ORGANOMETALLICS

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Group 1 Bis(iminophosphorano)methanides, Part 2: *N*-Aryl Derivatives of the Sterically Demanding Methanes $H_2C(PPh_2NR)_2$ (R = 2,4,6-trimethylphenyl or 2,6-diisopropylphenyl)

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Supporting Information

ABSTRACT: Treatment of $H_2C(PPh_2NMes)_2$ (Mes = 2,4,6-trimethylphenyl) with 1 equiv of [Na(Bn)] (Bn = $CH_2C_6H_5$) in THF gave the Lewis base adduct $[Na\{HC(PPh_2NMes)_2\}$ - $(THF)_2]$ (1). The heavy group 1 methanides $[Rb\{HC(PPh_2NMes)_2\}(DME)_2]$ (2) and $[Cs\{HC(PPh_2NMes)_2\}]_6$ (3) were prepared by the reaction of [MOR] (M = Cs, Rb; OR = 2-ethylhexoxide) with $[Li\{HC(PPh_2NMes)_2\}]$. The Lewis base adduct 2 is monomeric, but 3 exists as a novel cyclic 2.9 nm hexamer in the solid state even though it was recrystallized from the strong donor solvent THF. The reaction of $H_2C(PPh_2NDipp)_2$ (Dipp = 2,6-diisopropylphenyl) with [Na(Bn)] afforded $[Na\{HC(PPh_2NDipp)_2\}(THF)]$ (4). The potassium congener $[K\{HC(PPh_2NDipp)_2\}(THF)_2]$ (5) was prepared by the reaction of the parent methane with KH. In 5, the methanide ligand is bound to potassium through one N center, the methanide center, and an η^6 -Dipp interaction. However, the THF molecules in 5 are loosely bound, as evidenced by the isolation of dimeric $[\{K[HC(PPh_2NDipp)_2](THF)\}_2]$ (6) from hexane. In 6, the potassium is bound to the two N centers of one methanide ligand,



but no methanide–potassium interaction is observed, and a "loose" dimer is constructed by bridging $K \cdots C_{Dipp}$ interactions. The reaction of [MOR] (M = Rb, Cs) with [Li{HC(PPh_2NDipp)_2}] gave the heavy group 1 methanides [M{HC(PPh_2NDipp)_2}-(THF)_3] [M = Rb (7), Cs (8)]. The synthetic utility of these group 1 transfer agents has been demonstrated by the preparation of [Ln{HC(PPh_2NMes)_2}(I)_2(THF)_2] [Ln = Ce (9), Pr (10), Nd (11), Sm (12)] from [Ln(I)_3(THF)_n], employing a salt metathesis methodology. Complexes 1-12 have been characterized by X-ray crystallography, multielement NMR spectroscopy, FTIR spectroscopy, and CHN microanalyses.

INTRODUCTION

In the preceding paper,¹ we reported the synthesis of group 1 N-trimethylsilyl and N-adamantyl bis(iminophosphorano)methanides and demonstrated their synthetic utility by preparing lanthanum methanide complexes by a simple salt metathesis methodology, starting from $[La(I)_3(THF)_4]$.² This contribution is notable because previous attempts to install the N-trimethylsilyl bis(iminophosphorano)methanide ligand onto lanthanide iodides utilizing potassium reagents proved to be surprisingly difficult, but in contrast it was found to be straightforward with the rubidium and cesium methanide salts. Therefore, the availability of bis(iminophosphorano)methanides encompassing all alkali metals is desirable from a synthetic standpoint.³ The previous article also described previously reported structurally characterized group 1 methanides and methanediides of $H_2C(PPh_2NR)_2$ (R = Mes, $C_6H_2Me_3$ -2,4,6;^{4,5} Dipp = $C_6H_3Pr_2^i$ -2,6^{3,5}), namely, $[Li{HC(PPh_2NMes)_2}(OEt_2)],^5 [Li{HC(PPh_2NDipp)_2}],^6$ $[\{K(HC[PPh_2NMes]_2)\}_2]^7 [Li\{C(PPh_2NDipp)_2\}-Li(TMEDA)]$ (TMEDA = N, N'-tetramethylethylenediamine),⁶ and [{Li₂(C- $[PPh_2NMes]_2$, which have been summarized in two recent reviews.⁹ It is noteworthy that a related series of N-phenyl heavy group 1 methanediides $[\{M_2(C[PPh_2NPh]_2)\}_2]$ (M = K, Rb, Cs)

have also been reported.¹⁰ Realizing that no other alkali metal *N*-Mes or Dipp bis(iminophosphorano)methanide complexes have been reported, yet they represent valuable synthetic ligand transfer reagents, we describe here the synthesis and solid-state structures of sodium, rubidium, and cesium methanide derivatives of both ligand systems and the potassium methanide derivative of the *N*-Dipp analogue for completeness. We then demonstrate the synthetic utility of group 1 *N*-aryl bis(iminophosphorano)methanides by preparing a series of lanthanide methanides via a simple salt metathesis methodology from [{K(HC[PPh_2NMes]_2)}_2] and solvated lanthanide triiodides.

RESULTS AND DISCUSSION

Treatment of $H_2C(PPh_2NMes)_2^4$ with $[Na(Bn)]^{11}$ afforded the methanide complex $[Na{HC(PPh_2NMes)_2}(THF)_2]$ (1). Following workup, 1 was isolated in 86% yield (Scheme 1). Elemental analysis of 1 consistently gave low values for *C*, which we attribute to carbide formation as H and N values were

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

consistent with the proposed formulation and all spectroscopic data indicate that samples are pure. The ³¹P{¹H} NMR spectrum of 1 in *d*₆-benzene exhibits a singlet at δ 9.35 ppm, which is upfield of that observed for [Li{HC(PPh₂NMes)₂}(OEt₂)] (δ 14.1 ppm)⁵ and [{K(HC[PPh₂NMes]₂)}₂] (δ 16.3 ppm).⁷ The methine proton of 1 is observed as a singlet in its ¹H NMR spectrum at δ 2.02 ppm, which is between the values seen for [Li{HC(PPh₂NMes)₂}(OEt₂)] (δ 1.27 ppm, ²*J*_{PH} = 4.2 Hz)⁵ and [{K(HC[PPh₂NMes]₂)}₂] (δ 2.24 ppm, ²*J*_{PH} = 3.3 Hz),⁷ although these latter resonances, in contrast, are triplets. However, the corresponding methanide resonance in the ¹³C{¹H} NMR spectrum of 1 (δ 22.28 ppm, *J*_{PC} = 144.6 Hz) is a well-defined triplet, similar to that observed for [Li{HC(PPh₂NMes)₂](OEt₂)] (δ 18.9 ppm, *J*_{PC} = 150.1 Hz).⁵

The molecular structure of 1 is illustrated in Figure 1, and selected bond lengths and angles are listed in Table 1. Complex 1, like $[Na{HC(PPh_2NSiMe_3)_2}(THF)_2]$,¹² is monomeric in the solid state with two molecules of THF coordinated to the four-coordinate sodium cation. Although the six-membered metallocycle adopts a distorted twist-boat conformation, with sodium and the methanide carbon above the P_2N_2 mean least-squares

plane, no metal—methanide contact is apparent $[Na(1)\cdots C(1)$ 3.555(2) Å], a phenomenon observed in numerous group 1 methanide complexes, including $[Na{HC(PPh_2NSiMe_3)_2}-(THF)_2]$ $[Na\cdots C 3.739(7) Å]$.¹² The average Na–N distance [2.372 Å] and N(1)-Na(1)-N(2) angle $[102.2(15)^{\circ}]$ of 1 are shorter and larger, respectively, than the corresponding values for $[Na{HC(PPh_2NSiMe_3)_2}(THF)_2]$ [Na-N 2.416 Å mean, $N-Na-N 96.8(2)^{\circ}]$,¹² reflecting the less sterically demanding *N*-Mes substituents. However, endocyclic P–C and P–N bond distances and the P(1)-C(1)-P(2) angle of 1 $[129.39(15)^{\circ}]$ are similar to those observed in $[Na{HC(PPh_2NSiMe_3)_2}-(THF)_2]$ $[P-C-P 126.3(3)^{\circ}]$,¹² and their lack of variance underscores the ionic nature of the sodium—ligand bonding. In common with the potassium methanide $[{K(HC[PPh_2-NMes]_2)}_2]$,⁷ an $M \cdots C_{ipso}$ contact is apparent in 1 $[Na(1) \cdots C(35) = 3.008(3) Å]$.

Following the methodology that enabled the synthesis of rubidium and cesium N-silyl and alkyl-substituted bis(iminophosphorano)methanides,¹ H₂C(PPh₂NMes)₂ was converted to $[Li{HC(PPh_2NMes)_2}]_{2,5}$ by reaction with Bu^nLi , and subsequently treated with [MOR] (M = Cs, Rb; OR = 2-ethylhexoxide)¹³ and the coordinating solvent to afford $[Rb{HC(PPh_2 NMes_{2}(DME_{2}]$ (2) and $[Cs{HC(PPh_{2}NMes_{2})]_{6}$ (3) (Scheme 1). Analysis of ³¹P{¹H} NMR spectra revealed that the singlet resonance is shifted considerably upfield [δ 3.77 ppm (2); δ 2.53 ppm (3)] from that observed for [{K(HC[PPh₂-NMes]₂) $_{2}$] (δ 16.3 ppm).⁷ The methanide group is evidenced by broad singlets in the ¹H NMR spectra [δ 1.46 ppm (2); δ 2.17 ppm (3)] and triplet resonances in the ¹³C{¹H} NMR spectra $[\delta 23.20, J_{PC} = 140.9 \text{ Hz} (2); \delta 23.96, J_{PC} = 136.8 \text{ Hz} (3)] \text{ of}$ 2 and 3, which are similar to the corresponding values observed for 1 (vide supra).

To obtain crystals suitable for study by X-ray crystallography, 2 and 3 were crystallized from saturated DME and THF solutions, respectively, and their structures were determined by X-ray crystallography (Figures 2 and 3; selected bond lengths and angles are compiled in Table 1). Complex 2 required DME to crystallize, whereas 3 crystallizes as a remarkable hexanuclear, solvent-free wheel with a diameter of 2.9 nm. Unlike the sixmembered metallocycles of the *N*-silyl and alkyl rubidium and cesium methanides described in the previous paper, which adopt an atypical geometry,¹ the ligand frameworks of 2 and 3 exhibit a more standard distorted twist-boat conformation upon

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Table 1. Selected E	Bond Lengths	(Å) and Angles (°)	for 1-12		6		
	0			P(1)-N(1)	1.5973(11)	P(2)-N(2)	1.5976(10)
$C(1) = \mathbf{P}(1)$	1 710(2)	Γ	1 52 ((2))	K(1) - N(1)	2.7539(11)	K(1) - N(2)	2.6527(10)
C(1) - P(1)	1.710(2)	C(1) - P(2)	1.724(2)	K(1) - O(1)	2.6571(10)	$K(1) \cdots C(1)$	3.899(10)
P(1) = N(1)	1.591(2)	P(2) = N(2)	1.595(2)	$K(1)\cdots C(9)$	3.4701(13)	$K(1) \cdots C(38)$	3.3090(12)
Na(1) - N(1)	2.336(2)	Na(1) - N(2)	2.408(2)	$K(1) \cdots C(40A)$	3.5256(14)		
Na(1) = O(1)	2.31/(2)	Na(1) = O(2)	2.31/(2)	P(1)-C(1)-P(2)	131.92(7)	N(1)-K(1)-N(2)	93.43(3)
$Na(1) \cdots C(1)$	3.555(2)	$Na(1) \cdots C(35)$	3.008(2)	N(1)-P(1)-C(1)	123.54(6)	N(2)-P(2)-C(1)	113.07(6)
P(1) - C(1) - P(2)	129.39(15)	N(1) - Na(1) - N(2)	102.2(15)	P(1)-N(1)-K(1)	105.20(5)	P(2)-N(2)-K(1)	126.78(5)
N(1) - P(1) - C(1)	112.01(11)	N(2) - P(2) - C(1)	123.96(11)		7 · C.	H ₈ O	
P(1) - N(1) - Na(1)	121.86(11)	P(2) - N(2) - Na(1)	106.78(10)	C(1) - P(1)	1.720(3)	C(1) - P(2)	1.726(3)
C(1) = D(1)	1 52 61 (15)	\mathcal{L}		P(1) - N(1)	1.582(3)	P(2) - N(2)	1.592(3)
C(1) - P(1)	1.7251(17)	C(1) - P(2)	1.7115(17)	Rb(1) - N(1)	2.850(3)	Rb(1) - N(2)	3.092(3)
P(1) - N(1)	1.5942(15)	P(2) - N(2)	1.5841(15)	Rb(1) - O(1)	2.865(2)	Rb(1) - O(2)	3.053(2)
Rb(1) - N(1)	2.9321(14)	Rb(1) - N(2)	2.9369(14)	Rb(1) - O(3)	2.947(2)	$Rb(1)\cdots C(1)$	4.000(3)
Rb(1) - O(1)	2.9120(13)	Rb(1) - O(2)	3.0457(13)	$Rb(1)\cdots C(14)$	3.407(3)	$Rb(1)\cdots C(38)$	3.441(3)
Rb(1) - O(3)	2.8998(14)	Rb(1) - O(4)	3.3118(14)	P(1)-C(1)-P(2)	130.12(18)	N(1) - Rb(1) - N(2)	80.12(7)
$Rb(1)\cdots C(1)$	4.402(2)	$Rb(1)\cdots C(8)$	3.661(2)	N(1) - P(1) - C(1)	112.70(14)	N(2) - P(2) - C(1)	122.82(14)
$Rb(1)\cdots C(13)$	3.501(2)	$Rb(1)\cdots C(20)$	3.689(2)	P(1) - N(1) - Rb(1)	121.24(12)	P(2)-N(2)-Rb(1)	111.81(12)
$Rb(1)\cdots C(35)$	3.2898(16)	$Rb(1)\cdots C(40)$	3.612(2)	- (-) - (-) (-)	° C	ч о	
$Rb(1)\cdots C(41)$	3.712(2)			$C(1) = \mathbf{D}(1)$	$3 \cdot C_4$	Γ_{10}	1.710(2)
P(1)-C(1)-P(2)	128.31(11)	N(1)-Rb(1)-N(2)	77.63(4)	C(1) - P(1)	1.717(3)	C(1) - P(2)	1.710(3)
N(1)-P(1)-C(1)	124.77(8)	N(2)-P(2)-C(1)	110.49(8)	P(1) = N(1)	1.58/(3)	P(2) = N(2)	1.595(5)
P(1)-N(1)-Rb(1)	107.42(7)	P(2)-N(2)-Rb(1)	138.69(8)	$C_{s}(1) = N(2)$	3.023(3)	$C_{s}(1) = O(1)$	2.981(4)
	3.0.50	C_4H_8O		$C_{s}(1) = O(2)$	3.195(4)	$C_{s}(1) = O(3)$	3.010(8)
C(1)-P(1)	1.727(6)	C(1)-P(2)	1.705(6)	$C_{s}(1) \cdots C(1)$	4.182(4)	$C_{s}(1)\cdots C(14)$	3.893(4)
P(1)-N(1)	1.577(5)	P(2)-N(2)	1.568(5)	$C_{s}(1) \cdots C(1S)$	4.014(4)	$C_{s}(1)\cdots C(16)$	3.841(3)
Cs(1)-N(1)	3.065(4)	Cs(1)-N(2)	3.080(4)	$Cs(1)\cdots C(17)$	3.560(4)	$C_{s}(1) \cdots C(18)$	3.440(4)
$Cs(1)\cdots C(1)$	4.614(6)	$Cs(1) \cdots C(14)$	3.179(5)	$Cs(1)\cdots C(19)$	3.610(4)	$Cs(1)\cdots C(38)$	3.752(3)
$Cs(1) \cdots C(15)$	3.544(6)	$Cs(1) \cdots C(19)$	3.608(6)	P(1)-C(1)-P(2)	131.25(18)	N(1) - P(1) - C(1)	121.59(15)
$Cs(1) \cdots C(35)$	3.569(5)			N(2) - P(2) - C(1)	111.62(14)	P(2)-N(2)-Cs(1)	121.01(13)
P(1)-C(1)-P(2)	125.9(3)	N(1)-Cs(1)-N(2)	72.85(12)		9.30	C_7H_8	
N(1)-P(1)-C(1)	126.3(3)	N(2)-P(2)-C(1)	110.8(3)	C(1)-P(1)	1.730(3)	C(1)-P(2)	1.721(3)
P(1)-N(1)-Cs(1)	117.6(2)	P(2)-N(2)-Cs(1)	141.7(2)	P(1)-N(1)	1.619(3)	P(2)-N(2)	1.617(3)
	4.0.5	$6C_7H_8$		Ce(1)-N(1)	2.522(3)	Ce(1) - N(2)	2.529(3)
C(1) - P(1)	1.7149(15)	C(1)-P(2)	1.7257(15)	Ce(1) - O(1)	2.572(2)	Ce(1) - O(2)	2.540(2)
P(1)-N(1)	1.5963(13)	P(2) - N(2)	1.5961(13)	Ce(1)-I(1)	3.1742(3)	Ce(1) - I(2)	3.2006(3)
Na(1) - N(1)	2.2656(15)	Na(1) - N(2)	2.3026(14)	Ce(1) - C(1)	2.794(3)		
$Na(1)\cdots C(1)$	3.4780(16)	$Na(1) \cdots C(14)$	2.9372(17)	P(1)-C(1)-P(2)	133.76(19)	N(1)-Ce(1)-N(2)	110.76(8)
$Na(1)\cdots C(38)$	2.8308(17)	Na(1) - O(1)	2.2127(15)	N(1)-P(1)-C(1)	103.28(14)	N(2)-P(2)-C(1)	104.72(14)
P(1)-C(1)-P(2)	127.56(9)	N(1)-Na(1)-N(2)	103.73(5)	P(1)-N(1)-Ce(1)	101.15(12)	P(2)-N(2)-Ce(1)	104.14(12)
N(1)-P(1)-C(1)	112.08(7)	N(2)-P(2)-C(1)	121.39(6)		10.2	C II	
P(1)-N(1)-Na(1)	122.32(7)	P(2)-N(2)-Na(1)	110.80(6)	C(1) = D(1)	1 720(5)	$C_7 H_8$	1 722(5)
		5		C(1) - P(1)	1./29(5)	C(1) - P(2)	1./23(5)
C(1) - P(1)	1.715(5)	C(1) - P(2)	1.713(5)	P(1) - N(1)	1.623(4)	P(2) - N(2)	1.624(4)
P(1) - N(1)	1.589(4)	P(2) - N(2)	1.589(4)	Pr(1)-N(1)	2.499(4)	$\Pr(1)-N(2)$	2.500(4)
$K(1)\cdots C(1)$	3.501(6)	K(1) - N(2)	2.668(5)	Pr(1)-O(1)	2.528(4)	Pr(1)-O(2)	2.560(4)
K(1) - O(1)	2.801(7)	K(1) - O(2)	2.693(6)	Pr(1)-I(1)	3.1664(5)	Pr(1)-I(2)	3.1624(5)
$K(1) \cdots C(14)$	3.338(7)	$K(1) \cdots C(15)$	3.173(7)	Pr(1)-C(1)	2.795(5)		
$K(1) \cdots C(16)$	3.106(7)	$K(1) \cdots C(17)$	3.193(7)	P(1)-C(1)-P(2)	133.7(3)	N(1)-Pr(1)-N(2)	110.90(13)
$K(1) \cdots C(18)$	3.373(8)	$K(1) \cdots C(19)$	3.450(8)	N(1)-P(1)-C(1)	104.8(2)	N(2)-P(2)-C(1)	103.9(2)
$K(1) \cdots C(38)$	3,540(8)		5.100(0)	P(1)-N(1)-Pr(1)	104.31(19)	P(2)-N(2)-Pr(1)	101.5(2)
P(1) - C(1) - P(2)	133.5(3)	C(1) - K(1) - N(2)	49.85(13)		11.3	C ₇ H ₈	
N(1) - P(1) - C(1)	118.9(3)	N(2) - P(2) - C(1)	110.1(3)	C(1) - P(1)	1.731(4)	C(1) - P(2)	1.730(4)
P(2) = N(2) = K(1)	112.0(2)	(2) (2) (2) ((1)	10.1(3)	P(1) - N(1)	1.628(3)	P(2) = N(2)	1 634(3)
(2) $(2)^{-}$ (1)	112.0(2)	4		Md(1) M(1)	2514(2)	1(2) $1(2)Nd(1)$ $N(2)$	2514(2)
C(1) = D(1)	1 72 52 (12)	C(1) = D(2)	1711/(12)	$\operatorname{INU}(1) = \operatorname{IN}(1)$	2.314(3)	NU(1) = N(2)	2.314(3)
C(1) - P(1)	1.7252(12)	C(1) - P(2)	1.7116(12)	Nd(1) = O(1)	2.514(3)	Nd(1) = O(2)	2.518(3)

,	Table 1. Continued			
		11.3C7H	I_8	
	Nd(1) - I(1)	3.1853(3)	Nd(1)-I(2)	3.1604(3)
	Nd(1) - C(1)	2.770(3)		
	P(1)-C(1)-P(2)	134.1(2)	N(1)-Nd(1)-N(2)	112.05(9)
	N(1)-P(1)-C(1)	103.32(16)	N(2)-P(2)-C(1)	104.55(16)
	P(1)-N(1)-Nd(1)	100.57(14)	P(2)-N(2)-Nd(1)	103.40(14)
		12·3C	C_7H_8	
	C(1) - P(1)	1.725(5)	C(1) - P(2)	1.719(4)
	P(1)-N(1)	1.622(4)	P(2)-N(2)	1.620(4)
	Sm(1) - N(1)	2.472(4)	Sm(1)-N(2)	2.462(4)
	Sm(1) - O(1)	2.524(3)	Sm(1) - O(2)	2.485(3)
	Sm(1)-I(1)	3.1259(4)	Sm(1)-I(2)	3.1110(4)
	Sm(1) - C(1)	2.744(4)		
	P(1)-C(1)-P(2)	134.0(3)	N(1)-Sm(1)-N(2)	112.34(12)
	N(1)-P(1)-C(1)	103.8(2)	N(2)-P(2)-C(1)	104.5(2)
	P(1)-N(1)-Sm(1)	100.90(17)	P(2)-N(2)-Sm(1)	103.74(17)



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

coordination, as is observed for the lighter metals in the N-mesityl substituted series, including 1.^{5,7} However, in contrast to 1, the larger rubidium and cesium ions (effective ionic radii, coordination number 6: K⁺ 1.38 Å; Rb⁺ 1.52 Å; Cs⁺ 1.67 Å)¹⁴ display acute N(1)-M(1)-N(2) angles [77.63(4)° (2); 72.85(12)° (3)]. Additionally, their P(1)-C(1)-P(2) angles $[128.31(11)^{\circ}]$ (2); $125.9(3)^{\circ}$ (3)] are far smaller than that observed for $[\{Rb_2C(PPh_2NPh)_2\}_2(C_6H_6)_4] [P(1)-C(1)-P(1) 144.4(1)^\circ; Rb-N 2.923 (mean) Å], although 2 exhibits similar Rb-N 2.923 (mean) A 2$ distances [2.9321 (mean) Å] to the previously reported complex. Also, in common with $[\{Rb_2C(PPh_2NPh)_2\}_2(C_6H_6)_4]$ $[\eta^2$ phenyl Rb····C 3.520(3)-3.608(4) Å; methanide Rb····C 3.047(3) Å],⁹ 2 displays an intramolecular η^2 -aryl contact with one of the *P*-phenyl rings $[Rb \cdots C 3.501(2) - 3.661(2) Å]$ but does not exhibit a rubidium-methanide interaction [Rb···C 4.402(2) Å]. The methanide group of 3, similarly, does not coordinate to cesium $[Cs \cdots C 4.614(6) Å]$. A second intramolecular η^2 -aryl contact between rubidium and one of the Nmesityl groups is observed in 2 [Rb $\cdot \cdot \cdot C$ 3.290(2)-3.612(2) Å], whereas the cesium ion of 3 displays one η^{1} - [3.569(5) Å] and one η^{3} - [3.179(5)-3.608(6) Å] contact with its *N*-mesityl





Figure 3. Molecular structure of the monomer unit (a) and hexamer (b) of $3 \cdot 0.5C_4H_8O$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity.

substituents. Hydrogen atoms on two of the ortho-methyl groups of the N-mesityl substituents are in close proximity to the rubidium ion of **2** $[Rb(1)\cdots C(20) \ 3.689(2) \ Å; Rb(1)\cdots$ H(1A) 2.912(2) Å; $Rb(1) \cdots C(41)$ 3.712(2) Å; $Rb(1) \cdots$ H(1B) 2.981(2) Å], and although these intramolecular $Rb\cdots$ C distances are longer than those reported for [{RbSi- $(SiMe_3)_3$ ₂(toluene)] [Rb····C 3.44(2)-3.62(2) Å]¹⁵ and $[Rb(C_7H_8)_3][M{N(SiMe_3)_2}_3][M = Mg, Zn; Rb \cdots C 3.544(4) - 3.626(3) Å],^{16}$ they may be considered to be weak agostic interactions of C-H with Rb⁺, as discussed previously.¹ Although the coordination sphere of 2 is completed by two molecules of DME as would be anticipated, 3 adopts a novel hexameric structure in the solid state even in the presence of donor solvents, such as THF. This is a consequence of extensive intermolecular interactions in 3 of each cesium ion with two aryl rings $[\eta^6$ -*N*-mesityl: Cs···C 3.457(6)-3.579(6) Å; η^6 -*P*-phenyl: Cs···C 3.651(6) - 3.832(6) Å], which are favorable enough to prevent THF coordination cleaving the wheel into monomeric units. The intermolecular $Cs \cdots C$ distances of 3 are similar to those observed in $[{CsSi(SiMe_3)_3}_2(toluene)_3]$ $[Cs \cdots C 3.51(2) -$ 4.08(2) Å],¹⁵ though it is noteworthy that, in contrast to 3, addition of THF to the hypersilyl complex results in dissociation





Figure 4. Molecular structure of $4 \cdot 0.5C_7H_8$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity.

of toluene and formation of a structurally authenticated THF adduct. This is because the intermolecular interactions in 3 are stabilized by strong electrostatic forces between the anionic ligand and cesium and not just the donation of electron density from π -systems to the cesium ion.

With $H_2C(PPh_2NDipp)_2$ in hand, we studied its sodium and potassium methanide derivatives. Treatment of $H_2C(PPh_2-NDipp)_2$ with NaH did not effect deprotonation; however, [Na(Bn)] (Bn = $CH_2C_6H_5$) was found to react cleanly with $H_2C(PPh_2NDipp)_2$ under the same conditions in THF to give a red solution that yielded analytically pure $[Na{HC(PPh_2-NDipp)_2}(THF)]$ (4) in 71% yield following work up (Scheme 2). The ³¹P{¹H} NMR spectrum of 4 exhibits a singlet at δ 9.14 ppm, which compares to a chemical shift of -16.2 ppm for $H_2C(PPh_2NDipp)_2$.⁴ The proposed formulation of 4 is supported by the spectroscopic and analytical data, the methanide



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

resonance being observed in the ¹³C{¹H} NMR spectrum at δ 24.98 ppm (t, J_{PC} = 144.9 Hz) and in the ¹H NMR spectrum at δ 2.35 ppm. Colorless crystals of 4 · 0.5C₇H₈ were grown from a solution in toluene, and the structure was determined by X-ray crystallography.

The molecular structure of $4 \cdot 0.5C_7H_8$ is illustrated in Figure 4, and selected bond lengths and angles are listed in Table 1. Complex 4 is monomeric in the solid state. The sodium center is coordinated to both imino-nitrogens and the oxygen center of a coordinated THF molecule, but, like the lithium congener $[Li{HC(PPh_2NDipp)_2}],^6$ no metal—methanide bond is present $[Na(1)\cdots C(1) \ 3.4780(16) \ Å]$. Two interactions between the sodium center and the *ipso*-carbon of each *N*-Dipp group are apparent from $Na(1)\cdots C(14)$ and $Na(1)\cdots C(38)$ distances of 2.9372(17) and 2.8308(17) \ Å, respectively, reflecting the low-coordinate nature of the sodium center in 4. Furthermore, the Na(1)-N(1) and Na(1)-N(2) bond lengths of 2.2656(15) and



Figure 6. Molecular structure of **6** with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms are omitted for clarity. Symmetry operation: -x, -y, -z.

2.3026(14) Å are short compared with other bis(iminophosphorano)methanide–sodium complexes, which typically measure ~2.33–2.53 Å.^{12,17} The C(1)–P(1) and C(1)–P(2) bond lengths of 1.7149(15) and 1.7257(15) Å, respectively, are shorter than those observed in H₂C(PPh₂NDipp)₂, but longer than those observed in [Li{HC(PPh₂NDipp)₂}],⁶ reflecting the softer nature of sodium compared to lithium. The P(1)–N(1) and P(2)–N(2) bond distances of 1.5963(13) and 1.5961(13) Å are longer than the corresponding distances in H₂C(PPh₂NDipp)₂, but are statistically indistinguishable from the corresponding values in [Li{HC(PPh₂NDipp)₂}].⁶

Treatment of H₂C(PPh₂NDipp)₂ with an excess of KH in THF affords, after workup, [K{HC(PPh₂NDipp)₂}(THF)₂] (**5**) as a pale brown powder in 46% yield (not optimized, Scheme 2). This contrasts to the attempted preparation of 4 with NaH under the same conditions, which failed. The ³¹P{¹H} NMR spectrum of **5** in *d*₆-benzene exhibits a singlet at δ 3.85 ppm, suggesting that the structure observed in the solid state (vide infra) equilibrates in solution, which compares to a chemical shift of δ 9.14 ppm for **4**. All other spectroscopic and analytical data support the proposed formulation of **5**. Colorless crystals of **5** were grown from a solution in hexane, and the structure was determined by X-ray crystallography.

The molecular structure of 5 is illustrated in Figure 5, and selected bond lengths and angles are listed in Table 1. Complex 5 is monomeric in the solid state. The potassium center is coordinated to an imino-nitrogen, the methanide center, and the oxygen centers of two THF molecules, but the other iminonitrogen is noncoordinating. The coordination sphere of 5 is further supplemented by an η^6 -arene · · · K interaction and one contact from an *ipso*-carbon of an *N*-Dipp substituent $[K(1)\cdots$ C(38) 3.540(8) Å]. The K(1)-N(2) bond length is long at 2.668(5) Å, and the K(1) \cdots C(1) distance of 3.501(6) Å is also long and must be considered weak. Indeed, the η^{6} -arene · · · K bond lengths span a range of shorter distances of 3.106(7)-3.450(8) Å, which is typical for $K \cdots$ arene distances. For example, $K \cdots$ arene distances of 3.230(4)-3.418(3), 3.368(9) (av.), and 3.208(2)-3.597(2) Å were reported for [{(2,6-triisopropylphenyl)P(H)K(THF) $_2$],¹⁸ [HC{C(CH₃)N(Dipp)}_2K],¹⁹ and [2,6-(dimesitylphenyl)P(H)K]₄.²⁰ The C(1)-P(1) and C(1)-P(2) bond lengths of 1.715(5) and 1.713(5) Å are contracted compared to $H_2C(PPh_2NDipp)_{2,1}^{6}$ reflecting the methanide nature of 5 compared to the methylene nature of H₂C-(PPh₂NDipp)₂. Although one imino group is coordinated and



Figure 7. Molecular structure of $7 \cdot C_4 H_8 O$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity.



Figure 8. Molecular structure of $8 \cdot C_4 H_8 O$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity.

the other is not, the P(1)-N(1) and P(2)-N(2) bond lengths are both identical at 1.589(4) Å.

Although the characterization data for bulk 5 support its formulation, we have found that the THF molecules in 5 can be considered to be weakly bound. This is evidenced by the fact that standing a hexane solution of 5 for 5 days afforded a small crop of a dark green material that contains colorless crystals of a new complex formulated as $[{K[HC(PPh_2NDipp)_2](THF)}_2]$ (6) that are of a distinct crystal habit to 5 (Scheme 2). We, therefore, undertook an X-ray diffraction experiment to identify the new compound.

The molecular structure of **6** is illustrated in Figure 6, and selected bond lengths and angles are listed in Table 1. Complex **6** is a "loose" dimer in the solid state, resulting from the loss of one molecule of THF from **5**. The potassium center is coordinated to the two imino-nitrogen centers and the oxygen center of a THF molecule. Interactions with the *ortho*-aryl carbon of one *P*-phenyl group and the *ipso*-carbon of one *N*-Dipp group from the coordinated methanide ligand and an interaction with the *meta*-carbon of an *N*-Dipp group from another methanide ligand complete the coordination sphere of potassium, and the latter

Scheme 3. Synthesis of 9–12



interaction results in the formation of the "loose" dimer motif. The absence of a potassium—methanide contact in **6** is confirmed by a $K(1) \cdot \cdot \cdot C(1)$ distance of 3.899(10) Å. The K(1)—N(1) and K(1)—N(2) bond distances of 2.7539(11) and 2.6527(10) Å are longer overall compared with those in **5**. The $K \cdot \cdot \cdot C$ interactions span the range of 3.3090(12)—3.5256(14) Å and are comparable to the multihapto $K \cdot \cdot \cdot C_{arene}$ interactions observed in **5**. The C(1)—P(1), C(1)—P(2), P(1)—N(1), and P(2)—N(2) bond lengths of 1.7252(12), 1.7116(12), 1.5973(11), and 1.5976(10) Å, respectively, are similar to the corresponding distances in **5**, and this underscores the electrostatic nature of the bonding of potassium in these systems that renders the electronic structure of the methanide ligands, as adjudged from bond length considerations, to be relatively insensitive to changes in coordination mode to potassium.

The heavy group 1 analogues were prepared by reacting H₂C- $(PPh_2NDipp)_2$ with BuⁿLi to afford $[Li{HC(PPh_2NDipp)_2}]$, which, in turn, was reacted with [MOR] (OR = 2-ethylhexoxide; $M = Cs, Rb)^{13}$ in THF to yield $[M{HC(PPh_2NDipp)_2}(THF)_3]$ [M = Rb (7), Cs (8)] (Scheme 2), utilizing the same metathesis methodology that provided 2 and 3.²¹ The ³¹P{¹H} NMR spectra of 7 (δ 3.10 ppm, d_6 -benzene) and 8 (δ 0.73 ppm, d_8 -THF) exhibit resonances at similar chemical shifts to their N-mesityl congeners 2 and 3 (vide supra), as is the case for the methanide signals in their ¹H NMR [δ 2.14 ppm, ² J_{PH} = 3.4 Hz (7, d_6 -benzene); δ 1.59 ppm, ${}^2J_{\rm PH}$ = 3.8 Hz (8, d_8 -THF)] and ¹³C{¹H} NMR [δ 20.01 ppm, J_{PC} = 143.9 Hz (7, d_6 -benzene); δ 17.54 ppm, J_{PC} = 133.3 Hz (8, d_8 -THF)] spectra, although, in contrast, the methine protons are well-defined triplets in the ¹H NMR spectra of 7 and 8. Integration of the ¹H NMR spectra of 7 and 8 indicated that three molecules of THF were coordinated to the group 1 metal in these complexes; an X-ray diffraction study was undertaken to confirm this observation.

The molecular structures of $7 \cdot C_4 H_8 O$ and $8 \cdot C_4 H_8 O$ are depicted in Figures 7 and 8, and selected bond lengths and angles are compiled in Table 1. Like 1-4 and many other early metal bis(iminophosphorano)methanide complexes,⁹ 7 exhibits a distorted twist-boat conformation of its six-membered metallacycle; however, the cesium ion in 8 is coordinated less symmetrically by one nitrogen lone pair and by the N-Dipp π -system in an η^6 -fashion, similar to 5. As with 2 and 3, both 7 and 8 do not exhibit an interaction of the methanide with the metal ion $[M(1)\cdots$ C(1) 4.000(3) Å (7); 4.182(4) Å (8)]. Despite their differing coordination spheres, 7 and 8 both display three THF donors, as has been observed for the heavy group 2 methanediide complex $[Ba{C(PPh_2NDipp)_2}(THF)_3]$,²² and their P(1)-C(1)-P(2) angles are similar to each other $[130.12(18)^{\circ}(7); 131.25(18)^{\circ}$ (8)]. Although only one iminophosphorano-nitrogen of 8 donates electron density to the cesium ion, the P-N bond lengths are statistically identical [1.587(3)-1.593(3) Å], as was observed for 5. Like 2, 7 displays an acute N(1)-Rb(1)-N(2)

Table 2. Room-Temperature Magnetic Moment Data for9-12

complex	lanthanide	ground term	$\mu_{ m J}~(\mu_{ m B})^a$	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}}\right)$
9	Ce	${}^{2}F_{5/2}$	2.54	2.93
10	Pr	$^{3}H_{4}$	3.58	3.51
11	Nd	⁴ I _{9/2}	3.62	3.89
12	Sm	⁶ H _{5/2}	0.85	2.13
${}^{a}\mu_{J} = g_{J}\sqrt{J(J+1)}$, where $g_{J} = {}^{3}/_{2} + [S(S+1) - L(L+1)]/2J(J+1)$.				

angle [80.12(7)°], and the M–N distances of 7 [Rb–N 2.850(3)– 3.092(3) Å] and 8 [Cs(1)–N(1) 3.023(3) Å] are relatively short (previously reported ranges Rb–N 2.796–3.609 Å; Cs–N 2.915–3.678 Å).²³ The coordination sphere of the rubidium ion of 7 is completed by two contacts with the *ipso*-carbons of the *N*-Dipp substituents [Rb(1)···C(14) 3.407(3) Å; Rb(1)··· C(38) 3.441(3) Å], whereas 8, like 5, displays only one of these interactions [Cs(1)···C(38) 3.752(3) Å]. The Cs···C distances in 8 between cesium and the coordinated N-Dipp substituent vary considerably [3.440(4)–4.014(4) Å] and are similar to those observed in [{CsSi(SiMe₃)₃}₂(toluene)₃] [Cs···C 3.51(2)-4.08(2) Å],¹⁵ though they are typically longer than the intermolecular η^6 -arene contacts observed in 3 (vide supra).

To demonstrate the synthetic utility of 1-8, a series of lanthanide methanide complexes were prepared. The reaction of half an equivalent of $[\{K(HC[PPh_2NMes]_2)\}_2]^7$ with $[Ln(I)_3(THF)_n]$ (Ln = Ce, n = 4; Ln = Pr, n = 4; Ln = Nd, n = 3.5; L = Sm, n = 3.5)³ afforded $[Ln{HC(PPh_2NMes)_2}(I)_2(THF)_2]$ [Ln = Ce (9), Pr(10), Nd (11), Sm (12) following a straightforward salt metathesis reaction and workup (Scheme 3). Similar strategies have previously been employed in the preparation of $[La{HC-(PPh_2NMes)_2}(I)_2(THF)_2]^{24}$ and $[Sm{HC(PPh_2NMes)_2}_2]_2^{25}$ but this methodology has now been extended to yield a series of lanthanide N-aryl bis(iminophosphorano)methanide complexes. It is noteworthy that the reaction of the N-Silyl variant [K{HC- $(PPh_2NSiMe_3)_2$ $(THF)_n$ ^{12,26} with $[La(I)_3(THF)_4]^3$ was found to be sluggish,²⁴ and use of the heavier group 1 homologues $[Rb{HC(PPh_2NSiMe_3)_2}(THF)_2]$ or $[Cs{HC(PPh_2NSiMe_3)_2}-$ (DME)₂] is mandatory to prepare the expected lanthanum methanide in useful quantities.¹ In contrast, while the heavier *N*-Mes homologues 2 and 3 may be employed to synthesize 9-12, $[{K(HC[PPh_2NMes]_2)}_2]^7$ may also be utilized to prepare 9–12 in moderate-to-good yields. However, the use of 2 and 3 improves the efficiency of these reactions, so they are useful reagents.

The paramagnetic nature of 9-12 precluded meaningful assignment by NMR spectroscopy. Therefore, their solution magnetic moments (Evans method) were recorded at room temperature, and these are listed in Table 2 along with ground terms and theoretical magnetic moments. The Van Vleck equation for magnetic susceptibility approximates for many lanthanide complexes at room temperature to theoretical magnetic moments of $\mu_J = g_J \sqrt{J}(J+1)$ [where $g_J = \frac{3}{2} + [S(S+1) - L(L+1)]/$ 2J(J+1)].²⁷ A small crystal field splitting compared to kT results in the $^{2S+1}L_{I}$ ground term being the only significantly populated state, with higher-energy states not contributing to the susceptibility by temperature-independent second-order Zeeman effects. Lanthanide complexes display little crystal field splitting as their bonding is highly ionic and a large gap between ground and excited states results from the strength of spin orbit coupling. It follows that room-temperature magnetic moments exhibited by lanthanide complexes are largely unaffected by the coordination



Figure 9. Molecular structure of $9 \cdot 3C_7H_8$ with selective atom labeling. Displacement ellipsoids are set at 40%, and hydrogen atoms and lattice solvent are omitted for clarity. The structures of 10-12 are very similar.

environment.^{28,29} Complexes **9**–**11** follow the expected trend, but the magnetic moment displayed by **12** is higher than predicted. However, this is characteristic of samarium(III) complexes as the ${}^{6}\text{H}_{5/2}$ ground state (0.86 μ_{B}) is not well separated from higher-energy states, such as the ${}^{6}\text{H}_{7/2}$, and so the room-temperature magnetic moment of these complexes is raised to typically 1.36– 1.9 μ_{B} by thermal excitation, causing increased population of excited states.²⁸ It is noteworthy that **12** exhibits a slightly higher room-temperature magnetic moment than the related samarium-(III) methanide complex [Sm{C(PPh_2NSiMe_3)_2}{HC(PPh_2-NSiMe_3)_2}] (1.63 μ_{B}).³⁰

To confirm the formulations of 9-12, an X-ray diffraction study was undertaken and all complexes were structurally characterized. Complexes 9-12 were found to be structurally analogous, so, for brevity, they are discussed together. The molecular structure of 9 is depicted in Figure 9, and selected bond lengths and angles are compiled in Table 1. The bis(iminophosphorano)methanide scaffold of 9-12 adopts a typical distorted twist-boat conformation upon coordination to the lanthanide center.9 The coordination spheres of the lanthanide centers are completed by two iodide ligands and two molecules of THF in a highly distorted trigonal bipyramidal conformation. The intramolecular P-C and P-N distances and P-C-P and C-P-N angles of the ligand framework do not vary considerably between 9 and 12, and the Ln-C, Ln-N, Ln-O, and Ln-I distances decrease slightly across the series, following the lanthanide contraction. Complexes 9-12 are structurally analogous to $[La{HC(PPh_2NMes)_2}(I)_2(THF)_2]$, which exhibits the expected larger Ln-C [2.833(4) Å] and Ln-N [2.537 (mean) Å] distances.²⁴ All other distances and angles observed in 9-12 are as expected, but it is noteworthy that the closely related homoleptic samarium(II) complex $[Sm{HC(PPh_2NMes)_2}_2]^{25}$ displays much longer Sm-C [2.889 (mean) Å] and Sm-N distances [2.603 (mean) Å] than those observed in 12 [Sm(1) -C(1) 2.744(4) Å; Sm-N 2.467 (mean) Å], an expected consequence of the higher oxidation state and decreased steric demands of the ligand environment in 12.

SUMMARY AND CONCLUSIONS

Monomeric sodium and potassium salts of N-mesityl- and N-diisopropylphenyl-substituted bis(iminophosphorano)methanes, namely, $[Na{HC(PPh_2NMes)_2}(THF)_2]$ (1), $[Na{HC(PPh_2-Mes)_2}(THF)_2]$ $NDipp_{2}(THF)$ (4), and $[K{HC(PPh_2NDipp)_2}(THF)_2]$ (5), have been prepared by deprotonation of the parent methanes and have been structurally characterized. Complexes 1 and 4-5 complete the portfolio of light group 1 methanide complexes of H₂C $(PPh_2NMes)_2$ and $H_2C(PPh_2NDipp)_2$, allowing full comparison of the analytical and structural data of these series. Dissociation of THF molecules in monomeric 5 allows the facile formation of dimeric $[{K[HC(PPh_2NDipp)_2](THF)}_2]$ (6) in noncoordinating solvents, such as hexane. Employing a different synthetic methodology, lithium bis(iminophosporano)methanides were reacted with [MOR] (M = Rb, Cs) to afford the heavy group 1 methanides [Rb{HC(PPh₂NMes)₂}(DME)₂] (2), [Cs{HC(PPh₂- $NMes_{2}]_{6}$ (3), and $[M{HC(PPh_2NDipp)_2}(THF)_3]$ [M = Rb (7), Cs (8)] by metathesis. The synthetic utility of the N-Mes group 1 transfer agents has been demonstrated by the preparation of the *f*-block methanide series $[Ln{HC(PPh_2NMes)_2}]$ - $(I)_2(THF)_2$ [Ln = Ce (9), Pr (10), Nd (11), Sm (12)] from $[Ln(I)_3(THF)_4]$, employing a salt metathesis methodology. We are currently employing 1-5 and 7 and 8 in the preparation of a series of N-Aryl bis(iminophosphorano)methanide f-block complexes that may undergo a straightforward deprotonation reaction to afford methanediide derivatives. The results of these investigations will be disclosed in future publications.

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 [Na(Bn)], ¹¹ H₂C(PPh₂NR)₂ (R = Mes, Dipp),⁴ [Li{HC(PPh₂NR)₂}]₂ (R = Mes,⁵ Dipp⁶), [MOR] (M = Rb, Cs; OR = 2-ethylhexoxide), ¹³ [{K(HC[PPh₂NR)e₂}]₂],⁷ and [Ln(I)₃(THF)_n] (Ln = Ce, n = 4; Ln = Pr, n = 4; Ln = Nd, n = 3.5; L = Sm, n = 3.5)³ were prepared according to published procedures. KH was obtained from Aldrich as a 30 wt % dispersion in mineral oil and was washed thoroughly with hexanes and dried in vacuo before use.

The ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker 400 spectrometer operating at 400.2, 100.6, and 162.0 MHz, respectively; chemical shifts are quoted in parts per million and are relative to TMS (¹H and ¹³C) and external 85% H₃PO₄ (³¹P). 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. Compounds 1, 3, and 5 are poorly soluble in benzene, and 8 is completely insoluble in benzene. Therefore, spectra were also obtained in *d*₈-THF.

Synthesis of [Na{HC(PPh₂NMes)₂}(THF)₂] (1). THF (40 mL) was added to a precooled (-78 °C) mixture of H₂C(PPh₂NMes)₂ (6.51 g, 10.0 mmol) and [Na(Bn)] (1.14 g, 10.0 mmol) to give a yellow suspension. The mixture was slowly allowed to warm to room temperature with stirring over 24 h. Volatiles were removed in vacuo and the resultant solid washed with hexane to afford 1 as a yellow powder. Yield: 7.02 g, 86%. Recrystallization from hot THF afforded crystalline 1. Anal. Calcd for C₅₁H₅₉N₂NaO₂P₂: C, 74.98; H, 7.28; N, 3.43. Found: C, 69.07; H, 7.38; N, 3.17. ¹H NMR (d_8 -THF, 298 K): δ 1.77 (s, 1H, HCP₂), 1.80 (m, 8H, OCH₂CH₂), 1.85 (s, 12H, *o*-Ar-CH₃), 2.12 (s, 6H, *p*-Ar-CH₃), 3.65 (m, 8H, OCH₂CH₂), 6.57 (s, 4H, *m*-Ar-CH Mes), 7.22 (m, ³J_{HH} = 7.0 Hz, 12H, *m*- and *p*-Ar-CH), 7.89 (t, ³J_{HH} = 7.0 Hz, 8H, *o*-Ar-CH). ¹H NMR (d_6 -benzene, 298 K): δ 1.35 (m, 8H, OCH₂CH₂),

	1	2	3.0.5C ₄ H ₈ O	$4 \cdot 0.5 C_7 H_8$	
formula	$C_{51}H_{59}N_2NaO_2P_2$	C ₅₁ H ₆₃ N ₂ O ₄ P ₂ Rb	$C_{43}H_{43}C_8N_2P_2 \cdot 0.5C_4H_8O$	$C_{53}H_{63}N_2NaOP_2 \cdot 0.5C_7H_8$	
fw	816.93	915.44	818.70	875.05	
cryst size, mm	$0.12\times0.10\times0.09$	$0.45\times0.34\times0.15$	0.45 imes 0.41 imes 0.24	$0.32\times0.14\times0.09$	
cryst syst	monoclinic	triclinic	trigonal	triclinic	
space group	$P2_{1}/n$	$P\overline{1}$	R3	$P\overline{1}$	
<i>a,</i> Å	10.6126(11)	11.1549(4)	27.4890(16)	11.8167(7)	
<i>b,</i> Å	17.3394(18)	12.6068(4)	27.4890(16)	12.4338(7)	
<i>c,</i> Å	24.612(3)	17.4105(6)	28.0813(14)	18.4310(10)	
<i>α,</i> °		100.160(3)		73.701(2)	
<i>β</i> , °	97.076(2)	91.234(3)		80.258(2)	
γ, °		93.885(3)	120	72.164(2)	
<i>V,</i> Å ³	4494.4(8)	2403.05(15)	18 377(2)	2464.0(2)	
Z	4	2	18	2	
$ ho_{ m calcd,}~ m g~cm^{-3}$	1.207	1.265	1.332	1.179	
μ , mm ⁻¹	0.148	2.393	8.065	0.138	
no. of reflns measd	32 765	19 522	14 486	17 941	
no. of unique reflns, <i>R</i> _{int}	7918, 0.075	9539, 0.0268	8006, 0.055	8628, 0.0203	
no. of reflns with $F^2 > 2\sigma(F^2)$	6227	8750	6425	7685	
transm coeff range	0.495-0.746	0.47-0.73	0.115-0.434	0.62-0.75	
$R, R_{w}^{a} (F^{2} > 2\sigma(F^{2}))$	0.0547, 0.136	0.0332, 0.0841	0.0569, 0.141	0.0429, 0.1158	
R, R_{w}^{a} (all data)	0.0714, 0.146	0.0366, 0.0866	0.0720, 0.149	0.0471, 0.1192	
S ^a	1.05	1.023	1.05	1.077	
parameters	529	547	439	540	
max, min diff map, e Å $^{-3}$	0.90, -0.54	0.724, -0.546	1.33, -1.48	0.63, -0.30	
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.					

Table 3. Crystallographic Data for 1-4

2.02 (s, 1H, HCP₂), 2.07 (s, 12H, *o*-Ar-CH₃), 2.20 (s, 6H, *p*-Ar-CH₃), 3.45 (m, 8H, OCH₂CH₂), 6.81 (s, 4H, *m*-Ar-CH Mes), 7.03 (br m, 12H, *m*- and *p*-Ar-CH), 7.94 (m, 8H, *o*-Ar-CH). ¹³C{¹H} NMR (d_8 -THF, 298 K): δ 19.77 (*p*-Ar-CH₃), 21.00 (*o*-Ar-CH₃), 22.28 (t, J_{PC} = 144.6 Hz, HCP₂), 25.42 (OCH₂CH₂), 67.27 (OCH₂CH₂), 125.48 (*p*-Ar-C Mes), 126.88 (*m*-Ar-C Ph), 128.28 (Ar-C), 128.46 (Ar-C), 132.13 (Ar-C), 132.40 (Ar-C), 141.26, 142.01 (*ipso*-Ar-C Ph), 148.24 (*ipso*-Ar-C Mes). ³¹P{¹H} NMR (d_8 -THF, 298 K): δ 8.59 (s, HCP₂). ³¹P{¹H} NMR (d_6 -benzene, 298 K): δ 9.35 (s, HCP₂). FTIR ν/cm^{-1} (Nujol): 1589 (w), 1309 (m), 1206 (w), 968 (m), 696 (m).

Synthesis of [Rb{HC(PPh₂NMes)₂}(DME)₂] (2). Rubidium 2-ethylhexoxide (1.0 M in THF, 2.0 mL, 2.0 mmol) was added to a precooled (-78 °C) slurry of [Li{HC(PPh₂NMes)₂}] (1.38 g, 2.0 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 [Rb{HC(PPh₂- $NMes_{2}(THF)_{n}$ as a yellow powder. Recrystallization from hot DME (2 mL) afforded 2 as yellow crystals on cooling to $-30 \,^{\circ}\text{C}$. Yield: 1.14 g, 62%. Anal. Calcd for C₅₁H₆₃N₂O₄P₂Rb: C, 66.91; H, 6.94; N, 3.06. Found: C, 66.70; H, 6.83; N, 3.15. ¹H NMR (d_6 -benzene, 298 K): δ 1.46 (s, 1H, HCP₂), 2.25 (s, 12H, o-Ar-CH₃), 2.36 (s, 6H, p-Ar-CH₃), 3.17 (s, 12H, CH₃OCH₂), 3.35 (m, 8H, CH₃OCH₂), 6.95 (s, 4H, m-Ar-CH Mes), 7.05 (m, 4H, p-Ar-CH Ph), 7.16 (m, 8H, m-Ar-CH Ph), 8.15 (m, 8H, o-Ar-CH Ph). ${}^{13}C{}^{1}H$ NMR (d_6 -benzene, 298 K): δ 20.57 $(p-\text{Ar-CH}_3)$, 21.44 $(o-\text{Ar-CH}_3)$, 23.20 $(t, J_{PC} = 140.9 \text{ Hz}, \text{HCP}_2)$, 58.30 (CH₃OCH₂), 71.79 (CH₃OCH₂), 125.11 (*p*-Ar-C Mes), 127.34 (Ar-C), 127.97 (Ar-C), 128.72 (Ar-C), 129.03 (Ar-C), 129.30 (Ar-C), 130.59 (Ar-C), 131.27 (Ar-C), 132.22 (Ar-C), 134.76, 135.81 (o-Ar-C Mes), 142.10, 143.09 (ipso-Ar-C Ph), 143.99, 148.72 (ipso-Ar-C Mes). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (d_6 -benzene, 298 K): δ 3.77 (s, HCP₂). FTIR v/cm⁻¹ (Nujol): 1605 (w, br), 1306 (m), 850 (m), 695 (m).

Synthesis of [Cs{HC(PPh2NMes)2}]6 (3). Cesium 2-ethylhexoxide (1.0 M in toluene, 2.0 mL, 2.0 mmol) was added to a precooled (-78 °C) slurry of $[\text{Li}{\text{HC}(\text{PPh}_2\text{NMes})_2}]$ (1.38 g, 2.0 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 3 as a yellow powder. Recrystallization from THF (3 mL) layered with Et₂O (3 mL) afforded $3 \cdot 0.5C_4H_8O$ as yellow crystals on cooling to -30 °C. Yield: 0.61 g, 39%. Anal. Calcd for C43H43CsN2P2: C, 65.99; H, 5.54; N, 3.58. Found: C, 66.11; H, 5.68; N, 3.49. ¹H NMR (*d*₈-THF, 298 K): δ 1.76 (br s, 1H, HCP₂), 1.95 (s, 12H, o-Ar-CH₃), 2.11 (s, 6H, p-Ar-CH₃), 6.60 (s, 4H, m-Ar-CH Mes), 7.08 (m, 8H, m-Ar-CH Ph), 7.14 (m, 4H, p-Ar-CH), 7.78 (m, 8H, *o*-Ar-CH). ¹H NMR (*d*₆-benzene, 298 K): δ 2.13 (s, 12H, *o*-Ar-CH₃), 2.17 (br s, 1H, HCP₂), 2.24 (s, 6H, p-Ar-CH₃), 6.82 (s, 4H, m-Ar-CH Mes), 7.04 (m, 12H, m- and p-Ar-CH), 8.04 (m, 8H, o-Ar-CH). ¹³C{¹H} NMR (d_8 -THF, 298 K): δ 19.78 (p-Ar-CH₃), 22.51 (m-Ar-CH₃), 23.96 (t, J_{PC} = 136.8 Hz, HCP₂), 123.63 (p-Ar-C Mes), 126.60 (Ar-C), 127.85 (Ar-C), 128.48 (Ar-C), 131.66 (o-Ar-C Mes), 132.05 (o-Ar-C Ph), 142.38, 143.39 (ipso-Ar-C Ph), 148.75 (ipso-Ar-C Mes). ³¹P{¹H} NMR (d_8 -THF, 298 K): δ -0.70 (s, HCP₂). ³¹P{¹H} NMR $(d_6$ -benzene, 298 K): δ 2.53 (s, HCP₂). FTIR v/cm⁻¹ (Nujol): 1603 (w, br), 1331 (m), 1202 (m), 1177 (m), 963 (w), 943 (w), 863 (m), 745 (m), 697 (m).

Synthesis of $[Na{HC(PPh_2NDipp)_2}(THF)]$ (4). THF (20 mL) was added at room temperature to a mixture of $H_2C(PPh_2NDipp)_2$ (3.71 g, 5.0 mmol) and [Na(Bn)] (0.32 g, 5.0 mmol). The solution was stirred for 18 h, affording a pale pink solution. Volatiles were removed in vacuo, and the resulting pale pink solid was washed with hexane (10 mL) to afford 4 as a pale pink powder. Yield: 2.60 g, 71%. Colorless crystals of $4 \cdot 0.5C_7H_8$ were grown from a saturated toluene solution. Anal. Calcd for $C_{53}H_{63}N_4NaOP_2$: C, 76.79; H, 7.66; N, 3.38. Found: C, 76.48; H,

Table 4. Crystallographic Data for 5-8

	5	6	$7 \cdot C_4 H_8 O$	$8 \cdot C_4 H_{10} O$	
formula	C ₅₇ H ₇₁ KN ₂ O ₂ P ₂	C53H63KN2OP2	$C_{61}H_{79}N_2O_3P_2Rb \cdot C_4H_8O$	$C_{61}H_{79}CsN_2O_3P_2 \cdot C_4H_{10}O$	
fw	917.20	845.09	1107.78	1157.23	
cryst size, mm	$0.10\times0.09\times0.03$	$0.26\times0.19\times0.18$	$0.35\times0.16\times0.15$	0.32 imes 0.27 imes 0.24	
cryst syst	monoclinic	triclinic	triclinic	monoclinic	
space group	$P2_{1}/c$	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	
<i>a,</i> Å	10.4895(14)	11.7806(7)	12.7002(18)	10.7463(7)	
<i>b,</i> Å	12.6503(16)	13.3858(8)	13.3967(19)	20.3503(13)	
<i>c,</i> Å	40.112(5)	17.0995(10)	20.018(3)	28.0299(18)	
<i>α</i> , °		74.1230(10)	95.281(2)		
<i>β</i> , °	93.309(2)	74.5040(10)	106.173(2)	94.4670(10)	
γ, °		65.1220(10)	111.971(2)		
<i>V</i> , Å ³	5313.8(12)	2316.9(2)	2959.0(7)	6111.3(7)	
Z	4	2	2	4	
$ ho_{ m calcd,} { m g} { m cm}^{-3}$	1.146	1.211	1.243	1.258	
μ , mm ⁻¹	0.201	0.224	0.939	0.705	
no. of reflns measd	27 053	20 928	26 226	37 530	
no. of unique reflns, R _{int}	9338, 0.0816	10 526, 0.0156	13 495, 0.037	14 051, 0.0294	
no. of reflns with $F^2 > 2\sigma(F^2)$	5678	9413	9969	11 364	
transm coeff range	0.62-0.75	0.64-0.74	0.583-0.746	0.517-0.746	
$R, R_{w}^{a}(F^{2} > 2\sigma(F^{2}))$	0.0942, 0.2401	0.0378, 0.1038	0.0593, 0.157	0.0585, 0.1463	
$R, R_{\rm w}^{a}$ (all data)	0.1518, 0.2742	0.0419, 0.1074	0.0854, 0.175	0.0735, 0.1595	
S^{a}	1.019	1.031	1.02	1.037	
parameters	630	577	712	817	
max, min diff map, e ${\rm \AA}^{-3}$	1.04, -0.90	0.70, -0.35	2.12, -0.98	2.938, -2.536	
Conventional $R = \Sigma F_0 - F_c / \Sigma F_0 $; $R_w = [\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^{1/2}$; $S = [\Sigma w (F_0^2 - F_c^2)^2 / \text{no. data - no. params})^{1/2}$ for all data.					

7.50; N, 3.81. ¹H NMR (d_6 -benzene, 298 K): δ 1.16 (m, 4H, OCH₂CH₂), 1.18 (d, ³J_{HH} = 6.8 Hz, 24H, CH(CH₃)₂), 2.35 (s, 1H, HCP₂), 2.96 (m, 4H, OCH₂CH₂), 4.21 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 7.12 (m, 8H, Ar-CH Ph), 7.15 (m, 4H, Ar-CH Ph), 7.23 (d, ³J_{HH} = 6.8 Hz, 4H, Ar-CH Dipp), 7.27 (m, 2H, *p*-Ar-CH Dipp), 7.92 (m, 8H, *o*-Ar-CH). ¹³C{¹H} NMR (d_6 -benzene, 298 K): δ 23.89 (CH(CH₃)₂), 24.93 (OCH₂CH₂), 24.98 (t, J_{PC} = 144.9 Hz, HCP₂), 28.10 (CH(CH₃)₂), 67.53 (OCH₂CH₂), 119.92 (*m*-Ar-C Dipp), 123.56 (*p*-Ar-C Dipp), 128.31 (*m*-Ar-C Ph), 129.10 (*p*-Ar-C Ph), 132.19 (*o*-Ar-C Ph), 139.55 (*o*-Ar-C Dipp). ³¹P{¹H} NMR (d_6 -benzene, 298 K): δ 9.14 (*s*, HCP₂). FTIR v/cm⁻¹ (Nujol): 1589 (w), 1427 (*s*), 1324 (m, br), 1007 (m), 959 (m), 760 (m), 696 (m).

Synthesis of [K{CH(PPh₂NDipp)₂}(THF)₂] (5). THF (30 mL) was added to a mixture of H₂C(PPh₂NDipp)₂ (2.21 g, 3.0 mmol) and KH (0.24 g, 6.0 mmol) to give a yellow-brown suspension. The mixture was stirred for 3 h, affording an orange-brown solution that was then filtered, and the volatiles were removed in vacuo. The resultant brown solid was washed with hexane (30 mL) to afford 5 as a pale brown powder. Yield: 1.27 g, 46%. Crystals of 5 were grown from a saturated hexane solution. On prolonged standing, a small crop of 6 deposited. Anal. Calcd for C₅₇H₇₁KN₂O₂P₂: C, 74.56; H, 7.90; N, 3.05. Found: C, 75.13; H, 7.56; N, 3.25. ¹H NMR (d_8 -THF, 298 K): δ 0.90 (d, ³ $J_{\rm HH}$ = 6.8 Hz, 24H, CH(CH₃)₂), 1.77 (br s, 1H, HCP₂), 1.82 (m, 8H, OCH₂CH₂), 3.63 (sept, ${}^{3}J_{HH} = 6.8 \text{ Hz}, 4\text{H}, CH(CH_{3})_{2}$), 3.66 (m, 8H, OCH₂CH₂), 6.59 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 2H, *p*-Ar-CH Dipp), 6.88 (d, ${}^{3}J_{HH}$ = 7.6 Hz, 4H, *m*-Ar-CH Dipp), 7.10 (m, 12H, *m*- and *p*-Ar-CH Ph), 7.69 (m, 8H, *o*-Ar-CH). ¹H NMR (d_6 -benzene, 298 K): δ 1.07 (d, ³ J_{HH} = 6.8 Hz, 24H, CH(CH₃)₂), 1.41 (m, 8H, OCH₂CH₂), 2.06 (br s, 1H, HCP₂), 3.54 (m, 8H, OCH₂CH₂), 3.81 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 4H, CH(CH₃)₂), 6.83 $(dd, {}^{3}J_{HH} = 7.6 Hz, 2H, p-Ar-CH Dipp), 6.98 (m, 12H, m- and p-Ar-CH Ph),$

7.06 (d, ${}^{3}J_{HH} = 7.6$ Hz, 4H, *m*-Ar-CH Dipp), 7.86 (m, 8H, *o*-Ar-CH). ${}^{13}C{}^{1}H{}$ NMR (d_{8} -THF, 298 K): δ 18.85 (t, $J_{PC} = 134.9$ Hz, HCP₂), 20.19 (CH(CH₃)₂), 23.57 (OCH₂CH₂), 26.15 (CH(CH₃)₂), 65.41 (OCH₂CH₂), 114.77 (*m*-Ar-C Dipp), 120.82 (*p*-Ar-C Dipp), 124.83 (*m*-Ar-C Ph), 125.99 (*p*-Ar-C Ph), 130.20 (*o*-Ar-C Ph), 138.91 (*o*-Ar-C Dipp), 139.95 (*o*-Ar-C Dipp), 140.52 (*ipso*-Ar-C Ph), 146.52 (*ipso*-Ar-C Dipp). ${}^{31}P{}^{1}H{}$ NMR (d_{8} -THF, 298 K): δ 2.02 (*s*, HCP₂). ${}^{31}P{}^{1}H{}$ NMR (d_{6} -benzene, 298 K): δ 3.85 (*s*, HCP₂). FTIR *v*/cm⁻¹ (Nujol): 1585 (w), 1009 (*s*), 758 (m), 695 (m).

Synthesis of $[Rb{CH(PPh_2NDipp)_2}(THF)_3]$ (7). Rubidium 2-ethylhexoxide (1.0 M in THF, 2.0 mL, 2.0 mmol) was added to a precooled $(-78 \degree C)$ slurry of $[Li{HC(PPh_2NDipp)_2}]$ (1.49 g, 2.0 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 pale green powder. Recrystallization from hot THF (2.5 mL) afforded 7 · C₄H₈O as green crystals on cooling to -30 °C. Yield: 1.05 g, 48%. Anal. Calcd for $C_{63}H_{87}N_2O_4P_2Rb$ (7 · C_4H_8O): C, 70.47; H, 7.92; N, 2.53. Found: C, 70.56; H, 7.95; N, 2.65. ¹H NMR (d_6 -benzene, 298 K): δ 1.20 (d, ³ $J_{\rm HH}$ = 6.8 Hz, 24H, CH(CH₃)₂), 1.53 (m, 12H, OCH₂CH₂), 2.14 (t, ${}^{2}J_{PH} =$ 3.4 Hz, 1H, HCP₂), 3.65 (m, 12H, OCH₂CH₂), 3.88 (sept, ${}^{3}J_{HH} = 6.8$ Hz, 4H, $CH(CH_3)_2$), 6.92 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 2H, *p*-Ar-CH Dipp), 7.06 (t, ${}^{3}J_{HH}$ = 6.8 Hz, 4H, *p*-Ar-CH Ph), 7.11 (m, ${}^{3}J_{HH} = 6.8$ Hz, 8H, *m*-Ar-CH Ph), 7.18 (d, ${}^{3}J_{HH}$ = 7.6 Hz, 4H, *m*-Ar-CH Dipp), 8.02 (m, 8H, *o*-Ar-CH). ${}^{13}C{}^{1}H$ NMR (d_6 -benzene, 298 K): δ 20.01 (t, J_{PC} = 143.9 Hz, HCP₂), 24.13 (CH(CH₃)₂), 25.56 (OCH₂CH₂), 28.24 (CH(CH₃)₂), 67.56 (OCH₂CH₂), 117.58 (*m*-Ar-C Dipp), 123.44 (*p*-Ar-C Dipp), 127.36 (m-Ar-C Ph), 128.66 (p-Ar-C Ph), 132.10 (o-Ar-C Ph), 140.57, 141.62 (o-Ar-C Dipp), 142.95 (ipso-Ar-C Ph), 148.48 (ipso-Ar-C Dipp). ${}^{31}P{}^{1}H$ NMR (d_6 -benzene, 298 K): δ 3.10 (s, HCP₂). FTIR v/cm⁻¹ (Nujol): 1584 (w, br), 1202 (m), 1001 (m, br), 977 (w), 762 (m), 741 (m), 691 (m).

	9.3C ₇ H ₈	$10 \cdot 3C_7H_8$	$11 \cdot 3C_7H_8$	$12 \cdot 3C_7 H_8$
formula	$C_{51}H_{59}CeI_2N_2O_2P_2 \cdot 3C_7H_8$	$C_{51}H_{59}I_2N_2O_2P_2Pr \cdot 3C_7H_8$	$C_{51}H_{59}I_2N_2NdO_2P_2 \cdot 3C_7H_8$	$C_{51}H_{59}I_2N_2O_2P_2Sm \cdot 3C_7H_8$
fw	1464.26	1465.05	1468.38	1474.49
cryst size, mm	$0.08\times0.08\times0.04$	$0.08\times0.07\times0.04$	$0.17\times0.10\times0.09$	$0.12\times0.10\times0.03$
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
<i>a,</i> Å	12.6855(8)	12.7745(17)	12.7290(10)	12.7524(9)
<i>b,</i> Å	15.4244(10)	15.235(2)	15.5095(12)	15.1734(11)
<i>c,</i> Å	17.1748(11)	17.276(2)	17.2653(13)	17.2860(12)
α , °	83.079(1)	85.157(2)	82.868(2)	85.621(2)
β , °	77.224(1)	76.840(2)	77.062(2)	76.686(2)
γ, °	85.417(1)	87.327(2)	85.120(2)	87.418(2)
<i>V</i> , Å ³	3248.5(4)	3260.9(8)	3290.5(4)	3244.1(4)
Ζ	2	2	2	2
$ ho_{ m calcd,}~ m g~cm^{-3}$	1.497	1.492	1.482	1.509
μ , mm ⁻¹	1.746	1.789	1.821	1.952
no. of reflns measd	29 481	28 741	29 619	18 215
no. of unique reflns, R _{int}	14 843, 0.028	14 697, 0.045	15 179, 0.031	13 086, 0.0229
no. of reflns with $F^2 > 2\sigma(F^2)$	12 473	11 326	12 807	11 089
transm coeff range	0.66-0.75	0.87-0.93	0.634-0.746	0.643-0.746
$R, R_{w}^{a}(F^{2} > 2\sigma(F^{2}))$	0.0367, 0.0835	0.0549, 0.136	0.0417, 0.111	0.0428, 0.1049
$R, R_{\rm w}^{a}$ (all data)	0.0472, 0.0877	0.0695, 0.141	0.0509, 0.118	0.0523, 0.1096
S ^a	1.03	0.99	1.04	1.032
parameters	739	611	739	692
max, min diff map, e Å $^{-3}$	1.54, -0.68	5.52, -1.47	3.75, -2.15	1.972, -1.179
^{<i>i</i>} Conventional $R = \Sigma F_0 - R $	$F_{c}[/\Sigma F_{o}]; R_{w} = [\Sigma w (F_{o}^{2} - F_{o})]$	$(F_{0}^{2})^{2}/\Sigma w(F_{0}^{2})^{2}]^{1/2}; S = [\Sigma w(F_{0}^{2$	$F_0^2 - F_c^2)^2$ /no. data — no. pa	[rams) ^{1/2} for all data.

Synthesis of [Cs{CH(PPh₂NDipp)₂}(THF)₃] (8). Cesium 2-ethylhexoxide (1.0 M in toluene, 2.0 mL, 2.0 mmol) was added to a precooled $(-78 \,^{\circ}\text{C})$ slurry of $[\text{Li}{HC(PPh_2NDipp)_2}]$ (1.49 g, 2.0 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 8 as an analytically pure pale green powder. Yield: 1.38 g, 64%. Recrystallization from THF (3 mL) layered with Et₂O (3 mL) afforded 8 · C₄H₁₀O as crystals on cooling to $-30 \,^{\circ}$ C. Anal. Calcd for C₆₅H₈₉CsN₂O₄P₂ (8 · C₄H₁₀O): C, 67.46; H, 7.75; N, 2.42. Found: C, 67.50; H, 7.63; N, 2.49. ¹H NMR (d_8 -THF, 298 K): δ 0.84 (d, 24H, $^3J_{\rm HH}$ = 6.8 Hz, CH(CH₃)₂), 1.59 (t, $^3J_{\rm HH}$ = 3.8 Hz, 1H, HCP₂), 3.53 (sept, 4H, ${}^{3}J_{HH} = 6.8$ Hz, CH(CH₃)₂), 6.45 $(t, {}^{3}J_{HH} = 7.4 \text{ Hz}, 2H, p\text{-Ar-}CH \text{ Dipp}), 6.75 (d, {}^{3}J_{HH} = 7.4 \text{ Hz}, 4H, m\text{-Ar-}CH$ Dipp), 6.95 (m, 12H, m- and p-Ar-CH Ph), 7.57 (m, 8H, o-Ar-CH Ph). ¹³C{¹H} NMR (d_8 -THF, 298 K): δ 17.54 (t, J_{PC} = 133.3 Hz, HCP₂), 21.56 (CH(CH₃)₂), 26.09 (CH(CH₃)₂), 114.43 (*m*-Ar-C Dipp), 120.78 (p-Ar-C Dipp), 124.71 (o-Ar-C Ph), 125.96 (p-Ar-C Ph), 130.05 (o-Ar-C Ph), 139.08 (o-Ar-C Dipp), 140.14 (o-Ar-C Dipp), 140.63 (ipso-Ar-C Ph), 146.83 (ipso-Ar-C Dipp). ${}^{31}P{}^{1}H$ NMR (\hat{d}_{8} -THF, 298 K): δ 0.73 (HCP₂). FTIR v/cm⁻¹ (Nujol): 1582 (w, br), 1345 (s), 1283 (m), 1202 (m), 1044 (m), 978 (m), 878 (w), 763 (m), 741 (s), 691 (m).

Synthesis of [Ce{HC(PPh₂NMes)₂}(I)₂(THF)₂] (9). THF (25 mL) was added to a mixture of $[Ce(I)_3(THF)_4]$ (1.62 g, 2.00 mmol) and $[{K(HC[PPh_2NMes]_2)}_2]$ (1.40 g, 1.00 mmol), and the resultant yellow mixture was stirred for 20 h. The suspension was filtered, volatiles were removed in vacuo, and the resulting solid was recrystallized from toluene (12 mL) at -30 °C to afford 9 as colorless crystals. Yield: 1.16 g, 40%. Anal. Calcd for $C_{72}H_{83}CeI_2N_2O_2P_2$: C, 59.06; H, 5.71; N, 1.91. Found: C, 58.93; H, 5.51; N, 2.02. μ_{eff} (Evans method, 298 K, THF): 2.93 μ_{B} . FTIR ν/cm^{-1} (Nujol): 1590 (w, br), 1217 (m), 1158 (m), 985 (m), 853 (m), 696 (m), 531 (m).

Synthesis of [Pr{HC(PPh₂NMes)₂}(I)₂(THF)₂] (10). THF (25 mL) was added to a mixture of [Pr(I)₃(THF)₄] (1.21 g, 1.50 mmol) and [{K(HC[PPh₂NMes]₂)}₂] (1.05 g, 0.75 mmol), and the resultant yellow mixture was stirred for 20 h. The suspension was filtered, volatiles were removed in vacuo, and the resulting solid was recrystallized from toluene (8 mL) at -30 °C to afford 10 as pale green crystals. Yield: 1.22 g, 73%. Anal. Calcd for C₅₁H₅₉I₂N₂O₂P₂Pr: C, 51.53; H, 5.00; N, 2.36. Found: C, 51.27; H, 4.80; N, 2.16. μ_{eff} (Evans method, 298 K, THF): $3.51\mu_{\rm B}$. FTIR $\nu/{\rm cm}^{-1}$ (Nujol): 1614 (w), 1403 (m), 1261 (m), 1218 (w), 854 (w), 799 (s).

Synthesis of [Nd{HC(PPh_2NMes)_2}(I)_2(THF)_2] (11). THF (25 mL) was added to a mixture of $[Nd(I)_3(THF)_{3.5}]$ (1.55 g, 2.00 mmol) and $[{K(HC[PPh_2NMes]_2)}_2]$ (1.40 g, 1.00 mmol), and the resultant pale green mixture was stirred for 20 h. The suspension was filtered, volatiles were removed in vacuo, and the resulting solid was recrystallized from toluene (20 mL) at room temperature to afford 11 as purple crystals. Yield: 1.76 g, 78%. Anal. Calcd for $C_{72}H_{83}I_2N_2NdO_2P_2$: C, 58.89; H, 5.70; N, 1.91. Found: C, 58.62; H, 5.61; N, 1.89. μ_{eff} (Evans method, 298 K, THF): 3.89 μ_{B} . FTIR ν/cm^{-1} (Nujol): 1589 (w, br), 1403 (m), 1218 (w), 1183 (m), 1158 (w), 985 (m), 854 (m), 778 (m), 743 (m), 560 (m).

Synthesis of $[Sm{HC(PPh_2NMes)_2}(I)_2(THF)_2]$ (12). THF (25 mL) was added to a mixture of $[Sm(I)_3(THF)_{3.5}]$ (1.57 g, 2.00 mmol) and $[{K(HC[PPh_2NMes]_2)_2}]$ (1.40 g, 1.00 mmol), and the resultant yellow mixture was stirred for 20 h. The suspension was filtered, volatiles were removed in vacuo, and the resulting solid was recrystallized from toluene (17 mL) at -30 °C to afford 12 as colorless crystals. Yield: 1.52 g, 58%. Anal. Calcd for $C_{72}H_{33}I_2N_2O_2P_2Sm: C, 58.65; H, 5.67; N, 1.90. Found: C, 58.49; H, 5.52; N, 1.96. <math>\mu_{eff}$ (Evans method, 298 K, THF): 2.13 μ_{B} . FTIR ν/cm^{-1} (Nujol): 1604 (m, br), 1404 (m), 1215 (m), 1157 (m), 983 (m), 945 (m), 880 (w, br), 695 (m), 531 (m).

X-ray Crystallography. Crystal data for compounds 1-12 are given in Tables 3-5, 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 ($\lambda = 0.71073$ Å), or on an Oxford Diffraction SuperNova Atlas CCD diffractometer using mirror-monochromated Cu K α radiation $(\lambda = 1.5418 \text{ Å})$. 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 symmetry-equivalent and repeat reflections (APEX) or Gaussian grid face-indexed absorption correction 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 $U_{\rm eq}$ 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 3, 4, and 10 could not be modeled and were treated with the Platon SQUEEZE procedure.³¹ Programs were Bruker AXS SMART³² and CrysAlisPro³³ (control), Bruker AXS SAINT³² and CrysAlisPro³³ (integration), and SHELXTL³⁴ and OLEX2³⁵ were employed for structure solution and refinement and for molecular graphics.

ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data for 1-12. This material is available free of charge via the Internet at http://pubs.acs.org.

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