Synthesis and reactivity of the yttrium-alkyl-carbene complex [Y(BIPM)($CH_2C_6H_5$)(THF)] (BIPM = {$C(PPh_2NSiMe_3)_2$})†

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Reaction of [$YI_3(THF)_{3.5}$] with three equivalents of [KBz] (Bz = $CH_2C_6H_5$) affords the tri-benzyl complex [$Y(Bz)_3(THF)_3$] (**2**) in excellent yield. Complex **2** reacts with $H_2C(PPh_2NSiMe_3)_2$ (H_2BIPM) to afford the yttrium-alkyl-carbene complex [Y(BIPM)(Bz)(THF)] (**3**, BIPM = {$C(PPh_2NSiMe_3)_2$}). Compound **3** reacts with one equivalent of benzophenone to give the alkoxy 1,2-migratory insertion product [Y(BIPM)($OCPh_2Bz$)(THF)] (**4**) rather than the alkene Wittig-product $Ph_2C{=}C(PPh_2NSiMe_3)_2$. Reaction of **4** with one or more equivalents of benzophenone does not afford any detectable alkene products, rather it apparently catalyses rearrangement of monomeric **4** to afford dimeric [{Y(μ-BIPM)($OCPh_2Bz$)}$_2$] (**5**). Investigations reveal that formation of **5** is proportional to the amount of benzophenone added, but the benzophenone is recovered at the end of the reaction. Reaction of **3** with diphenyldiazene affords the 1,2-migratory insertion product [Y(BIPM){N(Ph)N(Ph)(Bz)}(THF)] (**6**) Compounds **2**, **3**, **4**, **5**, and **6** have been variously characterised by X-ray crystallography, multi-nuclear NMR spectroscopy, FTIR spectroscopy, and CHN micro-analyses. Density functional theory calculations on **3** reveal the HOMO to be localised at the $Y–C_{alkyl}$ bond which is commensurate with the observed reactivity.

Introduction

Compared to the well established chemistry of transition metal carbenes,[1] the chemistry of lanthanide carbenes is relatively undeveloped.[2] In recent years, the chemistry of lanthanide-N-heterocyclic carbenes has expanded,[3] but in these complexes the M–C bond may be regarded as a dative, Lewis base adduct of largely electrostatic character. Whilst lanthanide complexes which do not derive from stable free carbenes are sparse, they nevertheless promise novel reactivities due to the polar nature of their bonding,[4] yet paradoxically it is this very polarity of bonding which renders their synthesis a significant challenge due to the energetic mismatch of the relevant frontier orbitals.

Group 3 and lanthanide methylidene complexes have been detected by FTIR spectroscopy in frozen argon matrix isolation experiments by Andrews,[5] and [$Lu(CHSiMe_3)(CH_2SiMe_3)$][Li] and [$Er(CHSiMe_3)(CH_2SiMe_3)_2$] were postulated by Schumann.[6] Cavell reported the samarium carbene complex [Sm(BIPM)-(NCy_2)(THF)] (BIPM = {$C(PPh_2NSiMe_3)_2$}; Cy = cyclohexyl),[7] and [Ln{$C(PPh_2S)_2$}(μ-I)$(THF)_2]_2$ and [Ln{$C(PPh_2S)_2$}$_2$]-[$Li(THF)_4$] (Ln = Tm,[8] Sm[9]) have been reported by Nief, Le Floch, and Mézailles. Group 3/lanthanide methylidene/methandiide complexes have also emerged, including [{(Cp)(DME)-Lu}$_2$(PhCCPh=CPhCPh)],[10] and more recently, [{Ln(Cp*)-(THF)}$_3$(μ-Cl)$_3$(μ_3-Cl)(μ_3-CH_2)] (Ln = Y, La; Cp* = C_5Me_5),[11] [$Y(AlMe_4)$]{(μ-CH_2)(μ-Me)$AlMe_2$}$_2$($AlMe_2$)][$Al(Tp^{ButMe})$(Me)] (Tp^{ButMe} = hydrotris(pyrazoyl)borate),[12] [$La(Tp^{ButMe})$(μ_3-CH_2)-{(μ_2-Me)-$AlMe_2$}$_2$],[13] and [(PNP)Sc(μ_3-CH_2){(μ_2-Me)$AlMe_2$}$_2$] (PNP = N{2-P(Pr^i)$_2$-4-Me-C_6H_3}$_2$).[14]

Traditionally, transition metal carbenes are categorised as either Fischer or Schrock-type (alkylidene). The former category is characterised by a donor–acceptor interaction where the electrophilic carbene is stabilised by π-backbonding from an electron-rich metal and also by π-donor heteroatom substituents. The latter classification is characterised by the combination of a triplet metal with a triplet carbene and the nucleophilic carbene centre is stabilised only by the metal. However, where electropositive metals are concerned the designation of a carbene as Schrock becomes difficult because as the bonding becomes highly polarised the electron density becomes predominantly localised at the alkylidene centre which destabilises the carbene and ultimately renders the description of methandiide, *i.e.* a geminal dianion, more appropriate.[15]

Recently, we reported the synthesis of the alkyl-alkylidene complex [Y(BIPM)(CH_2SiMe_3)(THF)] (**1**).[16] Complex **1** contains a formally di-anionic carbene centre which is bound to yttrium. The ionic nature of the bonding was demonstrated by density functional theory (DFT) calculations to result in significant charge accumulation at the central carbon and the manifestation of a pseudo σ-bond, at which π-bonding was negligible. Thus, although the carbene centre in **1** possesses stabilising, electron withdrawing iminophosphorano groups, we referred to **1** as an alkylidene to emphasise its nucleophilic character, in common with alkylidenes, based on the high and negative calculated charge at the carbene centre. However, we have subsequently found that **1** apparently does not appear to react with benzophenone at the carbene centre, which is not consistent with charge accumulation at the carbene. Mézailles and Ephritikhine have suggested the term "nucleophilic carbene" for the {$C(PPh_2S)_2$}$^{2-}$ dianion[17] which is appropriate since the dianion charge is stabilised by the

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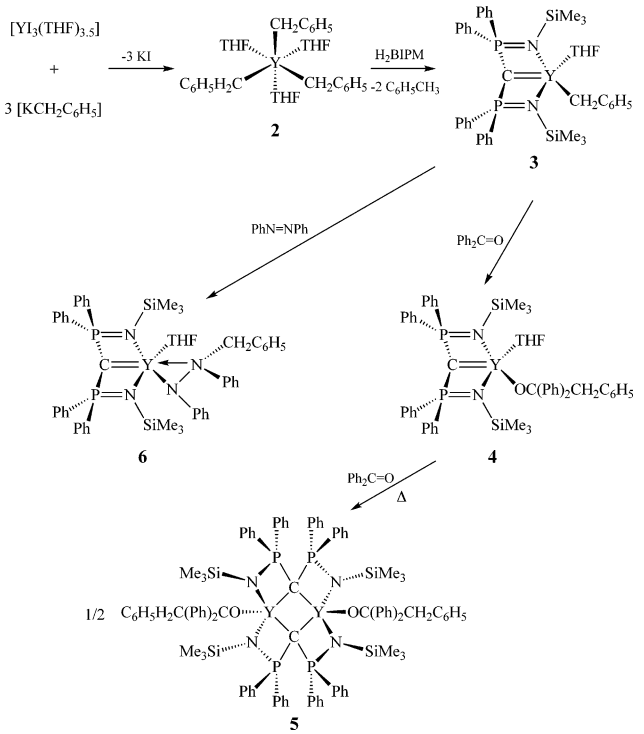
PPh_2S substituents and, in contrast to **1**, lanthanide and actinide complexes of this dianion react rapidly with benzophenone to give the expected alkene Wittig-product.[8,9,17] Since **1** does not exhibit Wittig-type reactivity with benzophenone, use of the term carbene would now appear to be more appropriate until Wittig-type reactivity is demonstrated by BIPM complexes such as **1**.[16]

Complex **1** represented a start point for our investigations in this area. However, we have found the synthesis of the tri-alkyl precursor to **1**, $[Y(CH_2SiMe_3)_3(THF)_3]$,[18] and its lanthanide congeners, to be occasionally capricious despite applying all the usual and routine precautions for anhydrous chemistry. Therefore, in order to expand the chemistry in this area at any speed to gain a full understanding of BIPM carbene complexes and their reactivity, we investigated an alternative, more amenable tri-alkyl system. Encouraged by recent reports of lanthanide tri-benzyls of lanthanum,[19] scandium,[20,21] lutetium,[20] and yttrium[22,23] we targeted yttrium tri-benzyl since yttrium affords diamagnetic complexes which are analogous to paramagnetic holmium, thus modelling the later lanthanides well. Very recently, a low yielding (24%) synthesis of *tris*-THF yttrium tri-benzyl was reported;[23] however, a higher yielding synthesis would clearly be desirable. Herein, we report a new, high yielding synthesis of *tris*-THF yttrium tri-benzyl, its utility in preparing a BIPM-based yttrium benzyl-carbene, and reactivity studies of this complex towards benzophenone and diphenyldiazaene, which are complemented by a DFT study of **3**.



Scheme 1 Synthesis of **2–6**.

Results and discussion

Synthesis and reactivity

The reaction between $[YI_3(THF)_{3.5}]$[24] and three equivalents of BzK (Bz = $CH_2C_6H_5$)[25] proceeds smoothly and reliably at 0 °C with concomitant elimination of potassium iodide, Scheme 1. Colourless crystals of $[Y(Bz)_3(THF)_3]$ (**2**), which had previously been reported to be light yellow,[23] were obtained in high (83%) yield following work up and recrystallisation from a hexane/THF mixture. The precipitation of potassium iodide is an excellent indicator as to the progress of the reaction and both precursors are cost effective and easy to prepare using Schlenk/Glove Box techniques. Maintaining the solution at 0 °C and employing yttrium triiodide rather than yttrium trichloride appears to be the key to obtaining a high yield of **2** reproducibly. NMR spectra of **2** were in good agreement with the previous report[23] despite the difference in reported colours. The benzylic protons in **2** were found to be co-incident with the β-methylene resonance of THF in the ^{1}H NMR spectrum (from a HMQC experiment), but the benzylic carbon was observed as a doublet at 54.4 ppm; the yttrium-carbon coupling constant of 32.2 Hz in **2** compares to 21.0 Hz in $[Y(CH_2C_6H_4\text{-}2\text{-}NMe_2)_3]$,[22] reflecting the presence of THF in the former as opposed to the more the basic amine substituents in the latter.

In order to verify the synthesis of **2**, we undertook an X-ray diffraction study to confirm its identity; since the data were collected at lower temperature and gave an improved residual compared to the previous report[23] we include it here. The molecular structure of **2** is illustrated in Fig. 1 and selected bond lengths and angles are in Table 1. The yttrium centre adopts

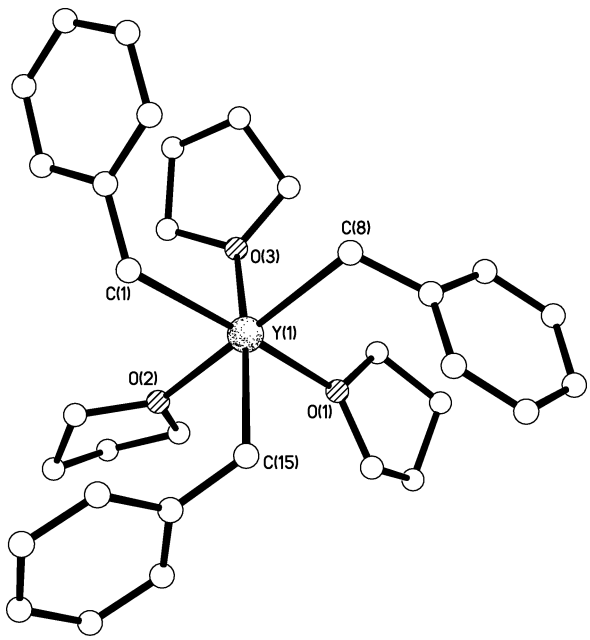


Fig. 1 Molecular structure of **2** with selective labelling; hydrogen atoms and minor disorder components of the THF molecules are omitted for clarity.

a distorted octahedral geometry and is bound to three benzylic carbons and three oxygen centres from THF molecules. The benzyl and THF groups are bound in a mutually *fac* manner. Multi-hapto interactions are not observed between yttrium and the three benzyl groups in the solid state, which contrasts to the closely related complex $[La(CH_2C_6H_4\text{-}4\text{-}Me)_3(THF)_3]$,[19] which

Table 1 Selected bond lengths (Å) and angles (°) for **2–6**

2			
Y(1)–C(1)	2.452(3)	Y(1)–C(8)	2.459(3)
Y(1)–C(15)	2.463(3)	Y(1)–O(1)	2.399(2)
Y(1)–O(2)	2.422(2)	Y(1)–O(3)	2.390(2)
3[a]			
Y(1)–N(1)	2.345(2)	Y(1)–O(1)	2.356(2)
Y(1)–C(1)	2.357(3)	Y(1)–C(17)	2.406(4)
Y(1)–C(18)	2.921(4)	C(1)–P(1)	1.6521(12)
P(1)–N(1)	1.627(2)	P(1)–C(8)	1.820(2)
P(1)–C(2)	1.824(2)	P(1)–C(1)–P(1A)	147.6(2)
4			
Y(1)–O(1)	2.0450(17)	Y(1)–O(2)	2.3153(18)
Y(1)–N(1)	2.340(2)	Y(1)–N(2)	2.358(2)
Y(1)–C(1)	2.393(2)	C(1)–P(2)	1.660(2)
C(1)–P(1)	1.671(2)	P(1)–N(1)	1.626(2)
P(1)–C(8)	1.821(3)	P(1)–C(2)	1.826(3)
P(2)–N(2)	1.632(2)	P(2)–C(14)	1.822(3)
P(2)–C(20)	1.832(3)	P(1)–C(1)–P(2)	137.58(16)
5[a]			
Y(1)–O(1)	2.034(4)	Y(1)–N(2A	2.316(4)
Y(1)–N(1)	2.329(5)	Y(1)–C(1)	2.592(6)
Y(1)–C(1A)	2.595(5)	C(1)–P(2)	1.721(5)
C(1)–P(1)	1.738(6)	P(1)–N(1)	1.616(6)
P(1)–C(8)	1.811(3)	P(1)–C(2B)	1.829(3)
P(1)–C(8B)	1.842(3)	P(1)–C(2)	1.842(3)
P(2)–N(2)	1.612(4)	P(2)–C(14)	1.833(3)
P(2)–C(20B)	1.833(3)	P(2)–C(14B)	1.838(3)
P(2)–C(20)	1.841(3)	P(1)–C(1)–P(2)	119.1(3)
6			
Y(1)–N(4)	2.200(4)	Y(1)–N(1)	2.341(4)
Y(1)–O(1)	2.373(3)	Y(1)–N(2)	2.388(4)
Y(1)–C(1)	2.408(5)	Y(1)–N(3)	2.581(4)
N(1)–P(1)	1.629(4)	P(1)–C(1)	1.674(5)
P(1)–C(2)	1.820(5)	P(1)–C(8)	1.829(5)
C(1)–P(2)	1.671(4)	P(2)–N(2)	1.635(4)
P(2)–C(14)	1.817(5)	P(2)–C(20)	1.821(5)
N(3)–C(39)	1.423(6)	N(3)–N(4)	1.447(5)
N(3)–C(32)	1.486(6)	N(4)–C(45)	1.402(6)
P(1)–C(1)–P(2)	135.5(3)		
3a			
Y(1)–N(1)	2.398	Y(1)–O(1)	2.451
Y(1)–C(1)	2.392	Y(1)–C(17)	2.481
Y(1)–C(18)	2.974	C(1)–P(1)	1.682
P(1)–N(1)	1.655	P(1)–C(8)	1.844
P(1)–C(2)	1.847	P(1)–C(1)–P(1A)	145.0

[a] Symmetry operation for **3**: $x, -y + \frac{1}{2}, z$; for **5**: $-x, -y + 1, -z$.

exhibits three η^2 La···C contacts, presumably due to the larger ionic radius of lanthanum. The Y–C bond lengths in **2** span the narrow range 2.452(3)–2.463(3) Å, which is in the middle of the range of the relatively small number of reported yttrium-benzyl distances.[23,26] Complex **2** is stable in crystalline form for weeks at room temperature in the absence of air, moisture, and solvent, and is thus an excellent reagent for the synthesis of organometallic yttrium complexes.

Compound **2** reacts cleanly with $H_2C(PPh_2NSiMe_3)_2$ in arene solvent to afford the alkyl-carbene complex [Y(BIPM)(Bz)(THF)] (**3**) in essentially quantitative yield, Scheme 1. Complex **3** may be isolated as pale yellow crystals in moderate yield from toluene. The benzylic protons resonate as a doublet at 2.78 ppm ($^2J_{YH}$ = 1.60 Hz) in the ^{1}H NMR spectrum of **3**. The $^{13}C\{^1H\}$ NMR spectrum exhibits a triplet of doublets at 61.8 ppm (J_{PC} = 207.30 Hz, J_{YC} = 5.03 Hz) which is similar to that observed in **1** and the $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at 4.80 ($^2J_{YP}$ = 13.12 Hz). Only one set of trimethylsilyl, aryl, benzyl, and THF resonances are observed in the NMR spectra, which implies that **3** exhibits C_s symmetry on the NMR timescale.

The molecular structure of **3** is illustrated in Fig. 2 and selected bond lengths and angles are in Table 1. The yttrium centre is five-coordinate, and may best be described as adopting a distorted trigonal bipyramidal geometry where the two N-atoms occupy axial sites and the O-, and two C-centres adopt equatorial sites. The distortion from ideal trigonal bipyramidal geometry originates from the bite angle of the BIPM ligand [N(1)–Y(1)–N(2) = 129.74(9)°], which compares to 125.36(10)° for the analogous angle in **1**. The crystal structure of **3** exhibits exact C_s symmetry and crystallises on a mirror plane which intersects C(1), Y(1), C(17), C(18), C(21) [the benzyl *para*-carbon atom] and O(1); consequently, the coordinated THF molecule exhibits significant disorder. The Y(1)–C(1) bond distance of 2.357(3) Å is significantly shorter than the analogous distance of 2.406(3) Å in **1**, reflecting the fact that benzyl may be considered a weaker carbanion than $Me_3SiCH_2^-$ due to more effective stabilisation of charge by delocalisation in the former as opposed to negative hyperconjugation in the latter. That said, the Y(1)–C(17) bond distance of 2.406(4) Å is statistically indistinguishable to the analogous Y–C bond distance of 2.408(3) Å in **1**, but it should be noted that bond length does not necessarily correlate with bond strength in such ionic systems. The Y(1)–N(1) and Y(1)–N(1A) bond lengths of 2.345(2) Å, are essentially the same as observed in **1** [2.331(3) and 2.33793) Å]. Additionally, an η^2 bonding mode of benzyl is suggested by a Y(1)···C(18) contact of 2.921(4) Å. For comparison, the non-bonding Y···C_{ipso} distances in **2** are in the range 3.258–3.467 Å.

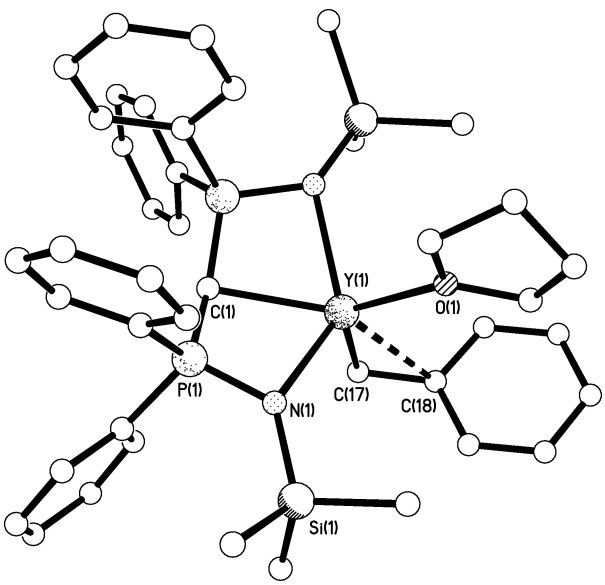


Fig. 2 Molecular structure of **3** with selective labelling of symmetry unique atoms; hydrogen atoms and minor disorder components of the THF molecules are omitted for clarity. Symmetry operation: $x, -y + \frac{1}{2}, z$.

We examined the reactivity of **3** with benzophenone in order to assess whether the alkene $Ph_2C{=}C(PPh_2NSiMe_3)_2$ would be produced by Wittig-type chemistry. Accordingly, treatment of **3** with one equivalent of benzophenone affords a red oil from which colourless crystals are isolated in high yield following work up, Scheme 1; however, no Wittig-type reactivity was

observed, *i.e.* alkene products were not detected. This parallels the lack of Wittig-type reactivity observed for [{Ca(BIPM)}$_2$][15] which exhibited virtually no reactivity towards benzophenone and only after prolonged heating to 60 °C in THF could small quantities of the alcohol $Ph_2C(OH)CH(PPh_2NSiMe_3)_2$ be identified.[15] Germane to these observations is the fact that whilst [2 + 2] cyclo-addition reactions between group 4-BIPM complexes and heteroallenes (*e.g.* isocyanates) are known, no reactivity of BIPM with benzophenone has been reported.[27] Collectively, these observations contrast with the reactivity of the $\{C(PPh_2S)_2\}^{2-}$ dianion which reacts rapidly with benzophenone to give the alkene $Ph_2C{=}C(PPh_2S)_2$.[8,9,17] The nucleophilicity, and hence reactivity, of these carbenes will, to a large extent, be dictated by competing stabilisation from a coordinated metal and the P-heteroatom substituents; nitrogen substituents would be expected to deplete the charge at the carbene centre more than sulfur substituents, thus leading to lowered reactivity which, for benzophenone, is commensurate with experimental observations. The colourless crystals isolated from the reaction between **3** and benzophenone were subsequently identified as the alkoxy 1,2-migratory insertion product [Y(BIPM)(OCPh$_2$Bz)(THF)] (**4**) (*vide infra*). The ^{1}H NMR spectrum reveals that the benzyl group now resonates at 4.04 ppm and does not exhibit coupling to yttrium. The $^{13}C\{^1H\}$ NMR spectrum exhibits a characteristic triplet of doublets at 51.0 ppm, which is shifted ~10 ppm to lower frequency compared to **3**; whilst the yttrium-carbon coupling constant is slightly higher (J_{YC} = 7.04 Hz) the phosphorus-carbon coupling constant is markedly smaller (J_{PC} = 134.85 Hz). The $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at 5.7 ppm ($^2J_{YP}$ = 12.96 Hz) which is very similar to **3**.

The molecular structure of **4** is illustrated in Fig. 3 and selected bond lengths and angles are in Table 1. Complex **4** is very similar to **3** except that the benzyl ligand is now replaced by the di-phenyl-benzyl-alkoxide ligand derived from the 1,2-migratory insertion of benzophenone into the yttrium-benzyl bond. The Y(1)–C(1) bond length of 2.393(2) Å is lengthened compared to **3** which reflects the replacement of an alkyl by an alkoxide. The Y(1)–O(1)–C(32) bond angle [172.73(17)°] is close to linear and together with the Y(1)–O(1) bond length of 2.0450(17) Å indicates strong binding of the alkoxide.[28] The Y(1)–N(1) and Y(1)–N(2) bond lengths of 2.340(2) and 2.358(2) Å are essentially the same as the analogous bond lengths in **1** and **3**.

Since the initial insertion reactivity had occurred at the Y–C$_{benzyl}$ bond we reasoned that addition of a second equivalent might furnish the alkene Wittig-reaction product. However, no reaction was observed between **4** and one equivalent of benzophenone at room temperature. Heating a 1:1 solution of **4** and benzophenone in C_6D_6 at 60 °C resulted in the growth of a complex subsequently identified as [{Y(μ-BIPM)(OCPh$_2$Bz)}$_2$] (**5**), Scheme 1, characterised by a multiplet at 21.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum, rather than the anticipated singlet for the anticipated alkene. The multiplet manifests as an AXX′ spin system with coupling constants tentatively assigned as $^2J_{YP}$ = 6.64 Hz and 17.82 Hz, and $^2J_{PP}$ = 26.73 Hz. Additionally, the resonance associated with the carbene centre was observed to have shifted to 19.20 ppm in the $^{13}C\{^1H\}$ NMR spectrum and appeared as a triplet (J_{PC} = 107.68 Hz).

The identity of **5** was confirmed by an X-ray diffraction study on crystals of **5** grown from benzene. The molecular structure of **5** is illustrated in Fig. 4 and selected bond lengths and angles are in Table 1. Complex **5** is dimeric, and, discounting the alkoxide groups, the gross structure is very similar to that observed for [{Ca(BIPM)$_2$}$_2$][15] and [{Cr(BIPM)$_2$}$_2$].[29] The carbene centre now bridges two yttrium centres and we suggest the BIPM ligand in this complex should be considered as a methandiide due to its bridging nature. Each yttrium centre is coordinated to one nitrogen and the methandiide centre from one BIPM ligand and one nitrogen and the methandiide centre from another BIPM ligand together with an alkoxide group. The yttrium centre adopts a distorted square-based pyramidal geometry where the alkoxide resides in the axial site. Despite wholesale disorder of all the BIPM phenyl and trimethylsilyl groups in the crystal structure, the bonding of the NPCPN fragment to yttrium is clear-cut. The methandiide

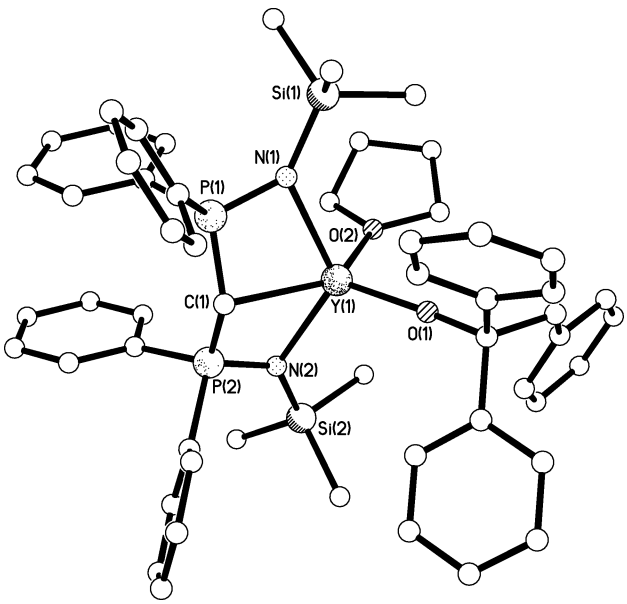


Fig. 3 Molecular structure of **4** with selective labelling; hydrogen atoms omitted for clarity.

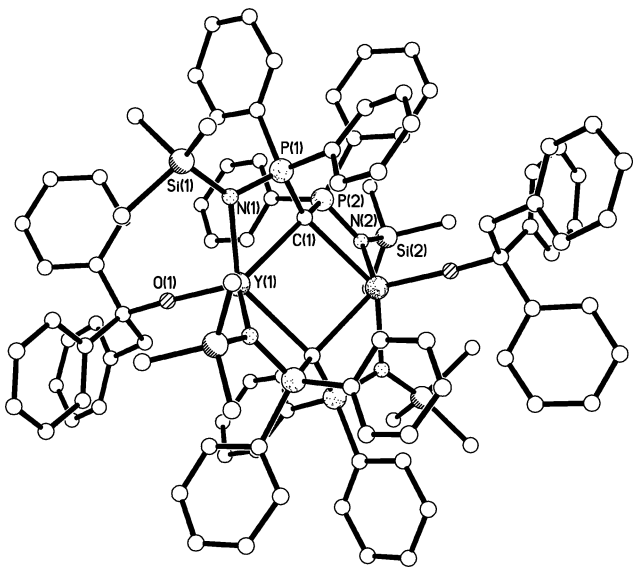


Fig. 4 Molecular structure of **5** with selective labelling; hydrogen atoms omitted for clarity. Symmetry operation: $-x, -y + 1, -z$.

centre bridges both yttrium centres with essentially identical bond lengths of 2.592(6) and 2.595(5) Å which are ~0.2 Å longer than in **1**, **3**, and **4** as a consequence of bridging. To compensate for the longer Y–C bonds, the Y(1)–N(1) and Y(1)–N(2A) bond lengths of 2.329(5) and 2.316(4) Å are shorter than the corresponding Y–N bond lengths in **3** and **4**. The Y(1)–O(1) bond length of 2.034(4) Å is, statistically speaking, unchanged from that observed in **4**.

An interesting feature of the formation of **5** is the role of benzophenone. Heating **4** in the absence of benzophenone does not result in formation of **5**. Once formed, **5** is apparently stable and does not react with benzophenone regardless of how many equivalents of benzophenone are added. However, the amount of **4** converted to **5** appears to be dependent on the quantity of benzophenone present, and, intriguingly, the percentage of **4** converted to **5** is always directly proportional to the percentage of benzophenone added. For example, addition of a half molar equivalent of benzophenone to **4** gives 50% conversion to **5** irrespective of how long the reaction mixture is heated for. Thus, benzophenone appears to be acting as an organocatalyst, promoting the conversion of **4** to **5** as a stoichiometric reagent, yet all of the benzophenone is recovered unchanged after the reaction is complete. We were able to monitor the conversion of **4** to **5** by ^{31}P NMR spectroscopy at 333 K. A plot of 1/[**4**] *versus* time (s) (Fig. 5) of a 0.05 M solution in d_6-benzene shows a reaction which is best modelled with second order kinetics, and which gives a rate constant of 8.41×10^{-4} mol^{-1} dm^3 s^{-1}. The mechanism of this reaction is clearly complicated since an overall second order reaction implies second order kinetics for one reaction component only or two reaction components which are each first order. Interestingly, the conversion of **4** to **5** does not appear to occur in THF, and, since THF is a stronger donor than benzophenone, this implies that coordination of benzophenone to yttrium may play a role in the dimerisation of **4** to **5**. Germane to this is the observation that addition of benzophenone to arene solutions of **4** results in an immediate colour change from colourless to red; however, THF solutions of benzophenone and **4** remain colourless.

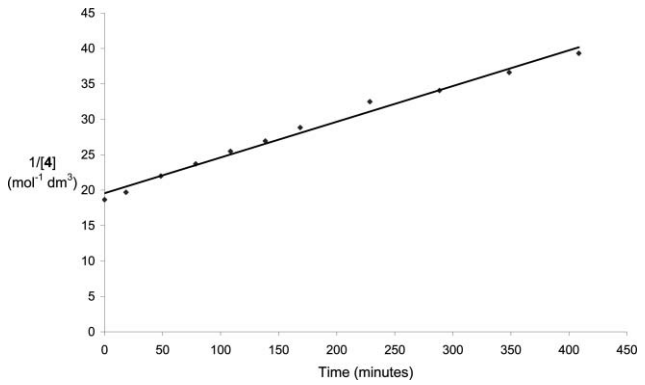


Fig. 5 Plot of 1/[**4**] *versus* time (s) for the thermal conversion of **4** to **5**.

Complex **4** was found to react cleanly with one equivalent of diphenyldiazene to give the insertion product [Y(BIPM){N(Ph)N(Ph)(Bz)}(THF)] (**6**), Scheme 1, isolated in low crystalline yield due to its high solubility. The ^{13}C{^{1}H} NMR spectrum exhibits a characteristic triplet of doublets at 60 ppm (J_{PC} = 207.30 Hz, J_{YC} = 5.03 Hz) and the benzyl protons now resonate at 5.5 ppm in the ^{1}H NMR spectrum (*cf*. 2.78 for **3**) and they are now diastereotopic, appearing as an AB quartet, which may be a consequence of the crystal structure being retained in solution (see below, *vide infra*).

Colourless crystals of **6** were obtained from diethyl ether; the molecular structure is illustrated in Fig. 6 and selected bond lengths and angles are in Table 1. The Y(1)–C(1) bond distance of 2.408(5) Å is comparable to that observed in **1**, but is longer than observed in **3** and **4**. The hydrazido ligand in **6** binds in an η^2 mode, through the anionic amide and neutral, dative amine centres with Y(1)–N(4) and Y(1)–N(3) bond lengths of 2.200(4) and 2.581(4) Å, which compare to Y(1)–N(1) and Y(1)–N(2) bond distances of 2.341(4) and 2.388(4) Å, respectively, in **6**. The N(3)–N(4) bond distance of 1.447(5) Å is unexceptional. The insertion of diphenyldiazene into a Ln–C bond is rare, since diphenyldiazene usually features in reduction reactions with low-valent lanthanides, *e.g.* [Sm(C$_5$Me$_5$)$_2$][30] and ytterbium naphthalenide.[31]

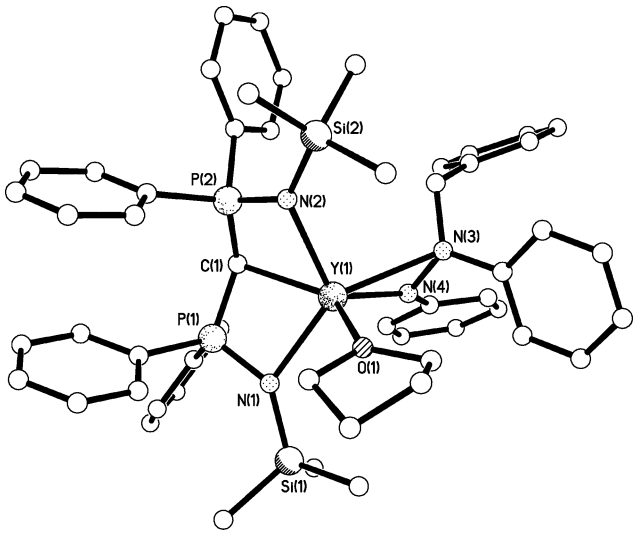


Fig. 6 Molecular structure of **6** with selective labelling; hydrogen atoms omitted for clarity.

Computational study of 3

The reactions discussed above occurred exclusively at the Y–C$_{alkyl}$ bond, as evidenced by the formation of **4** and **6**. This is an interesting observation because a DFT study of complex **1**[16] showed that the HOMO possesses carbene "lone pair" character and consequently the reactivity of **3** might also be associated with a nucleophilic carbene centre. In order to investigate this difference we undertook a DFT study on a full model of **3**, **3a**, using the ADF2007.01 code, Fig. 7.[32] Table 1 lists pertinent calculated bond lengths and angles for **3a**. Calculated bond lengths are generally longer (av. 0.05 Å) than those found within the experimental structure, and bond angles are within 3°. Nevertheless, the principal features of the co-ordination sphere about yttrium, as revealed by the X-ray crystallographic study of **3**, are reproduced in the calculation of **3a**. Thus, given the similarities between the calculated and experimental structures we conclude that the DFT calculations of **3a** provide a qualitative description of the electronic

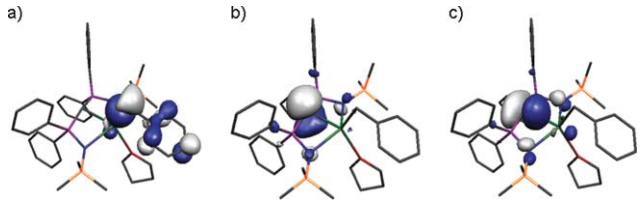


Fig. 7 The highest three occupied Kohn Sham orbitals of **3a**: a) HOMO (–4.248 eV); b) HOMO-1 (–4.463 eV); c) HOMO-2 (–4.753 eV).

structure of **3**. Inspection of the highest three occupied Kohn Sham orbitals, and consideration of their respective energies, shows that, compared to **1**, substitution of $Me_3SiCH_2^-$ by $C_6H_5CH_2^-$ results in a reordering of the frontier orbitals such that the Y–C_{alkyl} bond is now the HOMO (38% C 2p) which is in line with the observed reactivity of **3**. The carbene "lone pair" is now HOMO-1 (53% C 2p) and the HOMO-2 (53% C 2p) is the remaining carbene "lone pair" that forms the coordinate bond to the yttrium centre. An analysis of the Wiberg bond orders reveals Y–$C_{carbene}$, Y–C_{alkyl}, Y–N, and C–P bond orders of 0.66, 0.35, 0.29, and 1.27, respectively, which is congruent with values calculated for **1**. Mulliken charges for Y, $C_{carbene}$, C_{alkyl}, P, and N of +1.63, –1.04, –0.34, +1.31, and –1.12 clearly indicate accumulation of charge at the carbene centre, and a Lewis bonding picture consistent with the dipolar N^--P^+-C^{2-}-P^+-N^- resonance form, which has now emerged as the most accurate description of the bonding within BIPM,[15,16] and related, ligands,[8,9,17] although polarisation of charge from the carbene centre towards the iminophosphorano substituents is evident from a visual inspection of the Kohn Sham orbitals.

Summary and conclusions

The tribenzyl yttrium complex $[Y(Bz)_3(THF)_3]$ (**2**) is easily prepared in excellent yield, and is an excellent reagent for preparing organo-group 3 complexes, as evidenced by the quantitative preparation of [Y(BIPM)(Bz)(THF)] (**3**). Complex **3** reacts with one equivalent of benzophenone or diphenyldiazene to yield the insertion products [Y(BIPM)($OCPh_2Bz$)(THF)] (**4**) and [Y(BIPM){N(Ph)N(Ph)(Bz)}(THF)] (**6**), respectively. Complex **4**, in the presence of one or more equivalents of benzophenone rearranges to the dimeric complex $[\{Y(\mu\text{-BIPM})(OCPh_2Bz)\}_2]$ (**5**) and formation of the alkene Wittig-product is not observed. A DFT study of **3** shows the HOMO to be of Y–C_{alkyl} character, which is in line with the reactions of **3** to give **4** and **6**, and that the HOMO-1 and HOMO-2 orbitals are carbene based and predominantly of 2p-character.

Experimental

General

All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Solvents were dried by passage through activated alumina towers and degassed before use. All solvents were stored over potassium mirrors (with the exception of THF which was stored over activated 4 Å molecular sieves). Deuterated benzene was distilled from potassium, degassed by three freeze–pump–thaw cycles and stored under nitrogen. The compounds $[YI_3(THF)_{3.5}]$,[24] BzK,[25] and H_2-BIPM[33] were prepared according to published procedures. Benzophenone and diphenyldiazene were purchased from Aldrich and were dried *in vacuo* for 6 hours prior to use.

^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6, 162.0, and 79.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to TMS (^1H, ^{13}C, and ^{29}Si) and external 85% H_3PO_4 (^{31}P). FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. Elemental microanalyses were carried out by Mr Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK.

Preparation of $[Y(Bz)_3(THF)_3]$ (2)

THF (30 ml) was added to a pre-cooled (0 °C) mixture of $C_6H_5CH_2K$ (1.95 g, 15 mmol) and $[YI_3(THF)_{3.5}]$ (3.61 g, 5 mmol) and the resultant beige mixture was stirred at this temperature for 4 hours. The mixture was filtered and reduced in volume at 0 °C to *ca.* 5 ml, layered with hexane (5 ml) and stored at –25 °C overnight to afford **2** as colourless crystals. Yield: 2.40 g, 83%. Anal Calcd for $C_{33}H_{45}O_3Y$: C, 68.50; H, 7.84. Found: C, 68.62; H, 7.75. ^1H NMR (d_8-THF, 298 K): δ 2.03 (m, 18H, OCH_2CH_2 and CH_2Ph), 3.86 (m, 12H, OCH_2CH_2), 6.57 (t, $^3J_{HH}$ = 7.20 Hz, 3H, *p*-Ar-C*H*), 6.92 (d, $^3J_{HH}$ = 7.20 Hz, 6H, *o*-Ar-C*H*) and 7.07 (virtual t, $^3J_{HH}$ = 7.20 Hz, 6H, *m*-Ar-C*H*). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K): δ 25.62 (OCH_2CH_2), 54.38 (d, J_{YC} = 31.19 Hz, CH_2Ph), 67.70 (OCH_2CH_2), 115.37 (Ar-*C*), 122.91 (Ar-*C*), 127.62 (Ar-*C*) and 154.89 (*i*-Ar-*C*). IR ν/cm^{-1} (Nujol): 1587 (m), 1260 (w), 1211 (m), 1172 (w), 1017 (m), 896 (m), 853 (br, m), 795 (m), 740 (m), 698 (m), 671 (m).

Preparation of [Y(BIPM)(Bz)(THF)] (3)

A solution of $H_2C(PPh_2{=}NSiMe_3)_2$ (0.79 g, 1.42 mmol) in toluene (10 ml) was added drop-wise to a suspension of **2** (0.82 g, 1.42 mmol) in toluene (20 ml) at –78 °C. The mixture was allowed to slowly warm to room temperature with stirring over 18 hours. Volatiles were removed *in vacuo* and the resulting pale yellow solid was recrystallised from toluene (20 ml) at –30 °C to afford **3** as pale yellow crystals. Yield: 0.47 g, 47%. Anal Calcd for $C_{42}H_{53}N_2OP_2Si_2Y$: C, 62.36; H, 6.60; N, 3.46. Found: C, 62.23; H, 6.50; N, 3.39. ^1H NMR (d_6-benzene, 298 K): δ 0.13 (s, 18H, $NSi(CH_3)_3$), 1.43 (m, 4H, OCH_2CH_2), 2.78 (d, $^2J_{YH}$ = 1.60 Hz, 2H, CH_2Ph), 3.77 (m, 4H, OCH_2CH_2), 6.75 (t, $^3J_{HH}$ = 7.20 Hz, 1H, *p*-Ar-C*H*), 7.14 (br. m, 12H, Ar-C*H*), 7.30 (m, $^3J_{HH}$ = 7.20 Hz, 4H, Ar-C*H*) and 7.83 (br. m, 8H, Ar-C*H*). $^{13}C\{^1H\}$ NMR (d_6-benzene, 298 K): δ 4.03 ($NSi(CH_3)_3$), 25.28 (OCH_2CH_2), 52.21 (d, J_{YC} = 24.15 Hz, CH_2Ph), 61.81 (td, J_{PC} = 207.30 Hz, J_{YC} = 5.03 Hz, YCP_2), 70.61 (OCH_2CH_2), 117.13 (Ar-*C* Bz), 121.68 (Ar-*C* Bz), 127.62 (t, $^2J_{YC}$ = 5.64 Hz, *o*-Ar-*C*), 129.09 (Ar-*C*), 131.47 (t, $^2J_{YC}$ = 5.43 Hz, *ipso*-Ar-*C* Bz), 132.14 (Ar-*C*), 139.14 (br., *ipso*-Ar-*C*) and 152.19 (Ar-*C* Bz). $^{31}P\{^1H\}$ NMR (d_6-benzene, 298 K): δ 4.80 (d, $^2J_{YP}$ = 13.12 Hz, N*P*C). $^{29}Si\{^1H\}$ NMR (d_6-benzene, 298 K): δ –8.92 (s, N*Si*(CH_3)$_3$). IR ν/cm^{-1} (Nujol): 1589 (m), 1314 (m), 1242 (m), 1108 (m), 1045 (s), 836 (s), 766 (m), 715 (m), 694 (m).

Preparation of [Y(BIPM)(OCPh$_2$Bz)(THF)] (4)

Toluene (20 ml) was added to a pre-cooled (–78 °C) mixture of **3** (1.62 g, 2 mmol) and benzophenone (0.36 g, 2 mmol) and the mixture was allowed to slowly warm to room temperature with stirring over 18 hours. Volatiles were removed *in vacuo* and the resulting red oil was recrystallised from toluene (6 ml) at –30 °C to afford **4** as colourless crystals. A second crop was obtained following concentration and further storage at –30 °C. Yield: 1.42 g, 72%. Anal Calcd for $C_{62}H_{71}N_2O_2P_2Si_2Y$: C, 68.74; H, 6.61; N, 2.59. Found: C, 68.81; H, 6.54; N, 2.59. ^{1}H NMR (d_6-benzene, 298 K): δ 0.24 (s, 18H, NSi(CH_3)$_3$), 1.56 (m, 4H, OCH$_2$CH_2), 3.91 (m, 4H, OCH_2CH$_2$), 4.04 (s, 2H, CH_2Ph), 6.97–7.21 (m, 23H, Ar-CH), 7.26 (d, $^3J_{HH}$ = 6.80 Hz, 4H, Ar-CH), 7.62 (d, $^3J_{HH}$ = 7.20 Hz, 4H, Ar-CH) and 8.53 (br m, 4H, Ar-CH). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ 3.79 (NSi(CH_3)$_3$), 24.74 (OCH$_2$CH_2), 50.11 (OCPh$_2$CH_2), 51.04 (td, J_{PC} = 134.85 Hz, J_{YC} = 7.04 Hz, YCP_2), 70.03 (OCH_2CH$_2$), 83.21 (d, $^2J_{YC}$ = 5.03 Hz, OCPh$_2$CH$_2$), 125.45 (d, J_{PC} = 3.02 Hz, *ipso*-Ar-C), 125.57 (Ar-C), 127.31 (Ar-C), 127.54 (d, J_{PC} = 4.03 Hz, *ipso*-Ar-C) 128.22 (Ar-C), 129.11 (Ar-C), 130.95 (Ar-C), 131.41 (br, Ar-C), 137.54 (Ar-C), 139.57 (Ar-C) and 151.77 (Ar-C). One Ar-C resonance was obscured by the C_6D_6 solvent resonance. ^{31}P{^{1}H} NMR (d_6-benzene, 298 K): δ 5.68 (d, $^2J_{YP}$ = 12.96 Hz, NPC). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ –9.68 (s, NSi(CH$_3$)$_3$). IR ν/cm^{-1} (Nujol): 1603 (w), 1242 (m), 1104 (m), 1047 (s), 830 (m), 752 (m), 728 (m), 696 (m).

Preparation of [{Y(μ-BIPM)(OCPh$_2$Bz)}$_2$] (5)

Benzophenone (0.009 g, 0.05 mmol) was added to a Young's NMR tube containing **4** (0.05 g, 0.05 mmol) and C_6D_6 (0.6 ml) and the solution was heated to 60 °C overnight. Colourless crystals of **5** formed over one week at room temperature. ^{1}H NMR (d_6-benzene, 298 K): δ –0.17 (s, 18H, NSi(CH_3)$_3$), 0.21 (s, 18H, NSi(CH_3)$_3$), 4.13 (s, 4H, CH_2Ph) and 6.78–8.25 (m, 70H, Ar-CH). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ 3.62 (NSi(CH_3)$_3$), 4.83 (NSi(CH_3)$_3$), 19.20 (t, J_{PC} = 107.68 Hz, Y$_2$CP_2), 52.74 (OCPh$_2$CH_2), 84.30 (d, $^2J_{YC}$ = 5.03 Hz, OCPh$_2$CH$_2$), 125.47–132.45 (Ar-C), 137.79 (Ar-C), 148.64 (Ar-C), 150.79 (Ar-C) and 151.20 (Ar-C). Several Ar-C resonances were obscured by the C_6D_6 solvent resonance. ^{31}P{^{1}H} NMR (d_6-benzene, 298 K): δ 21.16 (ddd, $^2J_{YP}$ = 6.64 Hz and 17.82 Hz, $^2J_{PP}$ = 26.73 Hz, NPC). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ –9.51 (virtual t, $^2J_{PSi}$ = 45.63 Hz, NSi(CH$_3$)$_3$).

Preparation of [Y(BIPM){N(Ph)N(Ph)(Bz)}(THF)] (6)

Toluene (30 ml) was added to a pre-cooled (–78 °C) mixture of PhN=NPh (0.21 g, 1.17 mmol) and **3** (0.95 g, 1.17 mmol). The mixture was allowed to slowly warm to room temperature with stirring over 18 hours to afford a deep green solution. Volatiles were removed *in vacuo* and the resulting deep green oil was extracted with diethyl ether (2 ml) and stored at ambient temperature overnight to afford **6** as colourless crystals. Yield: 0.24 g, 21%. Anal Calcd for $C_{54}H_{63}N_4OP_2Si_2Y$: C, 65.44; H, 6.41; N, 5.65. Found: C, 65.31; H, 6.36; N, 5.57. ^{1}H NMR (d_6-benzene, 298 K): δ 0.13 (s, 18H, NSi(CH_3)$_3$), 1.44 (m, 4H, OCH$_2$CH_2), 3.73 (m, 4H, OCH_2CH$_2$), 5.46 (dd, br, $^2J_{HH}$ = 14.41 Hz, 2H, CH_2Ph), and 6.66–8.52 (m, br, 35H, Ar-CH). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ 4.31 (NSi(CH_3)$_3$), 25.12 (OCH$_2$CH_2), 60.00 (td, J_{PC} = 207.30 Hz, J_{YC} = 5.03 Hz, YCP_2), 61.55 (CH_2Ph), 65.68 (OCH_2CH$_2$), 115.28 (Ar-C), 116.13 (Ar-C), 116.32 (Ar-C), 119.71

Table 2 Crystallographic data for **2–6**

	2	**3**	**4**	**5**	**6**
Formula	$C_{33}H_{45}O_3Y$	$C_{42}H_{53}N_2OP_2Si_2Y$	$C_{59.38}H_{68}N_2O_2P_2Si_2Y$	$C_{110.10}H_{118.10}N_4O_2P_4Si_4Y_2$	$C_{56}H_{68}N_4O_{1.5}P_2Si_2Y$
Fw	578.60	808.89	1048.69	1943.45	1028.17
Cryst size/mm	0.70 × 0.31 × 0.26	0.34 × 0.34 × 0.18	0.58 × 0.29 × 0.19	0.22 × 0.20 × 0.20	0.22 × 0.21 × 0.13
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	*Cc*	*P*2$_1$/*m*	*C*2/*c*	*P*2$_1$/*n*	*Pbca*
a/Å	17.3179(14)	10.4711(7)	46.514(4)	13.2508(12)	21.719(2)
b/Å	20.8626(17)	19.2484(13)	10.2277(9)	19.8328(18)	19.171(2)
c/Å	8.4199(7)	10.6315(8)	26.579(2)	20.2611(18)	25.914(3)
α/°					
β/°	93.319(2)	93.894(2)	106.543(2)	106.039(2)	
γ/°					
V/Å^3	3037.0(4)	2137.9(3)	12121.3(19)	5117.4(8)	10790(2)
Z	4	2	8	2	8
ρ_{calcd}/g cm^{-3}	1.265	1.257	1.142	1.261	1.266
μ/mm^{-1}	1.950	1.527	1.094	1.288	1.227
no. of reflns measd	7439	11198	41978	23074	54011
no. of unique reflns, R_{int}	3574, 0.0208	3882, 0.0285	10641, 0.0517	6686, 0.0456	9557, 0.1355
no. of reflns with $F^2 > 2\sigma(F^2)$	3354	3388	8375	5270	5374
transmn coeff range	0.32–0.61	0.61–0.75	0.55–0.81	0.74–0.77	0.65–0.85
R, R_w[a] ($F^2 > 2\sigma$)	0.0250, 0.0575	0.0350, 0.0845	0.0432, 0.1142	0.0661, 0.1687	0.0522, 0.1117
R, R_w[a] (all data)	0.0282, 0.0587	0.0423, 0.0880	0.0556, 0.1199	0.0799, 0.1768	0.1251, 0.1428
S[a]	1.015	1.040	1.029	1.132	0.987
Parameters	334	256	583	715	628
max., min. diff map/e Å^{-3}	0.323, –0.182	0.528, –0.526	1.040, –0.253	0.928, –0.738	0.535, –0.479

[a] Conventional $R = \sum\|F_o| - |F_c\|/\sum|F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2/\text{no. data} - \text{no. params})]^{1/2}$ for all data.

(Ar-*C*), 127.10 (Ar-*C*), 128.24 (Ar-*C*), 129.00 (Ar-*C*), 129.65 (Ar-*C*), 130.23 (Ar-*C*), 130.43 (Ar-*C*), 130.90 (br, Ar-*C*), 131.52 (t, $^{2}J_{PC} = 5.03$ Hz, *o*-Ar-*C*), 132.25 (br, Ar-*C*), 138.74 (Ar-*C*), 150.74 (Ar-*C*) and 152.69 (d, $^{2}J_{PC} = 2.01$ Hz, *ipso*-Ar-*C*). $^{31}P\{^{1}H\}$ NMR (d_6-benzene, 298 K): δ 6.30 (d, $^{2}J_{YP} = 12.96$ Hz, N*P*C). $^{29}Si\{^{1}H\}$ NMR (d_6-benzene, 298 K): δ –9.14 (s, N*Si*(CH_3)$_3$). IR ν/cm^{-1} (Nujol): 1592 (br, m), 1261 (s), 1093 (s), 1020 (s), 800 (s).

X-Ray crystallography

Crystal data for compounds **2–6** are given in Table 2, and further details of the structure determinations are in the ESI.† Bond lengths and angles are listed in Table 1. Crystals were examined on a Bruker AXS CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Intensities were integrated from a sphere of data recorded on narrow (0.3°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semi-empirical absorption corrections were applied, based on symmetry-equivalent and repeat reflections. The structures were solved by direct methods and were refined by least-squares methods on all unique F^2 values, with anisotropic displacement parameters, and with constrained riding hydrogen geometries; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} of the parent atom. The largest features in final difference syntheses were close to heavy atoms. The Flack parameter for **2** refined to 0.007(4). Highly disordered solvent molecules of crystallisation in **4** and **5** could not be modelled and were treated with the Platon SQUEEZE procedure.[34] Programs were Bruker AXS SMART (control) and SAINT (integration),[35] and SHELXTL for structure solution, refinement, and molecular graphics.[36]

Density functional theory calculations

The calculations were performed using the Amsterdam Density Functional (ADF) suite version 2007.01.[37,38] The restricted relativistic geometry optimization DFT calculations for **3** employed a Slater type orbital (STO) triple-ζ-plus one polarization function basis set from the ZORA/TZP database of the ADF suite for all atoms. Frozen core basis sets were used for C (1 s), N (1 s), O (1 s), Si (2p), P (2p) and Y (4p). Scalar relativistic (SR) approaches were used within the ZORA Hamiltonian for the inclusion of relativistic effects. The local density approximation (LDA) with the correlation potential due to Vosko *et al* was used in all of the DFT calculations.[39] Gradient corrections were performed using the functionals of Becke[40] and Perdew[41] (BP). The Kohn–Sham orbitals were visualized in MOLEKEL.[42]

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