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Preliminary communication

Novel monoanionic di-*N*,*N*′-centred chelating ligands and their C_1 and C_2 symmetrical zirconium complexes

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Abstract

The novel lithium complexes $[Li\{N(SiMe_3)C(Ph)C(R)(C_5H_4N\text{-}2)\}]_2$ (R = H or $SiMe_3$) and $Li\{N(SiMe_3)C(Ph)C(R)(C_9H_6N\text{-}2)\}$ (R = H or $SiMe_3$), prepared from PhCN and $[Li\{C(SiMe_3)(R)(C_5H_4N\text{-}2)\}]_2$ or $Li\{C(SiMe_3)(R)(C_9H_6N\text{-}2)\}$, react with $ZrCl_4$ to afford racemic complexes $[Zr\{N(SiMe_3)C(Ph)C(R)(C_5H_4N\text{-}2)\}_2Cl_2]$ (R = H or $SiMe_3$, **3b**) and $[Zr\{N(SiMe_3)C(Ph)C(R)(C_9H_6N\text{-}2)\}_2Cl_2]$, respectively. Conproportionation of $ZrCl_4$ and **3b** or **4b** afforded $[Zr\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}Cl_3]$ and $[Zr\{N(SiMe_3)C(Ph)C(SiMe_3)(C_9H_6N\text{-}2)\}Cl_3]$, respectively. The compounds are characterised by NMR spectroscopy and X-ray data are provided for **3b**.

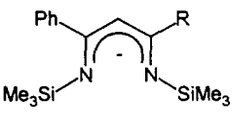
Keywords: Lithium; Zirconium; Chelating amide; Aza-allyl

1. Introduction

The search for good alternatives for cyclopentadienyl-type spectator ligands in Group 4 organometallic chemistry has led to the application of polydentate ligands like Schiff bases [1], benzamidinates [2], multidentate amides [3], macrocyclic nitrogen ligands [4], porphyrins and porphyrinogens [5], biphenoxide and binaphthoxide [6] ligands. Despite the numerous new ligands available, relatively few derived complexes have had catalytic activity. Recently we have shown that the new bidentate β-diketiminate ligands $[LL]^-$ **I** [7] and $[LL']^-$ **II** [8] have some η^5-character and are at least as bulky as the most highly substituted cyclopentadienyls, as exemplified by the existence of the mononuclear complexes $[\overline{Zr(LL')}Cl_3]$ [8], $[\overline{Yb(LL)}_2]$ [9] and $[\overline{L_n(LL)}_2Cl]$ [10]; some of the zirconium complexes were found to be olefin polymerisation catalysts [11]. Because of their different electronic and steric properties compared with cyclopentadienyls, β-diketiminate-type ligands might have considerable potential as spectator ligands especially in the area of catalysis. We now report on novel monoanionic bidentate 2-pyridyl- and 2-quinolyl-substituted 1-aza-allyl ligands, their lithium complexes **1** and **2**, and their racemic zirconium derivatives **3**, **4**, **8**, and **9**.

2. Results and discussion

The complexes $[Li\{N(SiMe_3)C(Ph)C(R)(C_5H_4N\text{-}2)\}]_2$ (R = H **1a** or $SiMe_3$ **1b**) or $Li\{N(SiMe_3)C(Ph)C(R)(C_9H_6N\text{-}2)\}$ (R = H **2a** or $SiMe_3$ **2b**), were prepared under mild conditions from PhCN and $[Li\{C(SiMe_3)(R)(C_5H_4N\text{-}2)\}]_2$ [12] (Scheme 1) or $Li\{C(SiMe_3)(R)(C_9H_6N\text{-}2)\}$ **5** (Scheme 2). The lithium derivatives **1** and **2** with $ZrCl_4$ under ambient conditions in Et_2O or THF gave the bis(ligand)zirconium dichloride complexes **3** and **4**. All of the eight compounds were



I $[LL]^-$ R = Ph
II $[LL']^-$ R = ^{t}Bu

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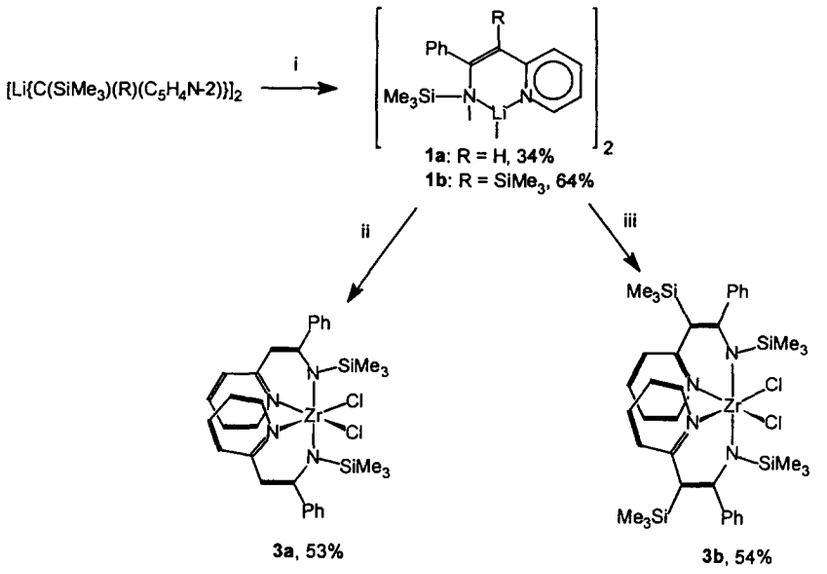
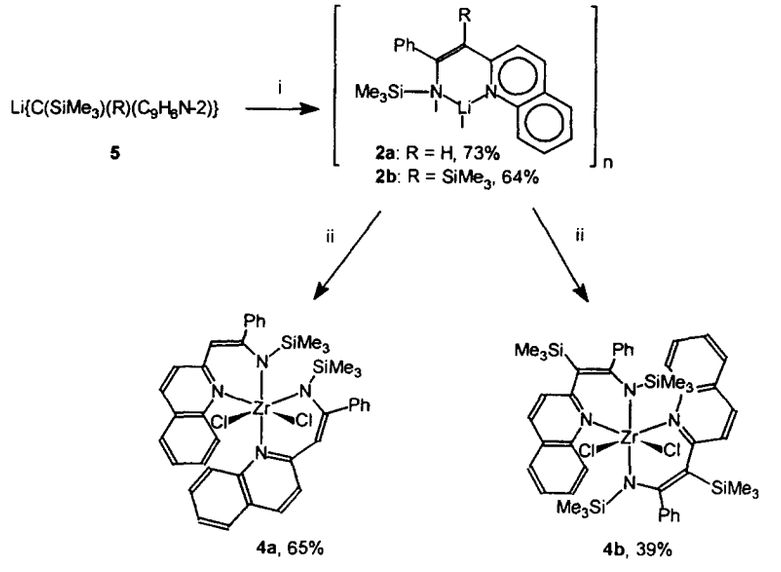


Scheme 1. Reagents and conditions (ca. 25°C, unless otherwise stated): (i) 2 PhCN, $Et_2O/n\text{-}C_6H_{14}$, 24 h; (ii) $ZrCl_4$, THF, 24 h, reflux 1.5 h; (iii) $ZrCl_4$, Et_2O, 24 h.

prepared in multigram quantities and gave satisfactory NMR (^1H, ^{13}C) [13] and MS data as well as good microanalytical results; X-ray data are available for two of the key compounds, **1b** and **3b**, but these are reported here only for **3b**. Compounds **3** and **4** were only sparingly soluble in alkanes or Et_2O but had good solubilities in THF, benzene, toluene or dichloromethane.

The lithiomethylquinoline compounds **5** were obtained from single and double silylation of 2-methylquinoline by $LiBu^n/SiMe_3Cl$ followed by metalation with $LiBu^n$. In the full paper we shall also report on inter alia (a) reactions analogous to (i) and (ii) (R = H) in Scheme 1, wherein $[Li\{HC(SiMe_3)(C_5H_4N\text{-}2)\}]_2$ was treated with Bu^tCN yielding $[Li\{N(SiMe_3)C(Bu^t)\text{-}C(H)(C_5H_4N\text{-}2)\}]_2$ **6**, which in turn with $ZrCl_4$ gave $[Zr\{N(SiMe_3)C(Bu^t)C(H)(C_5H_4N\text{-}2)\}_2Cl_2]$ **7**, and (b) the X-ray structure of **6**.

Based on NMR spectral data complexes **3** and **4b** are assigned as having either C_2 or C_S symmetry in solution to account for the equivalent NCCCN ligands. The higher substituted derivative **3b** showed two sets of



Scheme 2. Reagents and conditions (ca. 25°C): (i) PhCN, $Et_2O/n\text{-}C_6H_{14}$, 24 h; (ii) n/2 $ZrCl_4$, Et_2O, 24 h.

resonances for the *ortho* protons of the phenyl groups (δ 7.68 and 7.63, intensity ratio = 1 : 1) and 2 $CSiMe_3$ (δ 118.6 and 118.3) resonances. This is attributed to two different puckering modes of the highly substituted ZrNCCCN metallacycles (vide infra). In contrast to compounds **3** and **4b**, **4a** displayed two complete sets of ligand resonances (^1H and ^{13}C NMR) suggesting a lower symmetry of the complex [14]. It should be noted that no other isomers were observed in the NMR spectra of purified **3** and **4**.

To elucidate the molecular structure of complexes **3**, an X-ray crystal structure determination was carried out on **3b** [15]. In full agreement with the NMR spectral data the bonding geometry around zirconium is distorted octahedral with the zirconium centre situated on a crystallographic C_2 axis (Fig. 1). The best equatorial plane is defined by ZrN(1)N(1)$^{\#}$N(2)Cl (ΣZr = 358.4°) with Cl$^{\#}$ and N(2)$^{\#}$ in *trans*-apical positions. As in zirconocene chlorides, the chlorine atoms are *cis* which is a highly desirable situation from a catalytic point of view. Both the Zr–Cl (2.434(1) Å) distances and the Cl–Zr–Cl$^{\#}$ angle (95.06(7)°) are comparable with the corresponding values in four-coordinate zirconocene dichlorides (2.43–2.46 Å and 94–98°, respectively) [16]. The Cl–Zr–Cl$^{\#}$ plane is torsioned relative to the N2–Zr–N(2)$^{\#}$ plane by 16°. The bonding within the chelating NCCCN skeletons is highly localized with Zr–N(1) and C(2)–C(3) single and C(1)–C(2) double bonds. The pyridyl ring distances are regularly aromatic and Zr–N(2) is a dative σ-bond although the Zr atom is significantly displaced from the pyridyl plane (C(4)–C(3)–N(2)-Zr = −165.4(3)°). The Zr–N(1) distance (2.141(3) Å) is comparable with the Zr–N covalent bond in the amido complex $[Zr(\eta\text{-}C_5H_5)_2(Cl)\{N(H)SiMe_2Bu^t\}]$ (2.139(3) Å) [17] and close to the Zr–N values in $[\overline{Zr(LL')}Cl_3]$ (2.138(5) and 2.187(5) Å) [8]. The Zr–N(2) distance (2.354(3) Å) is slightly longer than the dative Zr–N interactions in Schiff base complexes $[Zr(CH_2\text{-}CMe_3)_2(F_6\text{-acen})_2]$ **III** (2.33(4) Å) [1a], $[ZrL_2Cl_2]$ **IV** (L = a norephedrine-derived ligand, 2.317(5) Å and 2.328(6) Å) [1c], and $[Zr(msal)_2Cl_2]$ **V** (2.317(5)–2.34(1) Å, msal = *N*-methylsalicylideneiminate) [1b]. This also indicates that N(2)–Zr π-d interactions are unimportant. The ZrNCCCN metallacycles are highly puckered most likely due to steric interactions between Ph and $SiMe_3$ substituents. In contrast to $[\overline{Zr(LL')}Cl_3]$ [8], there is no η^5-π-interaction with the bidentate nitrogen ligands in **3b**.

Complex **3b** is structurally similar to Schiff base complexes **IV** (Cl–Zr–Cl = 93.7(1)°) [1c], **V** (Cl–Zr–Cl = 96.9(1)°) and 98.8(1)°) [1b] and benzamidinate $[M\{N(SiMe_3)C(Ph)N(SiMe_3)\}_2Cl_2]$ (M = Ti, Zr; Cl–Ti–Cl = 98.6(1)°) [2c] in which the Cl atoms are also *cis*-positioned in distorted octahedral environments. On the basis of the close analogy in the NMR spectral data, we favour similar C_2 symmetrical distorted octahedral structures for **3a** and **4b**. The inequivalence of the nitrogen ligands in **4a** might be explained by an unsymmetrical (C_1) structure depicted in Scheme 2, although the reason for this deviation is not clear.

Mono(aza-allyl)zirconium trichloride complexes **8** and **9** were obtained by conproportionation of $ZrCl_4$

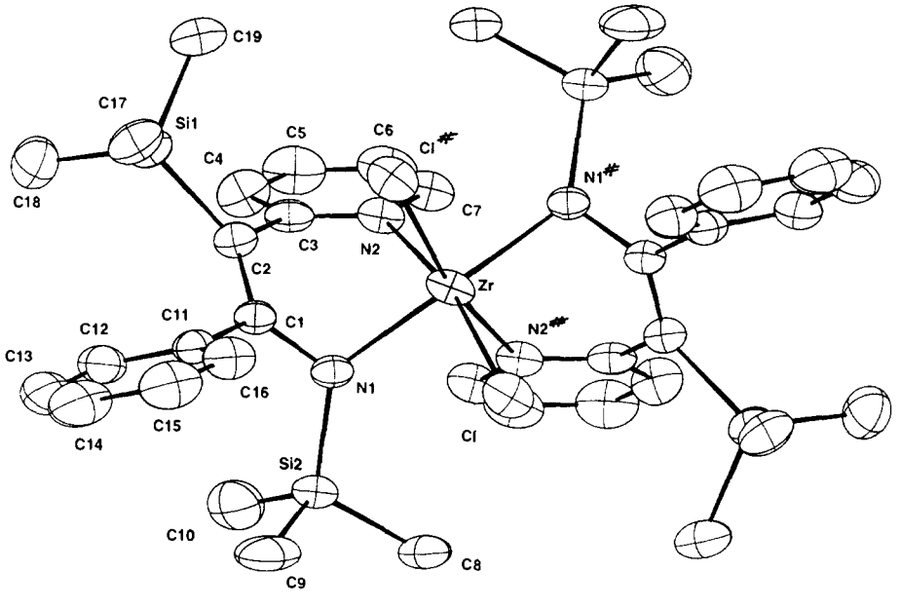
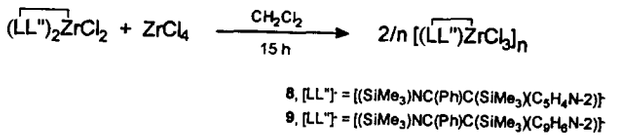


Fig. 1. The X-ray structure and atom labelling scheme for $[Zr\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2Cl_2]$ **3b**. Selected bond lengths (Å) and angles (°): Zr–N(1) 2.141(3), Zr–N(2) 2.354(3), Zr–Cl 2.434(1), N(1)–C(1) 1.397(5), N(2)–C(3) 1.338(5), N(2)–C(7) 1.348(5), C(1)–C(2) 1.369(6), C(2)–C(3) 1.475(6), N(1)–Zr-N(1)$^{\#}$ 165.0(2), N(2)–Zr–Cl 165.84(8), Cl–Zr–Cl$^{\#}$ 95.06 (7).



and **3b** or **4b**, respectively, in either dichloromethane or toluene (Eqn. (1)). Both compounds gave satisfactory ^{1}H NMR [18] and MS data. Compound **9** shows two sets of ligand resonances in the ^{1}H NMR spectrum suggesting that it is probably a dimer in solution.

All new zirconium compounds described above were tested on their activity in ethylene polymerisation with methylaluminoxane (MAO) as co-catalyst. However, neither of the complexes (**3** or **4**) had activity in ethylene polymerisation. In contrast, both **8** and **9** show moderate activity. We are currently further investigating this topic.

Acknowledgement

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[13] **1a**. ^{1}H NMR (360 MHz, C_6D_6): δ 8.05 (m, 1H, py), 7.90 (d, J = 7.4 Hz, 2H, Ph), 7.29 (t, J = 7.4 Hz, 2H, Ph), 7.20 (d, J = 7.2 Hz, 1H, py), 6.99 (t, J = 7.8 Hz, 1H, Ph), 6.73 (d, J = 7.9 Hz, 1H, py), 6.41 (ps t, 1H, py), 6.24 (s, 1H, CH), −0.02 (s, 9H, $SiMe_3$). ^{13}C NMR (62.9 MHz, C_6D_6/C_6H_6): δ 165.3 (*N*CPh), 160.5, 148.5, 147.2, 137.3, 129.2, 128.2, 127.9, 124.1 and 117.6 (aryl C), 107.1 (CH), 2.5 ($SiMe_3$).
1b. ^{1}H NMR (250 MHz, C_4D_8O): δ 8.13 (ddd, J = 5.2, 2.0, 0.9 Hz, 1H, py), 7.38 (ddd, J = 8.3, 7.1, 2.0 Hz, 1H, py), 7.33–7.29 (m, 2H, Ph), 7.18–7.15 (m, Ph), 7.11 (dt, J = 8.3, 1.0 Hz, 1H, py), 6.68 (ddd, J = 7.1, 5.2, 1.2 Hz, 1H, py), −0.36 (s, 9H, $SiMe_3$), −0.41 (s, 9H, $SiMe_3$). ^{13}C NMR (62.9 MHz, C_4D_8O): δ 174.2 (*N*CPh), 167.0, 151.5, 146.4, 135.0, 130.8, 127.6, 127.2, 125.8 and 115.7 (aryl C), 99.0 (*C*$SiMe_3$), 3.8 ($SiMe_3$).
2a. ^{1}H NMR (360 MHz, C_6D_6): δ 7.92 (dd, J = 7.9, 1.7 Hz, 2H, qui), 7.60 (d, J = 8.1 Hz, 1H, Ph), 7.39 (d, J = 8.8 Hz, 1H, Ph), 7.30–7.19 (m, 5H, qui), 7.04 (t, J = 7.7 Hz, 1H, qui), 6.87 (d, J = 8.7 Hz, 1H, qui), 6.33 (s, 1H, CH), −0.10 (s, 9H, $SiMe_3$). ^{13}C NMR (62.9 MHz, C_6D_6): δ 169.4 (*N*CPh), 160.6, 147.7, 147.6, 136.2, 129.7, 128.8, 128.6, 128.2, 127.8, 126.1, 126.0, 124.9 and 123.9 (aryl C), 106.4 (CH), 2.3 ($SiMe_3$).
2b. ^{1}H NMR (250 MHz, C_4D_8O): δ 7.80 (t, J = 9.0 Hz, 2H, qui), 7.60 (dd, J = 7.9, 1.2 Hz, 1H, Ph), 7.45 (m, 1H, Ph), 7.34 (m, 3H, aryl H), 7.20 (m, 4H, aryl H), −0.32 (s, 9H, $SiMe_3$), −0.38 (s, 9H, $SiMe_3$). ^{13}C NMR (62.9 MHz, C_4D_8O) δ 174.8 (*N*CPh), 167.7, 151.2, 148.6, 133.7, 130.9, 128.5, 128.0, 127.7, 127.5, 127.4, 126.8, 125.9 and 123.2 (aryl C), 100.6 (*C*$SiMe_3$), 4.1 ($SiMe_3$), 3.8 ($SiMe_3$).
3a. ^{1}H NMR (360 MHz, C_6D_6): δ 9.04 (d, J = 6.0 Hz, 2H, py), 7.66 (d, J = 7.2 Hz, 4H, Ph), 7.1–7.0 (m, 6H, Ph), 6.77 (t, J = 7.7 Hz, 2H, py), 6.35 (d, J = 7.9 Hz, 2H, py), 6.30 (t, J = 6.6, 2H, py), 6.05 (s, 2H, CH), 0.21 (s, 18H, $SiMe_3$). ^{13}C NMR (62.9 MHz, C_6D_6): δ 155.0 (*N*CPh), 154.2, 149.8, 141.2, 138.0, 129.2, 128.8, 127.9, 123.3 and 120.2 (aryl C), 111.2 (CH), 3.1 ($SiMe_3$).
3b. ^{1}H NMR (360 MHz, C_6D_6): δ 8.59–8.58 (m, 2H, py), 7.68 (d, J = 5.7 Hz, 2H, Ph), 7.63 (d, J = 6.6 Hz, 2H, Ph), 7.28 (d, J = 8.1 Hz, 2H, py), 7.12 (m, 6H, Ph), 6.87 (td, J = 7.7 Hz, 1.7 Hz, 2H, py), 6.00 (t, J = 6.0 Hz, 2H, py), 0.03 (s, 18H, $SiMe_3$), 0.01 (s, 18H, $SiMe_3$). ^{13}C NMR (62.9 Hz, C_6D_6): δ 165.0 (NCPh), 162.9, 149.8, 143.4, 137.9, 134.4, 130.4, 129.3, 128.6, 128.4, 128.3, 127.9, 127.0 and 125.8 (aryl C), 118.6 and 118.3 (*C*$SiMe_3$), 4.3 and 2.3 ($SiMe_3$).
4a. ^{1}H NMR (250 MHz, C_6D_6): δ 9.30 (d br, J = 8.3 Hz, 1H, qui), 9.04 (m br, 1H, qui), 8.21 (s br, 2H, qui), 7.69 (d br, J = 5.1 Hz, 2H, Ph), 7.31–6.82 (14H, qui and Ph), 6.20 (d, J = 8.6 Hz, 1H, qui), 5.65 (d, J = 8.7 Hz, 1H, qui), 5.63 (s, 1H, CH), 5.48 (s, 1H, CH), 0.36 (s, 9H, $SiMe_3$), 0.18 (s, 9H, $SiMe_3$). ^{13}C NMR (62.9 MHz, C_7D_8/C_7H_8): δ 165.1 (*N*CPh), 155.2, 152.5, 145.8, 145.4, 142.3, 138.4, 138.2, 138.1, 137.3, 130.8, 130.5, 130.2, 127.0, 126.9, 126.4, 125.3, 124.9, 121.9 and 120.4 (aryl C), 105.3 and 91.4 (CH), 4.3 and 3.7 ($SiMe_3$).
4b. ^{1}H NMR (360 MHz, C_6D_6): δ 8.82 (d, J = 8.3 Hz, 2H, qui), 8.28 (d, J = 8.4 Hz, 2H, qui), 7.80 (d, J = 6.9 Hz, 2H, Ph), 7.54 (d, J = 8.6 Hz, 2H, Ph), 7.26–7.17 (m, 8H, Ph and qui), 6.77–6.75 (m, 2H, qui), 6.60–6.57 (m, 4H, qui), 0.09 (s, 18H, $SiMe_3$), 0.08 (s, 18H, $SiMe_3$). ^{13}C NMR (62.9 MHz,

C_6D_6/C_6H_6): δ 166.5 (NCPh), 163.5, 145.8, 142.8, 138.7, 135.1, 131.5, 130.7, 129.8, 127.3, 126.9, 126.5, 125.3, 124.9, 119.5 and 118.4 (aryl C), 104.9 ($CSiMe_3$), 3.9 and 2.6 ($SiMe_3$).

[14] Another explanation would be that different isomers of **4a** are formed but this possibility seems less likely because the intensity ratio of the two sets of resonances in the NMR spectrum remains 1 : 1 after repeated recrystallisations.

[15] Enraf-Nonius CAD-4 diffractometer, λ (Mo-K α) 0.71073 Å. Crystal data for **3b**, $C_{38}H_{54}Cl_2N_4Si_4Zr(CH_2Cl_2)$. $M = 926.3$, monoclinic; space group $P2/n$ (No. 13); $a = 15.779(4)$, $b = 9.331(4)$, $c = 17.488(3)$ Å; $\beta = 112.46(2)°$; $U = 2380$ Å^3; $F(000) = 964$; $Z = 2$; $D_c = 1.29$ g cm^{-3}; μ(Mo-K α) = 5.9 cm^{-1}; $T = 293$ K; specimen $0.50 \times 0.30 \times 0.25$ mm^3; 4176 unique reflections for $2 < \theta < 25°$, 2914 reflections with $[I > 2\sigma(I)]$. Refinement on F^2 using SHELXL93; $R = 0.050$ (for $I > 2\sigma(I)$), $wR_2 = 0.14$ (all data), $S = 1.1$. Tables of thermal parameters and hydrogen atom coordinates and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre.

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[18] **8**. ^{1}H NMR (360 MHz, CD_2Cl_2): δ 8.88 (d, $J = 5.4$ Hz, 1H, py), 8.36 (t, $J = 8.1$ Hz, 1H, py), 7.79 (d, $J = 8.1$ Hz, 1H), 7.73–7.42 (6H, Ph and py), −0.09 (s, 9H, $SiMe_3$), −0.28 (s, 9H, $SiMe_3$). **9**. ^{1}H NMR (360 MHz, CD_2Cl_2): δ 8.80 (d, $J = 8.7$ Hz, 1H, qui), 8.75 (d, $J = 8.4$ Hz, 1H, qui), 8.0–7.5 (14H, Ph and qui), 7.40 (t, $J = 7.5$ Hz, 1H), 7.25 (t, $J = 7.7$ Hz, 1H), 6.95 (t, $J = 7.3$ Hz, 1H), 6.86 (t, $J = 7.6$ Hz, 1H), 6.65 (d, $J = 8.4$ Hz, 1H, qui), 6.34 (d, $J = 8.6$ Hz, 1H, qui), 0.26 (s, 9H, $SiMe_3$), −0.10 (s, 9H, $SiMe_3$), −0.20 (s, 9H, $SiMe_3$), −0.31 (s, 9H, $SiMe_3$).