Organometallics **1997,** *16,* 1247−1252 1247

Lithium Derivatives of Novel Monoanionic Di-*N*,*N*′-chelating Pyridyl- and Quinolyl-1-azaallyl Ligands

Berth-Jan Deelman,† Michael F. Lappert,† Hung-Kay Lee,‡ Thomas C. W. Mak,‡
Wing-Por Leung,‡ and Ping-Rong Wei‡

The Chemistry Laboratory, University of Sussex, Brighton, U.K. BN1 9QJ, and Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Received August 19, 1996⊗

The novel lithium complexes $[Li\{N(SiMe_3)C(R^2)C(R^1)(C_5H_4N\text{-}2)\}]_2$ ($R^1 = H$, $R^2 = Bu^t$ (**1b**); $R^1 = SiMe_3$, $R^2 = Ph$ (**1c**)) were prepared from the insertion of R^2CN into $[Li\{C(SiMe_3)(R^1)(C_5H_4N\text{-}2)\}]_2$. Similarly, $Li\{N(SiMe_3)C(Ph)C(R)(C_9H_6N\text{-}2)\}$ ($R = H$ or $SiMe_3$) was prepared from PhCN and $Li\{C(SiMe_3)(R)(C_9H_6N\text{-}2)\}$. X-ray data are provided for **1b**, **1c**, and $[Li\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}(Et_2O)(PhCN)]$ (**1c′**). Compounds **1b** and **1c** are dimers in the solid state, whereas **1c′** is monomeric.

Introduction

The continuing development of new spectator ligands in early transition metal chemistry, especially in group 4 metal chemistry, is stimulated by the search for new catalysts for α-olefin polymerization.[1] As a result, a range of new ligands has become available. Examples include polydentate Schiff bases,[2] benzamidinates,[3] multidentate amides,[4] macrocyclic nitrogen ligands,[5] porphyrins, porphyrinogens,[6] and biphenoxy[7] ligands. However, relatively few of their derived metal complexes have had catalytic activities that can match those of the cyclopentadienyl-based systems.

Following the successful introduction of bulky *N*,*N*′-bis(trimethylsilyl)-β-diketiminate ligands on zirconium[8] and the observation that some of the $[Zr\{N,N'\text{-bis(trimethylsilyl)-}\beta\text{-diketiminato}\}Cl_3]$ complexes show high activity in catalytic α-olefin polymerization when combined with methylaluminoxane (MAO) as a cocatalyst,[9] we decided to design a novel β-diketiminate-based ligand which posseses a nitrogen heterocycle as part of the ligand backbone (Figure 1). These monoanionic *N*,*N*′-bidentate ligands are less bulky than their parent *N*,*N*′-bis(trimethylsilyl)-β-diketiminates and are expected to have both good σ- and π-donating properties. Apart from being a variation on the β-diketiminate theme, we anticipated that because of the less sterically demanding nature of the ligands, formation of such bis(ligand)zirconium dichloride derivatives might place the zirconium center into a chiral coordination environment with the chloride ligands in a *cis* position.

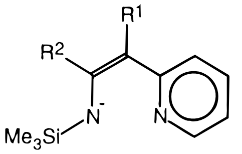


Figure 1. The newly developed 2-pyridyl-azaallyl ligand.

We recently briefly communicated results on some lithium and zirconium complexes of these pyridyl- and related quinolyl-1-azaallyl ligands,[10] and it was found that the bis(ligand)zirconium dichlorides with *cis*-positioned chloride ligands were indeed chiral, having either C_1 or C_2 symmetry. Here, we provide full details on the synthesis and characterization of the lithium complexes having new *N*,*N*′-chelating monoanionic ligands.

Several other *N*,*N*′-bidentate monoanionic $[LL]^-$ ligands are known, including the 1-azaallyls,[11] the β-diketiminates (cf. the lithium compound **I**[8]), the dipyrrolylmethanides, such as $[\{2\text{-}NC_4(X_2\text{-}3,4)(CO_2Et\text{-}5)\}_2CH]^-$ structurally characterized as the Ca^{2+} and Cu^{2+} complexes[12]), the dipyridylmethanides (X-ray data are available on the lithium compounds **II** and **III**),[13] the amidinates $[\{N(R)\}_2CR']^-$, including the structurally

---

† University of Sussex.

‡ The Chinese University of Hong Kong.

⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1997.

(1) For some recent reviews see: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1. (c) Horton, A. D. *Trends Polym. Sci.* **1994**, *2*, 158.

(2) (a) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 371. (b) Corazza, F.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1335. (c) Cozzi, P. G.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1995**, *34*, 2921 and references cited therein.

(3) (a) Herskovics-Korine, D.; Eisen, M. S. *J. Organomet. Chem.* **1995**, *503*, 307. (b) Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1995**, *14*, 1827. (c) Gómez, R.; Duchateau, R.; Chernega, A. N.; Teuben, J. H.; Edelmann, F. T.; Green, M. L. H. *J. Organomet. Chem.* **1995**, *491*, 153. (d) Roesky, H. W.; Meller, B.; Noltemeyer, M.; Schmidt, H.-G.; Scholz, U.; Sheldrick, G. M. *Chem. Ber.* **1988**, *121*, 1403.

(4) (a) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25. (b) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382.

(5) (a) Giannini, L.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2204. (b) Uhrhammer, R.; Black, D. G.; Gardner, T. G.; Olsen, J. D.; Jordan, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 8493 and references cited therein.

(6) (a) Solari, E.; Musso, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1994**, 2015. (b) Brand, H.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 95 and references cited therein.

(7) Van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.

(8) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699.

(9) Lappert, M. F.; Liu, D.-S. *Neth. Pat. Appl.* 9500085, 1995.

(10) Deelman, B.-J.; Hitchcock, P. B.; Lappert, M. F.; Lee, H.-K.; Leung, W.-P. *J. Organomet. Chem.* **1996**, *513*, 281.

(11) Hitchcock , P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2637.

(12) Clarke, E. T.; Squattrito, P. J.; Rudolf, P. R.; Motekaitis, R. J.; Martell, A. E.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *166*, 221.

(13) Gornitzka, H.; Stalke, D. *Organometallics* **1994**, *13*, 4398.

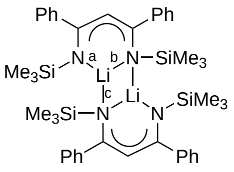
S0276-7333(96)00709-1 CCC: $14.00

Table 1. ^{1}H NMR Data

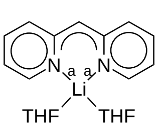
compound	aryl protons	CH	SiMe$_3$	others
1a^{a,c}	8.05 (m, 1H, 6-py), 7.90 (d, $J = 7.4$ Hz, 2H, *o*-Ph), 7.29 (t, $J = 7.4$ Hz, 2H, *m*-Ph), 7.20 (d, $J = 7.2$ Hz, 1H, 4-py), 6.99 (t, $J = 7.8$ Hz, 1H, *p*-Ph), 6.73 (d, $J = 7.9$ Hz, 1H, 3-py), 6.41 (m, 1H, 5-py)	6.24	−0.02	
1b^{b,c}	8.06−8.04 (m, 1H, 6-py), 7.03−6.96 (m, 1H, 4-py), 6.70−6.66 (m, 1H, 3-py), 6.43-6.38 (m, 1H, 5-py)	6.12	0.12	1.46 (s, 9H, Bu^t)
1c^{b,d}	8.13 (ddd, $J = 5.2$, 2.0, 0.9 Hz, 1H, 6-py), 7.38 (ddd, $J = 8.3$, 7.1, 2.0 Hz, 1H, 4-py), 7.33−7.29 (m, 2H, *o*-Ph), 7.18−7.15 (m, 3H, *m*-Ph, *p*-Ph), 7.11 (dt, $J = 8.3$, 1.0 Hz, 1H, 3-py), 6.68 (ddd, $J = 7.1$, 5.2, 1.2 Hz, 1H, 5-py)		−0.36, −0.41	
1c′^{b,c}	8.12−8.15 (m, 1H, 6-py), 7.69−7.66 (m, 2H, 4-py), 7.28−7.22 (m, 4H, *o*-Ph), 6.96−6.93 (dd, 3H, Ph), 6.81−6.76 (m, 1H, 3-py), 6.64−6.59 (d, 2H, Ph), 6.59 (m, 1H, 5-py)		0.02, −0.03	3.25 (q, 4H, OCH$_2$), 1.10 (t, 6H, Me)
2a^{a,c}	7.92 (dd, $J = 7.9$, 1.7 Hz, 2H, 9-qui), 7.60 (d, $J = 8.1$ Hz, 1H, *o*-Ph), 7.39 (d, $J = 8.8$ Hz, 1H, *o*-Ph), 7.30−7.19 (m, 5H, *m*-Ph, *p*-Ph, qui), 7.04 (t, $J = 7.7$ Hz, 1H, qui), 6.87 (d, $J = 8.7$ Hz, 1H, qui)	6.33	−0.10	
2b^{b,d}	7.80 (t, $J = 9.0$ Hz, 2H, 9-qui), 7.60 (dd, $J = 7.9$ Hz, $J = 1.2$ Hz, 1H, *o*-Ph), 7.45 (m, 1H, *o*-Ph), 7.34 (m, 3H), 7.20 (m, 4H)		−0.32, −0.38	

[a] 360 MHz. [b] 250 MHz. [c] In benzene-d_6. [d] In THF-d_8.

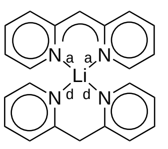
characterized compound **IV**,[14] and the *N*-alkyl-2-alkylaminotroponimates $[N(R)C(CH)_5CNR]^-$ [cf. $Sn(LL)_2$, R = Me);[15] for further examples of structurally characterized Li(LL) complexes, see ref 16.



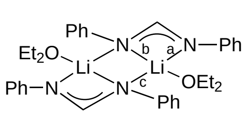
I



II



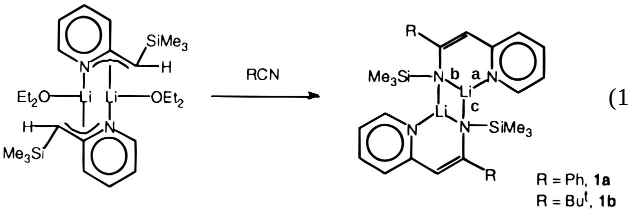
III



IV

Results and Discussion

Pyridyl substituted 1-azaallyls $[Li\{N(SiMe_3)C(R)C(H)(C_5H_4N\text{-}2)\}]_2$ (R = Ph, **1a**, or Bu^t, **1b**) were prepared under mild conditions from $[Li\{C(SiMe_3)(H)(C_5H_4N\text{-}2)(Et_2O)\}]_2$,[17] and PhCN or Bu^{t}CN, respectively (eq 1).



(1)

Diethyl ether or toluene was used as the solvent. Similarly $[Li\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}]_2$ (**1c**) was derived from $[Li\{C(SiMe_3)_2(C_5H_4N\text{-}2)\}]_2$[17] and PhCN. Such a reaction involves a 1,2-insertion of the nitrile into the Li−C bond as well as a 1,3-trimethylsilyl shift. This method is related to that previously employed in the synthesis of other 1-azaallyl complexes,[18] *e.g.*, $[Li\{N(SiMe_3)C(Bu^t)CHSiMe_3\}]_2$[11] from $LiCH(SiMe_3)_2$ and Bu^{t}CN. Other examples of nitrile insertion into metal−carbon bonds yielding a M(LL) complex ($[LL]^-$ being a monoanionic *N*,*N′*-bidentate ligand) include (i) $^1/_2[\{Cr(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Me\}_2] + MeCN \rightarrow [Cr(\eta^5\text{-}C_5Me_5)(Cl)\{N(H)C(Me)C(H)C(Me)NH\}]$,[19] (ii) $[Sc(\eta^5\text{-}C_5Me_5)_2Me] + 2ArCN \rightarrow [Sc(\eta^5\text{-}C_5Me_5)_2\{N(H)C(Ar)C(H)C(Ar)NH\}]$ (Ar = C_6H_4-Me-4),[20] and (iii) $[Yb\{CH(SiMe_3)_2\}_2(OEt_2)_2] + 4PhCN \rightarrow [Yb\{N(SiMe_3)C(Ph)C(H)C(Ph)NSiMe_3\}_2]$.[21]

Compounds **1a**−**c** were intensely yellow compounds, which were soluble in Et_2O, THF, or aromatic solvents but had fairly low solubility in an alkane. They were characterized by NMR spectroscopy, mass spectrometry, and elemental analysis. Mass spectra (electron ionization, EI) invariably showed signals due to the hydrolysis products $HN(SiMe_3)C(R^1)C(R^2)(C_5H_4N\text{-}2)\}$ (R^1 = Ph and R^2 = H or SiMe$_3$; R^1 = Bu^t and R^2 = H). The ^{1}H NMR spectroscopic data (Table 1) were straightforward, showing typical resonances for SiMe$_3$, pyridyl, and phenyl or Bu^t groups. Likewise, the ^{13}C NMR spectra (Table 2) were in agreement with the proposed structures;

---

(14) Cotton, F. A.; Haefer, S. C.; Matonic, J. H.; Wang, X.; Murillo, C. A. *Polyhedron* **1997**, *16*, 541.

(15) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 6546.

(16) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 469. Engelhardt, L. M.; Jacobsen, G. E.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc, Dalton Trans.* **1988**, 1011. Veith, M.; Goffing, F.; Huch, V. *Chem. Ber.* **1988**, *121*, 943. Pauer, F.; Stalke, D. *J. Organomet. Chem.* **1991**, *418*, 127. Chen, H.; Bartlett, R. A.; Rias, H. V. R.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1991**, *10*, 2487. Recknagel, A.; Steiner, A.; Noltemeyer, M.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *414*, 327. Edelmann, F. T.; Knössel, F.; Pauer, F.; Stalke, D.; Bauer, W. *J. Organomet. Chem.* **1992**, *438*, 1. Sato, D.; Kawasaki, H.; Shimada, I.; Arata, V.; Okamura, K.; Date, T.; Koga, K. *J. Am. Chem. Soc.* **1992**, *114*, 761. Detsch, R.; Niecke, E.; Nieger, M.; Schoeller, W. W. *Chem. Ber.* **1992**, *125*, 1119. Cragg-Hine, I.; Davidson, M. G.; Mair, F. S.; Raithby, P.; Snaith, R. *J. Chem. Soc., Dalton Trans.* **1993**, 2423. Freitag, S.; Kolodziejski, W.; Pauer, F.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1993**, 3479. Kosse, P.; Popowski, E.; Veith, M.; Huch, V. *Chem. Ber.* **1994**, *127*, 2103. Niecke, E.; Frost, M.; Nieger, M.; Gönna, V. v.d.; Ruban, A.; Schoeller, W.W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2111. Steiner, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1752. Bailey, P. J.; Blake, A. J.; Kryszczuk, M.; Parsons, S.; Reed, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1647.

(17) Papasergio, R. I.; Skelton, B. W.; Twiss, P.; White, A. H.; Raston, C. L. *J. Chem. Soc., Dalton Trans.* **1990**, 1161.

(18) Lappert, M. F.; Liu, D.-S. *J. Organomet. Chem.* **1995**, *500*, 203 and references cited therein.

(19) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics* **1989**, *8*, 2570.

(20) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

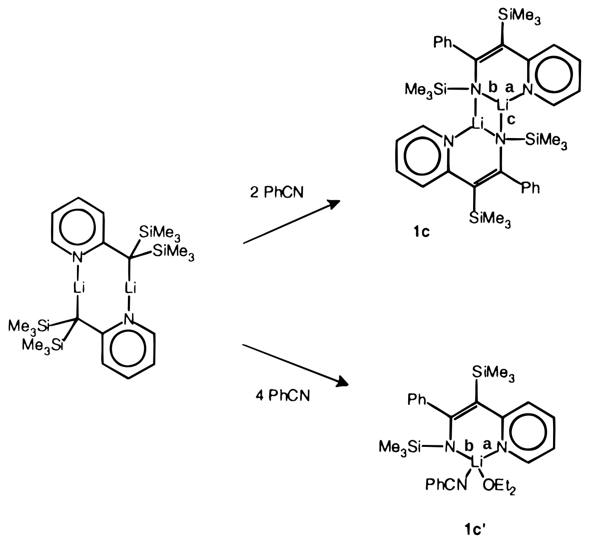
(21) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2691.

Table 2. ^{13}C NMR Data (62.9 MHz)

compound	aryl carbons	*C*H or *C*SiMe$_3$	N*C*Ph or N*C*Bu^t	C*Me*$_3$	Si*Me*$_3$
1a[a]	160.5, 148.5, 147.2, 137.3, 129.2, 128.2, 127.9, 124.1, 117.6	107.1	165.3		2.5
1b[b]	161.2, 146.7, 137.2, 123.8, 117.7	106.2	176.1	40.4, 30.9	3.4
1c[c]	167.0, 151.5, 146.4, 135.0, 130.8, 127.6, 127.2, 125.8, 115.7	99.0	174.2		3.8
2a[b]	160.6, 147.7, 147.6, 136.2, 129.7, 128.8, 128.6, 128.2, 127.8, 126.1, 126.0, 124.9, 123.9	106.4	169.4		2.3
2b[c]	167.7, 151.2, 148.6, 133.7, 130.9, 128.5, 128.0, 127.7, 127.5, 127.4, 126.8, 125.9, 123.2	100.6	174.8		4.1, 3.8

[a] In benzene/benzene-d_6. [b] In benzene-d_6. [c] In THF-d_8.

Scheme 1



N*C*Ph and N*C*Bu^t signals were observed at $\delta = 165.3$ (**1a**), 176.1 (**1b**), and 174.2 (**1c**) and the $=$CH or $=$*C*SiMe$_3$ resonances at $\delta = 107.1$ (**1a**)**,** 106.2 (**1b**), and 99.0 (**1c**). In each case, only one set of ligand resonances was observed, indicative of either a monomeric complex or a multinuclear structure with the ligands in symmetrically equivalent positions. X-ray analysis showed these complexes to be dimeric in the solid state (*vide infra*).

The preparation of these complexes in diethyl ether can be hindered by the formation of minor amounts of monomeric nitrile adducts, which are more soluble than dimeric **1**. Especially when an excess of nitrile was used, purification of **1** was severely hampered by the presence of significant amounts of these species. When a 4:1 stoichiometry of PhCN and [Li{C(SiMe$_3$)$_2$(C$_5$H$_4$N-2)}]$_2$ was used, [Li{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}(Et$_2$O)(PhCN)] (**1c′**) could be isolated in high yield and was characterized by NMR spectroscopy and X-ray analysis (Scheme 1, *vide infra*). The ^{1}H NMR data were very similar to those of dinuclear **1c** (Table 1).

The molecular structures of **1b**, **1c**, and **1c′** were determined by single-crystal X-ray crystallography. Compounds **1b** and **1c** are centrosymmetric dimers in the solid state (Figures 2 and 3) with central Li$_2$N$_2$ rhombi and bridging NSiMe$_3$ groups, the Li atoms being three coordinate. These features are similar to those of the molecular structure of [Li{N(SiMe$_3$)C(Ph)C(H)C(Ph)N(SiMe$_3$)}]$_2$.[8] The molecular structure of the mononuclear complex **1c′** is shown in Figure 4. The inner coordination sphere of the four-coordinate lithium atom is comprised of the two nitrogen atoms of the [N(SiMe$_3$)C(Ph)C(SiMe$_3$)C$_5$H$_4$N-2]$^-$ ligand, a benzonitrile nitrogen atom, and the oxygen atom of Et$_2$O. Selected bond distances for the three compounds are listed in Tables 3−5.

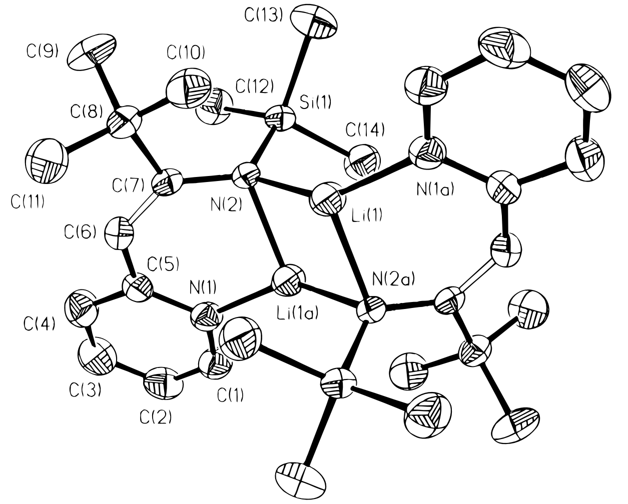


Figure 2. Molecular structure of **1b** showing atom-labeling scheme. The thermal ellipsoids are drawn at the 35% probability level. C(6)−C(7) is an olefinic bond.

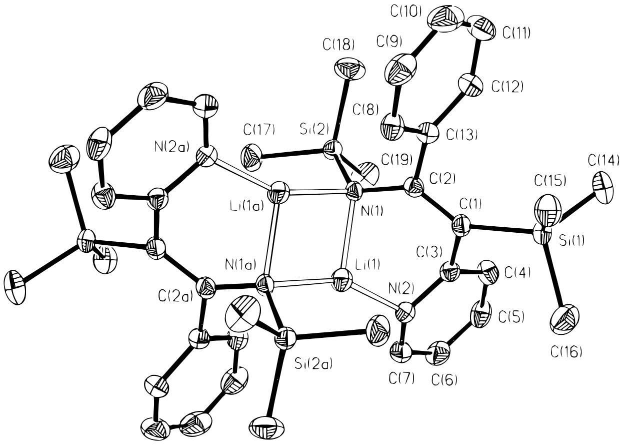


Figure 3. Molecular structure of **1c** showing atom-labeling scheme. The thermal ellipsoids are drawn at the 35% probability level.

A comparison of some relevant bond distances and angles for **1b**, **1c**, **1c′**, **I**,[8] **II**,[13] **III**,[13] and **IV**[14] is presented in Table 6. The bonding within the NCCCN ligand backbone is in each case highly localized with R^{1}C=C double bonds (R = Ph or Bu^t), leaving the aromaticity of the pyridyl ring largely unaffected. This is in contrast to [Li{N(SiMe$_3$)C(Ph)C(H)C(Ph)N(SiMe$_3$)}]$_2$, which displayed, at least to some extent, delocalization in the ligand backbone.[8] The Li−N distances of the bridging NSiMe$_3$ groups (Li1−N2) are almost identical and the Li−pyridyl bonds (1.968(6) (**1b**), 1.981(7) (**1c**), and 1.983(6) Å (**1c′**)) are considered to be unexceptional dative interactions and may be compared, for example, with the Li−pyridine distance in the three-coordinate lithium compound [Li{2-C(SiMe$_3$)$_2$C$_5$H$_4$N}{CH(SiMe$_3$)$_2$-C$_5$H$_4$N-2}] of 2.01(1) Å.[17] The LiNCCCN metallacycles

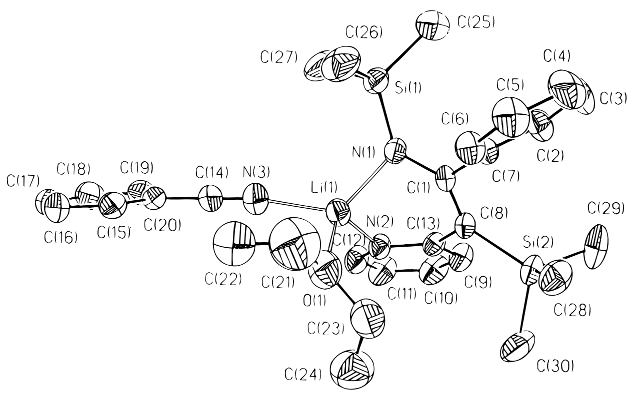


Figure 4. Molecular structure of **1c′** showing atom-labeling scheme. The thermal ellipsoids are drawn at the 35% probability level. Atoms C(21′) and C(22′), which represent an alternative orientation of one ethyl group in the disordered Et_2O ligand, have been omitted for the sake of clarity.

Table 3. Selected Bond Distances (Å) for $[Li\{N(SiMe_3)C(Bu^t)C(H)(C_5H_4N\text{-}2)\}]_2$ (1b)

Si1−N2	1.708(4)	C1−C2	1.373(5)
N1−C1	1.352(6)	C2−C3	1.362(8)
N1−C5	1.352(5)	C3−C4	1.380(8)
N1−Li1a[a]	1.968(6)	C4−C5	1.393(5)
N2−Li1	2.032(6)	C5−C6	1.461(6)
N2−C7	1.381(5)	C6−C7	1.356(5)
N2−Li1a	2.012(9)	C7−C8	1.568(6)

[a] Symmetry transformation: (a) $1 - x$, $1 - y$, $1 - z$.

Table 4. Selected Bond Distances (Å) for $[Li\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}]_2$ (1c)

Si1−C1	1.884(2)	N2−C7	1.343(5)
Si2−N1	1.700(2)	C1−C2	1.350(5)
Si2−Li1a[a]	2.971(5)	C1−C3	1.529(4)
Li1−N1	1.998(6)	C2−C13	1.515(4)
Li1−N2	1.981(7)	C3−C4	1.388(5)
Li1−N1a	2.026(6)	C4−C5	1.370(5)
N1−C2	1.405(2)	C5−C6	1.368(5)
N2−C3	1.338(3)	C6−C7	1.369(6)

[a] Symmetry transformation: (a) $(-x, -y, -z)$.

Table 5. Selected Bond Distances (Å) for $[Li\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}(Et_2O)(PhCN)]$ (1c′)

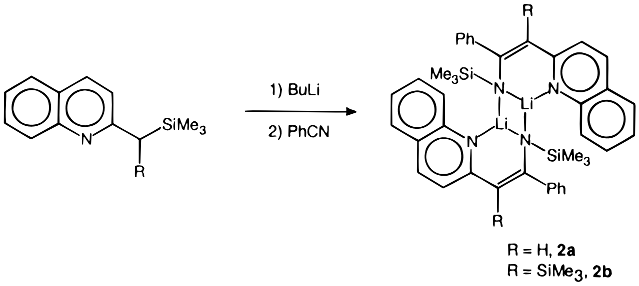
Li1−N1	1.994(4)	C8−Si2	1.876(3)
Li1−N2	1.983(6)	C9−C10	1.377(5)
Li1−N3	2.131(6)	C9−C13	1.402(5)
Li1−O1	2.028(5)	C10−C11	1.374(4)
N1−C1	1.349(4)	C11−C12	1.360(6)
N1−Si1	1.710(4)	C12−N2	1.349(5)
C1−C7	1.520(5)	N2−C13	1.356(3)
C1−C8	1.396(5)	N3−C14	1.140(4)
C8−C13	1.466(5)	C14−C20	1.433(4)

are highly puckered and, especially in the case of **1c**, the steric congestion at the NCCCN skeleton is revealed by the large out of plane rotation of the phenyl group relative to the C1−C2−C13 plane (C1−C2−C13−C8 = 120°), preventing effective conjugation with the C1=C2 double bond. This steric congestion has also been observed in the molecular structure of $[Zr\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2Cl_2]$.[10]

Table 6. Comparison of Selected Bond Distances (Å) for $[Li\{N(SiMe_3)C(Bu^t)C(H)(C_5H_4N\text{-}2)\}]_2$ (1b), $[Li\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}]_2$ (1c), $[Li\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}(Et_2O)(PhCN)]$ (1c′), and I−IV

Compound	a	b	c	d	ref
1b	1.968(6)	2.012(9)	2.032(6)		this work
1c	1.981(7)	1.998(6)	2.026(6)		this work
1c′	1.983(6)	1.994(4)			this work
I	1.952(10)	1.965(9)	2.095(9)		8
II	1.966(4) 1.973(4)				13
III	1.960(9) 1.976(9)			2.071(9) 2.058(8)	13
IV	2.045(8)	2.078(8)	2.231(9)		14

We reasoned that a quinoline instead of a pyridine substituent might be helpful in further increasing the stereo-directing properties of the ligand when it is introduced onto a group 4 metal center. In addition, the reactive 5,6-bond of the pyridine ring of the 1-azaallyl ligand would become less susceptible to nucleophilic attack. Therefore, the quinolyl-substituted 1-azaallyls, **2a** and **2b**, derived from the insertion of benzonitrile into lithiated mono- and bis(trimethylsilyl)-2-methylquinoline, respectively, were prepared (eq 2). Full experimental details for the synthesis of mono- and bis(trimethylsilyl)-2-methylquinoline are given in the Experimental Section. Solubility data for **2a** and **2b** were comparable to those of **1a**−**c**. Mass spectra, again, showed peaks due to the hydrolysis products $HN(SiMe_3)C(Ph)C(R)(C_9H_6N\text{-}2)$ (R = H (**2a**), $SiMe_3$ (**2b**)). On the basis of similarities in the NMR spectroscopic data, we assume that **2a** and **2b** are similar in structure to **1b** and **1c**. Notable features in the ^{13}C NMR spectrum of **2a** were the *C*H and N*C*Ph resonances at $\delta = 106.4$ and 169.4, respectively. Characteristic *C*$SiMe_3$ and N*C*Ph signals for **2b** were found at $\delta = 100.6$ and 174.8, respectively.



(2)

Conclusions

We have shown that the newly developed pyridyl- and quinolyl-substituted 1-azaallyl ligands are readily prepared from the lithiated 2-methylpyridine or 2-methylquinoline by 1,2-insertion of a suitable nitrile with a concomitant 1,3-trimethylsilyl shift. These monoanionic ligands complex lithium through both of their nitrogen atoms and are expected to be good σ- and π-donors. Like cyclopentadienyl ligands, they can formally be considered as six-electron donors. In addition, the substituents on the ligand backbone can be easily varied, which can be important for fine tuning of the ligands' steric and electronic properties. Because of these characteristics, pyridyl- and quinolyl-susbtituted 1-azaallyl ligands are expected to have significant potential in homogeneous catalysis; reports on this aspect will follow in due course.

Experimental Section

General Considerations. All experiments were performed under argon using standard Schlenk and vacuum line

Table 7. Details of the X-ray Structure Determinations of [Li{N(SiMe$_3$)C(Bu^t)C(H)(C$_5$H$_4$N-2)}]$_2$ (1b), [Li{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}]$_2$ (1c), and [Li{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}(Et$_2$O)(PhCN)] (1c′)

mol Form	$C_{28}H_{46}N_4Si_2Li_2$ (**1b**)	$C_{38}H_{54}N_4Si_4Li_2$ (**1c**)	$C_{30}H_{42}N_3OLiSi_2$ (**1c′**)
mol wt	508.8	693.1	523.8
color and habit	pale yellow prism	colorless prism	yellow prism
cryst size, mm^3	0.30 × 0.40 × 0.60	0.16 × 0.24 × 0.38	0.30 × 0.35 × 0.40
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	8.693(1)	10.126(2)	10.237(2)
b, Å	8.746(1)	10.261(2)	10.387(2)
c, Å	11.766(2)	12.073(2)	17.275(3)
α, deg	101.31(1)	99.44(4)	88.80(1)
β, deg	111.07(1)	9552(3)	87.56(1)
γ, deg	101.08(1)	117.31(3)	61.14(1)
V, Å^3	784.0(4)	1078.3(5)	1607.3(8)
D_{calcd}, g cm^{-3}	1.078	1.067	1.082
Z	1	1	2
F(000)	276	372	564
abs coeff, mm^{-1}	0.134	0.166	0.135
mean μr	0.24	0.081	0.024
scan type and rate	oscillation IP photos; 30 frames in total, $\phi = 0 - 180°$, $\Delta\phi = 6°$, 15 min per frame	oscillation IP photos; 39 frames in total, $\phi = 0 - 120°$, $\Delta\phi = 4°$, 9 min per frame	oscillation IP photos; 36 frames in total, $\phi = 0 - 180°$, $\Delta\phi = 5°$, 12 min per frame
cryst to detector distance, mm	69.334	69.56	69.218
background level	−50	−40	−50
collection range	$-10 \le h \le 10$, $-9 \le k \le 9$, $-14 \le l \le 9$	$-12 \le h \le 10$, $0 \le k \le 13$, $-15 \le l \le 15$	$0 \le h \le 12$, $-11 \le k \le 13$, $-19 \le l \le 20$
unique data measured	2892	3960	5631
observed data[a]	1780 ($\lvert F_0\rvert \ge 6\sigma(\lvert F_0\rvert)$, *n*)	3409 ($\lvert F_0\rvert \ge 6\sigma(\lvert F_0\rvert)$, *n*)	3011 ($\lvert F_0\rvert \ge 6\sigma(\lvert F_0\rvert)$, *n*)
no. of variables, *p*	163	218	353
extinction correction	not applied	$\chi = 0.015$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$	$\chi = 0.0023(2)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
weighting scheme	$w = [\sigma^2\lvert F_0\rvert + 0.00005\lvert F_0\rvert^2]^{-1}$	$w = [\sigma^2\lvert F_0\rvert + 0.0001\lvert F_0\rvert^2]^{-1}$	$w = [\sigma^2\lvert F_0\rvert + 0.000002\lvert F_0\rvert^2]^{-1}$
$R_F = \sum\lvert\lvert F_0 - \lvert F_0\rvert\rvert/\sum\lvert F_0\rvert$	0.060	0.058	0.055
$wR = [\sum w^2(\lvert F_0\rvert - \lvert F_c\rvert)^2/\sum w^2\lvert F_0\rvert^2]^{1/2}$	0.065	0.071	0.071
$S = [\sum w(\lvert F_0\rvert - \lvert F_c\rvert)^2/(n-p)]^{1/2}$	1.68	1.44	1.14
largest and mean Δ/σ	0.000, 0.000	0.000, 0.000	0.010, 0.008
residual extrema in final diff map, eÅ^{-3}	+0.32 to −0.39	+0.55 to −0.20	+0.41 to −0.26

[a] Owing to an error in the data conversion software, the numerical value of $\sigma(\lvert F_0\rvert)$ for **1c′** was underestimated by a factor of 2. In the tabulated structure factor tables for this compound, all entries under 10*s* [$10\sigma(\lvert F_0\rvert)$] should be multiplied by a factor of 2.

techniques. Pentane, Et$_2$O, THF, THF-d_8, cyclohexane, benzene, benzene-d_6, toluene, and toluene-d_8 were distilled from Na/K alloy and degassed prior to use. CH$_2$(SiMe$_3$)(C$_5$H$_4$N-2) and (SiMe$_3$)$_2$C(H)(C$_5$H$_4$N-2) were prepared according to the literature.[17] Other compounds were purchased and purified by standard procedures. NMR spectra were recorded on Bruker WM250, WM300, and WM360 spectrometers at ambient temperatures. Mass spectra (EI) were recorded on a VG Autospec instrument. Elemental analyses were carried out by Medac Ltd. (Brunel University).

[Li{N(SiMe$_3$)C(Ph)C(H)(C$_5$H$_4$N-2)}]$_2$ (1a). [Li{CH(SiMe$_3$)$_2$(NC$_5$H$_4$-2)}(Et$_2$O)]$_2$[17] was prepared by addition of CH$_2$(SiMe$_3$)(C$_5$H$_4$N-2) (5.13 g, 31 mmol) to a solution of BuLi (32 mmol) in hexane (20 mL) and Et$_2$O (20 mL), which was cooled in a water bath. After the mixture was stirred for 0.5 h at room temperature, the orange suspension was diluted with Et$_2$O (35 mL). Then, PhCN (3.3 mL, 32 mmol) was added dropwise, while the reaction mixture was kept at room temperature using a water bath. The orange reaction mixture was stirred for another 16 h, and volatiles were removed under vacuum. The residue was dried (0.5 h) at 50 °C under vacuum, and crystals were obtained by slowly cooling a hot hexane solution (50 mL) to 0 °C. The product **1a** was washed with pentane (10 mL). Yield of **1a**: 2.89 g, 5.3 mmol, 34%. Anal. Calcd for C$_{16}$H$_{19}$LiN$_2$Si: C, 70.0; H, 6.98; N, 10.21. Found: C, 69.5; H, 7.03; N, 10.03. MS (EI, 70 eV): *m/z* 268 (4, (HN(SiMe$_3$)C(Ph)CH(C$_5$H$_4$N-2))$^+$), 253 (100, (HN(SiMe$_3$)C(Ph)CH(C$_5$H$_4$N-2) − Me)$^+$).

[Li{N(SiMe$_3$)C(Bu^t)C(H)(C$_5$H$_4$N-2)}]$_2$ (1b). To a solution of [Li{CH(SiMe$_3$)(NC$_5$H$_4$-2)(Et$_2$O)}]$_2$[17] (2.00 g, 4.08 mmol) in toluene (40 mL) was added dropwise Bu^{t}CN (0.68 g, 8.2 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 6 h; a microcrystalline, yellow solid precipitated. The precipitate was washed with hexane and dried under vacuum affording **1b** (1.66 g, 3.26 mmol, 80%), which was recrystallized from warm toluene. Anal. Calcd for C$_{28}$H$_{46}$Li$_2$N$_4$Si$_2$: C, 66.1; H, 9.11; N, 11.01. Found: C, 65.9; H, 9.08; N, 11.01.

[Li{(N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}]$_2$ (1c). [Li{C(SiMe$_3$)$_2$(C$_5$H$_4$N-2)}]$_2$[17] was prepared by addition of CH(SiMe$_3$)$_2$(C$_5$H$_4$N-2) (8.0 mL, 7.4 g, 31 mmol) to a solution of BuLi (32 mmol) in hexane (20 mL) and Et$_2$O (50 mL), which was cooled in a water bath. After the orange mixture was stirred for 1 h at room temperature, PhCN (3.2 mL, 31 mmol) was added dropwise while the reaction mixture was kept at room temperature using a water bath. The mixture continued to stir for another 15 h, and volatiles were removed under vacuum. The yellow residue was suspended in hexane (50 mL), cooled to −30 °C, and collected on a frit. The yellow product **1c** was washed with pentane (30 mL). Yield of **1c**: 7.37 g, 10.6 mmol, 68%. Anal. Calcd for C$_{19}$H$_{27}$LiN$_2$Si$_2$: C, 65.9; H, 7.85; N, 8.08. Found: C, 65.7; H, 7.65; N, 8.13. MS (EI, 70 eV): *m/z* 340 (48, (HN(SiMe$_3$)CPhC(SiMe$_3$)(C$_5$H$_4$N-2))$^+$), 325 (22, (HN(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2) − Me)$^+$), 267 (28, (HN(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2) − SiMe$_3$)$^+$). Starting from CH(SiMe$_3$)$_2$(C$_5$H$_4$N-2) (26.7 g, 11.2 mmol), the total yield of **1c** was 30.0 g (8.83 mmol, 79%). Recrystallization from hot toluene gave pale yellow crystals suitable for X-ray analysis.

[Li{(N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_5$H$_4$N-2)}(Et$_2$O)(PhCN] (1c′). The procedure was similar to that for **1c**, using a 4:1 stoichiometry of PhCN and [Li{C(SiMe$_3$)$_2$(C$_5$H$_4$N-2)}]$_2$. After the reaction mixture had been stirred for 6 h, the mixture was filtered and concentrated. The mixture was cooled to −30 °C and afforded a mixture of yellow crystals of **1c′**. A suitable crystal of **1c′** was subjected to X-ray analysis.

CH$_2$(SiMe$_3$)(2-C$_9$H$_6$N). To a solution of BuLi (160 mmol) in hexane (100 mL) was added TMEDA (24.0 mL, 159 mmol).

Then, 2-quinaldine (22.0 mL, 163 mmol) was added dropwise at 0 °C. The resulting red suspension was stirred at room temperature for 1 h, and volatiles were removed under vacuum. The orange residue was dissolved in THF (125 mL) and was added to $SiMe_3Cl$ (30.0 mL, 240 mmol) in Et_2O (200 mL) in 1.5 h. The orange suspension was stirred for 16 h at room temperature. The solvent was removed under vacuum, and the remaining oil was extracted with hexane (2 × 100 mL). Vacuum distillation (10^{-3} mbar, 78−86 °C) gave the title product (30.4 g, 141 mmol, 87%) as a colorless liquid. ^{1}H NMR (250 MHz, chloroform-d_1): 7.94 (ps d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 7.9$ Hz, 1H), 7.62 (t, $J = 7.3$ Hz, 1H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.08 (d, $J = 8.4$ Hz, 1H), 2.54 (s, 2H, CH_2), 0.04 (s, 9H, $SiMe_3$).

Li{N(SiMe$_3$)C(Ph)CH(C$_9$H$_6$N-2) (2a). Li[CH($SiMe_3$)(C_9H_6N-2) was prepared by addition of $CH_2(SiMe_3)(C_9H_6N\text{-}2)$ (15.6 g, 72 mmol) to a solution of BuLi (72 mmol) in hexane (45 mL) and Et_2O (50 mL) at 0 °C. After the red suspension was stirred for 1 h at room temperature, PhCN (7.5 mL, 73 mmol) was added dropwise while the reaction mixture was kept at 0 °C. The dark red mixture was allowed to reach room temperature and was stirred for another 20 h, after which volatiles were removed under vacuum. The oily residue was dried (0.5 h) at 50 °C under vacuum and refluxed in hexane (100 mL). The yellow suspension was cooled to −30 °C, and filtration and washing with hexane (20 mL) gave the yellow, microcrystalline compound **2a** (14.3 g, 44.1 mmol, 61%). The combined washing and mother liquor were concentrated to $^3/_4$ of its volume, and cooling to −30 °C gave a second crop of **2a** (2.6 g, 8.1 mmol). Total yield: 73%. Anal. Calcd for $C_{20}H_{21}LiN_2Si$: C, 74.0; H, 6.52; N, 8.64. Found: C, 73.2; H, 6.48; N, 8.56. MS (EI, 70 eV): *m/z* 318 (63, $(HN(SiMe_3)C(Ph)CH(C_9H_6N\text{-}2))^+$), 303 (100, $(HN(SiMe_3)C(Ph)CH(C_9H_6N\text{-}2) - Me)^+$).

Li{N(SiMe$_3$)C(Ph)C(SiMe$_3$)(C$_9$H$_6$N-2)} (2b). $CH_2(SiMe_3)$-(C_9H_6N-2) (0.90 mL, 4.1 mmol) was added dropwise at 0 °C to a solution of BuLi (4.0 mmol) in hexane (2.50 mL) and Et_2O (5 mL). The orange solution was stirred at room temperature for 30 min, and then $SiMe_3Cl$ (0.50 mL, 4.0 mmol) was added. After 15 h at room temperature, the brown-red suspension was filtered, and BuLi (3.80 mmol) in hexane (2.40 mL) was added at 0 °C. The red solution was stirred at room temperature for 15 min, and then PhCN (0.40 mL, 3.9 mmol) was added at 0 °C. Again, the reaction mixture was stirred at room temperature for 15 h. Volatiles were removed, and the residue was dried (50 °C, 0.5 h) under vacuum, suspended in hexane (15 mL), isolated, and washed with hexane (10 mL) affording **2b** (1.02 g, 2.57 mmol, 64%) as a yellow powder. Anal. Calcd for $C_{23}H_{29}LiN_2Si_2$: C, 69.7; H, 7.37; N, 7.06. Found: C, 67.7; H, 7.22; N, 6.87. MS (EI, 70 eV): *m/z* 390 (50, $(M - Li + 1)^+$). Large scale synthesis starting from 22.3 mL (104 mmol) of $CH_2(SiMe_3)(C_9H_6N\text{-}2)$ afforded **2b** in 86% yield.

X-ray Structure Determinations of 1b, 1c, and 1c′. Selected single crystals were sealed in Lindemann glass capillaries under dinitrogen. X-ray intensities were measured on a MSC/Rigaku RAXIS-IIC imaging plate, using monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å, 50 kV, 150 mA) from a rotating-anode generator. The structures were solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms. Analytical expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1974). All calculations were performed using the computer program SHELXTL-PLUS program package (Sheldrick, 1985, 1990) on a PC 486 computer. One of the two ethyl groups in the coordinated Et_2O ligand in **1c′** exhibited 2-fold disorder, which was modeled by half-carbon atoms C(21), C(22) and C(21′), C(22′). Crystal data and experimental details of the structure determinations are listed in Table 7.

Acknowledgment. We thank the European Community for a Human Capital and Mobility Grant for B.-J.D, The Chinese University of Hong Kong for a Direct Grant for W.-P.L., and Dr. Ali Abdul-Sada for the MS measurements.

Supporting Information Available: Packing diagrams and tables of data collection and processing parameters, atomic coordinates and isotropic temperature factors, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates and assigned isotropic temperature factors (19 pages). Ordering information available on any current masthead page.

OM9607098