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Side-on Coordination of a P−P Bond in Heterobinuclear Tetraphosphorus Complexes with a $[\mathrm{Si}(\mu,\eta^{2:2}\text{-}\mathrm{P}_4)\mathrm{Ni}]$ Core and Nickel(I) Centers

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The synthesis and characterization of the first heterobinuclear tetraphosphorus complexes **3a** and **3b** with a $[\mathrm{Si}(\mu,\eta^{2:2}\text{-}\mathrm{P}_4)\mathrm{Ni}]$ core are reported. The latter result from conversion of the silylene-activated P_4 ligand LSiP_4 (**1**; L = $\mathrm{CH[(C{=}CH_2)CMe][N(2,6\text{-}^{i}Pr_2C_6H_3)]_2}$) with the β-diketiminatonickel(I) complexes $[(\mathrm{L'Ni})_2\cdot\mathrm{toluene}]$ (L′ = $\mathrm{CH[CMeN(2,6\text{-}\mathit{i}Pr_2C_6H_3)]_2}$) and $[(\mathrm{L''Ni})_2\cdot\mathrm{toluene}]$ (L″ = $\mathrm{CH[CMeN(2,6\text{-}Et_2C_6H_3)]_2}$), respectively. Unexpectedly, the complexes **3a** and **3b** feature a $[\mathrm{Si}(\mu,\eta^{2:2}\text{-}\mathrm{P}_4)\mathrm{Ni}]$ core with nickel(I) centers as shown by X-ray diffraction analysis, electron paramagnetic resonance, and magnetic measurements. The latter prove that the products are paramagnetic both in the solid state and in solution because of the presence of tetrahedral nickel(I) sites.

Cyclic silicon−phosphorus species (silaphosphanes) are electron-rich chelate ligands for transition metals, showing a versatile coordination chemistry and even finding applications in metal-mediated catalytic processes.[1] Thus, developing effective routes for the synthesis of versatile silaphosphane ligands is particularly desirable. The direct use of white phosphorus as a phosphorus source for the synthesis of such value-added compounds (phosphorus ligands, organophosphanes in organic synthesis, etc.) is an additional interesting task in contemporary phosphorus chemistry. The latter process requires facile P_4 activation, which can be achieved by mediation of the transition metals. In fact, numerous transition-metal complexes bearing a tetraphosphorus ligand have been reported since the isolation of the first transition-metal P_4 complex $[(\mathrm{PPh_3})_2\mathrm{ClRh}(\eta^2\text{-}\mathrm{P}_4)]$.[2,3] Meanwhile, the direct activation of white phosphorus by applying low-valent main-group elements has also achieved intriguing progress. For instance, reactions of P_4 with alkaline organometallic reagents and low-valent group 13 compounds lead to P_4-activated species.[4a,b] Recently, the activation of P_4 was even achieved by using N-heterocyclic carbenes (NHCs) and carbene-like compounds.[4c−f] Remarkably, the zwitterionic N-heterocyclic silylene LSi: (L = $\mathrm{CH[(C{=}CH_2)CMe][N(2,6\text{-}^{i}Pr_2C_6H_3)]_2}$),[5a] a heavier NHC homologue, is also capable of P_4 activation to give the cagelike complex $[\mathrm{LSiP_4}]$ (**1**; Scheme 1).[5b] Interestingly, one of the P−P bonds in **1** can be further activated by insertion of a second silylene molecule LSi: to give $[(\mathrm{LSi})_2\mathrm{P}_4]$ (**2**).[5b] The facile P−P bond activation in **1** prompted us to examine whether tricyclic **1** can also react with low-valent transition-metal centers to give the corresponding heterobinuclear tetraphosphorus complexes $[(\mathrm{LSi})(\mathrm{L'M})\mathrm{P}_4]$. Thus, we probed the reaction of **1** with the β-diketiminatonickel(I) complex $[(\mathrm{L'Ni})_2\cdot\mathrm{toluene}]$ (L′ = $\mathrm{CH[CMeN(2,6\text{-}\mathit{i}Pr_2C_6H_3)]_2}$),[6] which has been successfully employed for the activation of dioxygen, octasulfur, elemental selenium, and tellurium.[7] Herein, we report on the formation of the unusual heterobinuclear complexes

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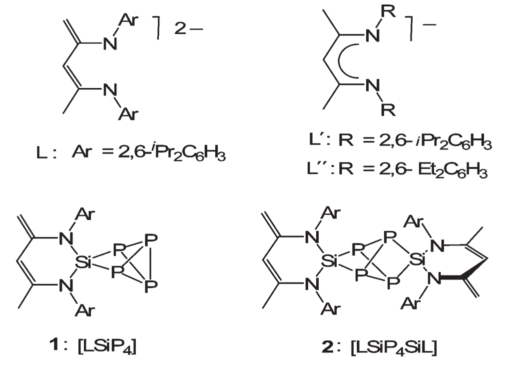
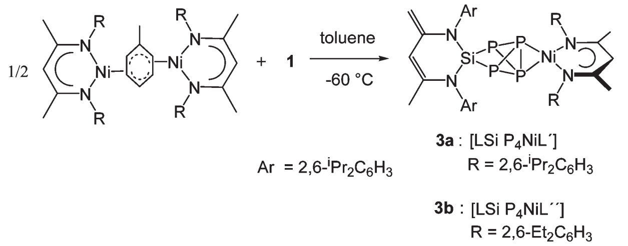
Scheme 1. C_3N_2 Ligands (L, L′, and L″) and the P_4 Activation Products **1** and **2**



Scheme 2. Synthesis of **3a** and **3b** from the $[(L'Ni^I)_2\cdot$Toluene] and $[(L''Ni^I)_2\cdot$Toluene] Precursor Complexes and **1**, Respectively



[LSiP$_4$NiL′] (**3a**) and [LSiP$_4$NiL″] (**3b**) (L″ = CH[CMeN(2,6-Et$_2$C$_6$H$_3$)]$_2$).

The complexes **3a** and **3b** are conveniently accessible from the reaction of **1** with $[(L'Ni)_2\cdot$toluene][6] and $[(L''Ni)_2\cdot$toluene][8] in toluene with a molar ratio of 1:1 at −60 °C, respectively. The completion of the reactions occurs through warming of the reaction mixture to room temperature. Subsequently, cooling of the concentrated solution of **3a** at −20 °C for 1 week affords red-brown single crystals in 86% yield (Scheme 2).

Red single crystals of **3b** can be obtained by changing the solvent to hexane/diethyl ether and cooling a concentrated solution at −20 °C for 1 week. Both **3a** and **3b** have been fully characterized by electron impact mass spectrometry, elemental analysis (see the Supporting Information), and single-crystal X-ray diffraction analysis. Compound **3a** crystallizes in toluene in the monoclinic space group $P2_1/c$ (Figure 1) with additionally one molecule of toluene in the unit cell, while complex **3b** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules and two diethyl ether molecules in the asymmetric unit; one of the molecular structures of **3b** is depicted in Figure 2.

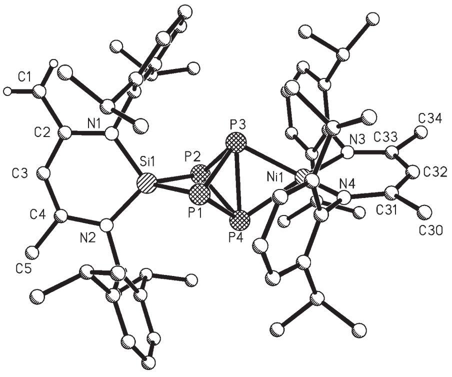


Figure 1. Molecular structure of **3a**. Hydrogen atoms except those at C1 are omitted for clarity. Selected interatomic distances (Å) and angles (deg): P1−P3 2.252(5), P1−P4 2.247(3), P2−P3 2.256(3), P2−P4 2.242(3), P3−P4 2.335(4), Si1−P1 2.215(3), Si1−P2 2.205(3), Ni1−P3 2.255(4), Ni1−P4 2.277(2), Si1−N1 1.800(3), Si1−N2 1.752(4), Ni1−N3 1.877(3), Ni1−N4 1.904(3); P1−Si1−P2 89.87(9), N1−Si1−N2 101.3(2), P3−Ni1−P4 62.03(9), N3−Ni1−N4 96.6(2).

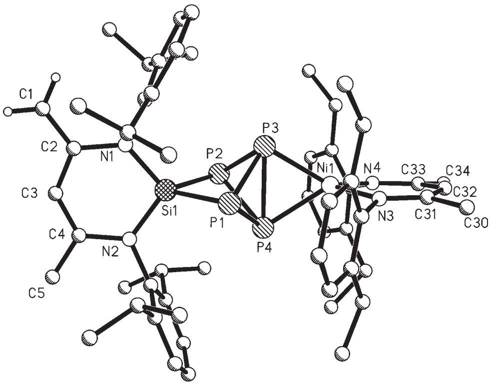


Figure 2. Molecular structure of **3b**. Only one of the two independent molecules in the asymmetric unit is shown. Hydrogen atoms except those at C1 are omitted for clarity. Selected interatomic distances (Å) and angles (deg) for the two independent molecules. *Mol.1*: P1−P3 2.244(2), P1−P4 2.242(2), P2−P3 2.251(2), P2−P4 2.248(2), P3−P4 2.351(3), Si1−P1 2.239(2), Si1−P2 2.262(2), Ni1−P3 2.258(2), Ni1−P4 2.241(2), Si1−N1 1.715(5), Si1−N2 1.725(5), Ni1−N3 1.921(4), Ni1−N4 1.890(5); P1−Si1−P2 87.35(8), N1−Si1−N2 104.2(2), P3−Ni1−P4 63.00(6), N3−Ni1−N4 94.8(2). *Mol.2*: P1−P3 2.251(2), P1−P4 2.233(3), P2−P3 2.251(2), P2−P4 2.253(2), P3−P4 2.354(2), Si1−P1 2.235(2), Si1−P2 2.254(2), Ni1−P3 2.249(2), Ni1−P4 2.250(2), Si1−N1 2.235(2), Si1−N2 2.254(2), Ni1−N3 2.249(2), Ni1−N4 2.250(2); P1−Si1−P2 87.58(8), N1−Si1−N2 104.6(2), P3−Ni1−P4 63.10(6), N3−Ni1−N4 95.4(2).

The molecular structure of **3a** reveals a heterobinuclear P_4 complex with a [Si(μ,$\eta^{2:2}$-P$_4$)Ni] core. Interestingly, the conformation of the LSiP$_4$ moiety in **3a** is reminiscent of that in the precursor **1**. However, one of the P−P bonds across the silicon atom in **3a** is coordinated to the nickel center in a "side-on" fashion. The silicon and nickel atoms are tetrahedrally coordinated. While the six-membered C_3N_2Si ring remains slightly puckered, the C_3N_2Ni ring is essentially planar. The latter two ring planes are strongly twisted but not perpendicular to each other. Although the [Si(μ,$\eta^{2:2}$-P$_4$)Ni] core in **3b** is similar to that of **3a**, the six-membered C_3N_2Si and C_3N_2Ni rings in **3b** are almost perpendicular to each other. Unexpectedly, the Ni$\cdots$Si distances in **3b** (4.649 and 4.642 Å) are even a little longer than that observed in **3a** (4.625 Å) despite the smaller steric congestion in **3b**. This suggests that crystal-packing effects are responsible for the less distinct twisting of the different β-diketiminate ligands in **3a**. The Si−N distances in **3b** [1.715(5)−1.725(5) Å] are shorter by 0.03−0.08 Å compared to those in **3a** [1.752(4)−1.800(3) Å]. However, the P−P distances in **3b** are essentially similar to the corresponding values of **3a**. The P−P distances (ave 2.245 Å), except those for P3−P4 in **3a** and **3b**, are only slightly longer than the respective values observed in the precursor **1** (2.228 Å). Because of the P−P bond coordination to the nickel center, the P3−P4 distances in **3a** [2.335(4) Å] and **3b** [2.351(3) and 2.354(2) Å] are longer than the other P−P distances in **3a**, **3b**, and **1** [2.159(2) Å], respectively.

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[8] Xiong, Y.; Yao, S.; Driess, M., unpublished results.

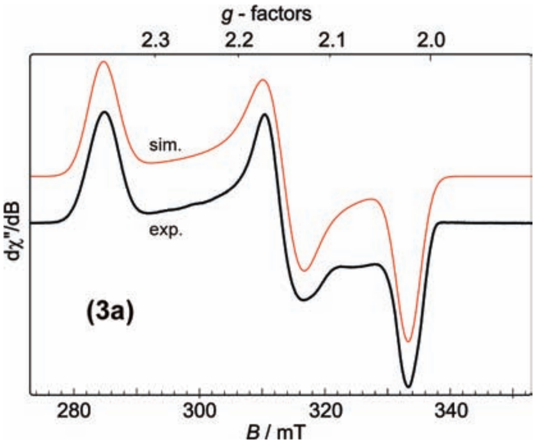

Figure 3. X-band EPR spectrum of **3a** in frozen toluene at 25 K. The red line is a powder simulation with anisotropic g values g_{max} = 2.367, g_{mid} = 2.150, g_{min} = 2.021 and Gaussian lines with angular dependent full widths at half-maximum (6.4 mT, 6.8 mT, 5.2 mT), given in the order of the g values.

However, the small P3−P4 bond elongation suggests coordination of the P−P bond to nickel(I) instead of the oxidative addition (electron transfer) of nickel(I) to **1**. This is in contrast to the result of the oxidative addition of silicon(II) to **1**, which furnishes **2** (with an analogous P−P distance of 3.00 Å) or the situation in a related β-diketiminatodialuminum P_4 complex.[4b] Thus, **3a** and **3b** represent nickel(I) complexes with a side-on η^2-silatetraphosphorus ligand. In other words, the coordination of the Ni[P_4Si] moiety is similar to the situation observed for related η^2-P_4 transition-metal complexes described previously.[9]

Because of the presence of a nickel(I) center, the complexes **3a** and **3b** are paramagnetic species both in the solid state and in solution. Accordingly, their ^{1}H NMR spectra in C_6D_6 display paramagnetically shifted resonances (see the Supporting Information). Magnetic measurements (the Evans method[10] using C_6D_6 as a solvent) for **3a** and **3b** revealed the μ_{eff} values of 1.83 and 1.43 μ_B at room temperature, respectively. In addition, the solid-state effective magnetic moment of **3a** shows a broad high-temperature plateau at about μ_{eff} = 1.74 μ_B, indicating a spin doublet state. In fact, X-band electron paramagnetic resonance (EPR) measurements of **3a** in a frozen toluene solution at 25 K reveal a paramagnetic ground state with spin $S = {}^1/_2$ (Figure 3). The rhombic spectrum has principal g values of 2.367, 2.150, and 2.021. The anisotropic g values are consistent with the nickel(I) oxidation state and resemble those values of nickel(I) complexes compiled by Saraev et al., including examples supported by the β-diketiminate ligands.[11] The presence of a nickel(II) site (with spin S_{Ni}=1 in tetrahedral symmetry) that is antiferromagnetically coupled to a {P_4} radical with $S_{rad} = {}^1/_2$ can be excluded as an explanation for the spin doublet ground state because ^{31}P NMR hyperfine coupling is elusive in the EPR spectrum. We can also exclude dissociation of the complexes and formation of the [LNi^I·toluene] starting compound because that is diamagnetic and EPR-silent in solution. Finally, also nickel(III) is not an option because the tetrahedral symmetry would afford high-spin, $S_{Ni} = {}^3/_2$, for the corresponding 3d^7 configuration, in contrast to the experiment. Thus, the magnetism of both **3a** and **3b** is entirely due to the properties of the tetrahedral nickel(I) site of the complexes, whereas the silicon site, as expected, is diamagnetic.

In summary, the novel heterobinuclear tetraphosphorus complexes **3a** and **3b** bearing a [Si(μ,$\eta^{2:2}$-P_4)Ni] core supported by different β-diketiminate ligands have been prepared and structurally characterized. Despite the different sizes of the substituents, in the solid state, **3a** and **3b** possess similar conformations with very close geometric parameters for the [Si(μ,$\eta^{2:2}$-P_4)Ni] core, in which the nickel centers are coordinated to a η^2-P_4Si moiety. Moreover, complexes **3a** and **3b** are paramagnetic species both in the solid state and in solution because of the presence of tetrahedral nickel(I) sites. The compounds **3a** and **3b** represent rare examples of heterobinuclear tetraphosphorus complexes with different stages of P−P bond activation. Investigations regarding utilization of the remarkable bonding features in **3a** and **3b** for the synthesis of new oligophosphorus ligands derived from P_4 activation are currently in progress.

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Supporting Information Available: Experimental details for the synthesis and spectroscopic data and X-ray crystallographic data in CIF format for **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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