catalytic properties in selected reactions in comparison to those of their chloride analogues.

2. Results and discussion

2.1. Synthesis of carbene iridium(I) complexes and structural studies

The 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene ligand was synthesized from bis(2,4,6-trimethylphenyl)imidazolium chloride according to a well known method [5] and was used for the reaction in the pure form. Treatment of imidazolin-2-ylidene ligand with binuclear complexes [$\text{Ir}(\mu\text{-X})(\text{cod})_2$] (where X = Cl, OSiMe₃) in benzene solution gave mononuclear complexes. Their formation occurs *via* a cleavage of bridging bonds in the dimeric form, according to the equation presented in Scheme 1, similarly to the procedure observed for nucleophilic ligands, e.g. PCy₃ [13b].

Both ¹H and ¹³C NMR support the complexation of the iridium atom with the carbene ligand. The ¹H NMR spectra show resonance lines coming from 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene ligand at 6.92; 6.80 (2,4,6-Me₃C₆H₂); 6.15 (=CHN); 2.59, 2.19, 1.90 (–CH₃, 2,4,6-Me₃C₆H₂) for **1** and 6.78; 6.81 (2,4,6-Me₃C₆H₂); 6.15 (=CHN); 2.59, 2.15, 2.05 (–CH₃, 2,4,6-Me₃C₆H₂) for **2**. For compound **1** the singlet at 0.40 ppm corresponds to the protons from the siloxyl ligand. In the ¹³C NMR spectrum the ligating carbon atom of carbene ligand was found at 185.4 ppm for **1** and at 182.11 ppm for **2**. Single crystals of **1** and **2** suitable for an X-ray diffraction study were grown from a toluene solution at –15 °C. The solid-state structure is shown in Figs. 1 and 2. Moreover, we have tried to synthesize iridium(I) complex containing

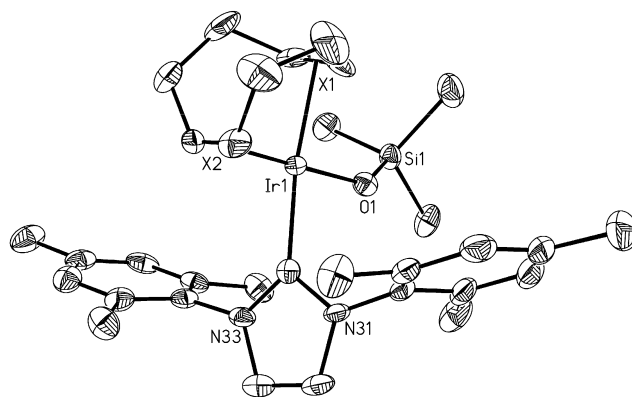


Fig. 1. Anisotropic ellipsoid representation of complex **1**. The ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. X1 and X2 are the midpoints of C=C bonds.

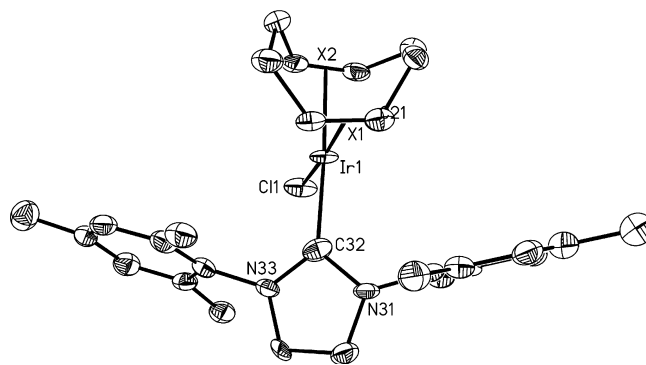
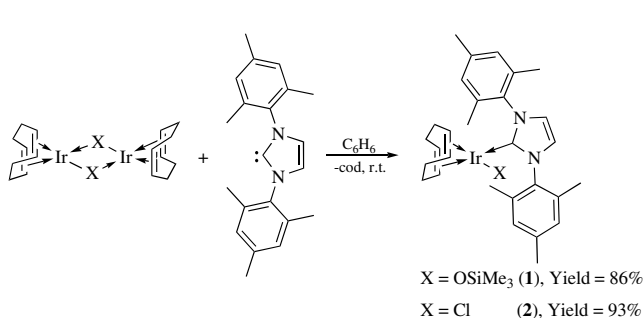


Fig. 2. Anisotropic ellipsoid representation of complex **2**. The ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. X1 and X2 are the midpoints of C=C bonds.

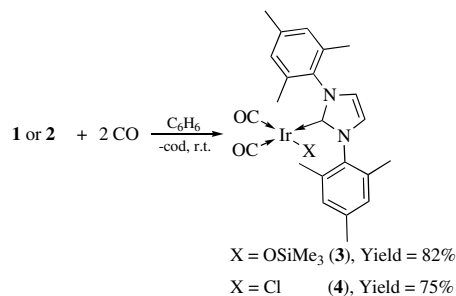
tert-butoxyl ligand, which is a structural analogue to iridium siloxide complex **1**. Unfortunately, treatment of **2** with typical reagents e.g. NaOBu^t or KOBu^t have not given the expected iridium *tert*-butoxide derivative, but instead, the iridium(I) hydroxide carbene complex **5** was obtained.

Reaction of **1** and **2** complexes with carbon monoxide affords iridium derivatives containing two carbonyl ligands, according to Scheme 2.

Due to a strong donor capability of carbene ligands, the cyclooctadiene ligand can be totally substituted by a



Scheme 1. Formation of iridium(I) mononuclear carbene complexes.



Scheme 2. Formation of iridium(I) carbonyl derivatives with bonded IMes ligand.

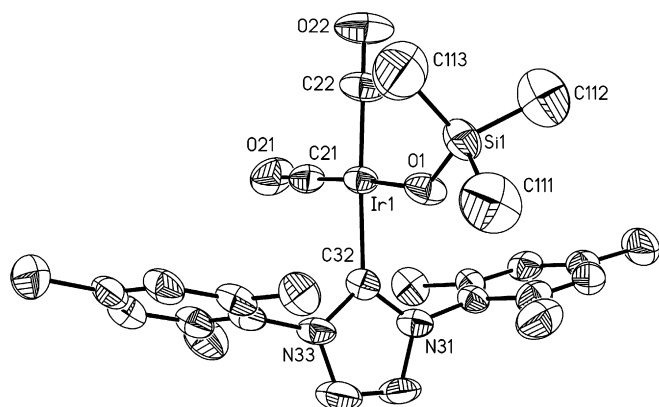


Fig. 3. Anisotropic ellipsoid representation of complex **3**. The ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity.

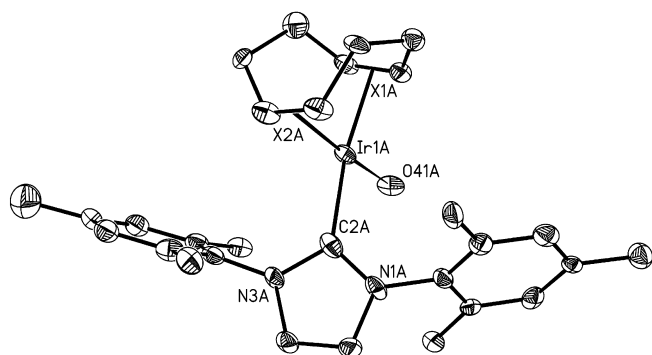


Fig. 4. Anisotropic ellipsoid representation of complex **5**. The ellipsoids are drawn at 50% probability level, hydrogen atoms are omitted for clarity. X1 and X2 are the midpoints of C=C bonds.

stronger acceptor ligand, carbon monoxide [6f]. Similar replacement of cyclooctadiene ligand by CO was observed in the case of $[\text{Ir}(\text{cod})(\text{PCy}_3)(\text{OSiMe}_3)]$ which we reported

previously [17]. In that case, both complexes were isolated and fully characterized by spectroscopic techniques. The ^1H NMR spectra of compounds **3** and **4** confirmed the presence of 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene ligand in the coordination sphere of iridium, evidenced by the appearance of characteristic lines, corresponding to IMes ligand: 6.77 (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$); 6.02 ($=\text{CHN}$); 2.05, 2.23 ($-\text{CH}_3$, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) for **3** and 6.75; 7.74 (2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$); 6.06 ($=\text{CHN}$); 2.04, 2.24 ($-\text{CH}_3$, 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$) for **4**. For compound **3** the singlet at 0.26 ppm was assigned to the protons from the siloxyl ligand. In the ^{13}C NMR spectra the ligating carbon atom of carbene ligand was found at 182.89 ppm for **3** and at 180.76 ppm for **4**. Additionally, single crystals of complex **3** suitable for an X-ray diffraction study were grown from a toluene solution at -20°C . Figs. 1–4 show the perspective views of the structure of complexes **1–3** and **5**; Table 1 presents some selected geometrical parameters. The coordination of iridium is square-planar, as in the majority of the four-coordinated iridium complexes. In the Cambridge Crystallographic Database [18] there are 193 iridium complexes with the coordination number four (Version 5.27, November 2005, May 2006 update); of those almost 90% are close to square planar. Fig. 5 shows the distribution of the sum of valence angles around the Ir atom in these structures; for the typical cases, the ideal values are 720° (square-planar), 660° (tetrahedral) and 630° (trigonal pyramid). However, the degree of distortion of the ideal square is different in the four complexes analyzed. In **1** and **5** the deviations from the plane calculated for the four coordination centers (including the middle points of the double bonds of cyclooctadiene moiety) are as large as 0.15 \AA , and the sum of valence angles is relatively far from the ideal value: 703.8° in **1** and 704.3° and 702.9° in the two symmetry-independent molecules of **5**. In contrast, in the other two complexes, the distortions are significantly less important: the maximum deviations from the

Table 1
Selected geometrical parameters (distances in Å and dihedral angles in $^\circ$)

	1	2	3	5A	5B
Ir–C(IMes)	2.050(5)	2.082(13)	2.055(9)	2.047 (6)	2.042(6)
Ir–X(cod)	1.996(5)	1.998(12)		2.003(7)	1.986(7)
	2.055(5)	2.098(12)		2.064(6)	2.056(6)
Ir–O	2.020(4)		1.993(5)	2.007(5)	1.998(5)
Ir–Cl		2.361(3)			
Ir–C(O)				1.756(11)	
				1.827(11)	
O–Si	1.612(4)		1.600(6)		
C=O				1.199(10)	
				1.156(10)	
(Si–C)	1.872				
(coord)/(Im)	74.0(2)	67.5(4)	74.4(3)	57.2(3)	55.3(3)
(Im)/(PhA)	86.0(2)	80.2(5)	83.2(3)	69.7(3)	68.7(3)
(Im)/(Ph2)	77.4(2)	79.4(5)	77.5(3)	72.1(3)	70.5(3)
(Ph1)/(Ph2)	36.3(2)	33.3(3)	31.0(4)	46.0(3)	48.0(3)

X is the midpoint of the double bond in the cyclooctadiene fragment; the planes are denoted as follows: (coord): the plane by Ir and four coordination centers; (Im): carbene plane and (Ph1) and (Ph2): phenyl rings.

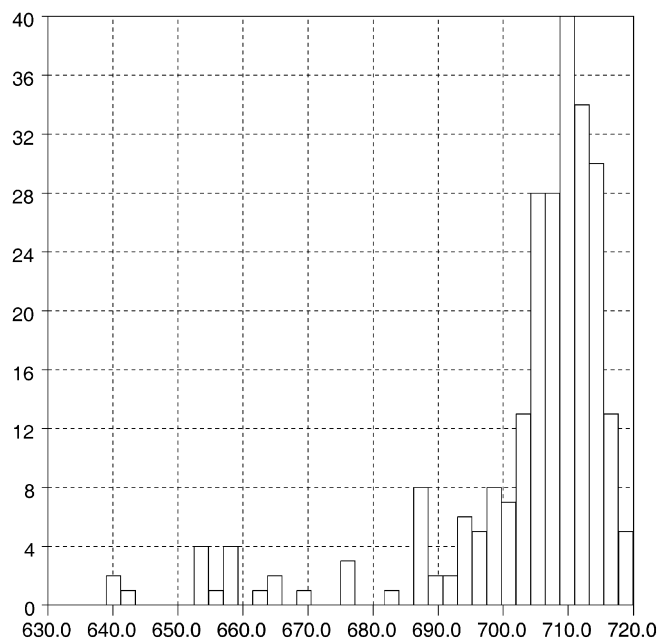


Fig. 5. The scattergram of the sum of valence angles around the Ir atom for all four-coordinated Ir found in Cambridge Crystallographic Database.

least-squares plane by four points are 0.009° (**2**) and 0.029° (**3**), and the sums of the valence angles are 711.5° (**2**) and 713.4° (**3**). It should be noted, however, that regardless of the degree of the square folding, the iridium atom always lies almost exactly in the least-squares plane. The other geometrical features of the molecules are similar in all four complexes and close to the typical values (for some examples, cf. Table 1). The cyclooctadiene fragments in **1**, **2** and **5** are close to a boat conformation (two torsion angles along the ring close to 0° , C_2 approximate symmetry). The overall conformations of the complexes are similar as can be shown by the dihedral angles between the planar fragments (Table 1).

The carbene plane is significantly twisted with respect to the iridium coordination plane and both phenyl rings are almost perpendicular to the carbene plane, certainly due to the steric stress caused by the substituents at *ortho*-positions. Only in two molecules of **5** these twists are smaller but still large. In the crystal structures of **2** and **5** there are toluene (solvent) molecules: two toluene molecules per one complex molecule in **2** and one toluene molecule per two complexes in **5**. The role of the solvent molecule is to stabilise the crystal structure, but there are no significant specific interactions; probably they just fill the voids thanks to the appropriate shape.

2.2. Catalytic properties of selected Ir-complexes in hydrogenation type reactions

As mentioned above, the synthesis of iridium complexes with monodentate carbene ligands and their application in catalysis were described previously [6–8]. Square-planar

cationic complexes with bonded carbene ligand and pyridine, $[\text{Ir}(\text{cod})(\text{py})(\text{L})]\text{PF}_6$ (where $\text{L} = \text{IMes}, \text{IPr}, \text{ICy}$), were applied in the transfer hydrogenation reaction [8a]. Structurally similar complexes $[\text{Ir}(\text{cod})(\text{L})(\text{L}')]\text{PF}_6$ (where $\text{L} = \text{Ime}, \text{IMes}$; $\text{L}' = \text{P}^t\text{Bu}_3, \text{PCy}_3, \text{PPh}_3$) containing simultaneously carbene and phosphine ligands [7c] were also used as catalyst precursors in hydrogenation of olefins. Neutral iridium-carbene complexes $[\text{Ir}(\text{Cl})(\text{cod})(\text{L})]$ (where $\text{L} =$ chiral carbene ligand) were successfully applied to asymmetric hydrogenation of *N*-acetylalanine methyl ester [6w] and transfer hydrogenation of acetophenone [8b].

Our neutral iridium(I) complexes **1** and **2** with bonded 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene ligand (IMes) were tested for catalytic activity in two reactions: transfer hydrogenation of acetophenone and hydrogenation of olefins. Selected results are presented in Table 2. The complexes appeared very active in reduction of acetophenone to the corresponding alcohol *via* hydrogen transfer from $^i\text{PrOH}$ with KOH as a promoter. In both cases full conversion was observed, however in the presence of siloxide precursor **1** a higher value of TOF was noted. Complexes **1** and **2** show high activity also in homogenous hydrogenation reaction. Under mild conditions full conversion of *cis*-cyclooctene was observed after 2 h. In the hydrogenation of *trans*-stilbene, both precursors demonstrated good activity and 72% yield was determined for complex **2**.

3. Experimental

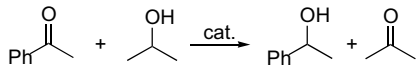
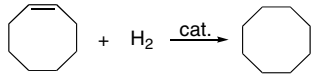
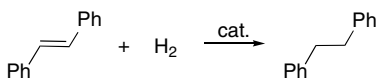
3.1. General methods and chemicals

All syntheses and manipulations were carried out under argon using standard Schlenk's and vacuum techniques. The imidazolin-2-ylidene ligand was synthesized according to a well-known method [5]. The binuclear complexes $[\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2]$ [19] and $[\{\text{Ir}(\mu\text{-OSiMe}_3)(\text{cod})\}_2]$ [13a] were synthesized according to methods described previously. ^1H , ^{13}C and ^{29}Si NMR spectra were recorded on a Varian Gemini 300 VT spectrometer and Varian Mercury 300 VT in C_6D_6 . The chemicals were obtained from the following sources: sodium trimethylsilylanolate, potassium *tert*-butanolate, paraformaldehyde, glyoxal, 2,4,6-trimethylaniline, hydrochloric acid diethyl ether solution, *cis*-cyclooctene, *trans*-stilbene, acetophenone and C_6D_6 from Aldrich Chemical Co., toluene, hexane, 2-propanol, and acetone from POCH Gliwice (Poland), hydrogen from Messer Co. All solvents were dried and distilled under argon prior to use.

3.2. Synthesis of $[\text{Ir}(\text{cod})(\text{IMes})(\text{OSiMe}_3)]$ (**1**)

Portions of 0.2 g $[\{\text{Ir}(\mu\text{-OSiMe}_3)(\text{cod})\}_2]$ (0.257 mmol) and 0.16 g of 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) (0.526 mmol) were placed in a Schlenk's flask equipped with a magnetic bar in argon atmosphere. Then 5 mL of dried and deoxygenated benzene was added. The reaction was carried out for 24 h at room temperature.

Table 2
Selected results of the catalytic activity of complex **1** vs. **2**

Complex	Time (h)	Yield (%)	TOF (h ⁻¹)
<i>Transfer hydrogenation</i>			
			
1	8	99	125 (222 ^a)
2	12	99	83 (143 ^a)
<i>Hydrogenation</i>			
			
1	2	100	50
2	2	100	50
			
1	2	51	25.5
2	2	72	36

Conditions of transfer hydrogenation: [ketone]:[Ir] = 1:10⁻³, [acetophenone]:[KOH] = 1:10⁻², 80 °C, 20 mL ^tPrOH. Conversion and yield were determined by ¹H NMR.

Conditions of hydrogenation reaction: [olefin]:[Ir] = 1:10⁻², CH₂Cl₂, 5 bars of H₂, 2 h.

TOF (h⁻¹) – total average turnover frequency.

^a Turnover frequency at 50% conversion.

After that time solution was filtered off by a cannula system and benzene was evaporated to dryness. To the crude product, 10 mL of dried and deoxygenated pentane was added. At the next step, the contents were cooled to -35 to -30 °C for crystallization. After this, time the solution was decanted and the precipitate was three times washed with pentane by decantation at -60 °C, than dried under vacuum (yield: 0.306 g (86%)).

Anal. Calcd. for C₃₂H₄₅N₂OSiIr (694.1): C, 55.38; H, 6.54; N, 4.04. Found: C, 55.59; H, 6.93; N, 3.85%.

¹H NMR (300 MHz, C₆D₆, 300 K) δ (ppm) = 6.92 (s, 2H, Mes); 6.80 (s, 2H, Mes); 6.15 (s, 2H, =CHN); 4.45 (m, 2H, cod); 2.85 (m, 2H, cod); 2.59 (s, 6H, CH₃ Mes); 2.19 (s, 6H, CH₃ Mes); 1.90 (s, 6H, CH₃ Mes); 1.80 (m, 4H, -CH₂-); 1.40 (m, 4H, -CH₂-); 0.40 (s, 9H, OSiMe₃).

¹³C NMR (75.42 MHz, C₆D₆, 300 K) δ (ppm) = 185.40 (:CN₂); 138.50; 138.10; 136.80; 134.10 (Mes); 122.38 (=CHN-); 79.47; 44.56 (=CH-, cod); 34.10; 29.75 (-CH₂-, cod); 21.06; 19.94; 18.126 (-CH₃, Mes); 5.95 (s, -OSiMe₃).

3.3. Synthesis of [Ir(Cl)(cod)(IMes)] (**2**)

Portions of 0.380 g (1.25 mmol) of 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) and 0.403 g (0.6 mmol) of [Ir(μ-Cl)(cod)]₂ were placed in a Schlenk's flask

equipped with magnetic bar in argon atmosphere. Then 10 mL of dried and deoxygenated benzene was added and the mixture was stirred with a magnetic stirrer. The reaction was continued for 2 h and then benzene was evaporated to 1/5 of the initial volume and 5 mL of dried and deoxygenated pentane was added. The precipitate was three times washed with pentane by decantation. The complex was dried under vacuum for about 4 h (yield: 0.714 g (93%)).

Anal. Calc. for C₂₉H₃₆N₂ClIr (640.28): C, 54.40; H, 5.67; N, 4.38. Found: C, 54.55; H, 5.91; N, 4.25%.

¹H NMR (300 MHz, C₆D₆, 300 K) δ (ppm) = 6.78 (s, 2H, Mes); 6.81 (s, 2H, Mes); 6.15 (s, 2H, =CHN); 4.70 (m, 2H, cod); 3.19 (m, 2H, cod); 2.59 (s, 6H, CH₃); 2.15 (s, 6H, CH₃); 2.05 (s, 6H, CH₃); 1.80 (m, 4H, cod); 1.35 (m, 4H, cod).

¹³C NMR (75.42 MHz, C₆D₆, 300 K) δ (ppm) = 182.11 (CN₂); 138.65; 137.96; 136.77; 134.40; 130.13 (Mes); 123.12 (=CHN-); 83.38; 50.77 (=CH-, cod); 34.07; 29.3 (-CH₂-, cod); 21.0; 20.13; 18.24 (-CH₃, Mes).

3.4. Synthesis of complex [Ir(CO)₂(IMes)(OSiMe₃)] (**3**)

To the complex [Ir(cod)(IMes)(OSiMe₃)] (0.2 g, 0.288 mmol) a portion of 3 mL of dried and deoxygenated benzene in the Schlenk's tube was added. Then to a vigorously stirred solution, 20 mL of carbon monoxide was introduced. The reaction was carried out for 0.5 h at room

temperature. After that time, the mixture was filtered off by a cannula system, and then the solvent and cyclooctadiene were evaporated. To the crude product (yellow solid) 4 mL of dried and deoxygenated pentane was added. The obtained solution was allowed at -35 to -30 °C for crystallization. The crystals obtained was washed by two small portions of pentane at -60 °C and dried under vacuum (yield: 0.151 g (82%)).

Anal. Calc. for $C_{26}H_{33}N_2O_3SiIr$ (641.85): C, 48.65; H, 5.18; N, 4.36. Found: C, 48.90; H, 5.63; N, 4.18%.

1H NMR (300 MHz, C_6D_6 , 300 K) δ (ppm) = 6.77 (s, 4H, Mes); 6.02 (s, 2H, =CHN-); 2.05 (s, 12H, -Me), 2.23 (s, 6H, -Me); 0.26 (s, 9H, -OSiMe₃).

^{13}C NMR (75.42 MHz, C_6D_6 , 300 K) δ (ppm) = 182.89 (:CN₂); 173.30 (CO); 139.72, 135.78, 129.69 (Mes); 122.77 (=CHN-); 21.36, 18.77 (-Me, Mes); 4.73 (-OSiMe₃).

^{29}Si NMR (59.59 MHz, C_6D_6 , 300 K) δ (ppm) = 9.37 (-OSiMe₃).

3.5. Synthesis of complex $[Ir(Cl)(CO)_2(IMes)]$ (**4**)

A portion of complex $[Ir(Cl)(cod)(IMes)]$ (0.2 g, 0.31 mmol) was dissolved in 3 mL of dried and deoxygenated benzene in the Schlenk's tube. Then to a vigorously stirred solution, 20 mL of carbon monoxide was introduced. The reaction was carried out for 0.5 h at room temperature, and then the solvent and cyclooctadiene were evaporated. To the crude product (pale yellow solid) 2 mL of dried and deoxygenated pentane was added, and then the solution was filtered off by a cannula system. The filtrate was allowed at -35 to -30 °C for crystallization. The crystals obtained was washed by two small portions of pentane at -60 °C and dried under vacuum (yield: 0.137 g (75%)).

Anal. Calc. for $C_{23}H_{24}N_2O_2ClIr$ (588.12): C, 46.97; H, 4.11; N, 4.76. Found: C, 47.21; H, 4.53; N, 4.58%.

1H NMR (300 MHz, C_6D_6 , 300 K) δ (ppm) = 6.75 (s, 2H, Mes); 7.74 (s, 2H, Mes); 6.06 (s, 2H, =CHN); 2.04 (s, 12H, CH₃); 2.24 (s, 6H, CH₃).

^{13}C NMR (75.42 MHz, C_6D_6 , 300 K) δ (ppm) = 180.76 (:CN₂); 139.56; 135.33; 129.58 (Mes); 123.22 (=CHN-); 21.03; 18.66 (-CH₃, Mes).

3.6. Synthesis of complex $[Ir(cod)(OH)(IMes)]$ (**5**)

Portions of 0.1 g (0.156 mmol) $[Ir(Cl)(cod)(IMes)]$ and 26.21 mg (0.243 mmol) $tBuOK$ were placed in a Schlenk's flask in argon atmosphere. Then 4 mL of dried and deoxygenated benzene were added. The reaction was conducted for 24 h at room temperature. After this time benzene was evaporated and 10 mL of dried and deoxidized pentane were added. The entire mixture was filtered off by a cannula system. From the obtained filtrate the solvent was evaporated leaving yellow-orange solid (yield: 0.0863 g (89%)).

Anal. Calc. $C_{29}H_{37}N_2OIr$ (621.83): C, 56.01; H, 6.00; N, 4.50. Found: C, 56.11; H, 6.43; N, 4.23%.

1H NMR (300 MHz, C_6D_6 , 300 K) δ (ppm) = 6.81 (m, 4H, Mes); 6.10 (s, 2H, =CHN); 4.71 (m, 2H, cod); 3.18 (m, 2H, cod); 2.60 (s, 6H, CH₃ Mes); 2.11 (s, 6H, CH₃ Mes); 2.05 (s, 6H, CH₃ Mes); 1.84 (m, 4H, -CH₂-); 1.36 (m, 4H, -CH₂-).

^{13}C NMR (75.42 MHz, C_6D_6 , 300 K) δ (ppm) = 181.95 (:CN₂); 138.63; 137.93; 136.73; 134.36 (Mes); 123.06 (=CHN-); 83.40; 50.78 (=CH-, cod); 34.09; 29.35 (-CH₂-, cod); 21.05; 20.17; 18.28 (-CH₃, Mes).

3.7. Catalytic tests

Catalytic tests were performed according to the following procedures.

3.7.1. Hydrogen transfer reactions

In a 25 mL round-bottomed flask equipped with reflux condenser, gas inlet, bubbler and a stir bar 10 mL of 2-propanol was placed via syringe under argon, then potassium hydroxide (1.12 mg, 0.02 mmol) and 10^{-3} mmol of iridium complex were added. After the mixture was stirred at room temperature for 15 min, then acetophenone (240 mg, 2.0 mmol) was added. The reaction mixture was stirred at 80 °C to completed conversion (reaction progress was controlled by 1H NMR). The solvent was removed under vacuum, and the residue was analyzed by 1H NMR spectroscopy.

3.7.2. Hydrogenation of olefins

In a Schlenk's tube 10 mL of dried and oxygen-free CH_2Cl_2 was placed then 8.0 mmol of *cis*-cyclooctene and 0.08 mmol of iridium precursor or 5.0 mmol of *trans*-stilbene and 0.05 mmol of iridium precursors were added. The obtained solution was transferred by a cannula system into the pressure reactor, which was flushed with argon prior to use. Then the reactor was pressurized with H_2 up to 5 bars. The reaction mixture was magnetically stirred at 40 °C for 2 h. After this time the reactor was allowed to cool to room temperature. The solvent was removed from the reaction mixture under vacuum, and the residue was analyzed by 1H NMR spectroscopy.

3.8. X-ray structure determination

X-ray data were collected at room temperature (compounds **1** and **3**) and at 100 K (**2** and **5**) by the ω -scan technique, on a KUMA KM4CCD diffractometer [20] with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz-polarization effects [21] as well as for absorption by SORTAV [22]. Accurate unit-cell parameters were determined by the least-squares fit of 8202 (**1**), 7139 (**2**), 3199 (**3**) and 5462 (**5**) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SHELXS97 [23] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97 [24]. Scattering factors incorporated in SHELXL97 were used. All non-hydrogen atoms were refined

Table 3
Crystal data, data collection and structure refinement

Compound	1	2	3	5
Formula	C ₃₂ H ₄₅ N ₂ OSiIr	C ₂₉ H ₃₆ ClN ₂ Ir · 2(C ₇ H ₈)	C ₂₆ H ₃₃ N ₂ O ₃ SiIr	C ₂₉ H ₃₇ N ₂ OIr · 1/2(C ₇ H ₈)
Formula weight	694.01	824.54	641.85	667.87
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.7545(5)	11.5383(14)	9.1157(7)	14.171(1)
<i>b</i> (Å)	17.7272(8)	17.068(2)	14.9832(10)	14.706(1)
<i>c</i> (Å)	18.1858(9)	18.8499(13)	21.2079(13)	15.499(1)
α (°)	90	90	90	68.73(1)
β (°)	92.596(3)	90	98.749(6)	69.94(1)
γ (°)	90	90	90	89.56(1)
<i>V</i> (Å ³)	3141.5(3)	3712.2(7)	2862.9(3)	2802.4(4)
<i>Z</i>	4	4	4	4
<i>D</i> _x (g cm ⁻³)	1.467	1.475	1.489	1.583
<i>F</i> (000)	1400	1672	1272	1340
μ (mm ⁻¹)	4.314	3.701	4.732	4.79
Crystal size (mm)	0.35 × 0.2 × 0.1	0.4 × 0.1 × 0.07	0.15 × 0.1 × 0.1	0.2 × 0.1 × 0.1
<i>T</i> (K)	293(2)	100(1)	293(2)	100(1)
Θ Range (°)	3.63–27.00	2.97–25.00	3.41–25.00	5.23–29.91
<i>hkl</i> Range	–12 ≤ <i>h</i> ≤ 12, –14 ≤ <i>k</i> ≤ 23, –23 ≤ <i>l</i> ≤ 23	–13 ≤ <i>h</i> ≤ 7, –20 ≤ <i>k</i> ≤ 20, –22 ≤ <i>l</i> ≤ 22	–10 ≤ <i>h</i> ≤ 10, –13 ≤ <i>k</i> ≤ 17, –25 ≤ <i>l</i> ≤ 25	–17 ≤ <i>h</i> ≤ 19, –19 ≤ <i>k</i> ≤ 19, –21 ≤ <i>l</i> ≤ 21
Reflections collected	17573	24531	14170	28537
Reflections unique (<i>R</i> _{int})	6698 (0.045)	6522 (0.083)	4975 (0.066)	14317 (0.054)
Reflections with <i>I</i> > 2σ(<i>I</i>)	5646	4952	2831	9229
Number of parameters	343	430	298	671
<i>R</i> (<i>F</i>) [<i>I</i> > 2σ(<i>I</i>)]	0.0396	0.0706	0.0506	0.0513
<i>wR</i> (<i>F</i> ²) [<i>I</i> > 2σ(<i>I</i>)]	0.0775	0.164	0.1074	0.1013
<i>R</i> (<i>F</i>) [all data]	0.0513	0.0841	0.0927	0.0892
<i>wR</i> (<i>F</i> ²) [all data]	0.0824	0.174	0.0782	0.1069
Goodness-of-fit	1.075	0.985	0.933	1.115
Maximum/minimum Δρ (e Å ⁻³)	1.58/–1.24	4.84/–3.23	0.861/–0.940	2.74/–2.85
CCDC deposition number	296879	296880	296881	296882

anisotropically, hydrogen atoms were placed geometrically, in idealized positions, and refined as rigid groups, *U*_{iso} of hydrogen atoms were set as 1.2 (1.3 for methyl groups) times *U*_{eq} of the appropriate carrier atom. Relevant crystal data are listed in Table 3, together with refinement details.

4. Supplementary material

CCDC 296879, 296880, 296881 and 296882 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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