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COMMUNICATION

A synthon for a 14-electron Ir(III) species: catalyst for highly selective β-(*Z*) hydrosilylation of terminal alkynes†

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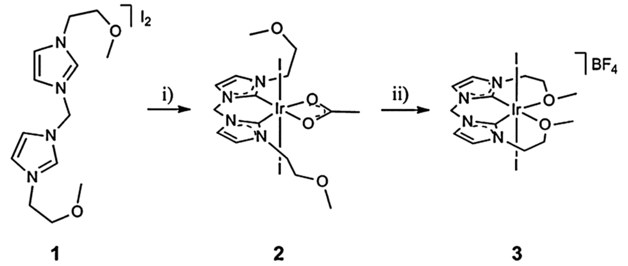
A synthon for a 14-electron Ir(III) species is described. The geometrical control exerted by the ligand system over the Ir–alkenyl intermediate in hydrosilylation of terminal alkynes precludes formation of the more thermodynamically stable β-(*E*)-vinylsilane, thus affording the β-(*Z*) isomer in excellent yields.

Bis-*N*-heterocyclic carbenes (bis-NHCs) are a fascinating class of ligands. The high σ-donor ability of NHCs and the strength of the resulting C–M bond, together with the inherent stability arising from the chelating nature of such ligands, render extremely robust electron rich transition metal species. In particular, [M(bis-NHC)(OAc)I_2] complexes (M = Rh^1 and Ir^2) have been demonstrated to be efficient air stable catalysts for transfer hydrogenation.

Transition-metal complexes containing latent coordination sites[3] have attracted much attention due to their central role as transient intermediates in many homogeneous catalytic processes.[4] Coordinating interactions with the solvent or fragments of the ligand system[5] generally stabilise coordinatively unsaturated complexes in solution. Hence, fine tuning of steric and electronic parameters of ligands with hemilabile character in order to achieve a truly reversible coordination—*i.e.* relatively small energy differences between open and closed conformations—is a matter of great interest.[6]

Hoping to shed some light on the effect of heterotopic ligands of hemilabile character on the generation of latent coordination sites, we envisaged a 14-electron bis-NHC iridium(III) fragment stabilised by two hemilabile side arms (Scheme 1), which would allow ready accessible coordination sites and concomitant protection of the active catalyst. Herein, we wish to report the synthetic route to such species and its remarkable β-(*Z*)-selectivity in catalysed hydrosilylation of terminal alkynes under mild conditions.



Scheme 1 Synthetic route for the preparation of complex **3**. Reaction conditions: (i) NaI, KOAc, [Ir(cod)Cl]$_2$ in acetonitrile, 2 days at 80 °C; (ii) $HBF_4 \cdot Et_2O$, in CH_2Cl_2 at 0 °C.

The aforementioned 14-electron metal fragment [Ir(bis-NHC)I_2]$^+$ was generated upon treatment of [Ir(L-*C*,*C*)(AcO)I_2] (L = methylenebis[(*N*-2-methoxyethyl)imidazole-2-ylidene], AcO = acetate) (**2**) with one equivalent of $HBF_4 \cdot Et_2O$ in dry dichloromethane at 0 °C. Stabilisation by coordination of the oxygen atoms in the wingtip groups to the metal centre permits isolation of [Ir(L-*C*,*C*,*O*,*O*)I_2]BF_4 (**3**), as a crystalline orange solid in 74% yield (Scheme 1 and ESI†).

Successful removal of the acetato ligand in **2** was indicated by loss of the peak corresponding to the methyl group of the acetate in ^{1}H and ^{13}C{^{1}H} NMR spectra at δ 1.85 and 25.9 ppm, respectively. Moreover, the A_2X_2 spin system ($^3J_{HH}$ = 4.8 Hz) corresponding to the protons of the methylene groups which appear at δ 3.75 (OCH_2) and 4.57 (NCH_2) ppm in **2** becomes an AA′XX′ spin system with resonances centred at δ 4.51 (OCH_2) and 4.74 (NCH_2) ppm in **3**. The singlet of the methoxy group undergoes a downfield shift similar to that observed for the OCH_2 groups upon coordination of the ethers (from δ 3.31 in **2** to 4.18 ppm in **3**).

Complex **3** was isolated by slow diffusion of diethyl ether into a saturated acetone solution. Its global connectivity pattern was confirmed by single crystal X-ray diffraction.[7] The molecular structure of cation **3** (Fig. 1) shows the expected octahedral geometry for the central Ir(III) metal ion. The two iodido ligands are located at the axial positions (Ir1–I1, 2.6750(3) Å; Ir1–I2, 2.6614(3) Å; I2–Ir1–I1, 179.396(18)°), while the equatorial sites are occupied by the "tetradentate" bis-NHC ligand. Both *cis*-positioned NHC-rings (Ir1–C12, 1.955(4) Å; Ir1–C22, 1.946(5) Å) extend their side arms toward the other two available positions, resulting in long distances between Ir1 and the oxygen atoms (Ir1–O43, 2.200(3) Å; Ir1–O53, 2.204(3) Å). Dihedral angles between both NHC-rings and the equatorial coordination plane of Ir1 are 16.2(2)° and

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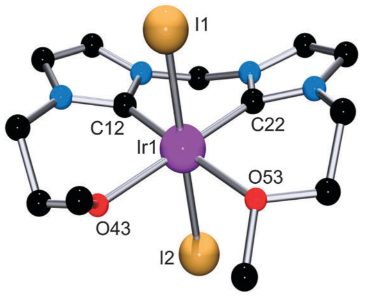


Fig. 1 View of **3** with two apical iodide ligands and a "tetradentate" bis-NHC ligand. Hydrogen atoms and BF_4^- counterion are omitted for clarity.

16.9(2)°. We are aware of only three additional examples in which a transition metal binds simultaneously an NHC-ring and its ether side arm.[8]

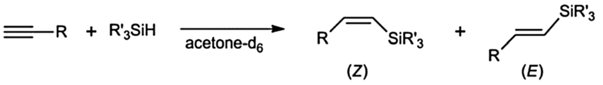
Complex **3** was tested in the hydrosilylation of terminal alkynes in order to explore the influence of the postulated latent coordination sites and the hypothetic generation of a cavity, formed by dissociation of the oxygen atoms, which would preclude formation of β-(*E*) isomers due to steric interactions with the ligands. The major issue concerning this reaction is that arising from its selectivity, which very much depends on the nature of the catalyst and the reaction conditions—the selective formation of one of the reaction products not being easily achievable in most cases. Among the three possible isomers obtainable from hydrosilylation of terminal alkynes, the β-(*E*) is the most thermodynamically stable and usually the major reaction product. Regarded as much more challenging targets, β-(*Z*)-vinylsilanes are highly valuable building blocks in organic synthesis, *e.g.* synthesis of natural products such as *cis*-retinoids *via* Hiyama cross-coupling.[9] However, examples of their selective metal-catalysed synthesis are scarce.[10]

Using **3** as catalyst, a range of terminal alkynes were converted in excellent yields and selectivities to their corresponding β-(*Z*)-vinylsilanes with Ph_2MeSiH, $PhMe_2SiH$ or Et_3SiH (1.1 equivalents) at 50 °C (Table 1). The corresponding alkyne was, in all cases, completely consumed within 5 h and no traces of catalyst decomposition were observed. The remarkably high activities and selectivities toward the β-(*Z*)-vinylsilanes presented in Table 1 are among the best hitherto reported for iridium catalysts.[10f] The steric hindrance of the silane seems to play a significant role in the selectivity of the reaction, the best selectivities being those obtained with Ph_2MeSiH (Table 1). Regarding the alkyne, no major effects on the selectivity of the reaction arise from electronic effects of *para* substitution in phenylacetylenes. Moreover, the β-(*Z*) selectivity was maintained for aliphatic alkynes, namely 1-hexyne (entry 16). Additionally, it is worth noting that the hydrosilylation reaction can be carried out on a preparative scale retaining high conversions and selectivities as demonstrated for the synthesis of (*Z*)-dimethyl(4-methylstyryl)(phenyl)silane.

Kinetic studies performed for representative alkynes (RC≡CH) with Ph_2MeSiH revealed conversions above 70% after 1.5 h, and $TOF_{1/2}$ (h^{-1}) values of 3333 (R = 4-CF_3-Ph), 1500 (R = 4-MeO-Ph) and 1250 (R = Ph).

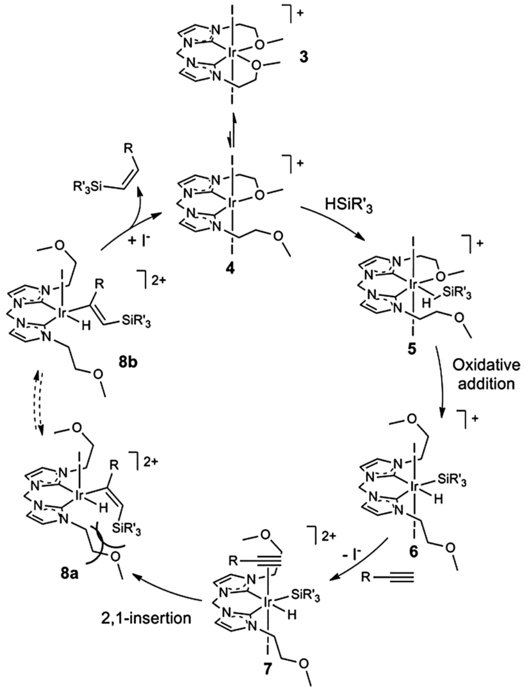
Under catalytic conditions ^{1}H-NMR spectroscopy shows that the percentage of **3**, the only metal species present in solution, remains constant throughout the reaction. This observation suggests an equilibrium between **3** and **4** (Scheme 2) caused by random dissociation of the oxygen atoms as the only conceivable option to generate an active catalyst which, at the end of the catalytic cycle, would convert back to **3**. This premise, in addition to the fact that no reaction between **3** and RC≡CH was observed, strongly points toward initial formation of Ir(σ-Si–H) complex[11] **5** followed by oxidative addition to give Ir(V)[10e,12] intermediate **6** as the first step of the catalytic cycle (Scheme 2). Therefore, in the overall process complex **3** could be regarded as a

Table 1 Hydrosilylation of terminal alkynes



Entry	Alkyne (R)	Silane	(*Z*)/(*E*)^a	Yield^a (%)
1	Ph	Ph_2MeSiH	91/9	94
2	Ph	$PhMe_2SiH$	90/10	95
3	Ph	Et_3SiH	92/8	93
4	4-^{t}Bu-Ph	Ph_2MeSiH	91/9	92
5	4-^{t}Bu-Ph	$PhMe_2SiH$	94/6	96
6	4-^{t}Bu-Ph	Et_3SiH	91/9	91
7	4-MeO-Ph	Ph_2MeSiH	100/0	94
8	4-MeO-Ph	$PhMe_2SiH$	92/8	91
9	4-MeO-Ph	Et_3SiH	95/5	98
10	4-CF_3-Ph	Ph_2MeSiH	100/0	98
11	4-CF_3-Ph	$PhMe_2SiH$	89/11	97
12	4-CF_3-Ph	Et_3SiH	95/5	98
13	4-Me-Ph	Ph_2MeSiH	98/2	94
14	4-Me-Ph	$PhMe_2SiH$	95/5	96
15	4-Me-Ph	Et_3SiH	92/8	99
16	*n*-Bu	Ph_2MeSiH	87/13	86
17	*n*-Bu	$PhMe_2SiH$	73/27	82
18	*n*-Bu	Et_3SiH	85/15	86

General conditions: alkyne (0.15 mmol), silane (0.16 mmol), **3** (5 mol%) in 0.5 mL of dry acetone-d_6 at 50 °C for 5 h.^{a} Yields and selectivities were calculated by ^{1}H NMR.



Scheme 2 Proposed catalytic cycle for the hydrosilylation of terminal alkynes.

synthon for the 14-electron fragment $[Ir(L\text{-}C,C)I_2]^+$ due to reversible coordination of the wingtip groups.[13]

We have observed that, in the ^1H DOSY spectrum,[14] the peak of residual acetone shows a higher diffusion coefficient for a sample of acetone-d_6 ($D^c = 4.323 \times 10^{-9}$ m^2 s^{-1}) than for a solution of **3** in acetone-d_6 (0.03 mmol in 0.5 mL of acetone-d_6; $D^c = 3.875 \times 10^{-9}$ m^2 s^{-1}). This behaviour can be ascribed to an interaction between **3** and the acetone molecules that results in a reduction of their mobility, which could be interpreted as a consequence of a certain degree of dissociation of the ether functions, an essential requisite to generate the coordination vacancies needed for the catalytic reaction to happen.

The second step of the catalytic cycle requires coordination of the alkyne to give **7**. For this to occur, we postulate substitution of an iodide by the corresponding alkyne, which we expect to be the rate limiting step. This assumption is supported by the fact that a significant reduction of reaction rate was observed upon addition of excess NaI to the reaction mixture. The $TOF_{1/2}$ (h^{-1}) decreases from 1250 to 706 in the case of the hydrosilylation of phenylacetylene with Ph_2MeSiH.

In order to explain the β-(*Z*) selectivity, a 2,1-insertion of the alkyne into the Ir–Si bond according to the modified Chalk–Harrod mechanism[15] must take place. Therefore, invoking a metal-assisted isomerisation,[10d,16] the cavity about the two coordination vacancies stabilises **8b** against **8a** through geometrical control exerted by the ligand system over the Ir–alkenyl intermediate (Scheme 2). This assumption is supported by the fact that the relative free energies of the postulated intermediates **8a** and **8b**, calculated by DFT (B3LYP) methods based on the model $[Ir(L\text{-}C,C)(CPh{=}CHSiMe_3)(I)(H)]BF_4$, show that the latter is more stable ($\Delta G = 4.9$ kcal mol^{-1}).[17] Finally, the last step of the proposed Ir(III)/Ir(V) catalytic cycle would be the reductive elimination of the β-(*Z*)-vinylsilane from **8b** and coordination of the iodido ligand. In this context, it seems to be interesting to mention that there is increasing support for the existence of Ir(III)/Ir(V) cycles in iridium catalytic chemistry.[18]

The proposed catalytic cycle rests on the following experimental observations and DFT calculations: (i) presence of **3** throughout the reaction and hints of an equilibrium between **3** and **4**, (ii) reduction of the reaction rate upon addition of NaI, and (iii) the unusual selectivity of the reaction, only explainable by a 2,1-insertion of the alkyne into the M–Si bond followed by reductive elimination of the vinylsilane from **8b**, which lies 4.9 kcal mol^{-1} below **8a**.

In summary, we have developed a straightforward synthetic route to a cationic bis-NHC iridium(III) complex (**3**) with two latent coordination sites accessible under catalytic conditions. As a first application, we have shown that the cavity created by dissociation of the side arms leads to unusually high β-(*Z*) selectivities in hydrosilylation of terminal alkynes under mild conditions. Remarkably, the X-ray structure of **3** represents the first example of a heterotopic Ir(NHC) complex featuring coordinated ether functions. Steric and electronic tuning of the ether functions in order to optimise the catalytic activity and a deeper mechanism insight are currently on-going.

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