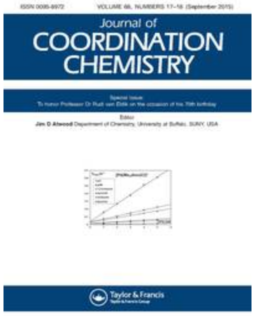

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An unsymmetrical phosphonium diylide with a fluorenylidene subunit and its lithium complexes

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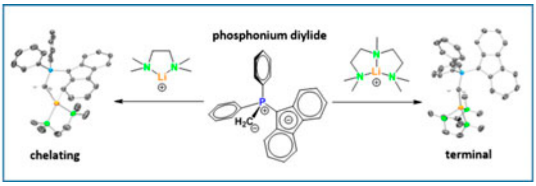

The phosphonium ylide $MePh_2P(flu)$ (**3**) (flu = $C_{13}H_8$, fluorenylidene) was conveniently prepared by reaction of $Ph_2P(fluH)$ (**1**) (fluH = $C_{13}H_9$, fluorenyl) with iodomethane, followed by subsequent dehydrohalogenation of the resulting phosphonium salt $[MePh_2P(fluH)]I$ (**2**) by potassium *tert*-butoxide. Compound **3** was further deprotonated by *n*-butyllithium, yielding the corresponding lithium complex $[Li\{CH_2PPh_2(flu)\}(tmeda)]$ (**4**) in presence of *N,N,N′,N′*-tetramethylethylenediamine (tmeda). This mononuclear lithium compound contains the monoanionic chelating diylidic ligand. An exchange of the neutral bidentate tmeda by tridentate *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdta) enforces a change in coordination mode. Consequently, the diylide is monodentate in $[Li\{CH_2PPh_2(flu)\}(pmdta)]$ (**5**). Compounds **1**–**5** were characterized by NMR spectroscopy and single-crystal X-ray diffraction experiments.

Keywords: Lithium; Phosphonium halides; Phosphonium ylides; Diylides; Phosphanes; Fluorenylidene; X-ray crystallography

1. Introduction

The fluorenide anion ($C_{13}H_9^-$) is able to adopt a variety of coordination modes in main group and transition metal complexes, allowing it to adapt to changes at its adjacent metal center. In comparison with the related cyclopentadienide ligand, such haptotropic rearrangements from a η^5 to a η^3 or even a η^1 coordination mode in transition metal complexes are more facile for the fluorenide ligand [1]. As a result, complexes containing

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Dedicated to Professor Rudi van Eldik on the occasion of his 70th birthday.

this anionic ligand show a pronounced “indenyl effect” that leads to an increased reaction rate for instance in (associative) substitution reactions at the metal centers [2].

In related s-block metal complexes, the fluorenide anion is a soft and easily polarizable *Lewis* base, due to extensive charge delocalization within the tricyclic aromatic ring system. Given the size of the anion, a vast number of coordination modes are possible and consequently, the fluorenide anion behaves as a “coordination chameleon” when interacting with *Lewis* acidic s-block metals. In lithium chemistry [3], the coordination modes range from non-coordinating in polymeric $[\mathrm{Li}(\mu\text{-en})_2][\mathrm{C}_{13}\mathrm{H}_9]$ (en = ethylenediamine) [3b] to a η^6: η^6 coordination mode in dimeric $[\{\mathrm{Li}(\mathrm{C}_{13}\mathrm{H}_9)\}_2]$ [3d] as shown by X-ray diffraction experiments. NMR techniques have been used to elucidate the structural features of these lithium complexes as well as the occurring dynamic processes in solid state and solution [4]. The driving force for formation of different aggregates, shown in chart 1, is the presence (or absence) of neutral *Lewis* bases that compete for coordination sites at lithium and limit the interaction with the anionic ligand in these contact ion pairs.

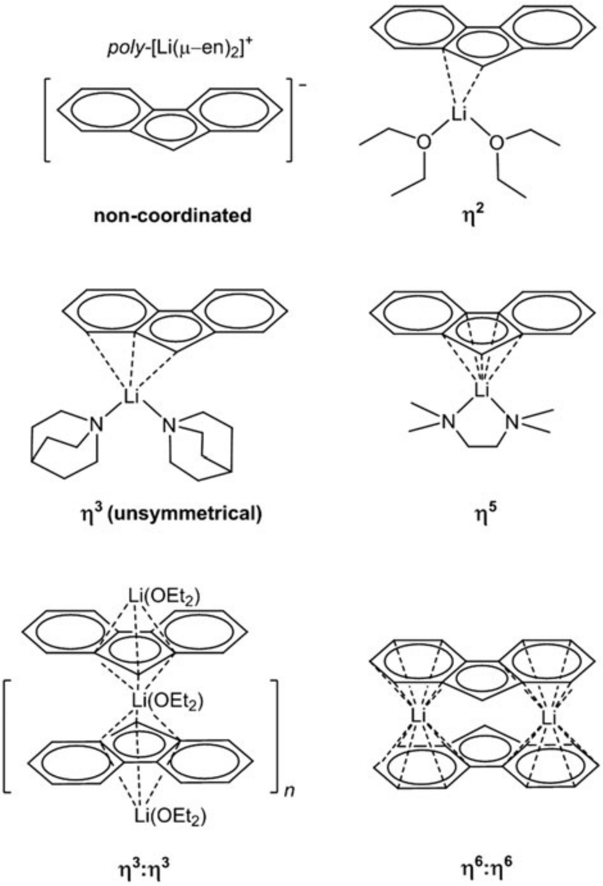


Chart 1. Synthesis of the phosphonium ylide **3**.

Continuing our previous investigations on phosphorus-stabilized methanide derivatives of s-block metals [5], we became interested in the incorporation of a fluorenyl moiety in such a ligand, in order to increase its ability to adapt to different metal centers. Additionally, such ligand might show hemilabile character.

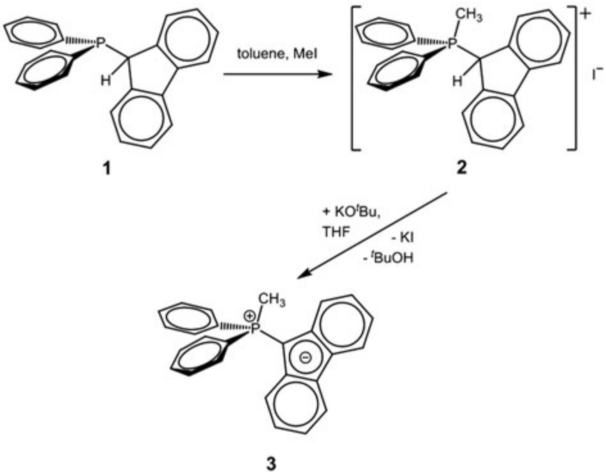
Here, we report the synthesis of the new phosphonium ylide $MePh_2P(flu)$ (flu = $C_{13}H_8$, fluorenylidene) and its deprotonation by *n*-butyl lithium, leading to an unsymmetrical monoanionic phosphonium diylide. During the preparation of this manuscript, the closely related derivative $[Li_2\{CH_2PMe_2(flu)\}_2(Et_2O)_2]$ was reported by Schröder and Sundermeyer [6].

2. Results and discussion

2.1. *Synthesis of the phosphonium ylide and its precursors*

The starting point of the synthesis of $MePh_2P(flu)$ (see scheme 1) is the phosphine $Ph_2P(fluH)$ (**1**) (fluH = fluorenyl; see figure 1), which can be conveniently prepared by reaction of *in situ* generated lithium fluorenide and chlorodiphenylphosphine, as reported by Escudie and co-workers [7].

Subsequent quaternization of **1** was achieved by reaction with iodomethane in toluene, leading to the colorless phosphonium iodide $[MePh_2P(fluH)]I$ (**2**) in excellent yield. The compound is sufficiently air stable for normal handling, but should be stored in the dark under an inert atmosphere for longer periods to avoid slow partial oxidation of the iodide by oxygen. In solution, such oxidation was noticed during recrystallization attempts from chloroform in order to obtain suitable crystals for X-ray diffraction experiments. Besides colorless crystals of the composition **2** $CHCl_3$ (see figure 2), a few yellow crystals of the closely related $[MePh_2P(fluH)]I_3$ (**2a**), containing a triiodide anion, were obtained under aerobic conditions.



Scheme 1. Synthesis of lithium derivatives **4** and **5**.

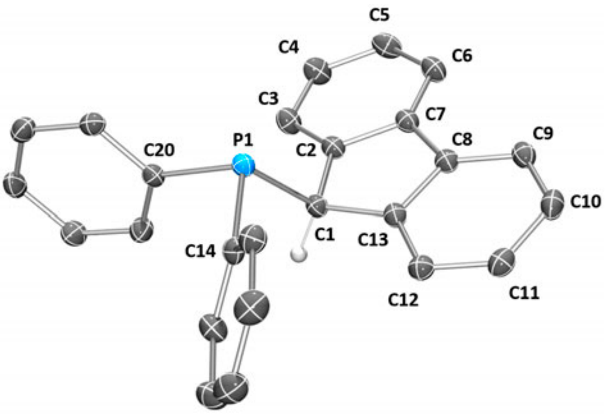


Figure 1. Molecular structure and numbering scheme of Ph_2P(fluH) (**1**). Hydrogens have been omitted for clarity, except at C1. The ellipsoids represent a probability of 50%. Selected bond lengths [Å]: C1–P1 1.8865(13), C14–P1 1.8403(13), C20–P1 1.8391(13), C1–H1 0.982(16), C1-C2 1.5179(17), C1–C13 1.5199(17). Angles [°]: C1–P1–C14 99.73(6), C1–P1–C20 102.61(6), C14–P1–C20 100.37(6).

The desired phosphonium ylide $MePh_2P$(flu) (**3**) was derived by dehydrohalogenation of **2** using potassium *tert*-butoxide as base. As expected from the vastly different equilibrium acidities of parent methane ($pK_{a,DMSO} = 56$) and fluorene ($pK_{a,DMSO} = 22.6$) [8], the proton was exclusively abstracted from the fluorenyl substituent. This deprotonation resulted in a high-field shift of 22.8 ppm for the signal of **3** ($\delta_p = 3.7$) in the $^{31}P\{^1H\}$ NMR spectrum, relative to the signal of **2** ($\delta_p = 26.5$). The ylidic carbon of **3**, which is now part of the aromatic system, showed a downfield shift to $\delta_C = 54.2$ in the $^{13}C\{^1H\}$ NMR spectrum

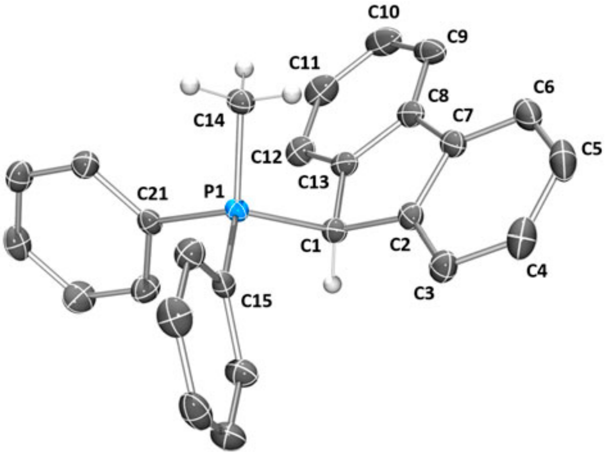


Figure 2. Molecular structure and numbering scheme of the cation of [$MePh_2P$(fluH)]I·$CHCl_3$ (**2**·$CHCl_3$). Hydrogens except at C1 and C14 have been omitted for clarity. Values for [$MePh_2P$(fluH)]I_3 (**2a**) are given in square brackets. The ellipsoids represent a probability of 50%. Selected bond lengths [Å]: C1–P1 1.8287(17) [1.834(4)], C14–P1 1.7878(17) [1.792(4)], C15–P1 1.7970(16) [1.795(4)], C21–P1 1.7976(16) [1.791(4)], C1–C2 1.524(2) [1.522(5)], C1-C13 1.523(2) [1.520(5)]. Angles [°]: C1–P1–C14 107.08(8) [107.73(19)], C1–P1–C15 110.74(8) [109.36(18)], C1–P1–C21 111.24(8) [108.74(17)].

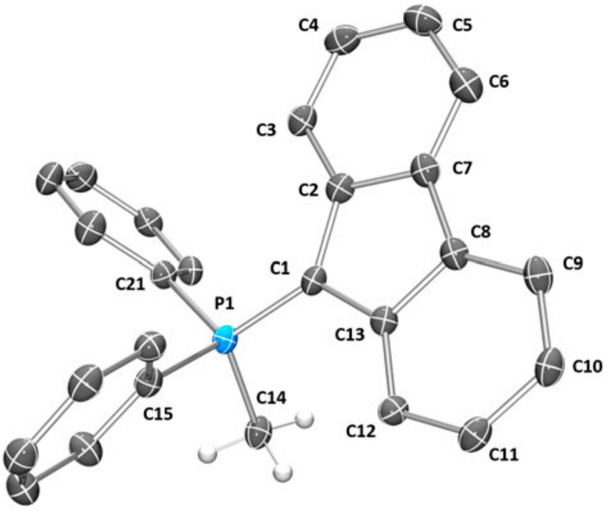


Figure 3. Molecular structure and numbering scheme of $MePh_2P(flu)$ (**3**). Hydrogens except at C14 have been omitted for clarity. The ellipsoids represent a probability of 50%. The values given in square brackets correspond to **3**·DME. Selected bond lengths [Å]: C1–P1 1.725(2) [1.717(3)], C14–P1 1.808(2) [1.803(3)], C15–P1 1.810(2) [1.813(3)], C21–P1 1.788(2) [1.797(3)], C1–C2 1.442(3) [1.452(4)], C1–C13 1.449(3) [1.449(3)]. Angles [°]: C1–P1–C14 112.90(10) [112.83(13)], C1–P1–C15 109.09(9) [112.33(12)], C1–P1–C21 110.04(10) [111.19(13)].

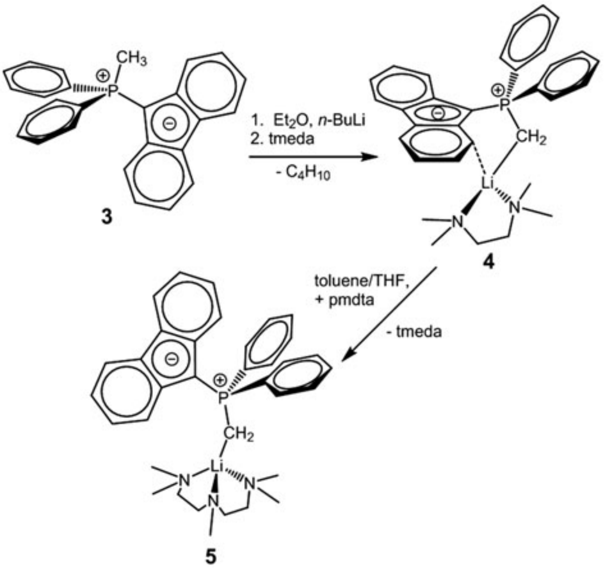
upon deprotonation (**2**: $\delta_C = 43.7$). In addition, an increased coupling constant to the neighboring phosphorus nucleus (**3**: ${}^1J_{C,p} = 126.2$ Hz; **2**: ${}^1J_{C,p} = 43.5$ Hz) was detected. This is in agreement with the increased s character of the bond between phosphorus and the now sp^2 hybridized ylidic carbon.

In order to gain further information about the structural changes induced by deprotonation, suitable crystals for X-ray diffraction analyses were grown from toluene or dimethoxyethane (DME). The determined molecular structure of **3** is depicted in figure 3.

A comparison with the structure of the parent phosphonium salt **2** shows that the distance between the phosphorus P1, carrying a positive charge, and C1 shortens upon deprotonation by 0.10–0.12 Å (**2**: 1.8287(17) Å; **2a**: 1.834(4) Å; **3**: 1.725(2) Å) as the result of an increased electrostatic attraction. However, this contraction is rather small in comparison with other phosphonium ylides [9]. This can be rationalized by the partial delocalization of the negative charge over the extended π-system, which weakens the electrostatic attraction. Nevertheless, the values of bond lengths and angles observed for **3** agree well with those reported for closely related systems [6, 10].

2.2. *Synthesis of lithium complexes 4 and 5*

Deprotonation of the phosphonium ylide **3** was performed with *n*-butyllithium (see scheme 2). In order to test the coordinating abilities of the newly formed unsymmetrical diylide ligand in the presence of a competitive neutral donor ligand, the *in situ* generated lithium complex was further treated with the bidentate nitrogen-donor ligand *N,N,N′,N′*-tetramethylethylenediamine (tmeda), a ligand commonly used for deaggregation of alkyllithium compounds [11]. Symmetrical dinuclear lithium complexes, in which the carbanionic



Scheme 2. Observed coordination modes of the fluorenide anion in its lithium complexes.

ligands bridge two neighboring lithium centers, were often observed in these experiments [12], although other tmeda-coordinated aggregates are also known [13].

In the deprotonation of **3**, utilization of tmeda enables isolation of the mononuclear derivative [Li{CH_2PPh_2(flu)}(tmeda)] (**4**) in crystalline form (see figure 4). In this compound, the lithium center is found in a distorted tetrahedral coordination sphere formed by two nitrogens of tmeda, the methylene carbon C14, and C12 of the fluorenylidene moiety. The observed bond length between Li1 and the methylene carbon C14 of 2.154(4) Å agrees well with those in closely related diylide complexes [Li{$(PhCH)_2PPh(CH_2Ph)$}(tmeda)] (Li–C2: 2.158(6) Å) [13h] and [Li{$CH_2PPh_2CHPPh_2$)}(tmeda)] (Li–C: 2.161(5) Å) [5e]. In contrast, the bridging methylene group in [Li_2{CH_2PMe_2(flu)}$_2$(Et_2O)$_2$] exhibits longer lithium carbon bonds (2.237(3) and 2.269(3) Å) [6].

The mainly electrostatic interaction between the fluorenylidene group and the cation in **4** leads to a distance of 2.507(4) Å between Li1 and C12 (see figure 4). It should be noted that this type of π-interaction is quite typical for diylidic derivatives with aryl substituents at the ylidic carbon. In related complexes, containing two benzylidene groups, the second benzylidene moiety also interacts with the lithium center via the *ortho*-carbon of the aryl substituent. The corresponding Li–C distances in [Li{4-$^tBuC_6H_4CHP(Ph)_2C(SiMe_3)$ C_6H_4_4-^{t}Bu}(thf)$_2$] [14] and [Li{$(PhCH)_2PPh(CH_2Ph)$}(tmeda)] [13h] are 2.463(5) and 2.639(6) Å, respectively.

In the dinuclear derivative [Li_2{CH_2PMe_2(flu)}$_2$(Et_2O)$_2$], the distance to the corresponding carbon is 2.592(3) Å [6]. However, in this case, a slightly shorter lithium carbon bond of 2.571(3) Å to the neighboring tertiary carbon was observed.

Much smaller values were found in related four-coordinate silyl-substituted benzyllithium derivatives, [Li{CH(Ar)SiR_2R'}(tmeda)] (Ar = aryl). In these derivatives, the attraction between the π-electron density of the benzene ring and the lithium cation results in short distances to the *ipso*-carbon in the range of 2.277(6)–2.352(5) Å [13g, j].

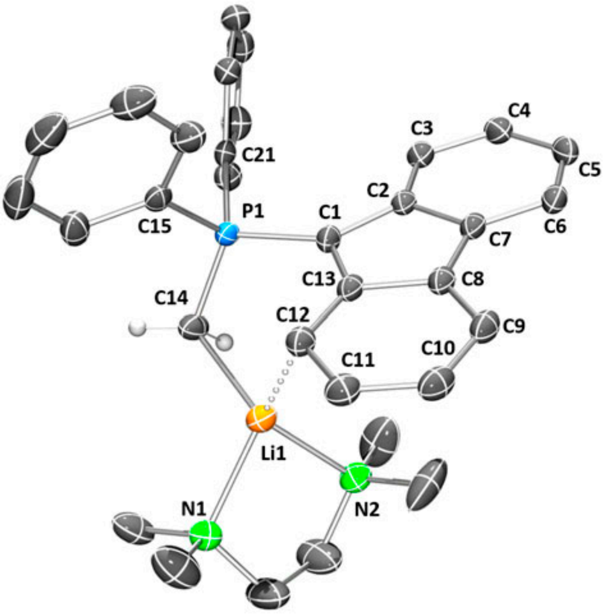


Figure 4. Molecular structure and numbering scheme of [Li{CH_2PPh_2(flu)}(tmeda)] (**4**). Hydrogens, except at C14, have been omitted for clarity. The ellipsoids represent a probability of 50%. Selected bond lengths [Å]: Li1–C14 2.154(4), Li1–C12 2.507(4), Li1–N1 2.090(4), Li1–N2 2.055(3), C1–P1 1.7510(17), C14–P1 1.7191(19), C15–P1 1.8216(18), C21–P1 1.8304(18), C1–C2 1.443(2), C1–C13 1.435(2). Angles [°]: N1-Li1-N2 87.74(13), C14-Li1-C12 101.68(13), C1–P1–C15 107.22(8), C1–P1–C21 107.13(8), Li1–C14–P1 105.26(13).

Nevertheless, the value observed for **4** falls within a range that has been considered as bonding in parent lithium fluorenide complexes [3]. Apparently, the interaction in **4** is sufficiently strong to suppress the formation of a dinuclear complex with bridging methylene moieties, as isolated for silyl derivatives like [{Li(μ-CH_2SiMe_3)(tmeda)}$_2$] [12e].

In addition, the use of a second equivalent of tmeda during the synthesis of **4** did not change the outcome of the reaction. A replacement of the coordinated fluorenylidene substituent at the lithium center by additional tmeda or even the liberation of the anionic ligand, as found for the related anionic diylide [$Me_2P(flu)_2$]$^-$ in [CaI(thf)$_5$][$Me_2P(flu)_2$] [15], was not observed.

However, the coordination mode of the diylide ligand can be altered by substitution of the bidentate tmeda by tridentate *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdta). In the presence of this neutral ligand, a lithium complex of composition [Li{CH_2PPh_2(flu)}(pmdta)] (**5**) was isolated. The molecular structure of this compound, which was determined by X-ray diffraction experiments, is depicted in figure 5. As with **4**, the lithium in **5** is in a distorted tetrahedral environment. Since the nitrogens of pmdta occupy three coordination sites at the lithium center, there is only one vacant coordination site left for the diylide ligand. Consequently, only an interaction with the rather hard *Lewis*-basic methylene moiety was observed, while no close contact between lithium and any carbon of the softer fluorenylidene subunit was detected. The distance between lithium and the methylene carbon C14 is not affected by the change in coordination mode of the ligand (**4**: 2.154(4) Å; **5**: 2.156(3) Å) and is in the typical range for pmdta ligated monomeric alkyllithium compounds [12e, 13f, 16]. For related lithium amide complexes, containing the neutral

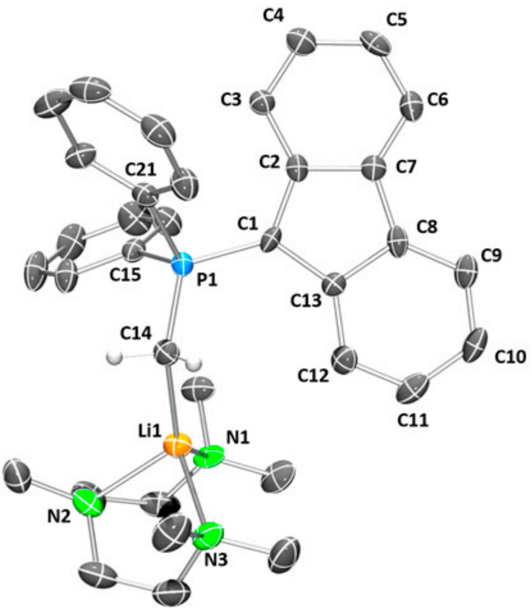


Figure 5. Molecular structure and numbering scheme of [Li{CH_2PPh_2(flu)}(pmdta)] (**5**). Hydrogens except at C14 as well as co-crystallized toluene have been omitted for clarity. A disorder of the pmdta ligand and of the fluorenylidene subunit is not shown. The ellipsoids represent a probability of 50%. Selected bond lengths [Å]: Li1–C14 2.156(3), Li1–N1 2.150(7), Li1–N2 2.110(3), Li1–N3 2.126(3), C1–P1 1.722(4), C14–P1 1.7275(14), C15–P1 1.8217(14), C21–P1 1.8364(13), C1–C2 1.437(5), C1–C13 1.448(4). Angles [°]: N1-Li1-N2 86.1(2), N1-Li1-N3 112.17(17), N2-Li1-N3 86.88(10), N1-Li1-C14 133.42(19), N2-Li1-C14 119.50(13), N3-Li1-C14 107.74(11), C1–P1–C14 116.67(9), C1–P1–C15 109.95(12), C1–P1–C21 103.85(11), Li1–C14–P1 127.53(10).

phosphonium ylide Ph_3PCH_2, which also binds exclusively via the methylene group, longer Li–C distances of 2.207(4) Å in [{Li(CH_2PPh_3)(μ-N{CH_2Ph}$_2$)}$_2$] and 2.285(9)–2.302(8) Å in [{Li(CH_2PPh_3)(μ-N{$SiMe_3$}$_2$)}$_2$] were reported [17].

In contrast to the unchanged bond lengths around C14, the angle P1–C14–Li1 in **5** has widened significantly to 127.53(10)° (**4**: 105.26(13)°), most likely for steric reasons. In [{$Li_2(CH_2PPh_2CH_2)_2$(dx)}$_2$(μ-dx)] (dx = 1,4-dioxane), in which the diylide moiety is incorporated in a twisted eight-membered ring, a value of 122(4)° for the P-CH_2-Li angle was reported [18]. In related monomeric benzyllithium derivatives, where an even more shielding tris(*N,N*-dimethyl-2-aminoethyl)amine ligand was used to limit the available coordination sites at lithium and disfavor π-interactions, the C_{ipso}-C_α-Li angle reaches similar values as in **5** [19].

Attempts to further investigate the different coordination modes of the diylide ligand in **4** and **5** in solution by NMR spectroscopy were hindered by the low solubility, especially of **5**, in hydrocarbon solvents. Therefore, the use of the rather strongly coordinating solvent THF-d_8 was necessary to dissolve both compounds under the same conditions. However, in this solvent, the diylidic moieties of **4** and **5** gave almost identical signals in the ^{1}H, ^{13}C, and ^{31}P NMR spectra (see section 4). In addition, the signals of the tmeda or pmdta ligands of **4** and **5** are close to the signals of the sole amines in this solvent. This indicates that THF-d_8 is able to substitute tmeda and pmdta in equilibrium in the coordination sphere of the lithium cation, when present in huge excess.

3. Conclusion

A convenient strategy for synthesis of the hitherto unknown phosphonium ylide $MePh_2P$(flu) (**3**), containing a fluorenylidene moiety, was developed. Its subsequent deprotonation with *n*-butyllithium led to the corresponding lithium complex, which was studied in the presence of the chelating nitrogen-donor ligands tmeda and pmdta. Together with the closely related compound $[Li_2\{CH_2PMe_2(flu)\}_2(Et_2O)_2]$, recently reported by Schröder and Sundermeyer [6], the obtained derivatives $[Li\{CH_2PPh_2(flu)\}(tmeda)]$ (**4**) and $[Li\{CH_2PPh_2(flu)\}(pmdta)]$ (**5**) nicely illustrate the possible coordination modes of such mono-fluorenylidene-substituted diylides. While s-block metal complexes containing chelating or bridging phosphonium diylides are well known, **5** appears to be the first example, where such an anion is a monodentate ligand. This binding mode closes the gap to $[Me_2P(flu)_2]^-$, which was found to be non-coordinating in $[CaI(thf)_5][Me_2P(flu)_2]$ [15].

The different properties of the present ylidic groups in $[CH_2PPh_2(flu)]^-$ with respect to *Lewis* basicity (hard *versus* soft) and the number of potential donor atoms, as well as the resulting preferences in metal binding (σ *versus* π interaction), suggest that this derivative could be an excellent candidate for the synthesis of heterobimetallic complexes.

4. Experimental

4.1. *General methods*

All manipulations were carried out under an inert argon or nitrogen atmosphere using standard Schlenk techniques. THF, diethyl ether, toluene, and benzene were dried over KOH and distilled over sodium/benzophenone in argon; $CHCl_3$ was dried over CaH_2 and distilled in an argon atmosphere. Deuterated THF was degassed, saturated with argon and stored over molecular sieves (3 Å). The yields given are not optimized. ^1H, $^7Li\{^1H\}$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance AC 300, 400 as well as Bruker Avance III HD 400 MHz and Bruker Avance III HD 600 MHz spectrometers. Chemical shifts are reported in parts per million relative to Me_4Si as an external standard. The residual signals of the used deuterated solvents were used as internal standards in the ^1H and ^{13}C NMR spectra. ^7Li and ^{31}P NMR shifts are referenced to LiCl in D_2O and 85% H_3PO_4 as external standard, respectively. Coupling constants are given in Hertz.

Elemental analyses of **2** and **3** were performed utilizing a Leco CHNS-932 Elemental Analyzer at the Institute of Organic Chemistry and Macromolecular Chemistry of the Friedrich Schiller University, Jena. The elemental analysis of **5** was obtained on a Euro Vector EA3000 Elemental Analyser.

The starting material $Ph_2P(C_{13}H_9)$ was synthesized according to a known procedure [7].

4.2. *Synthesis of [MePh$_2$P(fluH)]I (2)*

Ph_2P(fluH) (0.950 g, 2.71 mmol) was suspended in toluene (15 mL) and MeI (0.403 g, 2.84 mmol) was added via syringe to the colorless suspension at ambient temperature. The suspension was heated to 80 °C for 18 h. The white solid was filtered off, washed three times with toluene (3 × 5 mL), and dried under vacuum. The compound holds 0.5 equivalents of toluene even after prolonged drying. Yield 1.35 g (2.5 mmol, 92%).

Anal. Calcd for [MePh2P(fluH)]I·0.5 toluene (%): C 65.81, H 4.87; Found C 65.89, H 4.78. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 2.33$ (s, 1.5H, CH$_3$ toluene), 2.74 (d, $^2J_{\mathrm{H,p}}$ = 13.0 Hz, 3H, PCH$_3$), 7.14 (m, 4.5H, CH fluH + PCH + *o,p*-CH toluene), 7.21 (m, 3H, CH fluH + *m*-CH toluene), 7.36 (m, 2H, CH fluH), 7.49 (m, 4 H, CH Ph), 7.57 (m, 2H, CH fluH), 7.68 (m, 6H, CH Ph). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 25 °C): $\delta = 7.8$ (d, $^1J_{\mathrm{C,p}}$ = 55.8 Hz, 1C, PCH$_3$), 21.5 (s, 0.5C, CH$_3$ toluene), 43.7 (d, $^1J_{\mathrm{C,p}}$ = 43.5 Hz, 1C, PCH fluH), 117.5 (d, $^2J_{\mathrm{C,p}}$ = 84.2 Hz, 2C, *i*-C Ph), 120.8 (d, $J_{\mathrm{C,p}}$ = 1.2 Hz, 2 C, CH fluH), 125.4 (s, 1 C, *p*-CH toluene), 126.4 (d, $J_{\mathrm{C,p}}$ = 3.9 Hz, 2C, CH fluH), 127.8 (d, $J_{\mathrm{C,p}}$ = 3.0 Hz, 2C, CH fluH), 128.3 (s, 2C, *m*-CH toluene), 129.1 (s, 2C, *o*-CH toluene), 129.5 (d, $J_{\mathrm{C,p}}$ = 2.8 Hz, 2C, CH fluH), 129.9 (d, $^3J_{\mathrm{C,p}}$ = 12.3 Hz, 4C, *m*-CH Ph), 133.2 (d, $^2J_{\mathrm{C,p}}$ = 9.3 Hz, 4C, *o*-CH Ph), 135.0 (d, $^4J_{\mathrm{C,p}}$ = 3.0 Hz, 2C, *p*-CH Ph), 135.7 (d, $^3J_{\mathrm{C,p}}$ = 5.6 Hz, 2C, C fluH), 137.9 (s, 1C, *i*-C toluene), 142.1 (d, $^2J_{\mathrm{C,p}}$ = 4.7 Hz, 2C, PCHC$_2$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 25 °C): $\delta = 26.5$ (s). Suitable crystals of **2** for X-ray diffraction experiments were obtained by layering a saturated solution of **2** in CHCl$_3$ with *n*-heptane at ambient temperature.

4.3. *Synthesis of MePh$_2$P(flu) (3)*

[MePh$_2$P(fluH)]I·0.5 toluene (0.618 g, 1.15 mmol) was suspended in THF (10 mL) and KO^{t}Bu (0.131 g, 1.17 mmol) was added to the stirred colorless suspension at ambient temperature. The suspension immediately turned yellow and was heated for 30 min to 40 °C. Afterward, the yellow solid was collected on a Schlenk frit and dried in a vacuum. The dry residue of the filtration was extracted with CHCl$_3$ (5 × 10 mL). The mother liquor in THF was reduced to dryness and the resulting yellow solid was also dissolved in CHCl$_3$ (5 mL). All CHCl$_3$ solutions were combined and reduced to dryness. The resulting yellow solid was washed with *n*-heptane (10 mL), collected on a Schlenk frit and dried *in vacuo* afterward. Yield: 0.285 g (0.78 mmol, 67.8%).

Anal. Calcd for MePh$_2$P(flu) (%): C 85.69, H 5.81; Found C 85.39, H 5.67; ^{1}H NMR (400 MHz, THF-d$_8$, 25 °C): $\delta = 2.69$ (d, $^2J_{\mathrm{H,p}}$ = 13.2 Hz, 3H, PCH$_3$), 6.73 (m, 2H, CH flu), 6.82 (m, 4H, CH flu), 7.53 (m, 4H, *m*-CH Ph), 7.64 (m, 2H, *p*-CH Ph), 7.74 (m, 4H, *o*-CH Ph), 7.98 (m, 2H, CH flu); ^{13}C{^{1}H} NMR (101 MHz, THF-d$_8$, 25 °C): $\delta = 12.9$ (d, $^1J_{\mathrm{C,p}}$ = 61.7 Hz, 1C, PCH$_3$), 54.2 (d, $^1J_{\mathrm{C,p}}$ = 126.2 Hz, 1C, P=), 116.0 (s, 2C, CH flu), 116.7 (s, 2C, CH flu), 119.7 (d, $J_{\mathrm{C,p}}$=2.2 Hz, 2C, CH flu), 123.1 (s, 2C, CH flu), 128.9 (d, $^1J_{\mathrm{C,p}}$= 86.7 Hz, 2C, *i*-C Ph), 129.9 (d, $^3J_{\mathrm{C,p}}$= 11.9 Hz, 4C, *m*-CH Ph), 131.7 (d, $^3J_{\mathrm{C,p}}$= 14.0 Hz, 2C, C flu), 133.2 (d, $^4J_{\mathrm{C,p}}$= 2.9 Hz, 2C, *p*-CH Ph), 133.5 (d, $^2J_{\mathrm{C,p}}$= 10.5 Hz, 4C, *o*-CH Ph), 142.3 (d, $^2J_{\mathrm{C,p}}$= 15.4 Hz, 2C, P=CC$_2$); ^{31}P{^{1}H} NMR (162 MHz, THF-d$_8$, 25 °C): $\delta = 3.7$ (s). Suitable crystals of **3** for X-ray diffraction experiments were obtained from toluene (during the synthesis of **5**, see below) or DME.

4.4. *Synthesis of [Li{CH$_2$PPh$_2$(flu)}(tmeda)] (4)*

MePh$_2$P(flu) (0.320 g, 0.88 mmol) was suspended in Et$_2$O (15 mL) and a solution of *n*-butyllithium (0.58 mL of a 1.6 M solution in hexane, 0.93 mmol) was added via syringe to the stirred suspension at ambient temperature. The stirred yellow suspension was heated for 5 min–40 °C (bath temperature) until the yellow solid was dissolved. Afterward, tmeda (0.27 mL, 1.79 mmol) was added via syringe to the stirred yellow solution. Then, the reaction mixture was stored overnight at −20 °C. The resulting yellow crystals of **4** were collected on a cooled Schlenk frit and gently dried in a vacuum (prolonged drying leads to decomposition of the complex). Yield: 0.308 g (0.63 mmol, 71.6%). In some cases, orange-colored crystals of **4**·*n*Et_2O were isolated under almost identical conditions. These crystals rapidly lose the co-crystallized diethyl ether upon drying and are soluble in benzene while crystals of **4** are not.

4.4.1. Analytical data of 4. ^1H NMR (600 MHz, THF-d_8, 25 °C): $\delta = 0.24$ (d, $^2J_{H,p} = 12.7$ Hz, 2H, PCH_2Li), 2.16 (s, 12H, CH_3 tmeda), 2.31 (s, 4H, CH_2 tmeda), 6.61 (m, 2H, CH flu), 6.68 (m, 2H, CH flu), 6.79 (m, 2H, CH flu), 7.30 (m, 4H, *m*-CH Ph), 7.34 (m, 2H, *p*-CH Ph), 7.82 (m, 4H, *o*-CH Ph), 7.94 (m, 2H, CH flu); $^7Li\{^1H\}$ NMR (233 MHz, THF-d_8, 25 °C): $\delta = 0.6$ (s); $^{13}C\{^1H\}$ NMR (151 MHz, THF-d_8, 25 °C): $\delta = -1.4$ (d, $^1J_{C,p} = 37.2$ Hz, 1C, PCH_2Li), 46.2 (s, 4C, CH_3 tmeda), 58.9 (s, 2C, CH_2 tmeda), 68.1 (overlaps with solvent residual signal, 1 C, PCC_2), 113.0 (s, 2C, CH flu), 117.6 (s, 2C, CH flu), 119.1 (s, 2C, CH flu), 121.4 (s, 2C, CH flu), 128.4 (d, $^3J_{C,p} = 10.1$ Hz, 4C, *m*-CH Ph), 129.1 (d, $^3J_{C,p} = 12.3$ Hz, 2C, PCC_2), 130.1 (s, 2C, *p*-CH Ph), 133.2 (d, $^2J_{C,p} = 10.9$ Hz, 4C, *o*-CH Ph), 139.6 (d, $^1J_{C,p} = 75.0$ Hz, 2C, *i*-C Ph), 141.9 (d, $^2J_{C,p} = 14.3$ Hz, 2C, C flu); $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 25 °C): $\delta = 18.7$ (s).

4.4.2. Analytical data of 4·*n*Et_2O. ^1H NMR (400 MHz, C_6D_6): $\delta = 0.51$ (d, $^2J_{H,p} = 8.9$ Hz, 2H, PCH_2Li), 1.12 (t, $^3J = 7.0$ Hz, CH_3 Et_2O), 1.33 (br, 16H, $CH_3 + CH_2$ tmeda), 3.27 (q, $^3J = 7.0$ Hz, CH_2, Et_2O), 6.94–7.03 (m, 2H, CH), 7.05–7.14 (m, 6H, CH), 7.20 (m, 4H, CH flu), 7.87–8.05 (m, 4H, CH Ph), 7.24–7.17 (m, 4H), 8.48–8.54 (m, 2H, CH flu); $^{13}C\{^1H\}$ NMR (151 MHz, THF-d_8, 25 °C): $\delta = -3.0$ (d, $^1J_{C,P} \approx 44$ Hz, 1C, PCH_2Li), 15.6 (s CH_3 Et_2O), 45.0 (s, 4C, CH_3 tmeda), 56.3 (s, 2C, CH_2 tmeda), 67.7 (d, $^1J_{C,p} = 129.5$ Hz, 1 C, PCC_2), 114.5 (s, 2C, CH flu), 115.5 (s, 2C, CH flu), 120.4 (s, 2C, CH flu), 123.2 (s, 2C, CH flu), 128.4 (d, $^3J_{C,p} = 10.8$ Hz, 4C, *m*-CH Ph), 129.7 (d, $^3J_{C,p} = 12.1$ Hz, 2C, PCC_2), 130.3 (d, $^4J_{C,p} = 2.6$ Hz, 2C, *p*-CH Ph), 132.6 (d, $^2J_{C,p} = 10.0$ Hz, 4C, *o*-CH Ph), 137.1 (d, $^1J_{C,p} = 72.2$ Hz, 2C, *i*-C Ph), 140.4 (d, $^2J_{C,p} = 13.7$ Hz, 2C, C flu); $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 25 °C): $\delta = 13.4$ (s).

4.5. *Synthesis of [Li{CH_2PPh_2(flu)}(pmdta)] (5)*

[Li{CH_2PPh_2(flu)}(tmeda)] (110.4 mg, 0.22 mmol) was suspended in toluene (5 mL) and THF (1 mL). Pmdta (0.50 mL, 2.39 mmol) was added via a syringe to the suspension while stirring at ambient temperature. Afterward, THF (3 mL) was added to the stirred yellow suspension until the yellow solid was dissolved. The obtained yellow solution was reduced to a volume of 4 mL and stored overnight at −20 °C. Afterward, a small amount of **3** (bright yellow crystals) was removed by filtration. Further reduction of the volume of the mother liquor to 1.5–2 mL and storage at 5 °C overnight resulted in crystallization of an orange yellow solid. These crystals with composition **5**·0.5 toluene were isolated by decantation, rapidly washed with toluene (2 mL) and dried in vacuum afterward. Prolonged drying led to partial loss of incorporated toluene. Yield: 66 mg (0.11 mmol, 49.3%).

Anal. Calcd for [Li{CH2PPh2(flu)}(pmdta)]·0.5toluene (%): C 78.41, H 8.03, N 7.13; Found C 77.61, H 7.78, N 7.20; ^1H NMR (300 MHz, THF-d_8, 25 °C): $\delta = 0.24$ (d, $^2J_{H,p} = 12.0$ Hz, 2H, PCH_2Li), 2.10 (s, 12H, CH_3 pmdta), 2.20 (s, 3H, CH_3, pmdta), 2.25–2.34 (m, 5.5H, 2 × CH_2 pmdta + 0.5CH_3 toluene), 2.36–2.45 (m, 4H, CH_2 pmdta), 6.61 (m, 2H,

Table 1. Crystal data and refinement details for the X-ray structure determinations of **1**–**3** and **3a**–**5**.

Compound	**1**	**2**	**2a**	**3**
Formula	$C_{25}H_{19}P$	$C_{26}H_{22}P$, $CHCl_3$, I	$C_{26}H_{22}P$, I_3	$C_{52}H_{42}P_2$
fw (g mol^{-1})	350.37	611.67	746.11	728.80
T (°C)	−140(2)	−140(2)	−140(2)	−140(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\,2_1/n$	$P\,2_1/c$	$P\,2_1/n$	$P\,\bar{1}$
a (Å)	11.7065(2)	8.8601(1)	21.9923(4)	9.7188(9)
b (Å)	10.2244(2)	17.9612(3)	10.5807(2)	10.0431(7)
c (Å)	15.1952(3)	16.5671(3)	23.6759(4)	10.7480(9)
α (°)	90	90	90	93.102(5)
β (°)	93.864(1)	103.616(1)	109.032(1)	101.962(4)
γ (°)	90	90	90	110.492(5)
V (Å^3)	1814.61(6)	2562.36(7)	5208.08(16)	952.13(14)
Z	4	4	8	1
ρ (g cm^{-3})	1.282	1.586	1.903	1.271
μ (cm^{-1})	1.56	16.39	36.73	1.52
Measured data	12,256	15,513	36,753	5463
Data with $I > 2\sigma(I)$	3828	5561	10,499	3493
Unique data (R_{int})	4099/0.0220	5840/0.0173	11,853/0.0335	3856/0.0274
wR_2 (all data, on F^2) [a]	0.0886	0.0490	0.0576	0.1437
R_1 [$I > 2\sigma(I)$] [a]	0.0357	0.0208	0.0307	0.0532
S [b]	1.054	1.055	1.138	1.061
Res. dens./ (e Å^{-3})	0.303/−0.294	0.495/−0.576	0.703/−0.536	0.560/−0.394
Absorpt. method	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Absorpt. corr. $T_{min}/_{max}$	0.7126/0.7456	0.6867/0.7456	0.6311/0.7456	0.7145/0.7456
CCDC No.	1,057,334	1,057,335	1,057,310	1,057,311

Compound	**3a**	**4**	**5**
Formula	$C_{26}H_{21}P$, 0.5*$C_4H_{10}O_2$	$C_{32}H_{36}LiN_2P$	$C_{35}H_{43}LiN_3P$, 0.5*C_7H_8
fw (g mol^{-1})	409.46	486.54	589.70
T (°C)	−140(2)	−140(2)	−173(1)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\,\bar{1}$	$P\,21/c$	$P\,\bar{1}$
a (Å)	9.6368(3)	16.6877(2)	10.8672(3)
b (Å)	10.3941(4)	9.7869(1)	11.6016(4)
c (Å)	11.1641(5)	16.6877(3)	14.9434(6)
α (°)	79.533(2)	90	71.149(4)
β (°)	77.107(2)	99.261(1)	69.167(3)
γ (°)	83.095(2)	90	80.179(3)
V (Å^3)	1068.22(7)	2689.92(6)	1663.10(12)
Z	2	4	2
ρ (g cm^{-3})	1.273	1.201	1.178
μ (cm^{-1})	1.46	1.25	9.5
Measured data	6523	42,007	9624
Data with $I > 2\sigma(I)$	4230	5378	5258
Unique data (R_{int})	4778/0.0334	6190/0.0336	5973/0.0301
wR_2 (all data, on F^2)[a]	0.1689	0.1289	0.1043
R_1 [$I > 2\sigma(I)$][a]	0.0663	0.0523	0.0399
S[b]	1.132	1.044	1.026
Res. dens. (e Å^{-3})	0.444/−0.394	1.149/−0.620	0.347/−0.265
Absorpt. method	Multi-scan	Multi-scan	Multi-scan
Absorpt. corr. $T_{min}/_{max}$	0.6697/0.7456	0.7160/0.7456	0.9500/1.0000
CCDC No.	1057312	1057313	1057314

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$;
$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2]/3$.
[b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

CH flu), 6.68 (m, 2H, CH flu), 6.79 (m, 2H, CH flu), 7.04–7.24 (m, CH toluene), 7.24–7.38 (m, 6H, *m*-CH + *p*-CH Ph), 7.81 (m, 4H, *o*-CH Ph), 7.94 (m, 2H, CH flu); $^{13}C\{^1H\}$ NMR (75.48 MHz, THF-d_8, 25 °C): $\delta = -1.4$ (d, $^1J_{C,p} = 36.9$ Hz, 1C, PCH_2Li), 21.5 (s, CH_3 toluene), 43.6 (s, 1C, CH_3 pmdta), 46.2 (s, 4C, CH_3 pmdta), 57.0 (s, 2C, CH_2 pmdta), 58.0 (s, 2C, CH_2 pmdta), 113.0 (s, 2C, CH flu), 117.6 (s, 2C, CH flu), 119.2 (s, 2C, CH flu), 121.4 (s, 2C, CH flu), 126.0 (s, *p*-CH toluene), 128.4 (d, $^3J_{C,p} = 10.6$ Hz, 4C, *m*-CH Ph), 128.9 (s, *m*-CH toluene), 129.1 (d, $^3J_{C,p} = 57.4$ Hz, 2C, PCC_2), 129.7 (s, *o*-CH toluene), 130.1 (d, $^4J_{C,p} = 2.6$ Hz, 2C, *p*-CH Ph), 133.2 (d, $^2J_{C,p} = 9.7$ Hz, 4C, *o*-CH Ph), 139.6 (d, $^1J_{C,p} = 74.7$ Hz, 2C, *i*-C Ph), 142.0 (d, $^2J_{C,p} = 14.1$ Hz, 2C, C flu) (the *i*-C carbon atom of the co-crystallized toluene was not observed); $^{31}P\{^1H\}$ NMR (121 MHz, THF-d_8, 25 °C): $\delta = 18.6$ (s).

4.6. *Structure determinations*

The intensity data for **1**–**4** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans [20, 21]. The crystallographic data of **5** were collected on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer with monochromated Cu-Kα radiation (1.5418 Å). Absorption corrections were applied using CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (multi-scan).

The structures of **1**–**4** were solved by Direct methods (SHELXS [23]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [23]). The structure of **5** was solved by Direct Methods using Olex2 [24] with the ShelXT [25] structure solution program. Refinement was done with the ShelXL [23] refinement package using least squares minimization.

The hydrogens of **1**, **2**, **3**, **3a**, and **4** (with exception of the methyl group at C29, and methylene groups C27 and C28) at carbon C1A, C1B, C14A, and C14B of **2a** and at carbon C14 of **5** were located by difference Fourier synthesis and refined isotropically. All other hydrogens were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms of **1**–**4** were refined anisotropically [23]. In the case of **5**, the pmdta ligand as well as the fluorenylidene substituent showed positional disorder. A disorder model was therefore included. Some carbons of the less occupied site (site-occupancy factor constrained to 0.25) were only refined isotropically, all other non-hydrogen atoms were refined anisotropically.

A summary of cell parameters, data collection, structure solution, and refinement is given in table 1.

Supporting information

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC-1057334 for **1**, CCDC-1057310 for **2**, CCDC-1057335 for **2a**, CCDC-1057311 for **3**, CCDC-1057312 for **3a**, CCDC-1057313for **4**, and CCDC-1057314 for **5**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Email: deposit@ccdc.cam.ac.uk].

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Disclosure statement

No potential conflict of interest was reported by the authors.

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