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-η¹-η¹-P₄)] (1Mes, 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. phosphenium 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).⁶–⁹

Previous studies mainly focused on iron complexes.¹⁰ As reported by Scherer and Scheer, thermolysis or photolysis of [(CpFe(η¹-C₄H₄)₃)[μ-η¹-η¹-P₄]] (CpR = C₅H₅-1,2,4-tBu₃, C₅H₅-1,2,4-tBu₃, C₉H₆-1,3-tBu₂, C₅iPr₅, R₁ = R₂ = Me, Ph; R₁ = H, R₂ = Ph, tBu, SiMe₃, CO₂Me/Et, R₃ = tBu, C(CH₂)₅Me; (c) synthesis of 1₃Dipp and 1₃Mes and reactivity toward phenyl isothiocyanate.⁶–¹⁰

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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; Cp² = C₅H₅-1,2,4-tBu₃, C₅H₅-1,2,4-tBu₃, C₅H₅-1,3-tBu₂, C₅iPr₅, R₁ = R₂ = R₃ = Me, Ph; R₁ = H, R₂ = Ph, tBu, SiMe₃, CO₂Me/Et, R₃ = tBu, C(CH₂)₅Me; (c) synthesis of 1₃Dipp and 1₃Mes and reactivity toward phenyl isothiocyanate.⁶–¹⁰

† Electronic supplementary information (ESI) available. CCDC 1446071–1446073. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc01572g
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, \( \left[ \left( \eta^5\text{Cp} \right) \text{Ni[DiDipp]} \right]_2 \left( \mu-[\text{η}^1\text{P}-\text{η}^1\text{P}] \right) \) (1Dipp, DiDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene).\(^7\) This complex is formed in a quantitative reaction from two equivalents \( \left[ \left( \eta^5\text{Cp} \right) \text{Ni[DiDipp]} \right] \) and \( \text{P}_4 \) (Scheme 1c). Subsequent work showed that the slightly less encumbered mesityl-substituted complex \( \left[ \left( \eta^5\text{Cp} \right) \text{Ni[Mes]} \right]_2 \left( \mu-[\text{η}^1\text{P}-\text{η}^1\text{P}] \right) \) (1Mes) is obtained in an analogous fashion. 1Mes was isolated as dark red air-sensitive crystals in 71% yield (Scheme 1c) and shows a better solubility than 1Dipp, dissolving well in benzene, toluene, diethyl ether and tetrahydrofuran (ESI†).

In order to probe the reactivity of 1Dipp and 1Mes, we investigated reactions with heteroallenes. ADMX spin systems were observed by \(^{31}\text{P}\) 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 1Mes and PhNCS in [D\(_8\)]THF (Fig. 1) revealed that 7 equiv. PhNCS were necessary for full conversion of 1Mes after four hours, while a large amount of 1Mes (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 \(^{31}\text{P}\)\(^{\text{[1]}\text{H}}\) NMR spectrum of the reaction of 1Dipp 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), 1Dipp (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. 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\(_2\)S heterocycle (P1–P2–P3–S1–C1) is almost flat (\(\Sigma\)angles = 535.5 \(^\circ\)) 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.\(^11\).

The molecular structure of the regio isomer 2b (Fig. 2, bottom) features a flat CNP\(_3\) heterocycle (\(\Sigma\)angles = 539.0 \(^\circ\)) with a thiokeitone 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 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 $\tau_{FWHM}$ = 565 Hz); they become sharper when the temperature is decreased to −80 °C (av. $\tau_{FWHM}$ = 35 Hz). Experimental and fitted $^{31}$P{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 $P_X$ connected to three P atoms based on the observation of three large $\gamma(P,P)$-coupling constants for this multiplet ($\gamma(P,P_X) = −178$ Hz, $\gamma(P,P_M) = −185$ Hz and $\gamma(P,P_A) = −374$ Hz). The P atoms coordinated to nickel ($\delta(P_P) = −105.5$ ppm; $\delta(P_X) = 27.8$ ppm) show a common large $\gamma(P,P)$ coupling ($\gamma(P,P_X) = 82$ Hz), which may arise from an interaction of the lone pairs due to the conformational constraints of the bicyclo[3.1.0]heterohexane skeleton.

**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 $\tau_{FWHM} = 33$ 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{1H} NMR studies indicate that the formation of 2a, 2b and 2c is reversible; i.e. the products slowly equilibrate with the starting material 1Mes in solution (ESI†). A mixture of 2a (89%), 1Mes (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:1Mes) 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)† were performed to gain additional insight into the thermodynamics of the reaction. The optimized structures of the truncated model complexes 1Ph, 2aPh and 2bPh, 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 2aPh and 2bPh is exergonic, and the thermodynamic product of the reaction appears to be 2bPh (−15.2 kcal mol$^{-1}$ with respect to the starting materials), while 2aPh (−11.3 kcal mol$^{-1}$) is a kinetic product.¶

In conclusion, the reaction of 1Mes 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. Efficient preparative methods exist for a range of bicyclo[1.1.0]tetraphosphabutenes,1,6–9 therefore, such transformations may provide a fruitful avenue to the stepwise and selective degradation of the P$_4$ molecule.

We thank B. Sc. Thomas Maier for experimental assistance. Funding by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

**Notes and references**

† $^{31}$P{1H} NMR data of 2c ([D$_8$]THF; A$_2$MX spin system): $\delta = −321.2$ (dd, 2P, $P_X$), $\gamma(P,P_A) = −178$ Hz, $\gamma(P,P_M) = −188$ Hz, $\gamma(P,P_A) = −209$ Hz, $\gamma(P,P_M) = −282$ Hz, $\gamma(P,P_A) = −237$ Hz, $\gamma(P,P_M) = 57$ Hz, $\gamma(P,P_A) = 10$ Hz; expansions (inset) show the experimental (up) and fitted spectra (down). The signals assigned to 2b are labeled with an asterisk.

‡ $^{1}$H NMR data of 2e ([D$_8$]THF, A$_2$MX spin system): $\delta = −321.2$ (dd, 2P, $P_X$), $\gamma(P,P_A) = −178$ Hz, $\gamma(P,P_M) = −188$ Hz, $\gamma(P,P_A) = −209$ Hz, $\gamma(P,P_M) = −282$ Hz, $\gamma(P,P_A) = −237$ Hz, $\gamma(P,P_M) = 57$ Hz, $\gamma(P,P_A) = 10$ Hz; expansions (inset) show the experimental (up) and fitted spectra (down). The signals assigned to 2b are labeled with an asterisk.

§ 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 1Mes in a 94.5:0.5:5 ratio.
The structure and the mechanism of formation of the minor product 2e (A-MX 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 PnCNS (2e\textsuperscript{add} and 2e\textsuperscript{add}) or result from the insertion of the C=S or C=N double bonds into the Ni-P bond ([E]2e\textsuperscript{ins}, [Z]2e\textsuperscript{ins} and 2e\textsuperscript{ins}). Each of them has an energy significantly higher than that of 2a\textsuperscript{ins} and 2b\textsuperscript{ins}.


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