# Synthesis of $[(\mathrm{tmeda})\mathrm{LiCH_2PMe_2Li}(\mathrm{tmeda})\mathrm{CH_2PMe_2}]$ (tmeda = tetramethylethylenediamine) and of a Binuclear Zirconocene Phosphine Functionalized Ketene Complex, $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{ClZr}(\mathrm{PMe_2CH{=}CO})\mathrm{ZrCl}(\eta\text{-}\mathrm{C_5H_5})_2]$ (Both Structurally Characterized), the Latter *via* Carbonylation of '$[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{ZrCl}(\mathrm{CH_2PMe_2})]$'

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Reaction of $[(\mathrm{tmeda})\mathrm{LiCH_2PMe_2Li}(\mathrm{tmeda})\mathrm{CH_2PMe_2}]$, (**1**), (tmeda ≡ tetramethylethylenediamine) with $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{ZrCl_2}]$ in tetrahydrofuran at −78 °C yields $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Zr}(\mathrm{CH_2PMe_2})_n\mathrm{Cl}_{2-n}]$, $n$ = 1, (**2**), or $n$ = 2, (**3**); carbonylation of (**2**) affords exclusively a novel binuclear ketene complex, $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{ClZr}(\mathrm{PMe_2CH{=}CO})\mathrm{ZrCl}(\eta\text{-}\mathrm{C_5H_5})_2]$, (**4**), which in the crystal form possesses a Zr–P linkage [2.724(5) Å].

Carbonylations of zirconocene(IV) alkyl compounds, $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{ZrRX}]$, X = alkyl or halide, usually afford $\eta^2$-acylmetal products. For the combination of alkyl ligands R = $\mathrm{CHPh_2}$, X = $\mathrm{CH_3}$ or $\mathrm{CH_2SiMe_3}$, a metal ketene complex, $[\{(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Zr}(\mathrm{OCCPh_2})\}_2]$, is also formed.[1] The deprotonation of $\eta^2$-acylmetal complexes has been recently shown to be a more general route to early transition metal ketene complexes.[2]

We have now carried out the carbonylation of a thf (tetrahydrofuran) solution of $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Zr}(\mathrm{CH_2PMe_2})\mathrm{Cl}]$, (**2**), under ambient conditions and find it yields exclusively the metal ketene complex, $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{ClZr}(\mathrm{PMe_2CH{=}CO})\mathrm{ZrCl}\text{-}(\eta\text{-}\mathrm{C_5H_5})_2]$, (**4**). It is analytically pure, is moderately air-stable, and sparingly soluble in a variety of solvents, including thf. Its molecular structure has been determined by *X*-ray methods.† We have also re-investigated the carbonylation of the related compound $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Zr}(\mathrm{CH_2PPh_2})\mathrm{Cl}]$, reported to yield the $\eta^2$-acyl complex $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Zr}\text{-}(\eta^2\text{-}\mathrm{COCH_2PPh_2})\mathrm{Cl}]$,[3] and find it yields a complex of composition $\mathrm{Zr_2(C_5H_5)_4Cl_2PPh_2C(H)CO}$. It may have the same structure as (**4**). An i.r. band at 1520 cm⁻¹ was originally assigned as $\nu_{\mathrm{CO}}$ of an $\eta^2$-acyl group[3] and compares well with a band at 1528 cm⁻¹ for (**4**).‡

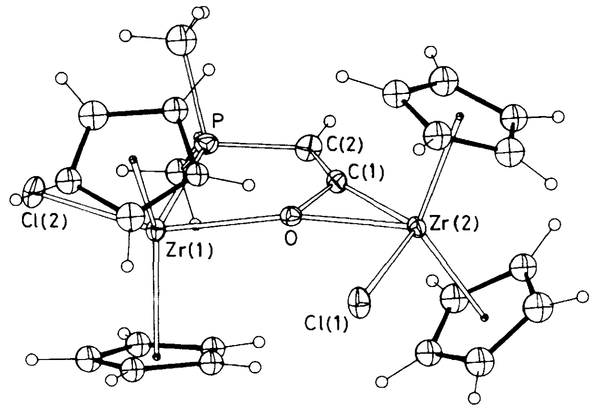

**Figure 1.** Molecular structure of $[(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{ClZr}(\mathrm{PMe_2CH{=}CO})\mathrm{ZrCl}\text{-}(\eta\text{-}\mathrm{C_5H_5})_2]$, (**4**), showing 20% ellipsoids for non-hydrogen atoms. Selected bond lengths (Å) and angles (°): Zr–centroids 2.23; Zr–Cl: 2.570(6) Zr(1); 2.561(5) Zr(2); Zr–O: 2.34(1) Zr(1), 2.26(1) Zr(2); Zr(1)–P 2.724(5); Zr(2)–C(1) 2.23(2); Zr–η-C 2.49(2)–2.56(2); centroid–Zr–centroid: 134.7 Zr(1), 128.1 Zr(2); O–C(1) 1.35(2); C(1)–C(2) 1.35(2); C(2)–P 1.76(2); Zr(1)–O–Zr(2) 161.7(5); Cl(1)–Zr(1)–O 143.0(3); Cl(2)–Zr(2)–O 84.0(3); Cl(1)–Zr(1)–P 73.6(2); P–Zr(1)–O 69.4(3); Cl(2)–Zr(2)–C(1) 119.1(4); O–Zr(2)–C(1) 35.1(4); Zr(1)–O–C(1) 127(1); O–C(1)–C(2) 123(2); C(1)–C(2)–P 116(1); C(2)–P–Zr(1) 103.8(6).

Compound (**4**) is a binuclear complex (Figure 1) in which the ketene ligand is bonded to both zirconium atoms: to Zr(2) as an $\eta^2$ ligand through the oxygen and adjacent carbon atoms, as in $[(\eta\text{-}\mathrm{C_5Me_5})_2\mathrm{Zr}\{\eta^2\text{-}\mathrm{C(O)CH{=}CH_2}\}(\mathrm{NC_5H_4})]$,[4] and to Zr(1) as a bidentate through the oxygen and phosphorus atoms so that the oxygen atom bridges both metal centres, as it does in the symmetrical binuclear complex $[\{(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Zr}(\mathrm{OCCPh_2})\}_2]$.[1] The plane defined by the ketene atoms O, C(1), C(2), and P is nearly coplanar with the planes

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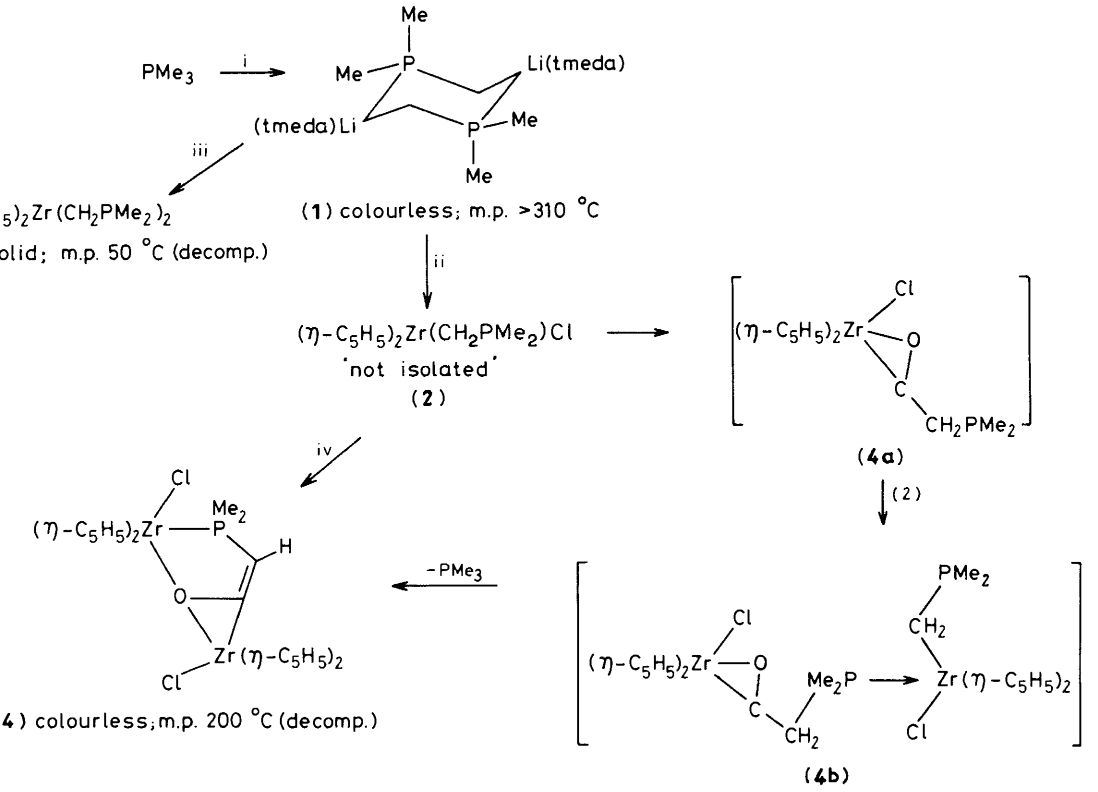
† *Crystal data*: (**1**), $\mathrm{C_9H_{24}N_2LiP}$, triclinic, space group $P\bar{1}$, $a$ = 14.918(7), $b$ = 11.567(5), $c$ = 9.621(4) Å, $\alpha$ = 113.94(3), $\beta$ = 91.92(3), $\gamma$ = 109.79(3)°, $Z$ = 4, $D_c$ = 0.94 g cm⁻³, $U$ = 1399(1) Å³. The structure was determined from 3019 [with $I > 3\sigma(I)$] 'observed' (out of 4501 independent) diffractometer reflections measured to $2\theta$ = 50° at room temperature. $R$ and $R_w$ are 0.059 and 0.078, respectively. (**4**), $\mathrm{C_{24}H_{27}Cl_2OPZr_2}$, triclinic, space group $P\bar{1}$, $a$ = 13.105(10), $b$ = 11.568(6), $c$ = 8.513(4) Å, $\alpha$ = 88.22(4), $\beta$ = 89.86(5), $\gamma$ = 70.59(5)°, $Z$ = 2, $D_c$ = 1.68 g cm⁻³, $U$ = 1217(1) Å³. The structure was determined from 1213 [with $I > 3\sigma(I)$] 'observed' (out of 1954 independent) diffractometer reflections measured to $2\theta$ = 40°, at room temperature. $R$ and $R_w$ are 0.048 and 0.054, respectively.

Atomic co-ordinates of this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Selected spectroscopic data: $^1$H n.m.r. (60 MHz, $\mathrm{C_6D_6}$) $\delta$: (**1**) 2.23 (s, $\mathrm{H_3C{-}N}$), 2.12 (s, $\mathrm{CH_2}$), 1.33 (s, $\mathrm{H_3C{-}P}$), −0.29 (s, $\mathrm{H_2C{-}P}$); (**3**) 5.24 (s, η-$\mathrm{C_5H_5}$), 0.93 [d, $\mathrm{H_3C{-}P}$, $J$(P) 4.2 Hz], 0.37 [d, $\mathrm{H_2C{-}P}$, $J$(P) 4.8 Hz]. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ n.m.r. ($\mathrm{C_6D_6}$, $\mathrm{SiMe_4}$) $\delta$: (**1**) 10.3 (d, $\mathrm{H_3C{-}P}$, $J$(P) 27.5 Hz], 24.5 [d, $\mathrm{H_3C{-}P}$, $J$(P) 9.2 Hz], 46.4 (s, $\mathrm{H_3C{-}N}$), 57.3 p.p.m. (s, $\mathrm{H_2C{-}N}$); (**3**) 20.4 [d, $\mathrm{H_3C{-}P}$, $J$(P) 16.0 Hz], 53.5 [d, $\mathrm{H_2C{-}P}$, $J$(P) 38.9 Hz], 111.0 p.p.m. [t, $\mathrm{C_5H_5}$, $J$(P) 3.4 Hz]. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ n.m.r. ($\mathrm{C_6D_6}$, $\mathrm{H_3PO_4}$) $\delta$: (**1**) −45.4 p.p.m. (s); (**3**) −37.8 p.p.m. (s). I.r. (KBr): (**4**), a sharp band at 1528 cm⁻¹ might be the C–O or OC=C stretch of the ketene ligand.



**Scheme 1.** *Reagents and conditions*: i, LiBu$^n$ (*ca.* 1.7 M in hexane), tmeda (1.0 equiv.), 12 h, 20 °C; ii, (**1**) in thf to a −78 °C thf solution of [(η-$C_5H_5$)$_2$Zr$Cl_2$] (1.0 equiv. or 0.5 equiv. for iii); iv, CO at 1 atm, 20 °C.

defined by Zr(1), C(1), O, and P, and Zr(2), O, C(1), and Cl(2), the dihedral angles being respectively 5.7 and 4.2°. The P–C(2) bond length is 1.76(2) Å, shorter than normal P–$CH_3$ bonds, as expected for a P–sp$^2$-C linkage. The Zr–P bond [2.724(5) Å] is similar to that in [ZrH(η-$C_8H_{11}$)($Me_2PCH_2CH_2PMe_2$)$_2$] [2.76(5) Å].[5] It is *cis* to both O and Cl(2), which is the least sterically encumbered position.

Compound (**2**) could not be isolated. In attempting to do so it readily redistributed to [(η-$C_5H_5$)$_2$Zr($CH_2PMe_2$)$_2$], (**3**), and zirconocene dichloride. The related compound [(η-$C_5H_5$)$_2$Zr($CH_2PPh_2$)Cl] is, however, stable with respect to redistribution[6] and its formation of a carbonylation product similar to that of (**4**) supports our proposal that (**2**) is initially present in solution.

The proposed pathway for the formulation of (**4**) (Scheme 1) is based on circumstantial evidence. It is the formation of an η$^2$-acylmetal derivative of (**2**), (**4a**), which rapidly reacts with another molecule of (**2**) yielding an intermediate, (**4b**), which eliminates trimethylphosphine. The phosphine bridge in (**4b**) would bring the Zr–$CH_2PMe_2$ and the η$^2$-acyl groups into close proximity, and would facilitate Zr–$CH_2PMe_2$ bond rupture. Positioning the Zr–P interaction to be *cis* to Cl and $CH_2PMe_2$ is based on steric considerations.

Compounds (**2**) and (**3**) were prepared from a new crystalline lithium alkyl [{(tmeda)Li$CH_2PMe_2$}$_2$] (tmeda ≡ tetramethylethylenediamine), (**1**), which ought to have general synthetic utility as a transfer reagent for $\bar{C}H_2PMe_2$. To date a variety of indirect methods for generating species containing η$^2$-co-ordinated $\bar{C}H_2PMe_2$ have been reported.[7] Compound (**1**) was obtained in 86% yield by the metallation of $PMe_3$ using LiBu$^n$(tmeda) and characterized by spectroscopic‡ and *X*-ray† methods. (The species 'Li$CH_2PMe_2$' has been prepared by the metallation of $PMe_3$ using LiBu$^t$.[8]) Its molecules, in the solid state, are centrosymmetric dimers, forming six-membered heterocycles in the chair conformation (Figure 2), in which the $\bar{C}H_2PMe_2$ moieties bridge successive lithium centres through the C and P atoms. The crystallographic asymmetric unit consists of two halves of two different molecules. The short Li–C bond [2.14(5) Å] is similar to that in [Li{CH(Si$Me_3$)$_2$}(pentamethyldiethylenetriamine)] [2.13(5) Å],[9] suggesting substantial covalent bonding.

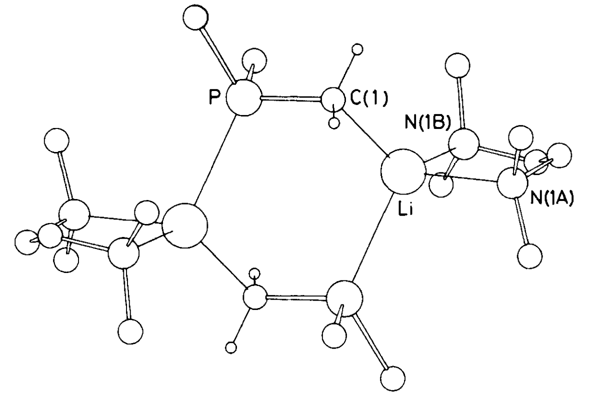


**Figure 2.** The structure of one molecule of [{(tmeda)Li$CH_2PMe_2$}$_2$], (**1**). Selected bond lengths (Å) and angles (°) (values for molecule 1 follow those of molecule 2): Li–C 2.150(8), 2.141(6); Li–P 2.593(7), 2.615(6); Li–N(1A) 2.218(5), 2.169(9); Li–N(1B) 2.177(8), 2.216(7); P–Li–C(1) 110.7(2), 108.2(3); Li–P–C(1) 114.4(2), 112.7(2); Li–C(1)–P 113.2(3), 111.8(3); P–Li–N(1A) 110.0(3), 109.7(3); P–Li–N(1B) 109.7(3), 109.5(2); C(1)–Li–N(1A) 113.0(4), 112.1(3); C(1)–Li–N(1B) 126.4(3), 130.2(3); N(1A)–Li–N(1B) 83.7(2), 84.1(3).

Compound (**3**) appears, from its n.m.r. spectra,‡ to be either a fluxional molecule with rapid $\eta^1$–$\eta^2$ interchange, or a molecule with two $\eta^1$-$\bar{C}H_2PMe_2$ ligands. Molecular orbital considerations predict the latter;[10] and in the compound $[(\eta\text{-}C_5H_5)_2ZrCl(\eta^1\text{-}CH_2PPh_2)]$,[6] the bonding is $\eta^1$, though the steric hindrance round the phosphorus atom might in this case dictate an $\eta^1$-interaction.

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