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Phosphorus Analogues of [Ni(bpy)\textsubscript{2}]: Synthesis and Application in Carbon–Halogen Bond Activation

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ABSTRACT: The neutral, homoleptic pyridylphosphininenickel(0) complex [Ni(2-Py-4,6-Ph\textsubscript{2}PC\textsubscript{5}H\textsubscript{2})\textsubscript{2}] (1) has been obtained by reaction of the formal Ni(0) source [(IPr)Ni(H\textsubscript{2}C\textsubscript{3}SiMe\textsubscript{3})\textsubscript{2}] with 2 equiv of 2-(2'-pyridyl)-4,6-diphenylphosphinine (L). Compound 1 can be oxidized both electrochemically and through the use of ferrocenium salts, to afford the corresponding Ni(I) complexes [1]Br, [1](THF)\textsubscript{2}, and [1](BAr\textsubscript{F}\textsubscript{4})\textsubscript{2}. The structures of these salts reveal an interesting dependence on the nature of the anion. While [1]Br\textsubscript{2} and [1](THF)\textsubscript{2}PF\textsubscript{6} show trigonal-bipyramidal coordination of Ni in the solid state, [1](BAr\textsubscript{F}\textsubscript{4})\textsubscript{2} exists as a dinuclear Ni(I) complex and possesses a bridging phosphinine moiety in a rare μ\textsubscript{3} mode. Reactions of 1 with halobenzenes highlight the noninnocent behavior of the aromatic phosphinine ligand, leading to the formation of oxidized Ni complexes but not to classical oxidative addition products. The reaction of 1 with bromobenzene affords the μ\textsubscript{3} phosphinine 2 and the bipyramidal Ni(I) complex [1]Br, whereas a more unconventional oxidation product 3 is formed from the reaction of 1 and iodobenzene.

INTRODUCTION

Nickel(0) complexes have become ubiquitous in homogenous catalysis and are used for a wide range of processes, including alkene and alkyne oligomerization reactions, as well as Kumada-type cross couplings. The complex bis(2,2'-bipyr-dine)nickel(0) (A; Figure 1) is an archetypal example of a Ni(0) species with versatile catalytic properties and has found diverse applications in various (electro)chemical reactions and catalysis.

Replacing the pyridyl moieties in A with valence isoelectronic phosphinine (also referred to as phosphaben-zene) units can have a significant impact on both the electronic structure and reactivity of the corresponding coordination compound. Considering the versatile applications of A and bipyr-dine complexes, as well as the fact that monophosphininenickel(0) complexes are well-investigated, it is quite surprising that phosphorus-containing analogues of A are extremely rare. In fact, the known examples appear to be limited to just a single species described by Le Floch and co-workers, who reported that reactions of 2,2'-[(4,5-dimethyl)-bipyrphosphinine\textsuperscript{26} with nickel(0) sources, such as Ni(cod), afford the homoleptic bis(bipyrphosphine) complex B (Figure 1). However, the reactivity of this complex—and almost all related chelating phosphininenickel complexes—remains unexplored.

We have recently become interested in the coordination chemistry of the donor-functionalized phosphinine 2-(2'-pyridyl)-4,6-diphenylphosphinine (L), a "hybrid" P,N ligand that can be considered to be a cross between previously explored biphosphinines and the ubiquitous bipyriddines. L possesses two electronically distinct binding sites—a "soft" P and a "hard" N donor site—which can have a significant impact on its coordination properties and reactivity. Although a large variety of 4d and 5d transition-metal complexes of L have been prepared, syntheses of 3d metal complexes remain scarce. Nevertheless, we have recently demonstrated that the combination of a late 3d metal with ligand L can lead to versatile coordination chemistry and, even more importantly, to useful reactivity, as exemplified by the facile cleavage of one C=O bond in CO\textsubscript{2} by the Fe complex C (Figure 1).
an (THF), toluene, diethyl ether, and n-hexane were purified, dried, and degassed using an MBrAin SPS800 solvent purification system. Benzene was distilled and degassed with Schlenk techniques. Deuterated THF and benzene were purchased from Sigma-Aldrich and used as received. H2Cp purchased from Sigma-Aldrich and degassed using a MBraun SPS800 solvent purification system. The assignment of 1H and 31P NMR spectra were determined by the analytical department of the University of Regensburg. Cyclic voltammograms were recorded with a CH Instruments electrochemical analyzer. Gas chromatography with a flame ionization detector (GC-FID); Shimadzu GC2010plus. Carrier gas: H2. Column: Restek Rxi (30 m × 0.25 mm × 0.25 μm). Carrier gas: H2. Temperature-controlled cryostat system (Oxford Instruments). The 1H and 13C NMR spectral parameters were determined by the Evans NMR method in THF-d8 at room temperature. UV–vis spectra were recorded using a Varian Cary 50 spectrometer. Elemental analyses were determined by the analytical department of the University of Regensburg. Cyclic voltammograms were recorded with a CH Instruments electrochemical analyzer. Gas chromatography with a flame ionization detector (GC-FID); Shimadzu GC2010plus. Carrier gas: H2. Column: Restek Rxi (30 m × 0.25 mm × 0.25 μm). Carrier gas: H2. Standard heating procedure: 50 °C (2 min), 25 °C min⁻¹ → 280 °C (5 min). Gas chromatography-mass spectrometry (GC-MS) HP6890 system with a 7683B injector and an Agilent 7820A system. Calibration of substrates and products with internal standard (THF), toluene, diethyl ether, and n-hexane (3 × 2 mL) and layered with n-hexane (12 mL). IPr was isolated as deep-purple crystals after decanting the mother liquor, washing with n-hexane (3 × 2 mL), and drying under vacuum. Crystals suitable for single-crystal XRD were grown from the slow diffusion of n-hexane into a benzene solution of I. Yield: 40 mg, 37%. Elemental calc. for CaH6N2P2Ni (M = 709.39 g mol⁻¹); C: 74.50; H: 4.55; N: 3.95. Found: C: 74.98; H: 4.70; N: 3.77. UV–vis [THF; λmax nm (εnmol L⁻¹ mol⁻¹ cm⁻¹)]: 290 (98632), 520 (27940), 816 (20814). 1H NMR (400.13 MHz, 300 K, THF-d8): δ 7.05–7.11 (m, 6H, H of C2,4−Ph), 7.18–7.21 (m, 2H, H of NC5H4), 7.33–7.37 (m, 2H, H of C2,4−Ph), 7.41–7.45 (m, 4H, H of C2,4−Ph), 7.79–7.81 (m, 4H, H of C2,4−Ph), 7.85–7.86 (m, 2H, H of NC5H4), 7.90 (d, 4H, H of C2,4−Ph), 8.30 (d, 4H, H of C2,4−Ph). 13C{1H} NMR (100.61 MHz, 300 K, THF-d8): δ 131.4 (s, C of C2,4−Ph), 137.4 (t, C of C2,4−Ph, J = 7 Hz), 143.2 (m, C of PC5H4Ph), 143.9 (m, C of PC5H4Ph), 146.6 (m, C of PC5H4Ph), 151.3 (m, C of C2,4−Ph). 31P{1H} NMR (161.98 MHz, 300 K, THF-d8): δ 179.4. 31P NMR (161.98 MHz, 300 K, THF-d8): δ 179.4. Synthesis of I [BF4] Compound I [BF4] was prepared in an MBrAin argon glovebox. I is sensitive toward moisture and air. [BF4] is soluble and stable in benzene, THF, and toluene. I (50 mg, 0.07 mmol) was dissolved in THF (1 mL), and complex [BF4] (12 mg, 0.07 mmol) was added dropwise to a solution of I (1 eq, 100 mg, 0.154 mmol) in benzene at room temperature. An immediate color change from yellow to deep purple was observed. The reaction mixture was stirred for 16 h at room temperature. Volatiles were completely removed, and the deep-purple residue was washed with n-hexane (3 × 2 mL) in benzene. The color changed further from deep purple to brown was observed. The color changed further to green-brown upon stirring overnight. The solvent of the green solution of I was completely removed, and ferrocene was removed by sublimation under high vacuum (50 °C, ca. 10⁻³ mbar). The remaining brown residue was extracted with THF (2 mL) and layered with n-hexane (4 mL). After crystallization for 2 days at 35 °C, [BF4] could be isolated as a brown powder. Crystals suitable for single-crystal XRD were grown from the slow diffusion of n-hexane.
into a toluene solution of [1]BF₄. Yield: 43 mg, 77%. Elem. anal. Calcd for C₁₅₁H₈₈B₂F₄₈N₄Ni₂P₄ (M₊ = 796.20 g mol⁻¹): C, 66.38; H, 4.05; N, 3.52. Found: C, 65.17; H, 4.26; N, 3.35. UV−vis [THF; λₘₒₐₓ(n)/μₐₓ (emₐₓ/L mol⁻¹ · cm⁻¹)] = 284 (38665), 338 (sh, 15363), 466 (8545). μ eff (THF-d₆): 2.0(1) μ β.

Synthesis of [1]THF[P₂]. Compound [1]THF[P₂] was prepared in an MBraun argon glovebox. [1]THF[P₂] is sensitive toward moisture and air. [1]THF[P₂] is soluble and stable in benzene, THF, and toluene. 1 (50 mg, 0.07 mmol) was dissolved in benzene (1 mL), and FeC₇P₆ (23 mg, 0.07 mmol) was added at room temperature. A deep-red color change from deep purple to brown was observed. After stirring overnight, the solution turned green, and the solvent of the reaction mixture was completely removed, and ferrocene was removed by sublimation under high vacuum (50 °C, ca. 10⁻² mbar). The remaining brown residue was extracted with THF (2 mL) and layered with hexane (6 mL). After crystallization for 1 day at −35 °C, [1]THF[P₂] could be isolated as a deep-brown powder. Crystals suitable for single-crystal XRD were grown from the slow diffusion of n-hexane into a THF solution of [1]THF[P₂]. Yield: 53 mg, 88%. Elem. anal. Calcd for C₁₅₁H₈₈B₂F₄₈N₄Ni₂P₄ (M₊ = 926.47 g mol⁻¹): C, 62.23; H, 4.35; N, 3.02. Found: C, 62.12; H, 4.41; N, 2.93. UV−vis [toluene; λₘₒₐₓ/n/μₐₓ (emₐₓ/L mol⁻¹ · cm⁻¹)] = 334 (sh, 6649), 450 (2617), 659 (1805). μ eff (THF-d₆): 1.7(1) μ β.

Synthesis of [1][BARF₄]. Compound [1][BARF₄] was prepared in an MBraun argon glovebox. [1][BARF₄] is sensitive toward moisture and air. [1][BARF₄] is soluble and stable in diethyl ether, benzene, THF, and toluene. 1 (50 mg, 0.07 mmol) and FeC₇P₆ (74 mg, 0.07 mmol) were dissolved in THF (2 mL) and layered with n-hexane (6 mL). After crystallization at room temperature overnight, a fluorescent pink solution was evaporated to dryness, and the remaining pink residue was extracted with n-hexane (2 × 2 mL) and drying under vacuum, 3 was isolated as a deep-green powder. Crystals suitable for single-crystal XRD were grown from the slow diffusion of n-hexane into a toluene solution of 3. Yield: 38 mg (64%). Elem. anal. Calcd for C₁₅₁H₉₁P₈Ni₂P₈ (M₊ = 843.96 g mol⁻¹): C, 53.80; H, 3.85; N, 1.66. Found: C, 53.99; H, 3.58; N, 1.98. UV−vis [THF; λₘₒₐₓ/n/μₐₓ (emₐₓ/L mol⁻¹ · cm⁻¹)] = 285 (24370), 450 (4788), 614 (2600). μ eff (THF-d₆): 3.2(1) μ β. The decanted fluorescent pink solution was evaporated to dryness, and the remaining pink residue was extracted with n-hexane (3 × 2 mL). Slow evaporation at room temperature gave pure 2 as a pink powder. Yield: 10 mg, 30%.

RESULTS AND DISCUSSION

Encouraged by our previous results with Fe, we were motivated to investigate the coordination compounds of the pyridophosphine ligand L with other late 3d metals. Given the paucity of prior Ni complexes containing chelating phosphinine ligands—and, in particular, the lack of corresponding reactivity studies—we were specifically motivated to study the reactivity of L toward suitable low-valent Ni sources and decided to start with the formal Ni(0) source toward suitable low-valent Ni sources.

Synthesis of 2 and 3. Compounds 2 and 3 were prepared in an MBraun argon glovebox. 3 is sensitive toward moisture and air. 3 is soluble and stable in benzene, THF, and toluene. 3 was added to a solution of 2 (50 mg, 0.07 mmol) in toluene (1 mL), and n-hexane was added to a solution of 2 (50 mg, 0.07 mmol) in benzene (1 mL). This reaction mixture was heated to 60 °C overnight. Crystals suitable for single-crystal XRD were grown from the slow diffusion of 2 into a THF solution of 3. Yield: 86 mg (78%). Elem. anal. Calcd for C₁₅₆H₉₈B₂F₄₈N₄Ni₂P₄ (M₊ = 1061.66 g mol⁻¹): C, 85.16; H, 5.46; N, 3.02. Found: C, 85.17; H, 5.47; N, 3.02. UV−vis [toluene; 265 (6456), 300 (8900), 516 (8023)]. H NMR (400.13 MHz, 300 K, C₆D₆): δ 6.21−6.25 (m, 1H, H of C₅ of PC₅H₂P₆), 6.86−7.00 (m, 10H, H(barren)), 7.08−7.12 (m, 2H, H(barren)), 7.21−7.23 (m, 1H, H(barren)), 7.32−7.36 (m, 2H, H(barren)), 7.81−7.82 (m, 1H, H of C₅ of PC₅H₂P₆), 7.91−7.97 (m, 4H, H(barren)), 8.11−8.19 (m, 2H, H(barren)). 13C{¹H} NMR: δ 161.98 MHz, 300 K, C₆D₆): δ 265 (6456), 300 (8900), 516 (8023). Inorganic Chemistry pubs.acs.org/IC
Scheme 1. Synthesis of 1 Using D as a Ni(0) Precursor

\[ \text{DippN}_{2} \text{SiMe}_{3} + 2.5 \text{Li} \rightarrow \text{Ph-P-Ni-P-Ph} \rightarrow \text{Ni-PPh}_{3} \text{L} \]

(i) TiCl4, C5H6, 25 °C, 16 h; Dipp = 2,6-diisopropylphenyl.

Single crystals suitable for XRD could be obtained by the slow diffusion of n-hexane into a solution of 1 in benzene. As anticipated, the solid-state molecular structure shows the expected homoleptic chelate complex, where the Ni center is coordinated by two 2-(2′-pyridyl)phosphinine ligands L (Figure 2). This leads to a distorted tetrahedral coordination sphere around the Ni center (the calculated geometry index for 1 is \( \tau_{4} = 0.80 \); see Table 1; cf. \( \tau_{4} = 0 \) and 1 for the ideal square-planar and tetrahedral geometries, respectively). The P–Ni–N bite angles are 84.05(17)° for P1–Ni1–N1 and 84.28(17)° for P2–Ni1–N2. The C1–P1–C5 angle of 1 is approximately 102°; close to the one in free phosphinines (ca. 100°). This is in line with earlier observations that electron-rich metal fragments cause only a marginal opening of the C1–P1–C5 angle in the coordinated phosphinine. In contrast, this effect is much more pronounced in coordination compounds, in which the phosphinine ligand is bound to more electron-poor metal centers with reduced π-back-donation ability. Those complexes are usually characterized by a high reactivity of the P==C double bond toward nucleophilic attack.

Complex 1 is the first example of a Ni complex containing a pyridylphosphinine ligand. The molecular structure of 1 is reminiscent of ubiquitous 2,2′-bipyridinenickel(0)53 complexes, which are known for their versatile redox properties and corresponding utilization in the electrochemical reduction of aryl halides, for example.54 Thus, in order to determine the redox properties of 1, cyclic voltammograms were recorded in THF using \( \left[n\text{Bu}_{4}\text{N}\right]\text{PF}_{6} \) as a supporting electrolyte. Several irreversible and quasi-reversible oxidation and reduction processes are apparent (Figure 2). However, perhaps the most interesting process is the quasi-reversible oxidation observed at \( E_{1/2} = -0.6 \text{ V} \) versus \( \text{Fc/Fc}^{+} \). Because this feature is well-behaved on the CV time scale, it was anticipated that 1 might also be oxidized in a preparative manner using a suitable chemical oxidant. Thus, 1 was treated with several different ferrocenium salts FcX [Fc = ferrocenium; X = BF4, PF6, and BArF4 where \( \text{Ar}^{4} = 3,5-(\text{CF}_{3})_{2}\text{C}_{6}\text{H}_{3} \)] in order to obtain the corresponding cationic Ni complexes \( [1]\text{BF}_{4}, [1](\text{THF})\text{PF}_{6}, \) and \( [1][\text{BArF}_{4}]_{2} \) (Scheme 2), which could all be characterized crystallographically.

**Figure 2.** Molecular structure of 1 in the solid state (left). Ellipsoids are drawn at the 40% probability level; H atoms are omitted for clarity; four phenyl groups are displayed in wireframe for clarity. Selected bond lengths [Å] and bond angles [deg]: Ni1–N1 2.005(6), Ni1–P1 2.091(2), Ni1–P2 2.092(2); P1–Ni1–P2 128.15(8), N1–Ni1–N2 124.67(18), N1–Ni1–P2 129.03(17), P1–Ni1–N1 84.05(17), P2–Ni1–N2 84.28(17), C1–P1–C5 102.2(3), C1′–P2–C5′ 102.0(3). Cyclic voltammograms of 1 (right; from E (V) = −3.4 to +1.1 and from E (V) = −1.1 to −0.2; scan rate 100 mV).

| Table 1. Geometry Indices (\( \tau_{4} \) and \( \tau_{5} \))55,56 and Magnetic Moments (\( \mu_{eff} \)) THF-d8, 300 K of Reported Ni Complexes |
|-----------------|--------|--------|-------------|
| compound       | \( \tau_{4} \) | \( \tau_{5} \) | \( \mu_{eff} \) |
| 1              | 0.80   |        | 2.0(1)      |
| [1]BF4         |        | 0.53   | 2.0(1)      |
| [1](THF)PF6    | 0.71   | 1.7(1) |             |
| [1]Br          | 0.79   | 2.1(1) |             |
| 2              | 0.95   | 3.2(1) |             |

The solid-state molecular structures of \( [1]\text{BF}_{4} \) and \( [1](\text{THF})\text{PF}_{6} \) reveal a common structural motif: trigonal-bipyrッドonal Ni(I) complexes coordinated by two ligands L and direct equatorial coordination of an additional ligand (Figure 3). In \( [1]\text{BF}_{4} \), the tetrafluoroborate anion shows an interaction of one F atom with the metal center [Ni1–F1 distance: 2.2729(9) Å]. The value of the geometry index for \( [1]\text{BF}_{4} \) (\( \tau_{5} = 0.53 \)) is between those expected for square-pyramidal (\( \tau_{5} = 0 \)) and trigonal-bipyrッドonal (\( \tau_{5} = 1 \); Table 1) complexes. For \( [1](\text{THF})\text{PF}_{6} \) the fifth coordination site at Ni is occupied by a THF solvent molecule [Ni1–O1 2.1355(15) Å], rather than by the counteranion, which can be attributed to the reduced donor strength of the PF6− anion relative to BF4− (Figure 3). A similar coordination motif was observed following the
The magnetic moments of $[1]_{\text{BF}_4}$ and $[1(\text{THF})]_{\text{PF}_6}$ [2.0(1) and 1.7(1) $\mu_\text{B}$, respectively, in THF $d_6$ at 300 K] were determined by the Evans NMR method and are consistent with $S = 1/2$ Ni(1) centers (Table 1). EPR measurements of $[1]_{\text{BF}_4}$ and $[1(\text{THF})]_{\text{PF}_6}$ were recorded in toluene glasses at 20 and 40 K, respectively, and also confirm the presence of a single unpaired electron at each Ni center (for full details, see the SI). The EPR signal of $[1]_{\text{BF}_4}$ appears almost isotropic because of the broad and overlapping signals of the $g$ tensor. However, it is better described as a rhombic system, which is indicated by the asymmetric shape of the signal. The observed $g$ tensor with the simulated principal components $g_{11} = 2.195$, $g_{22} = 2.127$, and $g_{33} = 2.060$ is consistent with a Ni-centered radical in a system with small $g$ anisotropy (for the spectrum, see Figure S20). The EPR spectrum of $[1(\text{THF})]_{\text{PF}_6}$ displays similarly overlapping signals of the $g$ tensor and can again be described as a rhombic system with small $g$ anisotropy. Poorly resolved hyperfine interactions were observed on (at least) one $g$ tensor, and satisfactory simulation was achieved after the inclusion of hyperfine coupling (135 and 150 MHz) to $^{31}\text{P}$ ($I = 1/2$) on two $g$ tensors. The observed $g$ tensor (simulated $g$ tensor: $g_{11} = 2.200$, $g_{22} = 2.129$, and $g_{33} = 2.035$) is again consistent with a Ni-centered radical (for the spectrum, see Figure S21). These results are consistent with the density functional theory (DFT) calculations carried out on $[1]_{\text{BF}_4}$, which show a large amount of spin density on Ni ($0.85$) and reproduce the experimental $g$ tensor quite well [TPSSH/IGLO-III+CP(PPP); see the SI].

The reaction of 1 with FcBa$^{2+}$ leads to a product with a notably different structure, at least in the solid state. In this case, the product $[1]_{\text{Ba}^{2+}}$ is formed, which crystallizes as a dicationic dinuclear Ni complex fragment with two Ni(1) centers bridged by one P atom of one phosphinine ligand L. The charge of the dication is balanced by two Ba$^{2+}$ anions, which show no close contacts with either Ni center (Figure 3).

Figure 3. Solid-state molecular structures of $[1]_{\text{BF}_4}$, $[1(\text{THF})]_{\text{PF}_6}$, and $[1]_{\text{Ba}^{2+}}$. Ellipsoids are drawn at the 40% probability level, H atoms are omitted for clarity; some phenyl groups are displayed in wireframe and are transparent for clarity. For $[1]_{\text{BF}_4}$, a toluene solvent molecule is omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ni1−P1 2.2328(4), Ni1−P2 2.2147(4), Ni1−N1 2.0449(12), Ni1−N2 2.0340(12), Ni1−F1 2.2729(9), P1−C1 1.7422(15), C1−C2 1.397(2), C2−C3 1.404(2), C3−C4 1.402(2), C4−C5 1.391(2), P1−C5 1.7409(14); C1−P1−C5 102.82(7), P1−Ni1−P2 108.070(16), P1−Ni1−F1 114.04(3), P1−Ni1−P2 137.73(3), P2−Ni1−N2 82.66(4), P1−Ni1−N1 82.92(4). For $[1(\text{THF})]_{\text{PF}_6}$, one THF molecule, which is not coordinated to the complex, was omitted for clarity. The crystal of $[1]_{\text{BF}_4}$ contains a second crystallographically independent molecule with very similar structural parameters, and only one of these molecules is shown. The structure of the metal core of $[1]_{\text{Ba}^{2+}}$ is shown in the inset. Selected bond lengths [Å] and bond angles [deg]: Ni1−N1 2.059(3), Ni1−N2 2.091(3), Ni1−P1 2.2275(11), Ni1−P2 2.2153(11), Ni1−P3 2.4071(11), Ni2−N3 1.968(4), Ni2−N4 1.960(4), Ni2−P3 2.2692(11), Ni2−P4 2.2360(13), Ni1−P3−Ni2 125.9074(10), P1−Ni1−N1 80.6936(11), P2−Ni1−N2 82.1127(13), P3−Ni2−N3 85.8814(12), P4−Ni2−N4 83.9324(11).
hyperfine coupling interactions are indicative for an isolated $S = \frac{1}{2}$ species. Thus, the EPR data might indicate that $[1_{12}](\text{BarF})_{22}$ dissociates in solution into two monocations $[\text{Ni}(I)\text{L}_{2}]^{+}$. This is also consistent with DFT calculations on the monocation, which yield a rhombic $g$ tensor ($g_{x} = 2.123$, $g_{y} = 2.116$, and $g_{z} = 2.015$) that is in good agreement with the experimental results.

When the EPR measurement of $[1_{12}](\text{BarF})_{22}$ is performed in a 2-methyltetrahydrofuran glass at 20 K instead of a toluene glass, a well-resolved rhombic system with small $g$ anisotropy is again observed (Figure 4). However, in this case, additionally resolved hyperfine couplings to two equivalent $^{31}\text{P}$ ($I = \frac{1}{2}$), two equivalent $^{14}\text{N}$ ($I = 1$), and two equivalent $^{1}\text{H}$ ($I = \frac{1}{2}$) nuclei are also observed. Calculations indicate that the proton hyperfine couplings are caused by the $\omega$-H atoms of the pyridyl groups (see the SI for details). The simulated $g$ tensor ($g_{x1} = 2.2135$, $g_{x2} = 2.1460$, and $g_{x3} = 2.0212$) is similar to that obtained in toluene and so is again consistent with a Ni-centered radical. The presence of monocationic Ni(I) centers is additionally confirmed by the magnetic moment of 1.7(1) $\mu_{B}$ (in THF-$d_{8}$ at 300 K) per Ni atom measured by the Evans NMR method.

In addition to simple outer-sphere oxidation, we were also interested in investigating more complex reactions of 1, particularly given the complete lack of analogous studies for other nickel phosphinine complexes. Ni(0) complexes, in general, are very versatile and find various applications in electrochemistry and catalysis. 69,70 For example, Ni(0) species play important roles in cross-coupling reactions (e.g., Kumada reaction) because of their redox properties and ability to undergo oxidative additions with substrates such as aryl halides. 71,72 Thus, we were motivated to investigate the reactivity of 1 with the simple model cross-coupling substrates bromobenzene and iodobenzene (Scheme 3). When 1 equiv of bromobenzene was added to 1 in benzene, no change was observed at room temperature, either by eye or by $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectroscopy. However, when the temperature was increased to 60 °C, a color change from deep purple to fluorescent red could be observed. According to GC-FID analysis, a maximum of ca. 70% bromobenzene was consumed (despite complete consumption of 1, as indicated by $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectroscopy) alongside the formation of a new species which shows a single $^{31}\text{P}\{^{1}\text{H}\}$ resonance arising as a sharp singlet at $\delta = 4.7$ ppm. This signal splits into a complex multiplet in the $^{31}\text{P}$ NMR spectrum. In order to characterize the corresponding species 2, the solvent of the fluorescent red reaction mixture was completely evaporated, and the remaining residue was extracted into $n$-hexane.

Crystals of 2 were obtained by slow evaporation of the resulting fluorescent orange $n$-hexane solution. Single-crystal XRD revealed its identity as a 1,1-diphenyl-$\lambda^{3}$-phosphinine (Figure 5), which accounts for the observed fluorescent properties. 73−76 This structure formally arises from the addition of two phenyl groups to the P center of the

![Figure 4](https://dx.doi.org/10.1021/acs.inorgchem.0c01115) Experimental (black) and simulated (red) EPR spectra of $[1_{12}](\text{BarF})_{22}$ recorded at 20 K in a 2-methyltetrahydrofuran glass. Simulation parameters: $g_{x1} = 2.2135$, $g_{x2} = 2.1460$, and $g_{x3} = 2.0212$; $W_{x1} = 3.0$, $W_{x2} = 2.5$, and $W_{x3} = 3.2$; $A_{11}^{xy} = A_{12}^{xy} = 210$ MHz, $A_{12}^{xy} = A_{13}^{xy} = 212$ MHz, $A_{13}^{xy} = A_{23}^{xy} = 207$ MHz, $A_{23}^{xy} = A_{33}^{xy} = 23$ MHz, $A_{11}^{xz} = A_{12}^{xz} = 28$ MHz, $A_{13}^{xz} = A_{23}^{xz} = 21$ MHz, $A_{11}^{yz} = A_{12}^{yz} = 20$ MHz, $A_{13}^{yz} = A_{23}^{yz} = 19$ MHz. Experimental conditions: microwave frequency 9.64567 GHz; power 1.589 mW; modulation amplitude 4.000 G.

![Scheme 3](https://dx.doi.org/10.1021/acs.inorgchem.0c01115)

Scheme 3. Reaction of 1 with Haloarenes PhX (X = Br, I) at 60 °C

(i) Reaction in benzene, 2 (15% isolated yield) and $[1]_{1}\text{Br}$ (45%). (ii) Reaction in toluene, 2 (30%) and 3 (64%). Possible contributions to the electronic structure of 3, including Ni d$^{9}$ (3-I), Ni d$^{8}$ (3-II), and Ni d$^{7}$ (3-III) centers.
phosphinine ligand L. As reported for other \(\lambda^2\)-phosphinines, the P1–C1/C5 bonds are slightly shortened compared to P–C single bonds (mean distance 1.763 Å vs sum of covalent radii 1.86 Å), while the C–C bonds are in the range of C=C double bonds (mean distance 1.395 Å vs sum of covalent radii 1.34 Å). The almost planar phosphorus heterocycle is characterized by the small fold angle of 1.50(8),77 while the phenyl substituents at the P atom show bond lengths consistent with P–C single bonds (mean distance 1.817 Å).77 Similar to the other \(\lambda^2\)-pyridylphosphine reported in the literature, the pyridyl group is essentially coplanar with the phosphinine ring [N1–C6–C5–C4 = 174.9(1)°], while the phenyl groups in 4 and 6 positions of the heterocycle are not in-plane with the central hexagon. This is in accordance with our expectations for the steric demand of the N lone pair, which is smaller than a CH group of a phenyl moiety.76,78

The \(n\)-hexane-insoluble material remaining after separation of 2 could be dissolved in THF to give a red NMR-silent solution. Single crystals suitable for XRD were obtained after layering with \(n\)-hexane. The molecular structure revealed the formation of a trigonal-bipyramidal Ni(I) complex, [1]Br, containing two L and one additional bromide ligand (Figure 5), in a structure very similar to those observed for [1]BF\(_4\) and [1(THF)]PF\(_6\). The σ bonds between the Ni center and the donor atoms of L (mean distances: Ni1–N 2.105 Å and Ni1–P 2.208 Å) are elongated compared to 1, most likely caused by the higher coordination number of the Ni atom. In comparison with the cationic complexes [1]BF\(_4\) and [1(THF)]PF\(_6\), [1]Br displays similar Ni–P distances but shortened Ni–N distances. The Ni1–Br1 bond length of 2.4889(4) Å is in the range of covalent Ni–Br bonds (sum of covalent radii 2.430 Å),77 while the geometry index of \(\tau_8\) = 0.79 is consistent with a distorted trigonal-bipyramidal structure (Table 1). The magnetic moment of [1]Br [2.14(1) \(\mu_B\) in THF-\(d_8\) at 300 K] was determined by the Evans NMR method and is consistent with an \(S = 1/2\) Ni(I) center (Table 1). Additionally, EPR measurements in a toluene glass at 20 K indicate the presence of a Ni(I) species with a metal-centered radical (Figure S24; simulated g tensor: \(g_{xx} = 2.190, g_{yy} = 2.125,\) and \(g_{zz} = 2.060)\), similar to [1]BF\(_4\) and [1(THF)]PF\(_6\). The calculated spin density on Ni (0.82) as well as the calculated g tensor are in good agreement with the experimental data (Table S5).

Although Ni-mediated cross-coupling reactions usually involve Ni(0) and Ni(II) species,79 Ni(I) complexes analogous to [1]Br have also been suggested as viable intermediates and may also show pronounced catalytic activity.79,80 Some other nickel(I) halide complexes have also been isolated from the reaction of Ni(0) complexes with PhX.79,80

The reaction of 1 was also investigated toward 1 equiv of iodobenzene under analogous conditions (toluene, 60 °C) but was found to lead to a significantly different outcome. In this case, full consumption (>99%) of iodobenzene took place according to GC-FID analysis. Compound 2 could again be isolated after extraction with \(n\)-hexane. However, the remaining residue showed a deep-green color rather than deep red, as had been observed using PhBr. Crystals were obtained from a toluene solution of this residue, after layering with \(n\)-hexane. Single-crystal XRD revealed a new product 3, which shows a significantly different structure in the solid state than [1]Br (Figure 5). Most notably, 3 has clearly lost one of its phosphinine ligands L. Moreover, the Ni center—which is tetrahedrally coordinated (\(\tau_8\) = 0.95; Table 1)—is bound to two iodide ligands, as well as by a formally anionic 1-Ph-\(\lambda^2\)-phosphinine ligand, which is derived by the addition of an extra phenyl substituent to ligand L. The Ni1–P1 distance (2.2509(6) Å) is in the range of Ni–P single bonds (sum of covalent radii 2.21 Å), while the Ni1–N1 [1.9941(19) Å] bond length is elongated in a manner similar to in 1. The Ni1–I distances (mean value 2.514 Å) are in the range of typical Ni–I bonds (sum of covalent radii 2.43 Å). We anticipate that 3 is formed by oxidative addition of the carbon–halogen bond to the Ni center and subsequent transfer of the aryl fragment to the ligand. A similar reaction of a (TPP)Ni(C\(_6\)H\(_5\)) (acac) complex (TPP = 2,4,6-triphenylphosphinine; acac = acetylacetonate) has been proposed by Lehmkuhl et al.22

Unlike [1]Br, the electronic structure of 3 cannot be assigned easily. The measured value of the magnetic moment

![Figure 5. Solid-state molecular structures of 2, [1]Br, and 3. Ellipsoids are drawn at the 40% probability level; H atoms are omitted for clarity; some phenyl groups are transparent for clarity. Selected bond lengths [Å] and bond angles [deg] for 2: P1–C1 1.7719(13), C1–C2 1.3724(17), C2–C3 1.4194(17), C3–C4 1.3858(18), C4–C5 1.4038(18), P1–C5 1.7553(13); C1–P1–C5 107.49(6), fold angle C1–P1–C5 1.50(8). Selected bond lengths [Å] and bond angles [deg] for [1]Br: Ni1–P1 2.2094(6), Ni1–P2 2.2055(6), Ni1–N1 2.1046(18), Ni1–N2 2.1045(18), Ni1–Br1 2.4889(4); P1–Ni1–P2 112.45(3), P1–Ni1–Br1 121.48(2), Br1–Ni1–P2 126.04(2), P1–Ni1–N1 80.61(4), P2–Ni1–N2 80.58(4). For 3, tolune solvent molecule is omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ni1–P1 2.2509(6), Ni1–I1 2.4893(4), Ni1–I2 2.5375(4), Ni1–N1 1.9941(19), P1–C1 1.774(2), C1–C2 1.387(3), C2–C3 1.414(3), C3–C4 1.417(3), C4–C5 1.370(3), P1–C5 1.779(2); C1–P1–C5 104.61(10), P1–Ni1–N1 82.59(6), I1–Ni1–I2 124.218(16), P1–Ni1–I1 116.93(2), N1–Ni1–I2 108.96(5).]
[3.2(1) in THF-$d_4$ at 300 K] lies between those expected for two and three unpaired electrons (Table 1). The magnetic susceptibility of a solid sample of 3 was measured with a SQUID magnetometer in the temperature range 100 K $< T <$ 400 K. The results are shown in Figure 6. These data reveal that the magnetic moment continuously increases from $\mu_{\text{eff}} = 2$ at 105 K to 4 at 400 K. These data suggest that a thermally activated spin transition occurs from an $S = 1/2$ ground state into an $S = 3/2$ excited state. The latter dominates at the upper limit of the accessible temperature window. In addition, it is noteworthy that the measured effective moment significantly exceeds the expected spin-only value for an $S = 3/2$ system at high temperature ($T > 350$ K). This observation might be explained by unquenched orbital contributions to the magnetic moment of the $S = 3/2$ species, which is a common phenomenon for complexes with a tetrahedral $d^3$ configuration at the metal atom.87

The EPR spectrum of 3 recorded at 20 K in a toluene glass shows overlapping and broad signals for the $g$ tensors. The simulated $g$ tensor ($g_{11} = 2.390$, $g_{22} = 2.242$, and $g_{33} = 2.120$) is consistent with a Ni-centered radical in a rhombic $S = 1/2$ system (Figure 7).

In the case of 3, the experimental data could not be reproduced in good agreement using standard DFT (for details, see the SI). Furthermore, a rather large spin density was calculated at the Ni atom (1.23), hinting at a broken-symmetry solution. Indeed, a broken-symmetry treatment at the TPSS0-D3BJ/def2-TZVP level shows an interesting electronic structure. Here, an intermediate-spin Ni center with a dicationic dinuclear $\lambda^2$-phosphininenickel(0) complex ($\lambda$-Ph-4,6-phosphininenickel(0) complex 1, which can be conveniently oxidized using ferrocenium salts FeCx. Oxidation with FeBF$_4$ and FePF$_6$ leads to the formation of Ni(1) complexes [1]BF$_4$ and [1(TTHF)]PF$_6$, which possess similar trigonal-bipyranyal structural motifs. Oxidation of 1 with FeBF$_4$ on the other hand, affords a dicationic dinuclear Ni(1) complex [1]$_2$[BArF$_2$$_2$$_2$] containing a bridging phosphine ligand in the rare $\mu_2$-coordination mode. The reaction of 1 with bromobenzene leads to formation of the $\lambda^2$-phosphinine 2 and the trigonal-bipyranyal Ni(I) complex [1]Br. In contrast, the reaction of 1 with iodobenzene results in the formation of 2 and the tetrahedral Ni complex 3, which is based on a formally anionic 1-Ph-$\lambda^2$-phosphinine. Quantum-chemical calculations on 3 highlight the redox-active behavior of the phosphinine moiety, which prohibits a clear assignment of an oxidation state to the Ni center. The carbon–halogen bond splitting by a transition-metal complex and transfer of the aryl fragment to the ligand highlights the chemical noninnocence of phosphine ligands in transition-metal complexes. Investigations on the mechanism of formation of [1]Br and 3 and further reactivity studies on 1 are currently underway in our laboratories.

## CONCLUSION

In summary, we have presented the synthesis and crystallographic characterization of the homoleptic 2-(2’-pyridyl)-4,6-phosphininenickel(0) complex 1. First reactivity studies on the phosphinine-based Ni complex 1 show that it can be conveniently oxidized using ferrocenium salts FeC$x$. Oxidation with FeBF$_4$ and FePF$_6$ leads to the formation of Ni(1) complexes [1]BF$_4$ and [1(TTHF)]PF$_6$, which possess similar trigonal-bipyramidal structural motifs. Oxidation of 1 with FeBF$_4$ on the other hand, affords a dicationic dinuclear Ni(1) complex [1]$_2$[BArF$_2$$_2$$_2$] containing a bridging phosphine ligand in the rare $\mu_2$-coordination mode. The reaction of 1 with bromobenzene leads to formation of the $\lambda^2$-phosphinine 2 and the trigonal-bipyranyal Ni(I) complex [1]Br. In contrast, the reaction of 1 with iodobenzene results in the formation of 2 and the tetrahedral Ni complex 3, which is based on a formally anionic 1-Ph-$\lambda^2$-phosphinine. Quantum-chemical calculations on 3 highlight the redox-active behavior of the phosphinine moiety, which prohibits a clear assignment of an oxidation state to the Ni center. The carbon–halogen bond splitting by a transition-metal complex and transfer of the aryl fragment to the ligand highlights the chemical noninnocence of phosphine ligands in transition-metal complexes. Investigations on the mechanism of formation of [1]Br and 3 and further reactivity studies on 1 are currently underway in our laboratories.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01115.
Full synthetic details, NMR, UV–vis, and EPR spectra, and crystallographic refinement and computational details (PDF)

Accession Codes
CCDC 2007973 and 1988434–1988439 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request cif, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes
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