

# Synthesis and structural characterisation of an yttrium–alkyl–alkylidene†‡

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**The first structurally authenticated yttrium-alkyl-alkylidene is reported; structural, spectroscopic, and theoretical analyses show that whilst the yttrium-alkylidene bond is short, it possesses a bond order less than one and is comparable to the Y–C<sub>alkyl</sub> single bond within the same molecule.**

Transition metal alkylidene/carbene complexes are extremely important due to fundamental issues regarding their structure and bonding (Schrock-type *vs.* Fischer), and their implicit roles in key synthetic transformations such as olefin metathesis,<sup>1</sup> cyclopropanations,<sup>2</sup> Wittig-type reactions,<sup>3</sup> and Fischer–Tropsch processes.<sup>4</sup> However, whilst mid- and late-transition metal–alkylidenes are now well studied,<sup>5</sup> and early-transition metal–alkylidenes have grown greatly in number recently,<sup>6</sup> lanthanide–alkylidenes remain scarce.<sup>7</sup>§

Schumann and Müller first reported lanthanide–alkyl–alkylidene complexes formulated as neutral [Er(CHSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)] and anionic [Lu(CHSiMe<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)] [Li(tmeda)<sub>2</sub>] in 1979, but an absence of structural data renders the extent of oligomerisation, and nature of the bonding of the alkylidene centres, in these compounds unknown.<sup>8</sup> Subsequently, Cavell *et al.* reported a lanthanide–amide–alkylidene complex [Sm{C(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>}(NCY<sub>2</sub>)(THF)],<sup>9</sup> and recently Le Floch, Mézailles, and Nief have reported the neutral lanthanide–halide–alkylidene complexes [Ln{C(PPh<sub>2</sub>S)<sub>2</sub>}(μ-I)(THF)<sub>2</sub>]<sub>2</sub> (Ln = Sm, Tm), and the ionic lanthanide–bis-alkylidene ‘ate’ complexes [Ln{C(PPh<sub>2</sub>S)<sub>2</sub>}]<sub>2</sub>[Li(THF)<sub>4</sub>] (Ln = Sm, Tm).<sup>10</sup> Germane to these examples are the two clusters [{Ln(Cp\*)(THF)}<sub>3</sub>(μ-Cl)<sub>3</sub>(μ<sub>3</sub>-Cl)(μ<sub>3</sub>-CH<sub>2</sub>)] (Ln = Y, La; Cp\* = C<sub>5</sub>Me<sub>5</sub>) reported by Anwander *et al.*, which are formulated as containing bridging methylidene moieties.<sup>11</sup>

Noting that, with the exception of Anwander’s clusters which contain bridging methylidene centres, all the above examples feature alkylidene centres stabilised by phosphorus or silicon (the carbanion stabilisation energies of SiH<sub>3</sub> and

PH<sub>2</sub> groups have been calculated to be –99.2 and –89.1 kJ mol<sup>–1</sup>, respectively<sup>12</sup>), we reasoned that P- or Si-stabilised alkylidenes represent an attractive strategy for a concerted expansion of lanthanide–alkylidenes. We selected the bis-(iminophosphorano)-methandiide scaffold used by Cavell *et al.*,<sup>9</sup> and more recently by Harder *et al.* to prepare calcium carbenes,<sup>13</sup> since it offers numerous substitution patterns and the opportunity of addressing two issues. Firstly, no monomeric lanthanide–alkyl–alkylidene has yet been structurally characterised. Secondly, a Sm=C double bond was postulated in Cavell’s report of a samarium–amide–alkylidene complex, but shorter Sm–C single bonds have been reported.<sup>7</sup> The synthesis and structural characterisation of a monomeric lanthanide–alkyl–alkylidene would, for the first time, enable direct comparison of lanthanide–alkyl and lanthanide–alkylidene bonds in the same molecule.

Herein, we report the synthesis and first structural authentication of a mononuclear yttrium–alkyl–alkylidene, **1**, and present a DFT analysis of its bonding.

Addition of toluene to a cold (–78 °C) 1 : 1 molar mixture of [Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (**2**)<sup>14</sup> and H<sub>2</sub>C(PPh<sub>2</sub>=NSiMe<sub>3</sub>)<sub>2</sub> (**3**)<sup>15</sup> afforded a clear, pale yellow solution on warming to room temperature with stirring overnight. Work-up and recrystallisation from a hexane–toluene mixture afforded colourless crystals of **1** (Scheme 1) in moderate yield (43%), but inspection of the crude mother liquor by NMR spectroscopy indicated that the reaction is essentially quantitative (*vide infra*) and the isolated yield is a result of the high solubility of **1**.¶

Selected data for **1**: yield: 1.21 g, 43%. Anal. calcd for C<sub>39</sub>H<sub>57</sub>N<sub>2</sub>OP<sub>2</sub>Si<sub>3</sub>Y: C, 58.19; H, 7.14; N, 3.48%. Found: C, 58.07; H, 7.09; N, 3.51%. <sup>1</sup>H NMR (*d*<sub>6</sub>-benzene, 298 K): δ –0.18 (d, <sup>2</sup>J<sub>YH</sub> = 2.88 Hz, 2H, CH<sub>2</sub>Si), 0.16 (s, 18H, NSi(CH<sub>3</sub>)<sub>3</sub>), 0.65 (s, 9H, CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>), 1.43 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 3.93 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 7.12 (m, br, 16H, *o*- and *m*-Ar-CH) and 7.81 (m, br, 4H, *p*-Ar-CH). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>6</sub>-benzene, 298 K): δ 3.78 (NSi(CH<sub>3</sub>)<sub>3</sub>), 4.86 (CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>), 24.92

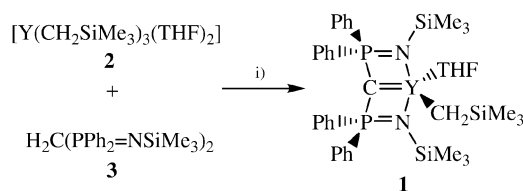
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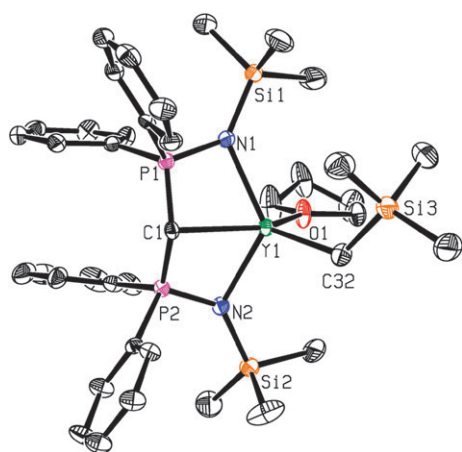
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‡ Electronic supplementary information (ESI) available: Full synthetic, spectroscopic and computational details for **1**. See DOI: 10.1039/b719633d



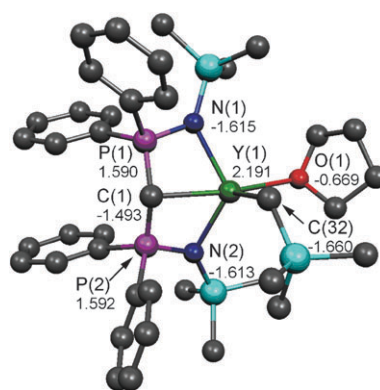
**Scheme 1** Reagents and conditions: (i) toluene, –2 SiMe<sub>4</sub>.



**Fig. 1** Molecular structure of **1** (thermal ellipsoids are shown at 30% probability levels). Selected bond distances (Å) and angles (°): Y(1)–C(1) 2.406(3), Y(1)–C(32) 2.408(3), Y(1)–N(1) 2.337(3), Y(1)–N(2) 2.311(3), Y(1)–O(1) 2.337(2), C(1)–P(1) 1.672(3), C(1)–P(2) 1.662(3), P(1)–N(1) 1.627(3), P(2)–N(2) 1.629(3); P(1)–C(1)–P(2) 138.4(2), N(1)–Y(1)–N(2) 125.36(10), C(1)–Y(1)–N(1) 68.41(10), C(1)–Y(1)–N(2) 68.31(10), C(1)–Y(1)–C(32) 115.32(13), C(1)–Y(1)–O(1) 135.87(9), C(32)–Y(1)–O(1) 108.49(12), C(1)–P(1)–N(1) 107.84(15), C(1)–P(2)–N(2) 107.18(15).

(OCH<sub>2</sub>CH<sub>2</sub>), 33.17 (d, <sup>1</sup>J<sub>YC</sub> = 43.90 Hz, CH<sub>2</sub>Si), 60.08 (td, <sup>1</sup>J<sub>PC</sub> = 131.86 Hz, <sup>1</sup>J<sub>YC</sub> = 4.88 Hz, YCP<sub>2</sub>), 69.86 (OCH<sub>2</sub>CH<sub>2</sub>), 129.14 (Ar-C), 131.36 (Ar-C) and 139.32 (t, <sup>1</sup>J<sub>PC</sub> = 50.34 Hz, *i*-Ar-C). One Ar-C resonance was obscured by the C<sub>6</sub>D<sub>6</sub> solvent resonance. <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>6</sub>-benzene, 298 K): δ 7.30 (d, <sup>2</sup>J<sub>YP</sub> = 11.53 Hz, NPC). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum exhibits a doublet at 7.30 ppm (<sup>2</sup>J<sub>YP</sub> = 11.53 Hz) and the <sup>1</sup>H NMR spectrum exhibits only one set of C<sub>silyl</sub>-methyl, N<sub>silyl</sub>-methyl, THF, and phenyl resonances consistent with pseudo-C<sub>s</sub> symmetry on the NMR time scale; the Y–CH<sub>2</sub> protons resonate as a doublet at –0.18 ppm (<sup>2</sup>J<sub>YH</sub> = 2.88 Hz) and there are no resonances associated with a P<sub>2</sub>CH group. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum the Y–CH<sub>2</sub>Si carbon resonates at 33.17 ppm (<sup>1</sup>J<sub>YC</sub> = 43.90 Hz). Of more interest is the YCP<sub>2</sub> carbon which resonates as a triplet of doublets at 60.08 ppm (<sup>1</sup>J<sub>PC</sub> = 131.86 Hz, <sup>1</sup>J<sub>YC</sub> = 4.88 Hz). Together, these data indicate that double deprotonation of **3** has occurred to afford an yttrium–alkyl–alkylidene. The facile double-deprotonation of **3** by **2** contrasts to the forcing conditions required to prepare related samarium<sup>9</sup> and Group 4 alkylidene derivatives of **3** by deprotonation strategies.<sup>16</sup> The low yttrium–carbon coupling constant<sup>17</sup> for the alkylidene centre, compared to the alkyl, indicated a high degree of p-character to the yttrium–alkylidene bond, and its <sup>13</sup>C NMR chemical shift indicated a high degree of shielding. We therefore undertook an X-ray diffraction study of **1** to further investigate the nature of the yttrium–alkylidene bond.¶

The molecular structure of **1** is illustrated in Fig. 1 along with selected bond lengths and angles. The yttrium centre is five-coordinate, adopting a heavily distorted trigonal bipyramidal geometry. Of immediate interest are the Y(1)–C(1) and Y(1)–C(32) bond lengths of 2.406(3) and 2.408(3) Å, respectively, which are statistically invariant with respect to each other. These two bond lengths are towards the lower end of the range of reported Y–C<sub>alkyl</sub> bond lengths but they are not

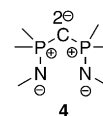


**Fig. 2** The geometry optimised structure of **1** and atomic charges estimated from a NBO analysis.

the shortest; for example, the mean Y–C bond length in [Y{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>] is 2.357(7) Å<sup>18</sup> (a search of the Cambridge Structural Database showed a range of 2.339–2.632 Å).<sup>19</sup> However, the Y(1)–C(1) bond is appreciably shorter than in related mono-deprotonated yttrium bis(iminophosphorano)methanides (~2.64 Å).<sup>20</sup> In **1**, the P–N and endocyclic P–C bonds are longer and shorter, respectively, compared to **3**,<sup>15</sup> but the exocyclic P–C bonds are essentially unchanged.

In order to gain a more detailed understanding of the nature of the yttrium–alkylidene bond in **1** we carried out DFT calculations on **1** with the ADF2006.01 code.<sup>21</sup> A model structure, based on the experimental crystallographic coordinates of **1**, was geometry optimised as described in the supplementary information.‡ The inclusion of the full ligand set was required to ensure that the optimised geometry reproduced the key features of the solid state structure. Key geometry optimised bond distances include: Y(1)–C(1) 2.39, Y(1)–C(32) 2.38, Y(1)–N(1) 2.30, Y(1)–N(2) 2.29, Y(1)–O(1) 2.42, C(1)–P(1) 1.67, C(1)–P(2) 1.67, P(1)–N(1) 1.65, and P(2)–N(2) 1.64 Å, which are in good agreement with those found by experiment.

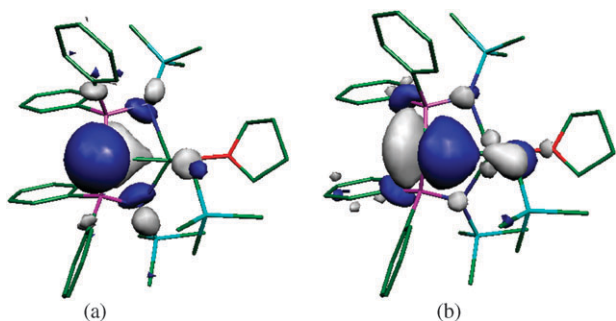
Calculated atomic charges derived from a NBO analysis are shown in Fig. 2. The atomic charge on Y (2.191) suggests that the Y–ligand bonds are dominated by ionic interactions and the charge distributions around the bis(iminophosphorano)methandiide ring are consistent with a resonance structure similar to **4**, which represents an extreme case.



The experimental bond distances (see above) and the bond orders for the P–N and C–P bonds in **1**, Table 1, are also consistent with this formulation and suggest there is little or no

**Table 1** Bond orders derived from a NBO analysis for **1**

Bond	Bond order	Bond	Bond order
Y(1)–N(1)	0.327	P(1)–N(1)	1.075
Y(1)–N(2)	0.340	P(2)–N(2)	1.085
Y(1)–C(1)	0.606	C(1)–P(1)	1.314
Y(1)–C(32)	0.509	C(1)–P(2)	1.245



**Fig. 3** Kohn-Sham orbital representations of (a) HOMO (−4.298 eV) and (b) HOMO-2 (−4.740 eV) in **1**.

$\pi$ -type electron delocalisation involving the central C and P atoms, and that two lone pairs are essentially localised on the central  $\gamma$ -C atom, Fig. 3. Thus, the contracted C–P bond lengths in **1** arise from dipolar  $R_2P^+C^{2-}$  attractions. A similar electronic structure has been proposed for a recently reported calcium–carbene complex derived from **3**,<sup>13</sup> and similar findings of charge accumulation at the  $\gamma$ -C position from NBO analysis of mono-deprotonated bis-(iminophosphorano)-methanides have been reported.<sup>22,23</sup>

The localisation of charge on the central C atom in **1** is supported by the compositions of the HOMO and HOMO-2. The HOMO is dominated by C 2p contributions (53.5%) with only 4.1% total P 3p participation, and the HOMO-2 possesses 49.0% C 2p character with only 3.7% Y contributions. Furthermore, the NBO-derived calculated bond order for the Y(1)–C(1) bond (0.606) is only moderately larger than for the Y(1)–C(32) formal single bond (0.509).<sup>24</sup>

To conclude, we have prepared and characterised the first structurally authenticated, monomeric yttrium–alkyl–alkylidene complex, **1**. DFT calculations show that the formal Y=C double bond in fact possesses a calculated bond order significantly lower than one, and this is only moderately larger than the *bona fide* Y–C single bond in the same molecule. The two lone pairs on the alkylidene centre remain essentially localised, and thus a dipolar description,  $Y^+C^-$ , is most appropriate. Studies of the chemistry of **1** are currently underway.

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## Notes and references

§ We include the group 3 elements Y and La in this definition due to the similar chemical properties of their +3 ions to those of the lanthanides.

¶ Crystal data for **1**:  $C_{39}H_{57}N_2OP_2Si_3Y$ ,  $M = 804.99$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 18.7425(11)$ ,  $b = 22.3897(13)$ ,  $c = 10.4415(6)$  Å,  $V = 4381.7(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.220$  g cm<sup>−3</sup>,  $\mu = 1.516$  mm<sup>−1</sup> (MoK $\alpha$ ,  $\lambda = 0.71073$  Å),  $T = 150$  K,  $R1$  ( $F^2$ ,  $>2\sigma$ ) = 0.0337,  $wR2$  ( $F^2$ , all data) = 0.0788, goodness-of-fit = 0.99 for all 7712 (which included Friedel pairs) unique data (42 305 measured,  $R_{int} = 0.0557$ ,  $2\theta < 50^\circ$ , CCD diffractometer) and 452 refined parameters, Flack parameter = −0.013(4). CCDC 667656.† Selected data for **1**: yield: 1.21 g, 43%. Anal. calcd for  $C_{39}H_{57}N_2OP_2Si_3Y$ : C, 58.19; H, 7.14; N, 3.48%. Found: C, 58.07; H, 7.09; N, 3.51%. <sup>1</sup>H NMR ( $d_6$ -benzene, 298 K):  $\delta$  −0.18 (d, <sup>2</sup> $J_{YH} = 2.88$  Hz,

2H,  $CH_2Si$ ), 0.16 (s, 18H,  $NSi(CH_3)_3$ ), 0.65 (s, 9H,  $CH_2Si(CH_3)_3$ ), 1.43 (m, 4H,  $OCH_2CH_2$ ), 3.93 (m, 4H,  $OCH_2CH_2$ ), 7.12 (m, br, 16H, *o*- and *m*-Ar-CH) and 7.81 (m, br, 4H, *p*-Ar-CH). <sup>13</sup>C{<sup>1</sup>H} NMR ( $d_6$ -benzene, 298 K):  $\delta$  3.78 ( $NSi(CH_3)_3$ ), 4.86 ( $CH_2Si(CH_3)_3$ ), 24.92 ( $OCH_2CH_2$ ), 33.17 (d, <sup>1</sup> $J_{YC} = 43.90$  Hz,  $CH_2Si$ ), 60.08 (td, <sup>1</sup> $J_{PC} = 131.86$  Hz, <sup>1</sup> $J_{YC} = 4.88$  Hz,  $YCP_2$ ), 69.86 ( $OCH_2CH_2$ ), 129.14 (Ar-C), 131.36 (Ar-C) and 139.32 (t, <sup>1</sup> $J_{PC} = 50.34$  Hz, *i*-Ar-C). One Ar-C resonance was obscured by the  $C_6D_6$  solvent resonance. <sup>31</sup>P{<sup>1</sup>H} NMR ( $d_6$ -benzene, 298 K):  $\delta$  7.30 (d, <sup>2</sup> $J_{YP} = 11.53$  Hz, NPC).

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