

Synthesis and Structure of *fac*-Tris[(8-quinolyl)dimethylsilyl]rhodium(III) and -iridium(III)

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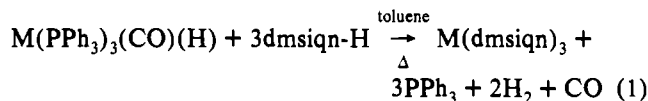
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Although the synthesis and study of metal–silicon-bonded species have been limited due to the lability of the metal–silicon bond, recent work has shown that the silyl group can be stabilized onto a metal center via chelation with a pendant alkylphosphine linkage.<sup>1–9</sup> The term “chelate-assisted hydrosilylation” has been coined to describe the synthesis of metal silyl complexes using this procedure. This method, applied here to reactions of Rh(I) and Ir(I) complexes with N,Si-chelating ligand precursors, has led to preparation of the first examples of tris-N,Si-ligated metal complexes.

(8-Quinolyl)dimethylsilane (dmsiqn-H)<sup>10</sup> was chosen as the N,Si-chelating ligand precursor because substitution in the 8-position of the quinoline ring allows for the formation of a thermodynamically stable five-membered chelate structure upon coordination to a metal center.<sup>12</sup> Furthermore, the fused aromatic quinoline ring system provides a low energy  $\pi$ -acceptor orbital, which, in conjunction with the strong  $\sigma$ -donating silyl group and an easily oxidized metal center, such as Ir(III), lends some assurance that the resulting complexes will display low-energy metal-to-ligand charge-transfer (MLCT) transitions. Prior work<sup>13–17</sup> with C,N-chelating 2-phenylpyridyl (ppy) complexes of Ir(III) indicates that the low-energy MLCT excited states in complexes such as *fac*-Ir(ppy)<sub>3</sub> result from the combination of the metal–carbon  $\sigma$  bonds with the ppy  $\pi$  system and that these Ir(ppy)<sub>3</sub> complexes are strong photoreductants when irradiated in their visible MLCT bands.

In a typical reaction, Ir(PPh<sub>3</sub>)<sub>3</sub>(CO)(H) (0.1 mmol) (Aldrich) is refluxed in toluene (12 mL) with a stoichiometric excess of dmsiqn-H (1.0 mmol) for 24 h. Removal of solvent and addition of hexanes (10 mL) results in the formation of orange crystals of *fac*-tris[(8-quinolyl)dimethylsilyl]iridium(III) [Ir(dmsiqn)<sub>3</sub>] in 60% yield. Similarly, if Rh(PPh<sub>3</sub>)<sub>3</sub>(CO)(H) is used as a starting material, yellow crystals of *fac*-tris[(8-quinolyl)dimethylsilyl]rhodium(III) [Rh(dmsiqn)<sub>3</sub>] are obtained in 50% yield (eq 1). The predominance of a tris-chelating complex obtained using dmsiqn-H can be contrasted with the favored bis-chelating

complex formed under similar conditions in a reaction of excess phosphinoalkylsilane with Ir(PPh<sub>3</sub>)<sub>3</sub>(CO)(H).<sup>3</sup>



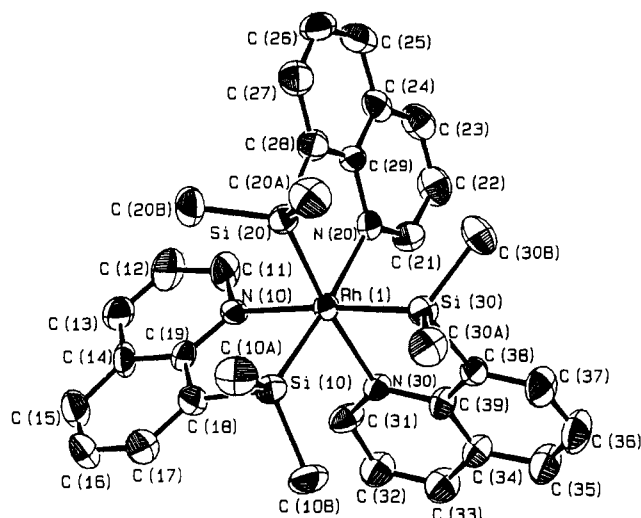
M = Ir, Rh

Both Ir(dmsiqn)<sub>3</sub> and Rh(dmsiqn)<sub>3</sub> are stable to air and moisture and can be heated to 150 °C without decomposition. The facial geometry is indicated by the simple <sup>1</sup>H NMR spectra, consisting of six aromatic and two methyl resonances, exhibited by the complexes.<sup>18</sup> The <sup>29</sup>Si NMR (59.63 MHz, DEPT) spectra show only one resonance occurring at  $\delta$  –10.14 for Ir(dmsiqn)<sub>3</sub> and  $\delta$  +23.60 for Rh(dmsiqn)<sub>3</sub> (<sup>1</sup>J<sub>Rh–Si</sub> = 41.7 Hz). Both complexes display absorption bands in the UV–visible region (350–450) which undergo hypsochromic shifts in polar solvents and have extinction coefficients ( $\sim 6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) consistent with MLCT transitions.

Crystals of Rh(dmsiqn)<sub>3</sub> and Ir(dmsiqn)<sub>3</sub>, grown from a THF solution by codiffusion of methanol, are isomorphous.<sup>19</sup> An ORTEP drawing of the structure of Rh(dmsiqn)<sub>3</sub> determined from a single-crystal X-ray diffraction study is shown in Figure 1. Extremely short metal–silicon bond lengths are found in both complexes (2.28–2.31 Å).<sup>20–24</sup> The strong trans influence exerted by the silyl group<sup>7</sup> leads to metal–nitrogen bond lengths that are longer than those found in metal 2-phenylpyridyl (ppy) chelates<sup>25</sup> (2.25 Å in Ir(dmsiqn)<sub>3</sub> vs 2.13 Å in *fac*-Ir(ppy)<sub>3</sub>). The 84° N–Me–Si “bite-angle” of the dmsiqn chelate is similar to the P–M–Si angles observed in phosphinoalkylsilyl metal complexes.<sup>1,5–7</sup> One set of

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- Data for Rh(dmsiqn)<sub>3</sub> are as follows. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  –0.68 (s, 9 H, CH<sub>3</sub>), 0.54 (s, 9 H, CH<sub>3</sub>), 7.01 (dd, 3 H, J = 8.1 and 4.7 Hz, H<sub>3</sub>), 7.56 (dd, 3 H, J = 7.9 and 6.7 Hz, H<sub>6</sub>), 7.72 (dd, 3 H, J = 8.0 and 1.4 Hz, H<sub>5</sub>), 7.78 (dd, 3 H, J = 4.7 and 1.6 Hz, H<sub>2</sub>), 7.94 (dd, 3 H, J = 6.6 and 1.4 Hz, H<sub>7</sub>), 8.14 (dd, 3 H, J = 8.2 and 1.6 Hz, H<sub>4</sub>). MS (FAB): *m/z* = 661 (M<sup>+</sup>). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) [ $\lambda_{\text{max}}$ , nm (M<sup>–1</sup> cm<sup>–1</sup>): 360 (7000)]. Data for Ir(dmsiqn)<sub>3</sub> are as follows. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  –0.75 (s, 9 H, CH<sub>3</sub>), 0.56 (s, 9 H, CH<sub>3</sub>), 6.97 (dd, 3 H, J = 8.1 and 4.9 Hz, H<sub>3</sub>), 7.55 (dd, 3 H, J = 7.9 and 6.7 Hz, H<sub>6</sub>), 7.71 (dd, 3 H, J = 8.0 and 1.2 Hz, H<sub>5</sub>), 7.86 (dd, 3 H, J = 4.8 and 1.5 Hz, H<sub>2</sub>), 7.96 (dd, 3 H, J = 6.5 and 1.2 Hz, H<sub>7</sub>), 8.20 (dd, 3 H, J = 8.2 and 1.5 Hz, H<sub>4</sub>). MS (FAB): *m/z* = 751 (M<sup>+</sup>). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>) [ $\lambda_{\text{max}}$ , nm (M<sup>–1</sup> cm<sup>–1</sup>): 372 (6700), 440 (sh) (3500)].
- Crystal data for Rh(dmsiqn)<sub>3</sub>: C<sub>33</sub>H<sub>36</sub>N<sub>3</sub>Si<sub>3</sub>Rh, monoclinic, Cc (No. 9), *a* = 12.1802 (5) Å, *b* = 14.8749 (6) Å, *c* = 18.5325 (7) Å,  $\beta$  = 108.287 (2)°, *V* = 3188.1 (2) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 1.38 g/cm<sup>3</sup>, *R*(*F*<sub>o</sub>) = 2.64%, *R*<sub>w</sub>(*F*<sub>o</sub>) = 3.48% on 3921 total reflections (3471 observed at *I* > 3 $\sigma$ (*I*)), *T* = 296 K. Crystal data for Ir(dmsiqn)<sub>3</sub>: C<sub>33</sub>H<sub>36</sub>N<sub>3</sub>Si<sub>3</sub>Ir, monoclinic, Cc (No. 9), *a* = 12.164 (1) Å, *b* = 14.876 (1) Å, *c* = 18.534 (2) Å,  $\beta$  = 108.604 (3)°, *V* = 3178.1 (3) Å<sup>3</sup>, *Z* = 4,  $\rho_{\text{calcd}}$  = 1.57 g/cm<sup>3</sup>, *R*(*F*<sub>o</sub>) = 5.7%, *R*<sub>w</sub>(*F*<sub>o</sub>) = 6.9% on 4211 total reflections (3479 observed at *I* > 3 $\sigma$ (*I*)), *T* = 296 K.
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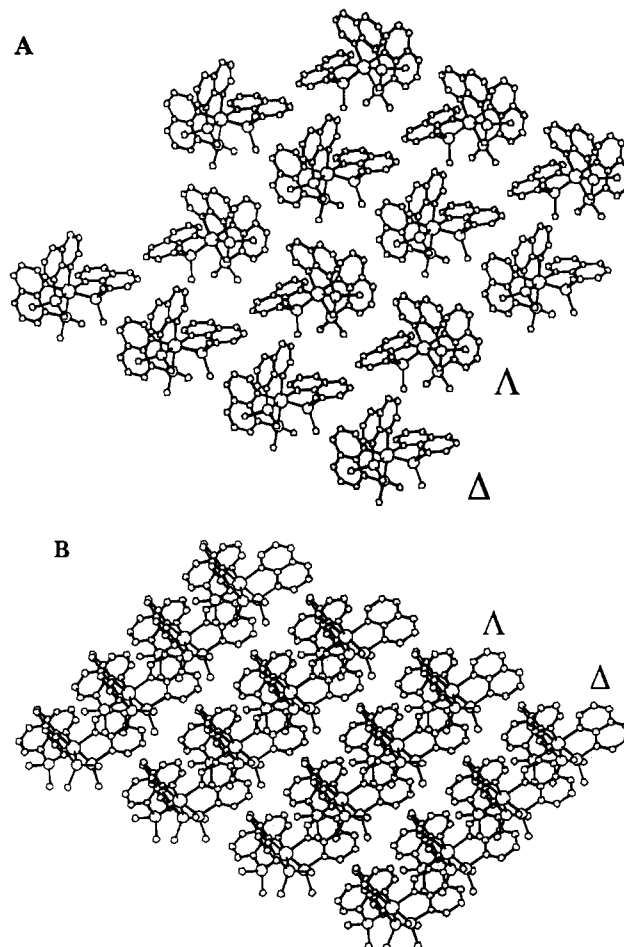


**Figure 1.** ORTEP diagram of  $\text{Rh}(\text{dmsiqn})_3$ . Selected bond distances (Å) and angles (deg):  $\text{Rh}-\text{Si}(10) = 2.278(1)$ ,  $\text{Rh}-\text{Si}(20) = 2.290(1)$ ,  $\text{Rh}-\text{Si}(30) = 2.301(1)$ ,  $\text{Rh}-\text{N}(10) = 2.252(3)$ ,  $\text{Rh}-\text{N}(20) = 2.259(3)$ ,  $\text{Rh}-\text{N}(30) = 2.256(3)$ ,  $\text{Si}-\text{C}_{\text{Me}}(\text{av}) = 1.898(5)$ ,  $\text{Si}-\text{C}_{\text{quin}}(\text{av}) = 1.917(4)$ ;  $\text{N}(10)-\text{Rh}-\text{Si}(10) = 84.20(9)$ ,  $\text{C}(18)-\text{Si}(10)-\text{Rh} = 99.6(1)$ ,  $\text{C}(19)-\text{N}(10)-\text{Rh} = 119.0(3)$ ,  $\text{C}(10\text{A})-\text{Si}(10)-\text{Rh} = 125.4(2)$ ,  $\text{C}(10\text{B})-\text{Si}(10)-\text{Rh} = 117.9(2)$ ,  $\text{C}-\text{Si}-\text{C}(\text{av}) = 103.8(2)$ . Selected bond distances (Å) for  $\text{Ir}(\text{dmsiqn})_3$ :  $\text{Ir}-\text{Si}(10) = 2.296(4)$ ,  $\text{Ir}-\text{Si}(20) = 2.301(4)$ ,  $\text{Ir}-\text{Si}(30) = 2.305(4)$ ,  $\text{Ir}-\text{N}(10) = 2.25(1)$ ,  $\text{Ir}-\text{N}(20) = 2.23(1)$ ,  $\text{Ir}-\text{N}(30) = 2.26(1)$ ,  $\text{Si}-\text{C}(\text{av}) = 1.90(2)$ . The bond angles in  $\text{Ir}(\text{dmsiqn})_3$  are similar to those in  $\text{Rh}(\text{dmsiqn})_3$ .

silylmethyl groups [C(10A), C(20A), C(30A)] points down in the direction of the molecular 3-fold axis, while the other set [C(10B), C(20B), C(30B)] points out from this axis allowing us to define and distinguish the two different sets of methyl groups as being either axial (ax) and equatorial (eq), respectively. The equatorial methyl groups lie over adjacent quinolyl rings which enable the hydrogens of these methyls to approach within 2.75 Å of the quinolyl nitrogen and result in the upfield shift observed for their  $^1\text{H}$  NMR resonances ( $\text{CH}_3^{\text{eq}} = \delta -0.75, -0.68$  vs  $\text{CH}_3^{\text{ax}} = \delta 0.56, 0.54$  for  $\text{Ir}(\text{dmsiqn})_3$  and  $\text{Rh}(\text{dmsiqn})_3$ , respectively).

An unusual feature of the complexes is the way in which the molecules pack into the crystal lattice. The two different enantiomers of the complex segregate into columns which are aligned in adjacent rows thereby creating alternating sheets of  $\Delta$  and  $\Lambda$  isomers (Figure 2A). These sheets are also arranged such that the 3-fold axes of the complexes orient parallel to each other so that the molecular dipoles point in the same direction (Figure 2B). The alignment of the molecules imparts the crystal with a net polarization which may lead to the observation of nonlinear optical behavior in the solid state.<sup>26</sup> This possibility is presently under investigation.<sup>27</sup>

*fac*-tris[(8-quinolyl)diorganosilyl]rhodium(III) and -iridium(III) derivatives with phenyl-substituted silyl groups as well as bis[(8-quinolyl)diorganosilyl]platinum(II) complexes have also



**Figure 2.** Chem-X<sup>28</sup> generated crystal packing diagrams for  $\text{M}(\text{dmsiqn})_3$  ( $\text{M} = \text{Rh}, \text{Ir}$ ): (A) View down the [110] plane showing segregation of enantiomers; (B) view down the  $b$ -axis showing alignment of the complexes in the direction of the molecular 3-fold axis.

been synthesized. The results on the preparation and UV-visible spectroscopy of these compounds will be reported in the near future.

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**Supplementary Material Available:** Tables listing details of the X-ray crystallographic structure determinations of  $\text{Ir}(\text{dmsiqn})_3$  and  $\text{Rh}(\text{dmsiqn})_3$ , atomic positions, bond distances and angles, and thermal parameters (24 pages). Ordering information is given on any current masthead page.

(26) Marder, S. R.; Sohn, J. E.; Stucky, G. N., Eds. *Materials for Nonlinear Optics*; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

(27) Preliminary results from powder second harmonic generation (SHG) studies with 1064-nm light show the efficiencies of  $\text{Rh}(\text{dmsiqn})_3$  and  $\text{Ir}(\text{dmsiqn})_3$  to be 1.5 and 2.5 times that of urea, respectively.

(28) Chem-X, developed and distributed by Chemical Design Ltd., Oxford, England.