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COMMUNICATION

SYNTHESIS AND X-RAY CRYSTAL STRUCTURES OF $[Ph_2PMe_2][(\eta^5–C_5H_4Bu^t)_2Li]$ and $[(\eta^5–C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2]$

WAI-KWOK WONG* and **LILU ZHANG**

Department of Chemistry, Hong Kong Baptist University, Kowloon, Hong Kong

and

WING-TAK WONG

Department of Chemistry, University of Hong Kong, Pokfulam Road,
Hong Kong

and

FENG XUE and **THOMAS C. W. MAK**

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories,
Hong Kong

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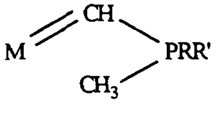
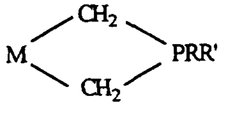
Abstract—The interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2YbCl \cdot LiCl]$ with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in tetrahydrofuran gave $[Ph_2PMe_2][(\eta^5\text{-}C_5H_4Bu^t)_2Li]$ (**1**) and $[(\eta^5\text{-}C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2]$ (**2**) in 10% and 30% yields, respectively. **1** could also be prepared in 70% yield from the reaction of $[Ph_2PMe_2][CF_3SO_3]$ with two equivalents of $(C_5H_4Bu^t)Li$. Both compounds have been fully characterized by analytical, spectroscopic and X-ray diffraction methods. The solid state structure of **1** reveals a sandwich structure for the $[(\eta^5\text{-}C_5H_4Bu^t)_2Li]^-$ anion. Copyright © 1996 Elsevier Science Ltd

Phosphorus ylides have been shown to possess an extensive coordination chemistry with main group and transition metal atoms and to form metal–carbon σ-bonds of unusual stability.[1] Schumann *et al.*[2] and Gilje *et al.*[3] have extended the ylidic chemistry to lanthanide and actinide metals, respectively. Gilje and co-workers have further demonstrated that the phosphorus ylidic ligand, depending on the reaction conditions, can act either as a monodentate or a bidentate ligand, as shown below.[3a]





We are interested in examining the factors that affect the mode of coordination of phosphorus ylidic ligand, particularly the steric and electronic effects of substituents of the cyclopentadienyl rings on the mode of coordination. Recently, we have shown that the interaction of $Cp'_2MCl \cdot LiCl$ (M = Nd, Sm) with $Li[(CH_2)(CH_2)PPh_2]$ gives the cyclic ylidic complex when Cp′ is the sterically bulky C_5Me_5 ring[4] and the ylide complex with Cp′ is the sterically less demanding C_5H_5 and $C_5H_4Bu^t$ rings.[5] We would like to further

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* Author to whom correspondence should be addressed.

examine the effect of lanthanide metal size on the mode of coordination of phosphorus ylidic ligand. In this communication we report the result of the interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2YbCl \cdot LiCl]$, a complex of relatively small metal size, with the ylidic ligand $Li[(CH_2)(CH_2)PPh_2]$.

The interaction of $[(\eta^5\text{-}C_5H_4Bu^t)_2YbCl \cdot LiCl]$ with one equivalent of $Li[(CH_2)(CH_2)PPh_2]$ in tetrahydrofuran at room temperature for 16 h, work up gave white crystals of stoichiometry $[Ph_2PMe_2][(C_5H_4Bu^t)_2Li]$ (**1**) and yellow crystals of stoichiometry $[(C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2]$ (**2**)[†] in 10% and 30% yields, respectively, after successive recrystallization from a tetrahydrofuran/toluene mixture. Both structures were established by X-ray diffraction studies.[‡] Crystals of **1** suitable for X-ray diffraction study were grown from a tetrahydrofuran/toluene mixture. A perspective drawing and selected bond lengths and bond angles of **1** are shown in Fig. 1 and its caption.

The solid state structure of **1** consists of a discrete cation and a discrete anion. In the $[Ph_2PMe_2]^+$ cation the phosphorus adopts a tetrahedral geometry. The P—C distances and C—P—C angles are normal and range from 1.777(4) to 1.789(3) Å and 107.9(2) to 110.5(2)°, respectively. The $[(C_5H_4Bu^t)_2Li]^-$ anion adopts a sandwich geometry if one considers that the Li atom is coordinated to the centroid of the two parallel *tert*-butylcyclopentadienyl rings. The two *tert*-butylcyclopentadienyl rings are bonded to the Li atom in a η^5-fashion with Li—C (ring) distances ranging from 2.255(7) to 2.382(7) Å with the longest distances being those carbon atoms bonded to *tert*-butyl groups. The mean Li—C distances for the two Cp rings are 2.31 and 2.32 Å. The Li—C (ring) distances are comparable to those of $[(\eta^5\text{-isodiCp})_2Li]^-$ [2.292(3)–2.389(3) Å][6] and $[(\eta^5\text{-}C_5H_5)_2Li]^-$ [2.262(3)–2.366(4) Å].[7] The spectroscopic data of **1** are consistent with its solid state structure. The ^{31}P NMR spectrum of **1** exhibited a singlet at δ 26.3 ppm. The

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[†] $[Ph_2PMe_2][(\eta^5\text{-}C_5H_4Bu^t)_2Li]$ (**1**): white crystals, m.p. 170–172°C dec. Found: C, 82.7; H, 9.2. Calc. for $C_{32}H_{42}PLi$: C, 82.8; H, 9.1%. IR (cm^{-1}, in KBr): 3566m, 2989w, 2952w, 1676m, 1602m, 1441m 1256vs, 1169s, 1119m, 1030s, 963w, 945m, 873w, 751m, 692m, 639s, 578w, 520m, 498m, 483m. $^{31}P\text{-}\{^1H\}$ NMR (THF–d_8): δ 26.3 (s) ppm. ^1H NMR (THF–d_8): δ 7.61–7.88 (10H, *m*), 5.40 (4H, m), 5.31 (4H, m), 2.27 (6H, d, $J = 14.0$ *Hz*), 1.18 (18H, s) ppm. $^{13}C\text{-}\{^1H\}$ NMR (THF-d_8): δ 135.0 (s), 134.0 (s), 133.2 (m), 132.6 (s), 131.6 (m), 130.7 (m), 129.4 (m), 129.0 (s), 124.4 (s), 123.5 (s), 122.9 (s), 122.0 (s), 102.6 (s), 100.6 (s), 41.4 (s), 40.6 (s), 33.9 (s), 31.3 (s), 30.1 (s), 8.6 (d, $J = 56.1$ *Hz*) ppm.

$[(C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2]$ (**2**): yellow crystals, m.p. 175–178°C dec. Found: C, 58.1; H, 6.4. Calc. for $C_{32}H_{41}PYbCl$: C, 57.8; H, 6.2%. IR (cm^{-1}, in KBr): 2940m, 2878m, 2804w, 1603w, 1438s, 1320w, 1302w, 1265m, 1166w, 1119s, 982m, 944s, 891s, 794m, 748vs, 687vs, 492m, 478s, 452m. $^{31}P\text{-}\{^1H\}$ NMR (toluene-d_8): δ 62.1 (s) ppm.

[‡] Crystal data for $[Ph_2PMe_2][(\eta^5\text{–}C_5H_4Bu^t)_2Li]$ (**1**): $F_w = 464.6$, triclinic, $P\bar{1}$ (No. 2) $a = 8.409(1)$, $b = 12.554(1)$, $c = 14.282(2)$ A[faaN], $\alpha = 92.09(1)°$, $\beta = 92.87(1)°$, $\gamma = 103.04(2)°$, $V = 1465.2(3)$ Å^3 $Z = 2$, $F(000) = 504$, $D_c = 1.053$ g cm^{-3}, $\mu = 1.10$ cm^{-1}. Crystal dimensions: $0.22 \times 0.34 \times 0.35$ mm. Intensity data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) using ω-2θ scans ($2\theta_{max} \leqslant 50°$) at room temperature. The data were corrected for Lorentz, polarization effects and absorption correction using ψ-scan method resulting in transmission factors ranging from 0.9419 to 1.0000. A total of 5121 unique reflections ($2\theta \leqslant 50°$) were measured; 2132 of these had $I \geqslant 3\sigma(I)$ and were considered to be observed. The structure was solved by Direct Methods (SIR92) and refined by full matrix least-squares analysis to give $R = 0.042$, $wR = 0.039$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated in their idealized positions (C—H bond fixed at 0.96 Å) and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were assigned appropriate isotropic thermal parameters and included in the structure factor calculations but not in the refinement. All calculations were performed on a Silicon–Graphics computer using program package Texsan from MSC.[13]

Crystal data for $[(C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2]$ (**2**): $F_w = 664.1$ orthorhombic, *Pbca*, $a = 20.874(4)$, $b = 10.586(2)$, $c = 27.028(5)$ Å, $V = 5972(2)$ Å^3, $Z = 8$, $F(000) = 2672$, $D_c = 1.477$ g cm^{-3}, $\mu = 32.93$ cm^{-1}. Crystal dimensions: $0.20 \times 0.30 \times 0.40$ mm. Intensity data were collected on a Siemens R3m/V diffractometer at 294 K with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). A total of 6842 unique reflections ($3° \leqslant 2\theta \leqslant 50°$) were measured; 2270 of these had $I \geqslant 4\sigma(I)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors and semi-empirical absorption correction was applied. The structure was solved by direct methods and refined by full matrix least-squares analysis to give $R = 0.079$, $wR = 0.105$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated in their idealized positions (C—H bond fixed at 0.96 Å) and allowed to ride on their respective parent carbon atoms. These hydrogen atoms were assigned appropriate isotropic thermal parameters and included in the structure factor calculations but not in the refinement. Computations were performed using the SHELTXL-PLUS (PC version) program package.[14]

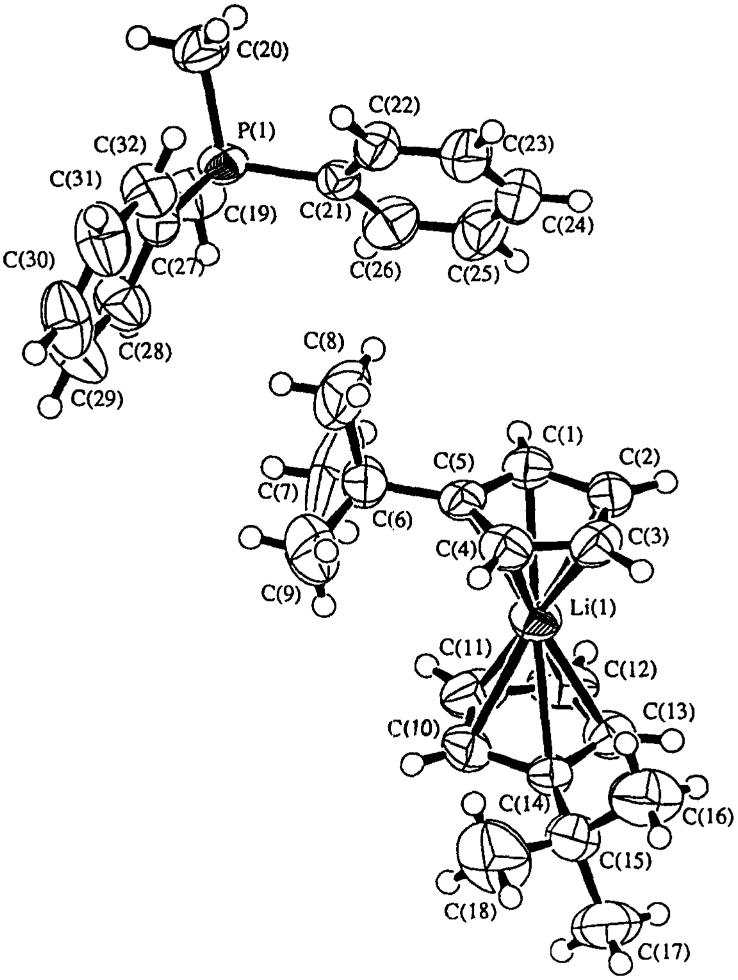

Fig. 1. A perspective view of the structure of $[Ph_2PMe_2][\eta^5\text{-}C_5H_4Bu^t)_2Li]$ (**1**). Selected bond lengths (Å) and bond angles (°) P(1)—C(19), 1.777(4); P(1)—C(20), 1.791(4); P(1)—C(21), 1.789(3); P(1)—C(27), 1.784(4); Li(1)—C(1), 2.326(7); Li(1)—C(2), 2.289(7); Li(1)—C(3), 2.281(7); Li(1)—C(4), 2.305(7); Li{1)—C(5), 2.358(7); Li(1)—C(10), 2.301(7); Li(1)—C(11), 2.255(7); Li(1)—C(12), 2.294(7); Li(1)—C(13), 2.360(7); Li(1)—C(14), 2.382(7); C(5)—C(6), 1.515(5); C(14)—C(15), 1.507(5); C(19)—P(1)—C(20), 108.3(2); C(19)—P(1)—P(1)—C(21), 110.4(2); C(19)—P(1)—C(27), 110.0(2); C(20)—P(1)—C(21), 107.9(2); C(20)—P(1)—C(27), 109.8(2); C(21)—P(1)—C(27), 110.5(2); C(1)—Li(1)—C(2), 35.0(1); C(1)—Li(1)—C(5), 34.8(1); C(2)—Li(1)—C(3), 35.3(2); C(3)—Li(1)—C(4), 35.6(1); C(4)—Li(1)—C(5), 35.1(1); C(10)—Li(1)—C(11), 35.7(2); C(10)—Li(1)—C(14), 34.7(1); C(11)—Li(1)—C(12), 35.6(2); C(12)—LI(1)—C(13), 34.7(2); C(13)—Li(1)—C(14), 34.7(1).

^{1}H NMR spectrum of **1** exhibited a multiplet and a doublet (J = 14.0 Hz) of relative intensity 10:6 at δ 7.61–7.88 and 2.27 ppm for the phenyl and methyl protons of the $[Ph_2PMe_2]^+$ cation, respectively; two multiplets of relative intensity 4:4 at δ 5.40 and 5.31 ppm for the —C*H* protons of the Cp ring and a singlet of relative intensity 18 at δ 1.18 ppm for the *tert*-butyl protons of the $[(\eta^5\text{-}C_5H_4Bu^t)_2Li]^-$ anion. **1** could also be prepared in 70% yield from the reaction of $[Ph_2PMe_2][CF_3SO_3]$ with two equivalents of $(C_5H_4Bu^t)$ Li. Although η^5-cyclopentadienyl alkali metal complexes are quite common, anionic *bis*(η^5-cyclopentadienyl) alkali metal complexes are rather rare.[8] **1** is the fourth example of anionic *bis*(η^5-cyclopentadienyl) alkali metal sandwich compounds that have been structurally characterized by X-ray diffraction studies.[8,9]

Crystals of **2** suitable for X-ray diffraction study were grown from a tetrahydrofuran/toluene mixture. A perspective drawing and selected bond lengths and bond angles of **2** are shown in Fig. 2 and its caption. The solid state structure of **2** can be described as a distorted tetrahedron if one considers that the metal is coordinated to the centroid of the *tert*-butylcyclopentadienyl rings. The *tert*-butylcyclopentadienyl rings are bonded to the Yb atom in a η^5-fashion with Yb—C (ring) distances ranging from 2.57(3) to 2.86(3) Å. The mean Yb—C distances for the two Cp rings are 2.66 and 2.67 Å. The Yb—C (ylide) distance is 2.51(3) Å. The Yb—Cl distance is

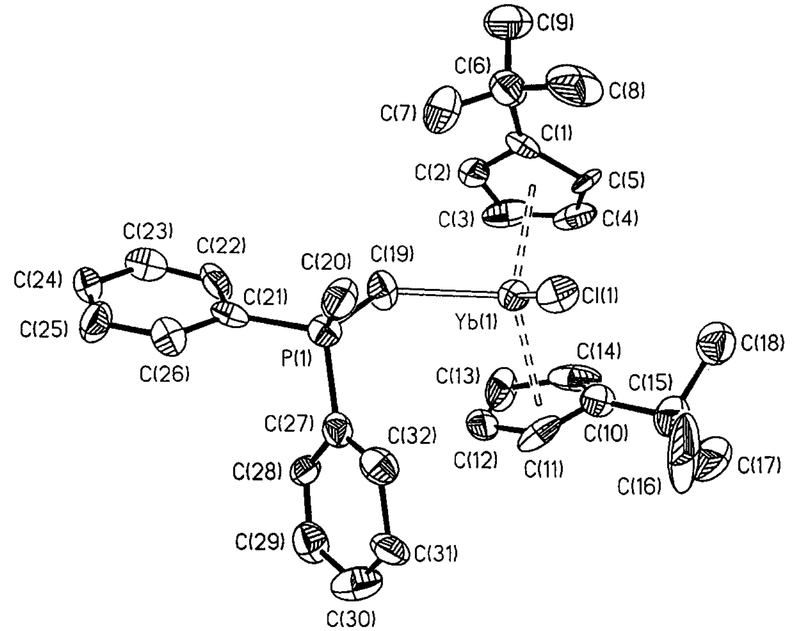

Fig. 2. A perspective view of the structure of [$(C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2$] (**2**). Selected bond lengths (Å) and bond angles (°): Yb(1)—Cl(1), 2.608(6); Yb(1)—C(1), 2.858(26); Yb(1)—C(2), 2.709(27); Yb(1)—C(3), 2.570(33); Yb(1)—C(4), 2.580(30); Yb(1)—C(5), 2.607(27); Yb(1)—C(10), 2.614(25); Yb(1)—C(11), 2.662(24); Yb(1)—C(12), 2.678(28); Yb(1)—C(13), 2.710(27); Yb(1)—C(14), 2.712(33); Yb(1)—C(19), 2.509(26); P(1)—C(19), 1.707(24); P(1)—C(20), 1.790(24); P(1)—C(21), 1.784(27); P(1)—C(27), 1.804(26); C(1)—C(6), 1.508(34); C(10)—C(15), 1.503(35); C(12)—Yb(1)—Cl(1), 88.4(5); C(19)—P(1)—C(20), 111.5(12); C(19)—P(1)—C(21), 114.3(12); C(19)—P(1)—C(27), 112.6(13); C(20)—P(1)—C(21), 104.8(12); C(20)—P(1)—C(27), 104.8(12); C(21)—P(1)—C(27), 108.1(11); P(1)—C(19)—Yb(1), 132.1(15).

2.608(6) Å and is comparable to the Yb—Cl distances of $YbCl_3(C_6H_{10}O_2)(THF)_2$ ranging from 2.521(1) to 2.532(2) Å.[10] The P—C(19) distance of 1.71(2) Å is within the range of a P═C double bond distance (1.665 Å)[11] and a P—C single bond distance (1.872 Å).[12] The P—C distances for the P—CH_2 [1.707(24) Å] and P—CH_3 [1.80(2) Å groups are in good agreement with comparable bond lengths in [$(\eta^5\text{-}C_5H_4Bu^t)_3NdCH_2P(Me)Ph_2$] [P—$CH_2$, 1.71(1); P—$CH_3$, 1.81(1) Å][5b] and [$(\eta^5\text{-}C_5H_5)_3SmCH_2P(Me)Ph_2$] [P—$CH_2$, 1.734(6); P—$CH_3$ 1.811(6) Å].[5a]

The results of our studies show that the large lanthanide metals such as Nd and Sm, the reaction of $(\eta^5\text{-}C_5H_4Bu^t)_2LnCl \cdot LiCl$ with $Li[(CH_2)(CH_2)PPh_2]$ gives $(\eta^5\text{-}C_5H_4Bu^t)_3LnCH_2P(Me)Ph_2$ (Ln = Nd, Sm); whereas with small lanthanide metals such as Yb, the reaction gives [$(\eta^5\text{-}C_5H_4Bu^t)_2Yb(Cl)CH_2P(Me)Ph_2$]. This suggests that the nature of the products from the reaction of $(\eta^5\text{-}C_5H_4Bu^t)_2LnCl \cdot LiCl$ with $Li[(CH_2)(CH_2)PPh_2]$ may be influenced by the size of the lanthanide metals. We are in the process of examining this effect further.

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