

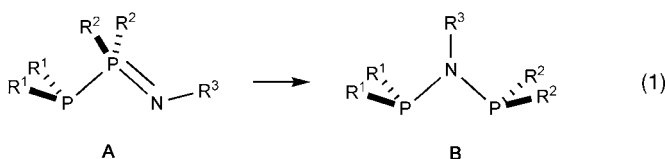
Phosphazanes

Synthesis and Solid-State Structure of a Metal Complex of a Diphosphineimine**

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Dedicated to Professor Michael Veith
on the occasion of his 60th birthday

Diphosphineimine compounds of the general structure $R_2P-PR_2=NR$ [**A**; Eq. (1)] have been known for some time,^[1] but



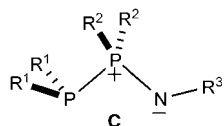
the pronounced tendency of these molecules to rearrange to the isomeric diphosphinoamines **B** has hampered the development of their chemistry and relegated them to structural curiosities. For example, the diphosphineimine $iPr_2P(=N-Ph)PEt_2$ was reported to completely rearrange to diphosphinoamine $iPr_2P-NPh-PEt_2$ in the presence of electrophiles or nucleophiles.^[1d] Similarly, the attempted synthesis of a palladium dichloride complex of $Ph_2P-PPh_2=N\{C_6H_4(o-CN)\}$ only furnished the diphosphinoamine complex $cis-[PdCl_2\{(o-CN)C_6H_4N(PPh_2)_2\}]$.^[2b] Diphosphinoamines, of course, have a

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long history as ligands for transition metals and as stable molecules in their own right.^[3] They have been used in late-transition-metal homogeneous polyolefin catalysis because they impart a greater stability to the complexes than the more conventional diimines.^[4,5] The asymmetric diphosphineimines have both electron-donating imine and electron-accepting phosphine functionalities, as exemplified in the ylidic form **C**, which may combine the best features of diimines and diphosphines and, thus, be superior ligands. Furthermore, these hemilabile phosphorus(III)/phosphorus(V) molecules should have applications in other important catalytic trans-

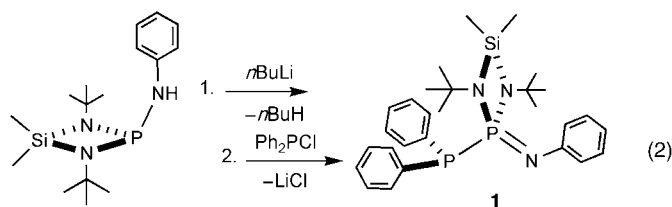
formations, such as hydroformylation and hydrogenation reactions,^[6] thus making the search for stable diphosphineimines an area of interest.



Herein, we report the synthesis and solid-state structure of the first diphosphineimine that is kinetically stable enough to allow the isolation of

a transition-metal complex. Our investigations also furnished the first solid-state structure of a diphosphineimine sulfide and of a metal complex in which the diphosphineimine has isomerized to the corresponding diphosphinoamine, thereby providing the rare opportunity to compare coordination compounds of both structural isomers.

Diphosphineimines are occasionally formed when amidophosphines are treated with halophosphines in the attempted synthesis of diphosphinoamines.^[1,2] Symmetrical diphosphinediimines can also be synthesized by the oxidative coupling of amidophosphines.^[7] The addition of $\{\text{Me}_2\text{Si}(\mu\text{-}i\text{PrBu})_2\text{PNPh}\}\text{Li}$ to Ph_2PCl in THF resulted in the nucleophilic attack of $\{\text{Me}_2\text{Si}(\mu\text{-}i\text{PrBu})_2\text{PNPh}\}^-$ on the phosphorus atom of Ph_2PCl to afford $\text{Me}_2\text{Si}(\mu\text{-}i\text{PrBu})_2\text{P(=NPh)PPh}_2$ (**1**) as the only phosphorus-containing product [Eq. (2)]. Treatment of



$(\text{Ph}_2\text{PNPh})\text{Li}$ with $\text{Me}_2\text{Si}(\mu\text{-}i\text{PrBu})_2\text{PCl}$,^[8] in contrast, gave only an intractable mixture.

A direct P–P bond in **1** was suggested by an AB pattern of doublets in the ^{31}P NMR spectrum at $\delta = 49.9$ and 44.9 ppm, respectively ($J(\text{P,P}) = 182$ Hz), but later findings showed that coupling constants of this magnitude are not diagnostic for direct P–P bonds in these systems (see below). A single-crystal X-ray analysis of the colorless product confirmed the assumed structure of **1**.

Figure 1 shows one of the two independent molecules, whose metric parameters are identical within experimental uncertainties. The P–P and P=N bonds (2.2092(7) and 1.5568(15) Å, respectively) are somewhat shorter than those of the previously characterized diphosphineimine of the type $(o\text{-X})\text{C}_6\text{H}_4\text{N=PPh}_2\text{-PPh}_2$ ($\text{X} = \text{CF}_3$, Ph, CN) in which they

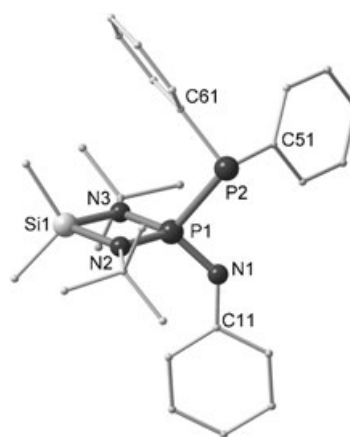
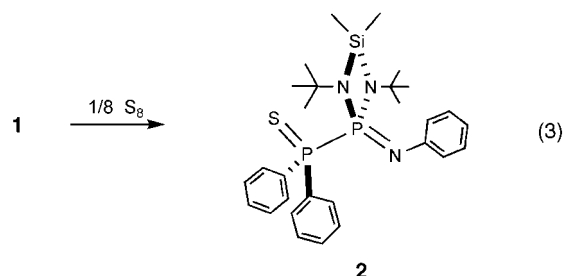


Figure 1. Solid-state structure of **1** (hydrogen atoms have been omitted). Selected bond lengths [Å] and angles [°]: P(1)–P(2) 2.2092(7), P(1)–N(1) 1.5568(15), P(1)–N(2) 1.6761(15), P(1)–N(3) 1.6804(16); N(1)–P(1)–P(2) 97.12(6), N(2)–P(1)–N(3) 86.67(8), C(61)–P(2)–P(1) 104.01(6), C(51)–P(2)–P(1) 106.44(7), C(51)–P(2)–C(61) 102.84(8).

ranged from 2.2379(16) to 2.2498(18) Å and from 1.571(3) to 1.578(3) Å, respectively.^[2] These bond-length contractions may be a reflection of the greater stability of **1**, which proved to be unusually thermally robust: it exhibited no tendency to decompose or rearrange to the corresponding diphosphinoamine on heating to reflux in toluene (24 hours).

Diphosphineimines are normally kinetic products that isomerize to the corresponding diphosphinoamines during attempted chemical transformations and metal coordination.^[1d,2] In notable contrast, the reaction of **1** with elemental sulfur produced the colorless compound **2** as the only product [Eq. (3)]. To the best of our knowledge, this diphosphine-



imine sulfide is only the second of its kind to have been reported and the first to have been characterized by X-ray structural analysis.^[1c]

The solid-state structure of **2** confirmed that the P–P bond had remained intact during the reaction (Figure 2). The molecule adopted a staggered conformation to minimize nonbonding interactions: the bulkiest substituent on one phosphorus atom is in a *gauche* conformation with the smallest substituents on the opposite phosphorus atom. This conformation renders **2** almost perfectly mirror-symmetric, with the phosphorus, sulfur, silicon, and nitrogen (imino) atoms all lying in a noncrystallographic mirror plane. The comparatively short P=S and P=N(imino) bonds (1.9563(8) and 1.5507(19) Å, respectively) form a torsion angle of

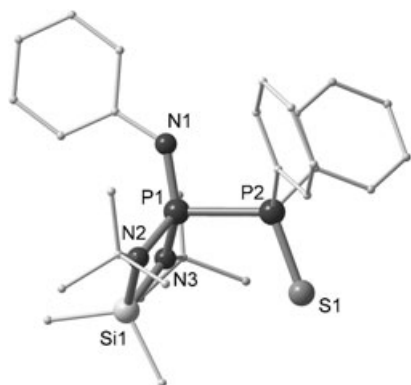


Figure 2. Solid-state structure of **2** (hydrogen atoms have been omitted). Selected bond lengths [Å] and angles [°]: P(1)-P(2) 2.2332 (7), P(1)-N(1) 1.5507(19), P(2)-S(1) 1.9563(8), P(1)-N(2) 1.6684(18), P(1)-N(3) 1.6677(17); N(1)-P(1)-P(2) 99.72(7), P(1)-P(2)-S(1) 110.71(3), N(2)-P(1)-N(3) 87.54(9), C(41)-P(2)-C(51) 103.19(10).

approximately 179° about the slightly elongated P-P bond (2.2332(7) Å).

Compound **1** did not isomerize on heating and oxidation, which encouraged us to explore its coordination chemistry. Treatment of **1** with *cis*-[Mo(CO)₄(piperidine)₂] in THF and heating to reflux afforded the light-yellow molybdenumtetracarbonyldiphosphineimine **3** [Eq. (4)]. The infrared spec-

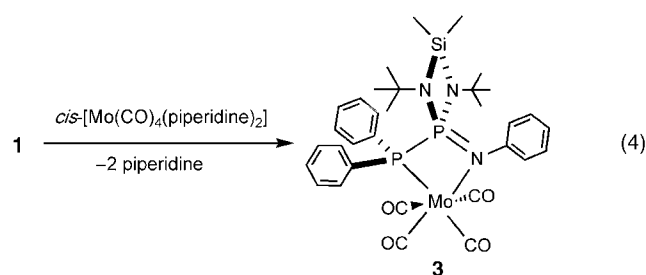


Figure 3. Solid-state structure of **3**. (Only one of the two independent molecules is shown; the toluene molecule and the hydrogen atoms have been omitted.) Selected bond lengths [Å] and angles [°]: Mo(1)-P(2) 2.4915(9), Mo(1)-N(1) 2.321(2), Mo(1)-C(1) 2.032(3), Mo(1)-C(2) 1.946(3), Mo(1)-C(3) 1.976(3), Mo(1)-C(4) 2.042(3), P(1)-P(2) 2.2362(11), P(1)-N(1) 1.599(2), P(1)-N(2) 1.661(2), P(1)-N(3) 1.669(2); N(1)-P(1)-P(2) 91.29(9), Mo(1)-N(1)-P(1) 111.16(11), Mo(1)-P(2)-P(1) 86.99(3).

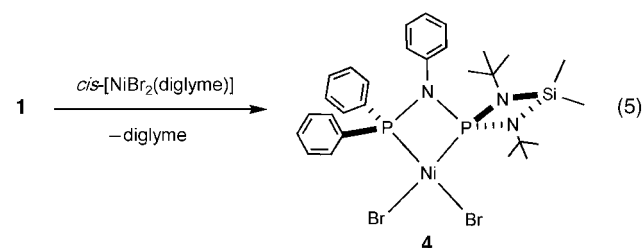
trum exhibited three $\nu(\text{CO})$ bands at 2010, 1890, and 1850 cm⁻¹, respectively, as is common for many molybdenumtetracarbonyl complexes with local C_{2v} symmetry. These carbonyl stretching vibrations are lower than for most complexes of the *cis*-[Mo(CO)₄(PP)] type (PP refers to alkanediyl- or amine-bridged bisphosphines),^[9] thus suggesting that **1** is the expected electron-rich chelating ligand.

Complex **3**, which crystallizes as a monotoluene solvate with two independent molecules in the asymmetric unit, was analyzed by single-crystal X-ray analysis. The spirocyclic molecule is composed of two almost-planar four-membered rings (Figure 3), but the trapezoidal Mo-P-P-N ring is much more irregular than the rhombus of the diazasilaphosphetidine. Thus, the *cis*-configured Mo-P and Mo-N bonds are 2.4915(9) and 2.321(2) Å, respectively, while the P-P and P=N bond lengths are 2.2362(11) and 1.599(2) Å, respectively. The Mo-P bond length is similar to those in the related *cis*-[Mo(CO)₄(PP)] and *cis*-[Mo(CO)₄(PN)] complexes,^[9,10] but the Mo-N and P=N bonds are rather long for an sp²-hybridized nitrogen atom,^[10] possibly because of ring strain. There is a distinct asymmetry in the Mo-CO bond lengths as

the axial bonds are significantly longer than the equatorial ones. Notably, the Mo-CO bond *trans* to the best electron donor, namely the imino nitrogen atom, is the shortest one of the four Mo-CO bonds. The bond parameters within the diazasilaphosphetidine are unremarkable and similar to those in related compounds.^[11]

Despite the direct P-P bond, the P-P coupling constant of **3** is only a third of the magnitude (ca. 69 Hz) as that of **1**, for reasons that are not yet clear.

Although the surprising thermal and chemical stabilities of **1** suggested that this diphosphineimine might be thermodynamically stable with respect to its isomer, its interaction with nickel salts proved otherwise. Compound **1** was treated with *cis*-[NiBr₂(diglyme)] (diglyme = diethyleneglycol dimethyl ether) to furnish the diphosphinoaminenickel dibromide complex **4** as the only product, even at room temperature [Eq. (5)].



The diamagnetism of the compound had indicated a square-planar coordination geometry about the nickel ion, and this arrangement was confirmed by the solid-state structure of **4** (Figure 4). The two planes defined by the nickel and phosphorus and the nickel and bromine atoms, respectively, are nearly coplanar (dihedral angle = 6°) and perpendicular to the diazasilaphosphetidine ring. Despite the dissimilar substituents on both phosphorus atoms, the Ni-P

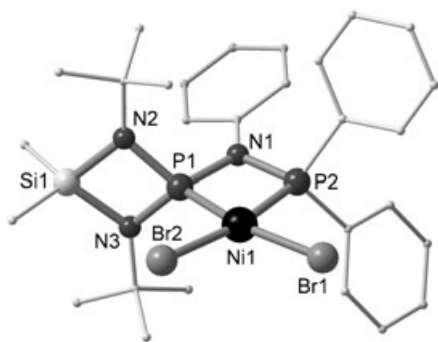


Figure 4. Solid-state structure of **4** (the THF molecule and the hydrogen atoms have been omitted). Selected bond lengths [Å] and angles [°]: Ni(1)–P(1) 2.1270(10), Ni(1)–P(2) 2.1151(10), Ni(1)–Br(1) 2.3481(6), Ni(1)–Br(2) 2.3302(6), P(1)–N(1) 1.714(3), P(2)–N(1) 1.714(3), P(1)–N(2) 1.658(3), P(1)–N(3) 1.670(3); P(1)–N(1)–P(2) 97.17(14), P(1)–Ni(1)–P(2) 74.62(4), Br(1)–Ni(1)–Br(2) 98.07(2), N(2)–P(1)–N(3) 87.67(15).

bonds are almost equidistant (the Ni–P1 and Ni–P2 bond lengths are 2.1270(10) and 2.1151(10) Å and are slightly shorter than those in the related *cis*-[NiBr₂{Ar₂PN(Me)PAr₂]} (Ar = *o*-tBuC₆H₄), which features symmetrical Ni–P bonds (2.1611(6) Å).^[4a] This latter nickel complex, with its bulky bis(diphenylphosphine)amine ligand, was shown to be a very good polyolefin catalyst, and the more electron-rich **4** may exhibit a similar reactivity.

The ³¹P NMR spectrum gave no indication that the isomerization of **1** had occurred as it showed two doublets at δ = 55.8 and 43.9 ppm for the P1 and P2 atoms, respectively, with larger coupling constants (*J*(P,P) = 137 Hz) than those seen in **3**. Thus, ³¹P NMR spectroscopy, which is usually considered a diagnostic tool, was neither reliable for predicting the connectivity in these phosphorus–nitrogen compounds nor did it show a correlation between the coupling constants and the P–P bond lengths. These results are in keeping with earlier studies that showed large and variable two-bond P–P coupling constants in diphosphinoamines that ranged from 15 to 665 Hz.^[12]

Given the catalytic activity of nickel and the inertness of the [Mo(CO)₄] moiety, it is not surprising that **1** isomerized in the presence of NiBr₂ even at room temperature, although it was unaffected by [Mo(CO)₄] when they were heated together to reflux in THF. However, it is surprising that the soft {Mo(CO)₄} fragment is coordinated by the hard nitrogen atom, although the harder NiBr₂ moiety is coordinated by the soft phosphorus atoms. This disparity further underlines the kinetic control demonstrated in Equations (4) and (5). Our results also suggest that attempts to stabilize diphosphineimines with certain Group 10 metal compounds, as had been done previously, may cause isomerization instead.^[2a] The ease with which **1** isomerizes in the presence of NiBr₂ clearly rules out its use as a diphosphineimine ligand in Group 10 metal catalysis.

In summary, the syntheses and solid-state structures of a kinetically stable diphosphineimine, its molybdenum complex, and its sulfide analogue have been reported. Whether the electronic properties or the cyclic structure of the

diazasilaphosphetidine give this particular diphosphineimine its unique stability remains to be seen. The potential rewards for finding stable diphosphineimines are clear, and we are currently exploring the reaction chemistry of **1** to understand the properties of these intriguing molecules.

Experimental Section

1: A solution of Me₂Si(μ-*Nr*Bu)₂PN(H)Ph^[11a] (11.2 mmol) in hexanes (20 mL) was treated dropwise at 0 °C with *n*BuLi (11.3 mmol) in hexanes (15 mL). The reaction mixture was heated at reflux for 1 h, cooled to RT, and then treated dropwise with a solution of Ph₂PCl (11.2 mmol) in hexanes. This caused a white precipitate to form. The mixture was stirred overnight and then filtered to afford a colorless, clear solution from which colorless, rectangular crystals separated upon cooling; yield: 3.69 g (64.9%). M.p. 170–172 °C; elemental analysis (%) calcd for C₂₈H₃₉N₃P₂Si: C 66.24, H 7.74, N 8.28; found: C 66.01, H 7.84, N 8.11; ¹H NMR (500.1 MHz, CD₂Cl₂, 21 °C): δ = 7.94 (m, 4H, Ph), 7.37 (m, 6H, Ph), 7.15 (t, *J* = 7.1 Hz, 2H, Ph), 7.06 (d, *J* = 8.1 Hz, 2H, Ph), 6.72 (t, *J* = 7.1 Hz, 1H, Ph), 1.13 (s, 18H, *t*Bu), 0.56 (s, 3H, Me), 0.20 ppm (s, 3H, Me); ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 21 °C): δ = 2.66 (d, *J*(P,P) = 182.4 Hz), –30.82 ppm (d, *J*(P,P) = 182.8 Hz).

2: Compound **1** (0.235 g, 0.486 mmol) and elemental sulfur (0.016 g, 0.50 mmol) were dissolved in THF (20 mL), and the mixture was heated at reflux for 3 h. Following removal of THF, the ensuing white powder was dissolved in toluene to afford colorless crystals upon cooling; yield: 0.213 g (81.2%). M.p. 202–206 °C; elemental analysis (%) calcd for C₂₈H₃₉N₃P₂SSi: C 62.31, H 7.28, N 7.79; found: C 61.94, H 7.35, N 7.72; ¹H NMR (500.1 MHz, C₆D₆, 21 °C): δ = 9.178 (dd, *J* = 12.4, 8.0 Hz, 4H, Ph), 7.43 (d, *J* = 8.3 Hz, 2H, Ph), 7.34 (t, *J* = 7.5 Hz, 2H, Ph), 7.11 (td, *J* = 8.0, 3.2 Hz, 2H, Ph), 6.99 (t, *J* = 7.4 Hz, 2H, Ph), 6.95 (t, *J* = 7.3 Hz, 1H, Ph), 0.94 (s, 18H, *t*Bu), 0.83 (s, 3H, Me), 0.38 ppm (s, 3H, Me); ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 21 °C): δ = 10.94 (d, *J*(P,P) = 238.8 Hz), –8.40 ppm (d, *J*(P,P) = 238.8 Hz).

3: Compound **1** (0.250 g, 0.500 mmol) and *cis*-[Mo(CO)₄](piperidine)₂ (0.195 g, 0.500 mmol) were dissolved in THF (50 mL) and the mixture was heated at reflux for 3 h. A yellow powder precipitated upon cooling, which was recrystallized from toluene to afford light-yellow crystals; yield: 0.263 g (65.1%). M.p. 176 °C (decomp); elemental analysis (%) calcd for C₃₉H₄₇MoN₃O₄P₂Si: C 57.99, H 5.86, N 5.20; found: C 58.04, H 5.98, N 5.34; ¹H NMR (500.1 MHz, CD₂Cl₂, 21 °C): δ = 8.09 (m, 4H, Ph), 7.52 (s, 6H, Ph), 7.39 (t, *J* = 7.6 Hz, 2H, Ph), 7.22 (m, 4H, Ph), 6.91 (t, *J* = 7.3 Hz, 1H, Ph), 2.34 (s, 3H, Me), 0.84 (s, 21H, *t*Bu, Me), 0.66 ppm (s, 3H, Me); ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 21 °C): δ = 49.93 (d, *J*(P,P) = 69.5 Hz), 44.97 ppm (d, *J*(P,P) = 69.0 Hz); ¹³C{¹H} NMR (CD₂Cl₂, 121.5 MHz, 21 °C): δ = 221.4 (s, CO_{eq}), 218.3 (d, *J* = 32.9 Hz, CO_{eq}), 210.2 (d, *J* = 8.5 Hz, CO_{ax}), 132.8 (d, *J* = 26.4 Hz, Ph), 131.9 (s, Ph), 129.6 (s, Ph), 128.9 (s, Ph), 126.1 (s, Ph), 122.4 (s, Ph), 32.4 (s, *t*Bu), 5.0 (s, Me), 4.4 ppm (s, Me); IR (nujol): $\tilde{\nu}$ = 2010.4 (s), 1889.9 (vs), 1850.4 cm^{–1} (vs).

4: A suspension of *cis*-[NiBr₂(diglyme)] (0.321 g, 0.912 mmol) in THF (10 mL) was treated dropwise with a solution of **1** (0.398 g, 0.816 mmol) in THF (25 mL) at RT. The ensuing orange mixture slowly turned red and was stirred overnight. The dark red–brown solution was filtered through a medium-porosity frit and stored in a freezer. Several crops of red–brown, needle-shaped crystals formed upon cooling; yield: 0.369 g (59.0%). M.p. 273–282 °C; elemental analysis (%) calcd for C₃₂H₄₇Br₂N₃NiOP₂Si: C 48.15, H 5.93, N 5.26; found: C 47.91, H 5.98, N 5.23; ¹H NMR (500.1 MHz, CD₂Cl₂, 21 °C): δ = 8.11 (dd, *J* = 12.4, 7.9 Hz, 4H, Ph), 7.77 (s, 2H, Ph), 7.49 (s, 4H, Ph), 7.23 (s, 4H, Ph), 7.01 (s, 3H, Ph), 3.58 (s, 4H, THF), 1.85 (s, 4H, THF), 1.50 (s, 18H, *t*Bu), 0.78 (s, 3H, Me), 0.401 ppm (s, 3H, Me);

$^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, CD_2Cl_2 , 21 °C): $\delta = 55.81$ (d, $J(\text{P,P}) = 137.0$ Hz), 43.88 ppm (d, $J(\text{P,P}) = 137.0$ Hz).

Crystal data for **1**, **3**, and **4** were collected on a Bruker Smart Apex CCD and those for **2** on a Stoe IPDS diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.71069 \text{ \AA}$). The structures were solved with direct methods and refined by full-matrix least-squares against F^2 using the SHELXTL program.

Crystal data for **1**: $\text{C}_{28}\text{H}_{39}\text{N}_3\text{P}_2\text{Si}$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.1274(7)$, $b = 15.3090(9)$, $c = 16.1150(9) \text{ \AA}$, $\alpha = 81.0053(11)$, $\beta = 72.7523(10)$, $\gamma = 82.8704(10)^\circ$, $V = 2812.6(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.199 \text{ g cm}^{-3}$, $T = 100 \text{ K}$, $2\theta_{\text{max}} = 50^\circ$, $\mu = 0.218 \text{ mm}^{-1}$, 13774 reflections measured, of which 9783 were unique ($R_{\text{int}} = 0.0632$), final R indices: $R1 = 0.0365$, ($I > 2\sigma(I)$), $wR2 = 0.0904$ (all data).

Crystal data for **2**: $\text{C}_{28}\text{H}_{39}\text{N}_3\text{SiP}_2\text{S}$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.0459(10)$, $b = 9.7581(9)$, $c = 33.246(4) \text{ \AA}$, $\beta = 93.604(13)^\circ$, $V = 2928.8(5) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.224 \text{ g cm}^{-3}$, $T = 200 \text{ K}$, $2\theta_{\text{max}} = 48^\circ$, $\mu = 0.282 \text{ mm}^{-1}$, 18452 reflections measured, of which 4522 were unique ($R_{\text{int}} = 0.0502$), final R indices: $R1 = 0.0370$ ($I > 2\sigma(I)$), $wR2 = 0.0997$ (all data).

Crystal data for **3**: $\text{C}_{39}\text{H}_{47}\text{MoN}_3\text{O}_4\text{P}_2\text{Si}$, monoclinic, space group $P2_1/n$ (no. 14), $a = 19.2663(16)$, $b = 11.4770(10)$, $c = 36.889(3) \text{ \AA}$, $\beta = 103.3213(14)^\circ$, $V = 7937.3(12) \text{ \AA}^3$, $Z = 8$, $\rho_{\text{calcd}} = 1.352 \text{ g cm}^{-3}$, $T = 100 \text{ K}$, $2\theta_{\text{max}} = 50^\circ$, $\mu = 0.483 \text{ mm}^{-1}$, 40213 reflections measured, of which 13998 were unique ($R_{\text{int}} = 0.0500$), final R indices: $R1 = 0.0401$ ($I > 2\sigma(I)$), $wR2 = 0.1006$ (all data).

Crystal data for **4**: $\text{C}_{32}\text{H}_{47}\text{Br}_2\text{N}_3\text{NiOP}_2\text{Si}$, monoclinic, space group $P2_1/c$ (no. 14), $a = 18.3666(13)$, $b = 12.1328(8)$, $c = 16.1095(11) \text{ \AA}$, $\beta = 90.4750(14)^\circ$, $V = 3589.7(4) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.477 \text{ g cm}^{-3}$, $T = 100 \text{ K}$, $2\theta_{\text{max}} = 50^\circ$, $\mu = 2.918 \text{ mm}^{-1}$, 18367 reflections measured, of which 6325 were unique ($R_{\text{int}} = 0.0375$), final R indices: $R1 = 0.0351$ ($I > 2\sigma(I)$), $wR2 = 0.0859$ (all data).

CCDC-254120–254123 (**1–4**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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