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Insertion of phenyl isothiocyanate into a P–P bond of a nickel-substituted bicyclo[1.1.0]tetraphosphabutane†

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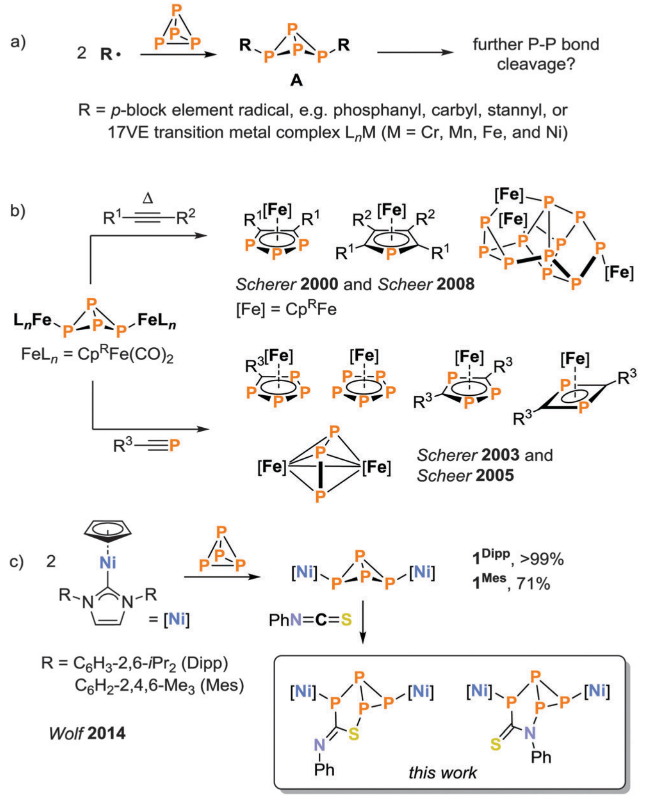
A new reaction mode for bicyclo[1.1.0]tetraphosphabutanes is reported. The C=S and C=N bonds of phenyl isothiocyanate reversibly insert into a P–P bond of [{CpNi(IMes)}$_2$(μ-η^1:η^1-P$_4$)] (1$^{\text{Mes}}$, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene), forming isomers 2a and 2b. X-ray crystallography and ^{31}P{^{1}H} NMR spectroscopy revealed similar bicyclo[3.1.0]heterohexane structures for these compounds.

Developing new, targeted and selective methods for the functionalisation of the P$_4$ molecule remains a topical challenge despite the extensive research efforts carried out in the past.[1,2] Recent reports have focused on the use of nucleophilic carbanions and carbenes,[3,4] insertion reactions of p-block elements, *e.g.* phosphenium cations[5] and the use of main group element or transition metal-based radicals.[6,7] The latter approach often gives rise to bicyclo[1.1.0]tetraphosphabutanes **A**, which may be seen as potential intermediates on the way to a stepwise P$_4$ degradation sequence (Scheme 1a). While various "P$_4$ butterfly" compounds of type **A** are known, it is interesting to note that their reactivity has only been explored to a small extent (Scheme 1b).[1,6–9] Previous studies mainly focused on iron complexes.[1d,7a,c,9–11] As reported by Scherer and Scheer, thermolysis or photolysis of [(Cp^{R}Fe(CO)$_2$)$_2$(μ-η^1:η^1-P$_4$)] (Cp^R = C$_5$H$_2$-1,2,4-*t*Bu$_3$, C$_5$H$_2$-1,2,4-*t*Bu$_3$, C$_9$H$_5$-1,3-*t*Bu$_2$ and C$_5$iPr$_5$) affords mixtures of polyphosphido complexes.[7a,c] Reactions with (phospha)alkynes evoked the P$_3$/P$_1$ fragmentation of the bicyclo[1.1.0]tetraphosphabutanediyl fragment, forming phosphide, phospholide and diphosphacyclobutadiene components.[9,10] Further studies revealed that the "P$_4$ butterfly" may be protonated reversibly and coordinates as a chelate ligand to copper(I).[11] Here, we disclose a new reaction mode for metal-substituted bicyclo[1.1.0]tetraphosphabutanes. We have found that phenyl isothiocyanate reversibly inserts into a P–P bond of the bicyclo[1.1.0]tetraphosphabutane scaffold of the dinuclear nickel complex [{(η^5-Cp)Ni(IMes)}$_2$(μ-η^1:η^1-P$_4$)] (**1$^{\text{Mes}}$**, Scheme 1c).[7b] This unprecedented reaction affords the isomers **2a** and **2b**, which display a bicyclo[3.1.0]heterohexane skeleton. We describe the single-crystal X-ray structures and ^{31}P{^{1}H} NMR data of these



Scheme 1 (a) Formation of bicyclo[1.1.0]tetraphosphabutanes amenable for further transformations; (b) selected reactions of iron-substituted bicyclo[1.1.0]tetraphosphabutanes; Cp^R = C$_5$H$_2$-1,2,4-*t*Bu$_3$, C$_5$H$_2$-1,2,4-*t*Bu$_3$, C$_9$H$_5$-1,3-*t*Bu$_2$, C$_5$iPr$_5$, R^1 = R^2 = Me, Ph; R^1 = H, R^2 = Ph, *t*Bu, SiMe$_3$, CO$_2$Me/Et, R^3 = *t*Bu, C(CH$_2$)$_5$Me; (c) synthesis of **1$^{\text{Dipp}}$** and **1$^{\text{Mes}}$** and reactivity toward phenyl isothiocyanate.[6–10]

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new complexes and analyse the possible nature of additional reaction products using DFT calculations.

We recently synthesised the first nickel-substituted bicyclo-[1.1.0]tetraphosphabutane, [{(η^5-Cp)Ni(IDipp)}$_2$(μ-η^1:η^1-P$_4$)] (**1$^{\text{Dipp}}$**, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene).[7b] This complex is formed in a quantitative reaction from two equivalents [(η^5-Cp)Ni(IDipp)] and P$_4$ (Scheme 1c). Subsequent work showed that the slightly less encumbered mesityl-substituted complex [{(η^5-Cp)Ni(IMes)}$_2$(μ-η^1:η^1-P$_4$)] (**1$^{\text{Mes}}$**) is obtained in an analogous fashion. **1$^{\text{Mes}}$** was isolated as dark red air-sensitive crystals in 71% yield (Scheme 1c) and shows a better solubility than **1$^{\text{Dipp}}$**, dissolving well in benzene, toluene, diethyl ether and tetrahydrofuran (ESI†).

In order to probe the reactivity of **1$^{\text{Dipp}}$** and **1$^{\text{Mes}}$**, we investigated reactions with heteroallenes. ADMX spin systems were observed by ^{31}P NMR spectroscopy with CS$_2$ (10 equiv.), suggesting an insertion into a P–P bond, but the products could not be isolated (ESI†). Isolable products were obtained with phenyl isothiocyanate, however. Monitoring the reaction of **1$^{\text{Mes}}$** and PhNCS in [D$_8$]THF (Fig. 1) revealed that 7 equiv. PhNCS were necessary for full conversion of **1$^{\text{Mes}}$** after four hours, while a large amount of **1$^{\text{Mes}}$** (55%) remained in the reaction mixture with one equiv. PhNCS after one day (Fig. S10, ESI†). Two main products **2a** and **2b** (ADMX spin systems) and one minor species **2c** were detected (approximate ratio **2a** : **2b** : **2c** 75 : 20 : 5).‡ The simultaneous formation of **2a**, **2b** and **2c** commences below 0 °C according to a VT NMR study ([D$_8$]THF, Fig. S8, ESI†). Prolonged reaction times and heating of the solution resulted in essentially the same product ratio, although the signal to noise ratio of the spectra decreased over time. In contrast, the ^{31}P{^{1}H} NMR spectrum of the reaction of **1$^{\text{Dipp}}$** with a large excess of PhNCS in [D$_8$]THF after two days at room temperature showed signals of a species similar to **2b** (15%, ADMX spin system), **1$^{\text{Dipp}}$** (50%) and P$_4$ (35%) (Fig. S9, ESI†).

Complex **2a** can be isolated as an analytically pure, dark brown solid in 31% yield by crystallising the crude product twice from toluene/*n*-hexane (ESI†). Crystallisation of the crude product from diethyl ether and recrystallization from toluene/*n*-hexane affords pure, crystalline **2b** in 16% isolated yield. Single-crystal XRD for **2a** (Fig. 2, top) revealed an unusual nickel-substituted bicyclo[3.1.0]-2-thia-1,4,5,6-tetraphosphahexane moiety (P1–C1 1.860(4) Å, P4–S1 2.1257(13) Å) with an exocyclic imino function. The C1–N1 (1.278(6) Å) and S1–C1 (1.794(4) Å) bonds of **2a** are elongated compared to free aryl isothiocyanates.[12] The P–P distances (2.1818(14)–2.2222(14) Å) are in the range of single bonds.[7] The five-membered CP$_3$S heterocycle (P1–P2–P4–S1–C1) is almost flat (Σ_{angles} = 535.8°) and orthogonal (89.60(7)°) to the plane formed by P2, P3 and P4. The scaffold of **2a** is analogous to that of 2,3,4,6-tetra-*tert*-butylbicyclo[3.1.0]hexaphosphane synthesised by Baudler *et al.*[13]

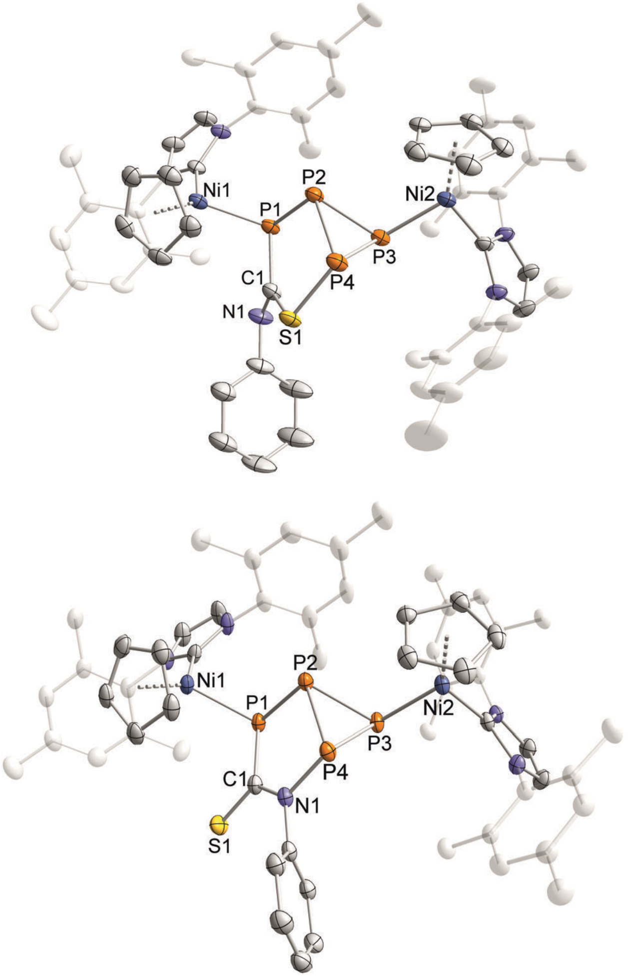

Fig. 2 Solid-state molecular structures of **2a** (top) and **2b** (bottom). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% level. Selected bond lengths [Å] and angles [°] for **2a**: P1–C1 1.860(4), P4–S1 2.1257(13), P1–P2 2.1818(14), P2–P3 2.2182(15), P2–P4 2.2222(14), P3–P4 2.1935(15), C1–S1 1.794(4), C1–N1 1.278(6), Ni1–P1 2.2036(13), Ni2–P3 2.1906(11), P1–P2–P4 102.89(5), P2–P4–S1 102.86(6), P4–S1–C1 104.82(14), S1–C1–P1 122.3(2), C1–P1–P2 102.88(14), P3–P2–P4 59.20(5), P1–C1–N1 116.4(3), S1–C1–N1 121.3(2); for **2b**: P1–C1 1.828(3), P4–N1 1.785(3), P1–P2 2.2157(11), P2–P4 2.1969(10), P2–P3 2.2233(10), P3–P4 2.206(1), C1–N1 1.359(4), C1–S1 1.678(3), Ni1–P1 2.2188(9), Ni2–P3 2.2192(9), P1–P2–P4 95.28(4), P2–P4–N1 99.75(9), P4–N1–C1 124.9(2), N1–C1–P1 118.6(2), C1–P1–P2 100.48(3), P3–P2–P4 59.88(3), P1–C1–S1 117.68(18), N1–C1–S1 123.6(2).

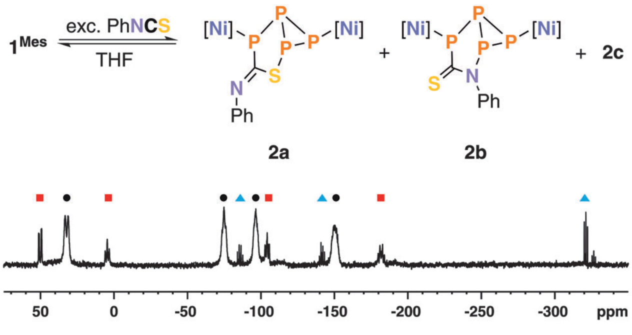

Fig. 1 Synthesis of **2a** and **2b** (top), and ^{31}P{^{1}H} NMR spectrum ([D$_8$]THF) of the reaction of PhNCS and **1$^{\text{Mes}}$** (7 : 1) at room temperature after four hours; ● = **2a**, 🟥 = **2b**, ▲ = **2c** (bottom).

The molecular structure of the regio isomer **2b** (Fig. 2, bottom) features a flat CNP$_3$ heterocycle (Σ_{angles} = 539.0°) with a thioketone function (C1–S1 1.678(3) Å) and single bonds between P1–C1 (1.828(3) Å) and P4–N1 (1.785(3) Å). The P–P distances in **2b** (2.1969(10)–2.2233(10) Å) are similar to those of **2a**. The CNP$_3$ ring forms an acute dihedral angle of 79.58(5)° with the P2–P3–P4 plane.

The ^{31}P{^{1}H} NMR spectrum of **2a** ([D$_8$]THF, room temperature) features four broad multiplets at −150.1, −96.4, −75.0 and 32.1 ppm consistent with four chemically different P atoms. The signals are broad at room temperature (average half-width τ_{FWHM} = 565 Hz); they become sharper when the temperature is decreased to −80 °C (av. τ_{FWHM} = 35 Hz). Experimental and fitted ^{31}P{^{1}H} NMR spectra in [D$_8$]THF at −80 °C along with the assignment of the chemical shifts and coupling constants are shown in Fig. 3. The resonance at −151.8 ppm is assigned to P$_\text{A}$ connected to three P atoms based on the observation of three large ^1J(P,P)-coupling constants for this multiplet (^1J(P$_\text{A}$P$_\text{D}$) = −178 Hz, ^1J(P$_\text{A}$P$_\text{M}$) = −185 Hz and ^1J(P$_\text{A}$P$_\text{X}$) = −374 Hz). The P atoms coordinated to nickel (δ(P$_\text{D}$) = −105.5 ppm; δ(P$_\text{X}$) = 27.8 ppm) show a common large ^2J(P,P) coupling (^2J(P$_\text{D}$,P$_\text{X}$) = 82 Hz), which may arise from an interaction of the lone pairs due to the conformational constraints of the bicyclo[3.1.0]heterohexane skeleton.[13]

Complex **2b** gives rise to four slightly broad ^{31}P{^{1}H} NMR resonances at −182.1, −104.5, 4.5 and 50.1 ppm in [D$_8$]THF at room temperature. The line width decreased from an average of τ_{FWHM} = 33 Hz at room temperature to τ_{FWHM} = 23 Hz upon cooling to −80 °C. The chemical shifts and coupling constants of **2b** lie in a similar range as observed for **2a** (Fig. 3, bottom) in agreement with the similar structure motif.

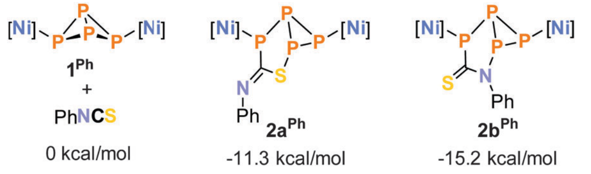

Fig. 4 Calculated, relative Gibbs free energies (kcal mol^{-1}) of **1**$^{\text{Ph}}$, **2a**$^{\text{Ph}}$ and **2b**$^{\text{Ph}}$. The relative Gibbs free energies refer to **1**$^{\text{Ph}}$ + PhNCS (kcal mol^{-1}).

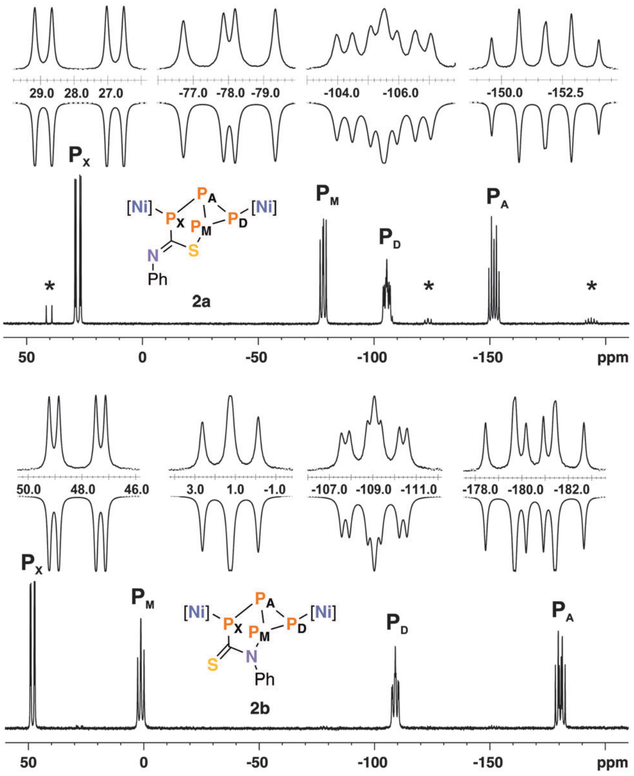

Fig. 3 ^{31}P{^{1}H} NMR spectra of **2a** (top) and **2b** (bottom, 161.98 MHz, [D$_8$]THF, 193 K); **2a** (ADMX spin system): δ_A = −151.8 ppm, δ_D = −105.5 ppm, δ_M = −78.0 ppm, δ_X = 27.8 ppm, ^1J(P$_\text{A}$P$_\text{D}$) = −178 Hz, ^1J(P$_\text{A}$P$_\text{M}$) = −185 Hz, ^1J(P$_\text{A}$P$_\text{X}$) = −374 Hz, ^1J(P$_\text{D}$P$_\text{M}$) = −238 Hz, ^2J(P$_\text{D}$P$_\text{X}$) = 82 Hz, ^2J(P$_\text{M}$P$_\text{X}$) = 9 Hz; **2b** (ADMX spin system): δ_A = −180.5 ppm, δ_D = −109.1 ppm, δ_M = 1.2 ppm, δ_X = 48.2 ppm, ^1J(P$_\text{A}$P$_\text{D}$) = −193 Hz, ^1J(P$_\text{A}$P$_\text{M}$) = −209 Hz, ^1J(P$_\text{A}$P$_\text{X}$) = −282 Hz, ^1J(P$_\text{D}$P$_\text{M}$) = −237 Hz, ^2J(P$_\text{D}$P$_\text{X}$) = 57 Hz, ^2J(P$_\text{M}$P$_\text{X}$) = 10 Hz; expansions (inset) show the experimental (up) and fitted spectra (down). The signals assigned to **2b** are labeled with an asterisk.

^{31}P{^{1}H} NMR studies indicate that the formation of **2a**, **2b** and **2c** is reversible; *i.e.* the products slowly equilibrate with the starting material **1**$^{\text{Mes}}$ in solution (ESI†). A mixture of **2a** (89%), **1**$^{\text{Mes}}$ (7%), **2c** (4%) and **2b** (traces) was detected upon storing a [D$_8$]THF solution of pure **2a** in an NMR tube at room temperature for two days, while a 65 : 10 : 5 : 20 mixture (**2a** : **2b** : **2c** : **1**$^{\text{Mes}}$) was present after one week.§ Additional multiplets of unidentified minor species can be observed upon prolonged storage (Fig. S11, ESI†). **2b** behaves similarly (Fig. S12, ESI†). IR monitoring of the decomposition of **2a** ([D$_8$]THF, 60 °C, 13.5 hours) shows the formation of free PhNCS (Fig. S13, ESI†).

DFT calculations (ωB97X-D/6-311G(d,p) level)[14] were performed to gain additional insight into the thermodynamics of the reaction. The optimized structures of the truncated model complexes **1**$^{\text{Ph}}$, **2a**$^{\text{Ph}}$ and **2b**$^{\text{Ph}}$, where the Mes substituents were replaced by phenyl groups for computational efficiency, are in good agreement with the experimental structures (Fig. 4). The formation of **2a**$^{\text{Ph}}$ and **2b**$^{\text{Ph}}$ is exergonic, and the thermodynamic product of the reaction appears to be **2b**$^{\text{Ph}}$ (−15.2 kcal mol^{-1} with respect to the starting materials), while **2a**$^{\text{Ph}}$ (−11.3 kcal mol^{-1}) is a kinetic product.¶

In conclusion, the reaction of **1**$^{\text{Mes}}$ with PhNCS affords the novel complexes **2a** and **2b** with an unusual bicyclo[3.1.0]heterohexane skeleton. To our knowledge, this represents the first example of an insertion of a heteroallene into a P–P bond of a cyclopolyphosphane. In future work, it will be of interest to investigate whether similar reactions with polar multiple bonds offer a general route toward "functionalized" polyphosphanes.[15] Efficient preparative methods exist for a range of bicyclo[1.1.0]tetraphosphabutanes,[1,6–9] therefore, such transformations may provide a fruitful avenue to the stepwise and selective degradation of the P$_4$ molecule.

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Notes and references

‡ ^{31}P{^{1}H} NMR data of **2c** ([D$_8$]THF, A$_2$MX spin system): δ = −321.2 (dd, 2P, P$_\text{A}$, ^1J(P$_\text{A}$P$_\text{M}$) = −178 Hz, ^1J(P$_\text{A}$P$_\text{X}$) = −188 Hz), −141.5 (dt, 1P, P$_\text{M}$, ^2J(P$_\text{M}$P$_\text{X}$) = 208 Hz), −85.8 (dt, 1P, P$_\text{X}$) ppm.

§ The ^{1}H NMR spectrum of a freshly prepared [D$_8$]THF solution of pure crystals of **2a** stored for one week at room temperature in an Ar-filled glove box also showed a mixture containing **2a**, **2b** and **1**$^{\text{Mes}}$ in a 94.5 : 0.5 : 5 ratio.

¶ The structure and the mechanism of formation of the minor product **2c** (A_2MX spin system, *vide supra*) presently remains unclear. Five potential candidates were identified by our computations (Fig. S14, ESI†). These calculated isomers are adducts of the starting material with PhNCS (**2c**$^{\mathbf{Add1}}$ and **2c**$^{\mathbf{Add2}}$) or result from the insertion of the C═S or C═N double bonds into the Ni–P bond ((*E*)-**2c**$^{\mathbf{Ins1}}$, (*Z*)-**2c**$^{\mathbf{Ins1}}$ and **2c**$^{\mathbf{Ins2}}$).[16] Each of them has an energy significantly higher than that of **2a**$^{\mathbf{Ph}}$ and **2b**$^{\mathbf{Ph}}$.

1 Reviews: (*a*) B. M. Cossairt, N. A. Piro and C. C. Cummins, *Chem. Rev.*, 2010, **110**, 4164; (*b*) M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. Rev.*, 2010, **110**, 4178; (*c*) M. Peruzzini, I. de los Rios, A. Romerosa and F. Vizza, *Eur. J. Inorg. Chem.*, 2001, 593; (*d*) M. Peruzzini, R. R. Abdreimova, Y. Budnikova, A. Romerosa, O. J. Scherer and H. Sitzmann, *J. Organomet. Chem.*, 2004, **689**, 4319; (*e*) M. Peruzzini, L. Gonsalvi and A. Romerosa, *Chem. Soc. Rev.*, 2005, **34**, 1038.

2 Selected publications on transformations of transition metal phosphide complexes derived from P_4 in one step: (*a*) P. Barbaro, C. Bazzicalupi, M. Peruzzini, S. Seniori Costantini and P. Stoppioni, *Angew. Chem., Int. Ed.*, 2012, **51**, 8628; (*b*) E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl and M. Scheer, *Angew. Chem., Int. Ed.*, 2014, **53**, 7643.

3 (*a*) W. T. K. Chan, F. García, A. D. Hopkins, L. C. Martin, M. McPartlin and D. S. Wright, *Angew. Chem., Int. Ed.*, 2007, **46**, 3084; (*b*) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg and K. Lammertsma, *Angew. Chem., Int. Ed.*, 2014, **53**, 12836; (*c*) M. Arrowsmith, M. S. Hill, A. L. Johnson, G. Kociok-Köhn and M. F. Mahon, *Angew. Chem., Int. Ed.*, 2015, **54**, 7882; (*d*) J. E. Borger, A. W. Ehlers, M. Lutz, J. C. Slootweg and K. Lammertsma, *Angew. Chem., Int. Ed.*, 2015, **55**, 613.

4 (*a*) J. D. Masuda, W. W. Schoeller, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 7052; (*b*) O. Back, G. Kuchenbeiser, B. Donnadieu and G. Bertrand, *Angew. Chem., Int. Ed.*, 2009, **48**, 5530.

5 Selected publications on the insertion of p-block elements into the P–P bonds of P_4: (*a*) Y. Xiong, S. Yao, M. Brym and M. Driess, *Angew. Chem., Int. Ed.*, 2007, **46**, 4511; (*b*) J. J. Weigand, M. Holthausen and R. Fröhlich, *Angew. Chem., Int. Ed.*, 2009, **48**, 295; (*c*) M. H. Holthausen and J. J. Weigand, *J. Am. Chem. Soc.*, 2009, **131**, 14210; (*d*) G. Prabusankar, A. Doddi, C. Gemel, M. Winter and R. A. Fischer, *Inorg. Chem.*, 2010, **49**, 7976; (*e*) M. H. Holthausen and J. J. Weigand, *Chem. Soc. Rev.*, 2014, **43**, 6639.

6 (*a*) J.-P. Bezombes, P. B. Hitchcock, M. F. Lappert and J. E. Nycz, *Dalton Trans.*, 2004, 499; (*b*) B. M. Cossairt and C. C. Cummins, *New J. Chem.*, 2010, **34**, 1533; (*c*) S. Khan, R. Michel, J. M. Dieterich, R. A. Mata, H. W. Roesky, J.-P. Demers, A. Lange and D. Stalke, *J. Am. Chem. Soc.*, 2011, **133**, 17889; (*d*) N. A. Giffin, A. D. Hendsbee, T. L. Roemmele, M. D. Lumsden, C. C. Pye and J. D. Masuda, *Inorg. Chem.*, 2012, **51**, 11837; (*e*) S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner and M. Scheer, *Angew. Chem., Int. Ed.*, 2014, **53**, 7639.

7 (*a*) O. J. Scherer, T. Hilt and G. Wolmershäuser, *Organometallics*, 1998, **17**, 4110; (*b*) S. Pelties, D. Herrmann, B. de Bruin, F. Hartl and R. Wolf, *Chem. Commun.*, 2014, **50**, 7014; (*c*) S. Heinl and M. Scheer, *Chem. Sci.*, 2014, **5**, 3221; (*d*) C. Schwarzmaier, A. Y. Timoshkin, G. Balázs and M. Scheer, *Angew. Chem., Int. Ed.*, 2014, **53**, 9077; (*e*) D. W. Agnew, C. E. Moore, A. L. Rheingold and J. S. Figueroa, *Angew. Chem., Int. Ed.*, 2015, **54**, 12673.

8 Selected main group element-substituted ''butterfly P_4'' compounds with an E_2P_4 core: (*a*) E. Niecke, R. Rüger and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 544; (*b*) R. Riedel, H.-D. Hausen and E. Fluck, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 1056; (*c*) S. L. Hinchley, C. A. Morrison, D. W. H. Rankin, C. L. B. Macdonald, R. J. Wiacek, A. Voigt, A. H. Cowley, M. F. Lappert, G. Gundersen, J. A. C. Clyburne and P. P. Power, *J. Am. Chem. Soc.*, 2001, **123**, 9045.

9 (*a*) O. J. Scherer, T. Hilt and G. Wolmershäuser, *Angew. Chem., Int. Ed.*, 2000, **39**, 1425; (*b*) C. Eichhorn, PhD thesis, Kaiserslautern, 2003; (*c*) S. Deng, C. Schwarzmaier, C. Eichhorn, O. J. Scherer, G. Wolmershäuser, M. Zabel and M. Scheer, *Chem. Commun.*, 2008, 4064.

10 M. Scheer, S. Deng, O. J. Scherer and M. Sierka, *Angew. Chem., Int. Ed.*, 2005, **44**, 3755.

11 C. Schwarzmaier, S. Heinl, G. Balázs and M. Scheer, *Angew. Chem., Int. Ed.*, 2015, **54**, 13116.

12 S. Biswas, S. Haldar, P. K. Mandal, K. Goubitz, H. Schenk and R. Dabrowski, *Cryst. Res. Technol.*, 2007, **42**, 1029.

13 (*a*) M. Baudler, Y. Aktalay, K.-F. Tebbe and T. Heinlein, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 967; in this context see also: (*b*) M. Baudler, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 492.

14 DFT calculations were performed using Gaussian09; see ESI† for further details.

15 (*a*) A. R. Jupp and J. M. Goicoechea, *Angew. Chem., Int. Ed.*, 2013, **52**, 10064; (*b*) R. S. P. Turbervill and J. M. Goicoechea, *Chem. Commun.*, 2012, **48**, 6100; (*c*) R. S. P. Turbervill, A. R. Jupp, P. S. B. McCullough, D. Ergöçmen and J. M. Goicoechea, *Organometallics*, 2013, **32**, 2234.

16 Selected examples for the insertion of isothiocyanates into transition metal–phosphorus bonds: (*a*) U. Segerer and E. Hey-Hawkins, *Polyhedron*, 1997, **16**, 2537; (*b*) U. Segerer, J. Sieler and E. Hey-Hawkins, *Organometallics*, 2000, **19**, 2445; (*c*) A. Antiñolo, S. García-Yuste, A. Otero and R. Reguillo-Carmona, *Eur. J. Inorg. Chem.*, 2009, 539; (*d*) W. Yi, J. Zhang, L. Hong, Z. Chen and X. Zhou, *Organometallics*, 2011, **30**, 5809.