Structures, dynamic behaviour, and reactivity of *P*-cyclopentadienyl-substituted 1,3,2-diazaphospholenes

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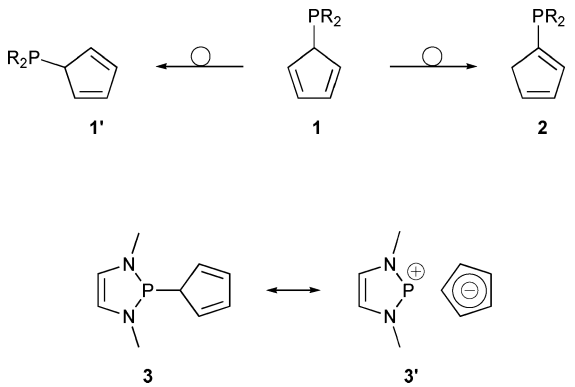
P-Cyclopentadienyl-substituted 1,3,2-diazaphospholenes were prepared by salt metathesis from NaCp or LiCp* and 2-chloro-1,3,2-diazaphospholenes. Comprehensive spectroscopic and X-ray diffraction studies revealed a significant lengthening of the phosphorus–carbon bonds as compared with typical P–C bond distances, and the presence of fluxional molecular structures in solution and solid state as a consequence of circumambulatory migration of the diazaphospholene moiety around the Cp-ring. The P–C bond lengthening is accompanied by the capability to react with transition metal complexes under P–C bond activation and cyclopentadienyl transfer. At the same time, 2-Cp-diazaphospholenes react with strong bases under deprotonation to afford a phosphinyl–cyclopentadienide anion that reacts further with $FeCl_2$ to a 1,1′-bisphosphinyl–ferrocene. The ambivalent behaviour of the diazaphospholenes offers interesting prospects to develop new synthetic methods for functional cyclopentadienyl complexes.

Introduction

The cyclopentadienyl (Cp) group is a versatile spectator ligand in complexes of transition metals, lanthanides, and actinides, and was also successfully introduced as a substituent into the chemistry of main-group elements.[1] The resulting compounds display a remarkable structural and electronic diversity as the cyclopentadienyl can act as a pure σ-donor (η^1-ligation mode) or a combined σ/π-donor (η^2-, η^3- or η^5-coordination). The η^1-bonded Cp groups frequently display fluxional behaviour as a consequence of degenerate intramolecular [1,5]-migration of the main-group moiety around the Cp ring ("circumambulatory rearrangement"). Alternatively, a non-degenerate [1,5]-shift of a hydrogen atom may occur (Scheme 1).[2]



Scheme 1

In the course of the investigation of cyclopentadienyls of main-group elements, several σ^3,λ^3-phosphines (Scheme 1) were synthesised and studies on their structure and dynamic behaviour carried out. Derivatives with dialkyl or diaryl phosphinyl moieties exist normally as vinylic isomers **2** and undergo no intramolecular dynamic processes at normal temperature.[3,4] Allylic structures **1** were observed for cyclopentadienyl phosphines with fluorine,[5] hydrogen, chlorine[6] or alkoxy substituents[7] at phosphorus, although most of these compounds exhibit very low thermal stability and decompose either at room temperature to give undefined products (R = H, F, Cl)[5,6] or rearrange slowly to a vinylic isomer **2** ($R_2 = (OCH_2)_2CMe_2$).[7] Still, a degenerate [1,5]-migration of the phosphinyl group (interconversion between **1** and **1′**) was detected at room temperature for $CpP(OCH_2)_2$ and $CpPF_2$.[5,7] The dioxophospholane $CpP(OCH_2)_2$ is sufficiently stable to be isolated as the allylic isomer but dimerises at 65 °C in an intermolecular Diels–Alder reaction rather than rearranging *via* hydrogen shift to a vinylic isomer **2**.[7]

The formal replacement of the cyclopentadienyl hydrogen atoms by methyl groups leads to pentamethylcyclopentadienyl (Cp*) σ^3,λ^3-phosphines. As these species lack a possibility to undergo [1,5]-hydrogen-shifts and rearrange to isomer **2**, the [1,5]-sigmatropic shift of the phosphinyl group is the only observable dynamic process.[9] The activation barrier for this process is determined by the substituents on the phosphorus atom:[8] electronegative halides or five membered ring systems with two directly attached oxygen, sulfur or nitrogen atoms which tend to stabilise the migrating phosphenium cation decrease the activation energy.

We have recently shown that 2-hydrido- and 2-phosphinyl-1,3,2-diazaphospholenes feature polarised P–H and P–P bonds, respectively.[11] The reasons for this effect are intimately related to the high stability of the diazaphospholenium cation and have been discussed elsewhere.[12] Applying the same concept to 2-Cp-1,3,2-diazaphospholenes leads to a description of the bonding in terms of bond/no-bond resonance between the canonical structures **3**, **3′**

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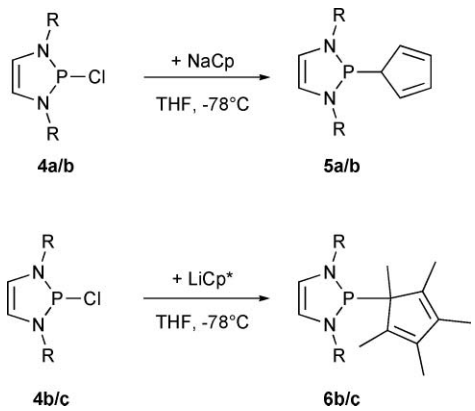
(Scheme 1). The high diazaphospholenium cation stability implies then an energetic stabilization, and thus an increased weight, for the ionic structure **3′**. As a consequence, one would expect not only a low activation barrier for circumambulatory migration of the 1,3,2-diazaphospholene fragment but also increased polarity of the exocylic phosphorus–carbon bond as compared to a "*normal*" PC-single bond which should in turn lead to enhanced chemical reactivity.

As, to the best of our knowledge, no Cp-substituted diaminophosphines and only a few examples of Cp*-substituted derivatives are known,[9,10] we set out to synthesise Cp- and Cp*-functionalised 1,3,2-diazaphospholenes, and to obtain experimental verification of the hypotheses outlined above from the results of spectroscopic, structural, and chemical reactivity studies.

Results and discussion

Syntheses

Salt metathesis of the 2-chloro-1,3,2-diazaphospholenes **4a–c** with sodium cyclopentadienide (NaCp) or lithium pentamethyl cyclopentadienide (LiCp*) in THF at −78 °C gave the *P*-Cp- or Cp*-diazaphospholenes **5a**,**b** and **6b**,**c**, respectively (Scheme 2). The crude products were purified by evaporation of the solvent, dissolving the residue in *n*-hexane, filtering off the insoluble part, and crystallisation at low temperature. Pure compounds were isolated as white to pale brown, air and moisture sensitive powders in yields from 78 to 85%.



Scheme 2 Synthesis of Cp- and Cp*-substituted 1,3,2-diazaphospholenes (**4**/**5a**: R = 2,6-iPr$_2$-C$_6$H$_3$; **4**–**6b**: R = Mes; **4**/**6c**: R = 2,6-Me$_2$C$_6$H$_3$, Dmp).

Spectroscopic studies

The room temperature ^{31}P NMR spectra of **5a** and **5b** display signals at 108.5 and 100.9 ppm whereas the signals of the Cp*-derivatives **6b** and **6c** are shifted to lower field and appear at 128.5 and 127.9 ppm. All ^{1}H- and ^{13}C NMR spectra show a single set of resonances for the hydrogen and carbon atoms of all CH and CCH$_3$ moieties in the Cp- and Cp*-substituents, indicating the occurrence of rapid dynamic exchange on the NMR time scale. The observation of a $^{2}J_{PH}$ coupling of 2 Hz for the signal of the Cp-protons of **5a**,**b** suggests further that this process is strictly intramolecular.

To gain deeper insight into the dynamic behaviour, variable temperature NMR studies of **5a** were carried out. However, ^{1}H and ^{13}C spectra recorded at the lowest accessible temperature (193 K) revealed only minor temperature induced shifts of the signals of the hydrogen and carbon atoms in the Cp group, and the lack of any dynamically induced change of line shapes indicated clearly that the slow exchange regime was not reached. Considering that the activation barriers for intramolecular dynamic processes are often higher in the solid state than in solution,[13] we also studied the ^{13}C CP-MAS NMR spectra of solid **5a**. Even though the observation, as in solution, of a single resonance for all five ring carbon atoms over the accessible temperature range (Fig. 1a,b) proves that the fluxional behaviour persists at low temperature in the solid state, we were able to verify qualitatively the slowing down of this process with decreasing temperature. This was feasible by recording a ^{13}C CP-MAS spectrum with delayed acquisition which is normally used to distinguish signals of quaternary and protonated carbon atoms ("non-quaternary suppression").

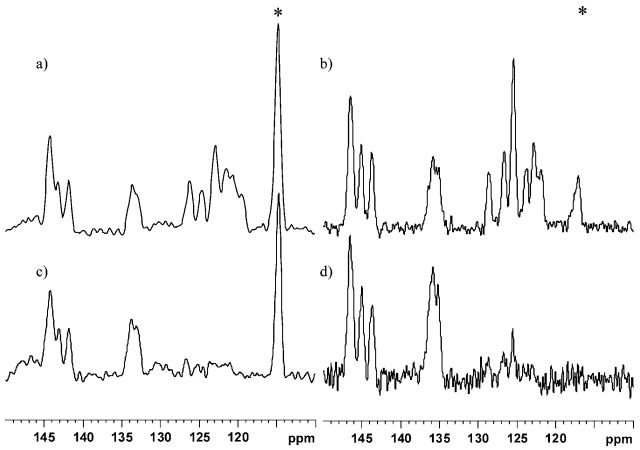


Fig. 1 Aromatic region of the CP-MAS ^{13}C NMR spectra of solid **5a** recorded with a normal CP pulse sequence (a,b) and a pre-acquisition delay to suppress non-quaternary carbons (c,d). The spectra on the left side (a,b) were recorded at ambient temperature and those on the right side (c,d) at 195 K. The signal attributable to the carbons in the Cp-substituent is marked with an asterisk.

The experiment is based on the fact that magnetisation of nuclei in CH and CH$_2$ moieties dephases rapidly under the influence of the large CH dipolar coupling and decays prior to acquisition whereas the signals of quaternary and methyl carbons survive as the dipolar interactions are smaller or are scaled by motional averaging introduced by methyl group rotation. In the case of **5a**, the signal of the Cp ring carbon atoms remains visible when the spectrum is recorded at ambient temperature (Fig. 1c) where rapid rotation of the Cp-ring induces a sizeable scaling of the CH dipolar interaction, and vanishes at low temperature where the fluxional process slows down and the effective dipolar interaction increases accordingly (Fig. 1d).

Room temperature solution NMR spectra of **6c** display likewise a single set of resonances for the methyl groups (δ^{1}H = 1.61, δ^{13}C = 11.8) and ring carbon atoms (δ^{13}C = 134.9) of the Cp* moiety. Cooling to 233 K induces broadening of the ^{1}H and likewise the ^{31}P NMR signals while the chemical shifts remain nearly unchanged. Further cooling to 193 K goes along with decoalescence of the ^{31}P

NMR signal into an intense singlet at 128.9 ppm and a second, slightly broadened one at 103.1 ppm. The ^{1}H NMR spectrum displays likewise two sets of signals (Fig. 2) attributable to two different species which can be assigned from examination of ^{1}H EXSY and ^{1}H,^{31}P HMQC spectra. Integration of the well separated signals in the olefinic region was used to determine the molar ratio of both species as 2 : 5. The more abundant isomer exhibits according to this analysis five different signals for methyl groups in the Cp* and four for those in the aryl substituents, and two signals of olefinic protons in the diazaphospholene unit. The less abundant isomer displays one set of resonances each for the methyls at the Cp* and aryl rings and one signal for the olefinic protons.

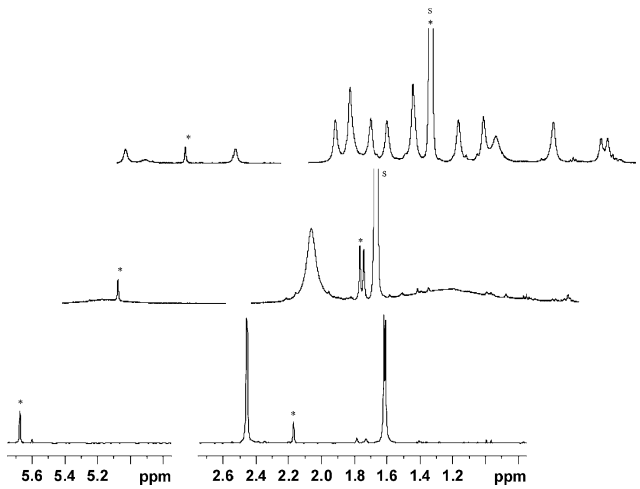
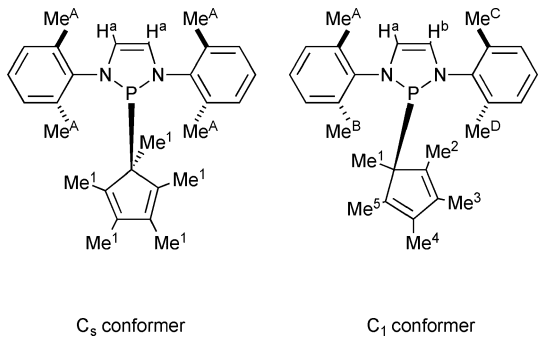


Fig. 2 Expansions of ^{1}H NMR spectra of **6c** at 303 K (bottom, in C_6D_6), 233 K (middle, in d_8-toluene) and at 193 K (top, in d_8-toluene). Labelled signals are due to solvents (s) or impurities (*).

Based on the number of observable signals we assign the abundant species as a rotational conformer with C_1 symmetry that displays a fixed *gauche*-orientation of the two five-membered rings at the central P–C bond (Scheme 3). The second isomer is attributed to a C_s symmetric conformer with a presumed transoid arrangement of the five-membered rings. The occurrence of both species can be ascribed to restriction of the free rotation of the Cp* substituents around the P–C bond whereas the splitting of the signals of the Cp* and Dmp groups in the major isomer is attributable to restricted rotation of the aryl rings around the C–N bonds and the slowing down of the [1,5]-sigmatropic migration of the phosphinyl group around the Cp* ring. Owing to the complexity of the dynamic processes and incomplete knowledge of spectral parameters in the slow-exchange regime (it remains unclear if the failure to resolve signals of methyl groups in different position of the Cp* ring depends on a failure to reach the slow-exchange regime or to the accidental near-degeneracy of chemical shifts) no quantitative assessment of activation parameters for the individual motional processes was attempted.



Scheme 3 Two rotamers of **6c** observed in solution at 193 K. The labels denote anisochronic hydrogen atoms at the diazaphospholene ring (H^a–H^b), and CH_3 groups in Dmp (Me^A–Me^D) and Cp* (Me^1–Me^5) substituents, respectively.

Even if the precise energetics of the Cp migration in **5a**,**b** remain unknown, the lack of evidence for a non-degenerate isomerisation to a vinylic isomer and the failure to freeze out the dynamics at low temperature suggest that the energy of the allylic isomer is much lower than that of the vinylic isomer, and that [1,5]-PR_2 shifts require significantly lower activation energy than [1,5]-H shifts. This is in accord with the high cation stability of a diazaphospholenium unit which should favour the circumambulatory rearrangement.[8] In this respect, **5a**,**b** differ from the thermally unstable species $CpPF_2$[5] and $CpP(OCH_2)_2$[7] which are the only phosphines showing a similar dynamic behaviour, and resemble more closely the cyclopentadienyls of heavier main group elements.[2] The dynamic behaviour of **6a**,**c** compares better with that of other known Cp* substituted phosphines.[2] The observation of spectra in the slow exchange regime at low temperature suggests that the [1,5]-PR_2 shift occurs in this case less facile, presumably as a consequence of steric interlocking of the bulky Cp* and *N*-aryl substituents.

Crystal structures

Suitable crystals for single-crystal X-ray diffraction studies of **5a** and **6b** were grown from *n*-hexane at −20 °C.

Crystalline **5a** (Fig. 3) contains discrete molecules that show no interaction with each other and the co-crystallised solvent (one molecule THF per formula unit). The diazaphospholene

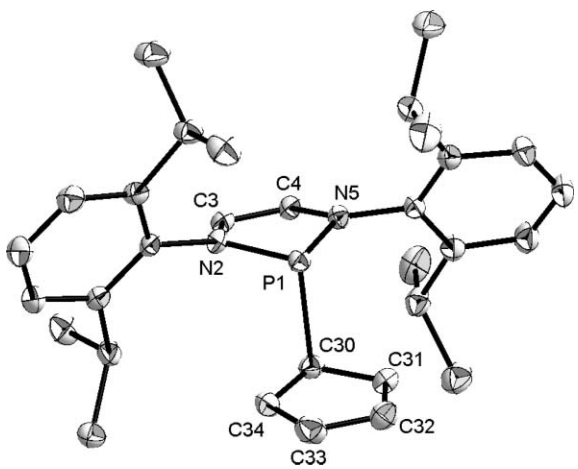


Fig. 3 Molecular structure of **5a**. Thermal ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°). P1–N1 1.715(2), P1–N5 1.724(2), P1–C30 1.949(2), N2–C3 1.413(2), N5–C4 1.414(2), C3–C4 1.332(3), C30–C31 1.472(3), C30–C34 1.472(3), C31–C32 1.356(3), C32–C33 1.438(3), C33–C34 1.346(3); N2–P1–N5 88.8(1), N2–P1–C30 101.8(1), N5–P1–C30 101.1(1).

ring exhibits a flat envelope conformation and adopts a transoid orientation relative to the planar Cp ring. The P–N, N–C, and C–C bond lengths compare with those in known *P*-hydrido- or *P*-phosphinyl-1,3,2-diazaphospholenes.[11] The C–C bonds in the Cp ring display the typical alternating pattern of a 1,3-diene system with similar distances as in solid cyclopentadiene.[15] All features together with the tetrahedral geometry at the C30 carbon atom support the proposed ground state structure of **5a** with an η^1-bound Cp ring that carries the PR_2 substituent in an allylic position.

A particularly remarkable aspect is the long exocyclic P1–C30 distance of 1.949(2) Å which compares with an average PC bond length in σ^3,λ^3-phosphines of 1.86 ± 0.03 Å[14] and is even longer than the corresponding bond in the only other structurally characterised cyclopentadienyl phosphine, $CpP(OCH_2)_2$ (PC 1.892(3) Å[7]). This effect is in accord with the prediction that the lower electrophilicity of a 1,3,2-diazaphospholenium as compared to a dioxaphospholenium cation[12] increases the weight of the ionic resonance structure **3′** in the bonding description outlined in Scheme 1 and thereby implies a lengthening of the exocyclic phosphorus–carbon bond.[11]

The crystal structure study of **6b** (Fig. 4) was carried out at 293 K as the crystals were found to undergo a phase transition upon cooling. This phenomenon was not studied in detail. The crystals contain discrete molecules of **6b** which differ from that of **5a** in showing a distinct *gauche* arrangement of the Cp and diazaphospholene rings relative to the central P–C bond. This distortion leads to a distinct pyramidalisation at N5 (sum of angles 350.5°) due to enhanced steric interaction between the methyl group at C24 of the Cp*-ring and the mesityl substituent at N5. The coordination geometry at the second nitrogen atom N2 remains planar (sum of angles 359.9°). The P–N, N–C, and C–C bond lengths in the diazaphospholene and the C–C single and double bond lengths in the Cp* ring resemble those in **5a**. Moreover, the latter are comparable to those in other Cp*-substituted phosphines.[16] The exocyclic P1–C24 bond (1.917(2) Å) in **6b** is still longer than a typical PC single bond although still shorter than in **5a**. This trend can be explained by considering that the additional methyl groups render the Cp* ligand a better nucleophile and increase thereby its interaction with the diazaphospholene fragment, leading to a concomitant PC bond shortening.

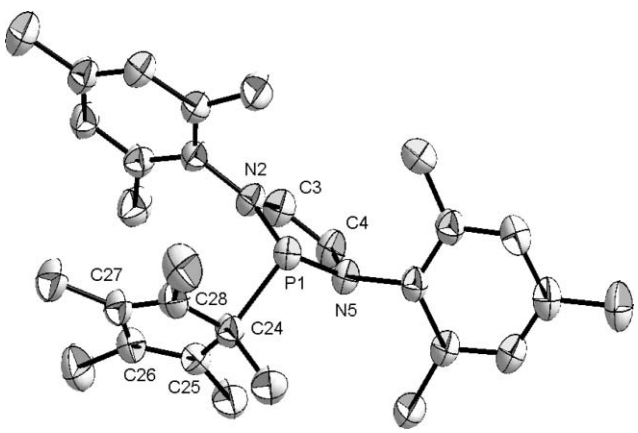
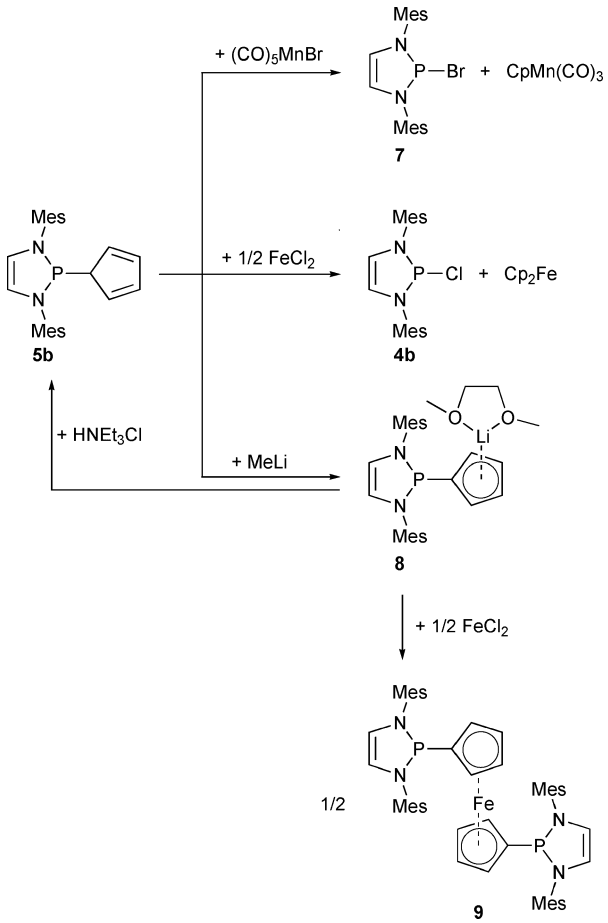


Fig. 4 Molecular structure of **6b**. Thermal ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°). P1–N2 1.738(2), P1–N5 1.720(2), P1–C24 1.917(2), N2–C3 1.406(3), N5–C4 1.418(2), C3–C4 1.319(3), C24–C25 1.497(3), C24–C28 1.512(3), C25–C26 1.346(3), C26–C27 1.458(3), C27–C28 1.339(3); N2–P1–N5 90.2(1), N2–P1–C24 105.1(1), N5–P1–C24 107.3(1).

Reactivity

The lengthening of the exocyclic phosphorus–carbon bonds in **5a** and **6b** is in accord with the postulated bond polarisation and weakening and leads to expect enhanced reactivity. In fact it was found that **5b** reacted with an equimolar amount of $Mn(CO)_5Br$ at room temperature *via* P–C/Mn–Br metathesis to yield the 2-bromo-diazaphospholene **7** and $CpMn(CO)_3$. Likewise, reaction with 1/2 equivalent of $FeCl_2$ gave **4b** and Cp_2Fe (Scheme 4). All products were identified by their ^1H and **4b** and **6b** also by their ^{31}P NMR data.[17,18]



Scheme 4

In order to establish if **5b** allows also the expected formation of a phosphinyl-substituted cylopentadienide anion *via* CH deprotonation[21] we further studied its reactivity toward methyllithium in DME at −78 °C. It was found that the reaction proceeded selectively to yield a single product with a ^{31}P NMR signal at 85.7 ppm that was isolated as colourless crystals by cooling a concentrated reaction mixture to 4 °C and identified by spectroscopic data and an X-ray diffraction study as the lithium cyclopentadienide **8** (Scheme 4). The ^1H and ^{13}C NMR

spectra display separate signals for the individual carbon and proton environments in the Cp substituent which indicate that the molecular structure is no longer fluxional.

The results of the X-ray diffraction study of **8** (Fig. 5) discloses the presence of isolated molecules without any intermolecular interactions. The lithium cation is coordinated by the carbon atoms of the η^5-bound cyclopentadienide unit (Li–C 2.24 to 2.32 Å) and the oxygen atoms of one molecule of DME. The C–C bonds in the Cp ring (C–C 1.38 and 1.43 Å) match those in other lithium cyclopentadienides[22] and display the typical bond equalisation of an aromatic π-system. The P–N bonds in the diazaphospholene ring are slightly longer than in **5a** and the N–C and C–C bonds have almost the same values. Quite striking, however, is the shortening of the P1–C24 bond (1.787(2) Å) in **8** by some 15 pm as compared to the P1–C30 bond in **5a** (1.949(2) Å). The observed distance compares well to a normal single bond (1.80 ± 0.03 Å[14]), thus indicating that the loss of hyperconjugation interactions with the π-system implies a substantial bond strengthening effect.

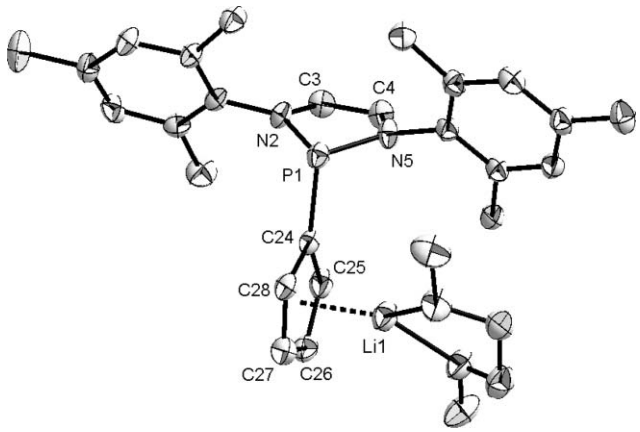


Fig. 5 Molecular structure of **8**. Thermal ellipsoids are drawn at 50% probability level and H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°). P1–N2 1.747(2), P1–N5 1.733(2), P1–C24 1.787(2), N2–C3 1.402(3), N5–C4 1.412(3), C3–C4 1.330(3), C24–C25 1.432(3), C24–C28 1.421(3), C25–C26, 1.381(3), C26–C27 1.404(4), C27–C28 1.392(3), C24–Li1 2.275(5), C25–Li1 2.302(5), C26–Li1 2.321(5), C27–Li1 2.283(5), C28–Li1 2.244(5), Z_{cp}–Li1 1.947(5); N2–P1–N5 87.6(1), N2–P1–C24 105.4(1), N5–P1–C24 105.2(1).

Whereas treatment of **8** with triethylamine hydrochloride lead to complete recovery of **5b** which was identified by ^{1}H and ^{31}P NMR data, reaction with half an equivalent of anhydrous iron dichloride yielded a new product the ^{31}P NMR signal of which displayed a slight deshielding (δ = 87.9) as compared to **8**. The product was isolated after work-up as a violet powder and identified by analytical and spectroscopic data as the 1,1′-bis-diazaphospholenyl ferrocene **9** (Scheme 4).

The observed reaction pattern suggests that **5b** behaves as a versatile reagent which permits, depending on the reaction conditions, either the transfer of a cyclopentadienyl fragment under similar conditions as metal cyclopentadienides[19] or stannyl cyclopentadienes[20] or, alternatively, of a phosphine-substituted cyclopentadienyl unit. This process allows the accomplishment, in one step, of the synthesis of novel metal cyclopentadienides with functional phosphine substituents. It can be expected that both reactions are more widely applicable and that combination of both processes permits the development of a novel synthetic methodology *e.g.* to access multiply substituted cyclopentadienyl complexes.

Conclusions

We have shown that thermally highly stable *P*-cyclopentadienyl-substituted 1,3,2-diazaphospholenes are easily accessible *via* salt elimination from *P*-chloro diazaphospholenes and metal cyclopentadienides. The products display fluxional molecular structures in solution and solid state. The experimental data suggest that the cyclopentadienyl migration proceeds preferably *via* reversible [1,5]-PR_2-shifts; no evidence for the occurrence of [1,5]-H-shifts was obtained. These effects, which are in accord with the high cation stability of the PR_2 fragment, are accompanied by a weakening of the P–C bonds which is further substantiated by the results of X-ray diffraction studies. The hypothesis that these results imply an increased activity of Cp diazaphospholenes in bond metathesis processes was proven by cyclopentadienide transfer reactions with transition metal halides. Moreover, deprotonation of a cyclopentadienyl diazaphospholene to give a stable phosphinyl–cyclopentadienide anion and further conversion of the latter to a bis-phosphinyl substituted ferrocene was demonstrated. The purposeful synthesis of both ferrocene and a 1,1′-bisphosphinyl ferrocene from the same starting material proves that precise control of the reactivity of these compounds is feasible and may offer interesting prospects for new developments in the synthetic chemistry of cyclopentadienyl compounds.

Experimental

General considerations

All manipulations were carried out under protective gas atmosphere (Ar) and in flame dried glassware. Solvents were dried prior to use by means of common procedures. **4a–c**[11b] and LiCp*[23] were synthesised according to literature procedures. All other chemicals were purchased from commercial suppliers. NMR Spectra (at 303 K if not specified otherwise): Bruker Avance 400 (^{1}H: 400.13 MHz, ^{31}P: 161.9 MHz, ^{13}C: 100.4 MHz) at 30 °C; chemical shifts referred to external TMS (^{1}H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P); positive signs of chemical shifts denote shifts to lower frequencies; coupling constants are given as absolute values; prefixes *i*-, *o*-, *m*-, *p*- denote atoms of aryl-substituents. CP-MAS NMR spectra of solids were recorded in 4 mm rotors using spinning speeds between 4 and 10 kHz. MS: Varian MAT 711, EI, 70 eV. Elemental analysis: Perkin Elmer 2400CHSN/O Analyser. Melting points were determined in sealed capillaries.

Preparations

Synthesis of 5a. NaCp (1 mL of a 2 M solution in THF, 2 mmol) was added at −78 °C to a stirred solution of **4a** (0.88 g, 2 mmol) in THF (30 ml). The reaction mixture was slowly warmed to room temperature and stirred for 1 h. The solvent was evaporated in vacuum, the residue dissolved in n-hexane (20 ml), and filtered. Storage of the filtrate at −20 °C produced pale yellow crystals of **5a**. Yield: 0.77 g (82%), mp 121 °C. ^{1}H NMR (C_6D_6)

δ = 7.20 to 7.10 (m, 6H, C*H*), 6.10 (s, 2H, N–C*H*), 6.06 (d, 5H, $^2J_{PH}$ = 2.2 Hz, C_5H_5), 3.76 (dsep, 4H, $^3J_{HH}$ = 6.8 Hz, $^5J_{PH}$ = 1.7 Hz, C*H*(CH_3)$_2$), 1.36 (d, 12, $^3J_{HH}$ = 6.8 Hz, CH_3), 1.20 (d, 12, $^3J_{HH}$ = 6.8 Hz, CH_3). ^{1}H NMR (C_7D_8, 193 K) δ = 6.97 to 6.89 (m, 6H, C*H*), 6.06 (s, 2H, N–C*H*), 5.99 (d, 5H, C_5H_5), 3.73 (sep, 4H, $^3J_{HH}$ = 6.3 Hz, C*H*(CH_3)$_2$), 1.31 (d, 12, $^3J_{HH}$ = 6.0 Hz, CH_3), 1.15 (d, 12, $^3J_{HH}$ = 5.7 Hz, CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ = 145.6 (d, $^3J_{PC}$ = 2.2 Hz, *o-C*), 135.6 (d, $^2J_{PC}$ = 9.5 Hz, i-*C*), 126.0 (d, $^5J_{PC}$ = 1.9 Hz, m-*C*H), 123.1 (d, $^4J_{PC}$ = 1.1 Hz, *p-C*H), 118.8 (d, $^2J_{PC}$ = 8.3 Hz, N–*C*H), 116.2 (d, $^1J_{PC}$ = 5.8 Hz, C_5H_5), 27.2 (d, $^4J_{PC}$ = 4.7 Hz, *C*H(CH_3)$_2$), 24.2 (s, *C*H_3), 23.9 (s, *C*H_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 108.5. ^{31}P{^{1}H} NMR (C_7D_8, 193 K) δ = 99.6. MS (EI, 70 eV, 375 K) *m/z* (%) = 472.3 ([M]$^+$, <1%), 407.3 ([M − C_5H_5]$^+$, 100%). Anal. Calcd for $C_{31}H_{41}N_2P$: C, 78.78, H, 8.74, N, 5.93. Found: C, 78.06, H, 8.67, N, 5.82%.

Synthesis of 5b. NaCp (1 mL of a 2 M solution in THF, 2 mmol) was added at −78 °C to a stirred solution of **4b** (0.72 g, 2 mmol) in THF (30 ml). The reaction mixture was slowly warmed to room temperature and stirred for 1 h. The solvent was evaporated in vacuum, the residue dissolved in n-hexane (20 ml), and the precipitate filtered off. Storage of the filtrate at −20 °C produced a precipitate of **5b** as a pale brown solid. Yield: 0.61 g (78%), mp 159 °C. ^{1}H NMR (C_6D_6) δ = 6.80 (s, 4H, *m*-C*H*), 6.04 (d, 5H, $^2J_{Ph}$ = 2.1 Hz, C_5H_5), 5.78 (d, 2H, $^3J_{PH}$ = 0.6 Hz, N–C*H*), 2.41(s, 12H, *o*-CH_3), 2.13 (s, 6H, *p*-CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ = 137.3 (d, $^2J_{PC}$ = 10.0 Hz, *i-C*), 135.8 (d, $^3J_{PC}$ = 2.5 Hz, *o-C*), 135.6 (d, $^4J_{PC}$ = 2.4 Hz, *m-C*), 130.3 (d, $^5J_{PC}$ = 1.5 Hz, *p-C*), 128.3 (s, C_5H_5), 118.1 (d, $^3J_{PC}$ = 8.1 Hz, N–*C*H), 20.8 (d, $^6J_{PC}$ = 0.9 Hz, *m*-CH_3), 19.5 (d, $^4J_{PC}$ = 5.3 Hz, *o*-CH_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 99.7. MS: (EI, 70 eV, 370 K) *m/z* (%) = 388.2 ([M]$^+$, 2%), 323.1 ([M − C_5H_5]$^+$, 100%). Anal. Calcd for $C_{25}H_{29}N_2P$: C, 77.29, H, 7.52, N, 7.21. Found C, 77.61, H, 7.63, N, 7.13%.

Synthesis of 6b. LiCp* (0.29 g, 2 mmol) dissolved in THF (10 ml) was slowly added to a stirred solution of **4b** (0.72 g, 2 mmol) in THF (30 ml) at −78 °C. The stirring was continued for 1 h. The mixture was then allowed to warm to room temperature and evaporated to dryness. The residue was dissolved in n-hexane (20 ml) and the precipitate removed by filtration. Crystallisation at −20 °C produced colourless crystals of **6b**. Yield: 0.57 g (62%), mp 133 °C. ^{1}H NMR (C_6D_6) δ = 6.77 (s, 4H, *m*-C*H*), 5.73 (s, 2H, N–C*H*), 2.48 (s, 12H, *o*-CH_3), 2.13 (s, 6H, *m*-CH_3), 1.66 (d, 15H, $^3J_{PH}$ = 2.3 Hz, CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ = 140.8 (d, $^2J_{PC}$ = 13.5 Hz, *i-C*), 135.0 (d, $^4J_{PC}$ = 1.3 Hz, *m-C*), 134.7 (d, $^3J_{PC}$ = 1.8 Hz, *o-C*), 130.6 (d, $^5J_{PC}$ = 1.0 Hz, *p-C*), 129.5 (s, broad, C_5Me_5), 120.1 (d, $^2J_{PC}$ = 7.1 Hz, *C*H), 21.1 (d, $^4J_{PC}$ = 9.4 Hz, *o*-CH_3), 21.1 (d, $^6J_{PC}$ = 0.5 Hz, *p*-CH_3), 12.2 (d, $^2J_{PC}$ = 6.1 Hz, *C*H_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 128.5. MS: (EI, 70 eV, 390 K) *m/z* (%) = 458.0 ([M]$^+$, 0.1), 323.1 ([M − $C_{10}H_{15}$]$^+$, 100.0), 135.2 ([M − $C_{20}H_{24}N_2P$]$^+$, 8.0). Anal. Calcd for $C_{30}H_{39}N_2P$: C, 78.57, H, 8.57, N, 6.11, Found: C, 77.95, H, 8.60, N, 6.04%.

Synthesis of 6c. LiCp* (0.29 g, 2 mmol) dissolved in THF (10 ml) was slowly added at −78 °C to a stirred solution of **4c** (0.66 g, 2 mmol) in THF (30 ml). The stirring was continued for 1 h, the mixture warmed to room temperature, and evaporated to dryness. The residue was dissolved in n-hexane (20 ml) and the precipitate removed by filtration. Storage of the filtrate at −20 °C produced **6c** as a colourless powder. Yield: 0.60 g (69%), mp 125 °C. ^{1}H NMR (C_6D_6) δ = 6.95 (m, 6H, *m/p*-C*H*), 5.67 (d, 2H, $^3J_{PH}$ = 0.6 Hz, N–C*H*), 2.46 (d, 12H, $^5J_{PH}$ = 1.3 Hz, *o*-CH_3), 1.61 (d, 15H, $^3J_{PH}$ = 2.6 Hz, CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ = 142.9 (d, $^2J_{PC}$ = 13.4 Hz, *i-C*), 137.6 (d, $^3J_{PC}$ = 15.9 Hz, *o-C*), 134.9 (d, $^1J_{PC}$ = 1.6 Hz, C_5Me_5), 129.6 (d, $^4J_{PC}$ = 1.0 Hz, *m-C*), 125.3 (d, $^5J_{PC}$ = 1.7 Hz, *p-C*), 119.5 (d, $^2J_{PC}$ = 6.9 Hz, N–*C*H), 20.8 (d, $^4J_{PC}$ = 9.4 Hz, *o-C*H_3), 11.8 (d, $^2J_{PC}$ = 6,3 Hz, *C*H_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 127.9. ^{31}P{^{1}H} NMR (C_7D_8, 193 K) δ = 129.8, 103.1. ^{1}H NMR (C_7D_8, 193 K): minor rotamer: δ = 6.97 to 6.66 (m, 6H, *m/p*-C*H*), 5.30 (s, broad, 2 H, N–C*H*), 2.49 (s, broad, 12 H, *o*-CH_3), 1.61 (s, broad, 15 H, CH_3); major rotamer: δ = 6.97 to 6.66 (m, 6 H, *m/p*-C*H*), 5.68 (s, 1 H, N–C*H*), 5.00 (s, 1 H, N–C*H*), 2.59 (s, 3 H, *o*-CH_3), 2.49 (s, 3 H, *o*-CH_3), 2.37 (s, 3 H, *o*-CH_3), 2.28 (s, 3 H, CH_3), 2.11 (s, 3 H, *o*-CH_3), 1.86 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 0.94 (d, 3 H, $^3J_{PH}$ = 15.5 Hz, CH_3).

Reaction of 5b with $FeCl_2$. **5b** (39 mg, 1 mmol) and $FeCl_2$ (7 mg, 0.5 mmol) were dissolved in C_6D_6 (0.5 ml). ^{1}H and ^{31}P NMR spectra revealed the quantitative formation of **4b** and ferrocene. **4b**: ^{1}H NMR (C_6D_6) δ = 6.71 (s, 4H, *m*-C*H*), 5.82 (s, 2H, N–C*H*), 2.37 (s, 12H, *o*-CH_3), 2.07 (s, 6H, *p*-CH_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 144.0. **$FeCp_2$**: ^{1}H NMR (C_6D_6) δ = 3.99 (s, 10 H).

Reaction of 5b with $Mn(CO)_5Br$. **5b** (39 mg, 1 mmol) and $Mn(CO)_5Br$ (55 mg, 1 mmol) were dissolved in C_6D_6 (0.5 ml). ^{1}H and ^{31}P NMR spectra revealed the quantitative formation of **7** and $CpMn(CO)_3$. **7**: ^{1}H NMR (C_6D_6) δ = 6.79 (s, 4H, *m*-C*H*), 5.78 (s, 2H, N–C*H*), 2.40 (s, 12H, *o*-CH_3), 2.12 (s, 6H, *p*-CH_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 175.2. **$CpMn(CO)_3$**: ^{1}H NMR (C_6D_6) δ = 6.01 (s, 5H).

Synthesis of 8. A solution of **5b** (0.72 g, 2 mmol) in DME (30 ml) was cooled to −78 °C and methyllithium (1.4 mL of a 1.4 M solution in THF, 2 mmol) added slowly while stirring. The reaction mixture was brought to room temperature and stirred for 1 h. The solvents were evaporated *in vacuo* and the residue dissolved in dimethoxyethane (10 ml). Crystallisation at 4 °C produced colourless crystals of **8**. Yield: 0.90 g (93%), mp 185 °C. ^{1}H NMR (C_6D_6) δ = 6.78 (s, 4H, *m*-C*H*), 6.71 (dt, 2H, $^{3/4}J_{HH}$ = 2.7 Hz, $^3J_{PH}$ = 3.8 Hz, 2-C*H*), 6.26 (dt, 2H, $^3J_{HH}$ = 2.7 Hz, $^4J_{PH}$ = 1.6 Hz, 3-C*H*), 5.94 (d, 2H, $^2J_{PH}$ = 1.7 Hz, N–C*H*), 2.96 (s, 4H, DME), 2.93 (s, 6H, DME), 2.55 (s, broad, 12H, *o*-CH_3), 2.13 (s, 6H, *p*-CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ = 140.4 (d, $^2J_{PC}$ = 14.3 Hz, *i-C*), 137.5 (s, broad, *o-C*), 133.7 (d, $^5J_{PC}$ = 2.0 Hz, *p-C*), 129.3 (d, $^4J_{PC}$ = 1.0 Hz, *m-C*H), 122.9 (d, $^1J_{PC}$ = 44.8 Hz, *C*), 116.8 (d, $^2J_{PC}$ = 6.0 Hz, N–*C*H), 111.3 (d, $^2J_{PC}$ = 24.6 Hz, *C*H), 107.0 (d, $^3J_{PC}$ = 7.5 Hz, *C*H), 69.1 (s, broad, CH_{2DME}), 58.7 (s, broad, CH_{3DME}), 20.7 (s, broad, *o*-CH_3), 19.7 (s, broad, *p*-CH_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 85.7. MS: (EI, 70 eV, 370 K) *m/z* (%) = 484.2 ([M]$^+$, 0.1), 323.2 ([M − $C_9H_{14}O_2Li$]$^+$, 11.6), 45.0 ([M − $C_{27}H_{33}N_2PLiO$]$^+$, 100.0). Anal. Calcd for $C_{29}H_{38}N_2PLiO_2$: C, 71.89, H, 7.91, N, 5.78, found: C, 70.82, H, 7.68, N, 5.82%.

Reaction of 8 with Et_3NHCl. **8** (48 mg, 0.1 mmol) and Et_3NHCl (12 mg, 0.1 mmol) were dissolved in C_6D_6 (0.5 ml). ^{1}H and ^{31}P NMR spectra revealed the quantitative formation of Et_3N and **5b**. **5b**: ^{1}H NMR (C_6D_6) δ = 6.80 (s, 4H, *m*-C*H*), 6.04 (d, 2 H, $^3J_{PH}$ = 1.6 Hz, N–C*H*), 3.11 (s, 5H, C_5H_5), 2.41 (s, 12H, *o*-CH_3), 2.13 (s, 6H, *p*-CH_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 99.7. **Et_3N**: ^{1}H NMR (C_6D_6) δ = 2.40 (q, 6H, $^3J_{HH}$ = 7.0 Hz, CH_2), 0.96 (t, 9H, $^3J_{HH}$ = 7.0 Hz, CH_3).

Synthesis of 9. **8** (0.97 g, 2 mmol) and $FeCl_2$ (0.13 g, 1 mmol) were dissolved in DME (30 ml) and stirred for 1 h. The solvents were evaporated *in vacuo*, the residue dissolved in n-hexane (30 ml) and the precipitate filtered off. The filtrated was concentrated to a volume of 5 mL and stored at 4 °C to produce violet crystals of **9**. Yield: 0.56 g (68%), mp 172 °C. ^{1}H NMR (C_6D_6) δ = 6.76 (s, broad, 8H, *m*-C*H*), 5.62 (t, 4H, $^3J_{PH}$ = 12 Hz, N–C*H*), 4.02 (t, 4H, $^3J_{HH}$ = 0.8 Hz, C*H*), 3.96 (t, 4H, $^3J_{HH}$ = 1.7 Hz, C*H*), 2.62 (s, broad, 24H, *o*-CH_3), 2.10 (s, 12H, *p*-CH_3). ^{13}C{^{1}H} NMR (C_6D_6) δ = 139.0 (s, *i*-*C*), 136.5 (s, broad, *o*-*C*), 134.9 (s, *p*-*C*), 130.1 (s, *m*-*C*H), 118.0 (t, $^2J_{PC}$ = 3.0 Hz, N–*C*H), 83.9 (dd, $^1J_{PC}$ = 62.0 Hz, $^3J_{PC}$ = 1.7 Hz, *C*H), 71.8 (t, $^{2/3}J_{PC}$ = 13.5 Hz, *C*H), 71.2 (t, $^{3/4}J_{PC}$ = 2.4 Hz, *C*H), 20.9 (s, *m*-*C*H_3), 19.9 (s, broad, *o*-*C*H_3). ^{31}P{^{1}H} NMR (C_6D_6) δ = 87.9. MS: (EI, 70 eV, 430 K) *m*/*z* (%) = 830.3 ([M]+, 2.0), 508.2 ([M − $C_{20}H_{23}N_2P$]$^+$, 24.0), 323.2 ([M − $C_{30}H_{32}N_2PFe$]$^+$, 100.0). Anal. Calcd for $C_{50}H_{56}N_4P_2Fe$: C, 72.28, H, 6.79, N, 6.74, found: C, 72.08, H, 6.88, N, 6.51%.

Crystal structure studies

All single-crystal X-ray diffraction studies were carried out on a Nonius Kappa-CCD diffractometer at 123(2) K (**5a**, **8**) or 293(2) K (**6b**) using MoKα radiation (λ = 0.71073 Å). Direct methods (SHELXS-97[24]) were used for structure solution; full-matrix least-squares on F^2 (SHELXL-97,[25]) for refinement. No absorption corrections were applied, and H atoms were refined using a riding model.

5a. Yellow crystals, $C_{35}H_{49}N_2OP$ ($C_{31}H_{41}N_2P$·thf), M = 544.7, crystal size 0.60 × 0.50 × 0.40 mm, monoclinic, space group $P2_1/n$ (No. 14): a = 9.9003(2) Å, b = 18.4544(4) Å, c = 17.5559(4) Å, β = 98.506(1)°, V = 3172.2(1) Å^3, Z = 4, ρ(calcd) = 1.141 Mg m^{-3}, F(000) = 1184, μ = 0.115 mm^{-1}, 17886 reflexes (2 θ_{max} = 55°), 7035 unique [R_{int} = 0.028], 352 parameters, 36 restraints, $R1$ ($I > 2\sigma(I)$) = 0.056, $wR2$ (all data) = 0.180, largest diff. peak and hole 0.660 and −0.680 e Å^{-3}.

6b. Colourless crystals, $C_{30}H_{39}N_2P$, M = 458.6, crystal size 0.50 × 0.35 × 0.20 mm, triclinic, space group $P\bar{1}$ (No. 2): a = 9.9703(2) Å, b = 10.6255(3) Å, c = 13.7990(4) Å, α = 75.585(1)°, β = 85.812(1)°, γ = 69.263(1)°, V = 1323.9(1) Å^3, Z = 2, ρ(calcd) = 1.150 Mg m^{-3}, F(000) = 496, μ = 0.124 mm^{-1}, 6707 reflexes (2 θ_{max} = 50°), 4456 unique [R_{int} = 0.023], 308 parameters, $R1$ ($I > 2\sigma(I)$) = 0.044, $wR2$ (all data) = 0.122, largest diff. peak and hole 0.199 and −0.217 e Å^{-3}.

8. Colourless crystals, $C_{29}H_{38}LiN_2O_2P$, M = 484.5, crystal size 0.20 × 0.10 × 0.05 mm, monoclinic, space group $P2_1/n$ (No. 14): a = 8.5950(3) Å, b = 21.7213(8) Å, c = 14.6049(6) Å, β = 92.711(2)°, V = 2723.6(2) Å^3, Z = 4, ρ(calcd) = 1.182 Mg m^{-3}, F(000) = 1040, μ = 0.128 mm^{-1}, 12355 reflexes (2 θ_{max} = 56.5°), 4776 unique [R_{int} = 0.041], 322 parameters, $R1$ ($I > 2\sigma(I)$) = 0.050, $wR2$ = 0.114, largest diff. peak and hole 0.632 and −0.275 e Å^{-3}.

CCDC reference numbers 631100–631302.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702720f

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