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Reactivity of the Yttrium Alkyl Carbene Complex $[Y(BIPM)(CH_2C_6H_5)(THF)]$ (BIPM = $\{C(PPh_2NSiMe_3)_2\}$)$^{2-}$: From Insertions, Substitutions, and Additions to Nontypical Transformations

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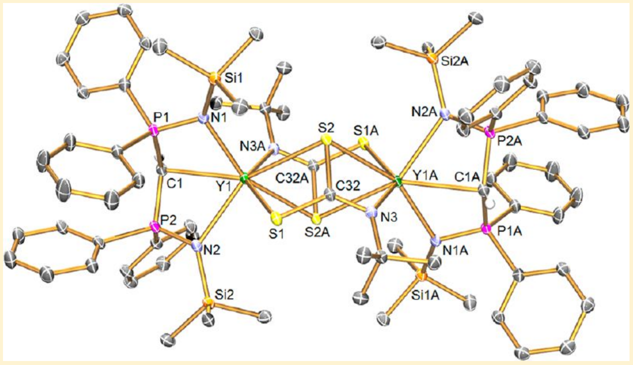
Supporting Information

ABSTRACT: The yttrium alkyl carbene complex $[Y(BIPM)(CH_2Ph)(THF)]$ (**1**; BIPM = $\{C(PPh_2NSiMe_3)_2\})^{2-}$) was treated with a series of unsaturated organic substrates, a bulky primary amine, and a group 1 metal alkyl to gauge and compare the reactivity of the $Y{=}C_{carbene}$ and $Y{-}C_{alkyl}$ bonds. Treatment of **1** with *tert*-butyl nitrile and 1-adamantyl azide gave the 1,2-migratory insertion products $[Y(BIPM)\{NC(Bu^t)(CH_2Ph)\}(THF)]$ (**2**) and $[Y(BIPM)\{N_3Ad\text{-}1,Bn\text{-}3\text{-}\kappa^2N^{1,3}\}(THF)]$ (**3**), respectively, with no reactivity observed at the Y═C double bond even when an excess of the relevant organic substrate was added. In contrast, the heteroallenes *N,N′*-dicyclohexylcarbodiimide and *tert*-butyl isocyanate reacted at both the $Y{=}C_{carbene}$ and $Y{-}C_{alkyl}$ bonds of **1** to afford $[Y\{C(PPh_2NSiMe_3)_2[C(NCy)_2]\text{-}\kappa^4C,N,N',N''\}\{C(NCy)_2(CH_2Ph)\text{-}\kappa^2N,N'\}]$ (**4**) and $[Y\{C(PPh_2NSiMe_3)_2[C(O)(NBu^t)]\text{-}\kappa^4C,N,N',O\}\{C(O)(NBu^t)(CH_2Ph)\text{-}\kappa^2N,O\}]$ (**5**), respectively. **4** and **5** form regardless of the molar ratio of **1** to heteroallene, with no intermediates observed; thus, it is not clear if the [2 + 2]-cycloaddition or the 1,2-migratory insertion reaction occurs first. The addition of 2 equiv of *tert*-butyl isothiocyanate to **1** yields dimeric $[Y(BIPMH)\{C(S)_2(NBu^t)\text{-}1\text{-}\kappa S,2\text{-}\kappa N{:}\mu,\kappa S'\}]_2$ (**6**), benzyl nitrile, and isobutylene by desulfurization and carbene-mediated deprotonation of a *tert*-butyl group of 1 equiv of heteroallene. The reaction between **1** and the bulky amine $DippNH_2$ (Dipp = $C_6H_3Pr^i_2$) gave $[Y(BIPM)(NHDipp)(THF)]$ (**7**) by alkane elimination, with no reactivity observed at the $Y{=}C_{carbene}$ bond. Finally, the addition of benzylpotassium to **1** afforded the yttriate polymer $[Y(BIPM)(\mu\text{-}\eta^1{:}\eta^6\text{-}CH_2Ph)(\mu\text{-}\eta^1{:}\eta^2\text{-}CH_2Ph)K]_\infty$ (**8**) by a formal carbopotassiation across the $Y{=}C_{carbene}$ bond. Complexes **2**−**8** have been characterized by X-ray crystallography, multielement NMR spectroscopy, FTIR spectroscopy, and CHN microanalyses.



■ INTRODUCTION

Transition-metal carbene complexes have been studied extensively in recent years, chiefly as a direct consequence of their applications in synthetic transformations.[1] While investigations into the chemistry of f-block carbenes are relatively few in number in comparison with their d-block counterparts,[2] they promise novel synthetic utility due to their highly polarized bonding.[3] There has been a recent surge in interest in the preparation of f-block carbene complexes that do not derive from stable free carbenes, which are distinct from Lewis base adducts such as f-block N-heterocyclic carbene complexes.[4] The isolation of stable early-metal carbenes with a formal M═C double bond (also referred to as geminal methanediides)[5] represents a synthetic challenge, as the highly polarized nature of the bonding requires additional stabilizing features, such as sterically bulky phosphorus substituents, to avoid polymetallic cluster formation.[6] To date, bis(diphenylthiophosphinoyl)methanediide ($\{C(PPh_2S)_2\}^{2-}$) and bis(diphenyliminophosphorano)methanediide ($\{C(PPh_2NR)_2\}^{2-}$; e.g., R = $SiMe_3$, BIPM) ligands have found the most utility in stabilizing lanthanide carbenes.[2]

The lanthanide bis(diphenylthiophosphinoyl)carbene complexes $[Ln\{C(PPh_2S)_2\}(\mu\text{-}I)(THF)_2]_2$ (Ln = Sm, Tm)[7] and $[Li(THF)_4]][Ln\{C(PPh_2S)_2\}_2]$ (Ln = Sm, Tm)[8] were found to exhibit classical metallo-Wittig chemistry with benzophenone, forming the alkene $PPh_2C{=}C(PPh_2S)_2$ and a metal oxide, although in the case of the anionic carbene complexes the "open" metallo-oxetane intermediates $[Ln\{C(PPh_2S)_2(Ph_2CO)\}_2\{Li(THF)\}]$ (Ln = Sm, Tm) could be isolated from the reaction mixtures. Uranium(IV) carbenes incorporating the bis(diphenylthiophosphinoyl)methanediide ligand, exemplified by $[U\{C(PPh_2S)_2\}(BH_4)_2(THF)_2]$,[9] and the uranyl(VI) carbene complex $[UO_2\{C(PPh_2S)_2\}(py)_2]$[10] have been reported and were also shown to react with ketones and aldehydes to generate the expected Wittig products.

The samarium(III) complex $[Sm(BIPM)(NCy_2)(THF)]$ was the first structurally characterized lanthanide carbene complex

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to be reported,[11] and a related neodymium(III) carbene complex, [Nd{C(PPh$_2$NPr^i)$_2$}{HC(PPh$_2$NPr^i)$_2$}],[12] has recently been prepared, but no reactivity studies have been reported in either case.

The entry point for our group into this field was the preparation of the yttrium alkyl carbene [Y(BIPM)(CH$_2$SiMe$_3$)(THF)],[13] which was then extended to include [Ln(BIPM)(I)(THF)$_2$] (Ln = Y,[14,15] Er[15]) and [Ln(BIPM)(CH$_2$Ph)(THF)] (Ln = Y (**1**);[16] Ln = Dy, Er[17]). These complexes were prepared by facile double deprotonation of BIPMH$_2$ by the respective lanthanide tri- or dialkyls, which is in contrast with the case for [Sm(BIPM)(NCy$_2$)(THF)], which required forcing conditions to prepare. Thus, the yttrium complexes represent convenient starting points from which to examine the reactivity of M=C double bonds. It is germane to note that this synthetic methodology was found to be inappropriate for the larger lanthanides, with [Ln(BIPM)(BIPMH)] (Ln = La, Ce, Pr, Nd, Sm, Gd) forming exclusively from the reactions between BIPMH$_2$ and the parent lanthanide trialkyls.[17] It was later found that salt metathesis strategies are more suitable for the preparation of related carbene complexes of both the larger lanthanides, e.g. [La{C(PPh$_2$NMes)$_2$}(I)(THF)$_3$] (Mes = C$_6$H$_2$Me$_3$-2,4,6),[18] and uranium.[19] DFT analysis of the bonding in [Y(BIPM)(CH$_2$SiMe$_3$)(THF)],[13] [Y(BIPM)(I)(THF)$_2$],[15] and **1**[16] suggests that the bonding is predominantly ionic in these systems and that the carbenes are essentially geminal methanediides with two localized lone pairs of electrons. Although the bonding was found to be similar for the three complexes, they differ according to the ordering of their frontier orbitals, with a carbene lone pair being the HOMO for [Y(BIPM)(CH$_2$SiMe$_3$)(THF)] and [Y(BIPM)(I)(THF)$_2$], whereas the HOMO of **1** is localized at the Y−C$_{\text{alkyl}}$ bond, which might vary its reactivity profile.

A reactivity study of [Y(BIPM)(CH$_2$SiMe$_3$)(THF)] and [Y(BIPM)(I)(THF)$_2$] with a selection of ketones has previously been reported.[20] While the expected 1,2-migratory insertion of benzophenone into the Y−C$_{\text{alkyl}}$ bond of [Y(BIPM)(CH$_2$SiMe$_3$)(THF)] occurred to generate the alkoxide [Y(BIPM){OC(CH$_2$SiMe$_3$)Ph$_2$}(THF)], the reaction of the Y=C bonds of these complexes with ketones did not furnish Wittig-type products. Instead, these reactions yielded a series of oxymethylbenzophenone and substituted isobenzofuran products from carbene-mediated C−H activation and C−C and C−O bond forming reactions. The reaction of [Y(BIPM)(I)(THF)$_2$] with PhCOMe was found to give the substituted cyclohexene dypnopinacol via C−H activation, cyclotetramerization, and dehydration. Both of these reactivity profiles are in contrast to known transition-metal carbene chemistry and encourage further investigations into the reactivity of lanthanide carbenes with unsaturated organic substrates. The synthetic utility of [Y(BIPM)(I)(THF)$_2$] was further demonstrated in the preparation of the first Ga−Y bond in [Y(BIPM){Ga[N(Dipp)CH]$_2$}(THF)$_2$],[14] which is part of a small family of f-element metal−metal-bonded complexes in the literature.[21]

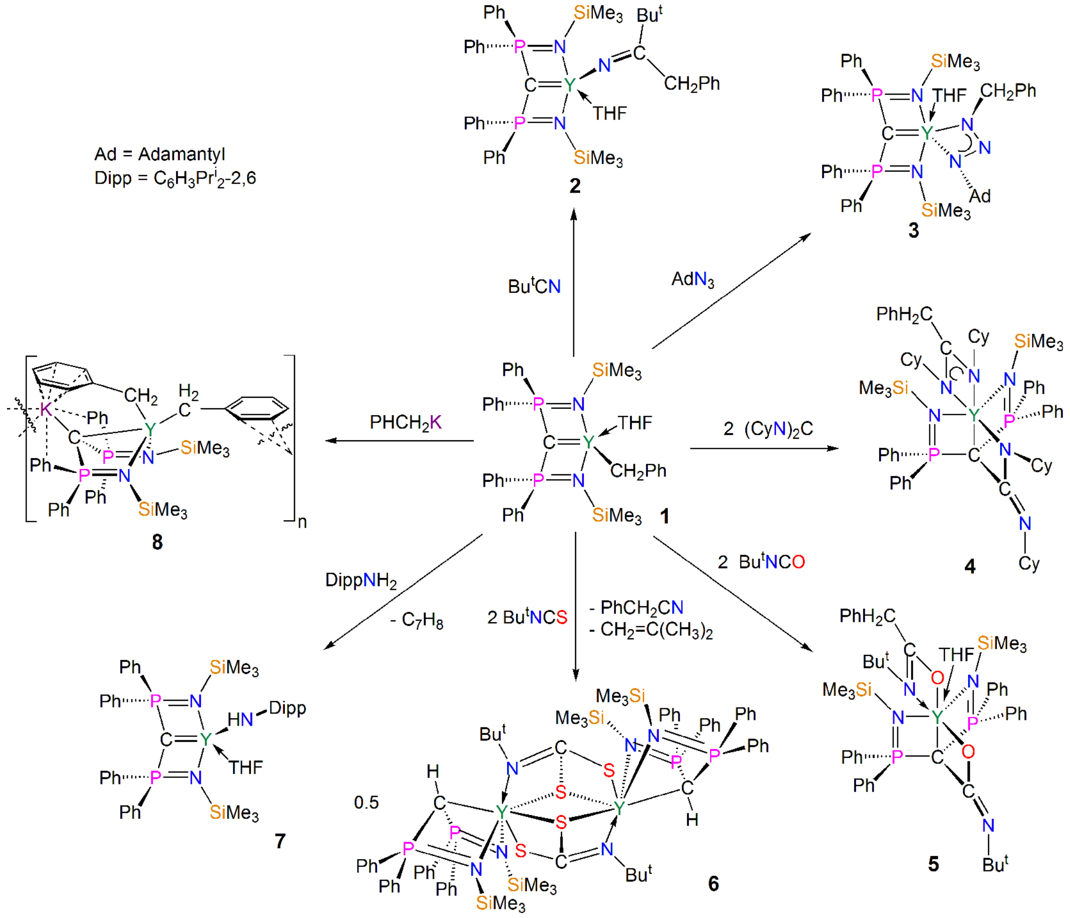
A preliminary reactivity study of **1** has been published,[16] with no reactivity at the formal Y=C double bond observed. **1** was shown to react separately with diphenyldiazene and benzophenone to afford [Y(BIPM){N(Ph)N(Ph)(CH$_2$Ph-κ^2N,N')}] and [Y(BIPM){OC(CH$_2$Ph)Ph$_2$}(THF)], respectively, by 1,2-migratory insertion reactions at the Y−C$_{\text{alkyl}}$ bond.[16] Further equivalents of diphenyldiazene or benzophenone did not result in reaction at the methanediide center, but in the case of the ketone dimerization to the bridging methanediide complex [Y(μ-BIPM){OC(CH$_2$Ph)Ph$_2$}]$_2$ was observed. We have now extended our investigations of **1** with a series of substrates including nitriles, amines, heteroallenes and a group 1 metal alkyl in order to gain a greater understanding of its reactivity, and our findings are presented herein.

■ RESULTS AND DISCUSSION

The separate additions of *tert*-butyl nitrile and 1-adamantyl azide to **1** afforded the 1,2-migratory insertion products [Y(BIPM){NC(Bu^t)(CH$_2$Ph)}(THF)] (**2**) and [Y(BIPM){N$_3$Ad-1,Bn-3-$\kappa^2N^{1,3}$}(THF)] (**3**), respectively (Scheme 1), in almost quantitative yield by ^{31}P NMR spectroscopy but in low crystalline yield due to their very high solubilities, which was a recurring issue in this study (**2**, 14%; **3**, 27%). The insertion of nitriles into Y−C σ bonds to form ketimides is well-known,[22] although examples of corresponding f-element alkyl azide insertion chemistry are surprisingly rare. The reaction of 1-adamantyl azide with [U(Cp*)$_2$(Me)$_2$] also furnished a triazenido alkyl complex, [U(Cp*)$_2${N$_3$Ad-1,Me-3-κ^2-$N^{1,3}$}(Me)],[23] and germane to this related triazenido complexes formed from the reaction between 1-adamantyl azide and [M{OCMe$_2$CH$_2$[C-(NCH$_2$CH$_2$NDipp)]}{N(SiMe$_3$)$_2$}$_2$] (M = Y, Ce) by insertion into the metal−carbene dative bond.[24] In common with the reactions of **1** with diphenyldiazene and benzophenone,[16] the addition of further equivalents of *tert*-butyl nitrile and 1-adamantyl azide to **2** and **3** did not result in reaction at the methanediide center. The formation of **2** and **3** was evidenced initially by ^{1}H NMR spectroscopy, with the benzyl methylene proton resonance shifting downfield from the value observed for **1** and no longer coupling with ^{89}Y (δ 3.88 (**2**), 4.93 (**3**) and 2.78 (**1**) ppm; $^2J_{\text{YH}}$ for **1** = 1.6 Hz). These values are comparable to the respective corresponding resonances observed in the ^{1}H NMR spectra of [Y(BIPM){OC(CH$_2$Ph)Ph$_2$}(THF)] (δ 4.04 ppm) and [Y(BIPM){N(Ph)N(Ph)(CH$_2$Ph-κ^2N,N')}] (δ 5.46 ppm).[16] It is also straightforward to monitor the formation of **2** by observation of the ketimide functional group in the FTIR spectrum (C=N stretch 1671 cm^{-1}). However, the ^{31}P{^{1}H} NMR spectra of **2** (δ 3.60 ppm (d, $^2J_{\text{YP}}$ = 13.0 Hz)) and **3** (δ 3.89 ppm (d, $^2J_{\text{YP}}$ = 11.3 Hz)) are not markedly different from the starting material **1** (δ 4.80 ppm (d, $^2J_{\text{YP}}$ = 13.1 Hz)).[16] Nonetheless, in the ^{13}C{^{1}H} NMR spectra the ketimide carbon (δ 175.27 ppm (d, $^2J_{\text{YC}}$ = 8.1 Hz)) of **2**, the methylene singlet (**2**, δ 43.02 ppm; **3**, δ 61.42 ppm) and methanediide doublet of triplets (**2**, δ 51.36 ppm (J_{PC} = 152.0 Hz, J_{YC} = 5.0 Hz); **3**, δ 59.81 ppm (J_{PC} = 185.1 Hz, J_{YC} = 4.0 Hz)) resonances of both complexes are diagnostic of their formation and compare well to the corresponding values reported for the yttrium ketimide [Y(Cp*)$_2${NC(Bu^t)(CH$_2$C$_6$H$_3$Me$_2$-3,5)}(NCBu^t)] (δ 168.96 ppm (d, $^2J_{\text{YC}}$ = 9.8 Hz, CNY))[22a] and the yttrium carbene complex [Y(BIPM){N(Ph)N(Ph)(CH$_2$Ph-κ^2-N,N')}] (δ 60.00 (dt (J_{PC} = 207.3 Hz, J_{YC} = 5.0 Hz, CP$_2$); 61.55 ppm (CH$_2$Ph)).[16]

The molecular structures of **2**·C$_7$H$_8$ (Figure 1) and **3** (Figure 2) were determined, and selected bond lengths and angles are compiled in Table 1. These structures will be discussed together for brevity. The BIPM ligands of both complexes adopt open-book conformations, with typical intramolecular distances and angles in the metallacycles and Y=C$_{\text{carbene}}$ distances (**2**, 2.428(2) Å; **3**, 2.482(5) Å) that confirm a methanediide formulation (cf. Y=C = 2.357(3) Å for **1**).[16] The yttrium centers of both complexes are coordinated by THF, with **2** being five-coordinate

Scheme 1. Synthesis of 2−8



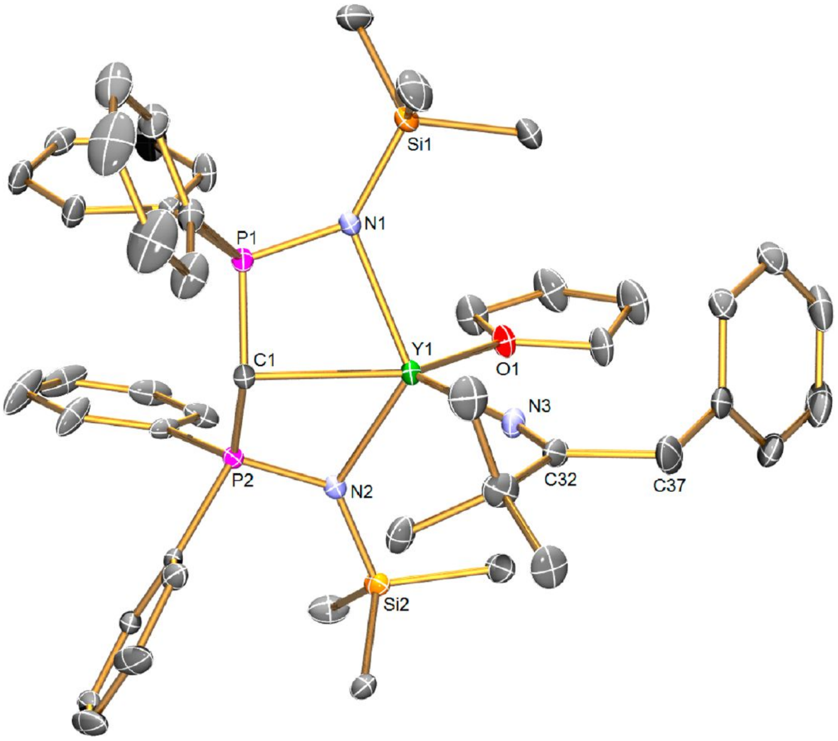


Figure 1. Molecular structure of $2\cdot C_7H_8$ with selective atom labeling. Displacement ellipsoids are set at the 40% probability level, and hydrogen atoms and lattice solvent are omitted for clarity.

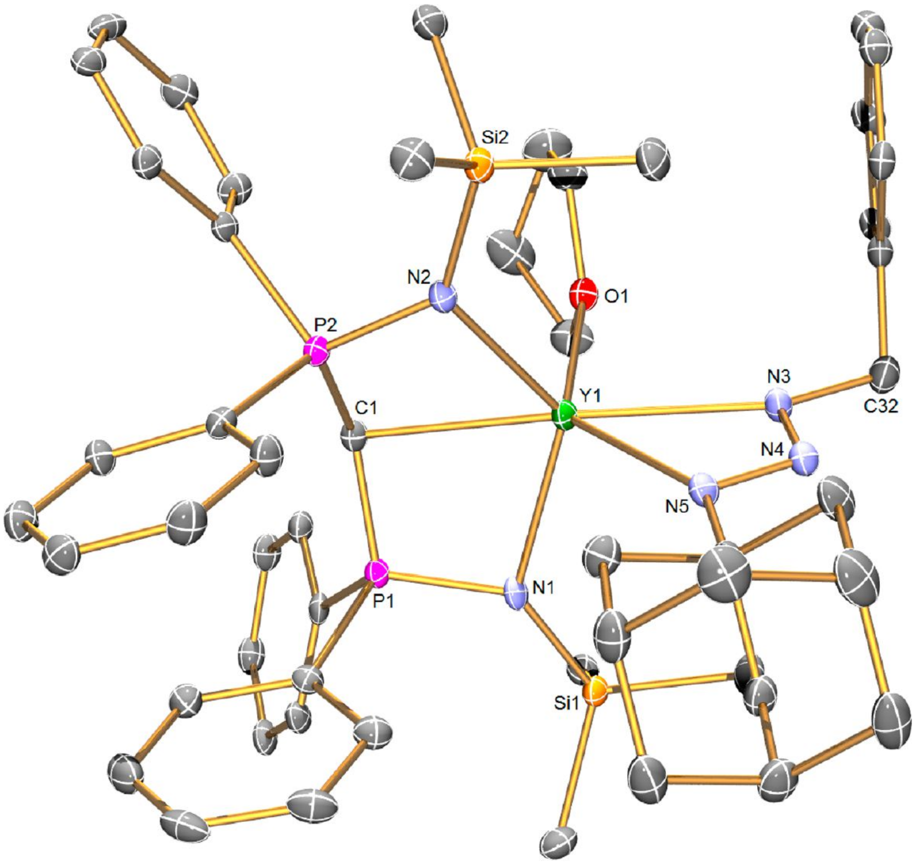


Figure 2. Molecular structure of **3** with selective atom labeling. Displacement ellipsoids are set at the 40% probability level, and hydrogen atoms are omitted for clarity.

and **3** six-coordinate according to the differing binding modes of the remaining ligands and with the N(3)−N(4)−N(5) triazenido fragment of **3** essentially orthogonal (96.7(6)°) to the P_2N_2 plane of the BIPM scaffold. As expected, the Y(1)−N(3) distance in **2** (2.165(2) Å) is shorter than the Y(1)−N(3) (2.433(5) Å) and Y(1)−N(5) (2.407(5) Å) distances in **3**. The Y(1)−N(3) and N(3)−C(32) (1.245(4) Å) distances and Y(1)−N(3)−C(32) angle (164.3(2)°) of **2** are remarkably similar to the corresponding parameters observed for the related imidazolin-2-iminato complex [Y{NC(NDippCH)$_2$}(η^8-C_8H_8)(THF)$_2$] (Y−N = 2.163(2) Å; N=C = 1.255(3) Å; Y−N−C = 163.51(19)°),[25] which itself is considered to exhibit a remarkably short Y−N distance. Delocalization about the N(3)−N(4)−N(5) framework of **3** (N−N = 1.316(6) Å mean, N−N−N = 111.7(5)°) is evidenced by the intermediacy of the N−N distances (idealized bond lengths from sum of covalent radii: N−N = 1.42 Å, N=N = 1.20 Å),[26] which compares well to the analogous metrics in the related complex [Ce{OCMe$_2$CH$_2$[AdN$_3$C(NCH$_2$CH$_2$NDipp)]-κ^3*O*,$N^{1,3}$}{N(SiMe$_3$)$_2$}$_2$] (N−N = 1.319(4) Å mean, N−N−N = 109.29(7)°).[24]

Treatment of **1** with 2 equiv of the heteroallenes *N*,*N*′-dicyclohexylcarbodiimide and *tert*-butyl isocyanate proceeded by a [2 + 2]-cycloaddition and a 1,2-migratory insertion reaction to afford [Y{C(PPh$_2$NSiMe$_3$)$_2$[C(NCy)$_2$]-κ^4*C*,*N*,*N*′,*N*″}{C(NCy)$_2$(CH$_2$Ph)-κ^2*N*,*N*′}] (**4**) and [Y{C(PPh$_2$NSiMe$_3$)$_2$[C(O)(NBu^t)]-κ^4*C*,*N*,*N*′,*O*}{C(O)(NBu^t)(CH$_2$Ph)-κ^2*N*,*O*}] (**5**), respectively (Scheme 1). In common with the formation of **2** and **3**, low-average crystalline yields of **4** (47%) and **5** (19%) were obtained despite the reactions being adjudged to be essentially quantitative by NMR spectroscopy. The ^{31}P NMR spectra exhibit a doublet for **4** (δ 17.96 ppm ($^2J_{YP}$ = 4.4 Hz)) and a broad singlet for **5** (δ 20.57 ppm), both downfield of the signals for **1** (δ 3.48 ppm ($^2J_{YP}$ = 13.0 Hz))[15] but comparable to the signal for [Zr{C(PPh$_2$NSiMe$_3$)$_2$[C(NCy)$_2$]-κ^4*C*,*N*,*N*′,*N*″}(Cl)$_2$] (δ 21.0 ppm).[27] It is not clear if the formations of **4** and **5** proceed initially by reaction at the Y=C$_{\text{carbene}}$ or Y−C$_{\text{alkyl}}$ sites, as no 1:1 products (1,2-migratory insertion or [2 + 2]-cycloaddition) could be detected at any molar ratio employed. Thus, when 1 equiv of substrate is reacted with **1**, a 50% yield of doubly reacted **4** or **5** is always observed, with 50% of **1** left unconsumed. Varying the stoichiometry simply returns different ratios of **4** or **5** and unreacted **1**, which suggests that once the heteroallene has reacted with **1** (be it by 1,2-migratory insertion or [2 + 2]-cycloaddition), this activates it to a rapid second reaction before the remaining heteroallene can react with any remaining **1**. This high reactivity is consistent with the electrophilic carbon centers present in dicyclohexylcarbodiimide and *tert*-butyl isocyanate. [2 + 2]-cycloadditions of heteroallenes to group 4 BIPM complexes have been observed previously, although while the formations of [M{C(PPh$_2$NSiMe$_3$)$_2$[C(NR)$_2$]-κ^4*C*,*N*,*N*′,*N*″}(Cl)$_2$] (M = Zr, R = Cy; M = Hf, R = *p*-tolyl)[27] are analogous to that of **4**, the formations of [M{C(PPh$_2$NSiMe$_3$)$_2$[C(O)(NAd)]-κ^4*C*,*N*,*N*′,*N*″}(Cl)$_2$] (M = Zr, Hf, Ad = adamantyl, $C_{10}H_{15}$)[27] are in contrast with that of **5**, where the isocyanate has added across the M=C bond to form an M−O bond, rather than an M−N bond. As with **2** and **3**, the methylene resonances of the benzyl group of **4** and **5** are shifted in their ^{1}H (**4**, δ 3.85 ppm; **5**, δ 3.64 ppm) and ^{13}C (**4**, δ 34.82 ppm; **5**, δ 41.99 ppm

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **2**−**8**

2·C_7H_8			
Y(1)−C(1)	2.428(2)	Y(1)−N(1)	2.340(2)
Y(1)−N(2)	2.346(2)	Y(1)−N(3)	2.165(2)
Y(1)−O(1)	2.3356(19)	C(1)−P(1)	1.659(3)
C(1)−P(2)	1.659(3)	P(1)−N(1)	1.630(2)
P(2)−N(2)	1.633(2)	N(3)−C(32)	1.245(4)
C(32)−C(37)	1.541(4)		
N(1)−Y(1)−N(2)	123.98(8)	P(1)−N(1)−Y(1)	94.00(10)
P(2)−N(2)−Y(1)	93.43(10)	N(1)−P(1)−C(1)	107.93(12)
N(2)−P(2)−C(1)	108.29(12)	P(1)−C(1)−P(2)	138.23(16)
Y(1)−N(3)−C(32)	164.3(2)		
3			
Y(1)−C(1)	2.482(5)	Y(1)−N(1)	2.339(5)
Y(1)−N(2)	2.324(5)	Y(1)−N(3)	2.433(5)
Y(1)−N(5)	2.407(5)	Y(1)−O(1)	2.349(4)
C(1)−P(1)	1.660(6)	C(1)−P(2)	1.649(6)
P(1)−N(1)	1.627(5)	P(2)−N(2)	1.641(5)
N(3)−N(4)	1.315(6)	N(4)−N(5)	1.317(6)
N(3)−C(32)	1.479(7)		
N(1)−Y(1)−N(2)	126.31(16)	P(1)−N(1)−Y(1)	95.1(2)
P(2)−N(2)−Y(1)	95.6(2)	N(1)−P(1)−C(1)	107.3(3)
N(2)−P(2)−C(1)	107.2(3)	P(1)−C(1)−P(2)	138.6(4)
N(3)−N(4)−N(5)	111.7(5)	N(4)−N(5)−Y(1)	98.0(3)
N(4)−N(3)−Y(1)	96.8(3)	N(5)−Y(1)−N(3)	53.50(16)
4·$C_4H_{10}O$			
Y(1)−C(1)	2.716(4)	Y(1)−N(1)	2.360(3)
Y(1)−N(2)	2.344(3)	Y(1)−N(3)	2.345(3)
Y(1)−N(5)	2.434(3)	Y(1)−N(6)	2.385(3)
C(1)−P(1)	1.754(4)	C(1)−P(2)	1.750(4)
P(1)−N(1)	1.616(3)	P(2)−N(2)	1.617(3)
C(1)−C(32)	1.531(5)	C(32)−N(3)	1.378(5)
C(32)−N(4)	1.300(5)	C(45)−N(5)	1.350(5)
C(45)−N(6)	1.320(5)	C(45)−C(46)	1.530(5)
N(1)−Y(1)−N(2)	112.38(11)	N(1)−Y(1)−N(3)	92.10(11)
N(2)−Y(1)−N(3)	96.75(11)	P(1)−N(1)−Y(1)	100.53(15)
P(2)−N(2)−Y(1)	99.94(15)	C(45)−N(5)−Y(1)	92.9(2)
C(45)−N(6)−Y(1)	95.9(2)	N(1)−P(1)−C(1)	109.49(17)
N(2)−P(2)−C(1)	110.26(17)	P(1)−C(1)−P(2)	128.4(2)
P(1)−C(1)−C(32)	114.5(3)	P(2)−C(1)−C(32)	114.6(3)
C(1)−C(32)−N(3)	111.6(3)	C(32)−N(3)−Y(1)	105.5(2)
C(32)−C(1)−Y(1)	85.9(2)	N(5)−C(45)−N(6)	115.3(3)
C(45)−N(5)−Y(1)	92.9(2)	C(45)−N(6)−Y(1)	95.9(2)
5			
Y(1)−C(1)	2.668(10)	Y(1)−N(1)	2.457(8)
Y(1)−N(2)	2.356(8)	Y(1)−N(4)	2.343(10)
Y(1)−O(1)	2.214(6)	Y(1)−O(2)	2.274(7)
Y(1)−O(3)	2.517(10)	C(1)−P(1)	1.738(10)
C(1)−P(2)	1.736(10)	P(1)−N(1)	1.613(8)
P(2)−N(2)	1.596(9)	C(1)−C(32)	1.523(13)
C(32)−N(3)	1.260(12)	C(32)−O(1)	1.354(12)
C(37)−N(4)	1.436(18)	C(37)−O(2)	1.157(14)
C(37)−C(42)	1.524(18)		
N(1)−Y(1)−N(2)	95.5(3)	N(1)−Y(1)−O(1)	103.4(3)
N(2)−Y(1)−O(1)	101.3(3)	N(4)−Y(1)−O(2)	56.4(3)
P(1)−N(1)−Y(1)	96.5(3)	P(2)−N(2)−Y(1)	99.0(4)
C(37)−N(4)−Y(1)	87.2(7)	C(37)−O(2)−Y(1)	97.9(8)
N(1)−P(1)−C(1)	109.5(4)	N(2)−P(2)−C(1)	110.4(5)
P(1)−C(1)−P(2)	122.8(6)	P(1)−C(1)−C(32)	116.9(7)
P(2)−C(1)−C(32)	118.0(7)	C(1)−C(32)−O(1)	111.6(8)
C(32)−O(1)−Y(1)	107.3(5)	C(32)−C(1)−Y(1)	83.5(6)
N(4)−C(37)−O(2)	114.3(12)		
6·3.5C_7H_8			
Y(1)−C(1)	2.633(3)	Y(1)−N(1)	2.393(2)
Y(1)−N(2)	2.455(2)	Y(1)−S(1)	2.7489(7)
Y(1)−S(2)	2.9011(7)	Y(1)−N(3A)	2.482(2)
C(1)−P(1)	1.748(3)	C(1)−P(2)	1.731(3)
P(1)−N(1)	1.611(2)	P(2)−N(2)	1.600(2)
C(32)−N(3)	1.304(3)	C(32)−S(1)	1.744(3)
C(32)−S(2)	1.770(3)		
N(1)−Y(1)−N(2)	107.46(8)	P(1)−N(1)−Y(1)	98.13(10)
P(2)−N(2)−Y(1)	98.95(10)	C(32A)−N(3A)−Y(1)	96.60(16)
C(32)−S(1)−Y(1)	86.73(9)	C(32)−S(2)−Y(1)	81.61(8)
S(1)−Y(1)−S(2)	63.025(19)	C(32)−N(3)−C(33)	122.2(2)
N(1)−P(1)−C(1)	107.77(12)	N(2)−P(2)−C(1)	106.35(12)
P(1)−C(1)−P(2)	126.80(17)	N(3)−C(32)−S(1)	130.0(2)
N(3)−C(32)−S(2)	115.3(2)	S(1)−C(32)−S(2)	114.54(15)
7			
Y(1)−C(1)	2.426(2)	Y(1)−N(1)	2.3504(19)
Y(1)−N(2)	2.3233(19)	Y(1)−N(3)	2.2519(19)
Y(1)−O(1)	2.3546(16)	C(1)−P(1)	1.665(2)
C(1)−P(2)	1.670(2)	P(1)−N(1)	1.6303(19)
P(2)−N(2)	1.6342(19)		
N(1)−Y(1)−N(2)	116.28(7)	P(1)−N(1)−Y(1)	93.58(8)
P(2)−N(2)−Y(1)	94.61(9)	C(32)−N(3)−Y(1)	145.43(17)
N(1)−P(1)−C(1)	107.68(10)	N(2)−P(2)−C(1)	106.87(10)
P(1)−C(1)−P(2)	139.24(14)		
8·2C_7H_8			
Y(1)−C(1)	2.453(2)	Y(1)−N(1)	2.357(2)
Y(1)−N(2)	2.359(2)	Y(1)−C(32)	2.443(3)
Y(1)−C(39)	2.467(3)	C(1)−P(1)	1.671(2)
C(1)−P(2)	1.672(2)	P(1)−N(1)	1.612(2)
P(2)−N(2)	1.625(2)	K(1)···C(1)	2.953(2)
K(1)···C(2)	3.118(2)	K(1)···C(3)	3.233(2)
K(1)···C(4)	3.521(2)	K(1)···C(5)	3.672(2)
K(1)···C(6)	3.567(2)	K(1)···C(7)	3.289(2)
K(1)···C(28)	3.353(3)	K(1)···C(33)	3.520(3)
K(1)···C(34)	3.421(3)	K(1)···C(35)	3.228(3)
K(1)···C(36)	3.108(3)	K(1)···C(37)	3.175(3)
K(1)···C(38)	3.368(3)	K(1A)···C(43)	3.140(3)
K(1A)···C(44)	3.122(3)		
N(1)−Y(1)−N(2)	126.05(7)	P(1)−N(1)−Y(1)	93.90(9)
P(2)−N(2)−Y(1)	94.14(9)	N(1)−P(1)−C(1)	108.37(11)
N(2)−P(2)−C(1)	108.59(11)	P(1)−C(1)−P(2)	140.43(14)

(d, $^3J_{YC}$ = 3.0 Hz)) NMR spectra compared to **1** (^{1}H, δ 2.78 ppm ($^2J_{YH}$ = 1.6 Hz); ^{13}C, δ 52.21 ppm (J_{YC} = 24.2 Hz)). Further analysis of the $^{13}C\{^1H\}$ NMR spectra of **4** and **5** allowed assignment of the respective amidinate and amidate carbons (**4**, δ 175.98 ppm (d, $^2J_{YC}$ = 2.0 Hz); **5**, δ 179.13 ppm (d, $^2J_{YC}$ = 2.0 Hz)) and the two quaternary carbons in each complex that derive from the [2 + 2]-cycloaddition reactions (**4**, δ 23.75 (dt, J_{PC} = 106.6 Hz, J_{YC} = 3.1 Hz), 153.30 ppm; **5** δ 29.31 (dt, J_{PC} = 108.1 Hz, J_{YC} = 2.3 Hz), 156.85 ppm (t, $^2J_{PC}$ = 5.0 Hz)). Carbodiimide and isocyanate insertions[22d,28] into yttrium−carbon σ bonds are common, and the values for the amidinate and amidate resonances in the ^{13}C NMR spectra may be compared with typical examples such as $[Y(PCp^*)\{C(NPr^i)_2\text{-}(CH_2SiMe_3)_2\text{-}\kappa^2N,N'\}_2]$ (PCp* = 1,2,3-trimethyl-1*H*-cyclopenta[*l*]phenanthrene) (δ 177.40 ppm) and $[Y(PCp^*)\text{-}\{C(O)(NSiMe_3)(CH_2SiMe_3)\text{-}\kappa^2N,O\}_2]$ (δ 188.54 ppm).[28d]

Resonances of the other quaternary carbons in **4** and **5** compare well with those reported for $[\mathrm{Zr}\{\mathrm{C}(\mathrm{PPh_2NSiMe_3})_2[\mathrm{C}(\mathrm{NCy})_2]\text{-}\kappa^4 C,N,N',N''\}(\mathrm{Cl})_2]$ (δ 15.5 (t, $J_{\mathrm{PC}} = 96.0$ Hz), 148.7 ppm (bt, $^2J_{\mathrm{PC}} = 4$ Hz)).[27]

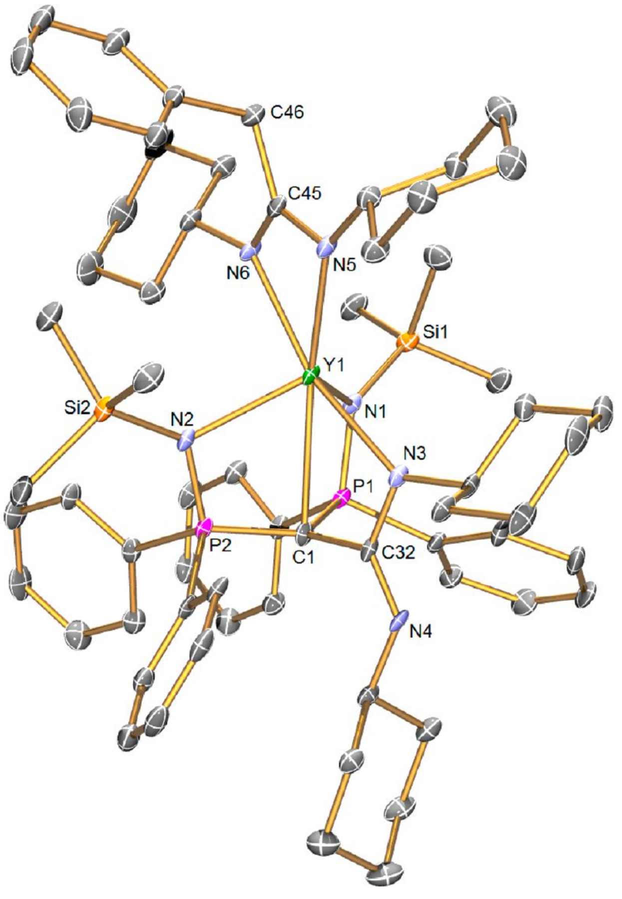


Figure 3. Molecular structure of $\mathbf{4}\cdot\mathrm{C_4H_{10}O}$ with selective atom labeling. Displacement ellipsoids are set at the 40% probability level, and hydrogen atoms and lattice solvent are omitted for clarity.

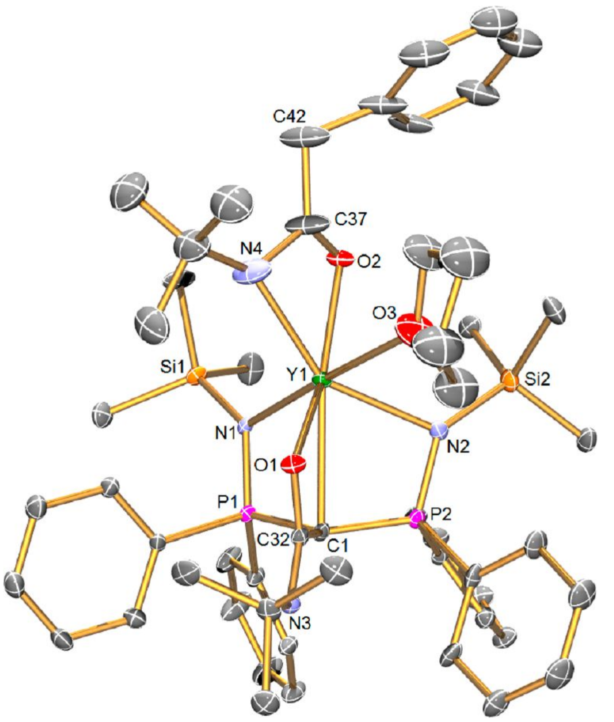


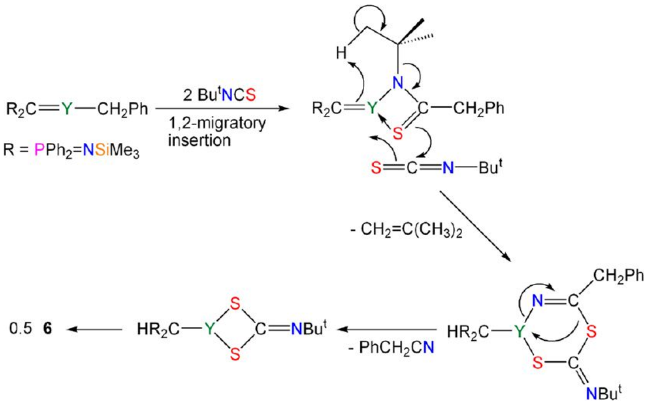
Figure 4. Molecular structure of **5** with selective atom labeling. Displacement ellipsoids are set at the 40% probability level, and hydrogen atoms are omitted for clarity.

The molecular structures of $\mathbf{4}\cdot\mathrm{C_4H_{10}O}$ (Figure 3) and **5** (Figure 4) were confirmed by single-crystal X-ray diffraction and are depicted here, with selected bond lengths and angles given in Table 1. As with **2** and **3**, the structures of **4** and **5** have similar bulk properties, with the yttrium centers of both complexes coordinated by one κ^4-dianionic and one κ^2-monoanionic ligand. Therefore, they will be discussed together, although the yttrium center of **4** is five-coordinate and that of **5** is six-coordinate, as the smaller steric bulk of the *tert*-butyl groups versus cyclohexyl groups allows the additional coordination of a THF molecule in **5**. The propeller-shaped geometry of the dianionic ligand systems, with N(1), N(2), and N(3) (**4**) or N(1), N(2), and O(1) (**5**) at the vertices of approximate triangles is comparable to that observed for $[\mathrm{Zr}\{\mathrm{C}(\mathrm{PPh_2NSiMe_3})_2[\mathrm{C}(\mathrm{NCy})_2]\text{-}\kappa^4 C,N,N',N''\}(\mathrm{Cl})_2]$[27] and the Y(1)−C(1) distances (**4**, 2.716(4) Å; **5**, 2.668(10) Å) and other intramolecular bond lengths and angles are similar to related yttrium methanide complexes.[14,20,29] Localized single (**4**, C(32)−N(3) = 1.378(5) Å; **5**, C(32)−O(1) = 1.354(12) Å) and double (**4**, C(32)−N(4) = 1.300(5) Å; **5**, C(32)−N(3) = 1.260(12) Å) bonds are observed in the dianionic ligand framework, and these are analogous to the related distances in $[\mathrm{Zr}\{\mathrm{C}(\mathrm{PPh_2NSiMe_3})_2[\mathrm{C}(\mathrm{NCy})_2]\text{-}\kappa^4 C,N,N',N''\}(\mathrm{Cl})_2]$ (C−N = 1.384(5) and 1.285(5) Å).[27] A localized C−N single bond (C(37)−N(4) = 1.436(18) Å) and C═O double bond (C(37)−O(2) = 1.157(14) Å) were also observed in the amidate ligand of **5**, in contrast to the corresponding delocalized distances found in $[\mathrm{Y}(\mathrm{Tp^{Me2}})(\mathrm{Cp})\{\mathrm{C}(\mathrm{O})(\mathrm{NPh})(\mathrm{CH_2Ph})\text{-}\kappa^2\text{-}N,O\}_2]$ (Tp = tris(pyrazolyl)borate) (C−N = 1.299(6) Å, C−O 1.276(6) Å).[28e] However, delocalization is evident in the amidinate ligand of **4** (C−N range 1.320(5)−1.350(5) Å) and these values compare well to the equivalent distances observed in $[\mathrm{Y}(\mathrm{Tp^{Me2}})(\mathrm{Cp})\{\mathrm{C}(\mathrm{NCy})_2(\mathrm{CH_2Ph})\text{-}\kappa^2 N,N'\}_2]$ (C−N range 1.314(4)−1.340(4) Å).[28e]

The reactions of **1** with heteroallenes was extended to *tert*-butyl isothiocyanate, which was found to react in a 2:1 molar ratio with **1** to afford a dimeric product, $[\mathrm{Y}(\mathrm{BIPMH})\{\mathrm{C}(\mathrm{S})_2(\mathrm{NBu^t})\text{-}1\text{-}\kappa S,2\text{-}\kappa N{:}\mu,\kappa S'\}]_2$ (**6**), which incorporates two dithiocarbonimidate ligands, in low (33%) yield (Scheme 1). Variation of the reaction stoichiometry from a 1:1 to a 2:1 molar ratio of $\mathrm{Bu^tNCS}$ to **1** did not lead to increased yields of **6**. It is noteworthy that Mindiola has reported that the reaction of phenyl isothiocyanate with a titanium carbene proceeds via a [2 + 2]-cycloaddition reaction,[30] while Grubbs has disclosed the desulfurization of phenyl isothiocyanate mediated by an iridium carbene complex.[31] However, the formation of **6** represents a novel mode of reactivity of isothiocyanates with early metal carbenes. The desulfurization of isothiocyanates to form dithiocarbonimidates mediated by transition-metal complexes has been observed previously,[32] but in all of these examples a low-valent metal complex or intermediate is present to mediate the reductive disproportionation of two isothiocyanate molecules, generally leading to the formation of the dithiocarbonimidate and an isocyanide. This is not a viable pathway for yttrium(III), which is typically redox-inert and yttrium(II) complexes are only formed under highly reducing conditions.[33] Analysis of the reaction mixture by multinuclear

NMR spectroscopy revealed that a number of products are formed in the reaction mixture, but only **6** could be isolated and identified. The reaction is proposed to proceed as described in Scheme 2, where initially 1,2-migratory insertion of *tert*-butyl isocyanate into the Y−C$_{alkyl}$ bond occurs. Deprotonation of the *tert*-butyl group is then effected by the methanediide, forming a methanide and a dianionic thioamidate and eliminating isobutylene. In support of this, C−H activation reactions mediated by the related complexes [Y(BIPM)(CH$_2$SiMe$_3$)(THF)] and [Y(BIPM)(I)(THF)$_2$] have been observed previously.[20] The sulfur of the thioamidate then nucleophilically attacks the electrophilic carbon of a second molecule of *tert*-butyl isocyanate to form a C−S bond. This then rearranges to form the dithiocarbonimidate, which subsequently dimerizes with concomitant elimination of benzyl nitrile, which appears to react with other species in the reaction mixture such as **1**[34] to form an intractable mixture of products that could not be conclusively identified by mass spectrometry methods.

Scheme 2. Proposed Mechanism of Formation of 6



The NMR spectra of **6** were recorded in d_8-THF due to the low solubility of **6** in arene solvents, but the coordination of d_8-THF to the yttrium centers of **6** results in an equilibrium mixture of complexes, presumably consisting of monomers and dimers, which results in complex NMR spectra that do not vary greatly with temperature. The ^{31}P NMR spectrum of **6** exhibits a broad singlet (δ 18.56 ppm) and two double doublets (δ 18.95 ppm ($^2J_{PP}$ = 12.2 Hz, $^2J_{YP}$ = 6.7 Hz, 21.04 ppm, $^2J_{PP}$ = 12.2 Hz, $^2J_{YP}$ = 6.7 Hz)) which derive from the monomeric and dimeric species. Germane to this observation, three signals are observed in the ^{29}Si NMR spectrum (δ −6.00, −4.69, and −3.66 ppm). Although the methanide proton was not observed in the ^{1}H NMR spectrum of **6**, the methanide carbon was observed in its ^{13}C{^{1}H} NMR spectrum (δ 14.90 ppm (t, J_{PC} = 106.6 Hz)) but the quaternary dithiocarbonimidate carbon was not observed.

The molecular structure of **6**·3.5C$_7$H$_8$ was obtained and is illustrated in Figure 5, and selected bond lengths and angles can be found in Table 1. **6** is the first structurally characterized example of a lanthanide dithiocarbonimidate complex and exhibits a novel bridging binding mode for this ligand class, as it additionally coordinates by a nitrogen lone pair.[35] The bis(iminophosphorano)methanide ligands in **6** are bound to yttrium in a tridentate pseudoboat conformation with typical metrical parameters.[14,20,29] Two dithiocarbonimidate ligands bridge the two seven-coordinate yttrium centers of **6**, with each {Bu^{t}NCS$_2$}$^{2-}$ unit in a mutually trans arrangement coordinating by one N-donor to one yttrium center and one S-donor to the other yttrium, with the final S-donor bridging the two metal centers. These contacts form a Y$_2$C$_2$N$_2$S$_4$ open cage structure formally made up of two YNCS and two YSCS four-membered rings that are alternately above and below the Y(1)−S(1)−Y(1A)−S(1A) plane. As would be expected, the terminal Y(1)−S(1) distance (2.7489(7) Å) is much shorter than the bridging Y(1)−S(2) value (2.9011(7) Å). The C−S (1.757(3) Å mean) and C=N distances (1.304(3) Å) observed in **6** are indicative of single- and double-bond character in these respective bonds, as is the case for other dithiocarbonimidate complexes such as [Pd(PMe$_3$)$_2${C(S)$_2$NPh-κ^2-$S^{1,3}$}] (C−S = 1.760(3) Å mean; C=N = 1.261(4) Å).[32h] It is notable that the C(32)−N(3)−C(33) angle of **6** (122.2(2)°) is not markedly different from that found for [Pd(PMe$_3$)$_2${C(S)$_2$NPh-$\kappa^2 S^{1,3}$}] (C−N−C = 123.1(3)°)[32h] despite its coordination to yttrium, and the Y(1)−N(3A) distance (2.482(2) Å) is slightly longer than the iminophosphorano Y−N distances (2.393(2)−2.455(2) Å).

Addition of 2,6-diisopropylaniline to **1** quantitatively afforded [Y(BIPM)(NHDipp)(THF)] (**7**) with the elimination of toluene, as evidenced by ^{31}P{^{1}H} NMR spectroscopy, but in a poor crystalline yield (13%) following workup (Scheme 1). Thus, the

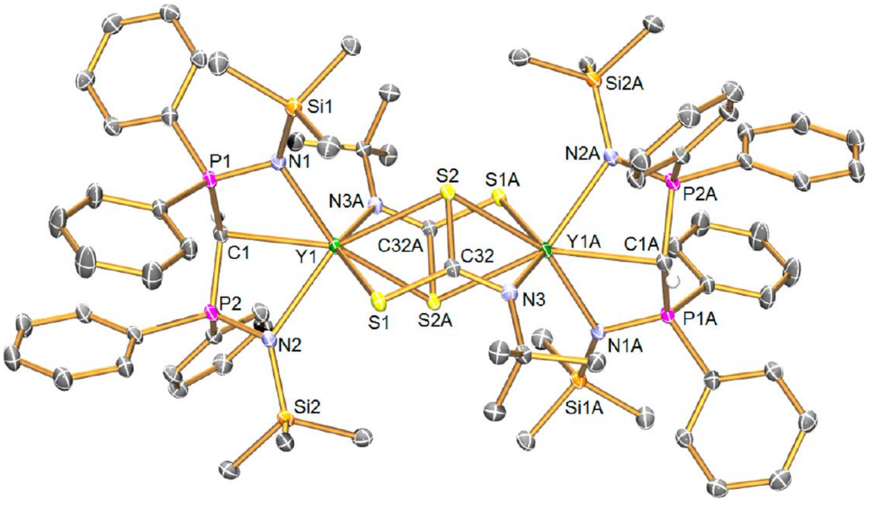


Figure 5. Molecular structure of **6**·3.5C$_7$H$_8$ with selective atom labeling. Displacement ellipsoids are set at the 40% probability level, and hydrogen atoms (except methanide hydrogens) and lattice solvent are omitted for clarity. Symmetry operation to generate complete molecule: −3 + *x*, −*y* + 1, −*z* +1.

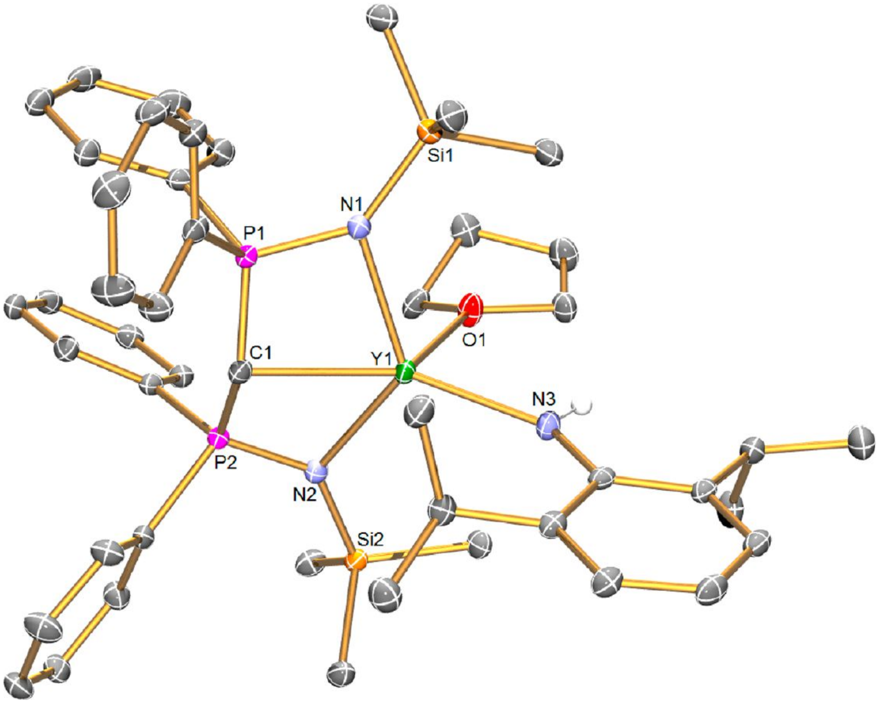


Figure 6. Molecular structure of **7** with selective atom labeling. Displacement ellipsoids are set at the 40% probability level, and hydrogen atoms (except amide hydrogen) are omitted for clarity.

Y−C_{alkyl} bond in **1** reacts in preference in this instance to 1,2-addition (hydroamination) across the Y═C bond, as was observed for [Hf(BIPMH)(NHC_6H_4Me-4)$(Cl)_2$], which was formed from a 1,2-addition reaction between *p*-tolylamine and [Hf(BIPM)$(Cl)_2$].[27] The spectroscopic data of **7** confirm the retention of the methanediide, with the resonance in the $^{31}P\{^1H\}$ NMR spectrum (*δ* 5.48 (d, $^2J_{YP}$ = 13.0 Hz)) exhibiting a chemical shift and coupling constant that is typical for yttrium bis(iminophosphorano)methanediide complexes.[13,15,16] The anilide proton was observed in the ^1H NMR spectrum of **7** at *δ* 4.85 ppm, which is comparable to the value reported for the related complex [Y{($C_6H_3Pr^i_2$-2,6)NC(Me)CH(C_5H_3N-1,SiMe$_2$CH$_2$-2)-κ^3-*C,N,N′*}(NHDipp)(THF)] (*δ* 4.75 ppm), which was also prepared by an alkane elimination reaction.[36] The potentially diagnostic signal arising from the methanediide carbon could not be observed in the $^{13}C\{^1H\}$ NMR spectrum of **7** even after long accumulations on highly concentrated samples. However, the anilide ipso carbon was readily observed (*δ* 152.32 ppm (d, $^2J_{YC}$ = 3.0 Hz)), and this resonance compares very well to the value reported for [Y{($C_6H_3Pr^i_2$-2,6)NC(Me)CH(C_5H_3N-1,SiMe$_2$CH$_2$-2)-κ^3*C,N,N′*}(NHDipp)(THF)] (*δ* 151.8 ppm).[36]

The methanediide formulation of **7** was confirmed by X-ray crystallography (depicted in Figure 6, with selected bond lengths and angles given in Table 1) by its short Y(1)−C(1) distance (2.453(2) Å) and P(1)−C(1)−P(2) angle (140.45(14)°), which are more comparable to those found for **1** (Y═C = 2.357(3) Å; P−C−P = 147.6(2)°)[16] than for related yttrium bis(iminophosphorano)methanide complexes, which exhibit longer Y−C distances and possess P−C−P angles that deviate further from linearity.[14,20,29] The BIPM framework of **7** adopts a boat conformation, and the five-coordinate yttrium center is additionally bound by the anilide and THF. The nonlinear Y(1)−N(3)−C(32) angle (145.43(17)°) and the Y(1)−N(3) distance (2.2519(19) Å) of **7** are in accord with the corresponding metrical parameters observed for the related complex [Y{($C_6H_3Pr^i_2$-2,6)NC(Me)CH(C_5H_3N-1,SiMe$_2$CH$_2$-2)-κ^3-*C,N,N′*}(NHDipp)(THF)] (Y−N = 2.197(5) Å; Y−N−C = 154.9(4)°).[36]

The reaction between benzylpotassium ($PhCH_2K$) and **1** results in a formal 1,2-carbopotassiation across the Y═$C_{carbene}$ bond to yield the yttriate polymer [Y(BIPM)(μ-η^1:η^6-CH_2Ph)(μ-η^1:η^2-CH_2Ph)K]$_\infty$ (**8**) (Scheme 1). As with other complexes reported here, the crystalline yield of **8** was low (29%), even though it is the only detectable product in the ^{31}P NMR spectrum of the reaction mixture. It is noteworthy that [Y(BIPM)(CH_2SiMe_3)(THF)] reacts with $PhCH_2K$ to form **8** by ligand scrambling, and we therefore conclude that **8** is the thermodynamic product, since it is stabilized by electrostatic interactions between potassium and *π*-basic aryl substituents (see below) and the polymer precipitates, driving the reaction to completion. Group 3 and lanthanide organometallic complexes commonly occlude salts within their coordination sphere due to their high Lewis acidity, and mixed-metal aggregates are commonplace.[37] In the majority of cases, these complexes occlude lithium halides, aryloxides, and alkyls and examples of potassium alkyl occlusion are rare, but the aryl substituents in **8** provide an ideal environment for the coordination of potassium cations, as is the case for related polymeric lanthanide heavier alkali metal chains.[38] Although **8** displays adequate solubility in arene solvents, it rapidly crystallizes once seeded; hence, the NMR spectroscopy was performed on d_8-THF solutions of **8**. The NMR spectra of **8** are more straightforward than would be expected from the solid-state structure (see below); therefore, we propose that THF coordinates to yttrium and/or potassium and breaks up the polymeric chain in solution into discrete units. Both methylene signals of the benzyl groups of **8** therefore resonate at the same chemical shift (^1H, *δ* 1.81 ppm (d, $^2J_{YH}$ = 6.0 Hz); ^{13}C, *δ* 51.31 ppm (br, s)), and only one resonance is observed in the ^{31}P NMR spectrum (*δ* 1.42 ppm (d, $^2J_{YP}$ = 11.3 Hz)). The methanediide signal in the $^{13}C\{^1H\}$ NMR of **8** (*δ* 57.46 ppm (dt, J_{PC} = 179.1 Hz, J_{YC} = 3.0 Hz)) is slightly upfield

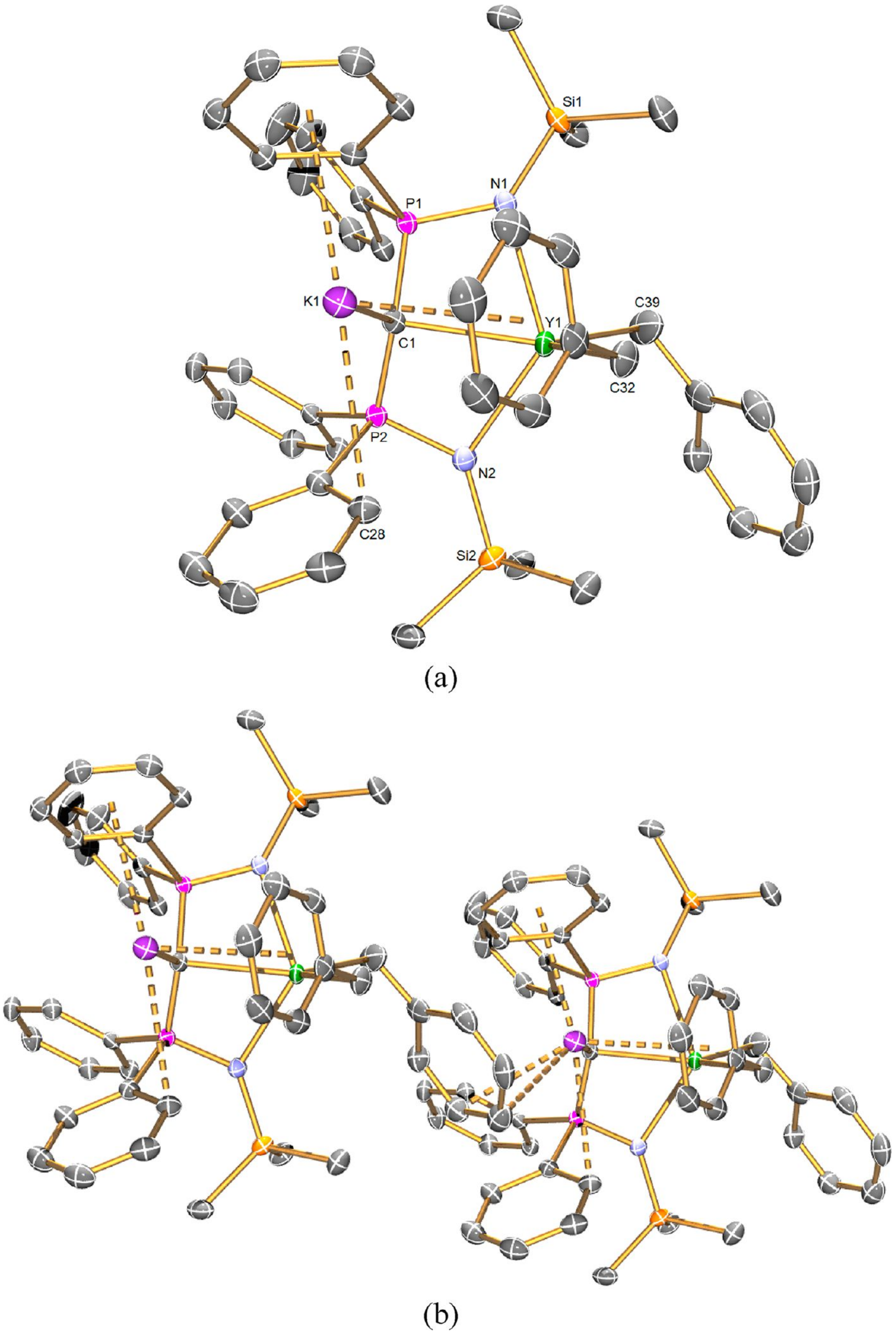


Figure 7. Molecular structure of the monomer with selective atom labeling (a) and part of the polymeric chain (b) of **8**·2C_7H_8. Displacement ellipsoids are set at the 40% probabilitly level, and hydrogen atoms and lattice solvent are omitted for clarity.

of, and exhibits smaller coupling constants than, the resonance observed for **1** (δ 61.81 ppm (dt, J_{PC} = 207.3 Hz, J_{YC} = 5.0 Hz)).

The solid-state structure of **8**·2C_7H_8 was determined by X-ray crystallography, and the monomer (a) and part of the polymeric chain (b) are depicted in Figure 7, with selected bond lengths and angles deposited in Table 1. The bond lengths and angles within the BIPM scaffold of **8** are not markedly different from those found in **1**, although the Y(1)−C(1) distance of **8** (2.453(2) Å) is longer than that observed in **1** (2.357(3) Å),[16] most likely due to an additional interaction of the carbene with potassium (K(1)···C(1) = 2.953(2) Å). This $K\cdots C_{carbene}$ distance is similar to that observed for $[K_2C(PPh_2NPh)_2]_2$ ($K\cdots C_{methanediide}$ = 2.910(3) Å)[39] but is much shorter than $K\cdots C_{methanediide}$ distances reported for other related potassium bis(iminophosphorano)methanediide complexes.[40] The five-coordinate yttrium center of **8** is additionally bound by two benzyl ligands (Y(1)−C(32) = 2.443(3) Å; Y(1)−C(39) = 2.467(3) Å), but no *ipso*-C-Ph contacts are evident; again, these are longer than that observed for **1** (2.406(4) Å), which in contrast exhibits a $Y-C_{ipso}$ interaction (2.921(4) Å).[16] The potassium center of **8** exhibits a contact with C(1) and multihapto interactions with a benzyl group and two *P*-phenyl groups of one monomeric unit and with a neighboring benzyl group to form the polymeric chain. These multihapto interactions can be assigned nominally as η^6 (range K(1)−{C(33)−C(38)} = 3.109(3)−3.422(3) Å), η^3 or η^6 (range K(1)−C(2),C(3),C(7) = 3.118(2)−3.289(2) Å; range K(1)−C(4),C(5),C(6) = 3.521(2)−3.672(2) Å), η^1 (K(1)−C(28) = 3.353(3) Å), and η^2 (K(1A)−C(43) = 3.140(3) Å; K(1A)−C(44) = 3.122(3) Å) by comparison with values observed for related complexes.[38−40] Both η^6 interactions are asymmetric, and one may perhaps be more accurately assigned as η^3, because there is a difference of over 0.2 Å between the two ranges.

■ SUMMARY AND CONCLUSIONS

A wide-ranging reactivity study of the yttrium alkyl carbene complex $[Y(BIPM)(CH_2Ph)(THF)]$ (**1**) has been performed. The reactions of **1** with alkyl nitriles and azides afforded $[Y(BIPM)\{NC(Bu^t)(CH_2Ph)\}(THF)]$ (**2**) and $[Y(BIPM)\{N_3Ad\text{-}1,Bn\text{-}3\text{-}\kappa^2N^{1,3}\}(THF)]$ (**3**) by 1,2-migratory insertion reactions into the $Y-C_{alkyl}$ bond, while the reactions of **1** with alkyl carbodiimides and isocyanates yielded $[Y\{C(PPh_2NSiMe_3)_2[C(NCy)_2]\text{-}\kappa^4C,N,N',N''\}\{C(NCy)_2(CH_2Ph)\text{-}\kappa^2N,N'\}]$ (**4**) and $[Y\{C(PPh_2NSiMe_3)_2[C(O)(NBu^t)]\text{-}\kappa^4C,N,N',O\}\{C(O)(NBu^t)(CH_2Ph)\text{-}\kappa^2N,O\}]$ (**5**) by additional [2 + 2]-cycloaddition reactions, following classical reactivity patterns. The synthesis of $[Y(BIPM)(NHDipp)(THF)]$ (**7**) from **1** and 2,6-diisopropylaniline by alkane elimination is also in accord with examples from the literature. In contrast, the treatment of **1** with an alkyl isothiocyanate afforded dimeric $[Y(BIPMH)\{C(S)_2(NBu^t)\text{-}1\text{-}\kappa S,2\text{-}\kappa N:\mu,\kappa S'\}]_2$ (**6**) via a proposed deprotonation and reductive disproportionation, which is a novel reactivity profile for early-metal carbene complexes with isothiocyanates. Finally, the addition of benzylpotassium across the $Y{=}C_{carbene}$ bond of **1** to produce $[Y(BIPM)(\mu\text{-}\eta^1{:}\eta^6CH_2Ph)(\mu\text{-}\eta^2{:}\eta^2\text{-}CH_2Ph)K]_\infty$ (**8**) represents another reactivity mode for early-metal carbenes. The results reported herein represent further examples of unexpected and unusual reactivities derived from highly polarized M═C double bonds that merit further investigation.

■ EXPERIMENTAL SECTION

General Considerations. 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 solvents were distilled from potassium, degassed by three freeze−pump−thaw cycles, and stored under nitrogen. **1**,[16] 1-adamantyl azide,[41] and benzylpotassium[42] were prepared according to published procedures. All other chemicals were purchased; all solid reagents were dried under vacuum for 3 h, and all liquid reagents were dried over 4 Å molecular sieves and distilled before use. ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6, 79.5, and 162.0 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, U.K., or by Dr. Tong Liu at the University of Nottingham.

Preparation of $[Y(BIPM)\{NC(Bu^t)(CH_2Ph)\}(THF)]$ (2). A solution of Bu^tCN (0.17 g, 2.00 mmol) in toluene (10 mL) was added dropwise to a precooled (−78 °C) solution of **1** (1.62 g, 2.00 mmol) in toluene (10 mL). The light brown mixture was slowly warmed to room temperature with stirring over 18 h. Volatiles were removed in vacuo, and the resulting light brown oil was extracted with toluene (2 mL) and stored at ambient temperature overnight to afford **2** as colorless crystals. Yield: 0.24 g, 14%. Anal. Calcd for $C_{47}H_{62}N_3OP_2Si_2Y$: C, 63.35; H, 6.91; N, 4.72. Found: C, 63.30; H, 6.91; N, 4.67. ^1H NMR (d_6-benzene, 298 K): δ 0.10 (s, 18H, $Si(CH_3)_3$), 1.48 (m, 4H, OCH_2CH_2), 1.55 (s, 9H, $C(CH_3)_3$), 3.76 (m, 4H, OCH_2CH_2), 3.88 (s, 2H, CH_2Ph), 7.16 (m, 13H, *m*- and *p*-Ph-C*H* and *p*-Bn-C*H*), 7.30 (vt, $^3J_{HH}$ = 7.6 Hz, 2H, m-Bn-C*H*), 7.35 (t, $^3J_{HH}$ = 6.8 Hz, 2H, o-Bn-C*H*), 7.89 (br, 8H, *o*-Ph-C*H*). $^{13}C\{^1H\}$ NMR (d_6-benzene, 298 K): δ 3.47 ($Si(CH_3)_3$), 25.00 (OCH_2CH_2), 29.13 ($C(CH_3)_3$), 43.02 (CH_2Ph), 43.86 ($C(CH_3)_3$), 51.36 (dt, J_{PC} = 152.0 Hz, J_{YC} = 5.0 Hz, CP_2), 70.77 (OCH_2CH_2), 124.75 (*p*-Bn-CH), 127.29 (t, $^2J_{PC}$ = 5.5 Hz, *o*-Ph-CH), 128.65 (*m*-Bn-CH), 130.42 (*o*-Bn-CH), 131.17 (t, $^3J_{PC}$ = 5.5 Hz, *m*-Ph-CH), 140.95 (br, *ipso*-Ph-C), 142.09 (*ipso*-Bn-C), 175.27 (d, $^2J_{YC}$ = 8.1 Hz, $PhCH_2C(Bu^t)N$). $^{31}P\{^1H\}$ NMR (d_6-benzene, 298 K): δ 3.60 (d, $^2J_{YP}$ = 13.0 Hz, CP_2). $^{29}Si\{^1H\}$ NMR (d_6-benzene, 298 K): δ −10.35 ($NSi(CH_3)_3$. FTIR ν/cm^{-1} (Nujol): 1671 (s, C═N stretch), 1600 (w), 1282 (s), 1243 (s), 1105 (s), 1077 (s), 1051 (s), 979 (w), 835 (s), 757 (m), 738 (m), 713 (m), 695 (m), 677 (m), 646 (w), 608 (m), 541 (m), 521 (m).

Preparation of $[Y(BIPM)\{N_3Ad\text{-}1,Bn\text{-}3\text{-}\kappa^2N^{1,3}\}(THF)]$ (3). A solution of AdN_3 (0.18 g, 1.00 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (0.81 g, 1.00 mmol) at −78 °C. The orange mixture was slowly warmed to room temperature with stirring over 24 h. Volatiles were removed in vacuo, and the resulting yellow oil was extracted with toluene (3 mL) to afford colorless crystals of **3** at −30 °C. Yield: 0.27 g, 27%. Anal. Calcd for $C_{52}H_{68}N_5OP_2Si_2Y$: C, 63.27; H, 6.94; N, 7.09. Found: C, 63.22; H, 6.86; N, 7.01. ^1H NMR (d_6-benzene, 298 K): δ 0.13 (s, 18H, $SiC(CH_3)_3$), 1.31 (m, 4H, OCH_2CH_2), 1.83 (br m, 6H, Ad-CH_2), 2.22 (br m, 3H, Ad-C*H*), 2.29 (br m, 6H, Ad-CH_2), 3.74 (m, 4H, OCH_2CH_2), 4.93 (s, 2H, CH_2Ph), 6.92 (m, $^3J_{HH}$ = 6.8 Hz, 4H, *m*-Ph-C*H*), 6.98 (m, 2H, *p*-Ph-C*H*), 7.13 (m, 7H, *m*- and *p*-Ph-C*H* and *p*-Bn-C*H*), 7.20 (vt, $^3J_{HH}$ = 7.6 Hz, 2H, *m*-Bn-C*H*), 7.39 (d, $^3J_{HH}$ = 7.6 Hz, 2H, *o*-Bn-C*H*), 7.45 (br m, 4H, *o*-Ph-C*H*), 7.96 (br m, 4H, *o*-Ph-C*H*). $^{13}C\{^1H\}$ NMR (d_6-benzene, 298 K): δ 3.96 ($Si(CH_3)_3$), 24.75 (OCH_2CH_2), 30.24 (Ad-CH), 37.15 (Ad-CH_2), 44.89 (Ad-CH_2), 56.83 (d, $^2J_{YC}$ = 3.0 Hz, NC-Ad), 59.81 (dt, J_{PC} = 185.1 Hz, J_{YC} = 4.0 Hz, CP_2), 61.42 (CH_2Ph), 70.60 (OCH_2CH_2), 126.65 (*p*-Bn-CH), 127.01 (vt, $^2J_{PC}$ = 6.6 Hz, *o*-Ph-CH), 127.22 (vt, $^2J_{PC}$ = 6.6 Hz, *o*-Ph-CH), 128.18 (*p*-Ph-CH), 128.44 (*m*-Bn-CH), 128.72 (*p*-Ph-CH), 129.08 (*o*-Bn-CH), 131.01 (vt, $^3J_{PC}$ = 5.9 Hz, *m*-Ph-CH), 131.56 (vt, $^3J_{PC}$ = 5.9 Hz, *m*-Ph-CH), 140.83 (vt, J_{PC} = 52.0 Hz, *ipso*-Ph-C), 142.19 (*ipso*-Bn-C), 142.38 (vt, J_{PC} = 45.4 Hz, *ipso*-Ph-C). $^{31}P\{^1H\}$ NMR (d_6-benzene, 298 K): δ 3.89 (d, $^2J_{YP}$ = 11.3 Hz, CP_2). $^{29}Si\{^1H\}$ NMR (d_6-benzene, 298 K): δ −10.60 ($Si(CH_3)_3$). FTIR ν/cm^{-1} (Nujol): 1589 (w), 1434 (m), 1243 (s), 1164 (w), 1106 (s), 1072 (s), 1062 (s), 1044 (s), 830 (s), 769 (m), 754 (m), 745 (m), 733 (m), 714 (m), 699 (m), 677 (s), 660 (m), 652 (m), 608 (m), 571 (m), 543 (m), 521 (m), 511 (m).

Preparation of $[Y\{C(PPh_2NSiMe_3)_2[C(NCy)_2]\text{-}\kappa^4C,N,N',N''\}\{C(NCy)_2(CH_2Ph)\text{-}\kappa^2N,N'\}]$ (4). Toluene (20 mL) was added to a precooled (−78 °C) mixture of **1** (1.62 g, 2.00 mmol) and $C(NCy)_2$ (0.83 g, 4.00 mmol). The yellow mixture was slowly warmed to room temperature with stirring over 18 h. Volatiles were removed in vacuo, and the resulting yellow oil was extracted with diethyl ether (2 mL) and stored at ambient temperature overnight to afford **4** as colorless crystals. Yield: 1.14 g, 47%. Anal. Calcd for $C_{64}H_{89}N_6P_2Si_2Y$: C, 66.87; H, 7.80; N, 7.31. Found: C, 66.79; H, 7.73; N, 7.25. ^1H NMR (d_6-benzene, 298 K):

δ 0.11 (s, 18H, $\mathrm{NSi(CH_3)_3}$), 0.39 (m, 2H, *C*H-2$_{\mathrm{ax}}$ NCy), 0.83 (m, 2H, *C*H-2$_{\mathrm{ax}}$ NCy), 0.96 (m, 2H, *C*H-2$_{\mathrm{ax}}$ NCy), 1.19−1.31 (m, 6H, C*H*$_{\mathrm{ax}}$ NCy), 1.36 (m, 4H, C*H*$_{\mathrm{ax}}$ NCy), 1.61 (m, 4H, C*H*$_{\mathrm{ax}}$ NCy), 1.78 (m, 6H, C*H*$_{\mathrm{eq}}$ NCy), 1.88 (m, 4H, C*H*$_{\mathrm{eq}}$ NCy), 2.06 (m, 4H, C*H*$_{\mathrm{eq}}$ NCy), 2.18 (m, 2H, C*H*$_{\mathrm{eq}}$ NCy), 2.65 (m, 4H, C*H*-2$_{\mathrm{eq}}$ NCy), 3.29 (m, 2H, C*H*-1$_{\mathrm{ax}}$ NCy), 3.52 (m, 1H, C*H*-1$_{\mathrm{ax}}$ NCy), 3.85 (s, 2H, $\mathrm{CH_2Ph}$), 4.27 (m, 1H, C*H*-1$_{\mathrm{ax}}$ NCy), 6.80 (vt, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 4H, *m*-Ph-C*H*), 6.88 (vt, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 2H, *p*-Ph-C*H*), 7.02 (vt, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 2H, *p*-Ph-C*H*), 7.09 (m, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 4H, *m*-Ph-C*H*), 7.11 (t, $^{3}J_{\mathrm{HH}}$ = 8.0 Hz, 1H, *p*-Bn-C*H*), 7.25 (vt, $^{3}J_{\mathrm{HH}}$ = 8.0 Hz, 2H, *m*-Bn-C*H*), 7.42 (d, 2H, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, *o*-Bn-C*H*), 7.67 (dd, $^{3}J_{\mathrm{PH}}$ = 12.4 Hz, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 4H, *o*-Ph-C*H*), 8.05 (dd, $^{3}J_{\mathrm{PH}}$ = 12.0 Hz, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 4H, *o*-Ph-C*H*). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ 3.77 ($\mathrm{NSi(CH_3)_3}$), 23.75 (dt, J_{PC} = 106.6 Hz, J_{YC} = 3.1 Hz, $\mathrm{CP_2}$), 25.96 (*C*-4 NCy), 26.23 (*C*-4 NCy), 26.89 (*C*-3 NCy), 27.21 (*C*-3 NCy), 27.30 (*C*-3 NCy), 27.75 (*C*-2 NCy), 32.75 (*C*-2 NCy), 34.66 (*C*-2 NCy), 34.82 ($\mathrm{CH_2Ph}$), 36.14 (*C*-2 NCy), 57.29 (*C*-1 NCy), 57.37 (*C*-1 NCy), 57.80 (*C*-1 NCy), 126.27 (*p*-Bn-CH), 127.31 (vt, $^{2}J_{\mathrm{PC}}$ = 6.0 Hz, *o*-Ph-CH), 127.46 (vt, $^{2}J_{\mathrm{PC}}$ = 6.0 Hz, *o*-Ph-CH), 127.69 (*m*-Bn-CH), 128.60 (*o*-Bn-CH), 130.49 (*p*-Ph-CH), 130.61 (*p*-Ph-CH), 130.63 (dd, J_{PC} = 118.8 Hz, $^{3}J_{\mathrm{PC}}$ = 23.1 Hz, *ipso*-Ph-C), 133.06 (vt, $^{3}J_{\mathrm{PC}}$ = 5.0 Hz, *m*-Ph-CH), 134.00 (vt, $^{3}J_{\mathrm{PC}}$ = 5.0 Hz, *m*-Ph-CH), 136.58 (d, J_{PC} = 14.1 Hz, *ipso*-Ph-C), 137.18 (*ipso*-Ph-C), 137.79 (dd, J_{PC} = 68.4 Hz, $^{3}J_{\mathrm{PC}}$ = 14.0 Hz, *ipso*-Ph-C), 138.47 (*ipso*-Bn-C), 153.30 ($\mathrm{CN_2}$), 175.98 (d, $^{2}J_{\mathrm{YC}}$ = 2.0 Hz, $\mathrm{PhCH_2CN_2}$). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ 17.96 (d, $^{2}J_{\mathrm{YP}}$ = 4.4 Hz, $\mathrm{C}P_2$). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ −5.87 (*Si*$\mathrm{(CH_3)_3}$). FTIR ν/cm^{-1} (Nujol): 1526 (s), 1246 (s), 1221 (s), 1191 (m), 1171 (m), 1110 (s), 1074 (s), 1029 (s), 996 (m), 932 (m), 890 (m), 834 (s), 741 (s), 709 (s), 695 (s), 660 (m), 608 (m), 557 (m), 535 (m).

Preparation of [Y{C(PPh$_2$NSiMe$_3$)$_2$[C(O)(NBu$^{\mathrm{t}}$)]-κ^4*C,N,N′,O*}{C(O)(NBu$^{\mathrm{t}}$)(CH$_2$Ph)-κ^2*N,O*}] (5). A solution of Bu$^{\mathrm{t}}$NCO (0.44 g, 4.00 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (1.62 g, 2.00 mmol) in toluene (10 mL) at −78 °C. The brown mixture was slowly warmed to room temperature with stirring over 18 h. Volatiles were removed in vacuo, and the resulting brown oil was extracted with toluene (2 mL) and stored at ambient temperature overnight to afford **5** as colorless crystals. Yield: 0.38 g, 19%. Anal. Calcd for $\mathrm{C_{52}H_{71}N_4O_3P_2Si_2Y}$: C, 62.01; H, 7.11; N, 5.57. Found: C, 61.88; H, 6.96; N, 5.58. ^{1}H NMR (d_6-benzene, 298 K): δ 0.29 (s, 18H, $\mathrm{Si(CH_3)_3}$), 0.95 (s, 9H, $\mathrm{C(CH_3)_3}$), 1.36 (m, 4H, $\mathrm{OCH_2CH_2}$), 1.46 (s, 9H, $\mathrm{C(CH_3)_3}$), 3.60 (m, 4H, $\mathrm{OCH_2CH_2}$), 3.64 (s, 2H, $\mathrm{CH_2Ph}$), 6.66 (vt, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 4H, *m*-Ph-C*H*), 6.71 (t, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 2H, *p*-Ph-C*H*), 7.13 (m, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 3H, *m*- and *p*-Bn-C*H*), 7.23 (t, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 4H, *m*-Ph-C*H*), 7.27 (m, 2H, *p*-Ph-C*H*), 7.41 (d, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 1H, *o*-Bn-C*H*), 7.57 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 1H, *o*-Bn-C*H*), 7.70 (dd, $^{3}J_{\mathrm{PH}}$ = 12.8 Hz, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 4H, *o*-Ph-C*H*), 8.26 (dd, $^{3}J_{\mathrm{PH}}$ = 12.4 Hz, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 4H, *o*-Ph-C*H*). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ 3.57 ($\mathrm{Si(CH_3)_3}$), 25.33 ($\mathrm{OCH_2CH_2}$), 28.80 ($\mathrm{C(CH_3)_3}$), 29.31 (dt, J_{PC} = 108.1 Hz, J_{YC} = 2.3 Hz, $\mathrm{CP_2}$), 29.89 ($\mathrm{C(CH_3)_3}$), 41.99 (d, $^{3}J_{\mathrm{YC}}$ = 3.0 Hz, $\mathrm{CH_2Ph}$), 51.38 ($\mathrm{C(CH_3)_3}$), 52.13 ($\mathrm{C(CH_3)_3}$), 69.28 ($\mathrm{OCH_2CH_2}$), 126.28 (*p*-Bn-CH), 126.67 (t, $^{2}J_{\mathrm{PC}}$ = 6.0 Hz, *o*-Ph-CH), 127.20 (t, $^{2}J_{\mathrm{PC}}$ = 6.0 Hz, *o*-Ph-CH), 127.82 (*m*-Bn-CH), 129.75 (*o*-Bn-CH), 129.99 (*p*-Ph-CH), 130.20 (*p*-Ph-CH), 132.12 (t, $^{3}J_{\mathrm{PC}}$ = 5.0 Hz, *m*-Ph-CH), 133.27 (dd, J_{PC} = 116.7 Hz, $^{3}J_{\mathrm{PC}}$ = 5.0 Hz, *ipso*-Ph-C), 134.60 (t, $^{3}J_{\mathrm{PC}}$ = 5.0 Hz, *m*-Ph-CH), 135.25 (dd, J_{PC} = 108.7 Hz, $^{3}J_{\mathrm{PC}}$ = 16.1 Hz, *ipso*-Ph-C), 136.49 (*ipso*-Bn-C), 156.85 (t, $^{2}J_{\mathrm{PC}}$ = 5.0 Hz, NCO), 179.13 (d, $^{2}J_{\mathrm{YC}}$ = 2.0 Hz, $\mathrm{PhCH_2NCO}$). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ 20.57 ($\mathrm{C}P_2$). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ −5.78 (*Si*$\mathrm{(CH_3)_3}$). FTIR ν/cm^{-1} (Nujol): 1592 (m), 1519 (m), 1294 (m), 1219 (m), 1170 (m), 1113 (s), 1069 (s), 1035 (s), 839 (s), 767 (m), 695 (m), 620 (m), 601 (m), 545 (m), 522 (m), 509 (m).

Preparation of [Y(BIPMH){C(S)$_2$(NBu$^{\mathrm{t}}$)-1-κ*S*,2-κ*N*:μ,κ*S′*}]$_2$ (6). A solution of Bu$^{\mathrm{t}}$NCS (0.25 g, 2.20 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (1.62 g, 2.00 mmol) in toluene (10 mL) at −78 °C. The orange mixture was slowly warmed to room temperature with stirring over 24 h. The mixture was filtered to isolate analytically pure **6** as a white solid. Yield: 0.52 g, 33%. X-ray-quality crystals were grown from a hot toluene solution. Anal. Calcd for $\mathrm{C_{36}H_{49}N_3P_2S_2Si_2Y}$: C, 54.39; H, 6.21; N, 5.29. Found: C, 54.29; H, 6.27; N, 5.31. ^{1}H NMR (d_8-THF, 298 K): δ 0.11, 0.14 (s, 36H, $\mathrm{Si(CH_3)_3}$), 1.23, 1.38, 1.41 (s, 18H, $\mathrm{C(CH_3)_3}$), 6.98 (vt, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 4H, Ph-C*H*), 7.14 (m, 8H, Ph-C*H*), 7.26 (m, 8H, Ph-C*H*), 7.29−7.51 (br m, 10H, Ph-C*H*), 7.68 (br m, 2H, Ph-C*H*), 8.00 (br m, 8H, Ph-C*H*), *H*CP$_2$ not observed. $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (d_8-THF, 298 K): δ 2.32, 2.56 ($\mathrm{Si(CH_3)_3}$), 14.90 (t, J_{PC} = 106.6 Hz, $\mathrm{HCP_2}$), 27.57, 27.92, 28.40 ($\mathrm{C(CH_3)_3}$), 56.27, 56.40, 56.45 ($\mathrm{C(CH_3)_3}$), 125.51 (d, $^{2}J_{\mathrm{PC}}$ = 13.8 Hz, *o*-Ph-CH), 125.87 (d, $^{2}J_{\mathrm{PC}}$ = 12.3 Hz, *o*-Ph-CH), 128.05, 128.11, 128.30, 128.84 (*p*-Ph-CH), 129.47 (vt, $^{3}J_{\mathrm{PC}}$ = 6.1 Hz, *m*-Ph-CH), 130.10 (vt, J_{PC} = 5.4 Hz, *m*-Ph-CH), 134.25, 135.26 (*ipso*-Ph-C), $\mathrm{NCS_2}$ not observed. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (d_8-THF, 298 K): δ 18.56 (br, $\mathrm{HC}P_2$), 18.95 (dd, $^{2}J_{\mathrm{PP}}$ = 12.2 Hz, $^{2}J_{\mathrm{YP}}$ = 6.7 Hz, $\mathrm{HC}P_2$), 21.04 (dd, $^{2}J_{\mathrm{PP}}$ = 12.2 Hz, $^{2}J_{\mathrm{YP}}$ = 6.7 Hz, $\mathrm{HC}P_2$). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (d_8-THF, 298 K): δ −6.00, −4.69, −3.66 (*Si*$\mathrm{(CH_3)_3}$). FTIR ν/cm^{-1} (Nujol): 1590 (br, w), 1417 (m), 1244 (m), 1164 (m), 1113 (s), 1082 (s), 1055 (s), 958 (m), 835 (s), 767 (m), 739 (m), 721 (m), 691 (m), 662 (w), 607 (w), 545 (w), 515 (w).

Preparation of [Y(BIPM)(NHDipp)(THF)] (7). A solution of DippNH$_2$ (0.72 g, 4.00 mmol) in toluene (10 mL) was added dropwise to a solution of **1** (3.24 g, 4.00 mmol) in toluene (10 mL) at −78 °C. The yellow mixture was slowly warmed to room temperature with stirring over 72 h. Volatiles were removed in vacuo, and the resulting yellow oil was washed with pentane (20 mL) to afford analytically pure **7**. Yield: 2.13 g, 60%. A small portion was recrystallized from toluene (0.45 g, 13%). Anal. Calcd for $\mathrm{C_{47}H_{62}N_3OP_2Si_2Y}$: C, 63.28; H, 7.01; N, 4.71. Found: C, 63.39; H, 7.12; N, 4.88. ^{1}H NMR (d_6-benzene, 298 K): δ 0.02 (s, 18H, $\mathrm{Si(CH_3)_3}$), 1.40 (m, 4H, $\mathrm{OCH_2CH_2}$), 1.61 (d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 12H, $\mathrm{CH(CH_3)_2}$), 3.31 (sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, 2H, $\mathrm{CH(CH_3)_2}$), 4.02 (m, 4H, $\mathrm{OCH_2CH_2}$), 4.85 (s, 1H, N*H*), 6.89 (t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 1H, *p*-Dipp-C*H*), 7.02 (br, 12H, *m*- and *p*-Ph-C*H*), 7.24 (t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 2H, *m*-Dipp-C*H*), 7.71 (br, 8H *o*-Ph-C*H*). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ 3.49 ($\mathrm{Si(CH_3)_3}$), 22.91 ($\mathrm{CH(CH_3)_2}$), 24.72 ($\mathrm{OCH_2CH_2}$), 30.47 ($\mathrm{CH(CH_3)_2}$), 70.47 ($\mathrm{OCH_2CH_2}$), 114.46 (*p*-Dipp-CH), 122.41 (*m*-Dipp-CH), 127.06 (t, $^{3}J_{\mathrm{PC}}$ = 61.3 Hz, *m*-PhCH), 128.72 (br, *p*-PhCH), 131.05 (br, *o*-PhCH), 131.69 (*o*-Dipp-C), 152.32 (d, $^{2}J_{\mathrm{YC}}$ = 3.0 Hz, *ipso*-Dipp-C), *ipso*-Ph-C and $\mathrm{CP_2}$ not observed. $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ 5.48 (d, $^{2}J_{\mathrm{YP}}$ = 13.0 Hz $\mathrm{C}P_2$). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (d_6-benzene, 298 K): δ −9.04 (*Si*$\mathrm{(CH_3)_3}$). FTIR ν/cm^{-1} (Nujol): 3062 (m, N−H stretch), 1590 (m), 1424 (s), 1333 (m), 1300 (m), 1106 (s), 1055 (s), 764 (m), 744 (m), 712 (m), 696 (m), 649 (w), 610 (m), 602 (m), 547 (m), 510 (m).

Preparation of [Y(BIPM)(μ-η^1:η^6-CH$_2$Ph)(μ-η^1:η^2-CH$_2$Ph)K]$_\infty$ (8). THF (30 mL) was added to a precooled (−78 °C) mixture of **1** (2.43 g, 3.00 mmol) and PhCH$_2$K (0.39 g, 3.00 mmol). The brown mixture was slowly warmed to room temperature with stirring over 18 h. Volatiles were removed in vacuo, and the resulting brown oil was recrystallized from hot toluene (5 mL) to afford **8** as yellow crystals. Yield: 0.76 g, 29%. Anal. Calcd for $\mathrm{C_{45}H_{52}KN_2P_2Si_2Y}$: C, 62.34; H, 6.05; N, 3.23. Found: C, 62.22; H, 5.97; N, 3.16. ^{1}H NMR (d_8-THF, 298 K): δ −0.19 (s, 18H, $\mathrm{Si(CH_3)_3}$), 1.81 (d, $^{2}J_{\mathrm{YH}}$ = 6.0 Hz, 4H, $\mathrm{CH_2Ph}$), 6.34 (t, $^{3}J_{\mathrm{HH}}$ = 6.4 Hz, 2H, *p*-Bn-C*H*), 6.80 (m, $^{3}J_{\mathrm{HH}}$ = 8.0 Hz, 8H, *m*-Ph-C*H*), 6.99 (m, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 6H, *m*- and *o*-Bn-C*H*), 7.07 (t, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 4H, *p*-Ph-C*H*), 7.15 (t, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 1H, *o*-Bn-C*H*), 7.23 (t, $^{3}J_{\mathrm{HH}}$ = 7.2 Hz, 1H, *o*-Bn-C*H*), 7.39 (dd, $^{2}J_{\mathrm{PH}}$ = 12.4 Hz, $^{3}J_{\mathrm{HH}}$ = 6.6 Hz, 8H, *o*-Ph-C*H*). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (d_8-THF, 298 K): δ 3.15 ($\mathrm{Si(CH_3)_3}$), 51.31 (br, $\mathrm{CH_2Ph}$), 57.46 (dt, J_{PC} = 179.1 Hz, J_{YC} = 3.0 Hz, $\mathrm{CP_2}$), 113.29 (*p*-Bn-CH), 122.35 (*p*-Bn-CH), 125.07 (*m*-Bn-CH), 126.36 (t, $^{2}J_{\mathrm{PC}}$ = 6.0 Hz, *o*-Ph-CH), 127.02 (*m*-Bn-CH), 127.66 (*p*-Ph-CH), 127.94 (*o*-Bn-CH), 128.71 (*o*-Bn-CH), 131.06 (t, $^{3}J_{\mathrm{PC}}$ = 5.0 Hz, *m*-Ph-CH), 141.27 (vt, J_{PC} = 48.3 Hz, *ipso*-Ph-C), 154.49 (*ipso*-Bn-C). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (d_8-THF, 298 K): δ 1.42 (d, $^{2}J_{\mathrm{YP}}$ = 11.3 Hz, $\mathrm{C}P_2$). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (d_8-THF, 298 K): δ −12.39 (*Si*Me$_3$). FTIR v/cm^{-1} (Nujol): 1586 (s), 1434 (m), 1246 (s), 1175 (m), 1106 (s), 1077 (s), 1051 (s), 830 (s), 772 (m), 754 (m), 739 (m), 728 (m), 717 (m), 698 (m), 645 (m), 609 (m), 539 (m), 512 (m).

X-ray Crystallography. Crystal data for compounds **2**−**8** are given in Tables 2 and 3, and further details of the structure determinations are in the Supporting Information. Bond lengths and angles are given in Table 1. Crystals were examined variously on a Bruker APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) or on an Oxford Diffraction

Table 2. Crystallographic Data for 2−5

	$2 \cdot C_7H_8$	3	$4 \cdot C_4H_{10}O$	5
formula	$C_{47}H_{62}N_3OP_2Si_2Y \cdot C_7H_8$	$C_{52}H_{68}N_5OP_2Si_2Y$	$C_{64}H_{89}N_6P_2Si_2Y \cdot C_4H_{10}O$	$C_{52}H_{71}N_4O_3P_2Si_2Y$
fw	984.16	986.14	1223.56	1007.16
cryst size, mm	0.24 × 0.38 × 0.62	0.004 × 0.008 × 0.014	0.22 × 0.25 × 0.45	0.02 × 0.19 × 0.22
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	10.5979(7)	12.725(7)	14.098(2)	11.5702(17)
b, Å	12.8692(8)	19.531(11)	14.224(2)	13.0541(19)
c, Å	20.1907(13)	20.748(11)	19.349(3)	18.880(3)
α, deg	82.257(2)		90.999(3)	80.088(3)
β, deg	87.160(2)	101.224(10)	90.104(3)	88.140(3)
γ, deg	80.411(2)		119.346(2)	72.461(2)
V, Å^3	2689.5(3)	5058(5)	3381.5(9)	2677.9(7)
Z	2	4	2	2
ρ_{calcd}, g cm^{-3}	1.215	1.295	1.202	1.249
μ, mm^{-1}	1.227	1.306	0.990	1.237
no. of rflns measd	20010	36791	17477	15606
no. of unique rflns, R_{int}	9460, 0.0173	8932, 0.1079	11229, 0.0381	6986, 0.0718
no. of rflns with $F^2 > 2\sigma(F^2)$	8254	5999	9163	4479
transmn coeff range	0.50−0.74	0.441−0.746	0.64−0.79	0.74−0.98
R, $R_w{}^a$ ($F^2 > 2\sigma(F^2)$)	0.0415, 0.1067	0.0708, 0.1771	0.0665, 0.1710	0.0946, 0.2388
R, $R_w{}^a$ (all data)	0.0495, 0.1119	0.1099, 0.2011	0.0789, 0.1791	0.1401, 0.2633
S^a	1.033	1.03	1.017	1.067
no. of params	693	574	727	589
max, min diff map, e Å^{-3}	1.145, −0.333	1.444, −1.132	2.078, −2.199	2.183, −0.877

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

Table 3. Crystallographic Data for 6−8

	$6 \cdot 3.5C_7H_8$	7	$8 \cdot 2C_7H_8$
formula	$C_{72}H_{96}N_6P_4S_4Si_4Y_2 \cdot 3.5C_7H_8$	$C_{47}H_{64}N_3OP_2Si_2Y$	$C_{45}H_{52}K\ N_2P_2Si_2Y \cdot 2C_7H_8$
fw	1910.32	894.04	1051.28
cryst size, mm	0.07 × 0.07 × 0.18	0.066 × 0.250 × 0.307	0.113 × 0.288 × 0.372
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	11.87174(19)	11.5102(3)	20.2089(3)
b, Å	18.9361(3)	23.0440(5)	11.4985(2)
c, Å	22.0918(4)	17.9369(5)	23.9442(4)
β, deg	97.8907(15)	97.652(3)	92.0323(17)
V, Å^3	4919.31(14)	4715.2(2)	5560.45(17)
Z	2	4	4
ρ_{calcd}, g cm^{-3}	1.290	1.259	1.256
μ, mm^{-1}	3.808	3.146	3.388
no. of rflns measd	28086	21664	21940
no. of unique rflns, R_{int}	8864, 0.0361	9391, 0.040	10928, 0.0341
no. of rflns with $F^2 > 2\sigma(F^2)$	7206	8016	9206
transmn coeff range	0.67−0.81	0.448−0.814	0.478−1.125
R, $R_w{}^a$ ($F^2 > 2\sigma(F^2)$)	0.0356, 0.0928	0.0348, 0.0820	0.0387, 0.0897
R, $R_w{}^a$ (all data)	0.0456, 0.0965	0.0442, 0.0885	0.0491, 0.0959
S^a	1.048	1.02	1.006
no. of params	488	526	653
max, min diff map, e Å^{-3}	0.429, −0.650	0.670, −0.480	0.786, −0.663

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

SuperNova Atlas CCD diffractometer using mirror-monochromated Cu Kα radiation (λ = 1.5418 Å). Intensities were integrated from data recorded on 0.3° (APEX) or 1° (SuperNova) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semiempirical absorption corrections based on symmetry-equivalent and repeat reflections (APEX) or Gaussian grid face-indexed absorption corrections with a beam profile correction (Supernova) were applied. The structures were solved variously by direct and heavy-atom methods and were refined by full-matrix least squares on all unique F^2 values, with anisotropic displacement parameters for all non-hydrogen atoms and with constrained riding hydrogen geometries; U_{iso}(H) was set at 1.2 (1.5 for methyl groups) times the U_{eq} value of the parent atom. The largest features in the final difference syntheses were close to heavy atoms and were of no chemical significance. Highly disordered solvent molecules of crystallization in **6**·3.5C_7H_8 could not be modeled and were treated with the Platon SQUEEZE procedure.[43] Programs used were Bruker AXS SMART[44] and CrysAlisPro[45] (control), Bruker AXS SAINT[44] and CrysAlisPro[45] (integration), and SHELXTL[46] and OLEX2[47] (structure solution and refinement and molecular graphics).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for **2**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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