

Merocyanine-Like Chromophores as Ligands for Catalytic Active Metals of Group VIII

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Keywords: N ligands / Chromophores / Palladium / Nickel / Electrochemistry

Nickel and palladium complexes that contain merocyanine-like 4*H*-imidazoles as ligands have been synthesized in good yields. The complexes were characterized by elemental analyses, mass spectrometry, ¹H NMR, ¹³C NMR spectroscopy and in the solid state by single crystal diffraction analyses. The new palladium complexes of type **4** can be regarded as new functional dyes as well as deeply coloured and redox active metallacycles that display catalytic activity.

In contrast to parent compounds **2**, the palladacycles of type **4** show two well-separated reductions that are fully reversible. The values of semiquinone formation constants of derivatives **4** (between 10¹¹ and 10¹²) are only somewhat lower than those reported for similar boracycles.

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Introduction

Nitrogen-containing ligands based on oxalic amidines **1** have recently attracted increasing interest.^[1–3] These bifunctional amidines can act as diamide or diamidinate ligands after deprotonation and the ligands can be easily modified in their electronic and steric effects by variation of the substituents on the nitrogen atoms. Moreover, they can adopt several possible coordination modes in their metal complexes. During the last decade we focussed our interests on the development of new cyclic versions of oxalic amidines. Thus, amidines without hydrogen in the α -position, such as benzamidines, can easily be cyclized with bis(imidoyl chlorides) derived from oxalic acid in order to yield 4*H*-imidazoles **2** (Figure 1).^[4] A new class of chromophores/fluorophores was developed employing these diazafulvene imines.^[5,6] In addition, the 4*H*-imidazoles **2** are reversible two-electron redox systems which have been optimized to powerful electron-accepting derivatives in the form of boratetraazapentalenes.^[7] Their radical anions are characterized by an unusual thermodynamic stability as can be seen from semiquinone formation constants K_{SEM} in the magnitude of 10¹⁵.

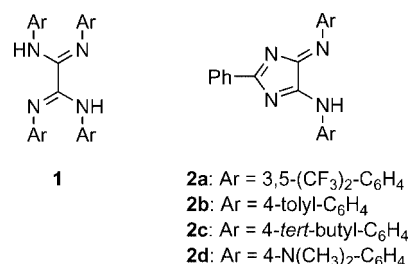


Figure 1. Oxalic amidines **1** and their cyclic versions 4*H*-imidazoles **2**.

The 4*H*-imidazoles **2** can therefore be regarded as multifunctional molecules in which the properties can easily be tuned by variation of the aryl substituents. Compared with derivatives of type **1**, they possess the same substructure which may serve as a donor site for metal complexation.

Because of the fact that open-chained oxalic amidines **1** have been successfully applied as ligands for cross-coupling methods,^[8] their cyclic versions “cycloamidines” 4*H*-imidazoles **2**, should also be promising candidates. Zinc complexes of 4*H*-imidazoles have previously been reported.^[9] Attempts to deprotonate derivatives **2** by lithium hydride^[10] yielded unusual lithium complexes that surprisingly contain one molecule of water in their first complexation sphere.

Apart from porphyrins, phthalocyanines and related systems metal complexes in which the ligand is identical with an efficient chromophore are quite rare. Our aim was therefore to combine the redox active chromophore of 4*H*-imidazoles **2** with the catalytic activity of selected d-metals.

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Results and Discussion

Synthesis and Characterization

First we attempted to synthesize Ni^{II} complexes starting from nickel^{II}-(acac)₂. This diketonato complex even reacts at room temperature with **2a**, the red solution changing to a deep purple. In order to complete the reaction, the mixture has to be heated under reflux for approx. 4 h (monitoring by TLC). It is remarkable that the complex formation takes place without addition of bases; most likely the acetylacetonato moiety functioned as a base for the deprotonation of the NH function. The X-ray structural analysis obtained from a single crystal of complex **3a** revealed a molecular structure as illustrated in Figure 2.

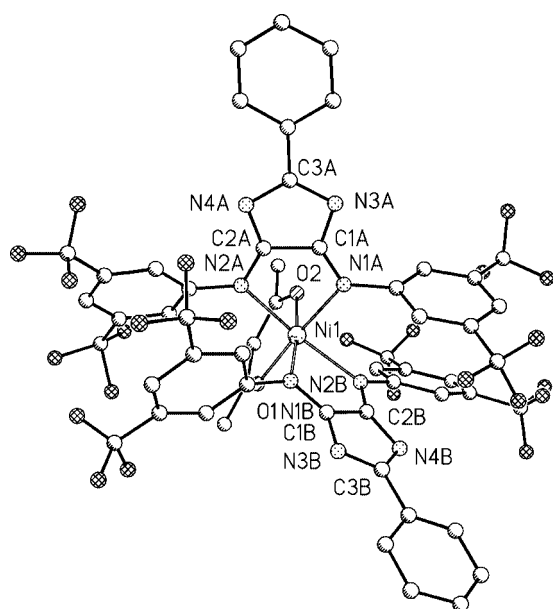
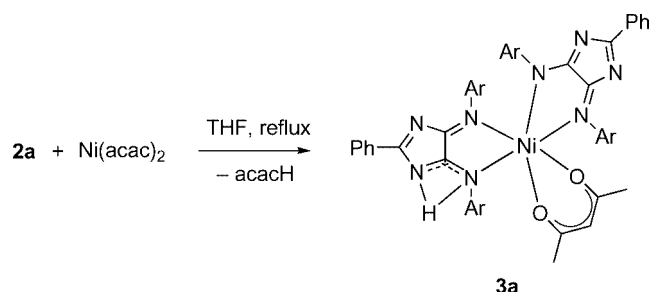


Figure 2. Molecular structure of complex **3a** (H atoms have been omitted for clarity). Selected bond lengths [Å]: Ni1–N1A 2.100(4), Ni1–N2A 2.197(4), Ni1–N1B 2.072(4), Ni1–N2B 2.201(4), Ni1–O1 2.009(3), Ni1–O2 2.042(3).

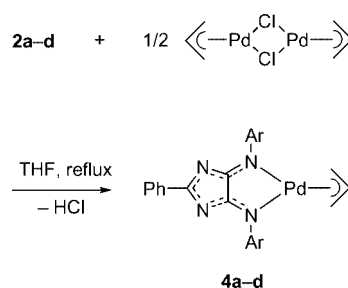
In the new chelate complex **3a** (Scheme 1) two 4*H*-imidazoles coordinate the nickel^{II} centre, whereby the two remaining coordination sites are occupied by an acetylacetonato ligand. While one 4*H*-imidazole is coordinated in the deprotonated form, the other is bound as a neutral ligand. This fact could be verified by determining the Ni–N distances of the coordinating nitrogen atoms. This molecule is in agreement with the stoichiometry of the reaction. The octahedral nickel centre in **3a** exhibits paramagnetism and therefore, no NMR-data could be obtained. Characterization of complex **3a** via mass spectroscopy confirmed the results of the X-ray analysis. A high-resolution mass spectrum verified the chemical composition of compound **3a** (C₅₅H₃₀F₂₄N₈NiO₂). In addition, the complex **3a** shows a characteristic fragmentation due to the split-up of the ligands.



Scheme 1. Synthesis of complex **3a**.

Because of the fact that palladium plays a vital role as a catalytically active metal in cross-coupling methods, further investigations were directed towards the synthesis of analogous Pd complexes. As a starting metal complex, the easily accessible allyl palladium(II) chloride dimer was applied. Because of its tendency to dissociate in solution into two coordinative unsaturated fragments, it enables easy complexation of other ligands at the palladium(II) centre. Furthermore, the allyl palladium-fragment preferably forms complexes with an almost square-planar geometry showing diamagnetism that allows a detailed structural elucidation by NMR spectroscopy.

Even at room temperature the complex formation is visible by a colour change from red to purple. After heating under reflux conditions, for 2–4 h, chromatographic purification allowed the isolation of new complexes of type **4**. Elemental analysis, NMR spectroscopic data and MS data confirmed the composition of a 1:1 complex in **4a**. According to Scheme 2, the dimeric palladium species reacted with one molecule of the ligands **2a–d** to yield palladacycles **4a–d**. A high symmetry of the molecule was indicated by the ¹H NMR spectrum of **4a**, which showed only five signals for the aromatic H-atoms in addition to the characteristic coupling pattern of the allyl substructure. Moreover, the ¹³C-NMR spectra confirm the symmetry of the molecule by a single set of signals. The signal for C-atom C4 is, compared to the ligand (δ = 190 ppm), shifted to a lower field in complex **4a** (δ = 199 ppm). This down-field shift is comparable to that in the corresponding boratetraazapentalenes,^[7] thus indicating the change from the merocyanine to the cyanine chromophore.



Scheme 2. Synthesis of complexes **4a–d**.

A single-crystal X-ray structure analysis of **4a** allowed an unambiguous assignment of these compounds, as shown in Figure 3. According to our presumptions, one 4*H*-imidazole is coordinated at the palladium(II) centre. Being a second ligand, the allyl-anion is η^3 -bonded and causes square-planar coordination geometry in view to the palladium(II) centre and shows C_2 symmetry. In analogy to the synthesis of the bis(3,5-trifluoromethyl) derivative **4a**, complexes of 4*H*-imidazoles could be prepared that possess electron-donating substituents. The various aryl substituents have no significant influence on the complexation ability of the corresponding 4*H*-imidazole. Interestingly, all new synthesized Pd complexes of type **4** show high stabilities as solids as well as in solution. They can be handled under normal atmospheric conditions and tolerate slightly acidic and basic conditions. In comparison with the 4*H*-imidazoles the UV/Vis maxima of the palladium complexes are shifted to higher wavelengths (**2a**: $\lambda_{\text{max}} = 460, 515 \text{ nm}$; **4a**: $\lambda_{\text{max}} = 549, 590 \text{ nm}$) as shown in Figure 4. Furthermore, complex **4a** shows a weak fluorescence at 623 nm (THF).

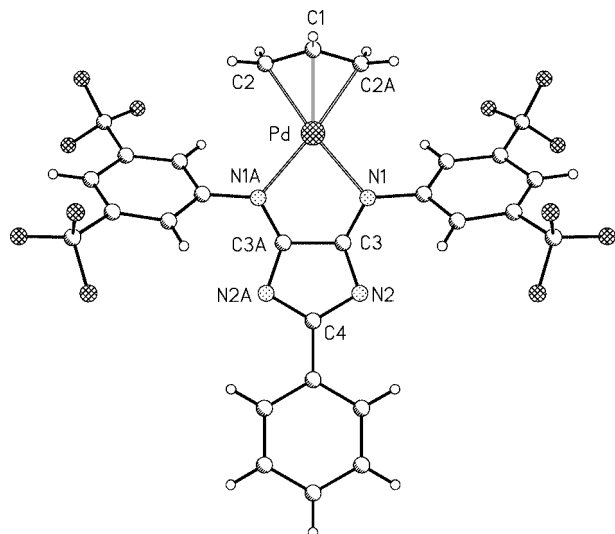


Figure 3. Molecular structure of complex **4a**. Selected bond lengths [Å]: Pd–N1 2.128(4), Pd–N1A 2.128(4), Pd–C2 2.120(5), Pd–C2A 2.120(5), Pd–C1 2.109(9).

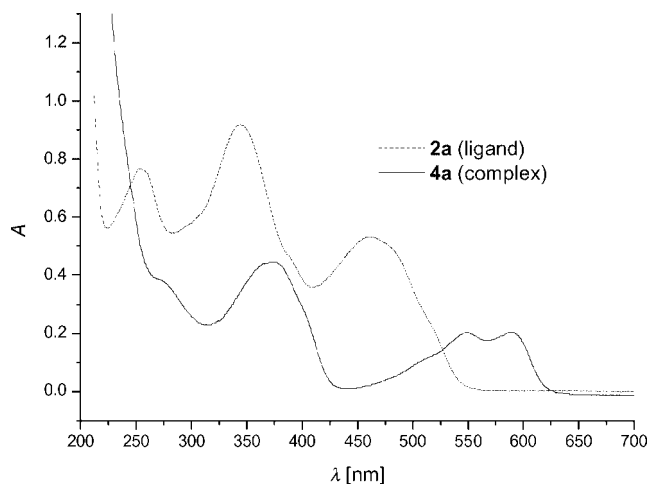


Figure 4. UV/Vis spectra of **2a** (···) and **4a** (—) in THF.

Electrochemical Measurements of Complexes **4**

The electrochemical reduction of the palladacycles **4** occurs in two one-electron steps. A typical series of cyclic square-wave voltammograms measured with square-wave frequencies from 25 to 800 Hz is shown in Figure 5. The half-wave potentials extracted from these measurements are summarized in Table 1.

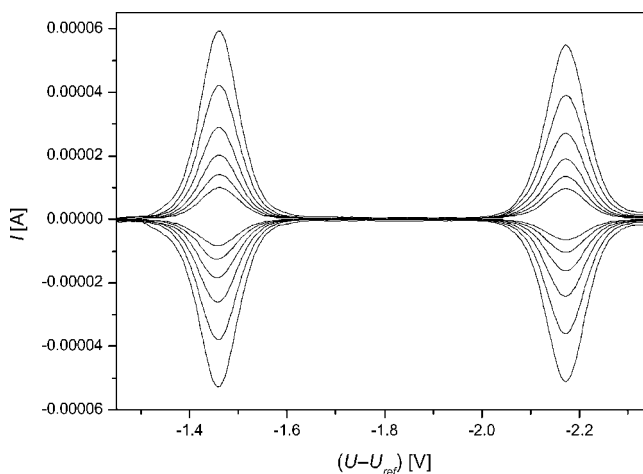


Figure 5. Cyclic square-wave voltammograms of the reduction of 1.5 mM of **4b** in DMF/tetrabutylammonium hexafluorophosphate at a mercury drop electrode using square-wave frequencies of 800, 400, 200, 100, 50 and 25 Hz. U_{ref} is the potential of the ferrocenium/ferrocene couple in the same electrolyte.

Table 1. Half-wave potentials and semiquinone formation constants of complexes **4a–c**.

Complex	$U_1^{1/2}$	$U_2^{1/2}$	K_{sem}
4b	–1.460 V	–2.175 V	$1.26 \cdot 10^{12}$
4a	–1.015 V	–1.670 V	$1.26 \cdot 10^{11}$
4c	–1.455 V	–2.175 V	$1.58 \cdot 10^{12}$

If only the first reduction process is measured (by reversing the potential scan before the second reduction takes place), the experimental curves agree very well with those simulated for a fast (fully reversible) charge-transfer process followed by a slow first-order decomposition reaction. This means, as far as the charge transfer steps are concerned, a deviation from Nernstian behaviour cannot be detected up to square-wave frequencies of approx. 1000 Hz. However, the one-fold reduced species is chemically not fully stable in the solvent system. A second, (much faster) follow-up reaction is induced upon scanning over a potential range including the second reduction step. Interestingly, this follow-up reaction has a much larger effect on the re-oxidation wave associated with the second charge transfer reaction. The ratio between cathodic and anodic peak current remains close to 1 for the first charge transfer step even when using relatively low square-wave frequencies such as shown in Figure 6 ($f = 25 \text{ Hz}$). In the case of **4b** an almost perfect agreement between experimental and simulated curves was obtained on the basis of the reaction shown in Scheme 3.

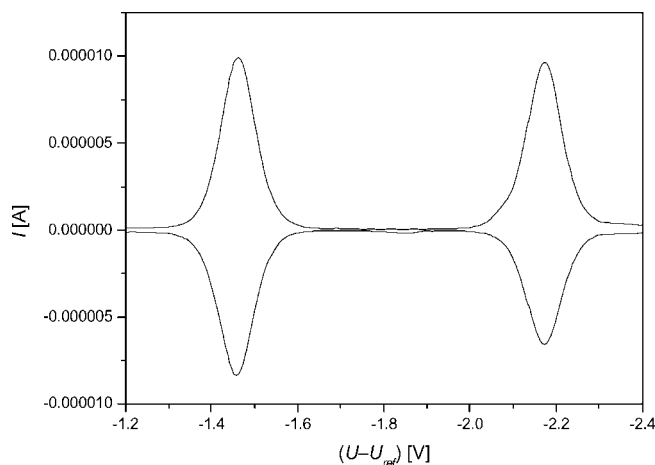
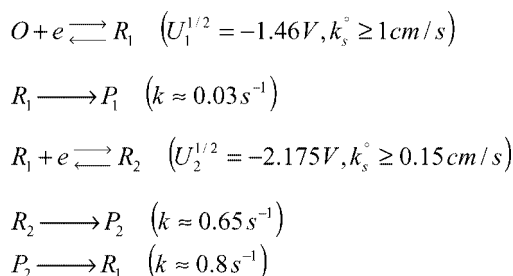


Figure 6. Cyclic square-wave voltammogram of the reduction of 1.5 mM of **4b** in DMF/tetrabutylammonium hexafluorophosphate at a mercury drop electrode using a square-wave frequency of 25 Hz. U_{ref} is the potential of the ferrocenium/ferrocene couple in the same electrolyte.



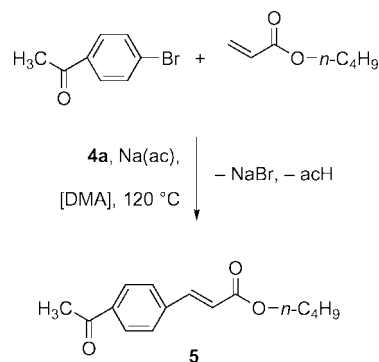
Scheme 3. Reaction scheme for an almost perfect agreement between experimental and simulated curves.

We assume that the twofold reduced species reacts to give an intermediate from which the onefold reduced species is formed in a subsequent reaction; the data determined for **4c** are virtually identical. In the case of **4a**, the first reduction process is accompanied by a pre-wave. Since the latter could not be reproduced by digital simulation, only the half-wave potentials are reported in Table 1.

The lack of success of the Sonogashira and Suzuki reactions with these cross-conjugated heterocycles can now be explained due to the fact that the 4*H*-imidazoles act as very efficient chelating ligands for palladium. This means that required catalytic amounts of palladium were immobilized immediately by complexation and consequently no catalytic activity was observed. However, the palladacycles themselves are able to catalyze other types of cross-coupling reactions as shown by the Heck reaction.

In an initial experiment we used the substrates 4-bromoacetophenone and acrylic acid *n*-butylester in dimethylacetamide as the solvent at 120 °C, yielding the 4-substituted cinnamic acidester **5** (Scheme 4) to evaluate the catalytic activity of palladium complex **4a**. This complex belongs to the very rare group of Pd-catalysts with *N,N*-chelate ligands that are active in this C–C-coupling method. After 2 h of

heating under reflux, 60% of the substrate was converted into cinnamic derivative **5**. Prolonged reaction times led to a nearly quantitative conversion.



Scheme 4. The Heck coupling as a model reaction for the determination of the catalytic activity of **4a**.

On the basis of these experimental findings the subject of further research will be the synthesis of homo- and heterobimetallic complexes of 4*H*-imidazoles and studies directed to the electronic communication between both metal centres. Applications of molecular architectures similar to those described above could prove to be light-driven reactions and catalyses.

Experimental Section

General Comments: All reactions were monitored by TLC, carried out on 0.25-mm Merck TLC aluminium sheets (aluminium oxide 150 F₂₅₄ neutral) using UV light. ¹H and ¹³C NMR spectra were recorded with a Bruker DRX 400 (400 MHz) or a Bruker AC 250 (250 MHz) spectrometer. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 19 spectrophotometer. MS spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer. Elemental analyses were carried out in-house with an automatic analyzer LECO CHNS 932.

Synthesis of the Nickel(II) Complex 3a: In a 100-mL one-necked round flask, equipped with a magnetic stirrer, **2a** (1 mmol) was dissolved in THF (50 mL). Then, bis(acetylacetonato)nickel(II) (1 mmol) dissolved in THF (10 mL) was added dropwise at room temperature. A darkening of the reaction mixture indicated a fast complexation reaction. The reaction mixture was heated to completion under reflux for 3–5 h. HRMS of **3a**: C₅₅H₃₁F₂₄N₈NiO₂; $M = 1349.15401113 \text{ g mol}^{-1}$ (calculated), $M = 1349.15494000 \text{ g mol}^{-1}$ (found).

Synthesis of the Palladium(II) Complexes 4a–d: In a 100-mL one-necked round flask, equipped with a magnetic stirrer, 1 mmol of the corresponding 4*H*-imidazole **2a** was dissolved in THF (50 mL). Then, allylpalladium(II) chloride dimer (0.5 mmol) dissolved in THF (10 mL) was added dropwise at room temperature. The reaction mixture was heated to completion under reflux for 3–5 h and the progress of the reaction was monitored by TLC. For complex **4a**, the solvent was removed in vacuo and the residue was suspended in acetone. The resulting precipitate was filtered off and dried in vacuo. The complexes **4b–d** were purified by column chromatography (alumina, activity V, toluene).

Complex 4a: Yield: 587 mg (79%). ¹H NMR (CD₂Cl₂, 250 MHz): $\delta = 8.34$ (m, 2 H, aryl-H), 8.16 (s, 4 H, aryl-H), 7.59 (m, 3 H, aryl-

H), 7.45 (m, 2 H, aryl-H), 5.50 (m, 1 H, allyl C-H), 3.55 (d, $J = 7.5$ Hz, 2 H, allyl CH₂), 3.03 (d, $J = 12.5$ Hz, 2 H, allyl CH₂) ppm. ¹³C NMR (CD₂Cl₂, 100 MHz): $\delta = 199.0, 178.8, 149.1, 134.9, 132.3, 131.5$ [q, ²J(C,F) = 33.2 Hz], 130.9, 128.6, 125.8, 123.3 [q, ¹J(C,F) = 272.7 Hz], 119.2, 116.1, 62.3 ppm. FAB-MS (NBA): m/z (%) = 743 [M]⁺, 702 [M – allyl]⁺, 597 [M – allyl – Pd + H]⁺. UV/Vis (THF): $\lambda_{\max}$ (lg ϵ) = 549 (4.0), 590 nm (4.0). C₂₈H₁₆F₁₂N₄Pd (742.86): calcd. C 45.27, H 2.17, N 7.54; found C 45.25, H 2.16, N 7.45.

Complex 4b: Yield: 274 mg (55%). ¹H NMR (CD₂Cl₂, 250 MHz): $\delta = 8.33$ (m, 2 H, aryl-H), 7.51 (m, 7 H, aryl-H), 7.21 (m, 4 H, aryl-H), 5.63 (m, 1 H, allyl-CH), 3.62 (d, $J = 6.9$ Hz, 2 H, allyl-CH₂), 3.16 (d, $J = 12.4$ Hz, 2 H, allyl-CH₂), 2.40 (s, 6 H, CH₃) ppm. Micro-ESI-MS (methanol): m/z (%) = 499 [M + H]⁺. UV/Vis (THF): $\lambda_{\max}$ (lg ϵ) = 560 (4.0), 600 nm (4.0). C₂₆H₂₄N₄Pd (498.92): calcd. C 62.59, H 4.85, N 11.23; found C 62.55, H 4.80, N 11.31.

Complex 4c: Yield: 291 mg (50%). ¹H NMR (CD₂Cl₂, 250 MHz): $\delta = 8.35$ (m, 2 H, aryl-H), 7.57 (m, 5 H, aryl-H), 7.43 (m, 6 H, aryl-H), 5.60 (m, 1 H, allyl-CH), 3.64 (d, $J = 6.9$ Hz, 2 H, allyl-CH₂), 3.15 (d, $J = 12.4$ Hz, 2 H, allyl-CH₂), 1.38 (s, 18 H, CH₃) ppm. Micro-ESI-MS (methanol): m/z (%) = 582 [M + H]⁺. UV/Vis (THF): $\lambda_{\max}$ (lg ϵ) = 563 (4.1), 604 nm (4.1). C₃₂H₃₆N₄Pd (583.08): calcd. C 65.92, H 6.22, N 9.61; found C 65.90, H 6.18, N 9.55.

Complex 4d: Yield: 362 mg (65%). ¹H NMR (CD₂Cl₂, 250 MHz): $\delta = 8.22$ (m, 2 H, aryl-H), 7.61 (m, 4 H, aryl-H), 7.39 (m, 3 H, aryl-H), 6.64 (m, 4 H, aryl-H), 5.53 (m, 1 H, allyl-CH), 3.56 (d, $J = 6.9$ Hz, 2 H, allyl-CH₂), 3.09 (d, $J = 12.4$ Hz, 2 H, allyl-CH₂), 2.91 [s, 12 H, N(CH₃)₂] ppm. Micro-ESI-MS (methanol): m/z (%) = 556 [M]⁺. UV/Vis (THF): $\lambda_{\max}$ = 630, 673 nm. C₂₈H₃₀N₆Pd (557.01): calcd. C 60.38, H 5.43, N 15.09; found C 60.40, H 5.48, N 15.05.

Heck Reaction Catalyzed by Complex 4a: In a typical experiment, 4-bromoacetophenone (6.25 mmol) and anhydrous sodium acetate (7 mmol) were placed in a 25-mL two-necked flask equipped with a stirring bar, reflux condenser and septum. The flask was degassed under vacuum and purged with argon to ensure an inert reaction atmosphere. Then, *N,N*-dimethylacetamide (10 mL) as the solvent and *n*-butyl acrylate (0.5 g) were added through the septum. The reaction mixture was thoroughly stirred and heated to the appropriate reaction temperature at which it was held for 5 min followed by treatment with the catalyst solution containing complex **4a** (1.25 μ mol in 0.5 mL of THF). After the appropriate time intervals samples (0.5 mL) of the reaction mixture were hydrolyzed with 2 M HCl (0.5 mL) and extracted with CH₂Cl₂ (0.5 mL). The organic phase was dried with K₂CO₃ and stored at –21 °C until GC analysis for determination of the yield.

Crystal Structure Determination: The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer, using graphite-monochromated Mo- K_{α} radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.^[11,12] The structures were solved by direct methods (SHELXS^[13]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97^[14]). The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.^[14] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 3a:^[15] 2C₅₅H₃₁F₂₄N₈NiO₂·C₅₀H₈₂Ni₈O₃₀·3CH₂Cl₂·H₂O, $M_r = 4649.27$ g mol^{–1}, red-brown prism, size 0.05 × 0.05 × 0.04 mm, monoclinic, space group $P2_1/c$, $a =$

15.8755(2), $b = 20.4987(3)$, $c = 32.8158(4)$ Å, $\beta = 101.482(1)^\circ$, $V = 10465.4(2)$ Å³, $T = -90$ °C, $Z = 2$, $\rho_{\text{calcd.}} = 1.475$ g cm^{–3}, μ (Mo- K_{α}) = 10.77 cm^{–1}, $F(000) = 4714$, 60125 reflections in $h(-18/20)$, $k(-26/26)$, $l(-42/36)$, measured in the range $1.18^\circ \leq \theta \leq 27.47^\circ$, completeness $\Theta_{\max} = 99.3\%$, 23821 independent reflections, $R_{\text{int}} = 0.030$, 18727 reflections with $F_o > 4\sigma(F_o)$, 1272 parameters, 0 restraints, $R_{\text{obs}} = 0.087$, $wR_{\text{obs}} = 0.271$, $R_{\text{1all}} = 0.111$, $wR_{\text{2all}} = 0.289$, GOOF = 2.184, largest difference peak and hole: 3.707/–1.610 e Å^{–3}.

Crystal Data for 4a:^[15] C₂₈H₁₆F₁₂N₄OPd·H₂O, $M_r = 759.86$ g mol^{–1}, red-brown prism, size 0.04 × 0.04 × 0.03 mm, monoclinic, space group $C2/m$, $a = 18.7198(8)$, $b = 18.9056(8)$, $c = 9.8808(2)$ Å, $\beta = 120.749(2)^\circ$, $V = 3005.29(19)$ Å³, $T = -90$ °C, $Z = 4$, $\rho_{\text{calcd.}} = 1.679$ g cm^{–3}, μ (Mo- K_{α}) = 7.22 cm^{–1}, $F(000) = 1500$, 10750 reflections in $h(-24/24)$, $k(-22/24)$, $l(-12/12)$, measured in the range $1.66^\circ \leq \theta \leq 27.50^\circ$, completeness $\Theta_{\max} = 99.4\%$, 3540 independent reflections, $R_{\text{int}} = 0.039$, 2996 reflections with $F_o > 4\sigma(F_o)$, 226 parameters, 0 restraints, $R_{\text{obs}} = 0.064$, $wR_{\text{obs}} = 0.186$, $R_{\text{1all}} = 0.077$, $wR_{\text{2all}} = 0.203$, GOOF = 1.055, largest difference peak and hole: 2.860/–0.943 e Å^{–3}.

Cyclovoltammetric Instrumentation and Procedures: Cyclic square-wave voltammetry was conducted with the 3-electrode technique using a home-built computer-controlled instrument based on the PCI 6110 data acquisition board (National Instruments). The experiments were performed in DMF containing 0.25-M tetrabutylammonium hexafluorophosphate (Merck, Darmstadt) under a blanket of solvent-saturated argon. The DMF was purified by stirring with NaH, distilled under reduced pressure and stored over molsieves 4A under argon.

The Ohmic resistance that had to be compensated was determined by measuring the impedance of the system at potentials where the Faradaic current was negligibly small. Background correction was accomplished by subtracting the current curves of the blank electrolyte (containing the same concentration of supporting electrolyte) from the experimental curves.

Working electrode: hanging mercury drop ($m_{\text{Hg-drop}} = 3.95$ –4.00 mg) produced by the CGME instrument (Bioanalytical Systems Inc., West Lafayette, USA). A platinum wire served as the counter electrode. Internal reference electrode: Ag/AgCl electrode in acetonitrile containing 0.25 M tetrabutylammonium chloride. However, for convenience all potentials reported in this paper refer to the ferrocenium/ferrocene couple. The latter was measured at the end of each experiment using a 1.5-mm Pt disk electrode. The evaluation of the experiments was accomplished by subjecting the experimental voltammograms to a nonlinear regression procedure using the freely available DigiElch software (<http://www.DigiElch.de>).

Acknowledgments

This work was supported by Deutsche Forschungsgemeinschaft (SFB 436).

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Received: August 25, 2006

Published Online: November 27, 2006