ORGANOMETALLICS

Group 1 Bis(iminophosphorano)methanides, Part 1: *N*-Alkyl and Silyl Derivatives of the Sterically Demanding Methanes $H_2C(PPh_2NR)_2$ (R = Adamantyl and Trimethylsilyl)

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Supporting Information

ABSTRACT: Treatment of $[Li{HC(PPh_2NSiMe_3)_2}]_2$ with 2 equiv of [MOR](M = Rb, Cs; OR = 2-ethylhexoxide) afforded the heavy group 1 methanides [Rb{HC(PPh_2NSiMe_3)_2}(THF)_2] (1) and $[Cs{HC(PPh_2NSiMe_3)_2}(DME)_2]$ (2), which do not exhibit methanide $C \cdots M$ contacts in the solid state. Following a literature procedure, $H_2C(PPh_2)_2$ was reacted with 2 equiv of AdN₃ (Ad = adamantyl) to give $H_2C(PPh_2NAd)_2$ (3). Reaction of 3 with 1 equiv of Bu^tLi in toluene afforded dimeric $[Li{HC(PPh_2NAd)_2}]_2$ (4). Treatment of 3 with 1 equiv of [M(Bn)] (M = Na, K; Bn = $CH_2C_6H_5$) in THF gave the Lewis base adducts $[M{HC(PPh_2NAd)_2}(THF)_2]$ [M = Na (5), K (6)]. The heavy group 1 methanides $[Rb{HC(PPh_2NAd)_2}(THF)_2]$ (7) and $[Cs{HC(PPh_2NAd)_2}(DME)_2]$ (8) were prepared by the reaction of [MOR] (M = Rb, Cs; OR = 2-ethylhexoxide) with 4 or reaction of [Cs(Bn)] with 3. The synthetic utility of these group 1 transfer agents has been demonstrated by the preparation of $[La{HC(PPh_2NR)_2}(I)_2(THF)]$ [R =



 $SiMe_3$ (9), Ad (10)] from $[La(I)_3(THF)_4]$, employing a salt metathesis methodology. Complexes 1–10 have been characterized by X-ray crystallography, multielement NMR spectroscopy, FTIR spectroscopy, and CHN microanalyses.

INTRODUCTION

Bis(iminophosphorano)methanides and methanediides¹ have received increasing attention over the last 12 years, as they are excellent ancillary ligands for a wide range of metal centers.¹ Although direct reaction of the parent methanes with metal alkyls and amides is often used to access the corresponding methanide and methanediide complexes, alkali metal methanide and methanediide complexes have found great utility as ligand transfer reagents for the stepwise construction of derivatives by salt elimination reactions. In addition to their extensive synthetic utility, alkali metal methanide and methanediide complexes are of interest because of their diverse structural chemistry. For example, the solvent-free complexes $[M{HC(PPh_2NSiMe_3)_2}]_2$ $(M = Li, Na, K)^{2,3}$ exist as methanide- (for lithium) and N-bridged dimers (for sodium and potassium) in the solid state. When N-aryl substituents are employed, multihapto interactions are observed for potassium, as exemplified by $[{K(HC[PPh_2 NMes_{2}^{2}$ (Mes = 2,4,6-trimethylphenyl),⁴ which was found to be an η° -arene-bridged dimer in the solid state. However, the addition of Lewis base solvents gives rise to structural modifications. For example, the ether adducts $[Li{HC(PR'_2NR)_2}(L)]$ (R = SiMe₃, Pr^{*i*}, Mes; R' = Ph, Cy; L = OEt₂, THF),^{3,5-8} [Li{HC(PPh₂NSi- $Me_3)(PPh_2S)$ (THF)₂],⁹ [Na{HC(PPh_2NSiMe_3)₂}(THF)₂],⁵ [K{HC(PPh₂NSiMe₃)₂}(diglyme)],³ and [K{HC(PPh₂NSi- $Me_3)_2$ (THF)₂⁵ all adopt monomeric structures in the solid state, but metal-methanide contacts are often absent. The latter

potassium complex is bound to the methanide ligand through the two imino groups and an η^2 -arene contact only. The methanediide derivatives $[\{MM'(C[PPh_2NR]_2)\}_2] (M = M' = Li, Na, K, Rb; R = SiMe_3, (S)-MeCHPr^i, Ph)^{7,10-14}$ are less structurally diverse and typically adopt structures where a belt of four alkali metals is capped top and bottom by mutually orthogonal methanediide ligands. The corresponding $[\{Li_2(C[PPh_2S]_2)\}_2 - (OEt_2)_n] (n = 2, 3)^{15}$ and $[\{Li_2(C[PPh_2NSiMe_3][PPh_2S]_2)\}_2 - (THF)]^9$ complexes adopt similar structures, but the replacement of one or more of the imino substituents with less sterically demanding thionyl groups results in the coordination of ethers.

In our early investigations into the chemistry of early metal methanide and methanediide complexes, we typically accessed the desired products, such as $[Y{C(PPh_2NSiMe_3)_2}(CH_2SiMe_3)_(THF)]$, by the straightforward reaction between the parent bis(iminophosphorano)methane and homo- and heteroleptic lanthanide alkyls.^{16–20} However, this synthetic methodology has its limitations; for example, larger rare-earth tribenzyls form complexes, such as $[Ln{C(PPh_2NSiMe_3)_2}{HC(PPh_2NSiMe_3)_2}]$, and larger rare-earth $[Ln(Bn)_2(I)(THF)_3]$ precursor complexes are apparently unstable.¹⁹ In addition, we were interested in the preparation of uranium methanide and methanediide complexes,

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Scheme 1. Synthesis of 1 and 2



and stable homoleptic neutral uranium(IV) alkyl precursors remain elusive.²¹ As a consequence, we have recently exploited previously reported group 1 methanides and methanediides as ligand transfer agents using a salt metathesis methodology.^{22–25} Gratifyingly, these studies have allowed the synthesis of an early rare-earth iodo-methanediide complex,²³ a comparison of the bonding and reactivity of U(IV) and U(V) carbenes,²⁴ and the preparation of a delocalized arene-bridged diuranium singlemolecule magnet.²⁵ Furthering this study, we have also prepared novel group 1 methanide and methanediide complexes.^{26,27} We demonstrated the synthetic utility of the dilithium methanediide complex $[{Li_2(C[PPh_2NMes]_2)}_2]$ by preparing the first homoleptic uranium carbene complex to exhibit two U=C double bonds.²⁶ We have also recently reported the monomeric methanide and methanediide complexes [Li{HC(PPh₂NDipp)₂}] and $[Li{C(PPh_2NDipp)_2}Li(TMEDA)]$ (TMEDA = N, N'-tetramethylethylenediamine), 2^{27} which exhibit a two-coordinate lithium with no methanide contact in the former and a remarkable distorted trans-planar tetracoordinate carbon in the latter.

We have found, however, that, in some cases, an apparently straightforward salt metathesis methodology to prepare lanthanide methanide complexes from known group 1 methanide precursors has, in fact, proven problematic.²⁸ For example, treatment of $[La(I)_3(THF)_4]$ with $[K{HC(PPh_2NSiMe_3)_2}]$ -(THF)₂] did not afford the desired monosubstituted lanthanide methanide.²³ We reasoned that this sluggish reactivity could be overcome by starting with cesium and rubidium methanide precursors, as the larger, more electropositive and polarizable Rb⁺ and Cs⁺ ions (effective ionic radii, coordination number 6: $\rm K^{+}$ 1.38 Å; $\rm Rb^{+}$ 1.52 Å; $\rm Cs^{+}$ 1.67 Å)^{29} should be more labile and hence their methanide complexes should exhibit greater reactivity. We have expanded this study by obtaining the solid-state structure of the corresponding N-Ad substituted bis(iminophosphorano)methane and its lithium, sodium, potassium, rubidium, and cesium methanide derivatives. The synthetic utility of these novel ligand transfer reagents has been proved by their use in the facile preparation of lanthanum methanide complexes. This provides an entry point to *N*-alkyl bis(iminophosphorano)methanide and -diide complexes by salt elimination, which provides a valuable alternative to amine and alkyl elimination methods.

RESULTS AND DISCUSSION

The reaction of half an equivalent of $[\text{Li}\{\text{HC}-(\text{PPh}_2\text{NSiMe}_3)_2\}]_2^{2,3}$ with [MOR] (M = Rb, Cs; R = 2-ethylhexoxide)³⁰ in the presence of the appropriate Lewis base gave the desired heavy group 1 methanides $[\text{Rb}\{\text{HC}(\text{PPh}_2\text{N-SiMe}_3)_2\}(\text{THF})_2]$ (1) and $[\text{Cs}\{\text{HC}(\text{PPh}_2\text{NSiMe}_3)_2\}(\text{DME})_2]$ (2), by simple metal exchange (Scheme 1). It is noteworthy that the closely related compound $[\text{Rb}\{\text{HC}(\text{PPh}_2\text{NPh})_2\}(\text{THF})_x]$



Figure 1. Molecular structure of 1 with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms are omitted for clarity.

has previously been prepared by Harder and its NMR spectroscopic data reported, though it was not isolated.¹⁴ The reaction to form 1 and 2 proceeds under mild conditions according to the HSAB principle, driven by the affinity of hard electropositive lithium to the alkoxide and the softer, more polarizable rubidium and cesium centers to the methanide ligand.³¹ Henderson^{12,13} and Harder¹⁴ have previously employed group 1 alkoxides to substitute the lithium cations of $[Li_2{C(PPh_2NSiMe_3)_2}]_2$ with heavier group 1 metals to prepare bimetallic methanediide complexes, and this method has been successfully adapted to prepare heavy group 1 methanides. This synthetic methodology was found to tolerate a variety of solvent systems, and the lithium alkoxide is easily separated from the products by extraction with hexanes, leaving the products behind, which are only sparingly soluble in this solvent. This procedure gives analytically and spectroscopically pure 1 and 2 in good (ca. 75%) yields as white powders. ⁷Li NMR spectroscopy indicated that no lithiumcontaining species remained in the reaction mixtures, and only a single resonance was observed in the ³¹P{¹H} NMR spectra of each reaction mixture [δ 11.87 (1); 10.73 (2) ppm], which are comparable to that observed for $[Rb{HC(PPh_2NPh)_2}(THF)_x]$ (δ 10.94 ppm).¹⁴ Complexes 1 and 2 each exhibit a virtual triplet resonance in their ²⁵Si{¹H} NMR spectra [δ , -17.08 ppm, ² $J_{SiP} = 6.4$ Hz (1); -17.19 ppm, ² $J_{SiP} = 6.7$ Hz (2)] from coupling to magnetically inequivalent phosphorus centers, a phenomenon we have previously observed in several other complexes of ${HC(PPh_2NSiMe_3)_2}^-$ and ${C(PPh_2NSiMe_3)_2}^{2-17,18,20,22}$ The expected triplet methanide resonances of 1 and 2 were observed in both their ¹H [1.92 ppm, ² J_{PH} = 2.6 Hz (1); 1.84 ppm, ² J_{PH} = 2.2 Hz (2)] and their ${}^{13}C{}^{1}H{}$ [23.39 ppm, $J_{PC} = 134.8$ Hz (1); 23.44 ppm, $J_{PC} = 145.9 \text{ Hz} (2)$] NMR spectra and again are comparable to resonances displayed by $[Rb{HC(PPh_2NPh)_2}(THF)_x](^{1}H \delta)$ 1.78 ppm, $^{2}J_{PH} = 3.2 \text{ Hz}; ^{13}C{^{1}H} \delta$ 15.3 ppm, coupling constant not reported).14

To confirm the formulations of 1 and 2, crystals were grown from saturated THF and DME solutions, respectively, to allow single-crystal X-ray determination of their solid-state structures (Figures 1 and 2; selected bond lengths and angles are listed in Table 1). The bis(iminophosphorano)methanide ligands of



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

both 1 and 2 exhibit an atypical conformation upon coordination to the group 1 metal through the nitrogen lone pairs. The bulk features are similar, so only the geometry of 1 is discussed in detail for brevity. 1 displays nearly perfectly defined P(1)-C-(1)-P(2)-M(1) and N(1)-C(1)-N(2)-M(1) planes (mean plane deviation of 0.0026 and 0.0174 Å, respectively) that bisect at an angle of $29.77(5)^\circ$. The coordination spheres of both 1 and 2 are completed by two molecules of solvent, the larger cesium center by bidentate DME. The mean M-N distances [Rb-N 2.8812 Å (1); Cs–N 3.185 Å (2)] lie within previously reported ranges (Rb-N 2.796-3.609 Å; Cs-N 2.915-3.678 Å)³² and, in the case of 1, are shorter than in the related methanediide complex $[\{Rb_2C(PPh_2NPh)_2\}_2(C_6H_6)_4]$ [Rb-N 2.923(3) Åmean].¹⁴ The mean endocyclic P-C distances [1.714 Å (1); 1.726 Å(2) and P–N distances [1.5733 Å(1); 1.572 Å(2)] are relatively long and short, respectively, when compared to $[\{Rb_2C(PPh_2NPh)_2\}_2(C_6H_6)_4]$ [P-C 1.648(2) Å; P-N 1.626(3) Å mean]. Both 1 and 2 do not exhibit a methanide-metal contact $[Rb(1)\cdots C(1) 4.276(2) \text{ Å } (1); Cs(1)\cdots$ C(1) 4.543(4) Å (2)], but each displays an electrostatic interaction of the metal with one of the *P*-phenyl rings, formally η^2 - in the case of 1 $[Rb(1)\cdots C(8) 3.639(2) \text{ Å}; Rb(1)\cdots C(13) 3.551(2) \text{ Å}]$ and η^1 - for **2** [Cs(1)···C(13) 3.763(4) Å]. An η^2 -interaction of rubidium with a P-phenyl ring was also observed in [{Rb₂C- $(PPh_2NPh)_2 (C_6H_6)_4] = [Rb \cdots C \quad 3.520(3) - 3.608(3) \quad A],^{14}$ which exhibits similar $Rb \cdots C$ distances, but this complex possesses two short methanide-rubidium contacts [Rb-C 3.047(3) Å], which are likely a result of the metal centers not being coordinated by Lewis base solvent molecules as they are in 1 and **2**. The intramolecular η^1 -*P*-phenyl contact found in **2** is more accurately described as coordination of a C-H bond to cesium, a phenomenon previously observed in $[{CsSi(SiMe_3)_3}_2-$ (biphenylene)] $[Cs \cdots C 3.683(7) Å]$,³³ although, unlike 2, this contact is intermolecular and the Cs···C distance is much shorter. Agostic interactions between methyl groups of the N-silyl substituents and the group 1 metal centers are observed for both 1 and 2. These s-block agostic interactions^{33,34} have been shown to differ from transition-metal agostic interactions³⁵

as they formally consist of the donation of electron density from the C-H bond to the metal cation as well as an electrostatic component deriving from the interaction of dipoles. The donation of electron density from methyl groups is maximized by a linear approach of the methyl group to the metal center, allowing all three $M \cdots H$ interactions.^{33,34} In the case of 1, there is significant rotational disorder of the N-silyl substituents, but the major component displays a "side-on" coordination of two methyl groups to rubidium, allowing four $Rb \cdot \cdot H$ contacts [3.065(2) - 3.338(2) Å]. The resultant $Rb \cdots C$ distances [3.397(2) - 3.632(2) Å] are similar to those observed in $[Rb(C_7H_8)_3][M{N(SiMe_3)_2}_3]$ $[M = Mg, Zn; Rb \cdots C \ 3.544(4) - 3.626(3) \ Å].^{34}$ Complex 2 displays two short [3.032(4)-3.111(4) Å] and two long [3.497(4) - 3.670(4) Å] Cs···H interactions from one methyl group of each silyl functionality, resulting in two short Cs···C distances [3.587(4)-3.696(4) Å]. An additional two Cs···H contacts between two methylene fragments of DME and the metal center [3.394(4)-3.417(4) Å] are exhibited by 2. The P(1)-C(1)-P(2) [121.11(11)° (1); 122.7(2)° (2)] and N(1)-M-N(2) [81.75(5)° (1); 77.58(10)° (2)] angles are extremely small considering the size of the group 1 metals and steric bulk of the methanide ligand [cf. P-C-P 144.4(1)° and N-Rb-N 119.2(1)° for $[\{Rb_2C(PPh_2NPh)_2\}_2(C_6H_6)_4]^{14}$ and are a direct consequence of the unusual geometry adopted by the ligand in these complexes.

Treatment of $CH_2(PPh_2)_2$ with 2 equiv of AdN₃ according to the previously described method of Cavell afforded the methane $H_2C(PPh_2NAd)_2$ (3) (Scheme 2).³⁶ Compound 3 was previously only characterized spectroscopically and analytically. During a routine purification procedure, we obtained colorless crystals of 3 and determined the structure by X-ray crystallography. The molecular structure of **3** is illustrated in Figure 3, and selected bond lengths and angles are listed in Table 1. 3 exhibits average endocyclic P-C and P-N bond distances of 1.8534 and 1.5465 Å, respectively, which are slightly longer than, but comparable to, the corresponding distances of 1.825(1) and 1.536(2) Å found in the solid-state structure of $H_2C(PPh_2-$ SiMe₃)₂,³⁷ as would be anticipated. The P(1)-C(1)-P(2)angle in 3 of 121.38(10)° is smaller than that displayed by $H_2C(PPh_2SiMe_3)_2$ [124.94(15)°],³⁷ but this is a consequence of the bulky N-adamantyl groups favoring a trans conformation of the N-substituents, rather than the cis conformation exhibited by $H_2C(PPh_2SiMe_3)_2$.³⁷

Compound 3 was treated with 1 equiv of Bu^tLi in toluene to afford the expected dimeric product $[Li{HC(PPh_2NAd)_2}]_2$ (4) (Scheme 2). The corresponding sodium and potassium methanides were prepared by the reaction of 3 with [M(Bn)] (M = Na,³⁸ K³⁹) in THF to give the respective Lewis base adducts [M- $\{HC(PPh_2NAd)_2\}(THF)_2\} [M = Na (5), K (6)] (Scheme 2).$ Compounds 4-6 all exhibited a single resonance in their $^{31}P\{^{f}H\}$ NMR spectra at δ 10.53, 9.45, and 4.90 ppm, respectively. These resonances are all upfield of those observed in the related complexes $[Li{HC(PPh_2NSiMe_3)_2}]_2$ (δ 17.4 ppm),² $[Na{HC(PPh_2NSiMe_3)_2}(THF)_2] (\delta 15.2 \text{ ppm}),^5 \text{ and } [K{HC-(PPh_2NSiMe_3)_2}(THF)_2] (\delta 12.6 \text{ ppm}).^5 \text{ The methanide pro-}$ ton resonance of 4 was not observed in its ¹H NMR spectrum as it was obscured by methylene signals of the N-adamantyl groups. This resonance was observed in the 1 H NMR spectra of 5 and 6, however, as a broad singlet in the spectrum of 5 (δ 1.61 ppm) and as a triplet in the spectrum of 6 (δ 1.64 ppm, ² $J_{\rm PH}$ = 3.40 Hz) from coupling to two equivalent ³¹P nuclei. These findings are in agreement with the ¹H NMR spectral data reported by Cavell for

Table 1. Selected Bond Lengths (Å) and Angles (°) for $1{-}10$

	1			6			
C(1) - P(1)	1.715(2)	C(1) - P(2)	1.713(2)	C(1)-P(1)	1.7163(15)	C(1)-P(2)	1.7245(15)
P(1)-N(1)	1.5733(17)	P(2)-N(2)	1.5732(17)	P(1)-N(1)	1.5848(13)	P(2)-N(2)	1.5802(12)
Rb(1) - N(1)	2.8562(17)	Rb(1) - N(2)	2.9061(17)	K(1) - N(1)	2.7970(13)	K(1) - N(2)	2.8524(13)
Rb(1) - O(1)	2.807(2)	Rb(1) - O(2)	2.845(2)	K(1) - O(1)	2.6840(12)	K(1) - O(2)	2.8804(13)
$Rb(1)\cdots C(1)$	4.276(2)	$Rb(1)\cdots C(8)$	3.639(2)	$K(1)\cdots C(1)$	4.082(2)	$K(1)\cdots C(2)$	3.264(15)
$Rb(1) \cdots C(13)$	3.551(2)	$Rb(1) \cdots C(15)$	3.632(2)	$K(1)\cdots C(7)$	3.297(15)	$K(1)\cdots C(17)$	3.209(15)
$Rb(1)\cdots C(30A)$	3.397(2)			$K(1)\cdots C(39)$	3.130(15)		
N(1)-Rb(1)-N(2)	81.75(5)	P(1)-C(1)-P(2)	121.11(11)	P(1)-C(1)-P(2)	128.28(9)	N(1)-K(1)-N(2)	88.27(4)
P(1)-N(1)-Rb(1)	108.95(9)	P(2)-N(2)-Rb(1)	112.94(8)	N(1) - P(1) - C(1)	125.83(7)	N(2) - P(2) - C(1)	112.96(7)
N(1) - P(1) - C(1)	119.34(10)	N(2) - P(2) - C(1)	116.95(10)	P(1) - N(1) - K(1)	100.40(6)	P(2) - N(2) - K(1)	120.32(6)
		-		C(1) = D(1)	7.0.5	C_7H_8	1 5000(1/)
	2	2		C(1) - P(1)	1.7263(17)	C(1) - P(2)	1.7283(16)
C(1) - P(1)	1.717(4)	C(1) - P(2)	1.734(4)	P(1) - N(1)	1.5837(14)	P(2) = N(2)	1.5750(14)
P(1)-N(1)	1.568(4)	P(2)-N(2)	1.575(4)	Rb(1) - N(1)	2.9641(13)	RD(1) - N(2)	2.933/(14)
Cs(1) - N(1)	3.160(4)	Cs(1)-N(2)	3.210(4)	RD(1) = O(1)	2.92/8(14)	RD(1) = O(2) Pb(1) = O(2)	2.8801(14)
Cs(1) - O(1)	3.147(4)	Cs(1)-O(2)	3.257(4)	$Rb(1) \cdots C(1)$	4.105(2)	$RD(1) \cdots C(8)$ $Pb(1) \cdots C(17)$	3.308/(10)
Cs(1) - O(3)	3.203(4)	Cs(1) - O(4)	3.131(4)	$Rb(1)\cdots C(37)$	3.4/43(10) 3.410(2)	$KD(1)\cdots C(1/)$	3.403(2)
$Cs(1) \cdots C(1)$	4.543(4)	$Cs(1) \cdots C(13)$	3.763(4)	N(1) - Rb(1) - N(2)	87 76(4)	P(1) = C(1) = P(2)	125 50(10)
$Cs(1) \cdots C(26)$	3.696(4)	$Cs(1) \cdots C(29)$	3.587(4)	P(1) = N(1) = Rb(1)	100.81(6)	P(2) = N(2) = Rb(1)	111 30(6)
N(1)-Cs(1)-N(2)	77.58(10)	P(1)-C(1)-P(2)	122.7(2)	N(1) - P(1) - C(1)	126.73(8)	N(2) - P(2) - C(1)	116.83(8)
P(1)-N(1)-Cs(1)	110.56(18)	P(2)-N(2)-Cs(1)	110.37(18)		8.050	.H.O.	
N(1)-P(1)-C(1)	120.2(2)	N(2)-P(2)-C(1)	122.1(2)	C(1) = P(1)	1 718(4)	C(1) = P(2)	1 725(4)
	-	2		P(1) = N(1)	1.713(4) 1.582(4)	P(2) = N(2)	1.723(4) 1.576(4)
$C(1) = \mathbb{P}(1)$	1 9/69(10)	C(1) $D(2)$	1 8600(10)	$C_{s}(1) - N(1)$	3.161(4)	$C_{s}(1) - N(2)$	3.160(4)
C(1) - F(1)	1.0+00(17)	C(1) - F(2)	1.6000(17)	$C_{s}(1) - O(1)$	3.205(3)	$C_{s}(1) - O(2)$	3.211(3)
P(1) = N(1) P(1) = C(1) = P(2)	1.3490(17)	P(2) = N(2)	1.3440(17)	$C_{s}(1) - O(3)$	3.172(3)	$C_{s}(1) - O(4)$	3.162(3)
P(1) - C(1) - P(2)	121.38(10)	C(1) = P(1) = N(1)	119.37(9)	$Cs(1)\cdots C(1)$	4.482(4)	$Cs(1)\cdots C(9)$	3.624(4)
C(1) - P(2) - N(2)	117.16(9)			$Cs(1)\cdots C(16)$	3.542(4)	$Cs(1)\cdots C(25)$	3.697(4)
	4	4		$Cs(1)\cdots C(39)$	3.633(4)		
C(1) - P(1)	1.743(4)	C(1)-P(2)	1.729(4)	N(1)-Cs(1)-N(2)	80.15(10)	P(1)-C(1)-P(2)	124.2(2)
C(46) - P(3)	1.737(4)	C(46) - P(4)	1.731(4)	P(1)-N(1)-Cs(1)	108.31(18)	P(2)-N(2)-Cs(1)	111.02(18)
P(1)-N(1)	1.595(3)	P(2)-N(2)	1.593(4)	N(1)-P(1)-C(1)	124.3(2)	N(2)-P(2)-C(1)	121.4(2)
P(3)-N(3)	1.597(3)	P(4) - N(4)	1.601(4)		9.0.5	C ₇ H ₈	
Li(1) - N(1)	1.986(8)	Li(1) - N(4)	2.009(8)	C(1) - P(1)	1.728(8)	C(1) - P(2)	1.739(8)
Li(2)-N(2)	1.998(8)	Li(2)-N(3)	1.981(8)	P(1) - N(1)	1.609(7)	P(2) - N(2)	1.611(7)
$Li(1) \cdots C(1)$	2.673(8)	$Li(1) \cdots C(46)$	2.339(8)	La(1) - N(1)	2.463(6)	La(1) - N(2)	2.412(6)
$Li(2)\cdots C(1)$	2.320(8)	$Li(2) \cdots C(46)$	2.685(8)	La(1) - O(1)	2.624(6)	La(1) - C(1)	2.859(8)
P(1)-C(1)-P(2)	136.5(2)	P(3)-C(46)-P(4)	134.0(3)	La(1) - I(1)	3.1800(6)	La(1)-I(2)	3.1981(6)
P(1)-N(1)-Li(1)	110.2(3)	P(2)-N(2)-Li(2)	95.4(3)	P(1)-C(1)-P(2)	135.9(5)	N(1)-La(1)-N(2)	111.9(2)
P(3)-N(3)-Li(2)	110.2(3)	P(4)-N(4)-Li(1)	94.9(3)	N(1)-P(1)-C(1)	109.2(4)	N(2)-P(2)-C(1)	107.9(4)
		-		P(1)-N(1)-La(1)	103.6(3)	P(2)-N(2)-La(1)	104.3(3)
C(1) = D(1)	1 7222(12)	C(1) $D(2)$	1 52(2)(12)	10 •1.5C ₄ H ₈ O			
C(1) - P(1)	1./233(13)	C(1) - P(2)	1.7252(13)	C(1) - P(1)	1.734(4)	C(1)-P(2)	1.731(4)
P(1) = N(1)	1.5819(12)	P(2) = N(2)	1.5931(11)	P(1)-N(1)	1.613(4)	P(2) - N(2)	1.614(4)
Na(1) - N(1)	2.4460(12)	Na(1) - N(2)	2.4528(12)	La(1)-N(1)	2.413(3)	La(1)-N(2)	2.410(3)
INA(1) = O(1)	2.3924(12)	INa(1) = O(2)	2.3495(12)	La(1)-O(1)	2.620(3)	La(1) - C(1)	2.826(4)
$\operatorname{Na}(1)\cdots \operatorname{C}(1)$	3.701(2)	$\operatorname{INa}(1)\cdots \operatorname{C}(25)$	3.396(2)	La(1)-I(1)	3.1928(4)	La(1)-I(2)	3.2167(4)
$Na(1)\cdots C(26)$	3.431(2)			$La(1) \cdots C(15)$	3.139(4)	$La(1) \cdots C(37)$	3.253(4)
P(1) - C(1) - P(2)	128.69(8)	N(1) - Na(1) - N(2)	102.68(4)	P(1)-C(1)-P(2)	137.1(2)	N(1)-La(1)-N(2)	114.73(12)
N(1)-P(1)-C(1)	117.17(6)	N(2)-P(2)-C(1)	123.09(6)	N(1)-P(1)-C(1)	104.5(2)	N(2)-P(2)-C(1)	105.54(19)
P(1)-N(1)-Na(1)	115.38(6)	P(2)-N(2)-Na(1)	101.98(5)	P(1)-N(1)-La(1)	105.26(17)	P(2)-N(2)-La(1)	106.06(16)

Scheme 2. Synthesis of 3-8





Figure 3. Molecular structure of 3 with selective atom labeling. Displacement ellipsoids are set at 30%, and hydrogen atoms are omitted for clarity.

[Na{HC(PPh₂NSiMe₃)₂}(THF)₂] (δ 1.95 ppm, br s) and [K{HC(PPh₂NSiMe₃)₂}(THF)₂] (δ 1.82 ppm, t, ²J_{PH} = 2.8 Hz).⁵ Although the corresponding methanide resonance was not observed in the ¹³C{¹H} NMR spectra of 4 or 5, the ¹³C{¹H} NMR spectrum of 6 exhibited the expected triplet at δ 26.95 ppm (J_{PC} = 141.86 Hz), which is similar to that observed for [K{HC(PPh₂NSiMe₃)₂}(THF)₂] (δ 24.1 ppm, J_{PC} = 134.0 Hz).⁵ Additionally, 4 displayed a single resonance in its ⁷Li{¹H} NMR spectrum at δ 2.32 ppm, which compares to the related complex [Li{HC(PPh₂NSiMe₃)₂]₂ (δ 0.70 ppm).²

The solid-state structures of **4**–**6** were determined by singlecrystal X-ray diffraction. Their molecular structures are illustrated in Figures 4–6, and selected bond lengths and angles are listed in Table 1. In the solid state, **4** is dimeric and exhibits a similar structure to that reported for $[\text{Li}{\text{HC}(\text{PPh}_2\text{NSiMe}_3)_2}]_2^2$, with the methanide carbons bridged by two lithium centers to form a distorted four-membered ring. Four nearly planar Li–N–P–C



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



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

four-membered rings are fused to the core metallacycle, two of which project above and two project below the Li(1)–C(1)–Li(2)–C(46) plane. The lithium atoms of 4 each display one short and one long C–Li distance [2.330(8) and 2.679(8) Å mean], complementary to [Li{HC(PPh₂NSiMe₃)₂}]₂, which exhibits significantly different C–Li distances [2.370(9)–2.784(10) Å].² Also in common with [Li{HC(PPh₂NSiMe₃)₂}]₂, the methine hydrogen atoms of 4 are in relatively close proximity to the lithium atoms [Li(1)···H(1) 2.221(8) Å and Li(2)···H(3) 2.301(8) Å, Li(1)–C(1)–H(1) 53.0(3)° and Li(1)–C(1)–H(1) 57.1(3)°], indicative of strong agostic interactions between C–H and Li.^{33–35} In contrast to [Li{HC(PPh₂NSiMe₃)₂}]₂, however, each lithium atom of 4 exhibits one strong agostic



Figure 6. Molecular structure of 6 with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms are omitted for clarity.

interaction, whereas one of the lithium centers in the N-silyl analogue exhibits two strong agostic interactions, explaining the greater variation in Li-C distances in the previously reported compound.² Despite the considerable steric bulk of the N-substituents of 4, its mean endocyclic C-P [1.735 Å], P-N [1.597 Å], and N–Li [1.994 Å] bond lengths are statistically identical to the mean distances exhibited by [Li{HC(PPh₂NSiMe₃)₂}]₂ [1.737, 1.588, and 2.012 Å, respectively], as are the metrical parameters of the four-membered rings.² The molecular structures of monomeric bis-THF-coordinated 5 and 6 both exhibit six-membered rings formed by chelation of the two imino nitrogen atoms to the alkali metal with the methanide carbanion remaining uncoordinated [the $C(1) \cdots M(1)$ distance is 3.701(2) Å in 5 and 4.082(2) Å in 6 in an analogous fashion to the methanide ligands in $[Na{HC(PPh_2NSiMe_3)_2}(THF)_2]$ $[C \cdots Na \ 3.739(7) \ \text{Å}]$ and $[K\{HC(PPh_2NSiMe_3)_2\}(THF)_2]$ $[C \cdots K 4.145(2) \text{ Å}].^{5}$ Although the bond distances and geometry of the bis(iminophosphorano)methanide scaffold of 5 $[P(1)-C(1)-P(2) 128.69(8)^{\circ}, N(1)-Na(1)-N(2) 102.68(4)^{\circ},$ P(1)-N(1)-Na(1) 115.38(6)°, P(2)-N(2)-Na(1) 101.98(5)°, N(1)-P(1)-C(1) 117.17(6)°, N(2)-P(2)-C(1) 123.09(6)°] are comparable to those observed for [Na{CH(PPh2NSi- Me_{3}_{2} (THF)₂ [P-C-P 126.3(3)°, N-Na-N 96.8(2)°, $P-N-Na 111.4(2)^\circ$, $N-P-C 116.4(2)^\circ$],⁵ it coordinates less symmetrically and as such exhibits nonequivalent P-N-Na and N–P–C bond angles. 6 displays an η^2 -aryl contact with one of the P-phenyl substituents of the ligand framework and the metal center in the solid state [K $\cdot \cdot \cdot C$ 3.264(15)-3.297(15) Å]. The sodium center of 5 exhibits a Na \cdots H contact with a methylene fragment of each of the N-adamantyl substituents [Na···H 2.421(2) - 2.758(2) Å]. The larger potassium cation of **6** allows more symmetrical agostic interactions, the corresponding methylene fragments in this complex donating electron density from both C–H bonds $[K \cdot \cdot \cdot H 2.748(15) - 2.943(15) Å]$, thus allowing close approach of the methylene carbon atoms $[K \cdots C]$ 3.130(15) - 3.209(15) Å]. The η^2 -aryl and agostic interactions observed in 6 are comparable to, but shorter than, those observed



Figure 7. Molecular structure of $7 \cdot 0.5C_7H_8$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity.

for $[K{CH(PPh_2NSiMe_3)_2}(THF)_2]$, in which the potassium center also exhibits an η^2 -aryl contact with one of the *P*-phenyl substituents $[K \cdots C \ 3.416(3) - 3.456(3) \text{ Å}]$ as well as agostic interactions with three C–H bonds of one silyl group $(K \cdots H \ 2.73 - 3.15 \text{ Å})$.⁵

Treatment of 4 with 2 equiv of [Rb(OR)] (OR = 2ethylhexoxide) in THF afforded $[Rb{HC(PPh_2NAd)_2}(THF)_2]$ (7) in 52% crystalline yield following workup (Scheme 2). The heavier cesium analogue could not be prepared by this method, however, as $[Cs(OR)]^{30}$ was found to not react with 4 under these conditions. [Cs{HC(PPh₂NAd)₂}(DME)₂] (8) was alternatively accessed by the treatment of **3** with $[Cs(Bn)]^{14}$ in THF, followed by treatment with DME (Scheme 2). The ${}^{31}P{}^{1}H$ NMR spectra of 7 (δ 4.06 ppm) and 8 (δ –0.58 ppm) displayed the expected singlet resonances upfield of 1-2 and 5-6 (vide supra). The methine proton produces a triplet resonance in the ¹H NMR spectrum of 7 (δ 1.59 ppm, ² $J_{\rm PH}$ = 2.9 Hz) but is only observed as a broad singlet for 8 (δ 2.15 ppm), although the chemical shifts are comparable with those observed for 1 and 2. Germane to this, the methanide carbons of 7 and 8 resonate at similar chemical shifts to 1-2 and 6 and exhibit comparable coupling constants [δ 25.58 ppm, J_{PC} = 133.8 Hz (7); δ 23.99 ppm, $J_{PC} = 134.8 \text{ Hz} (8)$].

X-ray single-crystal diffraction experiments on $7 \cdot 0.5C_7H_8$ and $8 \cdot 0.5C_4H_{10}O_2$ were performed, and their solid-state structures were determined (Figures 7 and 8. Selected bond lengths and angles are listed in Table 1). The bis(iminophosphorano)-methanide frameworks of 7 and 8 coordinate to the group 1 metals to form six-membered chelate rings that are comparable in their bulk geometry to 1 and 2 (vide supra), with essentially planar P(1)-C(1)-P(2)-M(1) and N(1)-C(1)-N(2)-M(1) units at an acute angle (<30°) with respect to each other. Despite the greater steric bulk of the *N*-substituents of 7 and 8 in comparison with 1 and 2, the mean endocyclic P-C and P-N bond lengths of the ligand scaffold are analogous as are the average M-N distances [M-N 2.9489 Å (7); 3.161 Å (8)],



Figure 8. Molecular structure of $8.0.5C_4H_{10}O_2$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity.

although the N(1)-M(1)-N(2) $[87.76(4)^{\circ}(7); 80.15(10)^{\circ}$ (8)] and P(1)-C(1)-P(2) $[125.50(10)^{\circ}(7); 124.2(2)^{\circ}(8)]$ angles are larger in 7 and 8 than in their N-silyl counterparts. The coordination sphere of the metal centers of 7 and 8 are completed by the same number and identity of donor solvent molecules as 1 and 2, respectively. In common with 1 and 2, but not with other related heavy s-block complexes, such as $[M{HC(PPh_2NSiMe_3)_2}(I)(THF)_n]_2$ (M = Sr, n = 1; M = Ba, n = 2)⁴⁰ and $[M{HC(PPh_2NSiMe_3)_2}_2]$ (M = Sr,⁴¹ Ba⁴²), no methanide-metal contacts were observed in the solid state $[M(1) \cdots C(1) 4.163(2) Å (7); 4.482(4) Å (8)]$. Like 1, 7 exhibits a π -base coordination of two carbon atoms of one of the *P*-phenyl rings to rubidium [Rb···C 3.509(2) - 3.475(2) Å], but 8 differs to 2 in that it displays two η^1 -aryl contacts with Pphenyl rings $[Cs(1)\cdots C(9) 3.624(2) \text{ Å and } Cs(1)\cdots C(25)]$ 3.697(2) Å], whereas 2 only exhibited one of these contacts (vide supra). Additionally, both 7 and 8 display four agostic interactions between the group 1 metal and C-H bonds of the *N*-adamantyl substituents, as was observed for **6**, as adjudged by close M···H distances [2.829(2)-3.276(2) Å (7); 2.937(4)-3.562(4) Å (8)] and acute M-C-H angles. As with 6, this causes the methylene carbon atoms to be in close proximity to the metal ions, the distances increasing with ionic radii as would be expected $[M \cdot \cdot \cdot C \ 3.405(2) - 3.419(2) \ \text{Å} (7); 3.542$ -(4) - 3.633(4) Å (8)].

To test our initial hypothesis, and the synthetic utility of these novel group 1 ligand transfer agents, **1** and **6** were reacted with $[La(I)_3(THF)_4]^{43}$ in THF, and gratifyingly, the lanthanide methanide complexes $[La{HC(PPh_2NSiMe_3)_2}(I)_2(THF)]$ (**9**) and $[La{HC(PPh_2NAd)_2}(I)_2(THF)]$ (**10**) were obtained following elimination of RbI and KI, respectively, and workup (Scheme 3). The isolation of **9** is noteworthy because this complex cannot be accessed from the reaction of $[La(I)_3-(THF)_4]$ with $[K{HC(PPh_2NSiMe_3)_2}(THF)_2]$,²³ but both **1** and **2** react with the same lanthanum triiodide precursor to afford **9** in good (77%) yield. It is important to note, however, that, for the corresponding *N*-adamantyl system, the potassium salt **6**





Figure 9. Molecular structure of $9 \cdot 0.5C_7H_8$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity.

reacts with $[La(I)_3(THF)_4]$ to yield 10, albeit in a poor (38%) yield, similar to the preparation of $[La{HC(PPh_2NMes)_2}]$ - $(I)_2(THF)_3$] from $[K[HC(PPh_2NMes)_2]$.²³ Interestingly, utilizing 7 or 8 instead of 6 makes very little difference to the isolated yield of 10, which contrasts to the synthesis of 9. Both 9 and 10 display a single resonance in their ${}^{31}P{}^{1}H{}$ NMR spectra at δ 17.63 and 12.11 ppm, respectively, the chemical shift for 9 being comparable to that for [La{CH(PPh₂NSiMe₃)₂}-{N(SiHMe₂)₂}₂] (δ 17.1 ppm)⁴⁴ The ¹H NMR spectra of 9 and 10 both exhibit the expected resonance for the methine proton, as a broad multiplet for 10 (δ 3.08 ppm), but as a welldefined triplet for 9 (δ 3.17 ppm, ²*J*_{PH} = 8.2 Hz), which is similar to that observed for [La{CH(PPh₂NSiMe₃)₂}{N(SiHMe₂)₂}₂] (δ 2.35 ppm, ²*J*_{PH} = 6.3 Hz).⁴⁴ The corresponding methanide triplet resonances in the ¹³C{¹H} NMR spectra of 9 (δ 12.86 ppm, J_{PC} = 118.9 Hz) and **10** (δ 11.15 ppm, J_{PC} = 139.5 Hz) are both well-resolved and considerably upfield of the N-mesitylsubstituted analogue, $[La{HC(PPh_2NMes)_2}(I)_2(THF)_3]$ (δ 58.76 ppm, $J_{PC} = 148.4 \text{ Hz}$).²³ Finally, the ²⁹Si{¹H} NMR spectrum of **9** displays a single resonance (δ –4.86 ppm) that is comparable to that observed for $[La{CH(PPh_2NSiMe_3)_2}{N(Ph_2P)_2}(Cl)]$ $(\delta - 1.2 \text{ ppm}).^{44}$

To confirm the formulation of 9 and 10, the structures were determined by X-ray crystallography (Figures 9 and 10; selected bond lengths and angles are listed in Table 1). The



Figure 10. Molecular structure of $10 \cdot 1.5C_4H_8O$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity.

bis(iminophosphorano)methanide scaffold adopts a typical distorted twist-boat conformation upon coordination in both 9 and 10^{1}_{2} with the methanide carbon displaced from the P₂N₂ leastsquares plane by 0.632 Å in both complexes and lanthanum displaced 0.429 Å for 9 and 0.721 Å for 10. The methanide framework of $[La{CH(PPh_2NSiMe_3)_2}{N(Ph_2P)_2}(Cl)]$ exhibits similar parameters, with the methanide carbon displaced 0.617 Å and lanthanum displaced 0.233 Å from the P₂N₂ leastsquares plane in this complex.⁴⁴ $[La{CH(PPh_2NSiMe_3)_2}]$ - ${N(SiHMe_2)_2}_2$ [La-C 2.875(4) Å and La-N 2.536 (mean) Å; P-C-P 135.7(2)° and N-La-N 112.05(9)°]⁴⁴ and [La{CH- $(PPh_2NSiMe_3)_2$ {N(Ph_2P)_2}(Cl)] [La-C 2.802(4) Å and La-N 2.500(4) (mean) Å; P-C-P 138.1(2)° and N-La-N $117.32(11)^{\circ}$ ⁴⁵ exhibit comparable P-C-P and N-La-N angles, La-C distances, and endocyclic P-C and P-N bond lengths to 9 [La(1)-C(1) 2.859(8) Å and La-N 2.438(6) (mean) Å; P(1)-C(1)-P(2) 135.9(5)° and N(1)-La(1)- $N(2) 111.9(2)^{\circ}$ and 10 [La(1)-C(1) 2.826(4) Å and La-N2.412(3) (mean) Å; P(1)-C(1)-P(2) 137.1(2)° and N(1)-La(1)-N(2) 114.73(12)°], although the La-N distances of 9 and 10 are considerably shorter. The La(1)-C(1) distances of 9 and 10 are relatively long, but within the reported range (2.277-3.388 Å).³² Two iodides and one molecule of THF complete the coordination spheres of 9 and 10, with 10 displaying four additional La····C-H agostic interactions with methylene units of the N-adamantyl groups, similar to 6-8. Again, this was evidenced by acute La-C-H angles, short La···H contacts [2.770(4)-3.069(4) Å] and short La···C distances [3.139(4) - 3.253(4) Å].

SUMMARY AND CONCLUSIONS

Heavy group 1 methanide complexes, namely, $[Rb{HC-(PPh_2NSiMe_3)_2}(THF)_2](1), [Cs{HC(PPh_2NSiMe_3)_2}(DME)_2](2), [Rb{HC(PPh_2NAd)_2}(THF)_2](7), and [Cs{HC(PPh_2N-Ad)_2}(DME)_2](8), have been prepared by treatment of the$

parent methanes with the appropriate metal alkoxide or benzyl precursor in the presence of coordinating solvents. The previously reported N-adamantyl bis(iminophosphorano)methane $H_2C(PPh_2NAd)_2$ (3) has been structurally characterized. Treatment of 3 with alkali metal reagents afforded dimeric lithium $[Li{HC(PPh_2NAd)_2}]_2$ (4) and monomeric sodium $[Na{HC-}$ $(PPh_2NAd)_2$ (THF)₂ (5) and potassium [K{HC(PPh_2NAd)_2}- $(THF)_2$] (6) salts. The synthetic utility of 1 and 2 has been demonstrated by their use in the preparation of [La{HC(PPh₂- $NSiMe_{3}_{2}(I)_{2}(THF)$ (9) from $[La(I)_{3}(THF)_{4}]$, overcoming a previous synthetic barrier. The corresponding N-adamantyl analogue $[La{HC(PPh_2NAd)_2}(I)_2(THF)]$ (10) was easily prepared from the reaction of $[La(I)_3(THF)_4]$ with lighter group 1 methanides, such as 6, proving the synthetic potential of the Nalkyl variant. We envisage that complexes 1-2 and 4-8 represent novel alkali metal transfer reagents that will prove useful in preparing other sterically constrained *d*- and *f*-block methanide complexes in the future. At present, we are utilizing 1-2 and 4-8 in the preparation of *f*-block methanide systems, which are proving to be suitable precursors for related methanediide systems by a simple deprotonation methodology. The findings of these studies will be published in due course.

EXPERIMENTAL SECTION

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 solvents were distilled from potassium, degassed by three freeze—pump—thaw cycles, and stored under nitrogen. The compounds $[Li{HC(PPh_2NSiMe_3)_2}]_2$,²³ [MOR] (M = Rb, Cs; OR = 2-ethylhexoxide),³⁰ H₂C(PPh_2NAd)₂,³⁶ [Na(Bn)],³⁸ [K(Bn)],³⁹ [Cs(Bn)],¹⁴ and $[La(I)_3(THF)_4]^{43}$ were prepared according to published procedures. Bu^tLi was purchased from Aldrich as a 1.7 M solution in pentane, the solvent was removed in vacuo, and the resultant white solid was stored in the glovebox.

The ¹H, ¹³C, ³¹P, ²⁹Si, and ⁷Li NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6, 162.0, 79.5, and 155.5 MHz, respectively; chemical shifts are quoted in parts per million and are relative to TMS (¹H, ¹³C, and ²⁹Si), external 85% H₃PO₄ (³¹P), and external 1.0 M LiCl (⁷Li). 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.

Synthesis of [Rb{HC(PPh2NSiMe3)2}(THF)2] (1). Rubidium 2-ethylhexoxide (1.0 M in THF, 2.0 mL, 2.0 mmol) was added to a precooled (-78 °C) slurry of $[\text{Li}{HC(PPh_2NSiMe_3)_2}]_2$ (1.27 g, 1.0 mmol) in THF (30 mL). The mixture was slowly allowed to warm to room temperature with stirring over 24 h. Volatiles were removed in vacuo and the resulting solid washed with hexane to afford 1 as a white powder. Recrystallization from hot THF (1 mL) afforded 1 as pale yellow crystals on cooling to room temperature. Yield: 0.53 g, 34%. Anal. Calcd for C₃₉H₅₅N₂O₂P₂RbSi₂: C, 59.49; H, 7.04; N, 3.56. Found: C, 59.35; H, 7.17; N, 3.49. ¹H NMR (d_6 -benzene, 298 K): δ 0.19 (s, 18H, $Si(CH_3)_3$), 1.54 (m, 8H, OCH₂CH₂), 1.92 (t, ²J_{PH} = 2.6 Hz, 1H, HCP_2), 3.67 (m, 8H, OCH_2CH_2), 7.24 (t, ${}^{3}J_{HH}$ = 7.2 Hz, 4H, p-Ar-CH), 7.27 (m, ${}^{3}J_{HH} = 7.2$ Hz, 8H, *m*-Ar-CH), 8.11 (m, 8H, *o*-Ar-CH). ¹³C{¹H} NMR (d_6 -benzene, 298 K): δ 4.50 (Si(CH₃)₃), 23.39 (t, J_{PC} = 134.8 Hz, HCP₂), 25.56 (OCH₂CH₂), 67.57 (OCH₂CH₂), 127.52 (m-Ar-C), 128.65 (p-Ar-C), 131.39 (o-Ar-C), 143.61, 144.59 (ipso-Ar-C). ³¹P{¹H} NMR (d_6 -benzene, 298 K): δ 11.87 (HCP₂). ²⁹Si{¹H} NMR (d_6 -benzene, 298 K): $\delta - 17.08$ (v t, ${}^2J_{SiP} = 6.4$ Hz, SiMe₃). FTIR v/cm⁻¹

(Nujol): 1589 (w, br), 1260 (s), 1173 (m), 1097 (m), 1054 (m, br), 862 (m), 826 (m), 803 (m), 743 (m), 696 (m).

Synthesis of [Cs{HC(PPh₂NSiMe₃)₂}(DME)₂] (2). Cesium 2-ethylhexoxide (1.0 M in toluene, 2.0 mL, 2.0 mmol) was added to a precooled (-78 °C) slurry of $[\text{Li}{HC(PPh_2NSiMe_3)_2}]_2$ (1.27 g, 1.0 mmol) in toluene (30 mL). The mixture was slowly allowed to warm to room temperature with stirring over 24 h. Volatiles were removed in vacuo and the resulting solid washed with hexane to afford [Cs{HC- $(PPh_2NSiMe_3)_2$ as a white powder. Yield: 1.04 g, 75%. Recrystallization from hot DME (1.5 mL) afforded 2 as pale yellow crystals on cooling to -30 °C. Anal. Calcd for C₃₉H₅₉CsN₂O₄P₂Si₂: C, 53.79; H, 6.83; N, 3.22. Found: C, 53.89; H, 6.97; N, 3.16. ¹H NMR (*d*₆-benzene, 298 K): δ 0.23 (s, 18H, Si(CH₃)₃), 1.84 (t, ²J_{PH} = 2.2 Hz, 1H, HCP₂), 3.22 (s, 12H, CH₃OCH₂), 3.39 (m, 8H, CH₃OCH₂), 7.27 (m, 4H, p-Ar-CH), 7.29 (m, 8H, *m*-Ar-CH), 8.10 (m, 8H, *o*-Ar-CH). ${}^{13}C{}^{1}H$ NMR $(d_6$ -benzene, 298 K): δ 4.63 (Si(CH₃)₃), 23.44 (t, J_{PC} = 145.9 Hz, HCP₂), 58.42 (CH₃OCH₂), 71.91 (CH₃OCH₂), 127.98 (m-Ar-C), 129.07 (p-Ar-C), 131.38 (o-Ar-C), 143.71, 144.65 (ipso-Ar-C). ³¹P{¹H} NMR (d_6 -benzene, 298 K): δ 10.73 (HCP₂). ²⁹Si{¹H} NMR (d_6 benzene, 298 K): δ -17.19 (v t, ² J_{SiP} = 6.7 Hz, SiMe₃). FTIR v/cm⁻ (Nujol): 1589 (w, br), 1260 (s), 1098 (s, br), 1022 (s, br), 863 (m), 800 (s), 741 (w), 724 (w), 696 (w).

Synthesis of $[Li{HC(PPh_2NAd)_2}]_2$ (4). Toluene (20 mL) was added to a precooled (-78 °C) mixture of 3 (0.477 g, 0.7 mmol) and Bu^tLi (0.045 g, 0.7 mmol), which turned orange upon warming to room temperature and stirring for 16 h. Volatiles were removed in vacuo to give crude 4 as an orange solid. Colorless crystals of 4 were obtained from a saturated toluene solution. Yield: 0.17 g, 35%. Anal. Calcd for C₉₀H₁₀₂Li₂N₄P₄: C, 77.54; H, 8.54; N, 4.02. Found: C, 77.67; H, 8.55; N, 3.97. ¹H NMR (d_6 -benzene, 298 K): δ 1.68 (br m, 12H, CH₂(CH)₂), 1.96 (br m, 12H, NCCH₂CH), 2.07 (br m, 6H, CH(CH₂)₃), 7.17 (br m, 12H, *m*- and *p*-Ar-CH), 7.97 (br m, 8H, *o*-Ar-CH), HCP₂ not observed. ¹³C{¹H} NMR (d_6 -benzene, 298 K): δ 30.81 (CH(CH₂)₃), 37.00 (CH₂(CH)₂), 49.56 (NCCH₂CH), 52.33 (NC(CH₂)₃), 127.57 (m-Ar-C), 129.01 (p-Ar-C), 132.56 (m, o-Ar-C), HCP₂ and ipso-Ar-C not observed. ³¹P{¹H} NMR (d_6 -benzene, 298 K): δ 10.53 (br s, HCP₂). ⁷Li{¹H} NMR (d_6 -benzene, 298 K): δ 2.32 (br s, LiHCP₂). FTIR v/ cm⁻¹ (Nujol): 1589 (w, br), 1261 (m), 1180 (m), 1096 (s), 1028 (s, br), 800 (m), 743 (m), 709 (m), 697 (m).

Synthesis of [Na{HC(PPh2NAd)2}(THF)2] (5). THF (30 mL) was added to a precooled $(-78 \,^{\circ}\text{C})$ mixture of 3 (2.05 g, 3.0 mmol) and [Na(Bn)] (0.34 g, 3.0 mmol) to give a yellow solution. The mixture was slowly allowed to warm to room temperature with stirring over 24 h. Volatiles were removed in vacuo and the resulting solid washed with hexane to afford crude 5 as a yellow powder. Recrystallization from hot THF (2 mL) gave crystalline 5. Yield: 1.10 g, 43%. Anal. Calcd for C₅₃H₆₇N₂NaO₂P₂: C, 74.97; H, 7.95; N, 3.30. Found: C, 74.99; H, 7.49; N, 3.18. ¹H NMR (d_6 -benzene, 298 K): δ 1.50 (m, 8H, OCH₂CH₂), 1.61 (br s, 1H, HCP₂), 1.70 (br m, 12H, CH₂(CH)₂), 1.95 (br m, 12H, NCCH₂CH), 2.10 (br m, 6H, CH(CH₂)₃), 3.68 (m, 8H, OCH₂CH₂), 7.23 (br m, 12H, *m*- and *p*-Ar-CH), 8.16 (br m, 8H, *o*-Ar-CH). ${}^{13}C{}^{1}H{}$ NMR (*d*₆-benzene, 298 K): δ 25.46 (OCH₂CH₂), 30.95 (CH(CH₂)₃), 37.03 (CH₂(CH)₂), 49.42 (NCCH₂CH), 51.95 (NC(CH₂)₃), 67.81 (OCH₂CH₂), 127.15 (*m*-Ar-*C*), 128.05 (*p*-Ar-*C*), 132.45 (*m*, *o*-Ar-*C*), 143.78, 144.53 (ipso-Ar-C), HCP2 not observed. ³¹P{¹H} NMR (d₆benzene, 298 K): δ 9.45 (br s, HCP₂). FTIR v/cm⁻¹ (Nujol): 1589 (w), 1261 (m), 1208 (m), 1094 (s), 1025 (s, br), 876 (w), 800 (s), 741 (w), 722 (w), 696 (w).

Synthesis of $[K{HC(PPh_2NAd)_2}(THF)_2]$ (6). THF (30 mL) was added to a precooled (-78 °C) mixture of 3 (1.37 g, 2.0 mmol) and [K(Bn)] (0.26 g, 2.0 mmol) to give a yellow solution. The mixture was slowly allowed to warm to room temperature with stirring over 24 h. Volatiles were removed in vacuo and the resulting solid washed with hexane to afford crude 6 as a yellow powder. Recrystallization from hot

THF (3 mL) afforded crystalline 6. Yield: 0.87 g, 50%. Anal. Calcd for $C_{53}H_{67}KN_2O_2P_2$: C, 73.72; H, 7.81; N, 3.24. Found: C, 73.68; H, 7.93; N, 3.19. ¹H NMR (d_6 -benzene, 298 K): δ 1.53 (m, 8H, OCH₂CH₂), 1.64 (t, ² J_{PH} = 3.4 Hz, 1H, HCP₂), 1.70 (br m, 12H, CH₂(CH)₂), 1.77 (br m, 12H, NCCH₂CH), 2.09 (br m, 6H, CH(CH₂)₃), 3.67 (m, 8H, OCH₂CH₂), 7.23 (t, ³ J_{HH} = 7.8 Hz, 4H, *p*-Ar-CH), 7.30 (m, ³ J_{HH} = 7.8 Hz, 8H, *m*-Ar-CH), 8.25 (t, ³ J_{HH} = 7.8 Hz, 8H, *o*-Ar-CH). ¹³C{¹H} NMR (d_6 -benzene, 298 K): δ 25.55 (OCH₂CH₂), 26.95 (t, J_{PC} = 141.9 Hz, HCP₂), 30.95 (CH(CH₂)₃), 37.13 (CH₂(CH)₂), 49.37 (NCCH₂CH), 52.09 (NC(CH₂)₃), 67.57 (OCH₂CH₂), 126.99 (*m*-Ar-C), 128.21 (*p*-Ar-C), 132.43 (br, *o*-Ar-C), 145.18, 146.05 (*ipso*-Ar-C). ³¹P₁{¹H</sup> NMR (d_6 -benzene, 298 K): δ 4.90 (s, HCP₂). FTIR v/cm⁻¹ (Nujol): 1558 (w, br), 1261 (m), 1168 (m), 1092 (s), 1026 (s, br), 873 (w), 800 (s), 736 (w), 722 (w), 696 (w).

Synthesis of [Rb{HC(PPh₂NAd)₂}(THF)₂] (7). Rubidium 2-ethylhexoxide (1.0 M in THF, 2.0 mL, 2.0 mmol) was added to a precooled $(-78 \text{ }^\circ\text{C})$ slurry of 4 (1.38 g, 1.0 mmol) in THF (30 mL). The mixture was slowly allowed to warm to room temperature with stirring over 24 h. Volatiles were removed in vacuo and the resulting solid washed with hexane to afford 7 as a yellow powder. Recrystallization from hot THF (1.5 mL) afforded 7 · 0.5C₇H₈ as crystals on cooling to -30 °C. Yield: 0.95 g, 52%. Anal. Calcd for C53H67N2O2P2Rb: C, 70.61; H, 7.22; N, 2.99. Found: C, 70.54; H, 7.27; N, 2.86. ¹H NMR (*d*₆benzene, 298 K): δ 1.54 (m, 8H, OCH₂CH₂), 1.59 (t, ²J_{PH} = 2.9 Hz, 1H, HCP₂), 1.76 (br m, 12H, CH₂(CH)₂), 1.81 (br m, 12H, NCCH₂CH), 2.23 (br m, 6H, CH(CH₂)₃), 3.68 (m, 8H, OCH₂CH₂), 7.23 (t, ${}^{3}J_{HH} =$ 7.6 Hz, 4H, *p*-Ar-CH), 7.31 (m, ${}^{3}J_{HH}$ = 7.6 Hz, 8H, *m*-Ar-CH), 8.28 (m, 8H, o-Ar-CH). ¹³C{¹H} NMR (d_6 -benzene, 298 K): δ 25.58 (t, J_{PC} = 133.8 Hz, HCP₂), 30.88 (CH(CH₂)₃), 36.99 (CH₂(CH)₂), 49.56 (NCCH₂CH), 52.34 (NC(CH₂)₃), 127.16, 127.69 (*m*-Ar-C), 128.17, 129.98 (p-Ar-C), 132.49, 132.64 (o-Ar-C), 145.41, 146.28 (ipso-Ar-C). ³¹P{¹H} NMR (d_6 -benzene, 298 K): δ 4.06 (s, HCP₂). FTIR v/cm⁻¹ (Nujol): 1600 (w, br), 1302 (w), 1261 (s), 1096 (s, br), 1026 (s, br), 871 (w), 801 (s), 737 (w), 721 (w), 697 (w).

Synthesis of [Cs{HC(PPh₂NAd)₂}(DME)₂] (8). THF (30 mL) was added to precooled (-78 °C) mixture of 4 (1.37 g, 1.0 mmol) and [Cs(Bn)] (0.45 g, 2.0 mmol) to give an orange solution. The mixture was slowly allowed to warm to room temperature with stirring over 24 h. Volatiles were removed in vacuo and the resulting solid washed with hexane to afford $[Cs{HC(PPh_2NAd)_2}(THF)_n]$ as an orange powder. Recrystallization from hot DME (4 mL) afforded crystalline $8 \cdot 0.5C_4H_{10}O_2$ on cooling to -30 °C. Yield: 0.95 g, 52%. Anal. Calcd for $C_{55}H_{76}C_{5}N_{2}O_{5}P_{2}$ (8.0.5 $C_{4}H_{10}O_{2}$): C, 63.50; H, 7.37; N, 2.69. Found: C, 63.68; H, 7.42; N, 2.86. ¹H NMR (d_8 -THF, 298 K): δ 1.71 (br m, 12H, CH₂(CH)₂), 1.83 (br m, 12H, NCCH₂CH), 1.95 (br m, 3H, CH(CH₂)₃), 2.03 (br m, 3H, CH(CH₂)₃), 2.15 (br s, 1H, HCP₂), 7.46 (br m, 8H, *m*-Ar-CH), 7.52 (d, ${}^{3}J_{HH}$ = 7.2 Hz, 4H, *o*-Ar-CH), 7.61 (t, ${}^{3}J_{HH} = 7.2 \text{ Hz}, 2H, p-\text{Ar-C}H), 8.05 (t, {}^{3}J_{HH} = 7.6 \text{ Hz}, 2H, p-\text{Ar-C}H), 8.28$ (br m, 4H, o-Ar-CH). ¹³C{¹H} NMR (d_8 -THF, 298 K): $\hat{\delta}$ 23.99 (t, J_{PC} = 134.8 Hz, HCP₂), 28.85, 29.00 (CH(CH₂)₃), 34.88, 35.09 (CH₂-(CH)₂), 46.66, 47.22 (NCCH₂CH), 49.89, 50.39 (NC(CH₂)₃), 124.58 (m-Ar-C), 125.25, 125.68 (p-Ar-C), 130.48, 130.71 (o-Ar-C), 143.92, 144.82 (ipso-Ar-C). ${}^{31}P{}^{1}H{}$ NMR (d_{8} -THF, 298 K): δ -0.58 (s, HCP₂). FTIR v/cm⁻¹ (Nujol): 1586 (w, br), 1348 (m), 1301 (m), 1260 (m), 1216 (s, br), 1093 (s), 1033 (m), 940 (m), 874 (m), 851 (m), 811 (m), 739 (m), 698 (m).

Synthesis of $[La{HC(PPh_2NSiMe_3)_2}(I)_2(THF)]$ (9). THF (25 mL) was added to a precooled (0 °C) mixture of $[La(I)_3(THF)_4]$ (4.04 g, 5.0 mmol) and 1 (3.43 g, 5.0 mmol). The resulting colorless suspension was allowed to warm to room temperature with stirring over 20 h. The suspension was filtered and solvents removed in vacuo to yield 9 as a white powder. Yield: 4.21 g, 77%. Crystallization of a small portion from toluene afforded colorless crystals of $9 \cdot 0.5C_7H_8$. Anal. Calcd for $C_{39}H_{55}I_2LaN_2O_2P_2Si_2$: C, 42.78; H, 5.07; N, 2.56. Found: C, 43.12; H,

	1	2	3	4	5	
formula	C ₃₉ H ₅₅ N ₂ O ₂ P ₂ RbSi ₂	C ₃₉ H ₅₉ CsN ₂ O ₄ P ₂ Si ₂	$C_{45}H_{52}N_2P_2$	C ₉₀ H ₁₀₂ Li ₂ N ₄ P ₄	$C_{53}H_{67}N_2NaO_2P_2$	
fw	787.44	870.91	682.83	1377.52	849.02	
cryst size, mm	$0.23\times0.17\times0.17$	$0.50\times0.36\times0.23$	$0.31\times0.20\times0.17$	$0.18\times0.11\times0.09$	$0.73 \times 0.30 \times 0.25$	
cryst syst	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	
space group	$P2_1/n$	P2 ₁ /c	$P\overline{1}$	$Pna2_1$	$P2_1/c$	
<i>a,</i> Å	10.5328(5)	13.8885(2)	10.5879(11)	27.3090(7)	29.1701(4)	
<i>b,</i> Å	17.2302(9)	16.7771(4)	11.1951(12)	12.5276(3)	20.3182(3)	
<i>c,</i> Å	23.0134(12)	38.3042(5)	16.3420(12)	22.2817(6)	23.9244(3)	
α , °			107.630(8)			
<i>β</i> , °	94.0980(10)	96.1663(13)	102.177(8)		105.7572(14)	
γ, °			92.073(9)			
<i>V</i> , Å ³	4165.8(4)	8873.6(3)	1794.1(3)	7622.9(3)	13 646.8(3)	
Ζ	4	8	2	4	12	
$ ho_{ m calcd,}~{ m g~cm}^{-3}$	1.256	1.304	1.264	1.200	1.240	
μ , mm ⁻¹	1.356	8.006	1.358	1.279	1.289	
no. of reflns measd	24 588	34 781	12 829	19 317	63 777	
no. of unique reflns, R _{int}	9393, 0.0213	17 323, 0.0408	7038, 0.0605	10 402, 0.0452	27 221, 0.025	
no. of reflns with $F^2 > 2\sigma(F^2)$	7269	15 797	6003	8860	23 818	
transm coeff range	0.637-0.746	0.134-0.574	0.749-1.185	0.876-1.008	0.571-1.863	
$R, R_{w}^{a} (F^{2} > 2\sigma(F^{2}))$	0.0372, 0.0906	0.0484, 0.1261	0.0511, 0.1356	0.0499, 0.1128	0.0379, 0.0965	
R, R_{w}^{a} (all data)	0.0559, 0.0990	0.0532, 0.1261	0.0596, 0.1449	0.0630, 0.1192	0.0445, 0.102	
S ^a	1.032	1.077	1.039	1.049	1.03	
parameters	514	926	442	902	1621	
max, min diff map, e ${\rm \AA}^{-3}$	0.676, -0.551	1.317, -1.260	0.675, -0.572	0.506, -0.514	0.53, -0.38	
Conventional $R = \Sigma F_o - F_c / \Sigma F_o $; $R_w = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$; $S = [\Sigma w (F_o^2 - F_c^2)^2 / \text{no. data - no. params})^{1/2}$ for all data.						

 parameters
 514
 926

 max, min diff map, e Å⁻³
 0.676, -0.551
 1.317, -1.260

 ^a Conventional $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|; R_w = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w$

NMR (d_6 -benzene, 298 K): δ 17.63 (s, HCP₂). ²⁹Si{¹H} NMR (d_6 -benzene, 298 K): δ -4.86 (s, SiMe₃). FTIR ν/cm^{-1} (Nujol): 1589 (w, br), 1310 (w), 1261 (s), 1114 (s), 1089 (s), 1025 (s), 984 (m), 836 (s), 801 (s), 722 (m), 693 (m), 659 (m), 606 (w). The preparation of **9** can be accomplished utilizing **2** instead of **1**, giving a similar yield of **9**. **Synthesis of [La{HC(PPh₂NAd)₂}(I)₂(THF)] (10).** THF (20 mL)

was added to a precooled (0 °C) mixture of $[La(I)_3(THF)_4]$ (1.62 g, 2.0 mmol) and 6 (1.60 g, 2.0 mmol). The resulting brown suspension was allowed to warm to room temperature with stirring over 20 h. The suspension was filtered and volatiles removed in vacuo to yield 10 as an offwhite powder. Recrystallization from hot THF (11 mL) afforded, on cooling, colorless crystals of 10 · 1.5C4H8O. Yield: 0.94 g, 38%. Anal. Calcd for C₅₅H₇₁I₂LaN₂O_{2.5}P₂ (10 · 1.5C₄H₈O): C, 52.65; H, 5.70; N, 2.23. Found: C, 52.58; H, 5.76; N, 2.08. ¹H NMR (d_6 -benzene, 298 K): δ 1.26 (br m, 12H, $CH_2(CH)_2$), 1.33 (br m, 6H, NCCH₂CH), 1.70 (m, 4H, OCH₂CH₂), 1.85 (br m, 6H, NCCH₂CH), 2.11 (br m, 6H, CH(CH₂)₃), 3.08 (br m, 1H, HCP_2), 3.95 (m, 4H, OCH_2CH_2), 6.64 (vt, ${}^{3}J_{HH} = 7.2$ Hz, 4H, *m*-Ar-CH), 6.72 (vt, ${}^{3}J_{HH} = 7.2$ Hz, 2H, *p*-Ar-CH), 6.89 (vt, ${}^{3}J_{HH} = 7.2$ Hz, 2H, *p*-Ar-CH), 6.95 (vt, ${}^{3}J_{HH} = 7.2$ Hz, 4H, *m*-Ar-CH), 7.64 (br m, 4H, o-Ar-CH), 7.98 (br m, 4H, o-Ar-CH). ¹³C{¹H} NMR (d₆-benzene, 298 K): δ 11.15 (t, J_{PC} = 139.5 Hz, HCP₂), 25.13 (OCH₂CH₂), 30.15 (CH(CH₂)₃), 36.19 (CH₂(CH)₂), 45.90 (NCCH₂CH), 57.32 (NC-(CH₂)₃), 71.14 (OCH₂CH₂), 127.53, 128.42 (*m*-Ar-C), 130.83, 131.07 (p-Ar-C), 131.67, 134.94 (o-Ar-C), 137.93, 138.41 (ipso-Ar-C). ³¹P{¹H}

NMR (d_6 -benzene, 298 K): δ 12.11 (s, HCP₂). FTIR ν /cm⁻¹ (Nujol): 1587 (w, br), 1304 (w), 1261 (m), 1226 (w), 1186 (w), 1143 (s), 1104 (s), 1020 (s), 992 (m), 875 (w), 846 (m), 801 (m), 764 (w), 745 (w), 720 (w), 712 (w), 693 (w), 627 (m).

X-ray Crystallography. Crystal data for compounds 1-10 are given in Tables 2 and 3, and further details of the structure determinations are in the Supporting Information. Bond lengths and angles are listed in Table 1. Crystals were examined variously on a Bruker APEX CCD area detector diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å), or on an Oxford Diffraction SuperNova Atlas CCD diffractometer using mirror-monochromated CuK α 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 correction based on symmetryequivalent and repeat reflections (APEX) or Gaussian grid face-indexed absorption correction with a beam profile correction (Supernova) was 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 $U_{\rm eq}$ of the parent atom. The methanide hydrogens were initially located in the Fourier difference map to confirm the methanide geometries and were subsequently idealized and refined using a riding model. The largest features in final difference syntheses were close to heavy atoms and were of no chemical significance. Highly disordered solvent molecules of crystallization in $7 \cdot 0.5C_7H_8$ and $8 \cdot 0.5C_4H_{10}O_2$ could not be modeled and were treated with the Platon SQUEEZE procedure.⁴⁶ Programs were Bruker AXS SMART⁴⁷ and CrysAlisPro⁴⁸ (control) and Bruker AXS SAINT⁴⁷ and CrysAlisPro⁴⁸ (integration), and SHELXTL⁴⁹ and OLEX2⁵⁰ were

Table 3. Crystallographic Data for 6–10

	6	7•0.5C ₇ H ₈	$8 \cdot 0.5 C_4 H_{10} O_2$	9 ⋅ 0.5C ₇ H ₈	10 • 1.5C₄H ₈ O		
formula	$C_{53}H_{67}KN_2O_2P_2$	C ₅₃ H ₆₇ N ₂ O ₂ P ₂ Rb ∙0.5C ₇ H ₈	$C_{53}H_{71}CsN_2O_4P_2$ • 0.5 $C_4H_{10}O_2$	$\begin{array}{c} C_{35}H_{47}I_{2}LaN_{2}OP_{2}Si_{2}\\ \bullet 0.5C_{7}H_{8} \end{array}$	$C_{49}H_{59}I_{2}LaN_{2}OP_{2}$ $\cdot 1.5C_{4}H_{8}O$		
fw	865.13	957.56	1040.03	1068.64	1254.79		
cryst size, mm	$0.46\times0.40\times0.36$	$0.32\times0.23\times0.17$	$0.68\times0.48\times0.33$	$0.16\times0.10\times0.01$	$0.15 \times 0.11 \times 0.06$		
cryst syst	monoclinic	triclinic	monoclinic	triclinic	monoclinic		
space group	$P2_1$	$P\overline{1}$	$P2_{1}/c$	$P\overline{1}$	$P2_{1}/c$		
<i>a,</i> Å	10.2558(11)	11.2873(9)	20.2678(17)	9.8191(4)	13.0440(8)		
<i>b,</i> Å	20.195(2)	14.3668(10)	13.4245(14)	11.9347(4)	39.599(2)		
<i>c,</i> Å	10.8602(11)	16.6811(12)	19.3640(11)	19.2510(9)	20.1193(12)		
lpha, °		80.260(6)		77.233(4)			
β , °	94.588(2)	73.219(7)	103.809(7)	77.040(4)	90.184(1)		
γ, °		71.248(7)		83.684(3)			
<i>V</i> , Å ³	2242.1(4)	2443.7(3)	5116.4(8)	2139.84(15)	10 392.2(11)		
Ζ	2	2	4	2	4		
$ ho_{ m calcd}$ g cm ⁻³	1.281	1.301	1.350	1.659	1.604		
μ , mm ⁻¹	0.234	2.344	6.616	20.520	2.115		
no. of reflns measd	13715	20 870	20 645	9638	21 329		
no. of unique reflns, R _{int}	9332, 0.0135	9705, 0.025	10016, 0.057	7226, 0.0513	53 355, 0.0247		
no. of reflns with $F^2 > 2\sigma(F^2)$	9115	8908	8295	6203	17 199		
transm coeff range	0.63-0.75	0.624-0.891	0.117-0.632	0.461-0.912	0.597-0.746		
$R, R_{w}^{a}(F^{2} > 2\sigma(F^{2}))$	0.0286, 0.0736	0.0316, 0.0811	0.0606, 0.163	0.0595, 0.160	0.0266, 0.0700		
$R, R_{\rm w}^{a}$ (all data)	0.0293, 0.0741	0.0342, 0.0829	0.0710, 0.173	0.0715, 0.170	0.0288, 0.0712		
S ^a	1.058	1.06	1.06	1.08	1.11		
parameters	546	545	594	441	1164		
max, min diff map, e ${\rm \AA}^{-3}$	0.373, -0.169	0.68, - 0.43	1.63, - 2.13	2.39, - 2.39	1.72, -0.54		
Conventional $R = \Sigma F_o - F_c / \Sigma F_o $; $R_w = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$; $S = [\Sigma w (F_o^2 - F_c^2)^2 / \text{no. data} - \text{no. params})]^{1/2}$ for all data.							

employed for structure solution and refinement and for molecular graphics.

ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data for 1-10. This material is available free of charge via the Internet at http://pubs.acs.org.

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