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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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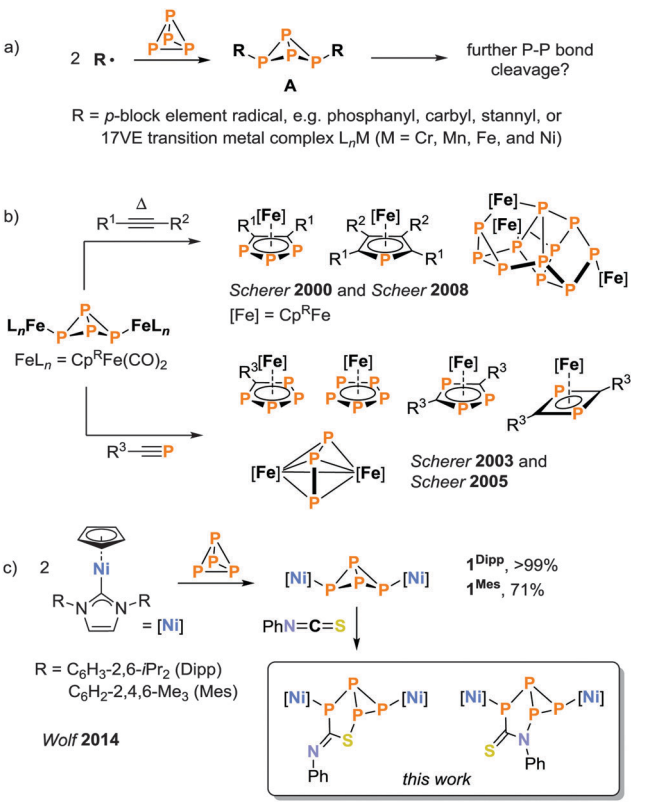
A new reaction mode for bicyclo[1.1.0]tetraphosphabutanes is reported. The C═S and C═N bonds of phenyl isothiocyanate reversibly insert into a P–P bond of [{CpNi(IMes)}$_2$(μ-η^1:η^1-P$_4$)] (1^{Mes}, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene), forming isomers 2a and 2b. X-ray crystallography 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^{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^{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, [{(η^5-Cp)Ni(IDipp)}$_2$(μ-η^1:η^1-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 [(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^{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 [D_8]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 ([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^{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^{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

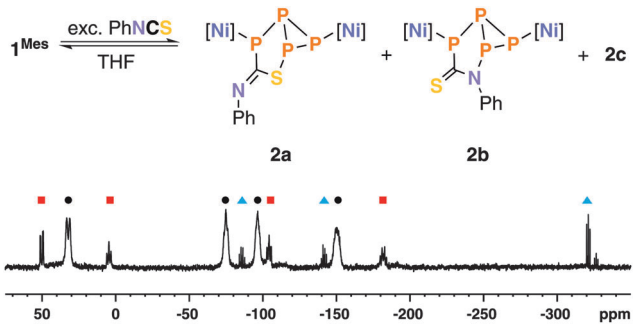

Fig. 1 Synthesis of **2a** and **2b** (top), and ^{31}P{^{1}H} NMR spectrum ([D_8]THF) of the reaction of PhNCS and **1^{Mes}** (7 : 1) at room temperature after four hours; ● = **2a**, ■ = **2b**, ▲ = **2c** (bottom).

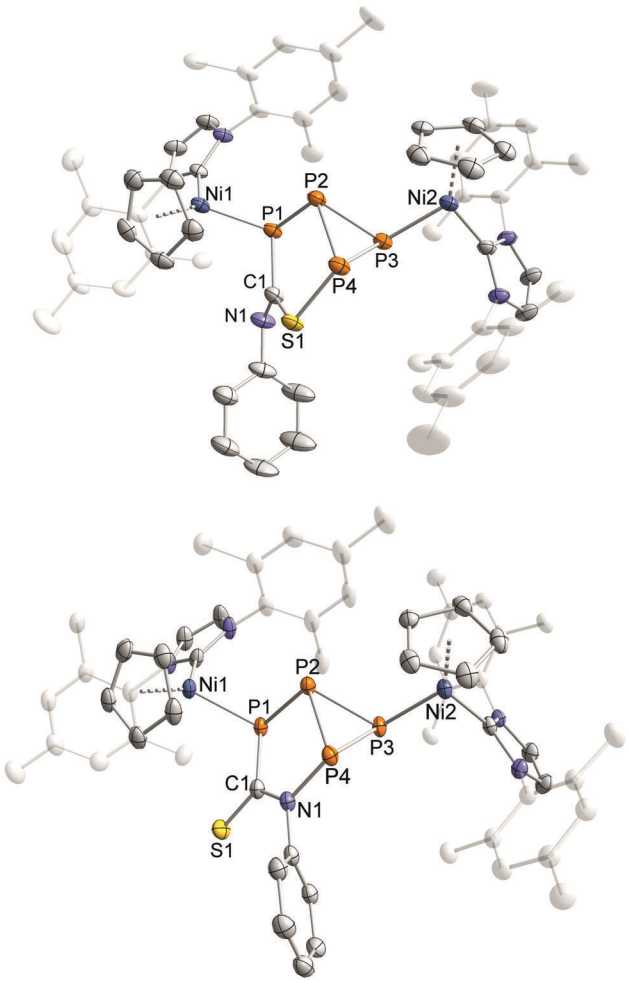

Fig. 2 Solid-state molecular structures of **2a** (top) and **2b** (bottom). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% level. Selected bond lengths [Å] and angles [°] for **2a**: P1–C1 1.860(4), P4–S1 2.1257(13), P1–P2 2.1818(14), P2–P3 2.2182(15), P2–P4 2.2222(14),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

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 (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]

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

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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 $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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_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 ($\delta(P_D)$ = −105.5 ppm; $\delta(P_X)$ = 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 $^{31}P\{^1H\}$ 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.

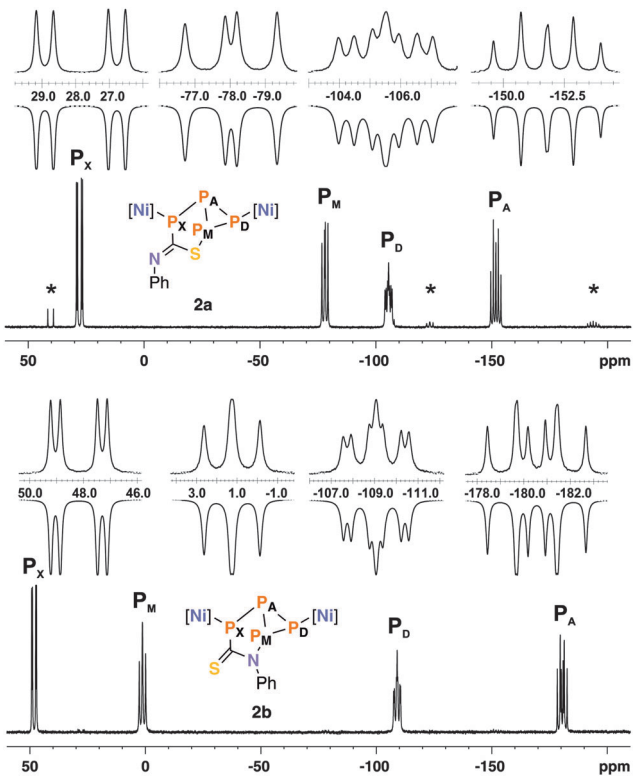

Fig. 3 $^{31}P\{^1H\}$ NMR spectra of **2a** (top) and **2b** (bottom, 161.98 MHz, [D_8]THF, 193 K); **2a** (ADMX spin system): δ_A = −151.8 ppm, δ_D = −105.5 ppm, δ_M = −78.0 ppm, δ_X = 27.8 ppm, $^1J(P_AP_D)$ = −178 Hz, $^1J(P_AP_M)$ = −185 Hz, $^1J(P_AP_X)$ = −374 Hz, $^1J(P_DP_M)$ = −238 Hz, $^2J(P_DP_X)$ = 82 Hz, $^2J(P_MP_X)$ = 9 Hz; **2b** (ADMX spin system): δ_A = −180.5 ppm, δ_D = −109.1 ppm, δ_M = 1.2 ppm, δ_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.

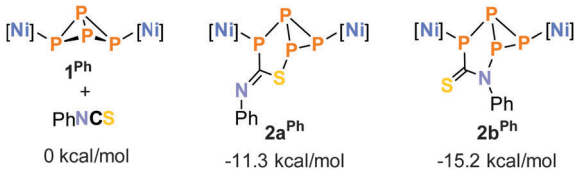

Fig. 4 Calculated, relative Gibbs free energies (kcal mol^{-1}) of $\mathbf{1}^{Ph}$, $\mathbf{2a}^{Ph}$ and $\mathbf{2b}^{Ph}$. The relative Gibbs free energies refer to $\mathbf{1}^{Ph}$ + PhNCS (kcal mol^{-1}).

$^{31}P\{^1H\}$ NMR studies indicate that the formation of **2a**, **2b** and **2c** is reversible; *i.e.* the products slowly equilibrate with the starting material $\mathbf{1}^{Mes}$ in solution (ESI†). A mixture of **2a** (89%), $\mathbf{1}^{Mes}$ (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** : $\mathbf{1}^{Mes}$) 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** ([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 $\mathbf{1}^{Ph}$, $\mathbf{2a}^{Ph}$ and $\mathbf{2b}^{Ph}$, 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 $\mathbf{2a}^{Ph}$ and $\mathbf{2b}^{Ph}$ is exergonic, and the thermodynamic product of the reaction appears to be $\mathbf{2b}^{Ph}$ (−15.2 kcal mol^{-1} with respect to the starting materials), while $\mathbf{2a}^{Ph}$ (−11.3 kcal mol^{-1}) is a kinetic product.¶

In conclusion, the reaction of $\mathbf{1}^{Mes}$ 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 P_4 molecule.

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Notes and references

‡ $^{31}P\{^1H\}$ NMR data of **2c** ([D_8]THF, A_2MX spin system): δ = −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 [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 $\mathbf{1}^{Mes}$ in a 94.5 : 0.5 : 5 ratio.

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¶ 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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