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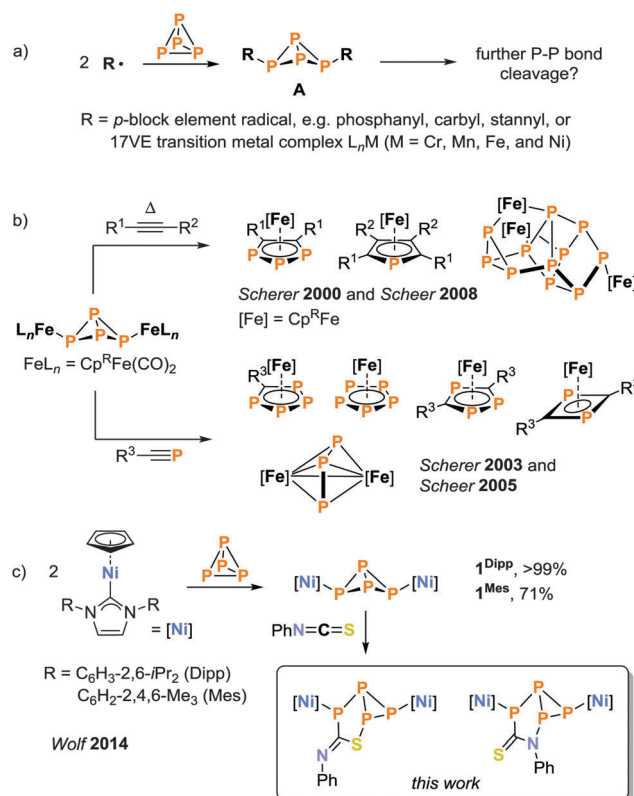
Insertion of phenyl isothiocyanate into a P–P bond of a nickel-substituted bicyclo[1.1.0]tetraphosphabutane†

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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 [(Cp^RNi(IMes))₂(μ-η¹:η¹-P₄)] (**1**^{Mes}, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene), forming isomers **2a** and **2b**. X-ray crystallography and ³¹P{¹H} NMR spectroscopy revealed similar bicyclo[3.1.0]heterohexane structures for these compounds.

Developing new, targeted and selective methods for the functionalisation of the P₄ 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. phosphonium cations⁵ 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 P₄ degradation sequence (Scheme 1a). While various “P₄ 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^RFe(CO))₂(μ-η¹:η¹-P₄)] (Cp^R = C₅H₂-1,2,4-*t*Bu₃, C₅H₂-1,2,4-*t*Bu₃, C₉H₅-1,3-*t*Bu₂ and C₅iPr₅) affords mixtures of polyphosphido complexes.^{7a,c} Reactions with (phospha)alkynes evoked the P₃/P₁ fragmentation of the bicyclo[1.1.0]tetraphosphabutenediyl fragment, forming phosphide, phospholide and diphosphacyclobutadiene components.^{9,10} Further studies revealed that the “P₄ 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 [(η⁵-Cp)Ni(IMes))₂(μ-η¹:η¹-P₄)] (**1**^{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 ³¹P{¹H} 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 = C₅H₂-1,2,4-*t*Bu₃, C₅H₂-1,2,4-*t*Bu₃, C₉H₅-1,3-*t*Bu₂, C₅iPr₅, R¹ = R² = Me, Ph; R¹ = H, R² = Ph, *t*Bu, SiMe₃, CO₂Me/Et, R³ = *t*Bu, C(CH₃)₅Me; (c) synthesis of **1**^{Dipp} and **1**^{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, $[(\eta^5\text{-Cp})\text{Ni}(\text{IDipp})]_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-P}_4)$ (**1^{Dipp}**, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene).^{7b} This complex is formed in a quantitative reaction from two equivalents $[(\eta^5\text{-Cp})\text{Ni}(\text{IDipp})]$ and P_4 (Scheme 1c). Subsequent work showed that the slightly less encumbered mesityl-substituted complex $[(\eta^5\text{-Cp})\text{Ni}(\text{IMes})]_2(\mu\text{-}\eta^1\text{-}\eta^1\text{-P}_4)$ (**1^{Mes}**) is obtained in an analogous fashion. **1^{Mes}** was isolated as dark red air-sensitive crystals in 71% yield (Scheme 1c) and shows a better solubility than **1^{Dipp}**, dissolving well in benzene, toluene, diethyl ether and tetrahydrofuran (ESI†).

In order to probe the reactivity of **1^{Dipp}** and **1^{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^{Mes}** and PhNCS in $[\text{D}_8]\text{THF}$ (Fig. 1) revealed that 7 equiv. PhNCS were necessary for full conversion of **1^{Mes}** after four hours, while a large amount of **1^{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 ($[\text{D}_8]\text{THF}$, 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction of **1^{Dipp}** with a large excess of PhNCS in $[\text{D}_8]\text{THF}$ after two days at room temperature showed signals of a species similar to **2b** (15%, ADMX spin system), **1^{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

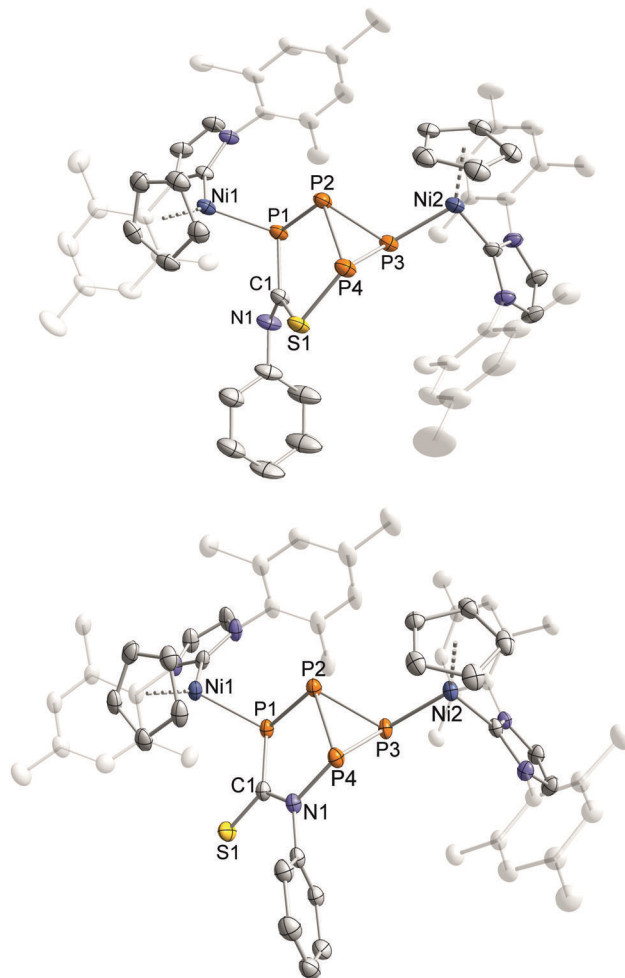


Fig. 2 Solid-state molecular structures of **2a** (top) and **2b** (bottom). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% level. Selected bond lengths [Å] and angles [°] for **2a**: P1–C1 1.860(4), P4–S1 2.1257(13), P1–P2 2.1818(14), P2–P3 2.2182(15), P2–P4 2.2222(14), 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).

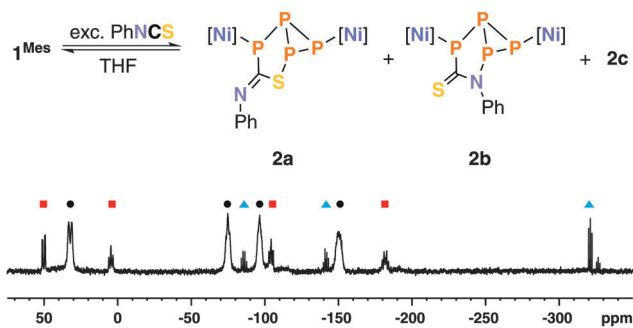


Fig. 1 Synthesis of **2a** and **2b** (top), and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum ($[\text{D}_8]\text{THF}$) of the reaction of PhNCS and **1^{Mes}** (7:1) at room temperature after four hours; ● = **2a**, ■ = **2b**, ▲ = **2c** (bottom).

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_3S heterocycle (P1–P2–P4–S1–C1) is almost flat ($\Sigma_{\text{angles}} = 535.8^\circ$) and orthogonal ($89.60(7)^\circ$) 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

The molecular structure of the regio isomer **2b** (Fig. 2, bottom) features a flat CNP_3 heterocycle ($\Sigma_{\text{angles}} = 539.0^\circ$) 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 CNP₃ ring forms an acute dihedral angle of 79.58(5)° with the P2–P3–P4 plane.

The ³¹P{¹H} NMR spectrum of **2a** ([D₈]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 $\tau_{\text{FWHM}} = 565$ Hz); they become sharper when the temperature is decreased to –80 °C (av. $\tau_{\text{FWHM}} = 35$ Hz). Experimental and fitted ³¹P{¹H} NMR spectra in [D₈]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_A connected to three P atoms based on the observation of three large ¹J(P,P)-coupling constants for this multiplet (¹J(P_AP_D) = –178 Hz, ¹J(P_AP_M) = –185 Hz and ¹J(P_AP_X) = –374 Hz). The P atoms coordinated to nickel ($\delta(\text{P}_\text{D}) = -105.5$ ppm; $\delta(\text{P}_\text{X}) = 27.8$ ppm) show a common large ²J(P,P) coupling (²J(P_D,P_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 ³¹P{¹H} NMR resonances at –182.1, –104.5, 4.5 and 50.1 ppm in [D₈]THF at

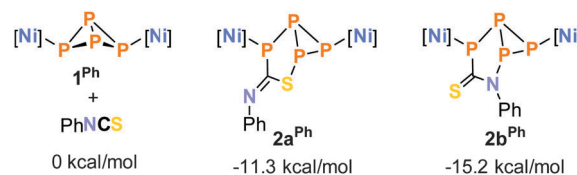


Fig. 4 Calculated, relative Gibbs free energies (kcal mol^{–1}) of **1^{Ph}**, **2a^{Ph}** and **2b^{Ph}**. The relative Gibbs free energies refer to **1^{Ph}** + PhNCS (kcal mol^{–1}).

room temperature. The line width decreased from an average of $\tau_{\text{FWHM}} = 33$ Hz at room temperature to $\tau_{\text{FWHM}} = 23$ 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.

³¹P{¹H} NMR studies indicate that the formation of **2a**, **2b** and **2c** is reversible; i.e. the products slowly equilibrate with the starting material **1^{Mes}** in solution (ESI[†]). A mixture of **2a** (89%), **1^{Mes}** (7%), **2c** (4%) and **2b** (traces) was detected upon storing a [D₈]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^{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** ([D₈]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^{Ph}**, **2a^{Ph}** and **2b^{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^{Ph}** and **2b^{Ph}** is exergonic, and the thermodynamic product of the reaction appears to be **2b^{Ph}** (–15.2 kcal mol^{–1} with respect to the starting materials), while **2a^{Ph}** (–11.3 kcal mol^{–1}) is a kinetic product. ¶

In conclusion, the reaction of **1^{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 P₄ molecule.

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Notes and references

‡ ³¹P{¹H} NMR data of **2c** ([D₈]THF, A₂MX spin system): $\delta = -321.2$ (dd, 2P, P_A, ¹J(P_AP_M) = –178 Hz, ¹J(P_AP_X) = –188 Hz), –141.5 (dt, 1P, P_M, ²J(P_MP_X) = 208 Hz), –85.8 (dt, 1P, P_X) ppm.

§ The ¹H NMR spectrum of a freshly prepared [D₈]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^{Mes}** in a 94.5:0.5:5 ratio.

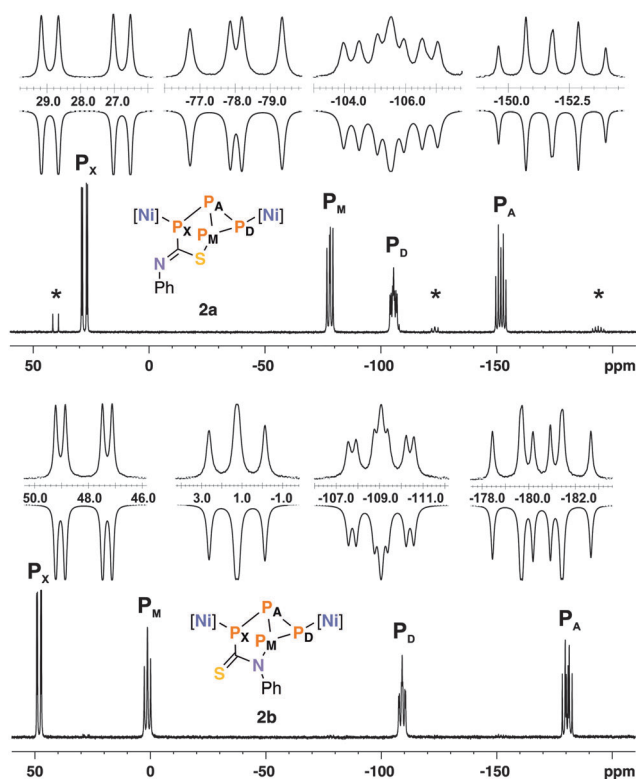


Fig. 3 ³¹P{¹H} NMR spectra of **2a** (top) and **2b** (bottom, 161.98 MHz, [D₈]THF, 193 K); **2a** (ADMX spin system): $\delta_\text{A} = -151.8$ ppm, $\delta_\text{D} = -105.5$ ppm, $\delta_\text{M} = -78.0$ ppm, $\delta_\text{X} = 27.8$ ppm, ¹J(P_AP_D) = –178 Hz, ¹J(P_AP_M) = –185 Hz, ¹J(P_AP_X) = –374 Hz, ¹J(P_DP_M) = –238 Hz, ²J(P_DP_X) = 82 Hz, ²J(P_MP_X) = 9 Hz; **2b** (ADMX spin system): $\delta_\text{A} = -180.5$ ppm, $\delta_\text{D} = -109.1$ ppm, $\delta_\text{M} = 1.2$ ppm, $\delta_\text{X} = 48.2$ ppm, ¹J(P_AP_D) = –193 Hz, ¹J(P_AP_M) = –209 Hz, ¹J(P_AP_X) = –282 Hz, ¹J(P_DP_M) = –237 Hz, ²J(P_DP_X) = 57 Hz, ²J(P_MP_X) = 10 Hz; expansions (inset) show the experimental (up) and fitted spectra (down). The signals assigned to **2b** are labeled with an asterisk.



¶ 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^{Add1}** and **2c^{Add2}**) or result from the insertion of the C=S or C=N double bonds into the Ni-P bond ((*E*)-**2c^{Ins1}**, (*Z*)-**2c^{Ins1}** and **2c^{Ins2}**).¹⁶ Each of them has an energy significantly higher than that of **2a^{Ph}** and **2b^{Ph}**.

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