Diphosphorus Release and Heterocumulene Oligomerisation by Nickel Complexes

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The generation of diphosphorus molecules \( \text{P}_2 \) under mild conditions in solution is a useful strategy to generate diphosphines via \([4+2]\) cycloadditions. We recently described the release of \( \text{P}_2 \) units from the nickel butterfly complex \( \left \{ (\text{IMes})\text{Ni} (\text{CO})_2 (\mu_2, \eta^2_2: \eta^2_2-\text{P}_2) \right \} \) (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) upon addition of CO gas. Herein, we developed an alternative protocol for the same process using heterocumulenes. In addition to formation of \( \text{P}_4 \) (the dimerisation product of \( \text{P}_2 \)), the reactions afford nickel complexes of novel pincer-type ligands. Aryl isothiocyanates undergo a trimerisation within the coordination sphere of nickel and afford square planar nickel complexes with \( \text{S}_3\text{C} \) pincer-ligand frameworks. Carbon disulfide coordinates to the \( \{(\text{IMes})\text{Ni}\} \)-fragment in an \( \eta^2 \)-fashion, affording a dinuclear complex. Similar products are formed when the N-heterocyclic carbene nickel(0) complex \( \left \{ (\text{IMes})\text{Ni}(\text{vtms}) \right \} \) is used as a precursor (vtms = vinyltrimethylsilane).

Introduction

The low tendency of the heavier members of the p-block elements to form multiple bonds is known as the double bond rule.[1] In the last decades, however, main group chemists have shown that this rule can be overcome, e.g. by introducing bulky substituents. A noteworthy example for this kinetic stabilisation is the isolation of a disilyne by Sekiguchi and co-workers.[2] For group 15 elements, the formation and detection of the \( \text{P}_2 \) molecule, showing a \( \text{P} \equiv \text{P} \) triple bond, has been investigated intensively. Diphosphorus can be stabilised in the coordination sphere of transition metal complexes.[3,4] In most of these cases \( \text{P}_2 \) acts as a ligand bridging two metal centres in an \( \eta^2 \)-mode. Only very recently, triply bonded \( \text{P} \equiv \text{P} \) was stabilised in the coordination sphere of a platinum complex.[5] Upon heating white phosphorus above 1000 K, dissociation into diphosphorus occurs.[6,7] However, the conditions of this gas-phase reaction render further reactions with \( \text{P}_2 \) difficult. Therefore, several compounds which generate \( \text{P}_2 \) under milder conditions in solution have been developed (Figure 1).

The group of Cummins showed that the niobium complex \( \text{A} \) transfers a \( \text{P}_2 \) unit to cyclohexadiene in a Diels-Alder reaction to afford the diphosphine \( \text{B} \).[8] The molecular structure was confirmed by single crystal X-ray structure analysis of a tungsten pentacarbonyl adduct of \( \text{B} \). A similar \([4+2]\)-cycloaddition was achieved by photolysis directly from \( \text{P}_4 \) in the presence of butadiene or dimethylbutadiene affording the diphosphines \( \text{B} \) and \( \text{C} \).[9,10] Moreover, Cummins and co-workers showed that the diphosphorus bis(anthracene) compound \( \text{D} \) efficiently transfers \( \text{P}_2 \) to butadienes. Under mild thermal activation, \( \text{D} \) releases \( \text{P}_2 \) which could be detected by molecular beam mass spectrometry and ultimately transforms to red phosphorus.[11] Recently, the group of Ghadwal showed that \( \text{P}_2 \)
units are released upon reaction of a phosphorus analogue of $p$-quinodimethane $\text{([IPr=C=P])}$ (IPr = 1,3-bis(2,6-di-iso-propylphenyl)imidazolin-2-ylidine) containing a planar P$_4$ ring with cyclohexadiene.$^{[12]}$ However, this reaction was not selective, affording both P$_4$ and the cycloaddition product B.

In 2018, we showed that the release of P$_2$ units is also viable using the dinuclear nickel butterfly complex $\text{([IMes]Ni(\text{CO})_2(\mu_4-P_2)])}$ (Figure 2) to an orange solution of $\text{([IMes]Ni(\text{CO})_2(\mu_4-P_2)])}$ in toluene resulted in a colour change to dark red. Analysis of the reaction mixture by $\text{^31P}$(H) NMR spectroscopy revealed complete consumption of $\text{([IMes]Ni(\text{CO})_2(\mu_4-P_2)])}$ and formation of a single species characterised by a singlet resonance at 34.7 ppm. It is noteworthy that no P$_2$ was detected in the spectrum. Orange needles suitable for single crystal X-ray diffraction (SCXRD) were formed by slow diffusion of 2,3-dimethylbutadiene (dmb) into a benzene solution and revealed the formation of the diphosphine C.

Results and Discussion

This study commenced with reactions of isonitriles with $\text{([IMes]Ni(\text{CO})_2(\mu_4-P_2)])}$. Isonitriles were chosen because they are isoelectronic to carbon monoxide and often show similar reactivity. Unfortunately, the reaction of Cy-N=C with $\text{([IMes]Ni(\text{CO})_2(\mu_4-P_2)])}$ afforded an intractable reaction mixture displaying multiple signals in the $\text{^31P}$(H) NMR spectrum. We therefore turned our attention towards other two-electron donor ligands such as carbenes. Addition of excess amounts (8 equiv.) of the carbene 2,3,4,5-tetramethylimidazolin-2-ylidene (TMC, Figure 3) to a toluene solution of $\text{([IMes]Ni(\text{CO})_2(\mu_4-P_2)])}$ resulted in a colour change to dark red. Analysis of the reaction mixture by $\text{^31P}$(H) NMR spectroscopy revealed complete consumption of $\text{([IMes]Ni(\text{CO})_2(\mu_4-P_2)])}$ and formation of a single species characterised by a singlet resonance at 34.7 ppm. It is noteworthy that no P$_2$ was detected in the spectrum. Orange needles suitable for single crystal X-ray diffraction (SCXRD) were formed by slow diffusion of n-hexane into a benzene solution and revealed the formation of the diphosphorus and white phosphorus from $\text{([IMes]Ni(\text{CO})_2(\mu_4-P_2)])}$.

Figure 2. P$_4$ release via P$_2$-type intermediates from a nickel butterfly complex$^{[10,14]}$ dmb = 2,3-dimethylbutadiene.
We next assessed the reactivity of \([\text{[(IMes)Ni(CO)]}_2(\mu_1^1\eta_1^1\eta_1^2-P_2)_2]\) toward heterocumulenes. While di-iso-propylcarbodiimide does not react with \([\text{[(IMes)Ni(CO)]}_2(\mu_1^1\eta_1^2\eta_1^2-P_2)_2]\) even at elevated temperatures, phenyl isothiocyanate reacts readily with \([\text{[(IMes)Ni(CO)]}_2(\mu_1^1\eta_1^2\eta_1^2-P_2)_2]\) to form a purple solution and \(P_2\) as observed by \(^{31}P\) NMR spectroscopy (singlet at \(-519.1\) ppm, see Figure S17 in the SI). Structural characterisation of deep purple crystals by SCXRD revealed the formation of the mononuclear complex \([\text{[(IMes)Ni(NHCS)]}_2(\text{PhNCS})_2]\) (3a, Figure 4a). The same compound 3a can also be synthesised by reacting the vinyltrimethylsilane \((\text{vttms})\) nickel(0) complex \([\text{[(IMes)Ni(vttms)]}_2]\) with phenyl isothiocyanate. Using this procedure, the compound was isolated in 44% yield. In a similar vein, the substituted aryl isothiocyanates 2,6-dimethylphenyl isothiocyanate and 3,5-bis(trifluoromethyl)phenyl isothiocyanate react with \([\text{[(IMes)Ni(vttms)]}_2]\) to form \([\text{[(IMes)Ni(\eta_1^1\eta_1^2\text{Ar-NRCS})]}(\text{Ar}=2,6-\text{Me}_2-C_6H_3\text{(3b)}\text{and} 3,5-(\text{CF}_3)_2C_6H_3\text{(3c)})\) in 77% \((3b)\) and 39% \((3c)\) yield, respectively. While complex 3c was also accessible from \([\text{[(IMes)Ni(CO)]}_2(\mu_1^1\eta_1^2\eta_1^2-P_2)_2]\) as a precursor, 2,6-Me_2C_6H_3NCS only reacted very slowly with the \(P_2\) complex at ambient temperature. Complexes 3a–c contain pincer-type ligands formed through trimerisation of three ArNCS molecules in the coordination sphere of nickel.

The molecular structures of 3a–c (Figure 4b) in the solid state show \(\eta_1^1\)-coordination of the nickel atom by two sulfur atoms and one carbon atom of the \((\text{ArNCS})_2\) ligands, resulting in a classical pincer-type architecture. The structural data for all three complexes are similar; thus, only the data for 3a will be discussed exemplarily in the following section. The coordination environment of the nickel atom is almost planar [sum of angles 360.1(1)°]. The two planar pentagons \(C2/N1/C1/Ni1/S2\) and \(C1/S3/C2/S1/Ni1\) are almost coplanar with a plane to plane twist angle of 3.1(1)° whereas the imidazole rings of the NHC are significantly displaced with respect to the planar \((\text{PhNCS})_3\) scaffold with a plane to plane twist angle of 73.0(2)°. The Ni–C(1) bond length of 1.8722(2) Å is shorter than the Ni1–C4 bond length (1.9352(2) Å), which can be attributed to a partial double bond character of the Ni1–C1 bond.

NMR spectra of complexes 3a and 3b were recorded at 0°C because the two complexes slowly decompose in solution at ambient temperature. Complex 3c was more stable at ambient temperature, allowing for NMR characterisation at 300 K. The \(^1H\) NMR spectra of all three complexes are in good agreement with their molecular structures determined by SCXRD. Three signals were observed for the methyl-groups of the IMes ligand, which indicates a hindered rotation around the N–C(IMes) bonds. Additional signals in the aromatic region (3a–c) and the aliphatic region (3b) arise from the aryl residues of the former isothiocyanates. In the \(^{13}C\) (\(^{1H}\)) NMR spectrum the two carbene resonances of C4 and C1 were detected at 173.5 and 238.8 ppm (3a), 179.2 and 239.1 ppm (3b) and 168.6 and 241.9 ppm (3c), respectively. The assignment of these resonances was confirmed by \(^1H-^{13}C\)-HMBC spectra. Complex 3c gives rise to three resonances in the \(^{19}F\) (\(^{1H}\)) NMR spectrum with chemical shifts of \(-62.6, -62.5\) and \(-62.4\) ppm in a 1:1:1 ratio, confirming the three different chemical environments of the CF3 groups. The UV/Vis absorption spectra of compounds 3a–c feature broad bands at 560–580 nm, which account for the purple colours in solution.

In order to gain further information on the electronic structure, density functional theory (DFT) calculations were performed on complex 3a. The optimised structure (BP86-D3BJ/def2-TZVP level of theory) compares well with the experimental data. The HOMO of 3a is mainly located at the two sulfur atoms coordinating to the Ni atom and the Ni atom.

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**Figure 4.** Synthesis (a) and molecular structures (b) of 3a, 3b and 3c in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms, the second molecular in the asymmetric unit, solvent of crystallisation and positional disorder for 3c are omitted for clarity. Selected bond lengths [Å] and angles [°] for 3a: Ni1–C1 1.872(2), Ni1–C4 1.935(2), Ni1–S1 2.130(1), Ni1–S2 1.214(1), S3–C1 1.733(2), Ni1–C1 1.337(2), Ni1–C2 1.447(2), S2–C2 1.734(2), N1–C2 1.269(2), S3–C3 1.789(2), S1–C1 1.736(2), N3–C3 1.276(2), S1–N1–S2 179.1(1), S1–N1–P2 91.7(1), C4–N1–S1 88.7(1), C1–N1–S2 87.4(1), C1–N1–S3 90.4(1), N1–C1–S1 121.3(1), Ni1–C1–S1 114.4(1), HNC to Ni/S/C/N plane to plane twist angle 73.0(2), C2/N1/C1/S2 to C1/S3/C3/S1/Ni plane to plane twist angle 3.1(1); for 3b: Ni1–C1 1.871(1), N1–C4 1.936(1), Ni1–S1 2.139(1), Ni1–S2 2.167(1), S3–C1 1.726(1), N1–C1 1.335(2), N1–C2 1.438(2), S2–C2 1.733(1), S2–N2 1.272(2), S3–C3 1.784(1), S1–C3 1.729(1), N3–C3 1.277(2), S1–Ni1–S2 177.1(1), C4–N1–S2 92.0(1), C4–Ni1–S3 89.7(1), C1–Ni1–S2 86.8(1), C1–Ni1–S1 91.5(1), C1–Ni1–C4 174.1(1), S3–C1–Ni1 124.9(1), N1–C1–Ni1 121.6(1), N1–C1–S1 113.2(1), HNC to Ni/S/C/N plane to plane twist angle 57.2(1), C2/N1/C1/Ni1/S2 to C1/S3/C3/S1/Ni1 plane to plane twist angle 2.9(1), for 3c: Ni1–C1 1.871(2), N1–C4 1.937(2), Ni1–S1 2.147(1), Ni1–S2 2.151(1), S3–C1 1.719(2), N1–C1 1.33(1), N1–C2 1.44(1), S2–C2 1.723(2), N2–C2 1.268(2), S3–C3 1.784(2), S1–C3 1.734(2), N3–C3 1.274(3), S1–Ni1–S2 178.4(1), C4–Ni1–S2 90.3(1), C4–Ni1–S1 90.4(1), C1–Ni1–S2 87.4(1), C1–Ni1–S1 91.7(1), C1–Ni1–C4 176.9(1), S3–C1–Ni1 125.0(1), Ni1–C1–Ni1 120.8(1), Ni1–C1–S3 114.0(1), HNC to Ni/S/C/N plane to plane twist angle 69.3(1), C2/N1/C1/Ni1/S2 to C1/S3/C3/S1/Ni1 plane to plane twist angle 0.7(1).
itself (Figure 5 top). The LUMO is mostly located at the C1 atom with contributions from the adjacent nitrogen and carbon atoms. Inspection of the Mayer bond orders reveals a significant delocalisation of electrons along the N1–C1–S3 motif, as anticipated for a Fischer-type carbene (Figure 5 bottom). Moreover, the N2–C2–S2 and N3–C3–S1 moieties can be considered as delocalised heteroallylic systems. This is also in agreement with the positive Löwdin atomic charges on the N2 and N3 atoms with values of 0.17 and 0.13, respectively.

In case of complex 3c, the supernatant solution of the crystallisation contained crystals of an additional complex 4, which was characterised by single crystal X-ray crystallography (Figure 6).

Complex 4 presumably forms upon prolonged storage of complex 3c at ambient temperature. The molecular structure is composed of two nickel atoms, a trimer (ArNCS), of three former aryl isothiocyanate molecules and an anisotride ligand (ArNC), which is presumably formed from a fourth ArNCS molecule via loss of elemental sulfur. One of the nickel atoms (Ni1) is in a strictly square planar coordination environment (bond angles from 87.0(1)–92.1(1)°), while the coordination environment of the second nickel atom (Ni2) is more distorted [50.1(1)–123.4(1)°]. The N4–C4 bond length of 1.157(3) Å compares well to related nickel isonitrile complexes (e.g. [Ni(NCPh)3] 1.162(4) Å).[15] The new C1–C2 bond in 4 has a bond length of 1.478(3) Å which is in the range commonly observed for double bonds.[16] This is in line with the bond angles on the C1 atom [117.6(2) to 123.3(2)°], which indicate an sp2-hybridised carbon atom in a trigonal planar environment. The C2 atom is tetracoordinate with a Ni1–C2 bond length of 1.922(2) Å. Unfortunately, compound 4 could not be isolated cleanly, preventing its full characterisation and further elucidation of its properties.

Notably, several reactions of organic isothiocyanates with transition metal complexes have been reported to date which result in insertions or oligomerisation reactions on the metal centre.[17,18] Only one system with a ligand comparable to the (ArNCS)3 scaffold as in 3a–c was described in the literature (complex E, Figure 7 left).[19] This complex contains rhodium in a similar coordination environment with two triphenylphosphine molecules, an additional chlorido ligand and an S–C–S pincer-type ligand obtained from ethoxycarbonyl isothiocyanate. However, in this case, a 1,3-shift of one of the substituents was observed, affording a two-coordinate N1-atom. Furthermore, it is noteworthy that a different, yet related P–C–S-type pincer complex F was reported recently by Gessner and co-workers.[20]

The successful reactions of (substituted) aryl isothiocyanates with [(IMes)Ni(tmtms)]+ inspired us to investigate similar reactions of cyclohexyl isothiocyanate CyNCS (Figure 8). In this case, a different product [(IMes)Ni(η3-CyNCS)2] (5) can be isolated in 73% yield, which results from the dimerisation of CyNCS in the coordination sphere of nickel. A similar species [(IPr)Ni(η3-PhNCS)2] was obtained in a recent study using [(IPr)Ni-
Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–S1 2.282(1), N1–S2 2.150(1), N1–C1 1.755(3), N1–C3 1.933(3), S2–C2 1.722(3), S1–C1 1.646(3), N1–C1 1.319(3), N1–C2 1.437(3), N1–C4 1.488(3), N2–C2 1.266(4), S2–N1–S1 129.8(1), C1–N1–S2 83.9(1), C1–Ni–N1–S2 166.5(1), C1–Ni–S2 83.9(1), C1–Ni–S2 112.0(2), C2–Ni–Ni 131.7(2), S2–Ni–Ni 129.8(1), C1–Ni–S2 112.0(2), C1–Ni–N1 45.8(1), C1–Ni–Ni 131.7(2), S2–Ni–Ni 129.8(1), C1–Ni–S2 83.9(1), C1–Ni–S1 130.3(2), Ni–Ni/S1/C1 plane to plane twist angle 90.1(1), Ni/S1/C1/N1/C2/S2 plane to plane twist angle 0.7(1).

Inspection of the coordination of the S–C–S pincer ligand in 3a–c suggests that the nitrogen atoms in ArNCS are not essential for metal coordination. Therefore, it was hypothesised that isoelectronic carbon disulfide, CS₂, might undergo a similar reaction with [[(IMes)Ni(CO)₃]]⁻(μ³-η¹-η¹-η¹-PS₂)⁻ or [[IMes]Ni(vtms)]⁻. Indeed, addition of a CS₂ solution to solutions of either of the complexes in benzene afforded a colour change from orange to red and precipitation of a red powder. ¹H NMR spectra of the red solid in THF-d₈ confirm the presence of one distinct IMes signal set, whereas the ³¹P(¹H) NMR spectrum reveals formation of P₂ when [[(IMes)Ni(CO)₃]]⁻(μ³-η¹-η¹-η¹-PS₂)⁻ is used as Ni-precursor. SCXRD analysis on crystals grown from fluorobenzene reveal the formation of the dinuclear complex [[IMes]Ni(η²-η²-η²-PS₂)]⁻ (6, Figure 9), which was isolated in 88% yield starting from [[IMes]Ni(CO)₃]]⁻(μ³-η¹-η¹-η¹-PS₂)⁻.

In the molecular structure of 6, two sulfur atoms and a carbene-like carbon coordinate to planar nickel atoms. In contrast to 3a–c, however, the complex is dinuclear and the CS₂-moieties are not directly connected, as was the case for the trimerised (PhNCS)₃ unit in 3a–c. Each CS₂ moiety in 6 is η²-coordinated via a C=S bond to one nickel atom and σ-bonded to the other nickel atom via the other sulfur atom. Similar to 3a–c, the Ni–Ni bond of 1.813(2) Å of the heterocumulene ligand is shorter than the Ni–C bond (1.937(2) Å) formed by the NHC, the difference being more pronounced in case of 6 due to the small NiS₃-ring.
The $^1$H NMR spectrum of 6 is in line with the molecular structure determined by SCXRD with a total of four singlet signals as expected for a C$_{2v}$-symmetric IMes ligand. The $^{13}$C($^1$H) NMR spectrum shows a strongly low-field-shifted carbene resonance for C1 at 285.6 ppm, which was assigned by $^1$H-$^{13}$C-HMBNMR spectroscopy. The NHC-carbene (C2) signal is observed at 189.2 ppm, similar to the shifts observed for HMBC NMR spectroscopy. The NHC-carbene (C2) signal is ligand. Aryl-substituted isocyanates ArNCS undergo a trimerisation to form the symmetric complex $\{[(TMC)Ni(CO)]_2(\mu^2,\eta^1: \eta^1-P_2)\}$.[20] A closely related example is the complex $\{([BuIm]Ni[\mu^2,\eta^1: \eta^1-C_5])_3\}$ (tBuIm=1,3-di-tert-butylimidazol-2-ylidene; N1–C1 1.810(2) Å, N1–C2 1.968(2) Å), which features similar structural and NMR parameters as compound 6.[18]

Having firmly established that $\{[(IMes)Ni(CO)]_2(\mu^2,\eta^1: \eta^1-P_2)\}$ readily forms P$_2$ upon reaction with isothiocyanates and CS$_2$, we finally sought to trap the P$_2$ intermediate with 2,3-dimethylbutadiene. Unexpectedly, the desired diphosphine C, which was the major product when CO gas, could not be detected by $^{31}$P NMR. Instead, the formation of several doublet resonances was observed (see Figures S15 and S16). Even though these signals hint towards the formation of nickel complexes of C, the isolation of cycloaddition products from $\{[(IMes)Ni(CO)]_2(\mu^2,\eta^1: \eta^1-P_2)\}$ unfortunately remains elusive.

**Conclusion**

Reactions of suitable two-electron donors with the Ni$_2$P$_2$ complex $\{[(IMes)Ni(CO)]_2(\mu^2,\eta^1: \eta^1-P_2)\}$ were investigated to study the utility of this complex as a source of P$_2$ units. While addition of tetramethylcarbene to $\{[(IMes)Ni(CO)]_2(\mu^2,\eta^1: \eta^1-P_2)\}$ only resulted in a ligand exchange reaction to form the symmetric complex 1, heterocumulenes replaced the P$_2$ ligand effectively to afford P$_2$ and the new complexes 3–6 which contain S–C–S pincer-type carbene ligands with planar coordination geometries around the nickel atom and an NHC ancillary ligand. Aryl-substituted isocyanates ArNCS undergo a reorganisation within the coordination sphere of nickel to form unusual (ArNCS)$_2$ scaffolds observed in the structures of 3–6 while CS$_2$ coordinates in an $\eta^1$-fashion and forms a dinuclear complex. The same complexes 3–6 can be prepared by the simple reaction of the heterocumulene with the readily available Ni(0) complex $\{[(IMes)Ni(vtms)]_2\}$.

While the P$_2$ ligand in $\{[(IMes)Ni(CO)]_2(\mu^2,\eta^1: \eta^1-P_2)\}$ appears to be easily liberated, trapping reactions with 2,3-dimethylbutadiene turned out to be unsuccessful. Although the reasons for this reactivity are currently not entirely unclear, it is tempting to speculate that the cycloaddition products coordinate to nickel fragments to form several unidentified complexes. Furthermore, it is possible that the P$_2$ type fragments undergo unselective reactions with the heterocumulenes themselves. Further investigations into the release of P$_2$ from Ni$_2$P$_2$ complexes and the subsequent trapping of the P$_2$ moiety therefore appear to be worthwhile.

**Experimental Section**

**General Synthetic Methods**

All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at $<$0.1 ppm H$_2$O and $<$0.1 ppm O$_2$). Tetramethylcarbene (TMC)[21], $\{[(IMes)Ni(CO)]_2(\mu^2,\eta^1: \eta^1-P_2)\}$[20] and $\{[(IMes)Ni(vtms)]_2\}$[22] were prepared according to procedures previously reported in the chemical literature. All other chemicals were purchased from commercial suppliers and used without further purification.

Solvents were dried and degassed with an MBraun SPS800 solvent purification system. Fluorobenzene was dried over sodium and distilled. All dry solvents except n-hexane were stored under argon over activated 3 Å molecular sieves in gas-tight ampules. n-Hexane was instead stored over a potassium mirror.

**General Analytical Techniques**

NMR spectra were recorded on Bruker Avance 300 or 400 spectrometers at 300 K unless otherwise noted and internally referenced to residual solvent resonances ($^1$H NMR: THF-d$_8$: 1.72 ppm, CDCl$_3$: 7.16 ppm, toluene-d$_8$: 2.08 ppm; $^{13}$C($^1$H) NMR: THF-d$_8$: 25.31 ppm, CDCl$_3$: 128.06 ppm, toluene-d$_8$: 20.43 ppm). Chemical shifts δ are given in ppm referring to external standards of tetramethysilane (H, $^{13}$C($^1$H)), 85% phosphoric acid ($^3$P and $^3$P ($^1$H)), $^1$H and $^{13}$C NMR signals were assigned based on 2D NMR spectra ($^1$H,$^1$H-COSY, $^1$H,$^{13}$C-HSQC, $^1$H,$^{13}$C-HMQC).

UV/Vis absorption spectra were recorded on an Ocean Optics Flame Spectrometer. Elemental analysis was performed by the Central Analytical Services department of the University of Regensburg.

Single-crystal X-ray diffraction data were recorded on a Rigaku Oxford Diffraction SuperNova Atlas or a XtaLAB Synergy R (DW system, Hypix-Arc 150) device with Cu-K$_\alpha$ radiation ($\lambda = 1.54184$ Å). Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow nitrogen cooling device. Either semi-empirical multi-scan absorption corrections[26] or analytical ones[24] were applied to the data. The structures were solved with SHELXT[25] solution program using dual methods and by using Olex2 as the graphical interface.[26] The models were refined with ShelXL[27] using full matrix least squares minimisation on F$_2$.[28] The hydrogen atoms were located in idealised positions and refined isotropically with a riding model.

**Synthesis of Compounds**

$\{[(TMC)Ni]_2(\mu^2,\eta^1: \eta^1-P_2)\}$ (1)

To a solution of $\{[(IMes)Ni(CO)]_2(\mu^2,\eta^1: \eta^1-P_2)\}$ (0.5 n-hexane) (110.0 mg, 0.124 mmol, 1.0 equiv.) in toluene (6 mL) was added TMC (61.6 mg, 0.50 mmol, 4.0 equiv.). Upon stirring at ambient temperature for 2 hours, a colour change from deep orange to deep red was observed. Subsequently, the solvent was removed, and the dark red residue was dried in vacuo. The residue was washed with n-hexane (5 mL) and benzene (5 mL) and the resulting bright orange solid was dried in vacuo to afford pure $\{[(TMC)Ni]_2(\mu^2,\eta^1: \eta^1-P_2)\}$. Crystals of $\{[(TMC)Ni]_2(\mu^2,\eta^1: \eta^1-P_2)\}$ (1) suitable for X-ray crystallography were grown by slow diffusion of n-
To a solution of [(IMes)Ni(vtms)] (100.0 mg, 0.177 mmol, 1.0 equiv.) in toluene (5 mL) was added phenyl isothiocyanate (0.1 mL, 113 mg, 0.84 mmol, 4.7 equiv.). The colour of the reaction mixture changed from yellow over burgundy to deep purple while stirring at ambient temperature for 1.5 h. Subsequently, the solvent was removed and the dark residue was dried in vacuo. The residue was washed with n-hexane (20 mL), extracted in toluene (3 mL) and layered with n-hexane (20 mL). Storage at −30 °C for 3 days afforded microcrystalline [(IMes)Ni(η^2-PHNCs)] which was isolated by decanting the supernatant and dried in vacuo. Crystals of [(IMes)Ni(η^2-PHNCs)] (3a) suitable for X-ray crystallography were grown by slow diffusion of n-hexane into a saturated solution of 3a in toluene.

C_{6}H_{5}N_{2}Ni_{2}P_{2} MW = 768.68 g/mol, yield: 60 mg (44%). 1H NMR (400 MHz, 273 K, toluene-d_{8}) δ = 2.03 (s, 6H, C\textsubscript{6}H\textsubscript{3}), 2.16 (s, 6H, C\textsubscript{6}H\textsubscript{3}), 2.19 (s, 6H, C\textsubscript{6}H\textsubscript{3}), 5.96–5.98 (m, 2H, H\textsubscript{8}), 5.99 (s, 2H, C\textsubscript{6}H\textsubscript{3}), 6.69–6.73 (m, 4H, H\textsubscript{2}), 6.75 (s, 2H, C\textsubscript{6}H\textsubscript{3}), 6.76 (s, 2H, C\textsubscript{6}H\textsubscript{3}), 7.22–7.34 (m, 9H, H\textsubscript{8}) ppm. 13C NMR (100 MHz, 273 K, toluene-d_{8}) δ = 19.17 (s, C\textsubscript{5}), 19.22 (s, C\textsubscript{5}), 21.0 (s, C\textsubscript{6}), overlapping with toluene signal), 122.2 (s, C\textsubscript{5}), 122.6 (s, C\textsubscript{5}), 123.6 (s, C\textsubscript{5}), 123.7 (s, C\textsubscript{5}), 124.5 (s, C\textsubscript{5}), 126.8 (s, C\textsubscript{5}), 128.47 (s, C\textsubscript{6}), overlapping with toluene signal), 128.5 (s, C\textsubscript{6}, overlapping with toluene signal), 129.5 (s, C\textsubscript{6}), 129.6 (s, C\textsubscript{6}), 135.7 (s, C\textsubscript{6}), 135.9 (s, C\textsubscript{6}), 136.0 (s, C\textsubscript{6}), 139.2 (s, C\textsubscript{6}), 143.1 (s, C\textsubscript{6}), 149.6 (s, C\textsubscript{6}), 151.5 (s, C\textsubscript{6}), 169.8 (s, C\textsubscript{6}), 173.5 (s, C\textsubscript{6}), 180.4 (s, C\textsubscript{6}), 238.8 (s, C\textsubscript{6}) ppm. 11 signals in the aromatic region (labelled with C\textsubscript{6}) could not be assigned to specific carbon atoms. The number of signals is smaller than expected in case of free rotation around C-NiPh and hindered rotation around C-NiMes (18 signals expected, 5 signals (assigned to the Mes-group) were assigned by 2D NMR spectroscopy). This could be explained by similar chemical environments of the phenyl groups and overlapping signals. Elemental Analysis calc. C 65.63, H 5.11, N 9.11, S 12.51; found C 65.66, H 5.15, N 8.70, S 11.31. UV/Vis (THF): $\lambda_{\text{max}}$ (nm, $\varepsilon_{\text{max}}$/L mol\(^{-1}\) cm\(^{-1}\)) 280 (19 000), 380 (30000), 560 (1500).

C\textsubscript{6}H\textsubscript{6}N\textsubscript{2}Ni\textsubscript{2}S\textsubscript{2} MW = 852.84 g/mol, yield: 35 mg (77%). 1H NMR (400 MHz, 273 K, toluene-d_{8}) δ = 1.86 (s, 6H, CH\textsubscript{3}), 1.97 (s, 6H, CH\textsubscript{3}), 1.99 (s, 6H, CH\textsubscript{3}), 2.11 (s, 6H, CH\textsubscript{3}), 2.16 (s, 6H, CH\textsubscript{3}), 2.26 (s, 6H, CH\textsubscript{3}), 5.86 (s, 2H, C\textsubscript{6}H\textsubscript{3}), 6.64–6.72 (m, 4H, C\textsubscript{6}H\textsubscript{3}), 6.75 (s, 2H, C\textsubscript{6}H\textsubscript{3}), 6.83 (t, J\textsubscript{H-H} = 7.6 Hz, C\textsubscript{6}H\textsubscript{3}), 6.93 (dd, 1H, J = 6.8, 8.0 Hz, C\textsubscript{6}H\textsubscript{3}), 6.99 (br s, 1H, overlapping with solvent signal, C\textsubscript{6}H\textsubscript{3}), 7.02–7.04 (m, 2H, overlapping with solvent signal, C\textsubscript{6}H\textsubscript{3}), 7.08–7.14 (m, 2H, overlapping with solvent signal, C\textsubscript{6}H\textsubscript{3}) ppm. 13C NMR (100 MHz, 273 K, toluene-d_{8}) δ = 17.4 (s, C\textsubscript{6}H\textsubscript{3}), 18.4 (s, C\textsubscript{6}H\textsubscript{3}), 19.0 (s, C\textsubscript{6}H\textsubscript{3}), 19.1 (s, C\textsubscript{6}H\textsubscript{3}), 19.2 (s, C\textsubscript{6}H\textsubscript{3}), 21.1 (s, C\textsubscript{6}H\textsubscript{3}), 123.0 (s, C\textsubscript{6}H\textsubscript{3}), 124.3 (s, C\textsubscript{6}H\textsubscript{3}), 127.2 (s, C\textsubscript{6}H\textsubscript{3}), 127.37 (s, C\textsubscript{6}H\textsubscript{3}), 127.43 (s, C\textsubscript{6}H\textsubscript{3}), 129.37 (s, C\textsubscript{6}H\textsubscript{3}), 129.41 (s, C\textsubscript{6}H\textsubscript{3}), 134.2 (s, C\textsubscript{6}H\textsubscript{3}), 135.5 (s, C\textsubscript{6}H\textsubscript{3}), 135.6 (s, C\textsubscript{6}H\textsubscript{3}), 135.88 (s, C\textsubscript{6}H\textsubscript{3}), 135.90 (s, C\textsubscript{6}H\textsubscript{3}), 139.6 (s, C\textsubscript{6}H\textsubscript{3}), 140.3 (s, C\textsubscript{6}H\textsubscript{3}), 144.7 (s, C\textsubscript{6}H\textsubscript{3}), 150.6 (s, C\textsubscript{6}H\textsubscript{3}), 167.9 (s, C\textsubscript{6}H\textsubscript{3}), 173.4 (s, C\textsubscript{6}H\textsubscript{3}), 179.2 (s, C\textsubscript{6}H\textsubscript{3}), 239.1 (s, C\textsubscript{6}H\textsubscript{3}) ppm. 15 signals in the aromatic region (labelled with C\textsubscript{6}) in the 13C NMR spectrum could not be assigned to specific carbon atoms. The number of signals is smaller than expected in case of free rotation around C-NiDmp and hindered rotation around C-NiMes (18 signals expected). This could be explained by similar chemical environments of the Dmp-groups and overlapping signals. Elemental Analysis calc. C 67.60, H 6.03, N 8.21, S 11.28; found C 68.43, H 6.08, N 8.12, S 11.60. UV/Vis (THF): $\lambda_{\text{max}}$ (nm, $\varepsilon_{\text{max}}$/L mol\(^{-1}\) cm\(^{-1}\)) 280 (19 000), 380 (30000), 560 (1500).

[(IMes)Ni(η^2-3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{4}NCS\textsubscript{2})] (3c)

To a solution of [(IMes)Ni(vtms)] (50.0 mg, 0.089 mmol, 1.0 equiv.) in toluene (2 mL) was added an excess amount of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (0.1 mL, 149 mg, 0.55 mmol, 10.4 equiv.). The colour of the reaction mixture immediately changed from yellow over burgundy to deep purple while stirring at ambient temperature for one hour. Subsequently, the solvent was removed and the dark residue was dried in vacuo. The residue was extracted with n-hexane (3 mL). Storage at
ambient temperature overnight afforded crystals of \([[\text{IMes}]\text{Ni(}1\text{-}(3,5-(CF_3)_2C_6H_4NCS)\text{)})\] (3c) suitable for X-ray crystallography. These crystals were isolated by decanting the supernatant and dried in vacuo. Storage of the supernatant solution at ambient temperature for 5 days afforded brown crystals of 4 suitable for X-ray crystallography along with crystals of 3c.

\[\text{C}_{28}\text{H}_{42}\text{Ni}_2\text{N}_2\text{S}_2\cdot 0.45(\text{n-hexane}), \text{MW} = 1176.67 \text{ (} +38.78\text{) g/mol, yield: } 42 \text{ mg (39%).}^1\text{H NMR (400 MHz, 300 K, C}_6\text{D}_6\text{)} \delta = 1.93 \text{ (s, 6H, C}_3\text{H}_3\text{)}, 2.12 \text{ (s, 6H, C}_3\text{H}_6\text{)}, 2.13 \text{ (s, 6H, C}_3\text{H}_3\text{)}, 5.92 \text{ (s, 2H, C}_2\text{H}_4\text{)}, 6.42 \text{ (s, 2H, C}_2\text{H}_2\text{ ortho-ortho-H), 6.80 \text{ (4H, C}_3\text{H}_4\text{)}, 7.45 \text{ (s, 1H, C}_2\text{H}_2\text{ para-H)}, 7.51 \text{ (s, 1H, C}_2\text{H}_2\text{ para-H)}, 7.58 \text{ (s, 1H, C}_2\text{H}_2\text{ ortho-H)}, 7.64 \text{ (s, 2H, C}_2\text{H}_2\text{ ortho-H)}, 7.65 \text{ (s, 2H, C}_2\text{H}_2\text{ ortho-H)}, 280 \text{ (48 000), 330 (30 000sh), 400 (7000sh)}\text{ppm.}^1\text{C}^1\text{H} \text{NMR (100 MHz, 300 K, C}_6\text{D}_6\text{)} \delta = 18.2 \text{ (s, C}_1\text{)}, 21.09 \text{ (s, C}_2\text{)}, 23.1 \text{ (s, C}_3\text{)}, 23.2 \text{ (s, C}_4\text{)}, 25.0 \text{ (s, C}_5\text{)}, 25.3 \text{ (s, C}_6\text{)}, 25.5 \text{ (s, C}_7\text{)}, 25.6 \text{ (s, C}_8\text{)}, 26.7 \text{ (s, C}_9\text{)}, 30.3 \text{ (s, C}_10\text{)}, 33.0 \text{ (s, C}_11\text{)}, 34.1 \text{ (s, C}_12\text{)}, 58.0 \text{ (s, C}_13\text{)}, 58.7 \text{ (s, C}_14\text{)}, 122.4 \text{ (s, C}_15\text{)}, 129.5 \text{ (s, C}_16\text{)}, 135.6 \text{ (s, C}_17\text{)}, 136.8 \text{ (s, C}_18\text{)}, 138.8 \text{ (s, C}_19\text{)}, 168.4 \text{ (s, C}_20\text{)}, 190.7 \text{ (s, C}_21\text{)}, 229.9 \text{ (s, C}_22\text{)} ppm. Elemental Analysis [for S-0.2(n-hexane), MW = 662.83 g/mol] calcld. C 65.60, H 7.42, N 9.67; found C 65.75, H 7.28, N 8.48. UV/Vis (THF): \(\lambda_{\text{max}}\) (nm, \(\varepsilon_{\text{max}}\)/L mol\(^{-1}\) cm\(^{-1}\)) 270 (28 000), 380 (4 300, tailing to 520 nm).

\[\text{[(IMes)}\text{Ni(}1\text{-}[\text{CyNCS}]\text{)] (6)}\]

To a suspension of \([[\text{IMes}]\text{Ni(CO)}(\mu_3\text{-}1\text{-}[\text{CyNCS}]\text{)])\] (0.5 \(n\)-hexane) (40.0 mg, 0.045 mmol, 1.0 equiv.) in \(n\)-hexane (5 mL) was added an excess amount of \(\text{CS}_2\) (0.1 mL, 5 mol\(^{-1}\) in THF, 0.5 mmol, 11.0 equiv.). While stirring at ambient temperature for 30 minutes a colour change from yellow to deep red and the formation of a red precipitate was observed. The reaction mixture was filtered, and the remaining red powder was dried in vacuo. Subsequently, the residue was stirred for 2 hours in total. Subsequently, the solvent was removed and the residue was dried in vacuo. The residue was extracted with \(n\)-hexane (5 mL) and stored at ambient temperature overnight to afford orange crystals of \([[\text{IMes}]\text{Ni(}1\text{-}[\text{CyNCS}]\text{)]}\) (5) suitable for single crystal X-ray diffraction. The crystals were isolated by decanting the supernatant and dried in vacuo.

\[\text{[(IMes)}\text{Ni(}1\text{-}[\text{CyNCS}]\text{)] (5)}\]

To a solution of \([[\text{IMes}]\text{Ni(vtms)}\text{)] (20.0 mg, 0.036 mmol, 1.0 equiv.) in toluene (5 mL) was added an excess amount of cyclohexyl isothiocyanate (0.1 mL, 99.6 mg, 0.71 mmol, 19.6 equiv.) at \(-30^\circ\text{C}.\) After stirring at ambient temperature for 5 minutes a colour change from yellow to orange was observed. The reaction mixture was stirred for 2 hours in total. Subsequently, the solvent was removed and the residue was dried in vacuo. The residue was extracted with \(n\)-hexane (5 mL) and stored at ambient temperature overnight to afford orange crystals of \([[\text{IMes}]\text{Ni(}1\text{-}[\text{CyNCS}]\text{)]}\) (5) suitable for single crystal X-ray diffraction. The crystals were isolated by decanting the supernatant and dried in vacuo.
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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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The reactivity of a nickel-phosphorus butterfly complex toward tetramethylcarbene and heterocumulenes was investigated. While the reaction with the carbene resulted in retention of the Ni₂P₂ core, reactions with isothiocyanates or carbon disulfide afforded phosphorus-free complexes with S–C–S pincer ligands. The same complexes were also isolated using a nickel(0) alkene complex as a precursor.