



Synthesis and structures of the transition metal(II) β -diketimines $[ML_2]$ ($M = Mn, Fe, Ni, Cu, Pd$), $[ML'_2]$ ($M = Ni, Cu$) and $[M(\eta^3-C_3H_5)L]$ ($M = Ni, Pd$); L or $L' = \{[N(SiMe_3 \text{ or } H)C(Ph)]_2CH\}^-$

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ARTICLE INFO

Article history:

Received 27 October 2008

Received in revised form 17 November 2008

Accepted 19 November 2008

Available online 30 November 2008

Keywords:

Late transition metals

β -Diketiminates

Structures

Magnetism

DFT calculations

ABSTRACT

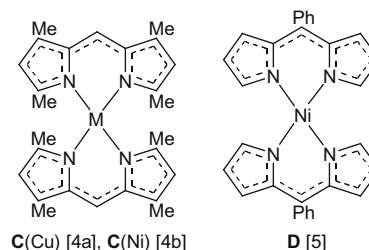
A series of crystalline late transition metal β -diketimines **1–10**, using the ligand $\{[N(SiMe_3)C(Ph)]_2CH\}^-$ ($\equiv L^-$) or $\{[N(H)C(Ph)]_2CH\}^-$ ($\equiv L'^-$) is reported. The homoleptic pseudo-tetrahedral crystalline complexes $[M(L)_2]$ [$M = Mn$ (**1**), Fe (**2**), Ni (**3**), Cu (**5**)] were prepared from $[Li(L)]_2$ and the appropriate anhydrous MCl_2 in thf. The planar metal analogues $[M(L')_2]$ [$M = Ni$ (**4**), Cu (**6**)] were obtained for **4** from $NiCl_2$ and $[Li(L)]_2$ in thf followed by chromatography on hydrated alumina, or for **6** from hydrated $CuSO_4$ and either $[Li(L)]_2$ or $H(L)$. The precursor for $[Pd(L)_2]$ (**7**) and $[Pd(L)(\mu-Cl)]_2$ (**8**) was $[Pd(cod)Cl_2]$ (one or two molar equivalents), while the allyl complexes $[Pd(\eta^3-C_3H_5)(L)]$ (**9**) or $[Ni(\eta^3-C_3H_5)(L)]$ (**10**) were prepared from $\{[Pd(\eta^3-C_3H_5)(\mu-Cl)]_2\}$ or $\{[Ni(\eta^3-C_3H_5)(\mu-Br)]_2\}$, respectively. Whereas in each of the crystalline complexes **1–6** the MNCCN rings are planar, in the centrosymmetric **7** and in **9** they are boat-shaped. The compounds **1, 2, 3, 5** and **6** (unlike **4, 7, 8** and **9**) are paramagnetic; the magnetic moment in $CDCl_3$ corresponds approximately to a low-spin complex for **1** and a high-spin complex for **2**. The molecular structures of the crystalline compounds (X-ray data) **2, 3, 4, 5, 6, 7** and **9** are presented. Quantum chemical calculations (B3LYP) on the Ni (**3**) and Pd (**7**) complexes correlated well with the experimental structures, although the calculated Gibbs free energy for both tetrahedral and square-planar geometries showed the latter configuration more stable than the former by *ca.* 60 (Ni) and 100 (Pd) $kJ\ mol^{-1}$ over a range of temperatures.

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1. Introduction

The homoleptic late 3d transition metal(II) β -diketimines were among the first metal complexes having such ligands to be examined. Particularly relevant to the present work are the results reported in 1968 by McGeachin [1] and Parks and Holm [2]; others [3] also made useful contributions in the 1960s. Their syntheses are summarised in Scheme 1. These early studies were designed to establish molecular structures, using the methods of magnetism, electronic spectra and isotropic 1H NMR spectral shifts for the paramagnetic compounds. Only the N–H containing complexes $[M\{(N(H)C(Me))_2CH\}_2]$ ($M = Co, Ni, Cu$) (**A**) were judged to have a planar four-coordinate metal environment [1], the others (**B**) being assigned as distorted tetrahedral [1–3]. The first X-ray structures were those of the distorted tetrahedral copper complex **C**(Cu) [4a] and the D_2 -symmetric nickel analogue **C**(Ni) [4b]; however, the distorted square-planar configuration was found in the less crowded Ni complex **D** [5]. Another pertinent development (from

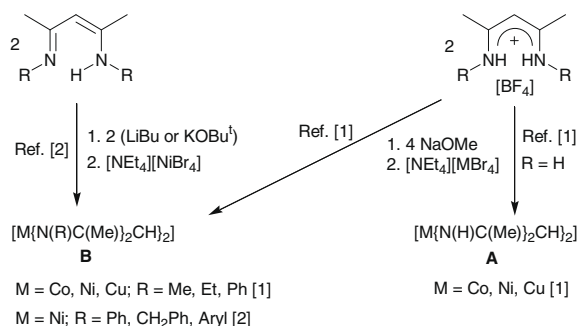
our laboratory) related to the synthesis and X-ray structures of the crystalline cobalt(II) complexes **E** and **F** of Scheme 2 [6]; the starting material for **E** and **F** were the lithium β -diketiminate **G** and the β -diketimine **H** [7]. The precursors to **G** were $LiCH(SiMe_3)_2 + 2PhCN$ [7].



Knorr and coworkers have published a series of papers on late transition metal(II) β -dialdiminates, including $[Ni\{(N(Ph)C(H))_2CCH(R^1)R^2\}_2]$ [8a] ($R^1 = H$ and $R^2 = H, Me, Et, Ph, CH_2Ph$; or $R^1 = Et$ and $R^2 = Me$ or Et ; or $CH(R^1)R^2 = C_5H_9-c, C_6H_{11}-c$) and $[M\{(N(C_6H_3Me_2-3,5)C(H))_2CCHO\}_2]$ ($M = Co, Ni, Cu, Zn, Pd$) [8b]. They studied

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Scheme 1. Synthesis of some homoleptic 3d⁷, 3d⁸, 3d⁹ metal β -diketiminates [1,2].

the nature of ligand to metal bonding, partly by measuring paramagnetically induced ¹H NMR spectral chemical shifts, using as reporter groups the prochiral alkyl [8a] or the formyl [8b] at the β -carbon atom of the ligand. Triplet–singlet spin-flip during thermal isomerisation of tetrahedral \rightarrow planar Ni(II) complexes was considered using orbital symmetry analysis [8c] (see also Refs. [8d,8e] and others cited therein). The detailed electronic structure of a large number of variously substituted paramagnetic Ni and Co β -diketiminates was studied by a combination of NMR spectroscopy and DFT calculations [8f].

Among the very few recent reports of homoleptic late transition metal(II) β -diketiminates and related compounds is [Cu{N(Me)C(Me)C(H)C(Me)NEt}₂], which, being volatile *in vacuo* at ambient temperature, was a useful precursor for Cu metal deposition via CVD or ALD [9a]. Noteworthy are homoleptic M^{II} (M = Mn, Fe, Co and Cu) complexes of the triazapentadienide ligand [N(Ar)C(NMe₂)NC(NMe₂)N(R)][−] (Ar = Ph or C₆H₃Pr₂^{−2,6}; R = SiMe₃ or H) [9b]. β -Diketiminates, especially [N(C₆H₃Pr₂^{−2,6})C(Me)₂CH][−] (\equiv [L¹][−]), have proved to be valuable spectator ligands due to their strong metal- κ^2 -ligand binding. Recent examples include [M(L¹){N(SiMe₃)₂}] (M = Mn, Fe, Co) [10a], [M(L¹)(μ -Me)₂] (M = Mn [10b], Fe [10c]), [Fe(L¹)₂(μ -S)] [10d], [Fe(L²)₂(μ -O)] [L² = {N(C₆H₃Pr₂^{−2,6})C(Bu^t)₂CH} [10e], [Ni(L¹)₂(μ - η^6 : η^6 -PhMe)] [10f], [Cu(L¹)(κ^2 -O₂)] [10g,10h], and [Pd(L³)(μ -Cl)₂] (L³ = {N(Ph)C(Me)₂CH} [10i].

2. Results and discussion

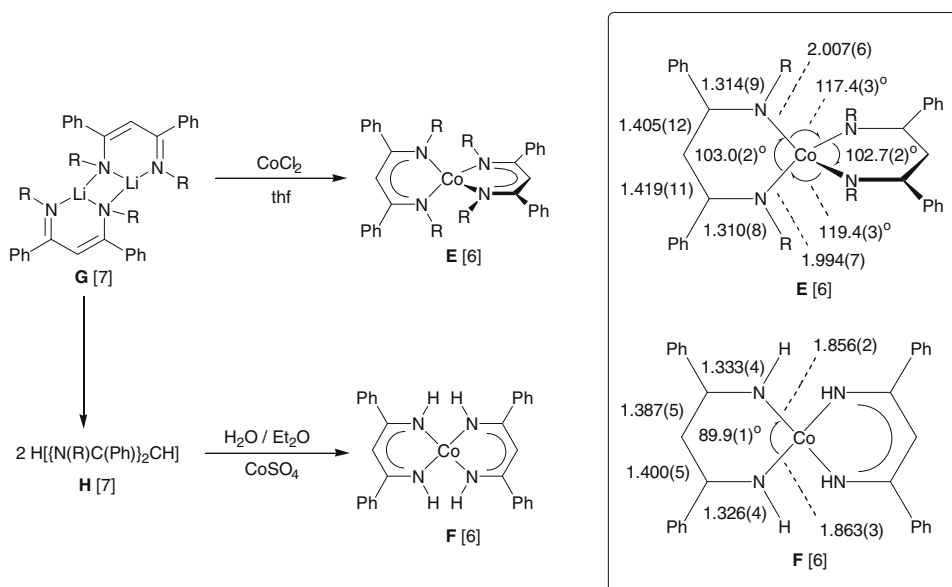
2.1. Introduction

In our recent review on metal β -diketiminates [11], we made brief mention of complexes of Mn(II), Fe(II), Ni(II), Cu(II) and Pd(II) using the ligand [N(R)C(Ph)₂CH] ([L]: R = SiMe₃ or [L']: R = H). This paper provides details of that chemistry.

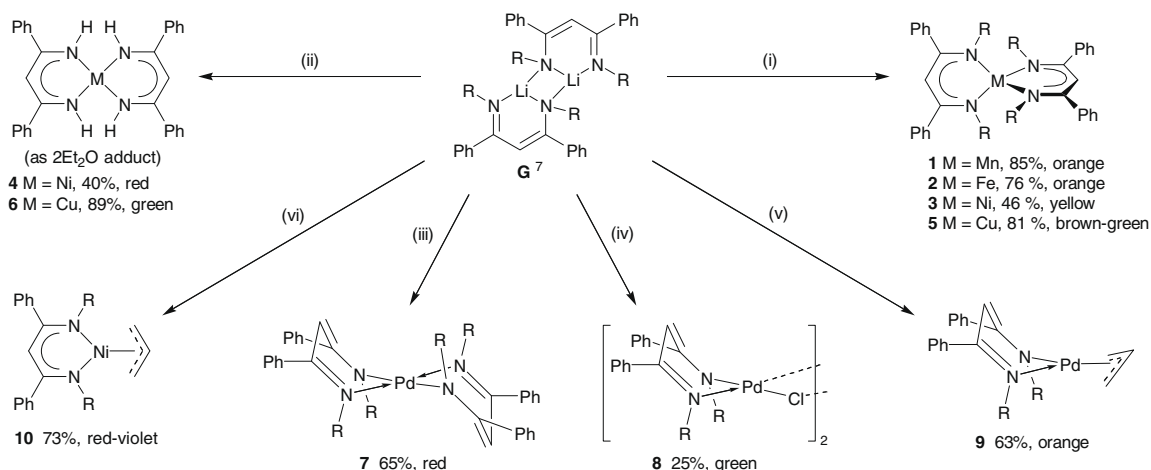
2.2. Synthesis and characterisation

Five types of crystalline late transition metal β -diketiminates have been synthesised. These are (i) the homoleptic crystalline quasi-tetrahedral, paramagnetic 3d⁵–3d⁹ metal(II) complexes [M(L)₂] (M = Mn (**1**), Fe (**2**), Ni (**3**) and Cu (**5**); for the cobalt complex **E**, see Scheme 2 [6]), (ii) the homoleptic quasi-square-planar diamagnetic 3d⁸ and paramagnetic 3d⁹ metal complexes [M(L')₂].2Et₂O (M = Ni (**4**) and Cu (**6**); for the 3d⁷ cobalt complex **F**, see Scheme 2 [6]), (iii) the bis(boat-shaped) diamagnetic 4d⁸ metal complex [Pd(L)₂] (**7**, planar at Pd), (iv) the heteroleptic diamagnetic d⁸ metal complexes [M(η^3 -C₃H₅)(L)] [M = Ni (**10**) and Pd (**9**)], and (v) the dinuclear complex [Pd(L)(μ -Cl)₂] (**8**). The metal β -diketiminates **2–10** were prepared from [Li(L)₂] (**G**)⁷ and an appropriate metal(II) salt; these reactions involved elimination of LiCl (for **1**, **2**, **4**, **5**, **7**, **8** and **9**), LiBr (for **3** and **10**) or Li₂SO₄ (for **6**) and additionally for **4** and **6** loss of (Me₃Si)₂O, as summarised in Scheme 3; thus, the NSiMe₃ \rightarrow NH hydrolysis proceeded under mild conditions. An alternative route to **6** is shown in Eq. (1). The cited yields were not optimised. It is interesting that [Pd{N(Ph)C(Me)₂CH}][Li] underwent ready hydrolysis yielding the β -ketoiminate [Pd{N(Ph)C(Me)C(H)C(Me)O}][Li] [12a].

The isolation (albeit in a low yield) of the heteroleptic Pd^{II} chloride **8** is noteworthy, as an attempted synthesis of an analogous compound using [Li{N(Pr^t)C(Me)₂CH}] and [Pd(cod)Cl₂] gave decomposition products along with a small amount of the homoleptic [Pd{N(Pr^t)C(Me)₂CH}][Li] [13]. Use of the *N,N*-diphenyl-substituted ligand L³ allowed the isolation of the heteroleptic complex [Pd(L³)(μ -Cl)₂], which proved to be a convenient precursor to other heteroleptic Pd^{II} compounds [10i,12b]. Analogues of the diamagnetic Ni complex **4** were prepared by reaction of hydrated

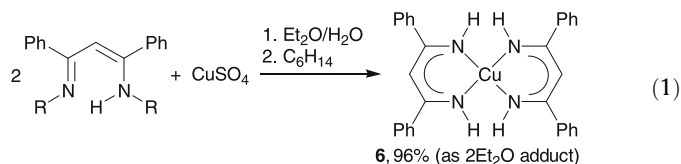


Scheme 2. Synthesis and selected geometric parameters for the crystalline cobalt(II) β -diketiminates **E** and **F** (R = SiMe₃) [6].



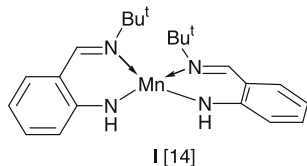
Scheme 3. Synthesis of **1–10**. *Reagents and conditions* (R = SiMe₃): (i), **1**: MnCl₂, thf, –78 °C → 20 °C, and crystn (CH₂Cl₂); **2**: FeCl₂(dme), thf, 20 °C, and crystn (PhMe); **5**: CuCl₂, Et₂O, –78 °C → 20 °C, and crystn (Et₂O); (ii), **4**: NiCl₂, thf, –78 °C → 20 °C, then chromatography (Al₂O₃ nH₂O/Et₂O), and crystn (Et₂O); **6**: CuSO₄, H₂O, C₆H₁₄, 20 °C, and crystn (Et₂O); (iii), [Pd(cod)Cl₂], Et₂O/thf, –78 °C → 20 °C, and crystn (PhMe); (iv) 2[Pd(cod)Cl₂], Et₂O/thf, 0 °C → 20 °C; (v) [[Pd(η³-C₃H₅)(μ-Cl)]₂], thf, 0 °C → 20 °C, and crystn (C₆H₁₄); (vi) [[Ni(η³-C₃H₅)(μ-Br)]₂], thf, 0 °C → 20 °C, and crystn (C₆H₁₄).

NiCl₂ with an appropriate lithium β-diketiminato [14a,14b]; the asymmetrically substituted [Ni{N(H)C(NC₅H₁₀-c)C(H)C(Bu^t)-N(H)}₂] showed moderate activity in ethene polymerisation [14b].



Each of the coloured compounds **1–10** was characterised by EImass spectra, which showed strong parent molecular ions, and satisfactory C, H, and N microanalyses for each except **3**, **7** and **8**. The nickel complexes **4** and **10** and the palladium compounds **7**, **8** and **9** were diamagnetic, and gave unexceptional ¹H and ¹³C{¹H} NMR spectra, while the signals for **3** were broadened and paramagnetically shifted. Compounds **4** and **6** showed sharp IR NH stretching modes at 3320 (**4**) and 3325 (**6**) cm⁻¹. Single crystal X-ray diffraction data were obtained for each of the crystalline complexes (*vide infra*), except **1**, **8** and **10**.

Magnetic moments of the paramagnetic complexes (except **3**) were measured on CDCl₃ solutions at 293 K, using Evans' NMR method. For the Mn complex **1**, the magnetic moment of 2.30 μ_B lies between the low-spin spin-only d⁵ value (1.73 μ_B) and the 2.7 μ_B recorded for the pseudo-tetrahedral manganese(II) complex **I** closely related to a β-diketiminato [15].



The magnetic moment of 5.06 μ_B for the Fe β-diketiminato **2** is appropriate for a high-spin d⁶ complex (*cf.* [16], 5.1–5.5 μ_B for tetrahedral Fe(II) species; spin-only value, 4.90 μ_B). The magnetic moments for the d⁹ Cu complexes **5** (1.98 μ_B) and **6** (1.89 μ_B) are similar to the range observed for [Cu{(N(R)C(Me))₂CH₂}], 1.86–1.94 μ_B [1].

2.3. Molecular structures of **2**, **3**, **4**, **5**, **6**, **7** and **9**

The molecular structures of the homoleptic metal(II) β-diketiminates [M{(N(R)C(Ph))₂CH₂}] [R = SiMe₃ and M = Fe (**2**), Ni (**3**),

Cu (**5**), or Pd (**7**); R = H and M = Ni (**4**) or Cu (**6**)] and the heteroleptic [Pd(η³-C₃H₅){(N(SiMe₃)C(Ph))₂CH}] (**9**) are illustrated in Figs. 1 (**2**), 2 (**3**), 3 (**5**), 4 (**4**), 5 (**6**), 6 (**7**), and 7 (**9**); selected geometric parameters are given in Tables 1–4. The six-membered metal-containing rings are planar in the 3d metal compounds, but shallow boat-shaped in the palladium β-diketiminates **7** and **9**. For the 3d metal complexes, the two six-membered rings, either tend to orthogonality (**2**, **3**, **5**) (*cf.* the dihedral angle at the metal M, which decreases in the sequence Fe > Ni > Cu, as shown in Table 2), illustrated for the nickel complex **3** in Fig. 2b, or coplanarity (**4**, **6**) as shown for the nickel complex **4** in Fig. 4b. The difference is attributed to steric effects. Thus, repulsion between the Me₃Si groups of one ring and those of the other is reduced when the metal environment is quasi-tetrahedral rather than planar (*cf.* for *N,N*-diphenyl substituted Ni compounds the change from the pseudo-tetrahedral to planar conformation would require *ca.* 96 kJ mol⁻¹ [8f]).

An alternative way of minimising such inter-ligand Me₃Si/SiMe₃ repulsions is by changing the conformation of the six-membered ring from planar (as in the 3d⁸ complex **3**) to the boat-shaped in the 4d⁸ complex **7** (*cf.* Fig. 6b); a similar outcome, avoiding excessive repulsions of bulky *N*-substituents, was found in [Pd{(N(C₆H₃Me₂-3,5)C(H))₂CCHO)}₂] [8b] and [Pd{(N(Pr^f)C(Me))₂CH₂}] [13].

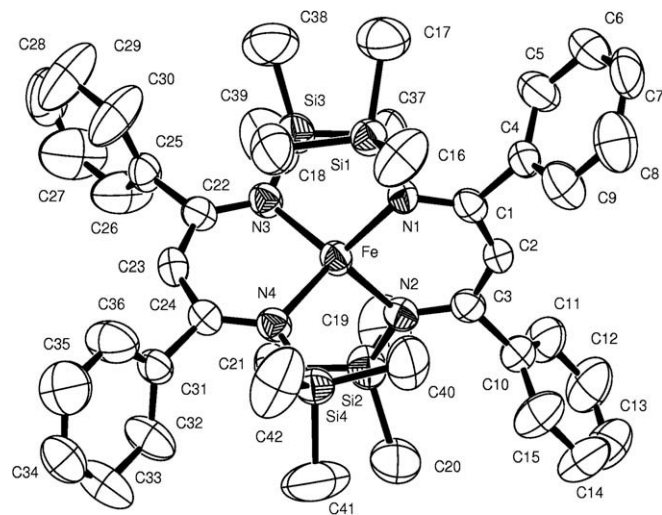


Fig. 1. Molecular structure of crystalline **2**.

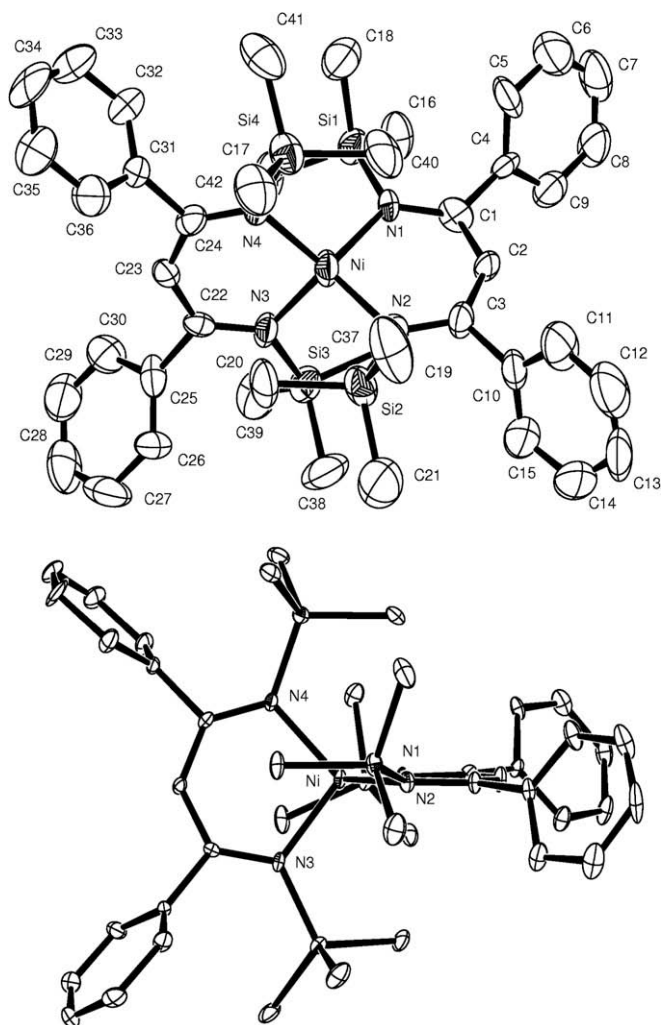


Fig. 2. (a) Molecular structure of crystalline **3** (top); and (b) an alternative ORTEP representation of **3** showing the distorted tetrahedral geometry at the Ni atom (bottom).

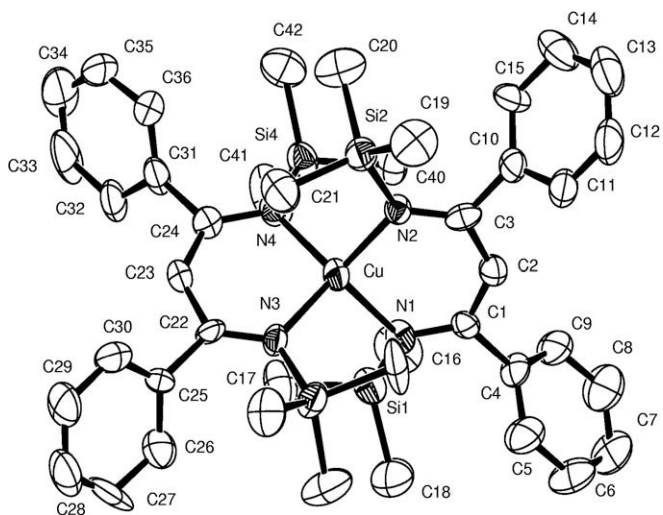


Fig. 3. Molecular structure of crystalline **5**.

We note that other tetrahedral paramagnetic $3d^8$ complexes are well documented but four-coordinate palladium(II) complexes normally have a planar environment at the metal; significant tetra-

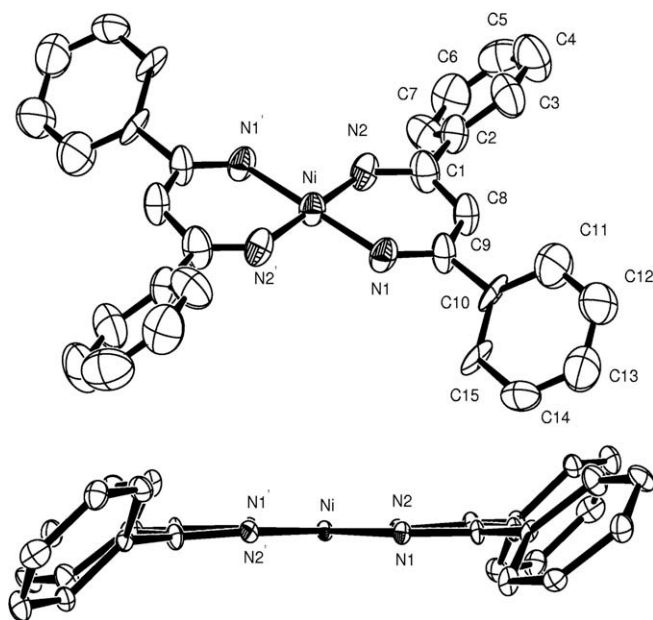


Fig. 4. (a) Molecular structure of crystalline **4** (top); and (b) an alternative ORTEP representation of **4** illustrating the geometry about the C8–Ni–C8' vector (bottom).

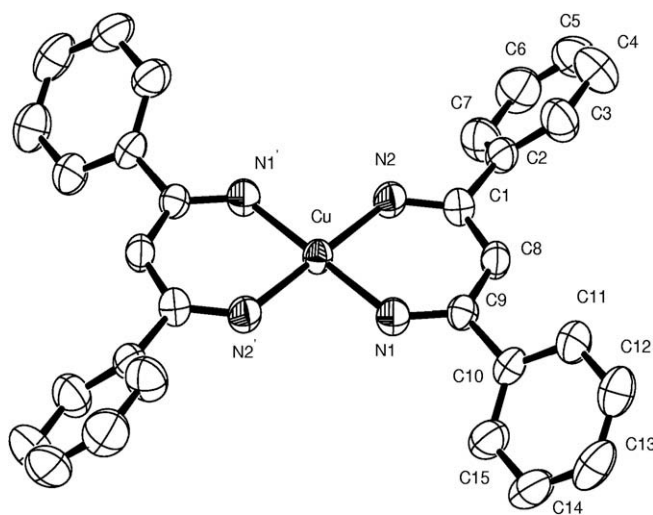


Fig. 5. Molecular structure of crystalline **6**; the torsion angle between (i) the CuN1C9C8C1N2 and the (C2–C7) planes and (ii) the (C2–C7) and the (C10–C15) planes: 45.9° (i) and 38.9° (ii).

hedral distortions were observed in sterically crowded compounds bearing substituted phosphazene [17a] or semicorrin [17b] ligands.

Endocyclic and selected exocyclic geometric parameters for each of the crystalline metal(II) β -diketiminates **2–7** and **9** are listed in Tables 1 and 2, respectively. The differences in MN bond lengths parallel those in four-coordinate M^{2+} ionic radii, with square-planar Ni^{2+} (0.49 Å) being notably smaller than tetrahedral (0.55 Å) [18]. The near identity within each pair of the endocyclic MN (a/a'), NC (b/b') and CC (c/c') bond lengths and MNC (β/β') and NCC (γ/γ') angles (Table 1) is consistent with there being π -delocalisation in each ligand's NCCCN backbone. Within the isoleptic series of N,N' -bis(trimethylsilyl) complexes **2** (Fe), **3** (Ni) and **5** (Cu), individual parameters are differentiated significantly only for the endocyclic CC bond lengths: Cu (**5**) > Ni (**3**) > Fe (**2**) (c and

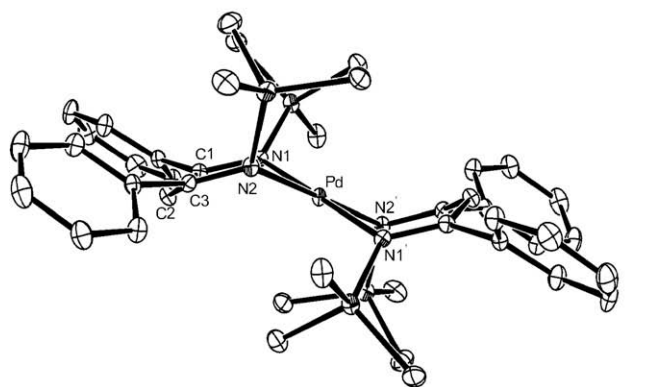
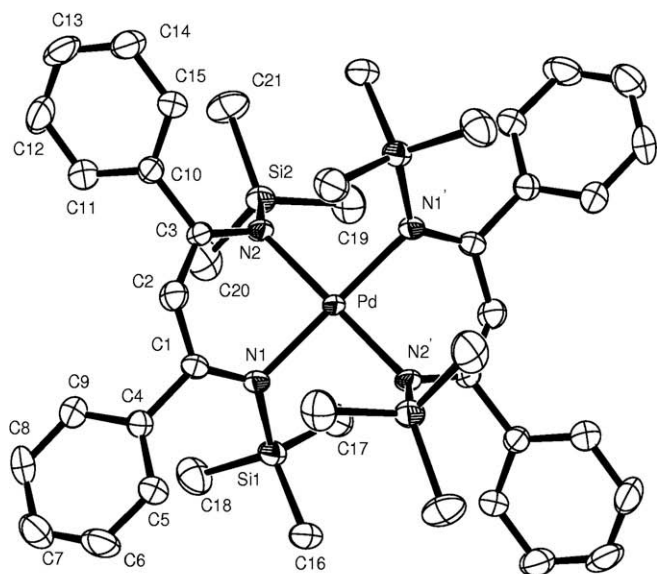


Fig. 6. (a) Molecular structure of crystalline **7**; and (b) an alternative ORTEP representation of crystalline **7**, emphasising its symmetry, planarity at the Pd atom and the boat-shaped PdNCCCN ring.

c' in Table 1). For the two compounds $[M\{(N(H)C(Ph))_2CH\}_2]$ [$M = Ni$ (**4**), Cu (**6**)], the following pairs differ significantly: the endocyclic MN [Cu (**6**) > Ni (**4**), a/a'] and CC [Ni (**4**) > Cu (**6**), b/b'] bond lengths and the MNC bond angle [Cu (**6**) > Ni (**4**), β/β'] (Table 1), and the exocyclic (Table 2) NCC [Ni (**4**) > Cu (**6**), γ/γ'] and CCC [Cu (**6**) > Ni (**4**), δ/δ'] bond angles. The effect of N,N' -substitution ($SiMe_3$ vs. H) for the two nickel complexes (**3** vs. **4**) and the pair of copper complexes (**5** vs. **6**) shows that the silyl complexes have significantly longer MN and NC bond lengths (a/a' and b/b' in Table 1) and narrower CCC bond angle (δ/δ' in Table 2). Dihedral angles relating to the phenyl groups and the endocyclic NCC plane are listed in Table 3.

Comparison of the β -diketiminatopalladium(II) ring(s) in the homoleptic compound **7** and the heteroleptic **9** reveals that significant differences appear in some of the bond angles. These are wider in **9** than **7** for the endocyclic PdNC (β/β' in Table 1) and the exocyclic (Table 2) SiNC (β/β') but narrower in **9** than **7** for the exocyclic PdNSi (α/α') and CCC (γ/γ'). The geometric features of **7** and **9** are broadly similar to those in $[Pd\{(N(Pr^i)C(Me))_2CH\}_2]$ and $[Pd(\eta^3-C_3H_5)\{(N(Pr^i)C(Me))_2CH\}]$, respectively [13]. Each of the Si atoms of **7** and **9** is further from its corresponding NCCCN plane (c and c' of Table 2) than is the case for **2**, **3** or **5**. The deviation of the *ipso*-carbon atom of each of the phenyl groups from the same plane (d and d' of Table 2) is greatest for **7** in comparison with **2**, **3**, **5** and **9**; in **4** and **9** these carbon atoms are essentially copla-

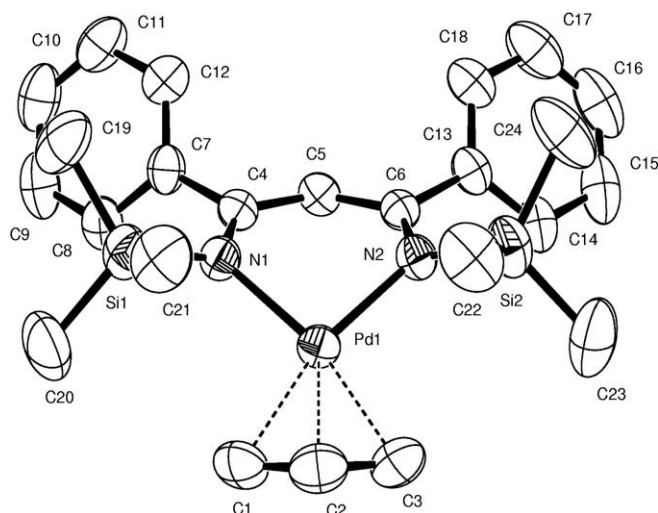


Fig. 7. Molecular structure of crystalline **9**.

nar with the appropriate NCCCN plane. Geometric parameters relating to the $Pd(\eta^3-C_3H_5)$ moiety of **9** are listed in Table 4.

2.4. Quantum chemical calculations

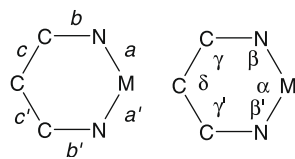
In an attempt to further understand the difference between the tetrahedral nickel complex **3** and the square-planar palladium analogue **7**, a series of quantum chemical calculations was undertaken on both structures and their corresponding geometries (Fig. 8). The square-planar and tetrahedral Ni- and Pd-complexes were fully optimised by the hybrid density functional B3LYP method [19] in combination with a triple-zeta valence basis set (def-TZVP) [20]. A 28 electron relativistic effective core potential (ECP) was used to describe the core electrons of palladium [21]. Each structure was verified as a true minimum in the potential energy surface by performing vibrational frequency calculations, also required for obtaining thermal corrections to the electronic energy. All calculations were carried out by TURBOMOLE version 5.10 [22]. Comparison between selected bond distances and angles for the X-ray structures and B3LYP calculated values for complexes **3** and **7** is shown in Table 5. Taking into account the possible presence of crystal packing effects the B3LYP data correspond quite well when compared to X-ray data for complexes **3** and **7**.

Values for the Gibbs free energy for the $[M\{(N(SiMe_3)C(Ph))_2CH\}_2]$ ($M = Ni$ or Pd) complexes were calculated for both tetrahedral and square-planar geometries over a range of temperatures (Table 6). The square-planar geometry was calculated to be more stable than the tetrahedral by *ca.* 60 and 100 kJ mol^{-1} for the nickel and palladium structures, respectively (Fig. 9). However, experimental work isolated only a tetrahedral geometry for the nickel complex **3**. One possible explanation is that a square-planar geometry is the global minimum for both nickel and palladium complexes, while the tetrahedral geometry is a distinct local minimum lying higher in energy. The two minima are separated by an activation barrier, and an energy α is required to overcome the barrier for conversion of the local minimum (tetrahedral) to the global minimum (square-planar). The existence of the tetrahedral geometry suggests that α is high; thus the tetrahedral complex is the kinetic product, although the square-planar isomer is thermodynamically preferred.

2.5. Conclusions

A series of crystalline Mn, Fe, Ni, Cu and Pd β -diketiminates **1**–**10** are reported. The X-ray crystallographic study of seven of the

Table 1
Endocyclic bond distances (*a–e*) (Å) and angles (α – δ) (°) in the M{(N(SiMe₃)C(Ph))₂CH} moieties of **2–7** and **9**; lettering corresponds to.

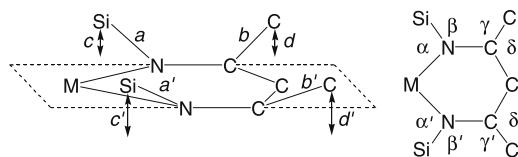


Parameters	2	3	4	5	6	7^a	9^b
<i>a</i>	2.027(4), 2.015(4)	1.979(8), 1.993(8)	1.888(11)	1.997(7), 1.976(8)	1.953(3)	2.065(4)	2.099(3)
<i>a'</i>	2.025(4), 2.020(4)	2.005(8), 2.011(7)	1.832(11)	1.998(7), 1.985(8)	1.937(3)	2.059(4)	2.088(3)
<i>b</i>	1.336(6), 1.344(6)	1.353(12), 1.331(11)	1.303(16)	1.353(11), 1.349(11)	1.311(5)	1.325(7)	1.320(4)
<i>b'</i>	1.343(6), 1.343(6)	1.362(12), 1.337(11)	1.281(17)	1.334(12), 1.315(11)	1.314(5)	1.333(7)	1.327(4)
<i>c</i>	1.336(6), 1.344(6)	1.364(14), 1.369(12)	1.409(18)	1.407(13), 1.433(12)	1.403(5)	1.414(8)	1.403(4)
<i>c'</i>	1.343(6), 1.343(6)	1.393(14), 1.391(12)	1.44(2)	1.412(12), 1.383(12)	1.390(5)	1.389(8)	1.395(5)
α	101.22(16), 100.54(16)	101.3(3), 100.3(3)	89.8(5)	101.2(3), 101.1(3)	89.14(14)	86.87(16)	92.07(11)
β	117.0(3), 116.5(3)	116.9(7), 117.5(6)	129.0(11)	118.1(6), 119.9(6)	130.1(3)	116.5(3)	116.9(2)
β'	117.9(3), 118.7(3)	117.8(7), 117.6(6)	134.3(11)	118.5(6), 122.8(7)	129.6(3)	114.9(3)	117.0(2)
γ	126.1(4), 124.9(5)	127.3(9), 126.9(9)	123.8(13)	125.2(8), 124.4(9)	122.6(4)	123.9(5)	126.4(3)
γ'	126.5(5), 125.7(5)	124.5(9), 126.3(9)	119.9(14)	125.4(9), 126.2(9)	123.8(4)	120.2(5)	126.2(3)
δ	132.5(5), 132.5(5)	132.0(9), 130.8(9)	122.3(12)	131.6(9), 130.8(9)	124.7(4)	122.7(5)	128.1(3)

^a Pd 1.12 Å and C2 0.11 Å out of plane.

^b Pd 0.73 Å and C5 0.11 Å out of plane.

Table 2
Selected bond distances (*a–d*) (Å), angles (α – δ) (°) and dihedral angles (°) at M for **2–7** and **9**; lettering corresponds to.



Parameters	2	3	4	5	6	7	9
<i>a</i>	1.775(4), 1.775(4)	1.733(9), 1.764(9)	–	1.777(8), 1.770(8)	–	1.774(5)	1.756(3)
<i>a'</i>	1.776(4), 1.770(4)	1.762(9), 1.767(8)	–	1.777(8), 1.770(8)	–	1.764(5)	1.748(3)
<i>b</i>	1.509(7), 1.501(7)	1.520(14), 1.515(12)	1.480(16)	1.512(14), 1.505(13)	1.499(6)	1.497(8)	1.502(5)
<i>b'</i>	1.508(7), 1.495(4)	1.506(15), 1.486(14)	1.487(16)	1.504(13), 1.478(12)	1.496(6)	1.509(7)	1.500(2)
<i>c</i>	0.13, –0.43	0.16, 0.27	–	0.28, 0.35	–	0.85	0.64
<i>c'</i>	0.10, –0.25	–0.395, –0.40	–	–0.51, –0.51	–	1.34	0.69
<i>d</i>	–0.10, –0.25	0.11, 0.23	–	0.05, 0.11	–	0.46	0.10
<i>d'</i>	0.23, 0.04	–0.19, –0.16	–	–0.11, –0.04	–	0.28	0.05
α	117.0(3), 118.4(3)	117.8(4), 116.9(4)	–	117.3(4), 116.5(4)	–	117.7(2)	115.74(14)
α'	116.5, 117.9(3)	117.0(5), 116.2(4)	–	118.5(6), 117.0(4)	–	118.9(2)	116.46(15)
β	124.7(3), 124.2(3)	125.3(7), 126.2(7)	–	122.2(6), 123.0(7)	–	124.9(4)	127.1(2)
β'	125.0(3), 124.7(3)	124.7(6), 123.8(7)	–	122.8(7), 124.6(6)	–	119.0(4)	126.4(2)
γ	120.5(5), 121.5(4)	119.3(9), 119.7(9)	119.0(13)	121.4(8), 122.9(8)	118.4(4)	120.2(5)	119.7(3)
γ'	119.4(5), 120.6(5)	119.5(8), 120.1(9)	123.2(15)	120.5(8), 120.8(8)	118.0(4)	120.8(5)	120.7(3)
δ	113.3(4), 113.5(4)	112.9(10), 113.8(9)	116.6(13)	112.7(8), 113.4(8)	118.2(4)	115.1(5)	113.8(3)
δ'	114.1(4), 113.7(4)	115.4(8), 114.1(9)	117.2(12)	113.8(9), 113.2(9)	118.6(4)	114.9(5)	113.1(3)
Dihedral angle at M	85.84(0.12)	78.45(0.29)	–	72.65(0.29)	–	–	–

complexes has shown that for the homoleptic compounds [M{(N(R)C(Ph))₂CH}₂] three distinct structural types exist: (i) pseudo-tetrahedral with planar MNCCCN rings [M = Fe (**2**), Ni (**3**), Cu (**5**) and R = SiMe₃], (ii) square-planar with planar MNCCCN rings [M = Ni (**4**), Cu (**6**) and R = H], and (iii) square-planar with boat-shaped MNCCCN rings [M = Pd (**7**) and R = SiMe₃]. The boat-shaped β -diketiminatopalladium ring was also found in the heteroleptic Pd allyl complex **9** showing that such a conformation is generally preferred in β -diketiminatopalladium compounds (a similar geometry was observed in the majority of previously reported Pd^{II} β -diketiminates [8b,10i,12,13]).

3. Experimental

3.1. General remarks

All manipulations were carried out under argon, using standard Schlenk and vacuum line techniques. Solvents were pre-dried over P₂O₅ (CH₂Cl₂, CHCl₃) or sodium wire, distilled from drying agents (light petroleum, Na/K alloy; diethyl ether and thf, Na/benzophenone) and stored under argon over molecular sieves (4 Å) or potassium mirrors. All solvents were freeze/thaw degassed prior to use. Deuterated solvents were likewise stored over such molecular

Table 3

Dihedral angles (°) between the C(*ortho*)C(*ipso*)C(*ortho*) and the endocyclic NCC planes of **2–7** and **9**.

Compound	Dihedral angles (°)
2	87.8, 80.7, 86.9, 68.6
3	71.1, 64.8, 73.3, 64.0
4	47.8, 41.1
5	69.9, 61.3, 66.1, 61.0
6	46.2, 39.5
7	58.0, 50.8
9	56.2, 53.4

Table 4

Selected bond lengths (Å) and angles (°) for **9** (see also Tables 1 and 2).

Bond lengths		Bond angles	
C1–C2	1.366(7)	N1–Pd–C1	99.89(16)
C2–C3	1.384(7)	N1–Pd–C2	133.31(16)
Pd–C1	2.151(4)	N1–Pd–C3	165.76(18)
Pd–C2	2.121(4)	N2–Pd–C1	165.39(17)
Pd–C3	2.138(5)	N2–Pd–C2	133.64(16)
		N2–Pd–C3	99.49(17)
		C1–Pd–C2	37.28(18)
		C1–Pd–C3	67.5(2)
		C2–Pd–C3	37.92(19)
		C1–C2–C3	120.2(5)

sieves and degassed prior to use. Compounds [NiBr₂(dme)] [23], [(Ni(η³-C₃H₅)(μ-Br))₂] [24], [PdCl₂(cod)] [25], [(Pd(η³-C₃H₅)(μ-Cl))₂] [26] and [Li{(N(R)C(Ph))₂CH}]₂ [1] were synthesised according to published procedures. The compounds MCl₂ (M = Mn, Fe, Ni, Cu) and CuSO₄ were commercial samples, which were dried before use.

The NMR spectra were recorded in C₆D₆ or CDCl₃ at 298 K using a Bruker DPX 300 instrument (¹H, 300.1; ¹³C 75.5 MHz) and referenced to residual ¹H and ¹³C solvent resonances. The magnetic moments were determined by Evans' method [27] at ambient temperature and diamagnetic corrections were made. IR spectra were recorded as nujol mulls on a Perkin-Elmer 1720 FT instrument. Electron impact mass spectra ([M]⁺ represents the parent molecular ion) were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries. Elemental analyses (except for **3** and **8**; samples were not submitted) were determined by Medac Ltd., Brunel University.

3.2. [Mn{(N(SiMe₃)C(Ph))₂CH}]₂ (**1**)

A solution of [(Li{N(SiMe₃)C(Ph))₂CH}]₂ (2.0 g, 2.7 mmol) in thf (ca. 15 cm³) was slowly added over a period of 30 min to a stirred suspension of MnCl₂ (0.34 g, 2.7 mmol, previously dried *in vacuo* at 140 °C for 4 h) in thf (ca. 10 cm³) at –78 °C. The suspension was allowed to warm to room temperature and was stirred for 16 h, a dark red solution being obtained. Tetrahydrofuran was removed *in vacuo* and the resultant brown oily solid was heated *in vacuo* at 75 °C for 3 h. The residue was washed with light petroleum (b.p. 60–80 °C, ca. 10 cm³), then extracted with CH₂Cl₂ (ca. 20 cm³). The bright red-orange extract was filtered and the filtrate concentrated *in vacuo* to ca. 1/3 and cooled to –30 °C affording bright orange crystals of complex **1** (1.85 g, 88%). Anal. Calc. for C₄₂H₅₈MnN₄Si₄ requires: C, 64.2; H, 7.44; N, 7.13. Found: C, 63.8; H, 7.37; N, 7.01%. M.p. 221–224 °C, μ_{eff} 2.30 μ_B. MS, *m/z* (% assignment): 785 (61, [M]⁺), 420 (92, [M–L]⁺), 365 (18, [L]⁺).

3.3. [Fe{(N(SiMe₃)C(Ph))₂CH}]₂ (**2**)

A solution of [(Li{N(SiMe₃)C(Ph))₂CH}]₂ (1.2 g, 1.6 mmol) in thf (ca. 20 cm³) was slowly added over a period of 20 min to a stirred suspension of FeCl₂ (0.21 g, 1.6 mmol, previously dried *in vacuo* at 160 °C for 4 h) in thf (ca. 15 cm³) at 40 °C. The suspension was allowed to warm to room temperature and was stirred for 4 h until no solid remained, a dark red solution being obtained. Tetrahydrofuran was removed *in vacuo* and the resultant dark red solid was heated *in vacuo* at 75–80 °C for 3 h. The residue was washed with light petroleum (b.p. 30–40 °C, ca. 10 cm³), then extracted with CH₂Cl₂ (ca. 20 cm³). The bright ruby extract was filtered and the filtrate concentrated *in vacuo* to ca. 10 cm³ and cooled to –30 °C affording bright orange crystals of complex **2** (0.96 g, 76%). Anal. Calc. for C₄₂H₅₈FeN₄Si₄ requires: C, 64.2; H, 7.44; N, 7.13. Found: C, 64.3; H, 7.66; N, 6.87%. M.p. 167–169 °C, μ_{eff} 5.06 μ_B. MS, *m/z* (% assignment): 786 (100, [M]⁺), 421 (60, [M–L]⁺), 365 (16, [L]⁺). Single crystals suitable for X-ray diffraction study were obtained by slow evaporation *in vacuo* of a toluene solution.

3.4. [Ni{(N(SiMe₃)C(Ph))₂CH}]₂ (**3**)

A solution of [(Li{N(SiMe₃)C(Ph))₂CH}]₂ (1.57 g, 2.11 mmol) was added to a stirred suspension of [NiBr₂(dme)] (1.30 g, 4.21 mmol) in thf (50 cm³) at room temperature; stirring was continued overnight. Volatiles were removed *in vacuo* and the residue "stripped" (this procedure refers to adding the solvent then removing it *in vacuo*) with diethyl ether (2 × 20 cm³) and the resultant yellow/

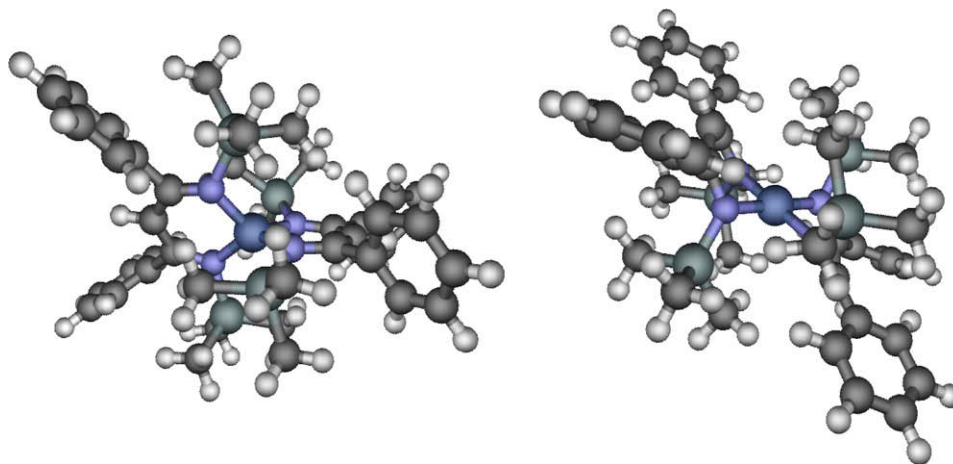
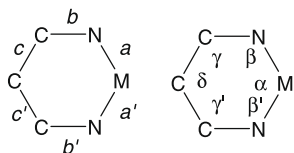


Fig. 8. (a) B3LYP generated structure for complex **3** (left); and (b) the hypothetical square-planar structure (right).

Table 5

Endocyclic bond distances (\AA) and angles ($^\circ$) from X-ray crystallography and B3LYP calculations in the $M(\{N(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH})_2$ moieties of **3** and **7**; lettering corresponds to.



Parameters	3 (X-ray)	3 (B3LYP)	7 (X-ray) ^a	7 (B3LYP) ^b
<i>a</i>	1.979(8), 1.993(8)	1.993	2.065(4)	2.122
<i>a'</i>	2.005(8), 2.011(7)	1.996	2.059(4)	2.114
<i>b</i>	1.353(12), 1.331(11)	1.333	1.325(7)	1.327
<i>b'</i>	1.362(12), 1.337(11)	1.326	1.333(7)	1.335
<i>c</i>	1.364(14), 1.369(12)	1.399	1.414(8)	1.414
<i>c'</i>	1.393(14), 1.391(12)	1.408	1.389(8)	1.403
α	101.3(3), 100.3(3)	98.3	86.87(16)	85.4
β	116.9(7), 117.5(6)	120.1	116.5(3)	114.6
β'	117.8(7), 117.6(6)	120.6	114.9(3)	113.7
γ	127.3(9), 126.9(9)	126.0	123.9(5)	124.4
γ'	124.5(9), 126.3(9)	125.5	120.2(5)	124.9
δ	132.0(9), 130.8(9)	129.3	122.7(5)	123.5

^a Pd 1.12 Å and C2 0.11 Å out of plane.

^b Pd 1.13 Å and C2 0.2 Å out of plane.

Table 6

B3LYP calculated values for the Gibbs free energy of tetrahedral and square-planar complexes $M(\{N(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH})_2$ over a range of temperatures.

<i>T</i> (K)	Gibbs free energy (a.u.)			
	M = Ni		M = Pd	
	Planar	Tetrahedral (3)	Planar (7)	Tetrahedral
98.15	-4519.270127	-4519.247989	-3138.842655	-3138.806598
198.15	-4519.302628	-4519.280188	-3138.876134	-3138.838878
298.15	-4519.348847	-4519.325993	-3138.923306	-3138.884800
398.15	-4519.407499	-4519.384241	-3138.982964	-3138.943189
498.15	-4519.477867	-4519.454208	-3139.054352	-3139.013305

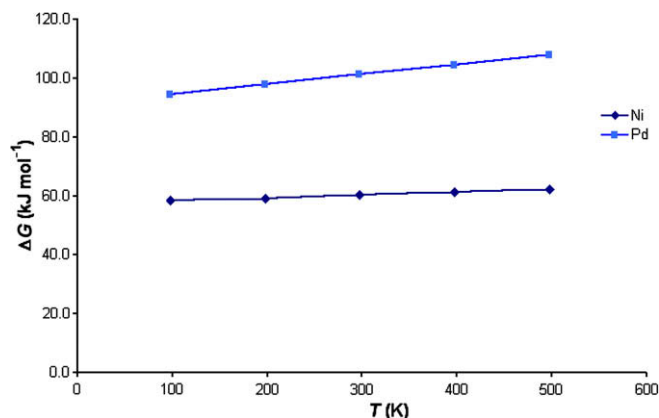


Fig. 9. Stabilities of the Ni (♦) and Pd (■) tetrahedral complexes with respect to the square-planar ones as a function of temperature.

brown solid was dissolved in refluxing hexane, filtered from a yellow precipitate and cooled to -30°C to afford a dark yellow/brown solid (1.52 g, 46%). Crystals of **3**, m.p. $250\text{--}252^\circ\text{C}$, suitable for X-ray analysis, were obtained from toluene. ^1H NMR (C_6D_6): δ 5.82 (s br, 2 H), 5.94 (s br, 4 H), 6.61 (s br, 3 H), 12.15 ppm (s br, $\text{Si}(\text{CH}_3)_3$), 18 H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): δ -6.3, 123.9, 126.2, 128.3, 140.3 ($\text{Si}(\text{CH}_3)_3$) and 267.3 ppm. MS, *m/z* (% assignment): 788 (5, $[\text{M}]^+$); 423 (4, $[\text{M}-\text{L}]^+$); 365 (10, $[\text{L}]^+$).

3.5. $[\text{Ni}(\{N(\text{H})\text{C}(\text{Ph})\}_2\text{CH})_2] 2\text{Et}_2\text{O}$ (**4**)

A solution of $[(\text{Li}\{N(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH})_2]$ (2.0 g, 2.7 mmol) in thf (*ca.* 20 cm^3) was slowly added to a stirred suspension of NiCl_2 (0.35 g, 2.7 mmol) in thf (*ca.* 10 cm^3) at -78°C . The suspension was allowed to warm to room temperature and was stirred for 16 h, a black solution being obtained. Tetrahydrofuran was removed *in vacuo* and the resultant oil was heated at $70\text{--}80^\circ\text{C}$. The residue was then stripped twice with light petroleum (b.p. $30\text{--}40^\circ\text{C}$, *ca.* 20 cm^3) to afford a glassy solid, which was extracted with Et_2O and the extract was passed down a chromatography column packed with alumina (5% H_2O). The diethyl ether was removed from the eluent *in vacuo* to afford the bright red solid **4** (0.51 g, 40%). Anal. Calc. for $\text{C}_{38}\text{H}_{46}\text{N}_4\text{NiO}_2$ requires: C, 71.3; H, 5.15; N, 11.1. Found: C, 71.4; H, 5.20; N, 10.9%. M.p. $<230^\circ\text{C}$ (decomp.). ^1H NMR (CDCl_3): δ 1.20 (t, 12 H, CH_2CH_3), 3.47 (q, 8 H, CH_2CH_3), 4.34 (s, 4 H, NH), 5.27 (s, 2 H, CH), 7.37–7.50 ppm (m, 20 H, C_6H_5); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 113.3 (s, CH), 128–132 ppm (m, C_6H_5). MS, *m/z* (% assignment): 500 (48, $[\text{M}]^+$), 279 (35, $[\text{M}-\text{L}]^+$). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a diethyl ether solution.

3.6. $[\text{Cu}(\{N(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH})_2]$ (**5**)

A solution of $[(\text{Li}\{N(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH})_2]$ (2.5 g, 3.36 mmol) in Et_2O (20 cm^3) was slowly added to a stirred suspension of CuCl_2 (0.44 g, 3.36 mmol, previously dried *in vacuo* at 120°C for 4 h) in Et_2O (10 cm^3) at -78°C . The suspension was allowed to warm to room temperature and was stirred for a further 3 h. The dark green mixture was filtered. The solvent was then removed from the filtrate *in vacuo* to afford a dark green solid, which was washed with light petroleum (b.p. $60\text{--}80^\circ\text{C}$, *ca.* 10 cm^3) and crystallised from Et_2O (20 cm^3) by slowly concentrating to *ca.* 5 cm^3 over a period of 4 h. Dark brown-green single crystals of **5** (2.13 g, 81%). Anal. Calc. for $\text{C}_{42}\text{H}_{58}\text{CuN}_4\text{Si}_4$ requires: C, 63.5; H, 7.30; N, 7.05. Found: C, 62.8; H, 7.20; N, 7.09%. μ_{eff} 1.98 μ_{B} , m.p. $254\text{--}256^\circ\text{C}$, were obtained. MS, *m/z* (% assignment): 793 (57, $[\text{M}]^+$), 428 (51, $[\text{M}-\text{L}]^+$), 365 (21, $[\text{L}]^+$).

3.7. $[\text{Cu}(\{N(\text{H})\text{C}(\text{Ph})\}_2\text{CH})_2] 2\text{Et}_2\text{O}$ (**6**)

(a) Distilled deoxygenated water (*ca.* 10 cm^3) and light petroleum (b.p. $60\text{--}80^\circ\text{C}$, 20 cm^3) were added to $[(\text{Li}\{N(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH})_2]$ (1.4 g, 1.90 mmol). The mixture was stirred until all the solid had dissolved. CuSO_4 (0.3 g, 1.90 mmol) was added and the mixture was stirred at room temperature for 10 h. The product at the junction of the two phases was collected and dried *in vacuo* to give the light green complex **6** (1.34 g, 89%). Anal. Calc. for $\text{C}_{38}\text{H}_{46}\text{CuN}_4\text{O}_2$ requires: C, 71.2; H, 5.18; N, 11.1. Found: C, 70.9; H, 5.18; N, 10.9%. M.p. $<260^\circ\text{C}$ (decomp.), μ_{eff} 1.89 μ_{B} . MS, *m/z* (% assignment): 505 (58, $[\text{M}]^+$), 284 (51, $[\text{M}-\text{L}]^+$). Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a diethyl ether solution.

(b) A solution of $[\text{H}\{N(\text{H})\text{C}(\text{Ph})\}_2\text{CH}]$ (2.0 g, 20 mmol) in Et_2O (*ca.* 50 cm^3) was added to a suspension of CuSO_4 (1.63 g, 10 mmol) in distilled deoxygenated water (*ca.* 5 cm^3). The mixture was stirred at room temperature for 18 h and the light green solid product at the junction of the two phases was collected, washed with light petroleum (b.p. $60\text{--}80^\circ\text{C}$, *ca.* 20 cm^3) and crystallised from diethyl ether to give complex **6** (3.9 g, 96%).

3.8. $[\text{Pd}(\{N(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH})_2]$ (**7**)

A solution of $[(\text{Li}\{N(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH})_2]$ (1.83 g, 2.46 mmol) in diethyl ether (100 cm^3) was slowly added to $[\text{PdCl}_2(\text{cod})]$ (0.70 g, 2.45 mmol) suspended in thf (*ca.* 40 cm^3) at -78°C . The suspen-

Table 7

Crystal data and refinement details for compounds 2–7 and 9.

	2	3	4	5	6	7	9
Empirical formula	C ₄₂ H ₅₈ FeN ₄ Si ₄	C ₄₂ H ₅₈ N ₄ NiSi ₄	C ₃₀ H ₂₆ N ₄ Ni 2(C ₄ H ₁₀ O)	C ₄₂ H ₅₈ CuN ₄ Si ₄	C ₃₀ H ₂₆ CuN ₄ 2(C ₄ H ₁₀ O)	C ₄₂ H ₅₈ N ₄ PdSi ₄	C ₂₄ H ₃₄ N ₂ PdSi ₂
<i>M</i>	787.13	789.99	649.50	794.82	654.33	837.68	513.11
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	P $\bar{1}$ (No. 2)	P2 ₁ /n (No. 14)	Pbca (No. 61)	P2 ₁ /n (No. 14)	Pbca (No. 61)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)
<i>a</i> (Å)	12.346(3)	12.788(12)	11.264(6)	12.814(3)	11.168(5)	9.816(5)	12.818(4)
<i>b</i> (Å)	13.222(2)	17.482(8)	17.225(15)	17.491(4)	17.299(4)	11.087(4)	12.436(4)
<i>c</i> (Å)	14.370(3)	20.623(9)	18.337(16)	20.599(5)	18.675(6)	11.995(4)	18.731(6)
α (°)	80.75(2)	90	90	90	90	115.63(3)	79.85(2)
β (°)	77.48(2)	104.23(6)	90	104.21(2)	90	113.10(3)	83.32(3)
γ (°)	83.84(2)	90	90	90	90	89.89(3)	69.01(2)
<i>U</i> (Å ³)	2253.8(8)	4469(5)	3558(5)	4475.6(18)	3608(2)	1060.2(8)	2603.3(15)
<i>Z</i>	2	4	4	4	4	1	4
<i>F</i> (000)	840	1688	1384	1692	1388	440	1064
μ (Mo K α) (mm ⁻¹)	0.47	0.57	0.58	0.63	0.64	0.59	0.82
Unique reflections, [R _{int}]	5483	5474, 0.115	2064	7849	5238	2600	15140
Reflections with $ I > 2\sigma(I)$	3547	2284	717	3216	1975	2134	9758
<i>R</i> ₁ [$ I > 2\sigma(I)$]	0.054	0.083	0.094	0.107	0.073	0.047	0.049
<i>wR</i> ₂ [$ I > 2\sigma(I)$]	0.105	0.148	0.197	0.228	0.131	0.103	0.100
<i>R</i> _{int} (all data) <i>R</i> ₁ , <i>wR</i> ₂	0.105, 0.125	0.213, 0.201	0.265, 0.283	0.256, 0.292	0.218, 0.181	0.065, 0.111	0.091, 0.117

sion was allowed to warm to room temperature and was stirred for a further 12 h, a deep red suspension being obtained. The mixture was filtered and the residual red brick solid was washed with diethyl ether (15 cm³) and pentane (15 cm³) and dried *in vacuo*; crystals of **7** (1.33 g, 65%). Anal. calc. for C₄₂H₅₈N₄PdSi₄ requires: C, 60.2; H, 6.98; N, 6.68. Found: C, 52.9; H, 6.41; N, 6.52%. M.p. 172–173 °C decomp., were isolated. ¹H NMR (CDCl₃): δ 0.23 (s, Si(CH₃)₃, 36 H), 5.86 (s, CH, 2 H), 7.30–7.38 (m, Ph, 12 H), 7.54–7.58 ppm (m, Ph, 8 H). ¹³C{¹H} NMR (CDCl₃): δ 4.7 (s, Si(CH₃)₃), 121.2 (s, CH), 127.6 (s, Ph, *o*- or *m*-CH), 129.3 (s, Ph, *p*-CH), 130.0 (s, Ph, *o*- or *m*-CH), 141.5 (s, Ph, C_{ipso}) and 175.1 ppm (s, CN). MS, *m/z* (% assignment): 836 (5, [M]⁺); 471 (12, [M–L]⁺); 365 (8, [L]⁺). Crystals of **7** suitable for X-ray analysis were obtained from toluene.

3.9. [Pd{(N(SiMe₃)C(Ph))₂CH}(μ-Cl)]₂ (**8**)

A solution of [Li{(N(SiMe₃)C(Ph))₂CH}]₂ (0.54 g, 0.73 mmol) in diethyl ether (25 cm³) was added to a suspension of [PdCl₂(cod)] (0.41 g, 1.44 mmol) in thf (20 cm³) at 0 °C. The resulting deep purple mixture was stirred for 30 min. The solvent was removed *in vacuo*, the residue “stripped” with diethyl ether (20 cm³) and then dissolved in diethyl ether (2 × 20 cm³). Filtration from a dark precipitate followed by evaporation of the volatiles from the filtrate yielded the deep green solid **8** which was washed with hexane and dried *in vacuo* (0.18 g, 25%), mp. 219–222 °C. ¹H NMR (C₆D₆): δ 0.58 (s, Si(CH₃)₃, 36 H), 5.60 (s, CH, 2 H), 7.01 (br m, Ph, 12 H), 7.45 ppm (br m, Ph, 8 H). ¹³C{¹H} NMR (C₆D₆): δ 6.1 (s, Si(CH₃)₃), 119.4 (s, CH), 126.6, 128.0, 129.9 (s, Ph, *o*-, *m*- and *p*-CH), 139.2 (s, Ph, C_{ipso}) and 172.3 ppm (s, CN). MS, *m/z* (% assignment): 1012 (3, [M]⁺); 836 (5, [PdL₂]⁺); 690 (19, [PdL₂–2SiMe₃]⁺); 365 (8, [L]⁺).

3.10. [Pd{η³-C₃H₅}{(N(SiMe₃)C(Ph))₂CH}] (**9**)

[Li{(N(SiMe₃)C(Ph))₂CH}]₂ (0.28 g, 0.38 mmol) in tetrahydrofuran (20 cm³) was added dropwise to a solution of [Pd(η³-C₃H₅)(μ-Cl)]₂ (0.14 g, 0.38 mmol) in tetrahydrofuran (20 cm³) at 0 °C. The resulting orange mixture was stirred for ca. 30 min. and allowed to warm to room temperature. The solvent was removed *in vacuo*, the residue “stripped” with hexane (2 × 10 cm³) and then dissolved in hexane (10 cm³). Filtration from a white precipitate followed by concentration of the filtrate to ca. 3–4 cm³ and cooling to –30 °C yielded orange crystals of **9** (0.23 g, 63%). Anal. Calc. for C₂₄H₃₄N₂PdSi₂ requires: C, 56.2; H, 6.68; N, 5.46). Found: C, 56.0; H,

6.70; N, 5.44%. M.p. 90–92 °C. ¹H NMR (C₆D₆): δ 0.01 (s, Si(CH₃)₃, 18 H), 2.35 (d, ³J_{HH} = 12.3, CH₂CHCH₂, 2 H), 3.49 (d, ³J_{HH} = 7.0, CH₂CHCH₂, 2 H), 4.90 (tt, ³J_{HH} = 12.3 and 7.0 Hz, CH₂CHCH₂, 1 H), 5.56 (s, CH, 1 H), 7.05–7.10 (m, Ph, 6 H), 7.55–7.60 ppm (m, Ph, 4 H). ¹³C{¹H} NMR (C₆D₆): δ 5.1 (s, Si(CH₃)₃), 55.4 (s, CH₂CHCH₂), 111.5 and 112.3 (s, CH₂CHCH₂ and CH), 126.3 (s, Ph, *p*-CH), 128.2 (s, Ph, *o*- or *m*-CH), 129.1 (s, Ph, *o*- or *m*-CH), 145.9 (s, Ph, C_{ipso}) and 172.0 ppm (s, CN). MS, *m/z* (% assignment): 512 (11, [M]⁺); 471 (47, [M–C₃H₅]⁺); 365 (69, [L]⁺).

3.11. [Ni{η³-C₃H₅}{(N(SiMe₃)C(Ph))₂CH}] (**10**)

[Li{(N(SiMe₃)C(Ph))₂CH}]₂ (0.63 g, 0.85 mmol) in tetrahydrofuran (ca. 10 cm³) was added slowly to a solution of [Ni(η³-C₃H₅)(μ-Br)]₂ (0.31 g, 0.86 mmol) in tetrahydrofuran (ca. 15 cm³) at 0 °C. The mixture was allowed to warm to room temperature and stirred for a further 2 h, a deep purple solution being obtained. Tetrahydrofuran was removed *in vacuo* and the residue was “stripped” with hexane (2 × 20 cm³) and then extracted into hexane. The extract was filtered. The filtrate was concentrated to ca. 5 cm³ and cooled to –30 °C, yielding deep red-violet crystals (0.38 g). A second crop of crystals of **10** was obtained from the mother liquor (0.35 g, combined yield 73%). Anal. Calc. for C₂₄H₃₄N₂NiSi₂ requires: C, 61.9; H, 7.36; N, 6.02). Found: C, 60.2; H, 7.16; N, 5.97%. M.p. 89–92 °C. ¹H NMR (C₆D₆): δ 0.15 (s, Si(CH₃)₃, 18 H), 1.59 (d, ³J_{HH} = 15.8, CH₂CHCH₂, 2 H), 2.73 (d, ³J_{HH} = 8.5, CH₂CHCH₂, 2 H), 5.1 (pent, ³J_{HH} = 7.9 Hz, CH₂CHCH₂, 1 H), 6.04 (s, CH, 1 H), 7.07–7.10 (m, Ph, 6 H), 7.51–7.54 ppm (m, Ph, 4 H). ¹³C{¹H} NMR (C₆D₆): δ 5.5 (s, Si(CH₃)₃), 49.6 (s, CH₂CHCH₂), 106.1 and 112.3 (s, CH₂CHCH₂), 116.7 (s, CH), 125.8 (s, Ph, *o*- or *m*-CH), 128.6 (s, Ph, *p*-CH), 128.9 (s, Ph, *o*- or *m*-CH), 144.9 (s, Ph, C_{ipso}) and 172.0 ppm (s, CN). MS, *m/z* (% assignment): 464 (28, [M]⁺); 423 (53, [M–C₃H₅]⁺); 365 (7, [L]⁺).

3.12. Crystal data and refinement details for 2, 3, 4, 5, 6, 7 and 9

Diffraction data were collected on a Enraf Nonius CAD-4 or for **4** a Nonius Kappa CCD diffractometer using monochromated radiation, λ 0.71073 Å, at 293(2) K. Crystals were mounted under argon into Lindemann capillaries and then sealed.

For **9** there were two independent molecules in the asymmetric unit, one of which had the allyl groups disordered “up” or “down”. Absorption corrections, other than for **4** or **6**, were applied using psi-scans. Drawings are ORTEP-3 for Windows, with 50% ellipsoids (hydrogen atoms are omitted for clarity). Structures were refined

on all F^2 with H atoms in riding mode, using SHELXL-97 [28]. Further details are in Table 7.

Acknowledgements

We are grateful to EPSRC and SPECS and BioSPECS BV for a CASE award for J.R.S. and the European Commission for the award to R.S. of a Marie Curie Fellowship. We thank Dr. A.V. Protchenko for useful discussions and assistance in the final preparation of the manuscript.

Appendix A. Supplementary material

CCDC 695618, 695619, 695620, 695621, 695622, 695623 and 695624 contain the supplementary crystallographic data for **2–7** and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.11.045](https://doi.org/10.1016/j.jorganchem.2008.11.045).

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