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Transfer Hydrogenation Catalysis by a N-Heterocyclic Carbene (NHC) Iridium Complex on a Polyoxometalate Platform

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Keywords: iridium / polyoxometalates / transfer hydrogenation / N-heterocyclic carbene / nanoscaffolds

A divacant Keggin polyanion has been decorated with a NHC iridium(I) organometallic complex in order to provide a molecular model of a Ir-based supported catalyst. The characterization of the hybrid compound has been performed by multinuclear NMR, infrared spectroscopy, cyclic voltammetry and mass spectroscopy, and it is in agreement with a bis fuctionalization of the polyoxometalate scaffold. The resulting supported homogeneous complex has been successfully used to catalyzes the hydrogen transfer hydrogenation from *i*PrOH to benzophenone (with TON=680 and TOF up to 540 h^{-1}).

Introduction

Decoration of bulk surfaces with organometallic domains is a powerful strategy to replicate single-site reactive units into functional arrays. The resulting catalytic surfaces can provide a combined tuning of steric and electronic features of the reactive sites, while offering opportunities for cooperativity, environment assistance and process intensification.

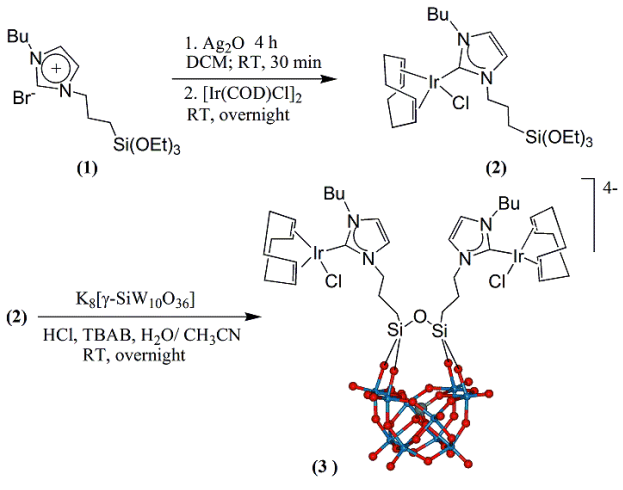
In this context, on-surface transfer hydrogenation catalysis (THC) may represent a valuable alternative to heterogeneous gas-phase protocols using dihydrogen. Indeed, THC exhibits a high synthetic appeal, stemming from the use of alcohols as organic hydrogen source for liquid phase reduction, under mild pressure and temperature conditions.[1]

Among molecular TH catalysts, iridium complexes with N-heterocyclic carbene ligands (Ir-NHC) show high thermal robustness and stability during multi-turnover catalysis.[2,3] However, heterogeneous THC by Ir-NHC species is limited to polymeric supports and plagued by irreversible leaching.[4]

We present herein a synthetic strategy for the immobilization of Ir-NHC domains on a molecular polyoxometalate (POM), resulting in the vicinal arrangement of two reactive sites (Scheme 1). POMs offer a unique nano-dimensional and totally inorganic platform, and they are often considered as a molecular fragment of metal oxide solid supports (oxides, zeolites, and mesoporous materials). Therefore, the use of POMs for the anchorage of hetero-catalytic sites has been proposed to bridge the gap between homogeneous and heterogeneous systems.[5] Moreover, POMs behave as ionic nano-tags and can impart a tunable solubility by tailored counter-ion association,[6] or they can be immobilized on cationic supports by electrostatic interactions.[7]

The design of POM-based supports for THC is unprecedented and holds great potential in terms of innovative functional nano-structures and advanced catalysis. In particular, THC protocols could benefits from metal oxide-assisted hydrogen translocation[8] and/or the possibility to tune reaction conditions in different H-donor media.[9]

Modification of the POM surface with organometallic substituents can be achieved by introduction of covalent tethers, providing binding motifs for hetero-metal centers.[10-12] According to this strategy, molecular catalytic species have been obtained upon POM decoration with phosphines and NHCs chelates for Rh[11] and Pd[12] ions, respectively.



Scheme 1. Synthesis of the Ir-NHC complexes

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Results and Discussion

The synthetic route to introduce Ir-NHC domains on POMs exploits the nucleophilic reactivity of surface oxygens on vacant polyoxotungstates with tailored organosilanes. Covalent grafting occurs in acetonitrile, in the presence of a lipophilic ammonium salt, usually nBu$_4$N$^+$Br$^-$, to promote the solubilization of the POM by counterion metathesis (Scheme 1).[13] Under these conditions, decoration of the divacant Keggin polyanion [γ-SiW$_{10}$O$_{36}$]$^{8-}$ is known to yield bis-functionalized hybrids with two surface-anchored organosilyl (RSi-) groups, each one linked to two oxygen atoms of two edge-shared WO$_6$ octahedra.[14]

To this end, the trialkoxysilyl-tagged imidazolium precursor **1**, was initially synthesized under strictly anhydrous conditions from (3-chloropropyl)-triethoxysilane and 1-butylimidazole (Scheme 1). Reaction of **1** with Ag$_2$O, followed by transmetallation with [Ir(C$_8$H$_{12}$)Cl]$_2$ (with C$_8$H$_{12}$ = 1,5-cyclooctadiene, COD) afforded the Ir–NHC complex **2** with a trialkoxysilyl tag in 78% yield.[15] The identity of **2** was confirmed by FT-IR, ^{1}H, ^{13}C, ^{29}Si NMR and ESI-MS analyses (see Supporting Information, Figures S1-S4). The absence of a resonance due to the C(2)-bound imidazolium proton (δ_H = 10.6 ppm for the imidazolium salt **1** in CDCl$_3$) is corroborated by the appearance of a new signal at δ_C = 178.7 ppm, which is characteristic of an iridium-bound carbene carbon (Figures S2 and S3).[15] Moreover, a single ^{29}Si NMR signal at –46.2 ppm is indicative of a pure product (Figure 1, inset).

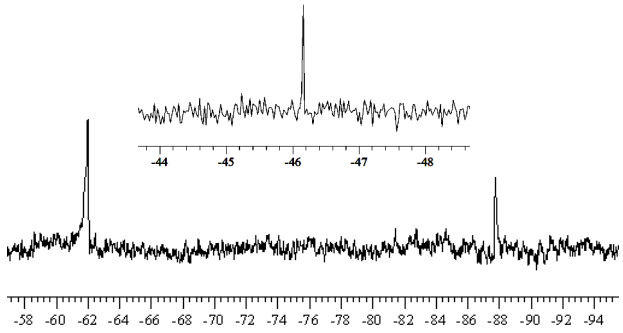


Figure 1: ^{29}Si-NMR (79.5 MHz, T=25°C) of **3** in CD$_3$CN and of **2** in CDCl$_3$ (inset).

The ESI-MS (positive mode) analysis confirms the formation of the desired iridium complex, bearing NHC and COD ligands, with signals centered at m/z = 628.9 and 670.6, corresponding to [M–Cl]$^+$ and [M–Cl+CH$_3$CN]$^+$ respectively (Figure S4).

The Ir complex **2** was then reacted with the decatungstosilicate K$_8$[γ-SiW$_{10}$O$_{36}$] in acetonitrile, under phase transfer conditions (Scheme 1), leading to the hybrid POM (nBu$_4$N)$_4${[Ir(C$_8$H$_{12}$)Cl(C$_{10}$H$_{17}$N$_2$Si)]$_2$O[γ-SiW$_{10}$O$_{36}$]} (**3**), in 75% yield. A different synthetic approach, consisting in post metalation of the POM-attached **1** with Ag$_2$O was also investigated. However, no carbene formation was obtained. Presumably, the inorganic POM interacts electrostatically with Ag$^+$ as well as with the imidazolium moieties, thus hampering the formation of the silver carbene intermediate. The resulting product was characterized by ^{1}H, ^{13}C, ^{183}W and ^{29}Si NMR, FT-IR spectroscopies, ESI-MS and cyclic voltammetry (Supporting Information, Figures S5-S11).

The ^{183}W NMR spectrum of POM–Ir hybrid **3** shows three resonances at -107.4, -135.8, and -142.1 ppm in 2:1:2 ratio, in agreement with a C$_2$v symmetry of the NHC decorated polyanion (Figure S5).[14] The ^{29}Si NMR spectrum reveals two signals at -62.8 and -88.4 ppm for the organosilane and the silicotungstate residues, respectively, in the expected 2:1 integration ratio (Figure 1). These results are consistent with a bis-substitution of the POM surface and indicate a diagnostic 14.6 ppm upfield shift for the organosilicon signal upon grafting to the POM.

FT-IR evidence is also in agreement with the expected functionalization, as shown by the RSi-O vibration band at 1102 cm^{-1} and by the diagnostic spectral pattern due to W-O bond vibrations, observed between 1000 and 700 cm^{-1} (Figure S6).[14] Upon exposure to a CO atmosphere, the resulting complex **3** undergoes a displacement of the COD ligand, providing an additional evidence of the presence of the Ir-NHC unit. Indeed, when a solution of **3** in CH$_3$CN (2 mM) was saturated with CO gas (1 atm) for 10 min, the FT-IR spectrum revealed two new bands at 2058 cm^{-1} and 1977 cm^{-1} (Figure S7) that are diagnostic for CO bonding at the iridium carbene moiety, as expected upon successful grafting of the bis-iridium site.[15,16]

An ESI-MS spectrum of **3** recorded in negative mode shows a dominant cluster centered at m/z = 1723, which was attributed to {[Ir(C$_8$H$_{12}$)(C$_{10}$H$_{17}$N$_2$Si)]$_2$O[γ-SiW$_{10}$O$_{36}$]}$^{2-}$, corresponding to [M-2Cl-4TBA]$^{2-}$ (Figure S8).[12]

Successful formation of the organometallic POM hybrid was also concluded from the ^{1}H NMR and ^{13}C NMR spectra, confirming the presence of the NHC ligand (heterocyclic protons at δ_H = 7.22 and 7.04 ppm), the COD residues (diagnostic olefinic

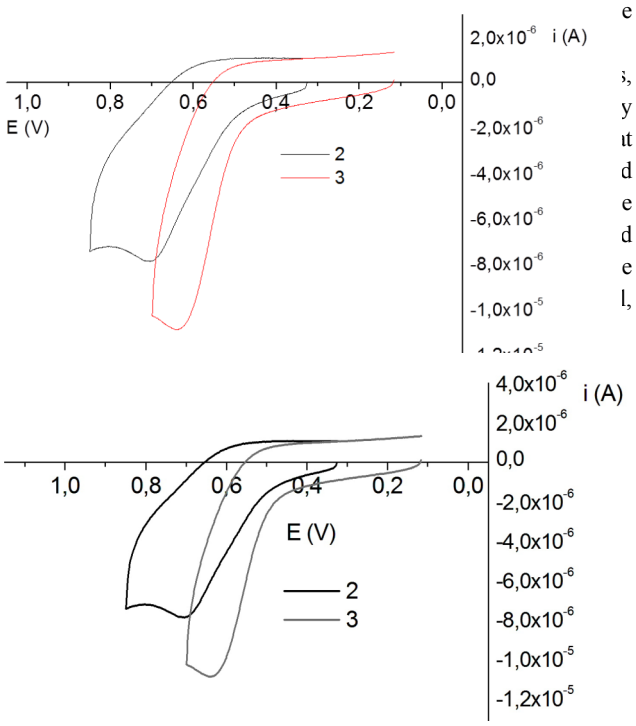
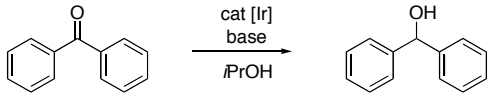


Figure 2: Cyclic voltammograms (anodic scan) of **2** and **3** (0.05 mM) in CH$_3$CN (nBu$_4$ClO$_4$; 0.1 M); scan rate 200 mV sec^{-1}, potentials *vs* Ag/AgCl.

The POM-grafted bis-NHC Iridium features a suitable manifold of redox states, which can leverage key catalytic steps involving alcohol oxidation and hydride transfer. Hybrid **3** was thus screened for catalytic transfer hydrogenation, by investigating the reduction

of benzophenone to diphenyl methanol in *i*PrOH as the model reaction (Scheme 2).

All catalyst manipulations were performed under air, since no special caution is needed for handling the POM-based system. The initial reaction set-up was designed with 1 mol% iridium loading.[18]



Scheme 2. Hydrogen transfer reaction to benzophenone by Ir catalysts

Product formation was monitored by ^{1}H NMR, to assess the overall catalytic efficiency (Table 1) and the relevant kinetic profiles (Figure 3).

Table 1. Hydrogen transfer reaction to benzophenone by NHC-Ir(I) complexes.[a]

entry	catalyst	Base	Conversion[b]	TON[c]	TOF[d] (h^{-1})
1	**4**	KOH	97	97	234
2	**5**	-	<2	<2	-
3	**4** + **5**	KOH	97	97	198
4	**3**	KOH	72	72	96
5	**3**	*t*BuOK	99	99	210
6	**3**	nBu$_4$NOH	23	23	24
7	**3**[e]	*t*BuOK	68	680	540

[a] 1 mol% catalyst (0.01 mmol), benzophenone (1.0 mmol) and base (10 mol%, 0.1 mmol) in *i*PrOH (5.0 mL), T=80°C. In all reactions, ketone was introduced after heating for 10 min; [b] % conversion of substrate monitored by ^{1}H NMR. [c] Turnover number (moles of converted substrate per mol of catalysts), at t=5h; [d] Turnover frequency (catalytic cycles per hours), calculated from initial rates at <30% conversion; [e] reaction with 0.1% mol Ir loading.

Inspection of data in Table 1 allows to benchmark catalyst **3** against the POM-free Ir–NHC complex [Ir(C_8H_{12})Cl(I*n*Bu)] (**4,** I*n*Bu = *N,N'*-dibutyl-imidazol-2-ylidene), and to confirm the competent role of the iridium sites (entry 1).

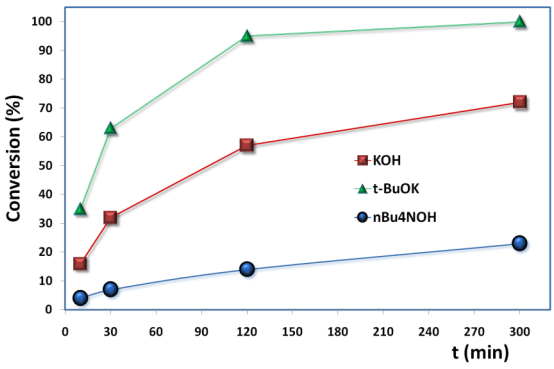


Figure 3. Kinetics of hydrogen transfer to benzofenone catalyzed by **3**, in the presence of different bases (entries 4, 5, 6 in Table 2).

Indeed, the Ir-free POM [γ-Si$W_{10}O_{36}$]$^{8-}$ (**5**) has no activity, both in *a-solo* conditions or in combination with **4** (entries 2, 3). THC works in the presence of a base additive. As shown in Figure 3, the nature of the base turns out to have a major impact on the reaction kinetics catalyzed by **3**.

Both turnover numbers and frequency (TON and TOF) decrease in the order *t*BuOK>KOH>nBu$_4$NOH (entries 4-6 and Figure 3). Indeed, quantitative conversion and performance, identical to that of homogeneous **4,** were observed after 2 h with the bulky organic base *t*BuOK (*cf* entries 1,5). In this case, the possibility to exclude aqueous bases is expected to preserve POM scaffold from irreversible hydrolysis.ref The base sensitivity of the POM-free **4** is less critical and *t*BuOK and KOH provided essentially identical results. Optimization of the process efficiency was achieved at lower iridium loading (0.1 mol%) with *t*BuOK as the base, providing 70% conversion after 5 h, with an overall TON=680 and maximum TOF=540 h^{-1} (entry 7). Such high activity underpins the efficiency of the immobilization strategy adopted here.

Conclusions

In summary, successful grafting of a NHC-bis-iridium(I) on a polyoxometalate surface has been demonstrated, so to provide a working model for heterogenized transfer hydrogenation catalysis. The catalytic efficiency has been preserved, when compared to the POM-free organometallic analogue, upon appropriate tailoring of reaction conditions. The POM nano-tag offers an added value, since it can foster solubility/immobilization in highly polar or ionic phases,[19] or it can take advantage of membrane separation processes.[20] Tailored POMs with diverse substituents/counterions will thus be considered to further address the reaction scope and the catalyst recycling potential.

Experimental Section

Generals: K$_8$[γ-Si$W_{10}O_{36}$] [21] 1-butyl-3-(3-triethoxysilylpropyl)-imidazolium bromide,[12] [Ir(C_8H_{12})Cl]$_2$ and [Ir(C_8H_{12})Cl(NHC')][15] (NHC' = *N,N'*-dibutyl-imidazol-2-ylidene) were prepared as described in the literature. Other reagents were purchased from commercial sources and used as received, without further purification. All syntheses were performed under nitrogen atmosphere using reagent grade solvents, which were used as received.

Synthesis of (nBu$_4$N)$_4${[Ir(C_8H_{12})Cl($C_{10}H_{17}N_2$Si)]$_2$O[γ-Si$W_{10}O_{36}$]} (3): 380 mg (0.13 mmol) of K$_8$[γ-Si$W_{10}O_{36}$] were suspended in 500 µL of H_2O, under nitrogen. 206 mg (65 mmol, 5 equiv.) of nBu$_4$NBr, and CH_3CN (5 mL) were added and the mixture was stirred at room temperature for 20'. The compound **2** (170 mg, 0.26 mmol) was dissolved in 3 mL of solution CH_2Cl_2/CH_3CN 1/2 under nitrogen, then the solution of **2** and 190 µl of HCl 4.05 M were added in rapid sequence. Upon addition of acid, immediate clearing of the solution was observed. The mixture was kept under vigorous stirring overnight at r.t., then filtered to remove the insoluble material. The mixture was concentrated to about 1 mL, and the product was precipitated by adding deionized water (20 mL). The product was collected by filtration on a fritted funnel, washed with few portions of deionized water and diethyl ether, and dried under vacuum. 298 mg (0.07 mmol) of product were obtained (54% yield). Full characterization (FT IR, ^{1}H NMR, ^{13}C{^{1}H} NMR, ^{29}Si NMR, ^{183}W NMR, ESI-MS (-), elemental analysis) is reported in the Supportin Information.

THC protocol: In a typical reaction, the iridium catalyst was stirred in *i*PrOH (5.0 mL) with the suitable base additive (0.1 mmol) at reflux temperature, for 10 min. The ketone (1.0 mmol) was added and aliquots (0.2 mL) were taken at fixed times, diluted with hexane (2 mL), filtered through a short pad of SiO_2 and analyzed by ^1H NMR spectroscopy.

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures and complete characterization are provided for compounds **2** and **3**.

Acknowledgments

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Entry for the Table of Contents

Key Topic

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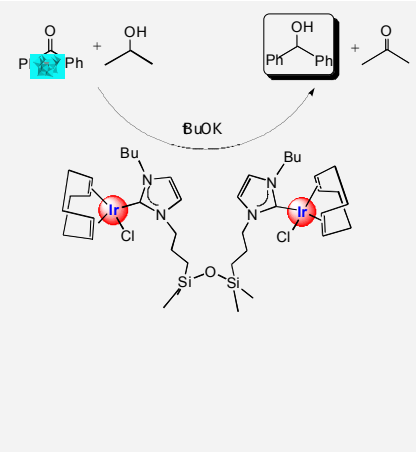

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Keywords: iridium / polyoxometalates / transfer hydrogenation / N-heterocyclic carbene / nanoscaffolds

Supporting Information

Transfer Hydrogenation Catalysis by a N-Heterocyclic Carbene (NHC) Iridium Complex on a Polyoxometalate Platform

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Generals

^{1}H NMR spectra were recorded with Bruker AV300 instrument operating at 300.13 MHz; ^{13}C NMR spectra were recorded with Bruker AV300 operating at 75.4 MHz. $Si(CH_3)_4$ was used as reference. ^{183}W NMR and ^{29}Si NMR spectra were recorded with a Bruker Avance DRX 400 instrument operating at 16.67 MHz and 79.50 MHz, respectively, using 2M Na_2WO_4 in D_2O and $Si(CH_3)_4$ in $CDCl_3$ as external references. FT-IR (KBr) spectra were collected on a Thermo Quest Nicolet 5700 instrument. ESI-MS spectra were obtained with a Agilent LC/MSD Trap SL spectrometer, by using a capillary potential of 1500V. CV analysis were performed on a BAS C3- instrument.

Synthesis of [1-butyl-3-(3-triethoxysilylpropyl)-imidazol-2-ylidene] [(1,2,5,6-η)-1,5 cyclooctadiene] chloro iridium $Ir(C_8H_{12})Cl(C_{10}H_{17}N_2)Si(OCH_2CH_3)_3$ (2): 1-butyl-3-(3-triethoxysilylpropyl)-imidazolium bromide **1** (0.5 g, 1.22 mmol) was introduced in a well dried Schlenk tube. Anhydrous CH_2Cl_2 (40 mL) and Ag_2O (0.142 g, 0.61 mmol) were then added. The reaction mixture, vigorously stirred, was allowed to react at room temperature, under nitrogen. After 5 h $[Ir(COD)Cl]_2$ (0.410 g, 0.61 mmol) was added and the mixture was stirred overnight, then filtered through celite. Evaporation of the solvent gives the desired product as a yellow oil. Yield: 0.69 g (85%).

FT-IR (KBr). ν= 3163 (w), 3126 (w), 3103 (w), 2961 (s), 2927 (s), 2876 (s), 2013 (w, b), 1456 (m), 1420 (m), 1257 (m), 1226 (m), 1201 (m), 1167 (m), 1102 (s), 1077 (s), 956 (m), 883 (w), 798 (m), 777(m), 703 (m), 690 (m) cm^{-1}. **^{29}Si-NMR** (79.5 MHz, CD_3CN, 25°C): δ = - 46.2 ppm **^{1}H-NMR** (360 MHz, CD_2Cl_2, 25°C) 6.87 (1H, s, CH imidazol-2-ylidene), 6.82 (1H, s, CH imidazol-2-ylidene), 4.58 (2H, s, b, CH_{cod}) 4.36 (4H, m, $Si(CH_2)_2\underline{CH_2}N$, $N\underline{CH_2}(CH_2)_2CH_3$), 3.84 (6H, q, $CH_3\underline{CH_2}O$), 2.92 (2H, s, b, CH_{COD}), 2.20 (4H, s, b, CH_{COD}), 2.06-1.38 (10H, m, CH_{COD}, $NCH_2CH_2\underline{CH_2}CH_3$, $SiCH_2\underline{CH_2}CH_2N$, $NCH_2\underline{CH_2}CH_2CH_3$), 1.24 (9H, t, $\underline{CH_3}CH_2O$), 1.00 (3H, t, $N(CH_2)_3\underline{CH_3}$), 0.71 (2H, m, $Si\underline{CH_2}$) ppm**.** **^{13}C{^{1}H}-NMR** (62.5 MHz, CD_2Cl_2, 25°C): 179.65 (C-Ir), 119.99, 119.68 (C4 and C5, imidazol-2-ylidene), 83.83 (1C, CH_{COD}), 83.52 (1C, CH_{COD}), 58.44 (3C, OCH_2), 52.79, 51.46, 51.14, 50.23 (4C, $CH_3(CH_2)_2\underline{CH_2}N$, $SiCH_2CH_2\underline{CH_2}N$ and CH_{COD}), 33.73, 33.35, 32.94, 29.69, 29.33, 24.50, 19.98 (7C, methylene groups and CH_{COD}), 18.27 (3C, $OCH_2\underline{CH_3}$), 13.70 (1C, $\underline{CH_3}(CH_2)_2CH_2N$), 7.77 (1C, $SiCH_2$) ppm. **ESI-MS(+)** (CH_3CN) m/z = 628.9 and 670.7, calcd. for $[Ir(C_8H_{12})\{C_{10}H_{17}N_2Si(OEt)_3\}]^+$ = 628.9 and for $[Ir(C_8H_{12})\{C_{10}H_{17}N_2Si(OEt)_3\}(CH_3CN)]^+$ = 670.0. **Elemental Analysis** calcd. (%) For $C_{24}H_{44}N_2O_3ClIrSi$: C 43.39, H 6.68, N 4.22; found: C 42.89, H 6.00, N 4.30.

Characterization of (nBu$_4$N)$_4$[(Ir(C$_8$H$_{12}$)ClC$_{10}$H$_{17}$N$_2$Si)$_2$O(γ-SiW$_{10}$O$_{36}$)] (3):

(For the synthesis, see main text).

FTIR (KBr): ν= 2960 (m), 2932 (m), 2872 (m), 1660 (m), 1482 (m), 1463 (m), 1418 (m), 1380 (m), 1105 (m), 964 (s), 902 (s), 886 (s), 820 (s), 733 (s), 544 (m), 508 (m) cm-1. **^{1}H NMR** (300 MHz, CD_3CN, 301 K) δ = 7.22 (2H, s, C<u>H</u> imidazol-2-ylidene), 7.04 (2H, s, C<u>H</u> imidazol-2-ylidene), 4.44-4.16 (24H, m, CH_{COD}, $Si(CH_2)_2C\underline{H_2}N$, $NC\underline{H_2}(CH_2)_2CH_3$, $CH_3\underline{CH_2}O$), 3.16 (32H, m, $(CH_3CH_2CH_2C\underline{H_2})_4N$), 2.79-2.13 (28H, m, CH_{COD}, $NCH_2CH_2\underline{CH_2}CH_3$, $SiCH_2\underline{CH_2}CH_2N$, $NCH_2\underline{CH_2}CH_2CH_3$), 1.65 (32H, m, $N(CH_2\underline{CH_2}CH_2CH_3)_4$), 1.40 (50H, $N(CH_2CH_2\underline{CH_2}CH_3)_4$, $OCH_2\underline{CH_3}$,), 0.98 (54H, $N(CH_2CH_2\underline{CH_2}CH_3)$, $N(CH_2)_3\underline{CH_3}$), 0.60 (4H, m, $Si\underline{CH_2}$) ppm. **^{13}C{^{1}H} NMR** (75.47 MHz, *d*-DMF, 301 K): δ = 178.7 (2C, C-Ir), 122.16, 121.40 (4C, C4 and C5, imidazol-2-ylidene), 82.75 (2C, CH_{COD}), 82.57 (2C, CH_{COD}), 59.27 (16C, $N(\underline{CH_2}CH_2CH_2CH_3)_4$), 58.93, 58.54, 58.17, 50.77 (8C, $CH_3(CH_2)_2\underline{CH_2}N$, $SiCH_2CH_2\underline{CH_2}N$ and CH_{COD}), 34.06, 33.89, 33.48, 30.46, 26.31 (14C, methylene groups and CH_{COD}), 24.36 (16C, $N(CH_2\underline{CH_2}CH_2CH_3)_4$), 20.6 (6C, $OCH_2\underline{CH_3}$), 20.33 (16C, $N(CH_2CH_2\underline{CH_2}CH_3)_4$), 13.90 (16C, $N(CH_2CH_2CH_2\underline{CH_3})_4$), 13.16 (2C, $\underline{CH_3}(CH_2)_2CH_2N$) **^{29}Si-NMR** (79.5 MHz, CD_3CN, 25°C): δ = -62.0 (2 Si), -87.8 (1 Si) ppm. **^{183}W-NMR** (16.7 MHz, CD3CN, 25°C): - 105.8 (4 W), -135.6 (2W), - 141.8 (4 W) ppm. **ESI-MS(-)** (CH_3CN) m/z = 1723.0, calcd. for $\{[(C_8H_{12})Ir(C_{10}H_{17}N_2Si)]_2O(\gamma\text{-}SiW_{10}O_{36})\}^{2-}$ = 1723.0. **Elemental Analysis** calcd. (%) for $C_{100}N_8O_{37}Cl_2Ir_2Si_3W_{10}$: C 26.75, H 4.50, N 2.50; found: C 25.25, H 4.00, N 2.54.

Transfer hydrogenation catalytic tests

Typically, the transfer hydrogen of benzophenone in *i*PrOH to yield diphenyl methanol was performed in glass reactors. Catalyst manipulation does not need particular precautions, and transfer hydrogenations were generally performed in air.

In a typical reaction, the catalyst (0.01 mmol, 1 mol%) was stirred, together with a base (0.05 mL of 2 M solution in H_2O, 0.1 mmol) and *i*PrOH (5.0 mL), under reflux for 10 min. Then the ketone (1.0 mmol) was added at once. Aliquots (0.2 mL) were taken at fixed times, diluted in hexane (2 mL), and filtered through a plug of silica, then the silica was washed with diethyl ether or *tert*-butyl methyl ether. The combined organic filtrates were evaporated and analyzed by ^{1}H NMR spectroscopy, monitoring the signal due to the C(OH)*H* proton, geminal to the hydroxyl group of the product, at 5.86 ppm.

Characterization of [1-butyl-3-(3-triethoxysilylpropyl)-imidazol-2-ylidene][(1,2,5,6-η)-1,5 cyclooctadiene] chloro iridium (2)

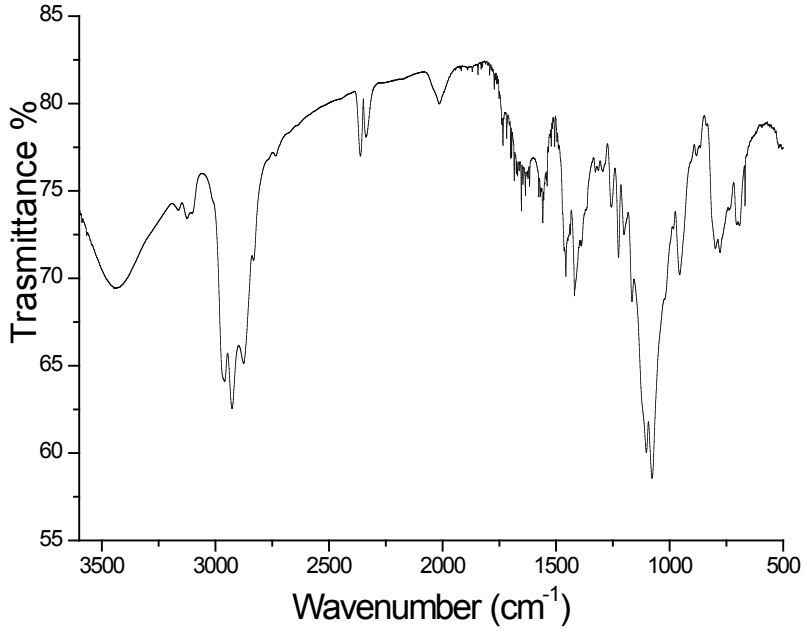

Figure S1: FT-IR (KBr) of **2**.

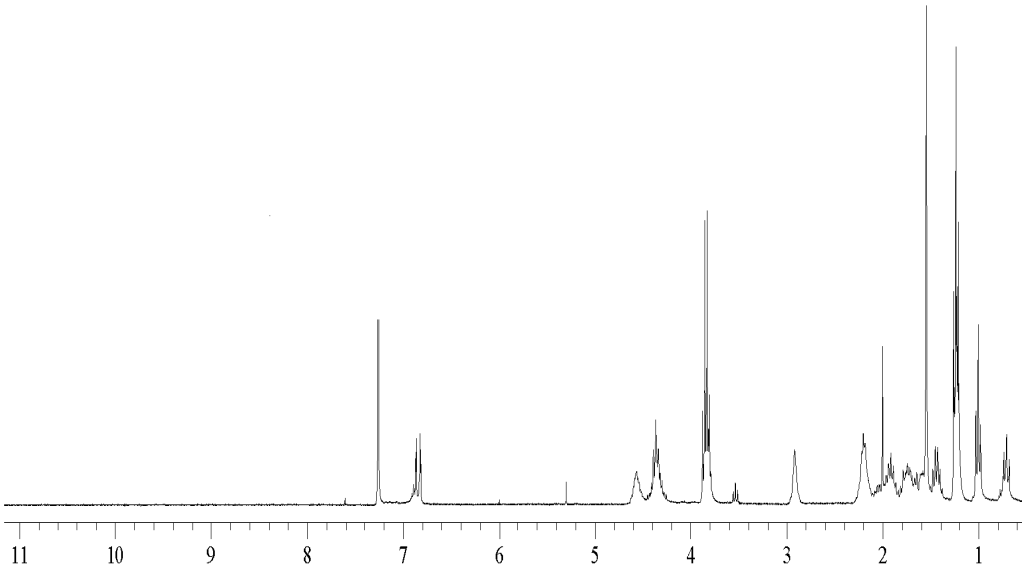

Figure S2: ^{1}H NMR ($CDCl_3$) of **2.**

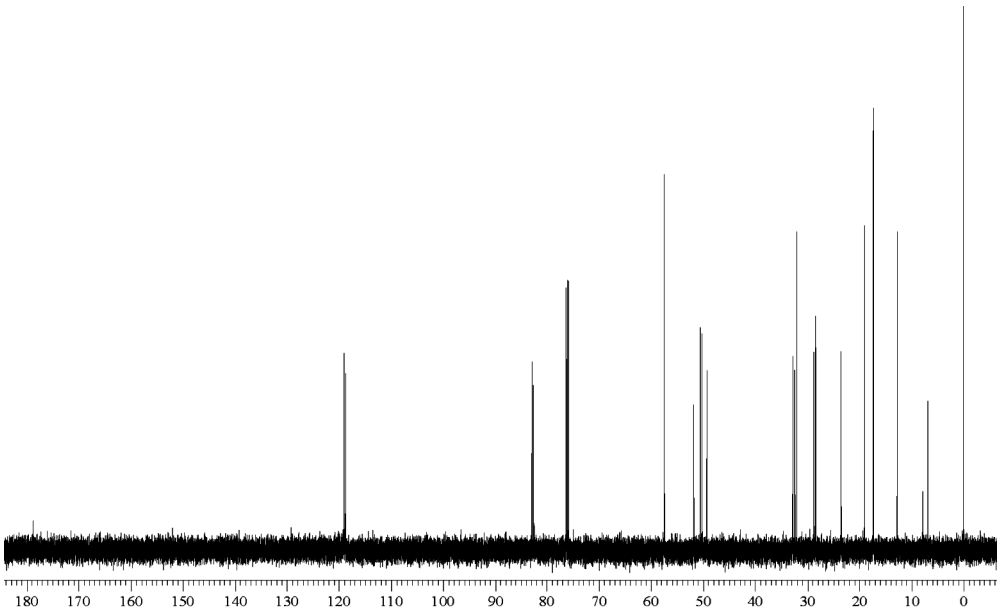

Figure S3: ^{13}C NMR ($CDCl_3$) of **2.**

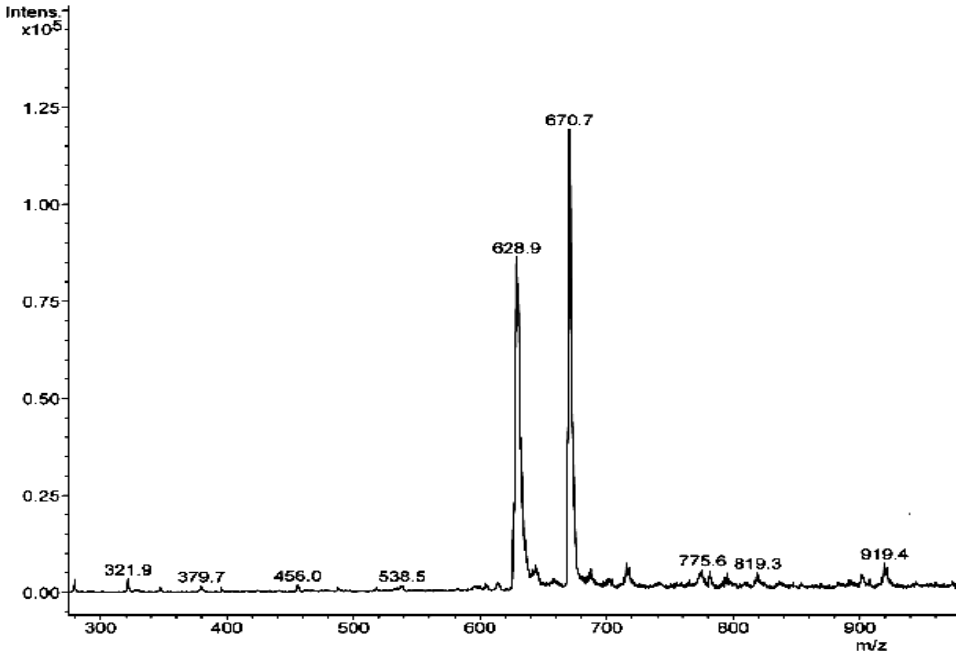

Figure S4: ESI-MS (-) (CH_3CN) of **2**.

Characterization of $(n\mathrm{Bu_4N})_4\{[\mathrm{IrCl}(\mathrm{C_8H_8})(\mathrm{C_{10}H_{17}N_2Si})]_2\mathrm{O}(\gamma\text{-}\mathrm{SiW_{10}O_{36}})\}$ (3)

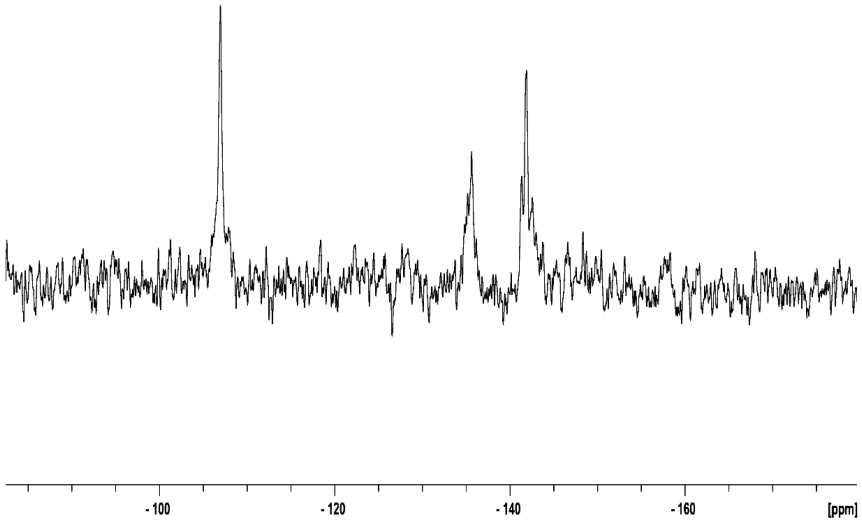

Figure S5: ^{183}W NMR (CH_3CN/CD_3CN) of **3**.

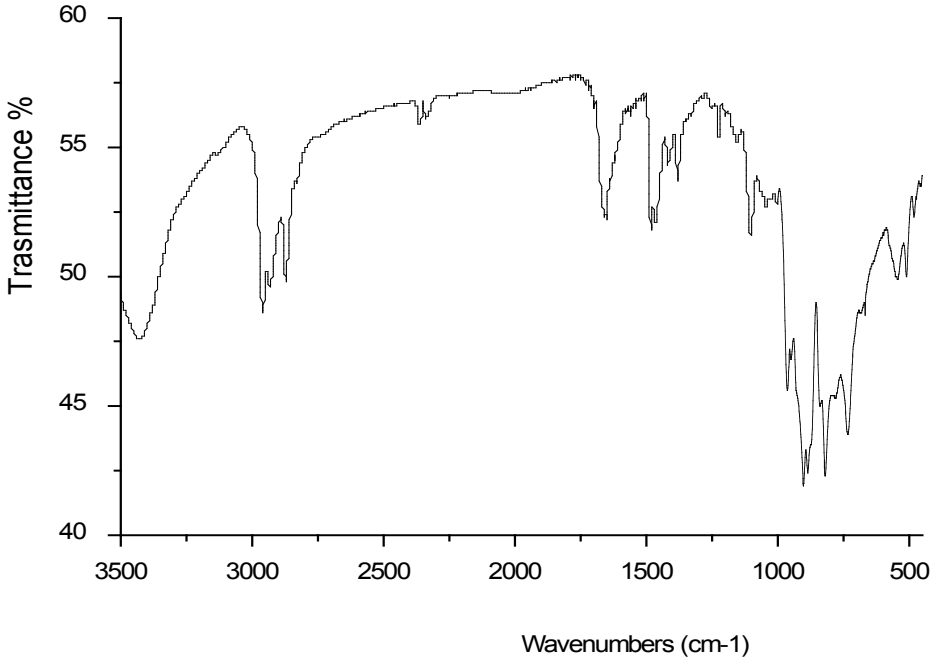

Figure S6: FT-IR (KBr) of **3**.

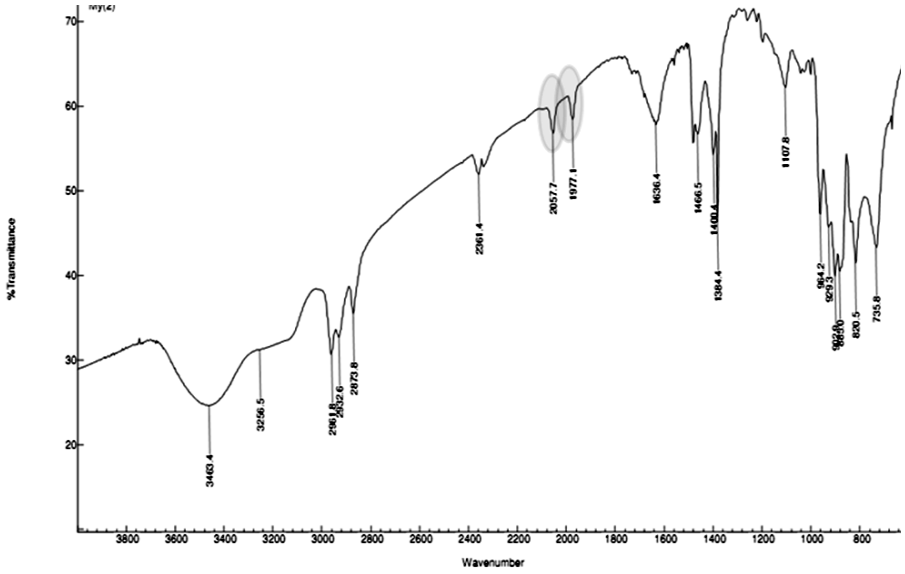

Figure S7: FT-IR (KBr) of **3** after reaction with CO.

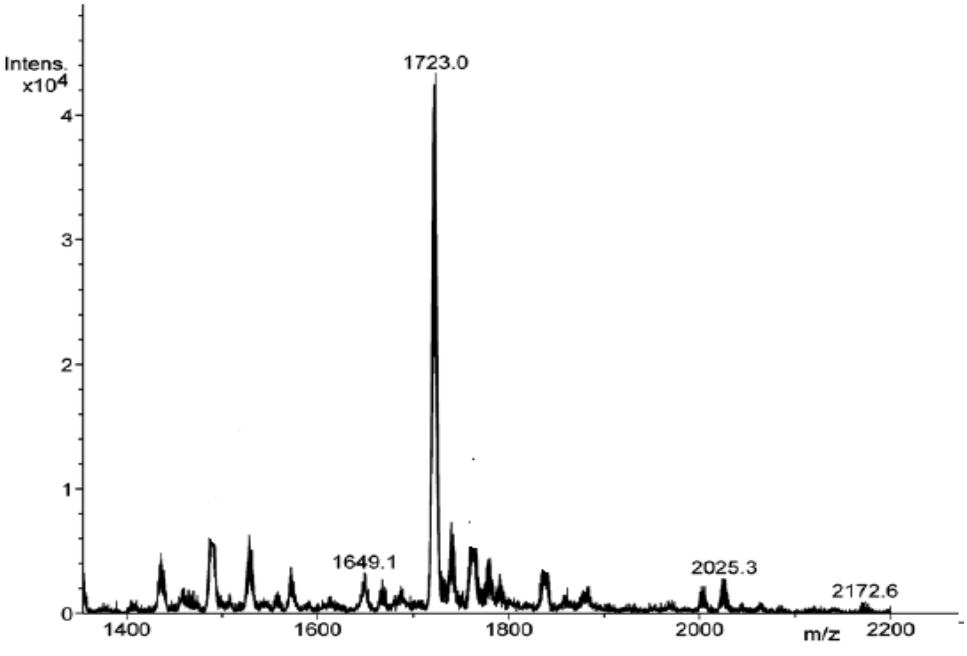

Figure S8: ESI-MS (-) (CH_3CN) of **3**.

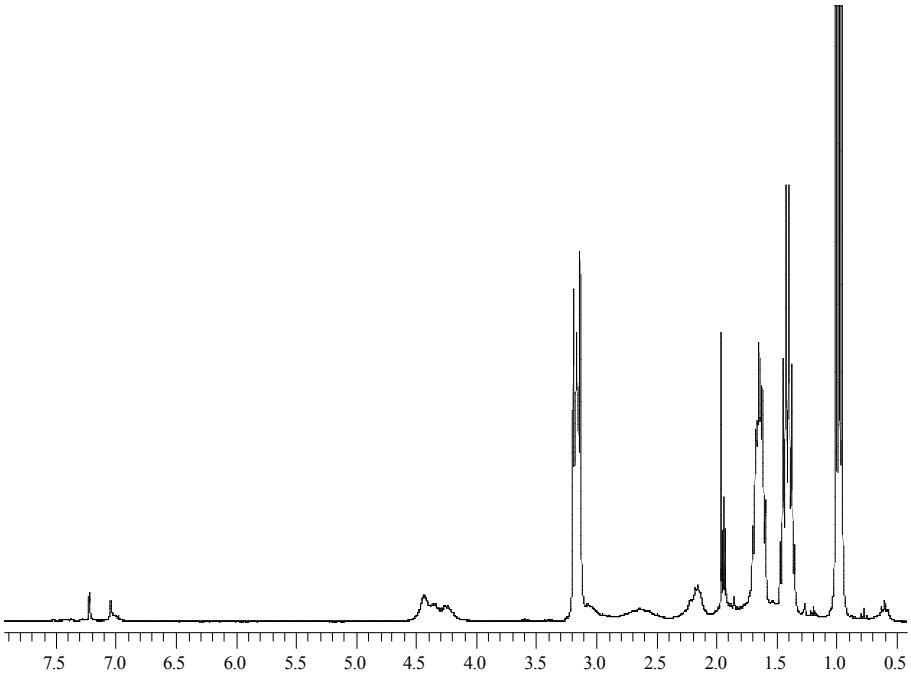

Figure S9: ^{1}H NMR (CD_3CN) of **3**.

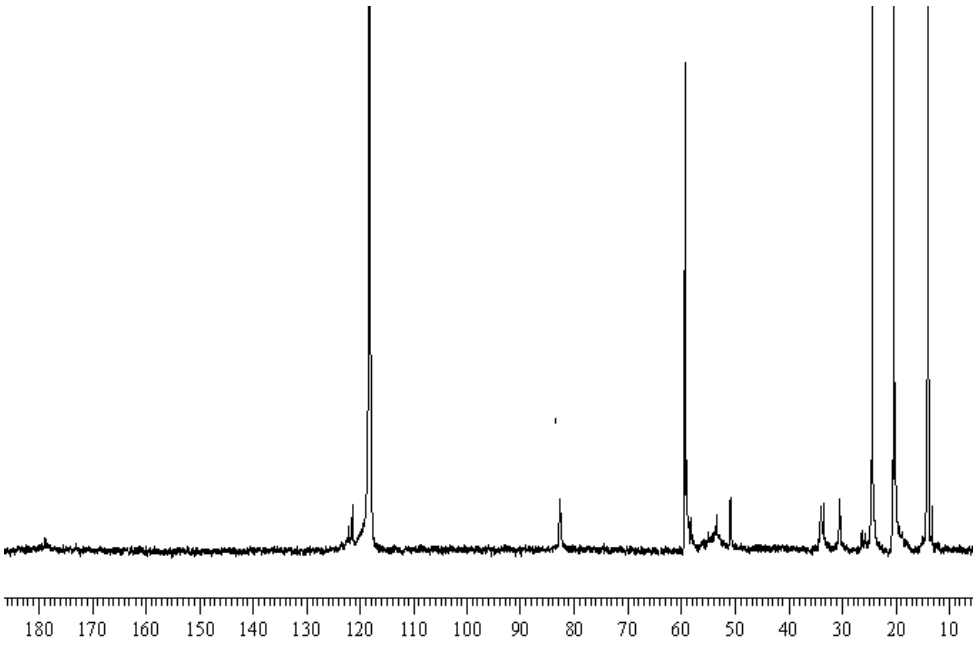

Figure S10: ^{13}C NMR (CD_3CN) of **3**.

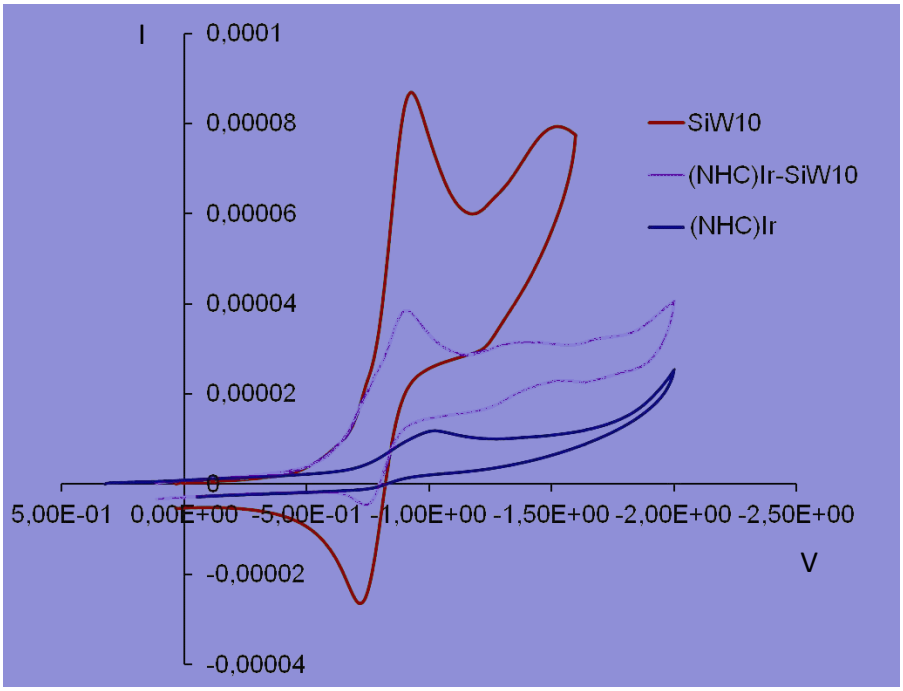

Figure S11: Cyclic voltammetries (cathodic scans): 0.5 mM of complexes **3**, **4**, **5** in CH_3CN (nBu_4ClO_4; 0.1M); 200 mV/sec.