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Phosphorus Analogues of [Ni(bpy)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-Ph2-PC5H2)2] (1) has been obtained by reaction of the formal Ni(0) sources [(IPr)Ni(H2C=CHSiMe3)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]BF4, [1](THF)PF6, and [1](BArF)3. The structures of these salts reveal an interesting dependence on the nature of the anion. While [1]BF4 and [1](THF)PF6 show trigonal-bipyramidal coordination of Ni in the solid state, [1](BArF)3 exists as a dinuclear Ni(1) complex and possesses a bridging phosphinine moiety in a rare μ3 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 μ3 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 homogeneous 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′-bipyridine)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 bipyridine 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)-biphosphinine with nickel(0) sources, such as Ni(cod), (cod = 1,5-cyclooctadiene), afford the homoleptic bis(biphosphinine) 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 bipyridines. 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 CO2 by the Fe complex C (Figure 1).

EXPERIMENTAL DETAILS

All experiments were performed under an atmosphere of dry argon using standard glovebox and Schlenk-line techniques. Tetrahydrofur-
an (THF), toluene, diethyl ether, and n-hexane were purified, dried, and degassed using an MBraun 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. Bromobenzene and iodobenzene were equipped with a He temperature-controlled cryostat system (Oxford Instruments). The 1H and 13C NMR spectra were recorded on Bruker Avance 400 spectrometers (Bruker BioSpin Rheinstetten) using a Varian Cary 50 spectrometer. Elemental analyses were performed with an Inorganic Mass (COSY, HSQC, and HMBC) experiments.

Magnetic susceptibilities in solution 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. Column: HP-5, 19091J-413 (30 m × 0.32 mm × 0.25 μm). Carrier gas: N2. Calibration of substrates and products with internal standard n-pentadecane and analytically pure samples. The experimental X-band electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX spectrometer (Bruker BioSpin Rheinstetten) equipped with a He temperature-controlled cryostat system (Oxford Instruments). The g values were calculated with the ORCA software package at the B3LYP/def2-TZVPP level of theory. The spectrum was analyzed and simulated using the W9SEPR program of Prof. Frank Neese.

Single-crystal X-ray diffraction (XRD) data were recorded on an Agilent Technologies SuperNova diffractometer with Cu KR radiation (λ = 1.54184 Å). Either semiempirical multisite absorption corrections or analytical ones were applied to the data. The structures were solved with SHELXT, 22 and least-squares refinements on F2 were carried out with SHELXL. 23 The H atoms were located in idealized positions and refined isotropically with a riding model. CCDC 2007973 (for [Ni(2-Py-4,6-Ph2-PC5H2)2] (1)), 1988434 (for [1BF4]), 1988435 (for [1THF]BF4), 1988436 (for [1](BArF)2), 1988437 (for [2]), and 1988438 (for [3]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre. The selected crystal of 1a was a nonmerohedral twin. The twinning was determined with the CrysAlisPro software (Rigaku Oxford Diffraction, 2019). Component 2 rotated by ~179°7003° around [−0.71, 0.71, −0.01] in reciprocal space and [−0.77, 0.64, 0.03] in direct space. The structure was refined with the corresponding HKLFS file (see the Supporting Information for further details). For compound [1]Br, a solvent mask was calculated, and 40 electrons were found in a volume of 160 Å3 in one void per unit cell. This is consistent with the presence of 0.5 equiv of THF per asymmetric unit, which accounts for 40 electrons per unit cell. A check cif report (http://checkcif.iucr.org/) for [1](BArF)2 shows a level B alert [PLAT910_ALERT_3_B: Missing # of FCF Reflection(s) Below Theta(Min)]. This alert was introduced during data collection and cannot be corrected by refinement. However, it will not affect the validity of the refined structure.

**Synthesis.** Synthesis of 1. Compound 1 was prepared in an MBraun argon glovebox. 1 is sensitive toward moisture and air, is soluble and stable in benzene, THF, and toluene. A solution of L (2.5 equiv, 125 mg, 0.385 mmol) in benzene (2 mL) was added dropwise to a solution of D (1 equiv, 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 order to remove IPr. The remaining residue was extracted with benzene (4 × 2 mL) and layered with n-hexane (12 mL). 1 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 1. Yield: 40 mg, 37%. Elem anal. Calc for C44H32N2P2Ni (Mw = 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/μm (εmax/L·mol−1·cm−1)]: 290 (98632), 320 (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, C of C2,4-Ph), 7.85–7.86 (m, 2H, H of NC5H4), 7.90 (d, 4H, H of C2,4-Ph)), 8.30 (2H, H of C2,4-Ph). Hε of PC5H4PhPy, JHBr = 5 Hz). 8.43 (2H, H of NC5H4Br, JBr = 8 Hz). 8.55 (pt, 2H, Hε of PC5H4PhPy). 8.66 (2H, H of NC5H4Br, JBr = 5 Hz). 13C{1H} NMR (100.61 MHz, 300 K, THF-d8): δ 119.3 (s, C of NC5H4). 122.5 (s, C of NC5H4), 126.7 (s, C of C2,4-Ph), 126.8 (s, C of C2,4-Ph), 127.0 (s, C of C2,4-Ph), 127.4 (t, 7H), 129.0 (s, C of C2,4-Ph), 129.6 (s, C of C2,4-Ph), 131.4 (s, C of C2,4-Ph), 133.7 (m, C of NC5H4), 137.4 (t, C of C2,4-Ph), 143.2 (m, C of PC5H4PhPy), 143.9 (m, C of PC5H4PhPy), 145.1 (m, C of PC5H4PhPy), 146.6 (m, C of PC5H4PhPy), 153.1 (m, C of 4-Ph), 161.9 (s, C of 3-Ph, J = 7 Hz). The Hε of PC5H4PhPy, JHBr = 5 Hz). 8.43 (2H, H of NC5H4Br, JBr = 8 Hz). 8.55 (pt, 2H, Hε of PC5H4PhPy). 8.66 (2H, H of NC5H4Br, JBr = 5 Hz). 13C{1H} NMR (100.61 MHz, 300 K, THF-d8): δ 119.3 (s, C of NC5H4). 122.5 (s, C of NC5H4), 126.7 (s, C of C2,4-Ph), 126.8 (s, C of C2,4-Ph), 127.0 (s, C of C2,4-Ph), 127.4 (t, 7H), 129.0 (s, C of C2,4-Ph), 129.6 (s, C of C2,4-Ph), 131.4 (s, C of C2,4-Ph), 133.7 (m, C of NC5H4), 137.4 (t, C of C2,4-Ph), 143.2 (m, C of PC5H4PhPy), 143.9 (m, C of PC5H4PhPy), 145.1 (m, C of PC5H4PhPy), 146.6 (m, C of PC5H4PhPy), 153.1 (m, C of 4-Ph), 161.9 (s, C of 3-Ph, J = 7 Hz). 19F NMR (161.98 MHz, 300 K, THF-d8): δ 179.4. 19F NMR (161.98 MHz, 300 K, THF-d8): δ 179.4.

**Synthesis of [1]BF4.** Compound [1]BF4 was prepared in an MBraun argon glovebox. [1]BF4 is sensitive toward moisture and air. [1]BF4 is soluble and stable in benzene, THF, and toluene. 1 (50 mg, 0.07 mmol) was dissolved in THF (1 mL), and FcBF4 (12 mg, 0.07 mmol) was added at room temperature. An immediate color change from yellow to deep purple was observed. The color changed further to green-brown upon stirring overnight. The solvent of the green reaction mixture was completely removed, and ferrocene was removed by sublimation under high vacuum (50 °C, ca. 10 Torr). 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, [1]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 \([1] \text{BF}_3\). Yield: 43 mg, 77%. Elem. anal. Calcd for \(\text{C}_3\text{H}_3\text{N}_2\text{P}_2\text{NiBF}_4\) (\(M_e = 926.47\) 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; \(\delta_{\text{max}}/\text{nm}(\varepsilon_{\text{max}}/\text{mol}^{-1}\cdot\text{cm}^{-1})\): 285 (24370), 450 (4788), 614 (2600), \(\mu_{\text{eff}}\) (THF·dioxane): 3.2(1) \(\mu_B\) for the purple solution. The decanted fluorescent pink solution was evaporated to dryness, and the remaining pink residue was isolated as \(n\)-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 pyridylphosphine 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 \(D\).\(^8\) While the 1:1 reaction of \(D\) and \(L\) resulted in a mixture of several inseparable products (Figure S11), the reaction of \(D\) with 2.5 equiv of \(L\) led to the selective formation of a single phosphorus-containing species (1), characterized by a singlet in the \(^{31}\text{P}\) NMR spectrum at \(\delta = 179.4\) ppm (Scheme 1, for the spectrum, see Figure S5). Isolation of 1 was achieved by the removal of volatiles (including \(\text{H}_2\text{C}=\text{CHSiMe}_3\)) under vacuum, the removal of \(\text{IPr}\) by washing with \(n\)-hexane, and the layering of a purple solution of 1 in benzene with \(n\)-hexane at room temperature for 2 days, to afford a pure, crystalline material in 35% yield.

**Compound 1** was fully characterized by NMR and UV–vis spectroscopy, elemental analysis, and cyclic voltammetry (CV; see the Supporting Information, SI). The collected data are all consistent with the formulation of 1 as the 1:2 homoleptic chelate complex \([\text{Ni}(L)_2]\) (Scheme 1), which is also in line with the reaction stoichiometry employed.
Scheme 1. Synthesis of 1 Using D as a Ni(0) Precursor

Scheme 2. Synthesis of Ni(I) Complexes [1]BF₄ (77% Isolated Yield), [1(THF)]PF₆ (88%), and [1₂][BArF₄]₂ (78%) via the Reaction of 1 with Ferrocenium Salts in THF at 25 °C

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–N2 1.998(6), Ni1–P1 2.092(2), P1–Ni1–P2 128.15(8), N1–Ni1–N2 104.5(2), P1–Ni1–N3 124.67(18), C1–P1–C5 102.2(3), C1′–P2–C5′ 102.0(3). Cyclic voltammograms of 1 (right; from +0.2 to +1.1 and from -1.1 to -0.2; scan rate 100 mV).

Table 1. Geometry Indices (τ₄ and τ₅) and Magnetic Moments (μₑff) THF-d₈, 300 K of Reported Ni Complexes

<table>
<thead>
<tr>
<th>compound</th>
<th>τ₄</th>
<th>τ₅</th>
<th>μₑff</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.80</td>
<td>0.53</td>
<td>2.0(1)</td>
</tr>
<tr>
<td>[1]BF₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[1(THF)]PF₆</td>
<td>0.71</td>
<td>1.7(1)</td>
<td></td>
</tr>
<tr>
<td>[1]Br</td>
<td></td>
<td>0.79</td>
<td>2.1(1)</td>
</tr>
<tr>
<td>3</td>
<td>0.95</td>
<td></td>
<td>3.2(1)</td>
</tr>
</tbody>
</table>

The solid-state molecular structures of [1]BF₄ and [1(THF)]PF₆ reveal a common structural motif: trigonal-bipyrildinencarbene Ni(I) complexes coordinated by two ligands L and direct equatorial coordination of an additional ligand (Figure 3). In [1]BF₄, 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]BF₄ (τ₅ = 0.53) is between those expected for square-planar (τ₅ = 0) and trigonal-bipyrildinencarbene (τ₅ = 1) Table 1) complexes. For [1(THF)]PF₆, 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
Figure 3. Solid-state molecular structures of [1]BF₄, [1(THF)]PF₆ and [1]((BAr)²)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]BF₄, 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), C5–P1 1.7409(14); C1–P1–C5 102.92(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(THF)]PF₆, one THF molecule, which is not coordinated to the complex, was omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ni1–P1 2.1871(6), Ni1–P2 2.1857(6), Ni1–N1 2.0611(16), Ni1–N2 2.0586(17), Ni1–O1 2.1355(15), P1–C1 1.734(2), C1–C2 1.389(3), C2–C3 1.407(3), C3–C4 1.396(3), C4–C5 1.387(3), P1–C5 1.738(2), C1–P1–C5 103.42(10), P1–Ni1–P2 103.49(2), P1–Ni1–O1 133.20(4), O1–Ni1–P2 123.20(4), P2–Ni1–N2 81.92(5), P1–Ni1–N1 81.91(5). For [1]((BAr)²)₂, two Ba(Br)₂ anions and n-hexane solvent molecule were omitted for clarity. The crystal of [1]((BAr)²)₂ contained 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]((BAr)²)₂ is shown in the inset. Selected bond lengths [Å] and bond angles [deg]: Ni1–Ni1 2.059(5), Ni1–N1–N2 2.091(3), Ni1–P1 2.2275(11), Ni1–P2 2.21531(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 125.9704(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).

electrophilic addition of Ph₃SnCl to anionic homoleptic biphosphininecobalt and -rhodium complexes, as described by Le Floch and co-workers.¹⁷

The magnetic moments of [1]BF₄ and [1(THF)]PF₆ [2.0(1) and 1.7(1) \(\mu_P\)] respectively, in THF-d₄ at 300 K were determined by the Evans NMR method and are consistent with \(S = \frac{1}{2}\) Ni(I) centers (Table 1). EPR measurements of [1]BF₄ and [1(THF)]PF₆ 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]BF₄ 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 \(g_{xx} = 2.195, g_{yy} = 2.127,\) and \(g_{zz} = 2.060\) 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(THF)]PF₆ 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 \(^{31}\)P (I = \(\frac{1}{2}\)) on two g tensors. The observed g tensor (simulated g tensor: \(g_{xx} = 2.200, g_{yy} = 2.129,\) and \(g_{zz} = 2.035\)) 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]BF₄, which show a large amount of spin density on Ni (0.85) and reproduce the experimental g tensor quite well [TPPSH/IGLO-III+CP(PPP); see the SI].

The reaction of 1 with FcBaB₄₂ leads to a product with a notably different structure, at least in the solid state. In this case, the product [1]((BAr)²)₂ is formed, which crystallizes as a dicatonic dinuclear Ni complex fragment with two Ni(I) centers bridged by one P atom of the phosphinine ligand L. The charge of the dication is balanced by two BArF₄⁻ anions, which show no close contacts with either Ni center (Figure 3). Compound [1]((BAr)²)₂ is a rare example of a complex in which the phosphinine ligand shows a \(\mu_P\) bridging coordination mode.⁶⁵ The corresponding bipyridine \(\mu_2\)-N bridging mode is even scarcer (despite the fact that these complexes were studied far more extensively) because of the reduced electronic versatility of the lighter heterocycle.⁷ The Ni–N and Ni–P distances in [1]((BAr)²)₂ are similar to those in [1]BF₄ and [1(THF)]PF₆, except for the bridging Ni–P3 distance, which is slightly elongated [2.4071(11) Å vs mean distance 2.246 Å], as expected for a bridging interaction. The bridging P3 atom is tetrahedrally coordinated between the two Ni(I) centers with a geometry index of \(\tau = 0.86\).

Also, in contrast to [1]BF₄ and [1(THF)]PF₆, the EPR signal of [1]((BAr)²)₂ in a toluene glass at 30 K is well resolved and shows a rhombic system with small g anisotropy and hyperfine coupling interactions with two \(^{31}\)P nuclei along three g tensors \([A_{P1_{11}} = A_{P2_{11}} = 205 MHz, A_{P3_{22}} = A_{P4_{33}} = 170 MHz,\) and \(A_{P3_{33}} = A_{P4_{22}} = 175 MHz\)]. The spectrum again indicates that a Ni-centered radical is present (simulated g tensors: \(g_{xx} = 2.2170, g_{yy} = 2.1450,\) and \(g_{zz} = 2.0195\); Figure S22). The found g values (close to 2) and well-defined
hyperfine coupling interactions are indicative for an isolated S = 1/2 species. Thus, the EPR data might indicate that [12][BARF]2 dissociates in solution into two monocations [Ni(I)L2]+. This is also consistent with DFT calculations on the monocation, which yield a rhombic g tensor (g = 2.123, g = 2.116, and g = 2.015) that is in good agreement with the experimental results.

When the EPR measurement of [12][BARF]2 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 unresolved hyperfine couplings to two equivalent 31P (I = 1/2), two equivalent 14N (I = 1), and two equivalent 1H (I = 1/2) nuclei are also observed. Calculations indicate that the proton hyperfine couplings are caused by the o-H atoms of the pyridyl groups (see the SI for details). The simulated g tensor (g = 2.2135, g = 2.1460, and g = 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) μB (in THF-d8 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 31P{1H} 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 31P{1H} NMR spectroscopy) alongside the formation of a new species which shows a single 31P{1H} resonance arising as a sharp singlet at δ = 4.7 ppm. This signal splits into a complex multiplet in the 31P 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-2,3-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. Experimental (black) and simulated (red) EPR spectra of [12][BARF]2 recorded at 20 K in a 2-methyltetrahydrofuran glass. Simulation parameters: g = 2.2135, g = 2.1460, and g = 2.0212; W = 3.0, W = 2.5, and W = 3.2; A = 210 MHz, A = 212 MHz, A = 210 MHz, A = 207 MHz, A = 23 MHz, A = 28 MHz, A = 21 MHz, A = 20 MHz, A = 20 MHz, and A = 19 MHz. Experimental conditions: microwave frequency 9.64567 GHz; power 1.589 mW; modulation amplitude 4.000 G.

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

(i) Reaction in benzene, 2 (15% isolated yield) and 1Br (45%). (ii) Reaction in toluene, 2 (30%) and 3 (64%). Possible contributions to the electronic structure of 3, including Ni d (3-I), Ni d (3-II), and Ni d (3-III) centers.
phosphinine ligand L. As reported for other \( \lambda^3 \)-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)°, and the phenyl substituents at the P atom show bond lengths consistent with P–C single bonds (mean distance 1.817 Å). Similar to the only other \( \lambda^3 \)-pyridylphosphinine 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.

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), while the geometry index of \( \tau_b = 0.79 \) is consistent with a distorted trigonal-bipyramidal structure (Table 1). The magnetic moment of \([1]Br\) [2.1(1) \( \mu_B \) in THF-\( d_8 \) at 300 K] was determined by the Evans NMR method and is consistent with an \( S = \frac{1}{2} \) 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,\(^{37,38} \) Ni(I) complexes analogous to \([1]Br\) have also been suggested as viable intermediates and may also show pronounced catalytic activity.\(^{39-41} \) Some other nickel(I) halide complexes have also been isolated from the reaction of Ni(0) complexes with PhX.\(^{53-56} \)

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 phosphininate ligands L. Moreover, the Ni center—which is tetrahedrally coordinated (\( \tau_b = 0.95; \) Table 1)—is bound to two iodide ligands, as well as by a formally anionic 1-Ph-\( \lambda^3 \)-phosphinine ligand, which is derived by the addition of an extra phenyl substituent to the ligand. A similar reaction of Ni(0) complexes with PhX.\(^{85,86} \) Lehmkuhl et al.\(^{23} \) have also reported the formation of a trigonal-bipyramidal Ni(I) complex, \([1]Br\), analogous to 3. The electronic structure of \([1]Br\) is best accounted for by a formal Ni(I) center (Table S5).
[3.2(1) in THF-d₄ 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 μₑff = 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 d⁸ 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 (g₁₁ = 2.390, g₂₂ = 2.242, and g₃₃ = 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 makes an assignment of the oxidation state of the Ni atom somewhat ambiguous. However, both broken-symmetry DFT and CASSCF clearly show the redox-active behavior of the anionic 1-phenylphosphacyclohexadienyl ligand in 3. Furthermore, the CASSCF-NEVPT2 estimation of the g tensor is in qualitative agreement with the experiment and reproduces the observed significant anisotropy of the g tensor (gₓ = 2.562, gᵧ = 2.227, and gₚ = 2.173).

### 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 FeC₅. Oxidation with FeC₅F₄ and FeCP₆ leads to the formation of Ni(I) complexes [1]BF₄ and 1[1(THF)]PF₆, which possess similar trigonal-bipyrimal structural motifs. Oxidation of 1 with FeC₅BF₄ on the other hand, affords a dications dicinuclear Ni(I) complex [1]₂[BAF₆]₄ containing a bridging phosphine ligand in the rare μₑff-coordination mode. The reaction of 1 with bromobenzene leads to formation of the λ²-phosphine 2 and the trigonal-bipyrimal 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-A⁻₄-phosphine. Quantum-chemical calculations on 3 highlight the redox-active behavior of the phosphine 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 highlight 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.
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