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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-tBu$_3$, C$_5$H$_2$-1,2,4-tBu$_3$, C$_9$H$_5$-1,3-tBu$_2$ 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
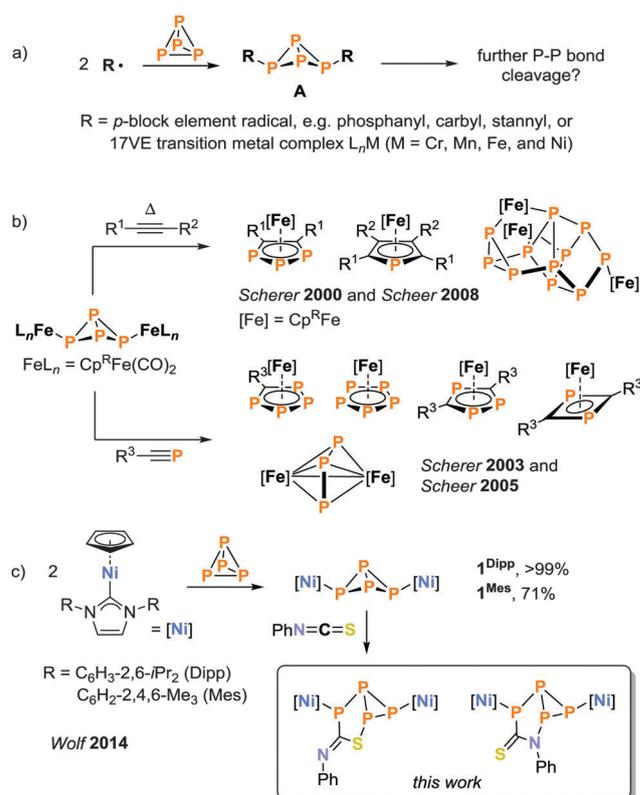


**Scheme 1** (a) Formation of bicyclo[1.1.0]tetraphosphabutanes amenable for further transformations; (b) selected reactions of iron-substituted bicyclo[1.1.0]tetraphosphabutanes; Cp$^R$ = C$_5$H$_2$-1,2,4-tBu$_3$, C$_5$H$_2$-1,2,4-tBu$_3$, C$_9$H$_5$-1,3-tBu$_2$, C$_5$iPr$_5$, R$^1$ = R$^2$ = Me, Ph; R$^1$ = H, R$^2$ = Ph, tBu, SiMe$_3$, CO$_2$Me/Et, R$^3$ = tBu, 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, [{($\eta^5$-Cp)Ni(IDipp)}$_2$($\mu$-$\eta^1$:$\eta^1$-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 [($\eta^5$-Cp)Ni(IDipp)] and P$_4$ (Scheme 1c). Subsequent work showed that the slightly less encumbered mesityl-substituted complex [{($\eta^5$-Cp)Ni(IMes)}$_2$($\mu$-$\eta^1$:$\eta^1$-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
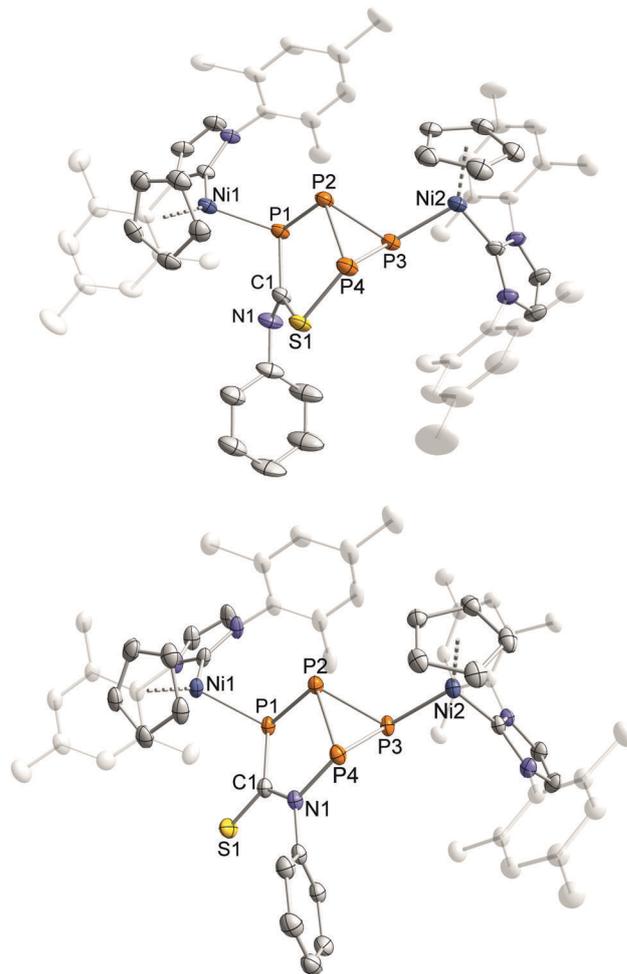


Fig. 2 Solid-state molecular structures of **2a** (top) and **2b** (bottom). The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 40% level. Selected bond lengths [Å] and angles [°] for **2a**: P1–C1 1.860(4), P4–S1 2.1257(13), P1–P2 2.1818(14), P2–P3 2.2182(15), P2–P4 2.2222(14),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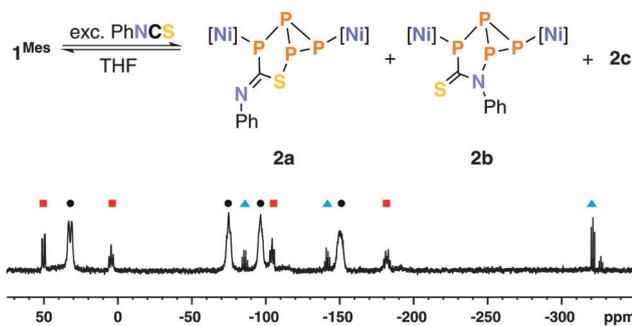


Fig. 1 Synthesis of **2a** and **2b** (top), and $^{31}$P{$^1$H} NMR spectrum ([D$_8$]THF) of the reaction of PhNCS and **1$^{Mes}$** (7:1) at room temperature after four hours; ● = **2a**, ■ = **2b**, ▲ = **2c** (bottom).

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$_3$S heterocycle (P1–P2–P4–S1–C1) is almost flat ($\Sigma_{angles}$ = 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 ($\Sigma_{angles}$ = 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 $\tau_{FWHM}$ = 565 Hz); they become sharper when the temperature is decreased to −80 °C (av. $\tau_{FWHM}$ = 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$_A$ connected to three P atoms based on the observation of three large $^1J$(P,P)-coupling constants for this multiplet ($^1J$(P$_A$P$_D$) = −178 Hz, $^1J$(P$_A$P$_M$) = −185 Hz and $^1J$(P$_A$P$_X$) = −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{$^1$H} NMR resonances at −182.1, −104.5, 4.5 and 50.1 ppm in [D$_8$]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 $\tau_{FWHM}$ = 33 Hz at room temperature to $\tau_{FWHM}$ = 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.

$^{31}$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$^{Mes}$** in solution (ESI†). A mixture of **2a** (89%), **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** : **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 **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 P$_4$ molecule.
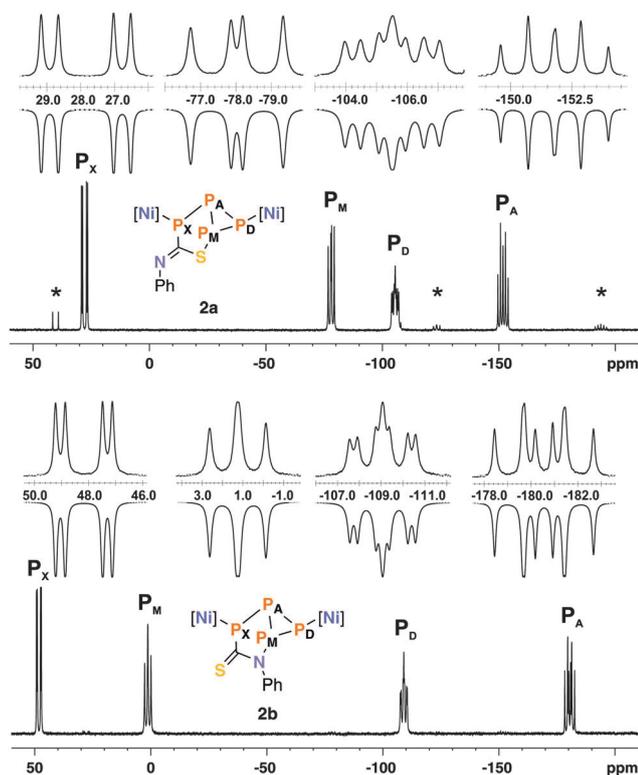
Fig. 3 $^{31}$P{$^1$H} NMR spectra of **2a** (top) and **2b** (bottom, 161.98 MHz, [D$_8$]THF, 193 K); **2a** (ADMX spin system): $\delta_A$ = −151.8 ppm, $\delta_D$ = −105.5 ppm, $\delta_M$ = −78.0 ppm, $\delta_X$ = 27.8 ppm, $^1J$(P$_A$P$_D$) = −178 Hz, $^1J$(P$_A$P$_M$) = −185 Hz, $^1J$(P$_A$P$_X$) = −374 Hz, $^1J$(P$_D$P$_M$) = −238 Hz, $^2J$(P$_D$P$_X$) = 82 Hz, $^2J$(P$_M$P$_X$) = 9 Hz; **2b** (ADMX spin system): $\delta_A$ = −180.5 ppm, $\delta_D$ = −109.1 ppm, $\delta_M$ = 1.2 ppm, $\delta_X$ = 48.2 ppm, $^1J$(P$_A$P$_D$) = −193 Hz, $^1J$(P$_A$P$_M$) = −209 Hz, $^1J$(P$_A$P$_X$) = −282 Hz, $^1J$(P$_D$P$_M$) = −237 Hz, $^2J$(P$_D$P$_X$) = 57 Hz, $^2J$(P$_M$P$_X$) = 10 Hz; expansions (inset) show the experimental (up) and fitted spectra (down). The signals assigned to **2b** are labeled with an asterisk.
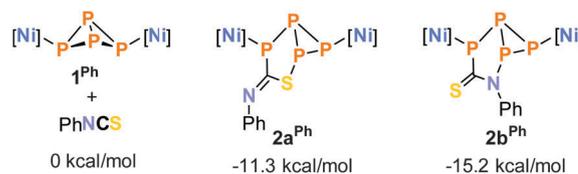
## Notes and references

‡ $^{31}$P{$^1$H} NMR data of **2c** ([D$_8$]THF, A$_2$MX spin system): $\delta$ = −321.2 (dd, 2P, P$_A$, $^1J$(P$_A$P$_M$) = −178 Hz, $^1J$(P$_A$P$_X$) = −188 Hz), −141.5 (dt, 1P, P$_M$, $^2J$(P$_M$P$_X$) = 208 Hz), −85.8 (dt, 1P, P$_X$) 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$^{Mes}$** 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$^{Add1}$** 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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