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2,6-Bis(oxazolinyl)phenylnickel(II) Bromide and 2,6-Bis(ketimine)phenylnickel(II) Bromide: Synthesis, Structural Features, and Redox Properties[☆]

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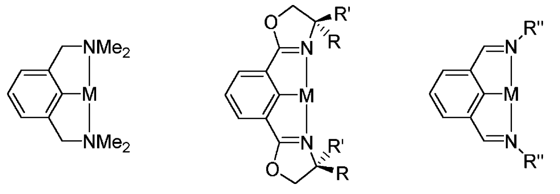
2,6-Bis(oxazolinyl)phenylnickel bromide complexes [NiBr(R,R′-Phebox)] (**2**) were synthesized via two synthetic routes (A and B). In route A, selective bis-*ortho* lithiation of [R,R′-PheboxBr], followed by a transmetalation reaction with [$NiBr_2(PEt_3)_2$], yielded not only complexes **2** with an η^3-*mer*-*N*,*C*,*N′*-bonded Phebox ligand but also [NiBr(R,R′-Phebox)(PEt_3)$_2$], **7**, where the nickel center is η^1-*C* bonded to the intra-annular C_{ipso} of the Phebox ligand. Coordination of two PEt_3 ligands completes the square-planar coordination sphere of the Ni center in **7**. When R = *t*-Bu, R′ = H, only complex **7c** was formed. Alternatively, when route B (oxidative addition with [$Ni(cod)_2$], cod = cyclooctadiene) was followed, selective formation of complexes **2** was observed. X-ray crystal structures were obtained for [NiBr(*i*-Pr,H-Phebox)] (**2b**) and [NiBr(bis(ketimine)phenyl)] (**3**). The Ni centers have square-planar geometries with a planar, η^3-*mer*-*N*,*C*,*N′* coordination of the terdentate ligand systems. Complexes **2** were found to be inactive as catalysts in the atom-transfer radical polymerization (ATRP) reaction of methyl methacrylate (MMA) and in the atom-transfer radical addition (ATRA, Kharasch addition) reaction of CCl_4 to MMA. This is ascribed to the relatively high oxidation potential of Ni^{II}−Phebox complexes, which excludes the (reversible) formation of a d^7-Ni^{III}−Phebox complex, a crucial condition for subsequent reactions. Cyclovoltammetry (CV) experiments (($(n\text{-Bu})_4NBr$ as supporting electrolyte) showed no electrochemical waves between −1.00 and +1.50 V (Ag/AgCl reference electrode, $(n\text{-Bu})_4NBr$ as supporting electrode). Theoretical calculations showed that the energy (E_{ox}) needed for the oxidation reaction occurring during the CV experiments is considerably higher for [NiBr(Me,Me-Phebox)] (1.87 eV) and [NiBr(bis(ketimine)phenyl)] (1.90 eV) than for [NiBr(NCN)] (**1**) (1.45 eV).

Introduction

Chelating aryl ligands have become an important class of ligands in homogeneous catalysis[1] and materials chemistry.[1b,2] We and others have extensively studied metal complexes derived from the so-called ECE pincer ligand (ECE is $[C_6H_3(CH_2E)_2\text{-}2,6]^-$ in which E is NR_2 (**A**,[1−3] Figure 1), PR_2, SR, OMe). The ECE pincer ligands have a rich coordination chemistry originating from the conformational flexibility of the CH_2E *ortho* substituents. The bis(*ortho*-oxazolinyl)phenyl or Phebox ligand (**B**,[4,5,6,7] Figure 1) and the bis(aldimine)phenyl ligand (**C**,[8] Figure 1) have *ortho* substituents with a pronounced restriction of conformational freedom; that is, only rotation about C_{aryl}−C_{imine} is possible as well as *syn*/*anti* configurations (for **C**). The



A M(NCN) **B** M(Phebox) **C** M(aldimine-NCN)

M = Ni, Pd, Pt, Rh, etc. M = Ni, Pd, Pt, Rh, Li M = Pd, Pt, Rh

Figure 1. *N*,*C*,*N′*-terdentate coordinating ligand systems applied in organometallic complexes.

[☆] Dedicated to Professor Miguel Yus on the occasion of his 60th birthday in recognition of his skills and contribution to the field of organic chemistry.

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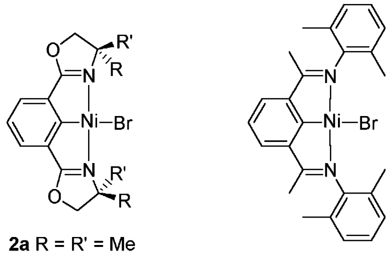
oxazolinyl $C{=}N$ groupings in these ligands have the tendency to be coplanar with the arene ring, thus creating a planar NCN-terdentate ligand system. This has been observed in Rh−,[4] Ni−,[5] Pd−,[4a,b,6] and Pt−Phebox[4b,7] derivatives and in Li−Phebox compounds in which C_{ipso} is three-center two-electron bonded to two lithium atoms in a dimeric structure.[9] Nevertheless, the Phebox ligand can also be η^1-*C* bonded to a metal center, as has been found for [Au(Me,Me-Phebox)-(PPh_3)][10] and [Sn(Me,Me-Phebox)Me_3].[9]

The Phebox ligand attracted much attention because of the ample opportunities to introduce chirality in the oxazoline ring by the use of readily available chiral amino alcohols in the oxazolinyl substituent synthesis. In 1997, the Phebox ligand was introduced in catalysis by Denmark (cyclopropanation with Phebox−Pd complexes)[6a] and was studied extensively by Nishiyama,[4,7a] who employed Phebox−Rh, −Pd, and −Pt complexes in catalysis (asymmetric aldol-type condensation of isocyanides and aldehydes,[4b,c] asymmetric Michael addition,[4e] enantioselective allylation of aldehydes,[4d,11] and asymmetric alkylation of aldimines[7a]).

In the search for catalytic properties of *E,C,E′*-pincer metal complexes, the unique atom-transfer radical addition (abbreviated as ATRA, 1:1 addition of $CClX_3$ to MMA)[12] and atom-transfer radical polymerization (abbreviated as ATRP, polymerization of MMA)[13] reactions catalyzed by [NiBr(C_6H_3-(CH_2NMe_2)$_2$-2,6)] (**1**, **A** (M = NiBr, see Figure 1)) were discovered. Extensive studies revealed that both the ATRP and ATRA reactions are catalyzed by these Ni compounds because of (i) the low and reversible $Ni^{II} \rightarrow Ni^{III}$ oxidation potential and (ii) the persistence of a d^7 Ni^{III} species [$Ni^{III}X_2$(C_6H_3-(CH_2NMe_2)$_2$-2,6)]. So far, this catalytic reactivity was not found for PCP- and SCS-nickel complexes and seems to be unique for the NCN-nickel complexes. Accordingly, we set out to study the synthesis and properties of other Ni^{II} complexes with *N,C,N′*-terdentate coordinating ligands related to **1**, i.e., the Ni−Phebox (**2**) and Ni−ketimine (**3**) NCN complexes, both with restricted conformational freedom as compared to [NiBr(C_6H_3-(CH_2NMe_2)$_2$-2,6)] (**1**, abbreviated as [NiBr(NCN)].



2a R = R' = Me
2b R = *i*Pr, R' = H
2c R = *t*Bu, R' = H

3

Figure 2. [NiBr(Phebox)] (**2**) and [NiBr(bis(ketimine)phenyl)] (**3**).

Here, the synthesis of [NiBr(R,R′-Phebox)] and [NiBr(bis-(ketimine)phenyl)] complexes (Figure 2) and analysis of their structural properties are described. The Ni−ketimine complex **3** is closely related to the 2,6-bis(aldimine)phenyl−Pd, −Pt, and −Rh complexes, recently described by Elsevier et al. (**C**, Figure 1).[8] In addition the catalytic activity of **2** in the radical polymerization of methyl methacrylate (MMA) and the Kharasch addition of CCl_4 to MMA has been tested. The redox properties of [NiBr(R,R′-Phebox)] (**2**) and [NiBr(bis(ketimine)-phenyl)] (**3**) are compared to those of [NiBr(NCN)] (**1**). Theoretical calculations provide further insight into the redox properties of **2** and **3**, which have implications for their reactivity in ATRA and ATRP.

Results and Discussion

Ligand Synthesis. Three different Phebox ligands (**5**) were synthesized using modified literature procedures.[14−16] One achiral Phebox ligand (**5a**) was derived from 2-amino-2-methyl-1-propanol, and the two chiral Phebox ligands (**5b**, **5c**, respectively, Scheme 1) were obtained from L-valinol and L-*tert*-leucinol, respectively. Synthesis of 2,6-bis(4,4′-R,R′-2′-oxazolinyl)phenyl bromide **5a** (R = R′ = Me), **5b** (R = *i*-Pr, R′ = H), and **5c** (R = *t*-Bu, R′ = H) (abbreviated as [R,R′-PheboxBr]) started with the oxidation of 1-bromo-2,6-dimethylbenzene with $KMnO_4$ to 2-bromoisophthalic acid.[14] The latter acid was chlorinated with $SOCl_2$, followed by reaction of the resulting 2-bromoisophthaloyl chloride (**4**) with the appropriate amino alcohol.[15] The resulting amide was cyclized *in situ* via a procedure of Vorbrüggen using a CCl_4/PPh_3 reagent.[16]

The synthesis of 2,6-bis[*N,N′*-(2′,6′-dimethylphenyl)ketimino]-phenyl bromide (**6**, abbreviated as [bis(ketimine)phenylBr])

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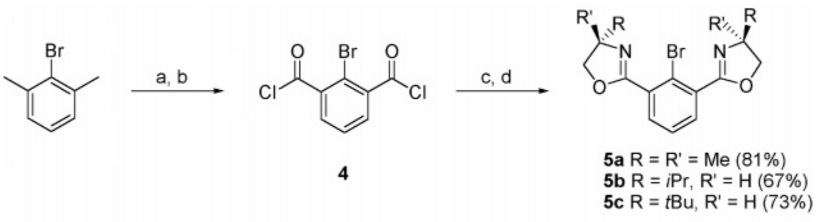
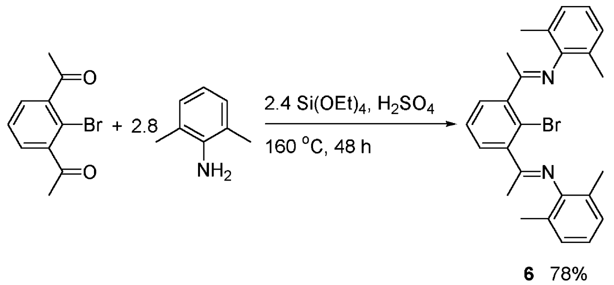
Scheme 1. Synthesis of [R,R′-PheboxBr] (5)



a) $KMnO_4$, *t*BuOH, H_2O, 76%; b) $SOCl_2$, quant.; c) amino alcohol, Et_3N, CH_2Cl_2, not isolated; d) PPh_3, CCl_4, Et_3N, CH_3CN.

Scheme 2. Synthesis of [Bis(ketimine)phenylBr] (6)



could not be accomplished via common condensation procedures: precipitation of the product, as was used for the 2,6-bis(ketimine)pyridine analogue,[17] or via removal of the generated H_2O by azeotropic distillation using a trap (Dean Stark). The synthesis of **6** was successfully accomplished by reacting 2,6-diacetylphenyl bromide[18] with 2.8 equiv of 2,6-dimethylaniline, in the presence of $Si(OEt)_4$, under removal of ethanol at high temperature (Scheme 2).

This procedure was developed for the synthesis of sterically hindered imines,[19] and these forcing conditions are necessary indeed to obtain the bis(ketimine)phenyl bromides such as **6**.

Synthesis of Ni Complexes 2 and 3. Starting from [R,R′-PheboxBr] **5**, synthesis of the Phebox−Ni complexes was accomplished via two different synthetic routes. Route A involved selective bis-*ortho* lithiation followed by transmetalation of the *in situ* formed Phebox−Li with, e.g., $[NiBr_2(PEt_3)_2]$. In a previous paper we demonstrated that selective bis-*ortho* lithiation of **5** via Br−Li exchange can be achieved with *n*-BuLi in Et_2O at −78 °C.[9] Reaction of either [Me,Me-PheboxBr] (**5a**) or [*i*-Pr,H-PheboxBr] (**5b**) with *n*-BuLi and subsequent reaction with $[NiBr_2(PEt_3)_2]$ resulted in the formation of [NiBr(Me,Me-Phebox)] (**2a**) and [NiBr(*i*-Pr,H-Phebox)] (**2b**), respectively, which could be isolated as pure products. A disadvantage of this route is that in addition to the desired η^3-*mer-N,C,N′*-Phebox−NiBr complexes **2**, η^1-*C*-Phebox−$NiBr(PEt_3)_2$ complexes of type **7** are also formed. The amount of **7** seems to be dependent on the nature of the oxazolinyl substituents R and R′. In the reactions to **2a** and **2b**, **7a** and **7b**, respectively, were formed as side products in relatively small amounts (max. 26%), while **7c** was formed exclusively in the transmetalation reaction of **5c** with $[NiBr_2(PEt_3)_2]$. In the latter reaction, formation of the desired product **2c** was not even observed.

Isolation of side products **7a** and **7b** was hampered because of similar solubility properties to the starting complex $[NiBr_2(PEt_3)_2]$. However, **7c** could be isolated pure as a dark red solid. $^{31}P\{^1H\}$ spectra (singlet at δ 1.4 ppm) showed that the two PEt_3 ligands are *trans*-coordinated. The $[NiBr(t\text{-Bu,H-Phebox})(PEt_3)_2]$ stoichiometry was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy of **7c** in benzene-d_6. Consequently the Phebox ligand in **7c** is η^1-*C* bonded to the Ni center and has a structure as proposed in Scheme 3. In this proposed structure, the plane of the aryl ring of the *t*-Bu,H-Phebox ligand is perpendicular to the square-planar coordination plane of the Ni^{II} center. The *meta*-aryl protons show a diagnostic downfield shift from 6.96 in square-planar complex **2c** with an η^3-*mer-N,C,N′*-coordinated *t*-Bu,H-Phebox ligand (*vide infra*) to 7.60 ppm in **7c**. The latter value corresponds to the chemical shift for the *meta*-aryl protons found in the starting *t*-Bu,H-Phebox bromide **5c**. Accordingly the formation of **7a** and **7b** in the corresponding reactions could be identified by the shifts of the respective *meta*-aryl protons in these compounds from 6.98 (**2a**) to 7.87 ppm for **7a** and 6.98 (**2b**) to 7.98 for **7b**, respectively. In the course of the formation of **2**, the PEt_3 ligands have to be replaced by bis-*ortho* coordination with the imine-N ligands. This feature was observed earlier in the transmetalation reaction of bis-*ortho*-amine chelating aryllithium compounds $[Li\{C_6H_3(CH_2NR^1R^2)\text{-}2,6\}]$ with $[NiBr_2(PEt_3)_2]$, yielding products with and without the phosphine ligands coordinated to the Ni^{II} center, depending on the R^1 and R^2 substituents of the ligand.[20] It is not clear yet why **2b** is formed in high yield, whereas in the case of the compound with a *t*-Bu instead of an *i*-Pr group the reaction stops at the stage of the bisphosphine compound **7c**.

The alternative route B (Scheme 4) consists of an oxidative addition reaction of the Phebox bromides **5** with $[Ni(cod)_2]$.

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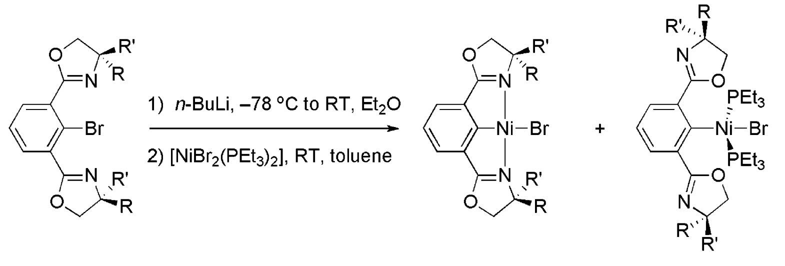
Scheme 3. Route A: Bis-*ortho* Lithiation/Transmetalation

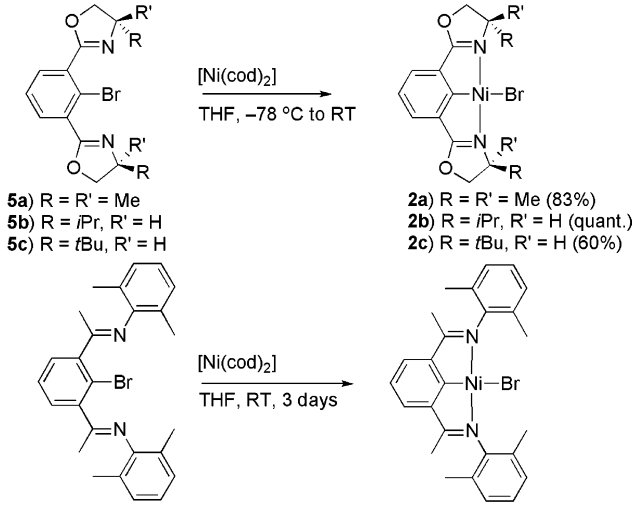


5a R = R' = Me
5b R = *i*Pr, R' = H
5c R = *t*Bu, R' = H

2a R = R' = Me (74%)
2b R = *i*Pr, R' = H (91%)

7a R = R' = Me
7b R = *i*Pr, R' = H
7c R = *t*Bu, R' = H (77%)

Scheme 4. Route B: Oxidative Addition with [Ni(cod)$_2$]



5a) R = R' = Me
5b) R = *i*Pr, R' = H
5c) R = *t*Bu, R' = H

2a) R = R' = Me (83%)
2b) R = *i*Pr, R' = H (quant.)
2c) R = *t*Bu, R' = H (60%)

6

3 72%

Because of the absence of potentially coordinating phosphine ligands, formation of complexes of type **7** is prevented. Therefore, route B is a preferred route for the synthesis of **2a** and **2b**, and **2c** in particular.

The ketimine−nickel complex **3** was prepared by the oxidative addition of [Ni(cod)$_2$] with aryl bromide **6**. The nickel complexes **2a**, **2b**, and **3** are stable as solids in air, whereas **2c** decomposes rapidly. In solution all complexes (**2a**−**c** and **3**) decompose upon exposure to air. Ultimately, the corresponding protonated arene ligand is observed. However, upon addition of a small amount of water to a solution of the Phebox−nickel complexes in benzene-d_6 under exclusion of oxygen, no decomposition through hydrolysis is observed. This suggests that these nickel complexes are stable toward water but react with oxygen in solution, subsequently followed by hydrolysis.

Structural Features. Single crystals of **2b**, suitable for X-ray crystallography, were obtained by vapor diffusion of pentane to a saturated solution in diethyl ether. The top and side-on views of the molecular structure of **2b** are depicted in Figure 3.

The X-ray crystal structure of **3** was determined from single crystals, obtained from slow evaporation of a saturated solution in pentane. The molecular structure of **3** is depicted in Figure 4.

The structure of **2b** is directly related to the recently published structure of [NiI(Me,Me-Phebox)][5] and the analogous Phebox−Pd,[4a,b,5]−Pt,[4b,7] and −Rh[4] complexes. The square-planar Ni^{II} centers in **2b** and **3** are four-coordinate, being bonded to C$_{ipso}$ of the aryl ring, the two *trans*-positioned oxazolinyl-N or imine-N ligands, and a bromide ligand that occupies the fourth coordination site.

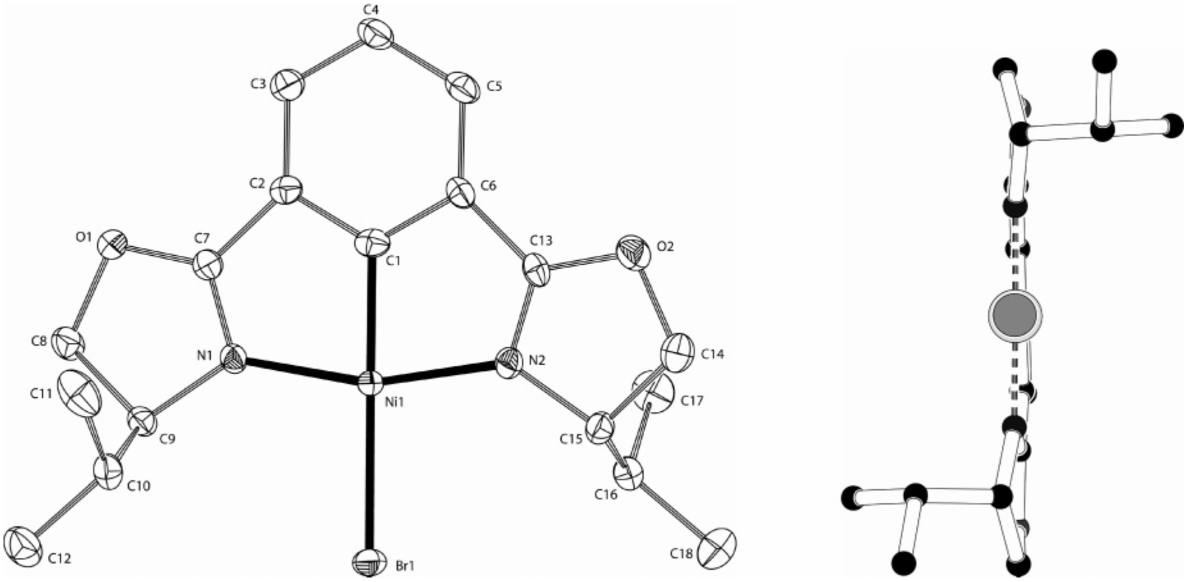


Figure 3. Displacement ellipsoid plot (50% probability) of [NiBr(*i*-Pr,H-Phebox)] (**2b**) showing full numbering scheme and a side-on view along the Ni(1)−C(1) bond. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−C(1) 1.8491(19), Ni(1)−Br(1) 2.3572(4), Ni(1)−N(1) 1.908(2), Ni(1)−N(2) 1.910(2), N(1)−C(7) 1.290(3), N(2)−C(13) 1.286(3), C(1)−Ni(1)−Br(1) 178.10(6), N(1)−Ni(1)−N(2) 162.20(8), C(1)−Ni(1)−N(1) 81.08(13), C(1)−Ni(1)−N(2) 81.15(13), Br(1)−Ni(1)−N(1) 99.86(6), Br(1)−Ni(1)−N(2) 97.93(6).

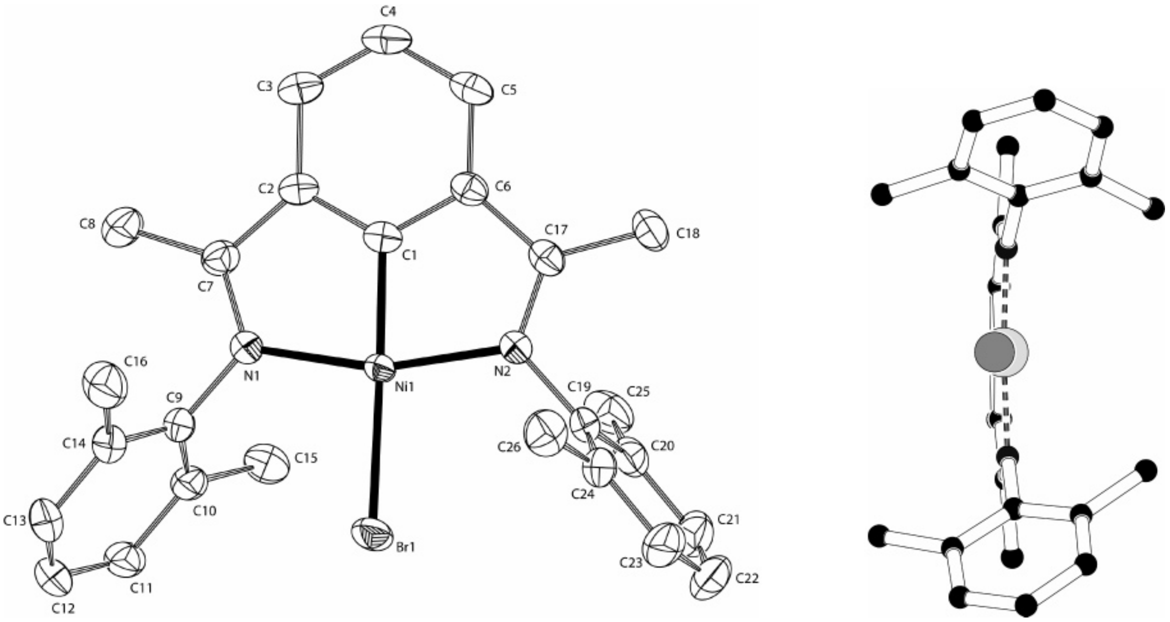


Figure 4. Displacement ellipsoid plot (50% probability) of **3**, showing full numbering scheme and a view onto the N−Ni−N moiety along the Ni(1)−C(1) bond. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (deg), and torsion angles (deg): Ni(1)−C(1) 1.819(2), Ni(1)−Br(1) 2.3419(3), Ni(1)−N(1) 1.9394(19), Ni(1)−N(2) 1.9318(19), N(1)−C(7) 1.307(3), N(1)−C(9) 1.435(3), N(2)−C(17) 1.311(3), N(2)−C(19) 1.439(3), C(1)−Ni(1)−Br(1) 174.63(7), N(1)−Ni(1)−N(2) 162.06(8), C(1)−Ni(1)−N(1) 81.26(9), C(1)−Ni(1)−N(2) 81.27(9), Br(1)−Ni(1)−N(1) 98.75(6), Br(1)−Ni(1)−N(2) 99.03(6), C(7)−N(1)−C(9) 120.4(2), C(17)−N(2)−C(19) 119.25(19), Ni(1)−N(1)−C(9)−C(10) −72.9(3), Ni(1)−N(2)−C(19)−C(20) 89.2(2), Br(1)−Ni(1)−N(1)−C(9) −7.96(18), Br(1)−Ni(1)−N(2)−C(19) 13.54(18).

The overall geometry of **2b** corresponds well to that of [NiI(Me,Me-Phebox)].[5]

The N(1)−Ni(1)−N(2) angles of **2b** and **3** are 162.20(8)° and 162.06(8)°, respectively. This acute angle reflects the distortion from the square-planar geometry around Ni, which is a common structural feature found in η^3-*mer-N,C,N′* pincer nickel(II) complexes (163.2−168.59°).[12a,20b,21]

The degree of planarity of the Phebox ligand skeleton (C═N substituent and aryl ring) is illustrated by the side-on views depicted in Figures 3 and 4. The largest deviation from the least-squares planes of the two five-membered rings forming the η^3-*mer-N,C,N′* chelate amounts to 0.012(3) Å for **2b** and 0.020(2) Å for **3**. The angles between these two planes are 1.61(12)° and 3.45(10)°, respectively. In **3**, the *ortho*-xylyl N substituents bend slightly to one side of the planar ketiminearyl skeleton, while the bromide is bending to the opposite side. This structural feature is illustrated by the torsion angles of Br(1)−Ni(1)−N(1)−C(9) and Br(1)−Ni(1)−N(2)−C(19) of −7.96(18)° and 13.54(18)°, respectively, and the C(1)−Ni(1)−Br(1) angle of 174.63(7)°.

The bond lengths about the Ni centers in **2b** and **3** follow the general trend as expected (Ni < Pd ∼ Pt) when comparing the Phebox−Pd and −Pt (**B**, Figure 1) and NCN−Ni, −Pd, and −Pt (**A**, Figure 1) and bis(aldimine)phenyl−Pd and −Pt (**C**, Figure 1) bond lengths (Table 1).

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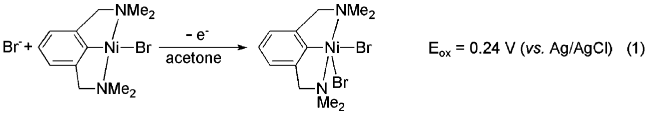
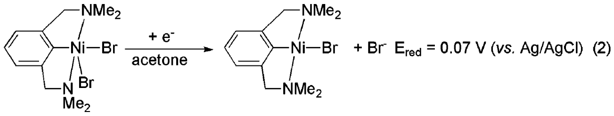
Catalysis and Redox Properties. The catalytic properties of Phebox−Ni complexes **2a**−**c** were investigated by testing their catalytic activity in both the radical polymerization reaction of MMA and the Kharasch addition reaction of CCl_4 to MMA. It appeared that all these nickel complexes were inactive as catalysts in these types of reactions. This is in concert with the observation that the complexes were stable in the presence of oxidating agents such as CCl_4, which excludes the possibility that the persistent "radical" d^7-Ni^{III} compound was irreversibly formed. This would block catalysis, as the occurrence of a fast electron-transfer back step is a crucial condition for the re-formation of the d^8-Ni^{II} catalyst.[12d]

These observations prompted us to investigate the redox properties of the Phebox− and ketimine−Ni^{II} complexes **2a**−**c** and **3** and compare them to [NiBr(NCN)] (**1**), which is a highly effective catalyst.[12,13] Cyclovoltammetric (CV) experiments with **2a**, **2c**, and **3** were performed in distilled acetone using $(n\text{-}Bu)_4NBr$ as supporting electrolyte in the −1.00 to +1.50 V region. The potentials are given against the Ag/AgCl reference electrode. For comparison, CV experiments were also performed on the [NiBr(NCN)] complex. The latter complex shows two distinct electron-transfer processes, which are coupled to chemical reactions (transfer of bromide) in the specified experimental region (eqs 1 and 2).[25]





Experiments with **2a**, **2c**, and **3** showed no electrochemical waves in the region where chemical reversible transformations of aryl−Ni^{II} to aryl−Ni^{III} complexes usually occur. This illustrates that Phebox−Ni and bis(ketimine)phenyl−Ni complexes are much more difficult to oxidize as compared to the [NiBr(NCN)] complex.

Table 1. Comparison of Selected Crystallographic Data of Phebox−M^{II}, NCN−M^{II}, and Bis(aldimine)phenyl−M^{II} Complexes

	C_{ipso}−M (Å)	N−M (Å)
bis(ketimine)Ph−Ni (**3**)	1.819(2)	1.9318(19), 1.9394(19)
*i*Pr,H-Phebox−Ni (**2b**)	1.8491(19)	1.908(2), 1.910(2)
Me,Me-Phebox−Ni[5]	1.857−1.859	1.968−1.977
R,R′-Phebox−Pd[4a,b,5]	1.845−1.956	2.056−2.072
R,R′-Phebox−Pt[4b,7]	1.892−1.963	2.026−2.066
bis(aldimine)Ph−Pt[8a,c,e]	1.889−1.945	2.036−2.097
bis(aldimine)Ph−Pd[8d]	1.905−1.918	2.087−2.143
NCN−Ni[12a,20b,21]	1.788−1.899	1.971−2.208
NCN−Pd[22]	1.900−2.017	2.007−2.136
NCN−Pt[14,22i,45,46]	1.901−2.025	2.036−2.168

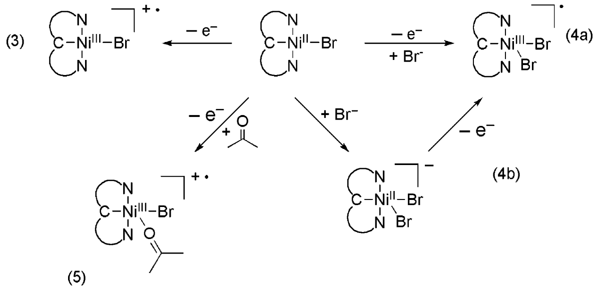
Table 2. Calculated IP_1's for 1, 2a, and 3

	1	**2a**	**3**
total energy (E_h)	−760.6755751	−1063.5225188	−1298.9355291
IP_1 (eV),[a] eq 3	6.95	7.33	6.92
IP_1 (eV),[b] eq 4a	1.45	1.87	1.90
IP_1 (eV),[c] eq 4b	2.19	2.52	2.53
IP_1 (eV),[d] eq 5	5.69	6.13	6.01

[a] Ionization potential, calculated as $E_{[NiBr]^+} - E_{[NiBr]^\bullet}$. [b] Ionization potential, calculated as $E_{[NiBr2]^\bullet} - \{E_{[NiBr]} + E_{[Br]^-}\}$. [c] Ionization potential, calculated as $E_{[NiBr2]^\bullet} - E_{[NiBr2]^-}$. [d] Ionization potential, calculated as $E_{[NiBr(ac.)]^{+\bullet}} - \{E_{[NiBr]} + E_{[ac.]}\}$.

Theoretical calculations on existing nickel(II) complexes **1**, **2a**, and **3** were performed to gain insight in the electronic structure of these complexes. All geometries were characterized as real minima by means of a numerical force constant calculation. The calculated geometries of **1**, **2a**, and **3** are in reasonable agreement with those obtained from X-ray crystallography data.[26−28] Only the Ni−Br bond length is systematically overestimated by about 0.1 Å in the calculations.

Equations 3, 4, and 5 schematically represent the processes for which theoretical calculations were performed regarding the ionization potential of the Ni^{II} complexes. The calculated energies for the first ionization potential (IP_1) for the depicted processes starting from the three d^8-Ni^{II} complexes [NiBr(NCN)] (**1**), [NiBr(Me,Me-Phebox)] (**2a**), and [NiBr(bis(ketimine)-phenyl)] (**3**) are depicted in Table 2.



The calculated ionization potentials for the electron-transfer reactions of d^8-Ni^{II} to d^7-Ni^{III} complexes (IP_1, eq 3, Table 2) show that for **2a** a higher oxidation potential is expected compared to **1** (7.33 vs 6.95 eV). However, according to these

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(26) Comparison of the calculated geometrical features of [NiBr(NCN)] and experimental[21c] geometrical features of $[NiBr(C_6H_3(CH_2NEt_2)_2\text{-}2,6)]$ (distances in Å, angles in deg) calcd (expt): Ni(1)−Br(1) 2.501 (2.420(1)), Ni(1)−N(1) 2.028 (2.002(5)), Ni(1)−N(2) 2.028 (2.006(4)), C(1)−Ni(1) 1.854 (1.825(5)), C(1)−Ni(1)−N(1) 83.67 (84.5(2)), C(1)−Ni(1)−N(2) 83.61 (84.2(2)), C(1)−Ni(1)−Br(1) 179.99 (176.6(2)), N(1)−Ni(1)−N(2) 167.27 (168.6(2)), N(1)−Ni(1)−Br(1) 96.33 (95.6(1)), N(2)−Ni(1)−Br(1) 96.40 (95.8(1)).

(27) Comparison of the calculated geometrical features of [NiBr(Me,Me-Phebox)] (**2a**) and experimental[5] geometrical features of [NiI(Me,Me-Phebox)] (distances in Å, angles in deg) calcd (expt): Ni(1)−Br(1) 2.472 (Ni(1)−I(1) 2.5804(5)), Ni(1)−N(1) 1.978 (1.972(3)), Ni(1)−N(2) 1.978 (1.977(3)), C(1)−Ni(1) 1.874 (1.859(4)), C(1)−Ni(1)−N(1) 81.06 (80.53(15)), C(1)−Ni(1)−N(2) 81.05 (80.73(15)), C(1)−Ni(1)−Br(1) 179.95 (C(1)−Ni(1)−I(1) 172.61(11)), N(1)−Ni(1)−N(2) 162.12 (161.04(13)).

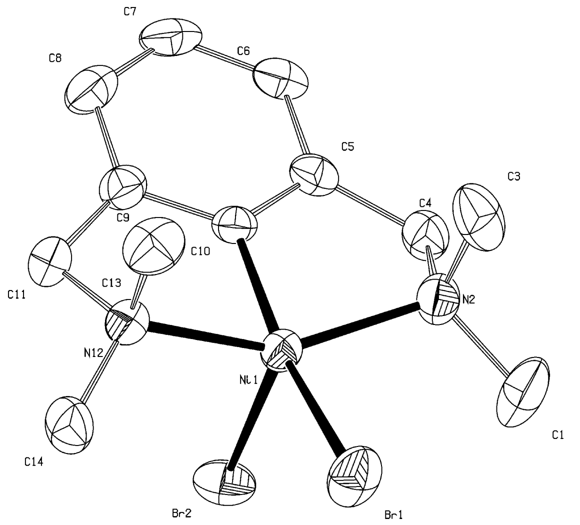

Figure 5. Displacement ellipsoid plot (50% probability) of **8**, showing full numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ni(1)−C(10) 1.894(3), Ni(1)−Br(1) 2.4373(6), Ni(1)−Br(2) 2.4272(6), Ni(1)−N(12) 2.041(2), Ni(1)−N(2) 2.036(3), C(10)−Ni(1)−Br(1) 166.19(9), C(10)−Ni(1)−Br(2) 90.85(9), N(12)−Ni(1)−N(2) 152.58(10), C(10)−Ni(1)−N(12) 82.15(11), C(10)−Ni(1)−N(2) 81.50(11), Br(1)−Ni(1)−N(12) 95.37(7), Br(2)−Ni(1)−N(12) 100.25(8), Br(1)−Ni(1)−N(2) 95.29(8), Br(2)−Ni(1)−N(2) 101.85(8), Br(1)−Ni(1)−Br(2) 102.96(2).

calculations, complex **3** should be as easy to oxidize as **1** (6.92 vs 6.95 eV), which is not in accordance with the cyclovoltammetric experiments. As stipulated in ref 25, the counterion (Br^-) plays an essential role in the cyclic voltammetric experiments (eqs 1, 2). In this process (eq 4a) [$NiBr_2$(NCN)] (**8**) is formed. Therefore, the reaction energies for reaction 4a are better measures for the ionization potential observed in the CV experiments than the IP_1's calculated for eq 3. Hence, the energies (IP_1) for the electron transfer and subsequent reaction with Br^- (eq 4a) were calculated for **1**, **2a**, and **3**. The calculated geometry of **8** is in reasonable agreement with the geometry obtained from an X-ray crystal structure determination.[29] The molecular structure of **8** (depicted in Figure 5; single crystals were obtained from slow evaporation of a saturated solution of **8** in xylene, RT[25]) is directly related to the molecular structure of [NiI_2(NCN)][30] and shows the same geometrical features: a square-pyramidal geometry with the Ni atom displaced ca. 0.34 Å out of the basal plane[31] toward the apical atom Br(2) and a distortion from an ideal square-pyramidal geometry toward trigonal bipyramidal (C(10) and Br(1) axial). A very similar crystal structure was also found for the corresponding iron(III) complex [$FeCl_2$(NCN)].[32]

The energies (IP_1) for this electron transfer and subsequent reaction with Br^- (eq 4a) were calculated as the difference between the total energies of, for example, **8** and the sum of **1** and Br^-. The ionization potentials thus calculated (1.45, 1.87, and 1.90 eV, respectively, Table 2) show that for **2a** and **3** a similar oxidation potential is expected, while for **1** a significantly lower energy is calculated, rationalizing the observed wave in the CV experiments for **1** and the absence of a wave for **2a** and **3** (in the region between −1.00 and +1.50 V).[33] However, in this calculation we assume that the Br^- anion is not associated with the Ni complex. Assuming that prior to the oxidation reaction the bromide anion interacts with the neutral nickel complex (eq 4b), theoretical calculations confirm that for **1** and **2a** this is indeed a plausible mechanism for the oxidation reactions. For **1** and **2a**, a [$Ni-Br_2$]$^-$ complex could be located with a Ni−Br^- distance of 3.283 and 2.998 Å, respectively, but for **3**−Br^- the Ni−Br^- distance is already 3.696 Å, indicating a very weak interaction with the Ni atom. The IP_1's calculated for these processes (eq 4b) lead to similar conclusions to those for the model reactions with Br^- at infinite distance (eq 4a).

If instead of a complexing bromide ion, coordination by a solvent molecule (acetone) is taken into account (eq 5), similar results to those for the process described in eq 4a are obtained (Table 2). This further corroborates the experimental result that the counterion or the solvent is involved in the charge-transfer process[25] as well as the absence of an electrochemical wave between −1.00 and +1.50 V in the cyclovoltammetric experiments with **2a** and **3**.

In conclusion, synthesis of the Phebox−Ni complexes was accomplished via two different synthetic routes. One route involves the selective bis-*ortho* lithiation of the corresponding Phebox−Br followed by transmetalation of the *in situ* formed Phebox−Li with, for example, [$NiBr_2(PEt_3)_2$] (route A). Following route A, a side product, characterized as [NiBr(R,R′-Phebox)$(PEt_3)_2$] (**7**), was formed. In the case of reaction with the most sterically hindered Phebox ligand **5c** (R = *t*-Bu, R′ = H) **7c** was formed exclusively. The second route, B, makes use of an oxidative addition reaction of the aryl bromide with [$Ni(cod)_2$]. This route leads to the exclusive formation of **2** and is also used for the synthesis of [NiBr(bis(ketimine)phenyl)] (**3**). The molecular structures of **2b** and **3** were determined by X-ray crystal structure determination. The Phebox and bis(ketimine)phenyl ligands are η^3-*mer-N,C,N′* bonded in these complexes. The terdentate *N,C,N′* ligands in these complexes have planar arrangements of the C=N and aryl plane. However, even these rigid ligands can bind in the monodentate η^1-*C* bonding mode, as was demonstrated for [NiBr(*t*-Bu,H-Phebox)-$(PEt_3)_2$] (**7c**). Complexes **2** are inactive in ATRP and ATRA, which is ascribed to the relatively high oxidation potential of Ni^{II}−Phebox complexes, which excludes the (reversible) formation of a d^7-Ni^{III} complex, a crucial condition for ATRP and ATRA. This was confirmed by cyclic voltammetry measurements with complexes **2a**, **2c**, and **3** using $(n\text{-Bu})_4NBr$ as electrolyte. Theoretical calculations showed that the energy (IP_1) needed for the oxidation reaction occurring during the CV experiments is considerably higher for [NiBr(Me,Me-Phebox)] (1.87 eV) and [NiBr(bis(ketimine)phenyl)] (1.90 eV) than for [Ni(NCN)Br] (1.45 eV).

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[28] Comparison of the calculated and experimental geometrical features of [NiBr(bis(ketimine)phenyl)] (**3**) (distances in Å, angles in deg) calcd (expt): Ni(1)−Br(1) 2.429 (2.3419(3)), Ni(1)−N(1) 1.985 (1.9394(19)), Ni(1)−N(2) 1.985 (1.9318(19)), C(1)−Ni(1) 1.838 (1.819(2)), C(1)−Ni(1)−N(1) 81.40 (81.26(9)), C(1)−Ni(1)−N(2) 81.40 (81.27(9)), C(1)−Ni(1)−Br 180.00 (174.63(7)), N(1)−Ni−N(2) 162.80 (162.06(8)), N(1)−Ni−Br 98.60 (98.75(6)), N(2)−Ni−Br 98.60 (99.03(6)).

[29] Comparison of the calculated and experimental geometrical features of [$NiBr_2$(NCN)] (**8**) (distances in Å, angles in deg) calc (expt): Ni(1)−Br(1) 2.516 (2.4373(6)), Ni(1)−Br(2) 2.526 (2.4272(6)), Ni(1)−N(12) 2.087 (2.041(2)), C(10)−Ni(1) 1.893 (1.894(3)), C(10)−Ni(1)−N(12) 82.79 (82.15(11)), C(10)−Ni(1)−N(2) 82.86 (81.50(11)), C(10)−Ni(1)−Br(1) 162.00 (166.19(9)), C(10)−Ni(1)−Br(2) 87.99 (90.85(9)), N(12)−Ni(1)−N(2) 157.50 (152.58(10)), N(12)−Ni(1)−Br(1) 94.16 (95.37(7)), N(12)−Ni(1)−Br(2) 98.35 (100.25(8)), Br(1)−Ni(1)−Br(2) 110.02 (102.96(2)).

[30] Grove, D. M.; van Koten, G.; Zoet, R. *J. Am. Chem. Soc.* **1983**, *105*, 1379.

[31] Defined by the atoms C(10), N(12), N(2), and Br(1).

[32] De Koster, A.; Kanters, J. A.; Spek, A. L.; van der Zeijden, A. A. H.; van Koten, G.; Vrieze, K. *Acta Crystallogr.* **1985**, *C41*, 893.

[33] On the basis of the theoretical calculations, the experimental oxidation wave for [NiBr(Me,Me-Phebox)] can be approximately expected at about IP_1([NiBr(Me,Me-Phebox)]) − IP_1([NiBr(NCN)]) = 0.42 V higher than E_{ox} for [NiBr(NCN)].

Experimental Section

Experiments were carried out under a dry, oxygen-free, nitrogen atmosphere, using standard Schlenk techniques. Solvents were dried and distilled from sodium (pentane, toluene), Na/benzophenone (diethyl ether, tetrahydrofuran), CaH_2 (CH_2Cl_2, CH_3CN), and KOH (Et_3N) prior to use. *n*-BuLi (1.6 M in hexanes) was ordered from Acros and used as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Inova 300 spectrometer; $^{31}P\{^1H\}$ NMR experiments, on a Varian Mercury 200 spectrometer. Benzene-d_6 was purchased from Cambridge Isotope Laboratories, distilled from sodium, and stored in a nitrogen-filled M-Braun glovebox. Other NMR solvents (acetone-d_6, $CDCl_3$) were used as received. ^1H and $^{13}C\{^1H\}$ chemical shifts (*δ*) are given in ppm relative to the solvent residual signal as an internal standard. $^{31}P\{^1H\}$ NMR chemical shifts are referenced externally to H_3PO_4. Electrochemical experiments were performed with an Autolab PGSTAT 10 cyclic voltammeter under an argon atmosphere. Acetone, used for cyclovoltammetry experiments, was distilled from $CaCl_2$ under an argon atmosphere prior to use. 2-Bromoisophthalic acid,[14] L-valinol, and L-*tert*-leucinol[34] were synthesized according to literature procedures. [R,R′-PheboxBr] was synthesized according to a combination of literature procedures.[15,16] All other chemicals were purchased from either Acros or Aldrich and used as received. Elemental analyses were performed by Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Theoretical calculations were performed at the (U)B3LYP/LANL2-DZ level,[35] using GAMESS-UK.[36]

Synthesis of [Me,Me-PheboxBr] (5a). Thionyl chloride (12 mL, 164 mmol) was added to 2-bromoisophthalic acid (9.8 g, 40.1 mmol). The mixture was refluxed overnight, and the residual $SOCl_2$ was removed *in vacuo*. Of the resulting 2-bromoisophthalic acid chloride, 6.9 g (24.5 mmol) was weighed in a 500 mL one-necked round-bottom flask, equipped with a nitrogen inlet, and dissolved in CH_2Cl_2 (25 mL). The temperature was cooled to 0 °C. In a separate Schlenk vessel, 2-amino-2-methylpropanol (5.07 g, 56.3 mmol) and triethylamine (14 mL, 100 mmol) were dissolved in CH_2Cl_2 (35 mL) and slowly added to the cooled 2-bromoisophthalic acid chloride solution. The reaction mixture was warmed to room temperature overnight, after which the solvent was removed *in vacuo*. Acetonitrile (200 mL), PPh_3 (23.7 g, 90.6 mmol), and triethylamine (15 mL, 108 mmol) were added to the residue. The temperature was reduced to 0 °C, after which CCl_4 (21 mL, 215 mmol) was slowly added via syringe. The reaction mixture was warmed to room temperature overnight, after which the mixture was quenched with H_2O (10 mL) and the volatiles were removed *in vacuo*. The residue was dissolved in H_2O (200 mL) and ethyl acetate (200 mL). After separation of the layers, the organic layer was washed with H_2O (100 mL). The combined aqueous layers were extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried on $MgSO_4$ and filtered. After the solvent was removed *in vacuo*, the residue was stirred for 3 h in diethyl ether (250 mL). The suspension was filtered, the residue was washed with diethyl ether (200 mL), and the filtrate was concentrated *in vacuo*. The crude product was filtered over alumina (neutral Merck 90) in diethyl ether (R_f 0.25), resulting in a white solid (6.95 g, 81%). IR (neat, cm^{-1}): ν_{max} 2966, 1663, 1643, 1423, 1351, 1192, 998, 952, 807, 736. ^1H NMR (300 MHz, acetone-d_6): *δ* 1.35 (s, 12H, C*Me*$_2$), 4.14 (s, 4H, C*H*$_2$), 7.52 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, Ar*H*), 7.67 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, Ar*H*). $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): *δ* 28.4 (C*Me*$_2$), 69.1 (*C*Me$_2$), 79.9 (O*C*H$_2$), 121.7 (Ar*C*), 128.1 (Ar*C*), 133.2 (Ar*C*), 133.7 (Ar*C*), 161.7 (O*C*N). Anal. Calcd for $C_{16}H_{19}BrN_2O_2$: C, 54.71; H, 5.45; N, 7.98. Found: C, 54.63; H, 5.38; N, 7.96.

Synthesis of [(*S*,*S*) *i*-Pr,H−PheboxBr] (5b).[4d] An analogous procedure to the synthesis of **5a** was employed with 2-bromoisophthalic acid (5.05 g, 21 mmol) and L-valinol (4.91 g, 48 mmol): light yellow oil (5.16 g, 67%), R_f value (diethyl ether) 0.28, $[\alpha]_D^{20}$ −63.2 (*c* 0.10 g/mL, CH_2Cl_2). IR (neat, cm^{-1}): ν_{max} 2958, 1660, 1362, 1123, 1069, 965, 728. ^1H NMR (300 MHz, $CDCl_3$): *δ* 0.98 (d, 6H, $^3J_{H-H}$ = 6.6 Hz, CH*Me*$_2$), 1.04 (d, 6H, $^3J_{H-H}$ = 6.6 Hz, CH*Me*$_2$), 1.91 (septet, 2H, $^3J_{H-H}$ = 6.6 Hz, C*H*Me$_2$), 4.18 (m, 4H, OC*H*$_2$), 4.45 (m, 2H, C*H*N), 7.37 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, Ar*H*), 7.65 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): *δ* 32.3 (C*Me*$_2$), 60.0 (*C*Me$_2$), 70.2 (*C*HN), 72.6 (O*C*H$_2$), 121.0 (Ar*C*), 126.6 (Ar*C*), 132.0 (Ar*C*), 132.2 (Ar*C*), 162.6 (O*C*N). Anal. Calcd for $C_{18}H_{23}BrN_2O_2$: C, 57.00; H, 6.11; N, 7.39. Found: C, 56.88; H, 6.07; N, 7.26.

Synthesis of [(*S*,*S*)-*t*-Bu,H-PheboxBr] (5c).[6a] An analogous procedure to the synthesis of **5a** was employed with 2-bromoisophthalic acid (4.08 g, 15 mmol) and L-*tert*-leucinol (3.52 g, 30 mmol): colorless oil (4.31 g, 73%), R_f value (1:1 diethyl ether/ethyl acetate) 0.71, $[\alpha]_D^{20}$ −60.2 (*c* 0.11 g/mL, EtOH). IR (neat, cm^{-1}): ν_{max} 2954, 1663, 1362, 970. ^1H NMR (300 MHz, $CDCl_3$): *δ* 0.96 (s, 18H, C*Me*$_3$), 4.06 (dd, 2H, $^3J_{H-H}$ = 10.1 Hz, $^2J_{H-H}$ = 8.3 Hz, OC*H*$_2$), 4.22 (t, 2H, $^3J_{H-H}$ = 8.7 Hz, C*H*N), 4.37 (dd, 2H, $^3J_{H-H}$ = 10.1 Hz, $^2J_{H-H}$ = 8.9 Hz, OC*H*$_2$), 7.33 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, Ar*H*), 7.60 (d, 2H, $^3J_{H-H}$ = 7.2 Hz, Ar*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): *δ* 26.1 (C*Me*$_3$), 34.0 (*C*Me$_3$), 69.2 (*C*HN), 76.7 (O*C*H$_2$), 121.4 (Ar*C*), 127.0 (Ar*C*), 132.4 (Ar*C*), 132.6 (Ar*C*), 163.0 (*C*N). Anal. Calcd for $C_{20}H_{27}BrN_2O_2$: C, 58.97; H, 6.68; N, 6.88. Found: C, 59.10; H, 6.74; N, 6.76.

Synthesis of 2,6-Bis[*N*-(2′,6′-dimethylphenyl)ketimino]phenyl Bromide (6). 2,6-Diacetylphenyl bromide (3.6 g, 15 mmol), 2,6-dimethylaniline (4.5 mL, 36 mmol), and $Si(OEt)_4$ (8 mL, 36 mmol) were combined in a Schlenk vessel equipped with a still head and treated with 20 drops of H_2SO_4 (95%). The solution was heated at 160 °C for 24 h. The distillate (EtOH) was discarded. 2,6-Dimethylaniline (1.2 mL, 5.4 mmol) and 10 drops of H_2SO_4 (95%) were added, and the mixture was heated for another 24 h at 160 °C. Ethanol (80 mL) and KOH_{aq} (10 mL, 2 M solution in H_2O) were added to the reaction mixture at room temperature and stirred for 4 h. The resulting suspension was concentrated *in vacuo*, diethyl ether was added, and the slurry was filtered. The filtrate was washed with brine and with water, dried on $MgSO_4$, and filtered. The filtrate was dried *in vacuo*. The residue was submitted to a Kugelrohr distillation at 160 °C for 30 min. The residue was purified by column chromatography (silica, hexane/EtOAc, 4:1, R_f 0.33): white solid (5.9 g, 78%). IR (neat, cm^{-1}): ν_{max} 1664, 1646, 1467, 1199, 793, 758. ^1H NMR (300 MHz, C_6D_6): *δ* 1.84 (s, 6H, NC*Me*), 2.28 (s, 12H, Ar*Me*), 7.08−7.11 (m, 3H, Ar*H*), 7.13 (d, 4H, $^3J_{H,H}$ = 15.3 Hz, Ar*H*), 7.40 (d, 2H, 7.5 Hz, Ar*H*). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): *δ* 18.5 (Ar*Me*), 21.4 (NC*Me*), 117.9 (Ar*C*), 123.6 (Ar*C*), 125.7 (Ar*C*), 128.6 (Ar*C*), 129.4 (Ar*C*), 145.0 (Ar*C*), 148.7 (Ar*C*), 169.2 (N*C*Me). Anal. Calcd for $C_{26}H_{27}BrN_2$: C, 69.80; H, 6.08; N, 6.26. Found: C,69.74; H, 6.07; N, 6.24.

Synthesis of [NiBr(Me,Me-Phebox)] (2a) via Route A. *n*-BuLi (1.2 mL, 1.92 mmol, 1.6 M solution in hexanes) was added to a solution of **5a** (0.60 g, 1.71 mmol) in toluene (30 mL) at −78 °C. After stirring for 3.5 h, the deep purple solution was added cold to a solution of $[NiBr_2(PEt_3)_2]$ (0.73 g, 1.61 mmol) in toluene (30 mL). After stirring for 16 h, the dark brown reaction mixture

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(35) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact David Feller or Karen Schuchardt for further information. Dunning, T. H., Jr.; Hay, P. J. *Methods of Electronic Structure Theory*, 2nd ed.; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

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containing a light precipitate was centrifugated and the supernatant was separated. The precipitate was extracted with toluene (20 mL). The toluene layers were dried *in vacuo* and washed with hexanes (2 × 20 mL), which yielded a bright orange solid (0.49 g, 74%). IR (neat, cm^{-1}): ν_{max} 2964, 1644, 1645, 1490, 1405, 1131, 981, 796, 783. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 1.49 (s, 12H, C*Me*$_2$), 3.59 (s, 4H, OC*H*$_2$), 6.69 (t, 1H, $^3J_{H-H} = 7.5$ Hz, Ar*H*), 6.98 (d, 2H, $^3J_{H-H} = 7.2$ Hz, Ar*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ 28.2 (C*Me*$_2$), 65.6 (*C*Me$_2$), 84.4 (O*C*H$_2$), 124.0 (Ar*C*), 124.5 (Ar*C*), 130.5 (Ar*C*), 168.7 (Ar*C*), 172.0 (O*C*N). Anal. Calcd for $C_{16}H_{19}BrN_2NiO_2$: C, 46.88; H, 4.67; N, 6.83. Found: C, 47.03; H, 4.73; N, 6.75.

Synthesis of (*S*,*S*)-[NiBr(*i*-Pr,H-Phebox)] (2b) via Route A. An analogous procedure to the synthesis of **2a** was employed with **5b** (0.60 g, 1.58 mmol), *n*-BuLi (1.1 mL, 1.76 mmol, 1.6 M in hexane), and [NiBr$_2$(PEt$_3$)$_2$] (0.68 g, 1.45 mmol): orange powder (0.58 g, 91%). IR (neat, cm^{-1}): ν_{max} 2960, 1607, 1586, 1489, 1404, 1387, 1146, 953, 726. ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ 0.54 (d, 6H, $^3J_{H-H} = 7.0$ Hz, CH*Me*$_2$), 0.65 (d, 6H, $^3J_{H-H} = 7.0$ Hz, CH*Me*$_2$), 3.23 (sp d, 2H, $^3J_{H-H} = 7.2$ Hz, 2.8 Hz, *C*HMe$_2$), 3.63 (m, 2H, NC*H*), 3.95 (m, 4H, OC*H*$_2$), 6.63 (t, 1H, $^3J_{H-H} = 7.0$ Hz, Ar*H*), 6.98 (d, 2H, $^3J_{H-H} = 7.4$ Hz, Ar*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ 13.8 (C*Me*$_2$), 18.6 (C*Me*$_2$), 29.5 (*C*Me$_2$), 66.1 (N*C*H), 72.4 (O*C*H$_2$), 124.0 (Ar*C*), 124.4 (Ar*C*), 129.9 (Ar*C*), 173.1 (Ar*C*), 173.3 (O*C*N).

Synthesis of (*S*,*S*)-[NiBr(*t*-Bu,H-Phebox)(PEt$_3$)$_2$] (7c) via Route A. *n*-BuLi (1.3 mL, 2.08 mmol, 1.6 M solution in hexanes) was added to a solution of **5c** (0.74 g, 1.82 mmol) in THF (25 mL) at −78 °C. After stirring for 10 min, the deep red solution was added dropwise to a solution of [NiBr$_2$(PEt$_3$)$_2$] (0.83 g, 1.82 mmol) in diethyl ether (30 mL) at −78 °C. The reaction mixture was warmed to room temperature. After stirring for 16 h, the dark brown reaction mixture was dried *in vacuo* and dissolved in toluene (50 mL). After centrifugation, the supernatant was separated. The precipitate was extracted with toluene (20 mL). The mixture was dried *in vacuo* and centrifugated after addition of pentane (50 mL). The supernatant was separated and dried *in vacuo*, which afforded a brown oil (0.99 g, 77%). A small quantity was further purified by crystallization from pentane at −20 °C, which yielded the product as a dark red powder. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.91 (m, 18H, P(CH$_2$C*H*$_3$)$_3$), 1.01 (s, 18H, C*Me*$_3$), 1.55 (m, 12H, P(C*H*$_2$CH$_3$)$_3$), 4.17 (m, 4H, OC*H*$_2$), 4.45 (t, 2H, $^3J_{H-H} = 9.2$ Hz, C*H*N), 6.77 (t, 1H, $^3J_{H-H} = 7.7$ Hz, Ar*H*), 8.18 (d, 2H, $^3J_{H-H} = 7.5$ Hz, Ar*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ 8.4 (P(CH$_2$*C*H$_3$)$_3$), 16.1 (t, $^1J_{C-P} = 11.3$ Hz, P(*C*H$_2$CH$_3$)$_3$), 26.4 (C*Me*$_3$), 34.2 (*C*Me$_3$), 68.9 (*C*HN), 76.4 (O*C*H$_2$), 122.0 (Ar*C*), 132.1 (Ar*C*), 137.0 (Ar*C*), 162.8 (Ar*C*), 166.8 (*C*N). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 81 MHz): δ 1.4. Anal. Calcd for $C_{32}H_{57}BrN_2NiO_2P_2$: C, 54.72; H, 8.18; N, 3.99. Found: C, 54.63; H, 8.07; N, 4.06.

Synthesis of [NiBr(Me,Me-Phebox)] (2a) via Route B. To a stirred suspension of Ni(cod)$_2$ (258 mg, 0.94 mmol) in THF (30 mL) at −78 °C was added [Me,Me-PheboxBr] (**5a**) (363 mg, 1.0 mmol) in THF (10 mL). The mixture was warmed to room temperature overnight. The mixture was centrifuged and separated. The supernatant was dried *in vacuo* and washed with pentane. The solid orange residue was characterized by ^{1}H NMR spectroscopy as pure **2a** (318 mg, 83%). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 1.49 (s, 12H, C*Me*$_2$), 3.59 (s, 4H, OC*H*$_2$), 6.69 (t, 1H, $^3J_{H-H} = 7.5$ Hz, Ar*H*), 6.98 (d, 2H, $^3J_{H-H} = 7.2$ Hz, Ar*H*).

Synthesis of (*S*,*S*)-[NiBr(*i*-Pr,H-Phebox)] (2b) via Route B. An analogous procedure to the synthesis of **2a** was employed with **5b** (623 mg, 1.64 mmol) and [Ni(cod)$_2$] (432 mg, 1.57 mmol): yellow-orange powder (697 mg, quant.). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.54 (d, 6H, $^3J_{H-H} = 7.2$ Hz, CH*Me*$_2$), 0.65 (d, 6H, $^3J_{H-H} = 7.2$ Hz, CH*Me*$_2$), 3.22 (septet d, 2H, $^3J_{H-H} = 7.0$ Hz, 2.7 Hz, C*H*Me$_2$), 3.64 (m, 2H, C*H*N), 3.95 (m, 4H, OC*H*$_2$), 6.63 (t, 1H, $^3J_{H-H} = 7.0$ Hz, Ar*H*), 6.98 (d, 2H, $^3J_{H-H} = 7.2$ Hz, Ar*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ 13.8 (CH*Me*$_2$), 18.6 (CH*Me*$_2$), 29.5 (*C*HMe$_2$), 66.1 (*C*HN), 72.4 (O*C*H$_2$), 124.0 (Ar*C*), 124.4 (Ar*C*), 129.9 (Ar*C*), 173.1 (Ar*C*), 173.3 (O*C*N). Anal. Calcd for $C_{18}H_{23}BrN_2NiO_2$: C, 49.36; H, 5.29; N, 6.40. Found: C, 49.38; H, 5.36; N, 6.33.

Synthesis of (*S*,*S*)-[NiBr(*t*-Bu,H-Phebox)] (2c) via Route B. An analogous procedure to the synthesis of **2a** was employed with **5c** (250 mg, 0.61 mmol) and [Ni(cod)$_2$] (160 mg, 0.58 mmol): yellow-orange powder (0.162 g, 60%). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.93 (s, 18H, C*Me*$_3$), 3.58 (t, 2H, $^3J_{H-H} = 7.8$ Hz, C*H*N), 3.83 (d, 2H, $^3J_{H-H} = 7.5$ Hz, OC*H*$_2$), 4.04 (d, 2H, $^3J_{H-H} = 7.5$ Hz, OC*H*$_2$), 6.63 (t, 1H, $^3J_{H-H} = 7.1$ Hz, Ar*H*), 6.96 (d, 2H, $^3J_{H-H} = 6.6$ Hz, Ar*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 75 MHz): δ 26.9 (C*Me*$_3$), 35.6 (*C*Me$_3$), 68.5 (*C*HN), 75.1 (O*C*H$_2$), 124.1 (Ar*C*), 124.2 (Ar*C*), 130.1 (Ar*C*), 170.6 (Ar*C*), 173.9 (O*C*N). Anal. Calcd for $C_{20}H_{27}BrN_2NiO_2$: C, 51.54; H, 5.84; N, 6.01. Found: C, 51.28; H, 5.97; N, 5.84.

Synthesis of 2,6-Bis[*N*-2′,6′-dimethylphenyl)ketimino]phenylnickel(II) Bromide (3) via Route B. A solution of **6** (171 mg, 0.38 mmol) in THF (10 mL) was added to a solution of [Ni(cod)$_2$] in THF (15 mL) at −60 °C. The reaction mixture was stirred for 3 days (at room temperature), after which it was centrifuged, the supernatant removed, and the residue extracted with THF (25 mL). The THF was removed *in vacuo*. The residue was washed with pentane (2 × 7 mL), yielding a bright orange solid, which was characterized as pure **3** (128 mg, 72%). IR (neat, cm^{-1}): ν_{max} 2965, 1576, 1534, 1465, 1333, 1261, 1092, 1017, 786, 766. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 1.32 (s, 6H, NC*Me*), 2.27 (s, 12H, Ar*Me*), 6.82 (m, 3H, Ar*H*), 6.92 (m, 6H, Ar*H*). ^{13}C{^{1}H} NMR (75 MHz, C$_6$D$_6$): δ 15.9 (NC*Me*), 19.33 (Ar*Me*), 123.0 (Ar*C*), 125.7 (Ar*C*), 126.5 (Ar*C*), 128.2 (Ar*C*), 128.4 (Ar*C*), 130.5 (Ar*C*), 145.5 (Ar*C*), 147.3 (Ar*C*), 180.3 (Ar*C*), 185.3 (N*C*Me). Anal. Calcd for $C_{26}H_{27}BrN_2Ni$: C, 61.70; H, 5.38; N, 5.54. Found: C, 61.61; H, 5.33; N, 5.42.

Typical Polymerization Experiment. Ethyl-2-bromoisobutyrate (11.5 μL, 0.078 mmol) was added to a mixture of **2a** (32 mg, 0.077 mmol) and degassed MMA (2.0 mL, 19 mmol) in toluene (7.5 mL) at 90 °C. The mixture was stirred for 16 h and then analyzed by ^{1}H NMR spectroscopy. No color change was observed (orange). Polymerization: 0%.

Kharasch Addition. CCl$_4$ (10 mL, 104 mmol) was added to a mixture of **2a** (32 mg, 0.077 mmol) and degassed methyl methacrylate (3.0 mL, 28 mmol) in CH$_2$Cl$_2$ (10 mL) at room temperature. The mixture was stirred for 16 h and then analyzed by ^{1}H NMR spectroscopy. No change of color was observed (orange). Conversion: 0%.

Cyclic Voltammetry. Cyclic voltammetry measurements were performed with an Autolab PGSTAT 10 cyclic voltammeter, using a Pt working electrode and a Ag/AgCl reference electrode in acetone with tetrabutylammonium bromide (0.1 M) as supporting electrolyte, at scan rates ranging from 0.025 to 1 V/s. Under these conditions the ferrocene/ferrocenium (Fc/Fc$^+$) couple was located at +0.44 V with a peak separation of 80 mV.

X-ray Crystal Structure Determination of (*S*,*S*)-[NiBr(*i*-Pr,H-Phebox)] (2b). $C_{18}H_{23}BrN_2NiO_2$, fw = 438.00, yellow plate, 0.18 × 0.12 × 0.03 mm^3, monoclinic, $P2_1$ (no. 4), $a = 6.2846(7)$ Å, $b = 12.0673(5)$ Å, $c = 12.0639(13)$ Å, $\beta = 100.695(8)°$, $V = 899.01(14)$ Å^3, $Z = 2$, $\rho = 1.618$ g/cm^3; 36 365 reflections up to a resolution of $(\sin \theta/\lambda)_{max} = 0.51$ Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator ($\lambda = 0.71073$ Å) at a temperature of 150(2) K. The crystal appeared to be nonmerohedrally twinned with a 2-fold rotation about *hkl* (10$\bar{2}$) as twin operation. This direction is approximately parallel to the Ni−Br bond. The intensity data were evaluated with EvalCCD,[37] taking the twin relation into account.

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An analytical absorption correction was applied ($\mu = 3.314$ mm^{-1}, 0.55−0.89 correction range), and the reflections were merged according to the twin law, resulting in 7979 unique reflections ($R_{\mathrm{int}} = 0.0637$). The structure was solved with automated Patterson methods (DIRDIFF-99[38]) based on the nonoverlapping reflections of the first twin domain. The structure was then refined as a HKLF-5[39] twin with SHELXL-97[40] on F^2 of all reflections, resulting in a twin fraction of 0.5141(4); 222 parameters were refined with one restraint for the origin shift in the polar space group. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0328/0.0611. R_1/wR_2 [all reflns]: 0.0492/0.0656. $S = 1.022$. Flack x parameter:[41] −0.008(6). Residual electron density was between −0.36 and 0.64 e/Å^3. Structure calculations, drawings, and checking for higher symmetry were performed with the PLATON[42] package.

X-ray Crystal Structure Determination of [NiBr(bis(ketimine)phenyl)] (3). $C_{26}H_{27}BrN_2Ni$, fw = 506.12, red needle, 0.42 × 0.09 × 0.09 mm^3, monoclinic, $P2_1/c$ (no. 14), $a = 11.7638(1)$ Å, $b = 10.9956(1)$ Å, $c = 18.2973(1)$ Å, $\beta = 101.7010(3)°$, $V = 2317.57(3)$ Å^3, $Z = 4$, $\rho = 1.451$ g/cm^3; 55626 reflections up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65$ Å^{-1} were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator ($\lambda = 0.71073$ Å) at a temperature of 150(2) K. An absorption correction based on multiple measured reflections was applied ($\mu = 2.576$ mm^{-1}, 0.58−0.79 correction range); 5318 reflections were unique ($R_{\mathrm{int}} = 0.0468$). The structure was solved with automated Patterson methods (DIRDIF-99[38]) and refined with SHELXL-97[40] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map and refined as rigid groups; 277 parameters were refined without restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0321/0.0736. R_1/wR_2 [all reflns]: 0.0461/0.0793. $S = 1.036$. Residual electron density was between −0.91 and 0.80 e/Å^3. Structure calculations, drawings, and checking for higher symmetry were performed with the PLATON[42] package.

X-ray Crystal Structure Determination of [NiBr$_2$(NCN)] (8). $C_{12}H_{19}Br_2N_2Ni$, fw = 409.82, monoclinic, space group $P2_1/c$, $a = 13.7870(16)$ Å, $b = 7.6995(9)$ Å, $c = 14.7377(17)$ Å, $\beta = 110.337(3)°$, $V = 1466.9(3)$ Å^3 (by least-squares refinement on 6099 reflection positions), $T = 220(2)$ K, $\lambda = 0.71073$ Å, $Z = 4$, D(calcd) = 1.856 Mg/m^3, $F(000) = 812$, μ(Mo Kα) = 6.751 mm^{-1}. Crystal character: dark block. Crystal dimensions: 0.50 × 0.28 × 0.12 mm. Data collection and processing: Siemens SMART[43] three-circle system with CCD area detector. The crystal was held at 220(2) K with the Oxford Cryosystem cryostream cooler.[44] Maximum theta was 28.88°. The *hkl* ranges were −18/12, −10/10, −16/19; 8704 reflections measured, 3539 unique [$R_{\mathrm{int}} = 0.0325$]. Semiempirical absorption correction from equivalents; maximum and minimum correction factors: 0.54; 0.89. No crystal decay. Structure analysis and refinement: Systematic absences indicated $P2_1/c$ and were shown to be correct by successful refinement. The structure was solved by direct methods using SHELXS-97[45] (TREF) with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0339P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on F^2 was 0.927, R_1[for 2681 reflections with $I > 2\sigma(I)$] = 0.0322, $wR_2 = 0.0711$. Data/restraints/parameters: 3539/0/159. Extinction coefficient: 0.0004(2). Largest difference Fourier peak and hole: 0.65 and −0.50 e/Å^3. Refinement used SHELXTL.[46]

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