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Iridium(III) complexes of the new tridentate bis(8-quinolyl)silyl ('NSiN') ligand†

Mark Stradiotto, Kyle L. Fujdala and T. Don Tilley*

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720-1460, USA.
E-mail: tdtilley@socrates.berkeley.edu

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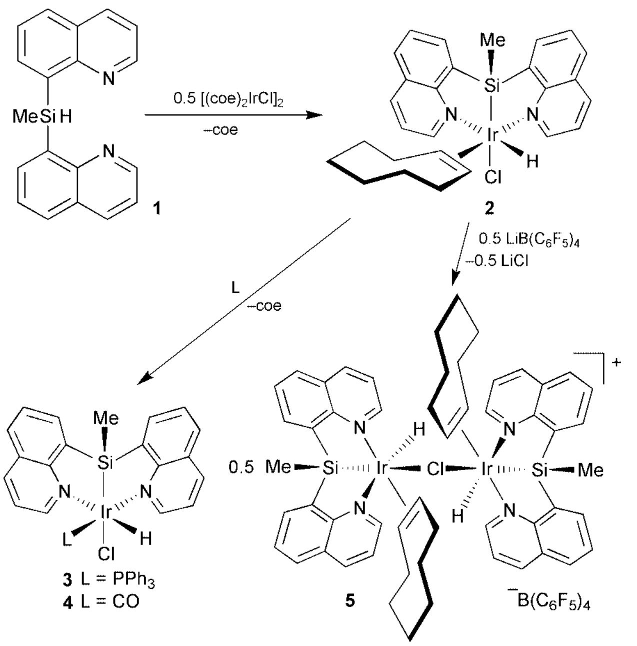
Bis(8-quinolyl)methylsilane reacts cleanly with $[Ir(coe)_2Cl]_2$ (coe = cyclooctene) to give a complex containing an NSiN tridentate ligand, [Ir(NSiN)(coe)(H)(Cl)]; preliminary reactivity studies indicate that the (NSiN)Ir fragment is chemically robust.

Multidentate ligands have featured prominently in the recent development of new transition metal chemistry. Such ligands provide stability to a metal complex, and offer diverse possibilities for the manipulation of steric and electronic properties in controlling reactivity at the metal center. Notwithstanding the significant advances in transition metal–silicon chemistry over the past several years,[1,2] multidentate ligands containing silicon as part of the chelate architecture have received little attention. The incorporation of silicon into such structures may offer certain advantages, given (for example) the high strength of metal–silicon bonds and the strong *trans*-effect for silicon ligands.[1,3] Stobart and coworkers[4] have synthesized a number of metal complexes supported by a PSiP ligand framework; tridentate connectivity is attained in these systems *via* oxidative addition of an Si–H functionality. This general strategy should provide synthetic routes to various silicon-containing multidentate ligands.

With the goal of developing reactive metal fragments supported by new tridentate ancillary ligands, we identified nitrogen-based NSiN chelates as potential synthetic targets. A tridentate system based on the bis(8-quinolyl)silyl framework appeared particularly attractive, since the resulting five-membered metallacyclic rings are expected to stabilize a complex towards reductive elimination of the silyl unit, while providing a rather rigid ligand binding arrangement. Support for the viability of such a ligation strategy comes from the work of Watts and coworkers,[5] who have prepared Rh(III) and Ir(III) complexes of the bidentate (8-quinolyl)dimethylsilyl ligand. In this contribution, synthesis of the tridentate ligand precursor bis(8-quinolyl)methylsilane **1** and Ir(III) complexes supported by this NSiN fragment are reported.

Addition of 0.5 equivalents of methyldichlorosilane to 8-lithioquinoline in THF, followed by purification, provided **1** as pale yellow crystals in moderate yield.†‡ The characterization of **1** is based on IR and NMR spectroscopic data. Notably, the C_S symmetry of this compound results in observation of only one set of quinoline ^1H and ^{13}C NMR resonances.

Treatment of **1** with 0.5 equivalents of $[Ir(coe)_2Cl]_2$ in CH_2Cl_2 resulted in rapid liberation of cyclooctene (coe) and near quantitative formation (by NMR spectroscopy) of the new coordination complex **2** as a *single* diastereomer (Scheme 1). Vapor diffusion of diethyl ether into the reaction mixture permitted isolation of **2** as analytically pure, yellow crystals in 87% yield. As expected, two sets of NMR resonances are observed for the quinoline groups of compound **2**. Evidence for the presence of the hydride ligand in **2** was obtained from IR (2172 cm^{-1}) and ^1H NMR (−15.6 ppm) spectroscopic data.



Scheme 1

The crystallographically determined structure of compound **2** is shown in Fig. 1.†‡ The non-equivalence of the quinoline groups noted in the ^1H and ^{13}C NMR spectra is consistent with the observed facial binding mode of the NSiN fragment. Constraints imposed by this ligand give rise to an Ir(III) center which is distorted considerably from ideal octahedral geometry. The chelate ligand 'bite' angles [N–Ir–N 87.5(3), N–Ir–Si 83.2(3) and 83.2(2)°] are all significantly compressed, underscoring the 'pinned-back' nature of the NSiN chelating framework. Geometric distortions are also observed at the silicon center. For example, the C(Me)–Si–Ir angle [131.2(4)°] is expanded well beyond the normal tetrahedral value. The Ir–Si distance [2.275(3) Å] in **2** can be compared to those in *fac*-tris[(8-quinolyl)dimethylsilyl]iridium (av. 2.30 Å),[5] and falls within the previously observed range (2.235–2.454 Å) for such

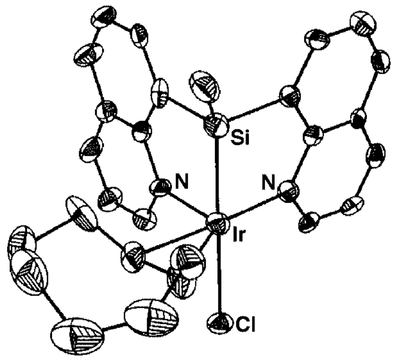


Fig. 1 Crystallographically determined structure of **2**, depicted with 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity.

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† Electronic supplementary information (ESI) available: synthetic and crystallographic details for **1**–**5**. See http://www.rsc.org/suppdata/cc/b1/b102821a/

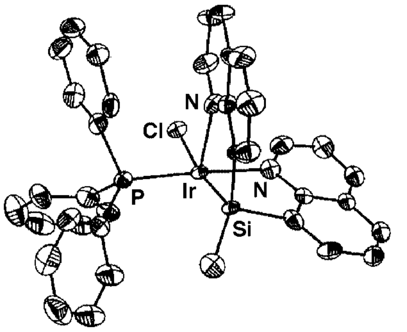

Fig. 2 Crystallographically determined structure of **3**, depicted with 50% thermal ellipsoids; all hydrogen atoms have been omitted for clarity.

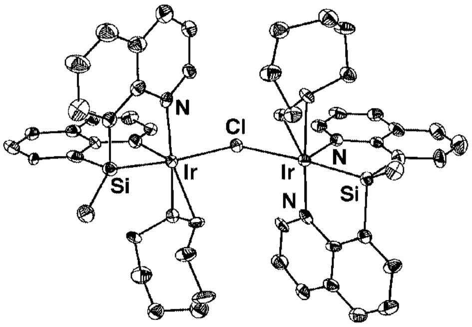

Fig. 3 Crystallographically determined structure of **5**, depicted with 50% thermal ellipsoids; the anion, solvates and all hydrogen atoms have been omitted for clarity. Only one component of the disordered coe fragment is shown.

bonds.[2] In contrast, the *trans*-labilizing nature[1–3] of the silyl group is manifested in a long Ir–Cl bond [2.572(3) Å].[6] The *trans*-influence of the hydride ligand is also indicated by elongation of an Ir–N bond [2.191(9) Å], relative to the other Ir–N bond [2.120(8) Å] in this complex.[7]

Preliminary reactivity studies reveal that the NSiN moiety is a robust ancillary ligand. Treatment of **2** with either PPh_3 or CO resulted in substitution of the coe ligand, yielding compounds **3** and **4**, respectively. Compound **3** gives rise to a singlet (17.0 ppm) in the $^{31}P\{^1H\}$ NMR spectrum and a phosphorus-coupled doublet (−19.1 ppm) in the hydride region of the ^1H NMR spectrum. The solid-state structure of compound **3** (Fig. 2) confirmed that the conversion of **2** to **3** occurs with retention of configuration at the Ir(III) center. In general, the geometric features associated with **3** parallel those described for **2** (*vide supra*). However, the Ir–P distance in **3** [2.234(3) Å] is noteworthy, since it appears to be contracted relative to Ir–P bonds found in related Ir(III) compounds (2.264–2.381 Å).[4,6,7] The coordination of a terminal carbonyl ligand to the Ir(III) center in **4** was confirmed by observation of a strong IR absorption attributed to this fragment (2010 cm^{-1}) and by the presence of a resonance at 169.9 ppm in the ^{13}C NMR spectrum. In contrast to the aforementioned transformations, no reaction was observed when a degassed CD_2Cl_2 solution of **2** was exposed to an atmosphere of H_2—even after prolonged heating (72 h at 90 °C). Collectively, these observations indicate that the Ir–Si linkage in **2** is relatively stable toward reductive elimination of Si–H.

In an attempt to prepare a cationic NSiN complex of iridium, CH_2Cl_2 was added to an equimolar mixture of **2** and $LiB(C_6F_5)_4·2.5Et_2O$. Surprisingly, the major product obtained from this reaction was not that resulting from simple anion exchange, but rather the dinuclear complex **5**, which formally results from *in situ* trapping of the anticipated cationic species by an additional molecule of **2**. Complex **5** is formed exclusively as the racemic (C_2-symmetric) diastereomer, as confirmed by X-ray crystallography (Fig. 3).†‡ The overall connectivity pattern in **5** mirrors that found in **2**, with the exception that both of the Ir–Cl distances in the former [2.638(2) and 2.645(2) Å] are significantly longer than the Ir–Cl distance in the latter. Subsequently, compound **5** was prepared in 93% yield *via* treatment of **2** with 0.5 equiv. of the lithium borate. However, slow addition of **2** to an equiv. of $LiB(C_6F_5)_4·2.5Et_2O$ under more dilute conditions led to clean formation (by NMR spectroscopy) of a new product, which we assume to be the desired mononuclear complex. Attempts are currently underway to isolate this species in pure form.

In conclusion, Ir(III) complexes containing the new bis(8-quinolyl)methylsilyl ligand have been prepared as single diastereomers in excellent yield. The diastereoselectivity associated with the clean formation of **2** and its derivatives indicates that the NSiN chelating ligand may have a directing effect on transformations at the Ir(III) center.[4] The synthesis and reactivity of various metal complexes supported by NSiN hybrid ligands will be the subject of future reports.

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‡ CCDC 164004–164006. See http://www.rsc.org/suppdata/cc/b1/b102821a/ for crystallographic data in CIF or other electronic format.

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