ORGANOMETALLICS

Communications

The First Structurally Authenticated Rb−PR₃ and Cs−PR₃ Contacts. Synthesis and Crystal Structures of [Rb{(Me₃Si)₂CP(C₆H₄-2-CH₂NMe₂)₂}]ₙ and [Cs{(Me₃Si)₂CP(C₆H₄-2-CH₂NMe₂)₂}(toluene)]ₙ

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*Summary: Metathesis between [Li{([Me₃Si]₂C)P(C₆H₄-2-CH₂NMe₂)₂}] (**1**) and either RbOR or CsOR (R = 2-ethylhexyl) gives the heavier alkali metal phosphinomethanide complexes [Rb{([Me₃Si]₂C)P(C₆H₄-2-CH₂-NMe₂)₂}]ₙ (**4**) and [Cs{([Me₃Si]₂C)P(C₆H₄-2-CH₂NMe₂)₂}-(toluene)]ₙ (**5**), respectively, after recrystallization. Compounds **4** and **5** represent the first examples of complexes containing a Rb−PR₃ or Cs−PR₃ bond.*

Interactions between alkali metal cations and P-donor ligands are expected to be weak due to the mismatch between the hard alkali metal cations and soft donor ligands.[1,2] Indeed, binding energies for the reaction $M^+ + PH_3 \rightarrow M^+-PH_3$ for M = Li or Na have been calculated to be −26.7 and −17.4 kcal mol⁻¹, respectively, compared to Li⁺−NH₃ and Na⁺−NH₃ binding energies of −40.2 and −28 kcal mol⁻¹.[3] The strength of the M⁺−P interaction may be enhanced by incorporating the P-donor site into a ligand which either (i) has a negative charge localized on phosphorus (i.e., primary and secondary phosphides, PHR and PR₂, and phospholides), (ii) has a significant degree of charge delocalization from an adjacent atom to the phosphorus center

(i.e., phosphinomethanides and phosphinoamides), or (iii) has a negative charge localized on an atom remote from the phosphorus center, enabling chelate ring formation (i.e., tertiary phosphine-functionalized alkoxides, amides, alkyls, etc.). Complexes of the heavier alkali metals rubidium and cesium with P-donor ligands have, until now, been limited to a very few examples with primary and secondary phosphide ligands in which a negative charge is localized on the phosphorus atom.[1,4] There has been no report of a rubidium or cesium complex in which there is a direct contact between the metal and a tertiary phosphine center.
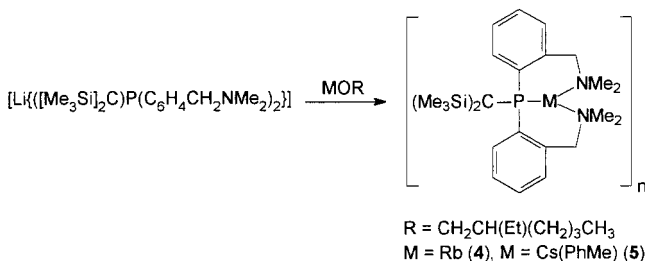
We recently reported that the coordination behavior of phosphinomethanide ligands could be directed by incorporating suitable donor functionality within the substituents on phosphorus. Thus, in the complexes [M{([Me₃Si]₂C)P(C₆H₄-2-CH₂NMe₂)₂}L]ₙ (**1**, M = Li, L

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Scheme 1

$$[Li\{([Me_3Si]_2C)P(C_6H_4CH_2NMe_2)_2)\}] \xrightarrow{MOR}$$

R = CH$_2$CH(Et)(CH$_2$)$_3$CH$_3$
M = Rb (**4**), M = Cs(PhMe) (**5**)

= none, n = 1; **2**, M = Na, L = (Et$_2$O)$_{0.5}$(DME)$_{0.5}$, n = 1; **3**, M = K, L = none, n = infinity), the metals are primarily bound by the N and P centers of the phosphinomethanide ligand and there is no contact between the metal and the carbanion centers.[5] This is in marked contrast to alkali metal complexes of nonfunctionalized monophosphinomethanides, such as [Li{(Me$_3$Si)$_2$CPMe$_2$}-(THF)]$_2$,[6] which exhibit strong M–C contacts.

In **1**–**3** the presence of three charge-stabilizing substituents at the carbanion center both reduces the nucleophilicity of the carbanion and increases its steric hindrance. At the same time the presence of additional donor functionality at the periphery of the ligands leads to the formation of two six-membered chelate rings. These two factors combine to favor coordination of the metals by phosphorus rather than by the carbanion center, enabling the isolation of complexes with a direct contact between a soft tertiary phosphine center and a hard alkali metal cation. We have now used this strategy to synthesize the first rubidium and cesium complexes containing a direct contact between these metals and a tertiary phosphine center.

Metathesis between **1** and either rubidium or cesium 2-ethylhexoxide in diethyl ether gives the heavier alkali metal phosphinomethanides [Rb{([Me$_3$Si]$_2$C)P(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$}]$_n$ (**4**) and [Cs{([Me$_3$Si]$_2$C)P(C$_6$H$_4$-2-CH$_2$-NMe$_2$)$_2$}(toluene)]$_n$ (**5**), respectively, after recrystallization from hot toluene (Scheme 1).[7] The highly soluble

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(7) **4**: To a solution of **1** (0.72 g, 1.55 mmol) in ether (20 mL) was added RbOCH$_2$CH(Et)(CH$_2$)$_3$CH$_3$ (5.16 mL of a 0.3 M solution in hexane, 1.55 mmol; ref 11). This mixture was stirred for 12 h, and then solvent was removed in vacuo. The solid was washed with light petroleum (4 × 20 mL), and residual solvent was removed in vacuo. The yellow-orange solid was recrystallized from hot toluene as yellow rectangular prisms. Yield: 0.67 g. 79%. Anal. Calcd for C$_{25}$H$_{42}$N$_2$-PRbSi$_2$: C, 55.27; H, 7.79; N, 5.16. Found: C, 55.75; H, 7.78; N, 5.00. ^{1}H NMR (500 MHz, THF-d_8, 210 K): δ −0.47 (s, 9H, SiMe$_3$), 0.01 (s, 9H, SiMe$_3$), 1.98 (s, 6H, NMe$_2$), 2.31 (s, 6H, NMe$_2$), 2.87 (d, J_{HH} = 14.8 Hz, 1H, CH$_2$N), 3.52 (dd, J_{HH} = 14.8 Hz, J_{PH} = 6.4 Hz, 1H, CH$_2$N), 3.98 (d, J_{HH} = 15.5 Hz, 1H, CH$_2$N), 4.25 (dd, J_{HH} = 15.5 Hz, J_{PH} = 6.7 Hz, 1H, CH$_2$N), 6.56 (m, 1H, ArH), 6.69 (m, 1H, ArH), 6.82 (m, 1H, ArH), 6.91 (m, 1H, ArH), 7.03 (m, 1H, ArH), 7.35 (m, 2H, ArH), 8.29 (m, 1H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, THF-d_8, 300 K): δ −8.8. Compound **5** was prepared by an identical procedure to **4** from **1** (0.86 g, 1.85 mmol) and CsOCH$_2$CH(Et)(CH$_2$)$_3$CH$_3$ (9.25 mL of a 0.2 M solution in hexane, 1.85 mmol; ref 11). Yield: 0.83 g. 66%. Anal. Calcd for C$_{32}$H$_{50}$CsN$_2$PSi$_2$: C, 56.29; H, 7.38; N, 4.10. Found: C, 55.75; H, 7.22; N, 4.79. ^{1}H NMR (500 MHz, THF-d_8, 205 K): δ −0.46 (s, 9H, SiMe$_3$), 0.02 (s, 9H, SiMe$_3$), 1.99 (s, 6H, NMe$_2$), 2.30 (s, 6H, NMe$_2$), 2.31 (s, 3H, PhCH$_3$), 2.90 (d, J_{HH} = 14.8 Hz, 1H, CH$_2$N), 3.54 (dd, J_{HH} = 14.8 Hz, J_{PH} = 6.2 Hz, 1H, CH$_2$N), 3.98 (d, J_{HH} = 15.5 Hz, 1H, CH$_2$N), 4.27 (dd, J_{HH} = 15.5 Hz, J_{PH} = 6.3 Hz, 1H, CH$_2$N), 6.58 (m, 1H, ArH), 6.70 (m, 1H, ArH), 6.84 (m, 1H, ArH), 6.94 (m, 1H, ArH), 7.05 (m, 1H, ArH), 7.10−7.24 (m, 5H, PhCH$_3$), 7.37 (m, 2H, ArH), 8.30 (m, 1H, ArH). ^{31}P{^{1}H} NMR (121.5 MHz, THF-d_8, 300 K): δ −7.8. ^{133}Cs NMR (39.3 MHz, THF-d_8, 300 K): δ 1.97.
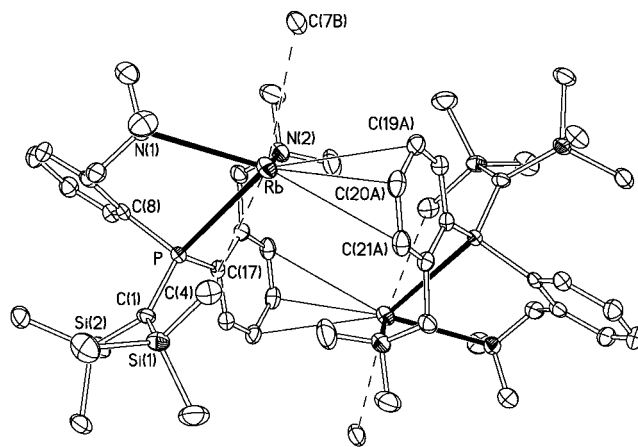

Figure 1. Dimeric molecular structure of **4** with 50% probability ellipsoids, with additional atoms to complete the coordination of Rb, and with H atoms omitted for clarity. Selected bond lengths (Å): Rb–P 3.3437(8), Rb–N(1) 3.042(2), Rb–N(2) 2.915(2), Rb–C(19A) 3.519(3), Rb–C(20A) 3.257(3), Rb–C(21A) 3.686(3), Rb···C(4) 3.539(3), Rb···C(7B) 3.459(3), P–C(1) 1.752(3), P–C(8) 1.866(3), P–C(17) 1.877(3), C(1)–Si(1) 1.822(3), C(1)–Si(2) 1.822(3), Si–C(Me) 1.887 (average).
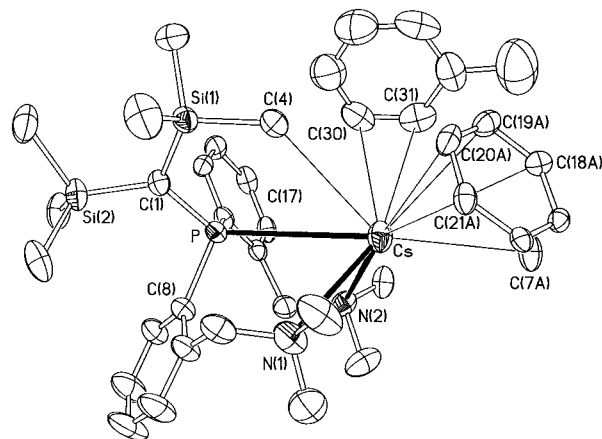

Figure 2. Molecular structure of **5** with 50% probability ellipsoids, with some symmetry-related atoms to complete the coordination of Cs, and with H atoms omitted for clarity. Selected bond lengths (Å): Cs–P 3.6053(6), Cs–N(1) 3.2758(19), Cs–N(2) 3.1039(17), Cs–C(18A) 3.809(2), Cs–C(19A) 3.577(2), Cs–C(20A) 3.585(2), Cs–C(21A) 3.823(2), Cs···C(4) 3.545(2), Cs···C(7A) 3.800(2), Cs–C(30) 3.794(2), Cs–C(31) 3.864(2), P–C(1) 1.757(2), P–C(8) 1.8582(19), P–C(17) 1.872(2), C(1)–Si(1) 1.813(2), C(1)–Si(2) 1.8201(19), Si–C(Me) 1.889 (average).

lithium 2-ethylhexoxide side-product is readily separated from the sparingly soluble heavier alkali metal phosphinomethanides by extraction into light petroleum.

The molecular structures of **4** and **5** are shown in Figures 1 and 2, respectively.[8,9] Complex **4** is essentially isostructural with its potassium analogue (**3**); the rubidium atom is bound by the two amino substituents and the phosphorus atom of the ligand in a PN$_2$ coordination mode. There is no contact between the metal and the essentially planar carbanion center (sum of angles at C(1) = 358.33°). The Rb{([Me$_3$Si]$_2$C)P(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$} units form dimers through η^3-interactions between the metal center and one of the aryl

groups of an adjacent unit. The coordination sphere of each Rb is completed by two Si−CH$_3$···Rb interactions, one intramolecular and one intermolecular; the intermolecular Rb···CH$_3$ contacts link the dimeric units into a two-dimensional sheet arrangement identical to that observed for **3**.

To our knowledge, the Rb−P distance of 3.3437(8) Å is the shortest such distance to be reported. The Rb−P distances in the ladder-type secondary phosphide complex [Rb{P(SiMe$_3$)$_2$}(THF)]$_x$ are 3.461(1), 3.484(2), and 3.486(2) Å,[4a] while the Rb−P distances in the primary phosphide complexes [Rb{PH(mes)}]$_x$,[4b] [Rb{PH(mes*)}-(18-crown-6)],[4c] and [Rb{PH(Dmp)}]$_4$(toluene)[4d] range from 3.381(1) to 3.756(2) Å (mes = 2,4,6-Me$_3$−C$_6$H$_2$; mes* = 2,4,6-tBu$_3$−C$_6$H$_2$; Dmp = 2,6-dimesitylphenyl). The short Rb−P distance in **4** is consistent with the tridentate nature of the ligand and with a significant degree of charge delocalization from the carbanion center to the phosphorus atom.

Complex **5** adopts a different structure from **3** and **4** in the solid state, although the phosphinomethanide ligand once again adopts a PN$_2$ coordination mode. There is no contact between the metal and the essentially planar carbanion center (sum of angles at C(1) = 359.48°). Unlike **4**, the Cs{([Me$_3$Si]$_2$C)P(C$_6$H$_4$-2-CH$_2$-NMe$_2$)$_2$} units do not form dimers but adopt a one-dimensional polymeric arrangement in which individual Cs{([Me$_3$Si]$_2$C)P(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$} units are joined by η^4-interactions between the Cs atom and an aryl group from an adjacent ligand. Each Cs atom is further bound in an η^2-fashion by a molecule of toluene. The C(SiMe$_3$)$_2$ group of the phosphinomethanide ligand is involved in two Si−CH$_3$···Cs contacts, one intramolecular [C(4)−Cs = 3.545(2) Å] and one intermolecular [C(7)···Cs(A) = 3.800(2) Å]. The coordination sphere of the Cs atoms is thus completed by one intra- and one intermolecular Si−CH$_3$···Cs contact to give each Cs atom 11 ligand donor atom contacts. The Cs−P distance of 3.6053(6) Å lies within the range of previously reported Cs−P contacts. For example, the Cs−P distance is 3.6084(13) Å in [Cs{PH(Dmp)}(18-crown-6)],[4e] and the Cs−P distances range from 3.577(1) to 3.993(1) Å in the polymeric complexes [Cs{PH(mes*)}]$_n$ and [Cs{PH(mes*)}(N-Me-Im)]$_n$ (N-MeIm = N-methylimidazole).[4b]

In both **4** and **5** the M−N distances are typical of complexes in which Rb or Cs is complexed by a tertiary amine center. Similarly, the M−C(aryl) [M = Rb, 3.275(3)−3.686(3) Å; M = Cs, 3.577(2)−3.864(2) Å] and M···Me-Si distances lie within the range of distances previously reported for such contacts.[10] The greater hapticity of the aryl rings in **5** (η^4) compared to **4** (η^3) and **3** (η^2) is a function of the increasing ionic radius on descending the group 1 elements.

Compounds **4** and **5** provide the first examples of crystallographically authenticated complexes in which a rubidium or cesium cation is bound by a formally tertiary phosphine center.

As was observed for **1**, **2** and **3**, compounds **4** and **5** are highly fluxional in THF-d_8 solutions. The ^{1}H NMR spectra of both compounds at room temperature in this solvent are extremely broad, although in both cases signals for all of the ligand protons are resolved. At low temperatures the SiMe$_3$ and NMe$_2$ signals each split into two peaks, and all of the aromatic and benzylic protons on the two chelating arms of the ligand are well resolved as separate signals. This behavior exactly parallels that observed for compounds **1**−**3**.[5c] Line-shape analysis of the SiMe$_3$ and NMe$_2$ regions in the variable-temperature ^{1}H NMR spectra of **4** and **5** yields $\Delta H^{\ddagger}$(SiMe$_3$) = 38(1) and 43(2), $\Delta H^{\ddagger}$(NMe$_2$) = 41(1) and 44(3) kJ mol^{-1}, $\Delta S^{\ddagger}$(SiMe$_3$) = −57(4) and −31(9), $\Delta S^{\ddagger}$(NMe$_2$) = −46(5) and −29(9) J K^{-1} mol^{-1} for **4** and **5**, respectively. Values of $\Delta G^{\ddagger}$ at the coalescence temperatures for both the SiMe$_3$ and NMe$_2$ groups are close to 50 kJ mol^{-1} for both compounds, as was observed for compounds **1**−**3** in this solvent. Similarly, values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the process affecting the SiMe$_3$ groups in each complex are close to those for the process affecting the NMe$_2$ groups, suggesting that the same process is responsible for the fluxionality of both groups. A similar trend was noted for **1**−**3** and was ascribed to rapid, reversible M−N and/or M−P bond cleavage and subsequent conformational changes in the chelate arms of the ligands.

Supporting Information Available: For **4** and **5** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

(8) Crystal data for **4**: C$_{25}$H$_{42}$N$_2$PRbSi$_2$ (monomer formula), fw = 543.23, monoclinic, space group P2$_1$/n, a = 9.9751(7), b = 17.7100(12), c = 15.9534(11) Å, β = 93.565(2)°, V = 2812.9(3) Å^3, Z = 4, D_{calcd} = 1.283 g cm^{-3}, μ = 1.917 mm^{-1}, T = 160 K, crystal size 0.54 × 0.46 × 0.44 mm. Bruker SMART CCD diffractometer, structure solution by direct methods, refinement on F^2 (2θ < 28.59°); R_w = {$\Sigma[w(F_o^2 - F_c^2)^2]$/$\Sigma[w(F_o^2)^2]$}$^{1/2}$ = 0.0943 (all 6601 unique data), conventional R = 0.0421 on F values of 4415 reflections with F_o^2 > 2$\sigma(F_o^2)$, goodness of fit = 0.967, final difference synthesis within ±0.42 e Å^{-3}.

(9) Crystal data for **5**: C$_{32}$H$_{50}$CsN$_2$PSi$_2$ (monomer formula), fw = 682.80, monoclinic, space group Cc, a = 20.0291(8), b = 11.2852(4), c = 16.6256(6) Å, β = 102.999(2)°, V = 3661.6(2) Å^3, Z = 4, D_{calcd} = 1.239 g cm^{-3}, μ = 1.141 mm^{-1}, T = 160 K, crystal size 0.80 × 0.38 × 0.32 mm. Bruker SMART CCD diffractometer, structure solution by direct methods, refinement on F^2 (2θ < 28.52°); R_w = {$\Sigma[w(F_o^2 - F_c^2)^2]$/$\Sigma[w(F_o^2)^2]$}$^{1/2}$ = 0.0394 (all 8181 unique data), conventional R = 0.0192 on F values of 7640 reflections with F_o^2 > 2$\sigma(F_o^2)$, goodness of fit = 0.919, final difference synthesis within ±0.41 e Å^{-3}.

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(11) The alkoxides MOCH$_2$CH(Et)(CH$_2$)$_3$CH$_3$ (M = Rb or Cs) were prepared by the direct reaction of 2-ethylhexanol with the respective alkali metal in diethyl ether. Removal of solvent gave the alkali metal alkoxides as colorless solids in quantitative yields.