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# Synthesis of New Porphyrins with Peripheral Conjugated Chelates and Their Use for the Preparation of Porphyrin Dimers Linked by Metal Ions

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This article describes the preparation of several new porphyrins bearing chelating peripheral groups fully conjugated with the macrocyclic $\pi$-system. Treatment of a 2-nitro-*meso*-tetraarylporphyrin with phosphite gave a cyclic enamine, whose formylation gave an enaminoaldehyde. The thio analogue was obtained on treatment with Lawesson's reagent. The same reagent was also used to obtain the isomeric thioenaminoketone chelates. A enaminoketone ligand was prepared from a porphyrinic pyrrolone. All these ligands, as internal nickel complexes, could be metalated with palladium to yield porphyrinic dimers. The dimers obtained from enaminoketones and thioketones show a trans geometry, while in the enaminoaldehyde and -thioaldehyde series the cis isomer is thermodynamically favored. The bathochromic shifts of the electronic spectra of the aldehyde-derived dimers illustrate the strong electronic effect of peripheral metalation and dimerization. However, in the case of the pyrrolone-derived ligand, opposite effects were observed, due to partial reconstitution of the porphyrin chromophore on complexation. As with the dimers derived from enaminoketones, the dimers derived from the new ligands show typical splitting (up to 190 mV) of the electrochemical waves confirming large porphyrin–porphyrin interactions.

## Introduction

Porphyrins bearing external coordination sites conjugated to the macrocycle $\pi$-system are developed in our group in order to build oligomers. The research field of conjugated oligomers is in constant expansion due to the promise offered by these new molecular materials in many applications (electronic or photonic devices). Oligomers containing heterocycles (thiophene, pyrrole, etc.) have been widely studied.[1] More recently, porphyrin oligomers have also been prepared to obtain materials for optical, electronic or magnetic applications.[2] These oligomers were mainly built with covalent linkages between the individual components.[3−5] However, due to the sometimes very tedious syntheses, noncovalent linkages (coordination bonds, hydrogen bonds, etc.) have also been realized.[6,7] These types of linkages made generally use of *meso*-heteroaryl or aryl groups of synthetic

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(1) (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (b) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (c) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (d) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350.

(2) (a) Vicente, M. G. H.; Jaquinod, L.; Smith, K. M. *Chem. Commun.* **1999**, 1771. (b) Anderson, H. L. *Chem. Commun.* **1999**, 2323.

(3) Arnold, D. P. *Synlett* **2000**, 296. Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, *101*, 2751. Selected recent references on oligomers showing little porphyrin−porphyrin interactions (for earlier references, see also articles cited in ref 9 in this article): Yoshida, N.; Ishizuka, T.; Osuka, A.; Jeong, D. H.; Cho, H. S.; Kim, D.; Matsuzaki, Y.; Nogami, A.; Tanaka, K. *Chem.—Eur. J.* **2003**, *9*, 58. Segawa, H.; Machida, D.; Senshu, Y.; Nakazaki, J.; Hirakawa, K.; Wu, F. *Chem. Commun.* **2002**, 3032. Nakano, A.; Aratani, N.; Furuta, H.; Osuka, A. *Chem. Commun.* **2001**, 1920. Takase, M.; Ismael, R.; Murakami, R.; Ikeda, M.; Shinmori, H.; Furuta, H.; Osuka, A. *Tetrahedron Lett.* **2002**, *43*, 5157. Aratani, N.; Osuka, A. *Org. Lett.* **2001**, *3*, 4213. Uno, H.; Kitawaki, Y.; Ono, N. *Chem. Commun.* **2002**, 116. Bonifazi, D.; Diederich, F. *Chem. Commun.* **2002**, 2178. Kubo, Y.; Ikeda, M.; Sugasaki, A.; Takeuchi, M.; Shinkai, S. *Tetrahedron Lett.* **2001**, *42*, 7435. Ayabe, M.; Ikeda, A.; Kubo, Y.; Takeuchi, M.; Shinkai, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2790.

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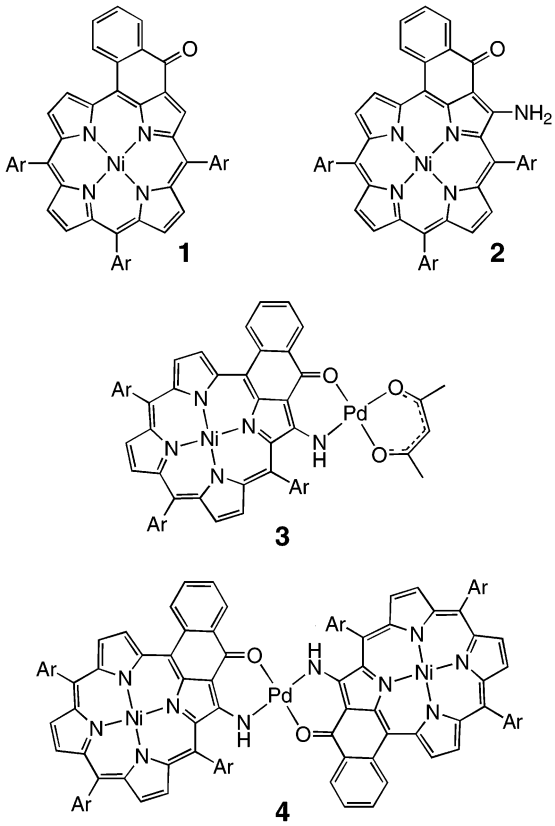
porphyrins. These starting materials are easily accessible using the highly versatile Adler or Lindsey condensations of pyrrole and aromatic aldehydes. As a consequence, due to the noncoplanarity of the porphyrin and the *meso*-aryl groups, the interactions between individual components of the oligomers are very weak. By using chelating coordination sites positioned at the periphery of the porphyrin macrocycle, one might expect that linkages through coordination bonds to be more efficient in terms of interactions between individual porphyrins or other related macrocycles.[8]

We demonstrated[9] that such interactions can be observed by using porphyrins bearing enaminoketones fully conjugated with the aromatic ring. The synthetic route was based on the initial preparation of a cyclic ketone **1** and the subsequent




addition of various nitrogen nucleophiles at the $\beta$-pyrrolic position of this conjugated system[10] resulting in the formation of the enaminoketone moiety like in **2**. Metal ions coordination resulted in the formation of metalated monomers **3** and dimers **4**. Higher oligomers were later obtained from porphyrins bearing two enaminoketone chelates.[11]

We aimed at increasing the number of available ligands in order to (a) improve the stability of the metal to ligand

(4) (a) Arnold, D. P.; Johnson, A. W.; Mahendran, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 366. (b) Bonfantini, E. E.; Officer, D. L. *Tetrahedron Lett.* **1993**, *34*, 8531. (c) Higuchi, H.; Shimizu, K.; Takeuchi, M.; Ojima, J.; Sugiura, K.; Sakata, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1923. (d) Sugiura, K.; Fujimoto, Y.; Sakata, Y. *Chem. Commun.* **2000**, 1105. (e) Anderson, H. L. *Inorg. Chem.* **1994**, *33*, 972. (f) Susumu, K.; Therien, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 8550. (g) Wytko, J.; Berl, V.; McLaughlin, M.; Tykwinski, R. R.; Schreiber, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1998**, *81*, 1964.

(5) (a) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1987**, 39. (b) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1569. (c) Kobayashi, N.; Numao, M.; Kondo, R.; Nakajima, S.; Osa, T. *Inorg. Chem.* **1991**, *30*, 2241. (d) Jaquinod, L.; Siri, O.; Khoury, R. G.; Smith, K. M. *Chem. Commun.* **1998**, 1261. (e) Paolesse, R.; Jaquinod, L.; Della Sala, F.; Nurco, D. J.; Prodi, L.; Montalti, M.; Di Natale, C.; D'Amico, A.; Di Carlo, A.; Lugli, P.; Smith, K. M. *J. Am. Chem. Soc.* **2000**, *122*, 11295. (f) Vicente, M. G. H.; Cancilla, M. T.; Lebrilla, C. B.; Smith, K. M. *Chem. Commun.* **1998**, 2355. (g) Tsuda, A.; Nakano, A.; Furuta, H.; Yamochi, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 558. (h) Tsuda, A.; Furuta, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2549. (i) Tsuda, A.; Furuta, H.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 10304. (j) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79. (k) Tsuda, A.; Nakamura, Y.; Osuka, A. *Chem. Commun.* **2003**, 1096. (l) Sugiura, K.-i.; Matsumoto, T.; Ohkouchi, S.; Naitoh, Y.; Kawai, T.; Takai, Y.; Ushiroda, K.; Sakata, Y. *Chem. Commun.* **1999**, 1957. (m) Sendt, K.; Johnston, L. A.; Hough, W. A.; Crossley, M. J.; Hush, N. S.; Reimers, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 9299. (n) Susumu, K.; Therien, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 8550. (o) Rubtsov, I. V.; Susumu, K.; Rubtsov, G. I.; Therien, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 2687. (p) Screen, T. E. O.; Thorne, J. R. G.; Denning, R. G.; Bucknall, D. G.; Anderson, H. L. *J. Am. Chem. Soc.* **2002**, *124*, 9712. (q) Blake, I. M.; Krivokapic, A.; Katterle, M.; Anderson, H. L. *Chem. Commun.* **2002**, 1662. (r) Higuchi, H.; Maeda, T.; Miyabayashi, K.; Miyake, M.; Yamamoto, K. *Tetrahedron Lett.* **2002**, *43*, 3097. (s) Arnold, D. P.; Hartnell, R. D.; Heath, G. A.; Newby, L.; Webster, R. D. *Chem. Commun.* **2002**, 754. (t) Ikeda, C.; Nagahara, N.; Motegi, E.; Yoshioka, N.; Inoue, H. *Chem. Commun.* **1999**, 1759. Kobayashi, K.; Koyonagi, M.; Endo, K.; Masuda, H.; Aoyama, Y. *Chem.—Eur. J.* **1998**, *4*, 417.

(6) Collman, J. P.; Arnold, H. *Acc. Chem. Res.* **1993**, *26*, 586. Collman, J. P.; Fish, H. T. *Inorg. Chem.* **1996**, *35*, 7922. Buchler, J. W.; Ng, D. K. P. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 3, p 245.

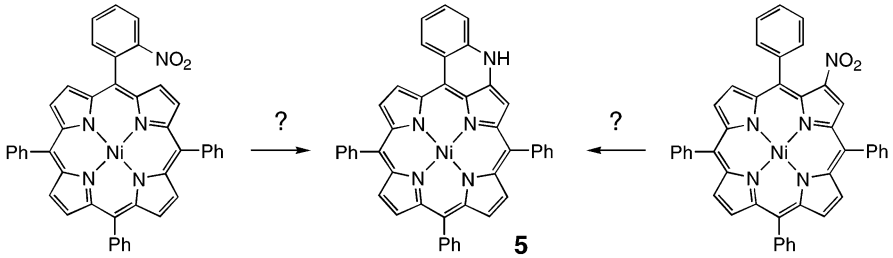
(7) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133. Wojaczynski, J.; Latos-Grazynski, L. *Coord. Chem. Rev.* **2000**, *204*, 113. Sanders, J. K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 3, p 347. Selected recent references on oligomers connected by coordination bonds (for earlier references see also articles cited in ref 9b in this article): Ikeda, A.; Ayabe, M.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *Org. Lett.* **2000**, *2*, 3707. Fujita, N.; Biradha, K.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1718. Twyman, L. J.; King, A. S. H. *Chem. Commun.* **2002**, 910. Lengo, E.; Zangrando, E.; Minatel, R.; Alessio, E. *J. Am. Chem. Soc.* **2002**, *124*, 1003. Lo Schiavo, S.; Serroni, S.; Puntoriero, F.; Tresoldi, G.; Piraino, P. *Eur. J. Inorg. Chem.* **2002**, 79. Kumar, P. P.; Maiya, B. G. *New J. Chem.* **2003**, *27*, 619. Bhyrappa, P.; Vaijayanthimala, G.; Verghese, B. *Tetrahedron Lett.* **2002**, *43*, 6427. Ballester, P.; Gomila, R. M.; Hunter, C. A.; King, A. S. H.; Twyman, L. J. *Chem. Commun.* **2003**, 38. Carlucci, L.; Ciani, G.; Proserpio, D. M.; Porta, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 317. Tsuda, A.; Nakamura, T.; Sakamoto, S.; Yamaguchi, K.; Osuka, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 2817. Ogura, H.; Walker, F. A. *Inorg. Chem.* **2001**, *40*, 5729. Cheng, K. F.; Drain, C. M.; Grohmann, K. *Inorg. Chem.* **2003**, *42*, 2075. Nomoto, A.; Mitsuoka, H.; Ozeki, H.; Kobuke, Y. *Chem. Commun.* **2003**, 1074. Nomoto, A.; Kobuke, Y. *Chem. Commun.* **2002**, 1104. Takahashi, R.; Kobuke, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2372. Ikeda, C.; Fujiwara, E.; Satake, A.; Kobuke, Y. *Chem. Commun.* **2003**, 616. Furuta, H.; Youfu, K.; Maeda, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 2186.

(8) (a) Kobayashi, N.; Muranaka, A. *Chem. Commun.* **2000**, 1855. (b) Michel, S. L. J.; Hoffman, B. M.; Baum, S. M.; Barrett, A. G. M. *Prog. Inorg. Chem.* **2001**, *50*, 473. (c) Baumann, T. F.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **1997**, *36*, 5661. (d) Michel, S. L. J.; Goldberg, D. P.; Stern, C.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 4741. Wang, H. J. H.; Jaquinod, L.; Nurco, D. J.; Vicente, M. G. H.; Smith, K. M. *Chem. Commun.* **2001**, 2646. Prasad, R.; Kumar, A.; Murguly, E.; Branda, N. R. *Inorg. Chem. Commun.* **2001**, *4*, 219. Prasad, R.; Murguly, E.; Branda, N. R. *Chem. Commun.* **2003**, 488. Zhao, M.; Stern, C.; Barrett, A. G. M.; Hoffman, B. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 462. Michel, S. L. J.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **2003**, *42*, 814.

(9) (a) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2001**, 91. (b) Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Am. Chem. Soc.* **2002**, *124*, 6168.

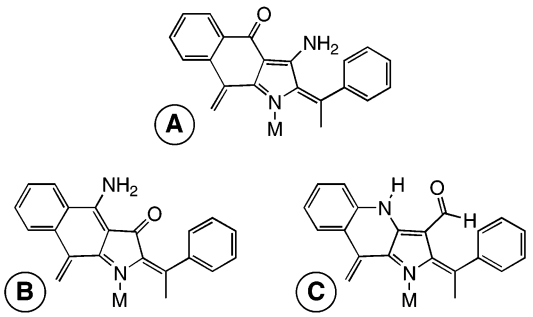
(10) (a) Henrick, K.; Owston, P. G.; Peters, R.; Tasker, P. A.; Dell, A. *Inorg. Chim. Acta* **1980**, *45*, L 161−163. (b) Callot, H. J.; Schaeffer, E.; Cromer, R.; Metz, F. *Tetrahedron* **1990**, *46*, 5253. (c) Ishkov, Y. V.; Zhilina, Z. I. *Zh. Org. Khim.* **1995**, *31*, 136. (d) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Tetrahedron Lett.* **2001**, *42*, 2103.

**Scheme 1.** Possible Synthetic Routes to Enamine **5**




bonds, (b) modify the geometry of the chelating group, i.e., to change the steric interactions between the vicinal *meso* aryl group and the chelated metal + porphyrin moiety and (c) modulate the electronic properties of the metal linked porphyrin dimers.

In this article,[12] we describe how the first requirement was fulfilled by replacing in **A** oxygen by sulfur, which was




expected to strengthen the metal ligand bonds, in particular when second or third row late transition metals are concerned. This substitution would also result in longer metal porphyrin distances and thus reduce the steric interactions caused by *meso*-aryl groups and this was indeed observed. We also describe the synthesis of two new porphyrin series bearing enaminocarbonyl moieties: an enaminoketoporphyrin **B** derived from an isomeric naphthoporphyrin, as well as an enaminoaldehyde **C** and the corresponding enaminothioaldehyde which were expected to show significant differences in steric hindrance around the chelating site. To our surprise, these seemingly minor modifications resulted in (a) a change in stereochemistry of the dimeric species from trans to cis in the case of enaminoaldehydes and (b) a hypsochromic shift of the visible absorption of metalated monomeric and dimeric species derived from the isomeric enaminoketone, in contrast to the effect of previously known metalation reactions.

## Results and Discussion

**1. Synthesis of the Enaminoaldehyde Ligand.** The reaction of nitro compounds with trialkyl phosphites is a very efficient route to nitrogen heterocycles.[13] In the hope to form a *N*-containing six-membered ring fused to the *meso*-tetraarylporphyrin macrocycle, we thought of reacting either a $\beta$-nitroporphyrin with a *meso*-aryl group or a porphyrin bearing a *meso*-*o*-nitroaryl group with trialkyl phosphite (see Scheme 1). Both reactions should give the same cyclic enamine **5**. The next steps would take advantage of the reactivity of enamines to introduce a substituent at the pyrrolic position adjacent to the new ring. Extension of this reaction to substrates bearing several nitro groups could in turn give porphyrins bearing several external coordination sites.

The route starting with a *meso*-*o*-nitroaryl substituent was tested first. A mixture of *meso*-*o*-nitrophenylporphyrins was easily prepared from *o*-nitrobenzaldehyde, 3,5-di-*tert*-butylbenzaldehyde and pyrrole under Adler's or Lindsey's conditions.[14] The products were separated by chromatography, and the mono(*o*-nitrophenyl)porphyrin base was selected for the next step and reacted with triethyl phosphite at 155 °C. Although almost total conversion was obtained, the product proved to be a complex mixture and this route was abandoned in favor of that starting with $\beta$-nitroporphyrins.

The starting material, nickel 2-nitroTPP (TPP = *meso*-tetraphenylporphyrin) was prepared in high yield (90−95%) by nitration of NiTPP (Scheme 2) or, better, of the more soluble CuTPP, with lithium nitrate in $CHCl_3/Ac_2O/AcOH$, followed by a demetalation−metalation sequence. These mild and inexpensive reaction conditions were inspired by the earliest nitration method for porphyrins[15] and avoid the use of dinitrogen tetroxide.[16] When nickel 2-nitroTPP was reacted with excess triethyl phosphite at 155 °C in 1,2-dichlorobenzene, green enamine **5** was obtained as the major product (75%).

The proposed structure of enamine **5** was confirmed by its NMR and crystal data (Figure 1). The N−H signal was found as a broad singlet at 9.2 ppm and the adjacent pyrrolic proton shifted upfield to 8.01 ppm. In addition, the four protons of the cyclized phenyl were differentiated and the aromatic proton close to the adjacent pyrrole ring shifted downfield to 8.91 ppm. Cyclization led to a downfield shift

(11) (a) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2002**, 266. (b) Richeter, S.; Jeandon, C.; Sauber, C.; Gisselbrecht, J.-P.; Ruppert, R.; Callot, H. J. *J. Porphyrins Phthalocyanines* **2002**, *6*, 423.

(12) Selected results were presented at the 2nd International Conference on Porphyrins and Phthalocyanines (ICPP2), Kyoto (Japan), June 30−July 5, 2002.

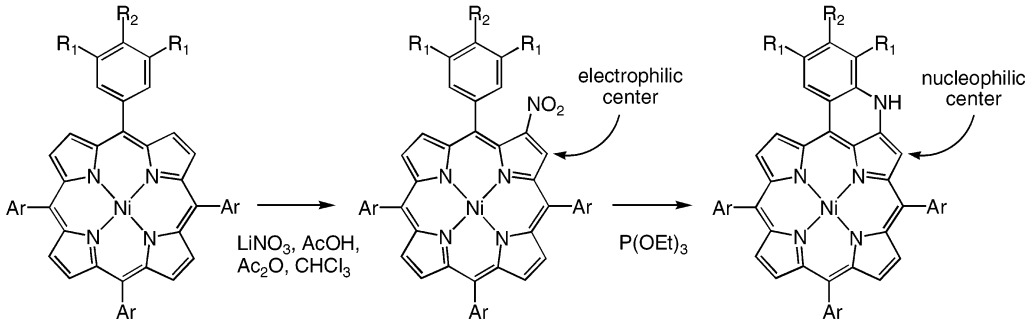
(13) Cadogan, J. I. G. *Q. Rev.* **1968**, *22*, 222.

(14) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827. Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864. Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 1, p 45.

(15) Giraudeau, A.; Callot, H. J.; Jordan, J.; Ezahr, I.; Gross, M. *J. Am. Chem. Soc.* **1979**, *101*, 3857. Johnson, A. W.; Oldfield, D. *J. Chem. Soc.* **1965**, 4303.

(16) Catalano, M. M.; Crossley, M. J.; Harding, M. M.; King, L. G. *J. Chem. Soc.* Chem. Commun. **1984**, 1535.

**Scheme 2.** General Synthetic Route to Enaminoporphyrins



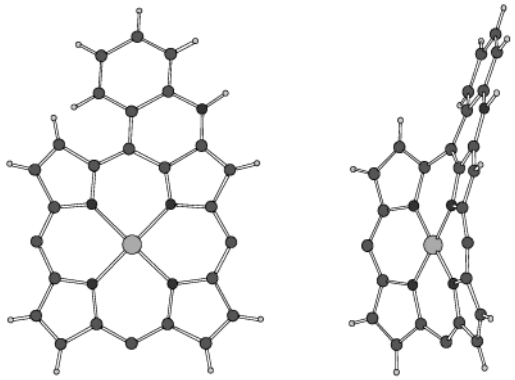



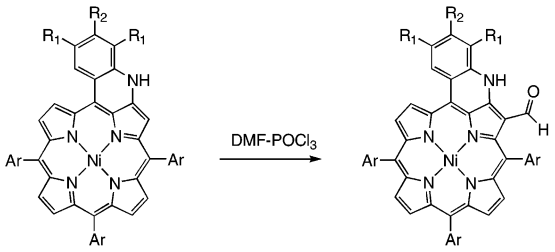
**Figure 1.** X-ray structure of enamine **5** (top and side view: *meso*-phenyl omitted for clarity).

of the two protons of the pyrrole adjacent to the cyclized phenyl. The nickel(II) cation was found in an almost perfect square planar environment. The four Ni−N distances are similar (1.902, 1.915, 1.913, and 1.93 Å), the four N−Ni−N angles were close to 90° (89.8, 90.6, 90.2, and 89.4°) and the deviation from the plane of each nitrogen atom is less than 2°. The porphyrin itself is far from being planar. The geometry of the aromatic core is best described as ruffled, the angles C5−Ni−C15 and C10−Ni−C20 being both close to 160°. The cyclized *meso*-phenyl group, the additional six-membered ring and the adjacent pyrrole are in contrast almost coplanar (less than 5° deviation from planarity between the three rings).

At this stage, it is of importance to stress the fact that the reactivity of nucleophilic enamine **5** opens a general route to 1,2-substituted porphyrins which is complementary to that starting from electrophilic 2-nitroporphyrins developed earlier by other groups.[17] (Scheme 2).

Under Vilsmeier−Haack conditions (DMF + $POCl_3$ in dichloromethane) the formylation of enamine **5** proceeded smoothly at 20 °C to give enaminoaldehyde **8** in 90% yield (Scheme 3). The reaction conditions had to be carefully adjusted, since the conditions first used (2−8 equiv; 45 °C) led to complex mixtures along with starting material. On the contrary, a large excess of reagent (100 equiv; dichloromethane at room temperature) and very short reaction times yielded the enaminoaldehyde in 90% yield. Enaminoaldehyde

**Scheme 3.** Formylation of Enamine **5**, **6**, and **7**




**5** : Ar = Ph, $R_1 = R_2 = H$
**6** : Ar = 4-$CH_3$-Ph, $R_1 = H$, $R_2 = CH_3$
**7** : Ar = 3,5-*t*-$Bu_2$-Ph, $R_1$ = *t*-Bu, $R_2 = H$

**8** : Ar = Ph, $R_1 = R_2 = H$
**9** : Ar = 4-$CH_3$-Ph, $R_1 = H$, $R_2 = CH_3$
**10** : Ar = 3,5-*t*-$Bu_2$-Ph, $R_1$ = *t*-Bu, $R_2 = H$

**8** showed typical NMR signals for the aldehyde group (singlet at 9.09 ppm) and a broad N−H singlet shifted to 12.5 ppm, due to H bonding.

The structure of enaminoaldehyde **8** was confirmed by an X-ray study. The porphyrin geometry is very similar to the one found for enamine **5**. The *meso*-phenyl group, the additional six-membered ring, the adjacent pyrrole, and the aldehyde group are almost coplanar. In the case of the aldehyde, this is probably due to the intramolecular hydrogen bond formed between the carbonyl oxygen atom and the enamine N−H ($d_{CO-HN}$ = 2.15 Å). Conjugation of the aldehyde group with the enamine functionality (vinylogous of a formamide) is also reflected in the shortening of the C−N bond and lengthening of the pyrrolic C−C bond compared to the same bonds in the enamine. This is also reflected in the electronic properties: whereas the addition of a carbonyl function to a chromophore should lead to a bathochromic shift, we observed a slight decrease of the longest wavelength (from 630 nm for enamine **5** to 626 nm for enaminoaldehyde **8**).

**2. Thionation of Porphyrins Bearing Enaminoketone and Enaminoaldehyde Groups.** The reagent of choice for the conversion of a carbonyl into a thiocarbonyl group is Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide).[18] Since thioamides are notably more stable than the corresponding thioketones, we expected the thio analogues of enaminoketones and -aldehydes to be stable enough to be isolated and characterized prior to be complexed by metal ions. This proved to be true,

(17) Crossley, M. J.; King, L. G. *J. Org. Chem.* **1993**, *58*, 4370. Crossley M. J.; Harding, M. M.; Tansey, C. W. *J. Org. Chem.* **1994**, *59*, 4433. For a review, see: Jaquinod, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 1, p 201.

(18) Lawesson, S. O.; Shabana, R.; Rasmussen, J. B. *Tetrahedron* **1980**, *36*, 3047. Pradere, J.-P.; N'Guessan, Y. T.; Quiniou, H. *Tetrahedron* **1975**, *31*, 3059. Walter, W.; Proll, T. *Synthesis* **1979**, *12*, 941. For a review, see: Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061.

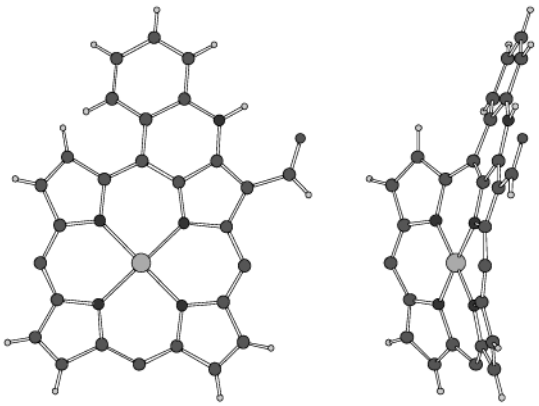
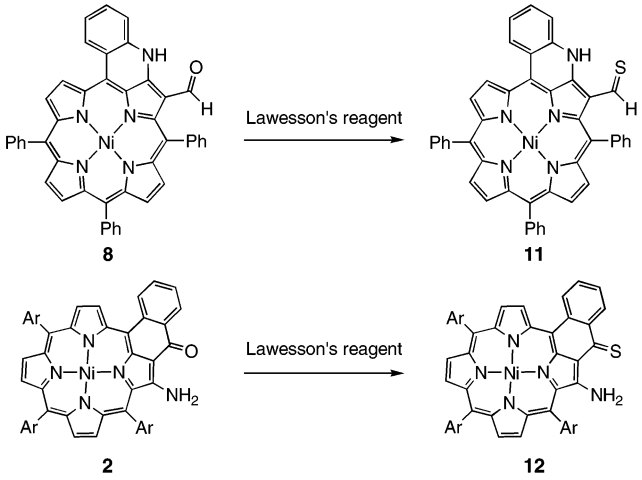


**Figure 2.** X-ray structure of enaminoaldehyde **8** (top and side view: *meso*-phenyl omitted for the seek of clarity).

**Scheme 4.** Thionation of Enaminoaldehyde **8** and Enaminoketone **2**




and the treatment of enaminoketone **2** and enaminoaldehyde **8** (both as nickel complexes) with Lawesson's reagent (Scheme 4) under standard conditions (refluxing benzene) gave thioenaminoketone **12** and thioenaminoaldehyde **11** in 97 and 78% yield, respectively.

Both **11** and **12** are stable enough to be chromatographed and fully characterized. Their NMR data are similar to that of the starting materials, differing mainly for the aldehyde signal (10.37 ppm for **11**, to be compared with 9.09 ppm for **8**) and the N−H signal (15.4 ppm for **11**, to be compared with 12.5 ppm for **8**). Replacement of oxygen by sulfur led also to a significant bathochromic shift of the lowest energy band, respectively 43 or 24 nm for the enaminothioketone or -aldehyde vs the starting enaminoketone or -aldehyde.

**3. Isomeric Enaminoketones 17 and 18.** The starting materials, nickel ketones **15 (**and **16)**, were obtained from the porphyrin free bases (prepared from aldehydes **13** and **14** according to the procedure described by Ishkov[19]) after metalation with nickel acetylacetonate. Treatment of the resulting nickel complexes with 4-amino-4H-1,2,4-triazole[20] gave the required ligands in 61% (and 83%) yield (Scheme 5). While nickel ketone **15** showed exceptionally high absorbance at low energy ($\lambda$ = 720 nm, $\epsilon$ = 17 000), the amination led to a large hypsochromic shift of the lowest energy band to 678 nm (see detailed discussion of the electronic spectra of ligands and metal complexes below).

In the case of enaminoketones **17** and **18**, we were unable to prepare the corresponding thioderivatives. Reaction of enaminoketones **17** and **18** with Lawesson's reagent led to complex mixtures of products, most of them still containing phosphorus (originating from the reagent).

**4. Preparation of Acetylacetonatopalladium Derivatives and Porphyrin Dimers.** We have observed that, although they can be characterized, dimers of porphyrin enaminoketones connected with nickel ion are of moderate stability and will decompose under attempted chromatography or in dilute solution.[9] In the case of the thio derivatives (thioenaminoketones or -aldehydes), the dimers connected with first row transition metal ions were found to be by far more stable. However, to ensure that comparisons could be made between pairs of stable and well characterized dimers, we chose to restrain this study to dimers of nickel porphyrins linked by palladium ions (Scheme 6). The nickel(II) ion in porphyrins usually does not coordinate axial ligands and remains in a square planar geometry as does palladium(II) with chelates like enaminoketones.

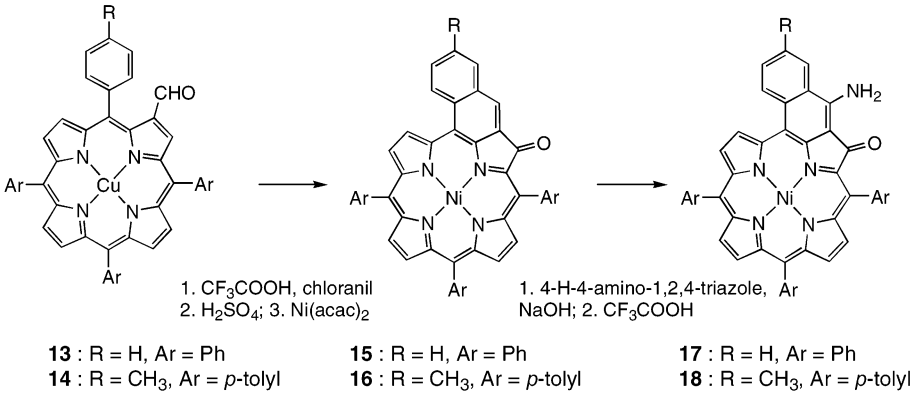
In the already studied dimers **4** of enaminoketone **2**, the square planar complexes were found as trans isomers in all cases.[9b] It is known, since the initial publications of Chatt and Wilkins,[21] that the cis−trans isomerism is governed by different factors: electrostatic interactions, steric effects, difference in bond energies, and solvation. Modification of the external chelate, in a geometric or electronic way, might therefore modify the geometry around the connecting metal ion and as a consequence the extent of the interaction between the two connected porphyrins. The replacement of the oxygen atom by the softer sulfur atom in the chelate should, for example, favor the cis isomer.[22]

The reaction of thioenaminoketone **12** with palladium(II) bis(acetylacetonate) ($Pd(acac)_2$) led quantitatively to a single compound identified as the trans isomer **19** (analogue of dimer **4**) by $^1H-^1H$ COSY and ROESY NMR experiments. The cis isomer has a plane of symmetry and the trans isomer a center of symmetry: as a consequence NOE correlations between protons belonging to different porphyrins can be observed only in the case of the trans isomer. We were unable to isolate the externally metalated porphyrin monomer. Because of the presence of the soft sulfur atom, which should destabilize the remaining acac ligand as soon as the first porphyrin is coordinated, even the use of a large excess of $Pd(acac)_2$ led almost quantitatively to the porphyrin dimer.

The reaction of enaminoketones **17** or **18** with excess $Pd(acac)_2$ led as excepted to the metalated porphyrin monomers **20** or **21** and to palladium(II)-connected dimers **22** or **23**

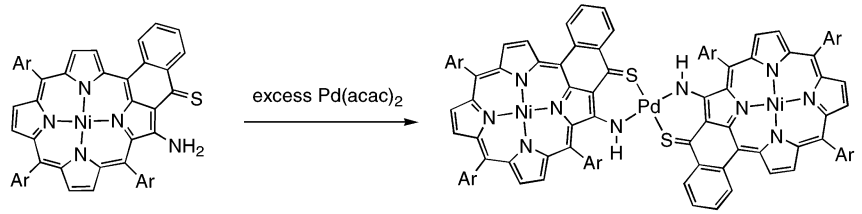
(19) Ishkov, Y. V. *Russ. J. Org. Chem.* **2001**, *37*, 288.
(20) (a) Bakke, J. M.; Svensen, H.; Trevisan, R. *J. Chem. Soc., Perkin Trans. 1* **2001**, 376. (b) Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1986**, *51*, 5039. (c) Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1988**, *53*, 3978.
(21) Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* **1952**, 273 and 4300. Harvey, J. N.; Heslop, K. M.; Orpen, A. G.; Pringle, P. G. *Chem. Commun.* **2003**, 278. Anderson, K. M.; Orpen, A. G. *Chem. Commun.* **2001**, 2682.
(22) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

**Scheme 5.** Preparation of Enaminoketones **17** and **18**



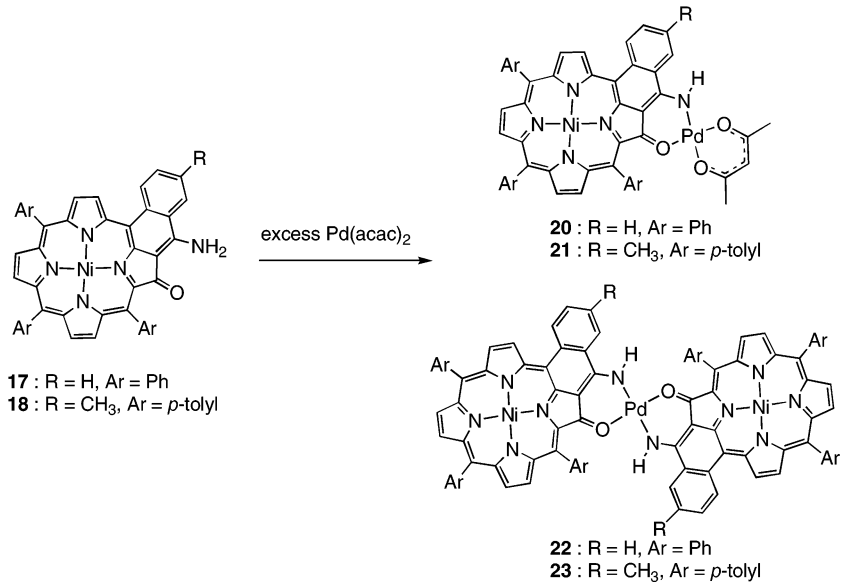

**13** : R = H, Ar = Ph
**14** : R = $CH_3$, Ar = *p*-tolyl
**15** : R = H, Ar = Ph
**16** : R = $CH_3$, Ar = *p*-tolyl
**17** : R = H, Ar = Ph
**18** : R = $CH_3$, Ar = *p*-tolyl

**Scheme 6.** Preparation of Palladium(II)-Linked Enaminothione Dimer **19**




**12** **19**

**Scheme 7.** Preparation of Metalated Porphyrin Monomers **20** and **21** and Palladium-Linked Dimers **22** and **23** from Enaminoketones **17** and **18**




**17** : R = H, Ar = Ph
**18** : R = $CH_3$, Ar = *p*-tolyl

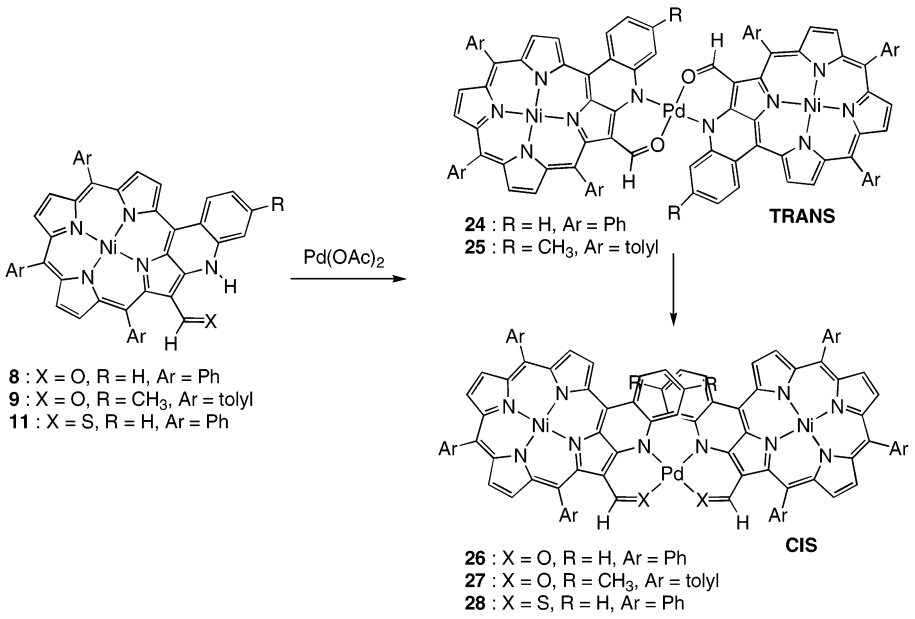
**20** : R = H, Ar = Ph
**21** : R = $CH_3$, Ar = *p*-tolyl

**22** : R = H, Ar = Ph
**23** : R = $CH_3$, Ar = *p*-tolyl

(Scheme 7). These dimers, as for the dimer built with enaminoketone **2**, were established to be the trans isomer by $^1H-^1H$ COSY and ROESY NMR experiments. Although metalation of the external coordination site, to give acetylacetonatopalladium derivatives or dimers, led in all previously studied compounds to a large bathochromic shift of the UV−visible bands, the opposite was observed in this series, and led us first to doubt the structure of the dimer. The lowest energy absorption band found at 678 nm for enaminoketone **18** shifted to 658 nm for metalated monomer **21** and to 662 nm for dimer **23**.

In contrast to both enaminoketone series which only yielded trans dimers, the reaction of enaminoaldehyde **8** with $Pd(OAc)_2$ led to the formation of two dimeric products (TLC monitoring of the advancement of the reaction clearly showed their formation) (Scheme 8). Stopping the reaction before complete conversion of the starting enaminoaldehyde, allowed to separate and isolate the two dimers by careful silica gel chromatography. Both isomeric dimers presented almost superimposable electronic spectra, within a 3−4 nm range, with broadening and splitting of the Soret bands and bathochromic shifts of the lower wavelength bands. One isomer could be obtained in only 90−95% purity (checked by $^1H$ NMR) in all attempts. This dimer was found unstable and led quantitatively to the other dimer when kept in solution for a few hours (followed by NMR, see Supporting Information). Once again, since we were unable to grow single crystals suitable for an X-ray structure determination,

**Scheme 8** Cis and Trans Isomeric Dimers Obtained from Enaminoaldehydes **8** and **9** and Cis Dimer Obtained from Enaminothioaldehyde **11**




**8** : X = O, R = H, Ar = Ph
**9** : X = O, R = $CH_3$, Ar = tolyl
**11** : X = S, R = H, Ar = Ph

**24** : R = H, Ar = Ph
**25** : R = $CH_3$, Ar = tolyl

**26** : X = O, R = H, Ar = Ph
**27** : X = O, R = $CH_3$, Ar = tolyl
**28** : X = S, R = H, Ar = Ph

the structure of the dimers (cis or trans isomer) was established by $^1H-^1H$ COSY and ROESY NMR experiments.

The most stable dimer showed at high field (6.69 ppm) a signal attributed to the cyclized phenyl (in all monomers and dimers so far studied the corresponding signals are located in the 9−7.5 ppm range). This strongly suggested that the two cyclized phenyl rings were overlapping, and that, in contrast to the other series, the cis dimer **26** was the most stable isomer. Because of overlapping signals the $^1H$ NMR spectra of dimers **24** and **26** could not be fully assigned, and $^1H-^1H$ COSY and ROESY NMR experiments that confirmed the stereochemical assignments were run on the *meso*-tolyl-substituted dimers **25** and **27** (see Supporting Information). The geometry of the cis dimers must induce a distortion around the palladium(II) ion, which can no longer stay in a true square planar environment, as shown in Scheme 8. As a direct consequence, these dimers exists as two enantiomeric chiral Δ and Λ species. The trans isomer was clearly the kinetic product since NMR of the reaction medium after 24% conversion showed that the trans/cis isomer ratio was close to four (19 and 5%). However, due to isomerization during the course of the reaction and the purification of the products, the cis isomer was the major product recovered.

Reaction of enaminothioaldehyde **11** with $Pd(OAc)_2$ led to a single dimeric compound identified as the cis isomer **28**. The overlap of the two cyclized phenyl rings was again reflected in the $^1H$ NMR spectrum by the presence of an aromatic signal at 6.14 ppm. The fact that we could not observe the presence of the trans isomer reflects the much stronger trans effect induced by the soft sulfur atom in the enaminothioaldehyde chelate.[22]

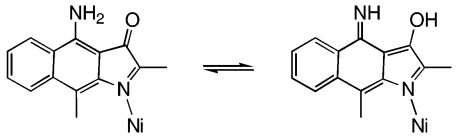
**5. Spectroscopic Properties.** Metalation of the external coordination site led in the previously studied series (for example: enaminoketone **2**, metalated monomer **3**, and dimer **4**)[9b] to a large bathochromic shift of the UV−visible bands. The electronic spectra shown in Table 1 demonstrate that either a bathochromic or a hypsochromic shift was observed depending on the starting porphyrins used to build the metalated monomers or the dimers. Using enaminothioketone **12**, enaminoaldehyde **8**, or enaminothioaldehyde **11** to build dimers **19**, **26**, or **28**, led as expected to bathochromic shifts upon formation of the palladium(II)-linked dimers. These effects are due to the delocalization of the electron density in the six-membered ring formed by the chelates and the metal(II) ions. In these cases, the metal chelation might be seen as the addition of a new six-membered ring, almost aromatic in character, thus leading to the observed bathochromic shifts. These effects (generally called "metalloaromaticity") have been reviewed recently[23] and first described by M. Calvin for simple copper bis(acetylacetonate) complexe.[24]

Metalation of enaminoketone **18** to build metalated monomer **21** or dimer **23** led to hypsochromic shifts in the electronic spectra (see Table 1). However, the same electronic delocalization effects might be invoked to explain these

**Table 1.** Electronic Spectra and Selected IR Wave Numbers of Porphyrin Monomers and Dimers

| compound | wavelength $\lambda$ > 400 nm | $\nu$(CO) ($cm^{-1}$) | $\nu$(N−H) ($cm^{-1}$) | ref |
|---|---|---|---|---|
| **1** | 462, 650, 686 | 1650 | | 11b |
| **2** | 458, 599, 649 | 1628 | 3311, 3473 | 10b |
| **3** | 420, 458, 484, 640, 686 | 1611 | 3355 | 10b |
| **4** | 439, 470, 500, 638, 696 | 1607 | 3353 | 10b |
| **12** | 428, 473, 496, 654, 692 | | | this work |
| **19** | 450, 524, 654, 682, 732 | | | |
| **16** | 406, 462, 490, 657, 720 | 1698 | | this work |
| **18** | 414, 450, 476, 624, 650, 678 | 1655 | 3309, 3467 | |
| **21** | 412, 446, 466, 606, 636, 658 | 1570 | 3366 | |
| **23** | 416, 450, 472, 486, 608, 640, 662 | 1568 | 3344 | |
| **8** | 446, 560, 626 | | | this work |
| **26** | 450, 478, 560, 622, 668 | | | |
| **11** | 422, 470, 568, 598, 650 | | | this work |
| **28** | 432, 506, 572, 628, 714 | | | |

**Scheme 9**




surprising results. A clue for this unexpected behavior is found in the IR data for the corresponding starting ketones and enaminoketones.

If one considers the carbonyl wavenumbers of the starting ketones, that of **16** falls in the normal range for aryl−alkyl or diaryl ketones, and it makes sense to describe **16** as a ketochlorin, with very little contribution from mesomeric form of the aromatic ring current involving the $\beta$ positions of the modified pyrrole. In contrast that of ketone **1** is atypical and suggests a strong polarization of the carbon−oxygen bond and a significant delocalization of the $\pi$ electron density on the $\beta,\beta$-bond of the modified pyrrole. Amination of the two ketones **1** and **16** gave the isomeric enaminoketones **2** and **18**. The extent of the modification of the carbonyl wavenumbers of **2** and **18** vs **1** and **16** ($-22$ and $-43$ cm$^{-1}$) reflects the different nature of the ketones. The amination of ketone **16** leads to a large delocalization of the carbonyl electron density in the enaminoketone group thus diminishing the bond order of the carbonyl bond and increasing the bond order of the $\beta,\beta$-pyrrolic bond (more double bond character and thus a more porphyrin-like spectrum; see Scheme 9). Metalation of enaminoketone **18** increases this delocalization to a much larger extent (shift of $-85$ cm$^{-1}$ after metalation), bringing the carbonyl wavenumbers in the range of acetylacetonate complexes (Pd(acac)$_2$: 1568 cm$^{-1}$).

Complexation of the external coordination site is not expected to modify significantly the macrocyclic chromophore of enaminoketone **2**, and the bathochromic shift of UV−visible data will reflect the extension of the conjugation to the acetylacetonatopalladium in monomer **3** and then to the porphyrinatopalladium group in dimer **4**, as earlier presented.[9b] On the other hand, the same operations, when performed with enaminoketone **18** will have a large effect on the macrocyclic chromophore. Starting with **18**, which has still a ketochlorin character, the extension of the delocalization on metalation will, as did the amination, modify the chromophore which will end even more porphyrin-like. Expected are then porphyrin-like bands, less intense and at shorter wavelengths. The resulting spectrum will reflect the relative and opposite contributions from the organic chromophore being more porphyrin-like, which results in a hypsochromic effect, and the metalation which determines a bathochromic effect.

**6. Electrochemical Studies.** The electrochemistry of nickel porphyrins is well documented.[25] In general, the nickelporphyrins are oxidized in two one-electron steps and reduced in two one-electron steps (sometimes a third oxidation or reduction step might be observed, but close to the electrolyte oxidation or reduction). In most cases, the initial oxidations and reductions are not localized on the nickel(II) ion but involve the aromatic $\pi$ system. We have studied by cyclic voltammetry the electrochemical behavior of a series of porphyrin monomers bearing an external enaminoketone chelate and the metal ion linked dimers build from these compounds. In the case of nickel porphyrins, we observed the usual reversible two oxidation and reduction steps. For the dimers, the oxidation and reduction steps were splitted, indicating that the resultant charge was delocalized over both porphyrin rings (one example is reported in Table 2: monomer **2** and dimer **4**).[9b] The redox splitting of the electrochemical oxidation or reduction steps is generally accepted as a proof of strong interactions in the ground state between the two porphyrins.[26]

For the new nickel porphyrin monomers or dimers presented in this study, it must be taken into account that reducible or oxidizable functions are present at the periphery of the macrocycle, thus giving rise to irreversible processes or additional redox steps. It is well-known that aromatic amines or sulfur compounds are easily oxidized or that aromatic aldehydes might be reduced in the potential range used in our experiments.[28] Isomeric enaminoketone **17** and metalated monomer **20** gave two reversible well-defined reduction and oxidation signals. For dimer **22**, the first and the second reduction signals involve an uptake of two electrons for each step. The first two oxidation steps each involve one electron, whereas the third peak involves two overlapping one-electron steps. The value of the redox splitting found for the first oxidations in the new dimer **22** (140 mV) is very close to the value found for dimer **4** (160 mV). The same type of chelate, even in an isomeric form, should give the same kind of interaction. For thioenaminoketone **12**, the situation on the oxidation side is complicated by a first irreversible oxidation probably localized at the sulfur atom. Dimer **19**, where the sulfur atom is protected by the complexation with palladium(II), has a well-defined reversible electrochemistry on the oxidation side. As expected, the first steps are one electron processes and the value of the splitting is found equal to 190 mV. Moreover, on the reduction side, although the interpretation was made difficult

(23) Masui, H. *Coord. Chem. Rev.* **2001**, *219*−*221*, 957, and references therein. The "aromatic character" of the metal(acac) six-membered rings is reflected in their reactivity and in the ring-current effects observed in NMR spectra. The electrophilic substitution on the acac ligand is well-known (see, for example: Reihlen, H.; Illig, R.; Wittig, R. *Ber. Dtsch. Chem. Ges.* **1925**, *58B*, 12; Collman, J. P. *Angew. Chem.* **1965**, *77*, 154). If several acac ligands surround the metal ion, J. P. Collman described also intramolecular-interannular electronic effects through the metal center, illustrated by chemical reactivity and physical properties.

(24) Calvin, M.; Wilson, K. W. *J. Am. Chem. Soc.* **1945**, *67*, 2003.

(25) Kadish, K. M.; Van Caemelbecke, E.; Royal, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Boston, MA, 2000; Vol. 8, p 3. Kadish, K. M.; Lin, M.; Van Caemelbecke, E.; De Stefano, G.; Medforth, C. J.; Nurco, D. J.; Nelson, N. Y.; Krattinger, B.; Muzzi, C. M.; Jaquinod, L.; Xu, Y.; Shyr, D. C.; Smith, K. M.; Shelnutt, J. A. *Inorg. Chem.* **2002**, *41*, 6673.

(26) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105.

(27) Callot, H. J. *Tetrahedron* **1973**, *29*, 899. Chen, H. L.; Ellis, P. E., Jr.; Wijesekera, T.; Hagan, T. E.; Groh, S. E.; Lyons, J. E.; Ridge, D. P. *J. Am. Chem. Soc.* **1994**, *116*, 1086.

(28) See, for example: *Encyclopedia of Electrochemistry of the Elements. Organic Section*; Bard, A. J., Lund, H., Eds.; Marcel Dekker Inc.: New York: 1979, Vol XII; 1980, Vol. XIV. Weinberg, N. L.; Weinberg, H. R. *Chem. Rev.* **1968**, *68*, 449.

**Table 2.** Cyclic Voltammetry Data[a]

| compound | reduction $E'^{\circ}$ in V vs $Fc/Fc^+$ (no. of electrons exchanged) | | | | oxidation $E'^{\circ}$ in V vs $Fc/Fc^+$ (no. of electrons exchanged) | | | |
|---|---|---|---|---|---|---|---|---|
| **2** | | −1.63 (1) | | −1.26 (1) | 0.60 (1) | | 0.95 (1) | |
| **4** | −1.94(1) | −1.86 (1) | | −1.45 (2) | 0.32 (1) | 0.48 (1) | 0.82 (2) | |
| **17** | | −1.79 (1) | | −1.44 (1) | 0.37 (1) | | 0.78 (1) | |
| **20** | | −1.85 (1) | | −1.48 (1) | 0.40 (1) | | 0.78 (1) | |
| **22** | | −1.82 (2) | | −1.46 (2) | 0.41 (1) | 0.55 (1) | 0.81 (2) | |
| **12** | | −1.61 (1) | | −1.26 (1) | 0.44[b] | | 0.80 (1) | |
| **19** | ≈−1.95[f] | ≈−1.85 | −1.45 (1) | −1.35 (1) | 0.30 (1) | 0.49 (1) | 0.80 (2) | |
| CHO[c] | | −1.87 (1) | | −1.53 (1) | 0.67 (1) | | 0.73 (1) | |
| **5**[d] | | −2.04 (1) | | −1.64 (1) | 0.32 (1) | | 0.63 (1) | 1.20 |
| **8** | | −2.05[b] | | −1.62 (1) | 0.32 (1) | | 0.62 (1) | 1.18 |
| **26** | −2.18[b] | −1.83 (1) | −1.70 (1) | −1.39 (1)[e] | 0.25 (1) | 0.36 (1) | 0.60 (2) | 1.25 |
| **11** | | −1.88 (1) | | −1.55 (1) | 0.35[b] | | 0.64 (1) | |
| **28** | −2.02 | −1.80 | −1.58 | −1.42[b] | 0.27(1) | 0.41(1) | 0.60 | |

[a] Experimental conditions: see Experimental Section. The number of exchanged electrons is indicated in parentheses following the peak potential when it could be determined accurately and confirmed by rotating disk voltammetry (RDV) experiments. [b] Peak potentials. [c] CHO = nickel 2-formyl-*meso*-tetraphenylporphyrin.[27] [d] For enamine **5**, it was necessary to deaerate the electrolyte carefully, since the presence of traces of oxygen led to additional waves (at −1.84 and −2.24 V) during the reduction process. This was probably due to the generation of the oxygen radical anion in situ, which may further react with enamine **5** to generate the corresponding hydroxylamine. [e] Only reversible if the potential scan is reverted after this first reduction step. [f] Approximative values due to the low solubility of the reduced forms of dimer **19**.

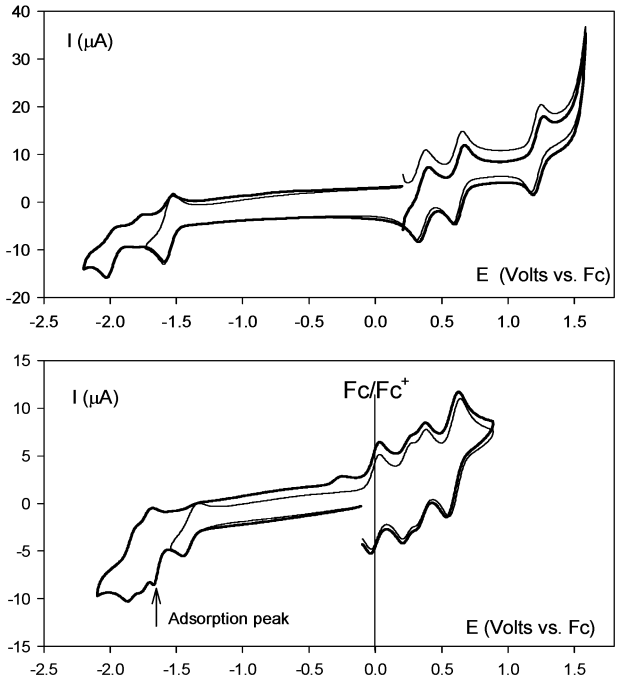



**Figure 3.** Typical cyclic voltammetry of monomeric and dimeric porphyrins (top, monomer **8**; bottom, dimer **26**). Plain line: inversion of the potential sweep after the first reduction. Bold line: inversion of the potential sweep after the fourth reduction step.

by the rather low solubility of the reduced forms of dimer **19**, it is possible to conclude that **19** is reduced in four independent one electron steps at approximately −1.35, −1.45, −1.85, and −1.95 V. A spectroelectrochemical study during reductive electrolysis at a potential of −1.9 V also confirmed that the dimeric structure is maintained after reduction. The enaminothioketone chelate complexing the palladium(II) connecting ion seems to be a better link in term of extent of interaction than the enaminoketone chelate, although the distance between the two porphyrin rings is probably larger since Pd−S bonds are longer than Pd−O bonds.For enaminoaldehyde **8**, enaminothioaldehyde **11** and dimers **26** and **28** build from these monomers, the electrochemical behavior allows to draw the same conclusions. For dimer **26** ("enaminoaldehyde dimer"), the redox splitting on the oxidation side was found equal to 110 mV. However, the behavior on the reduction side was complicated by decomplexation problems. The first step is reversible only if the potential scan is reverted after the first reduction. Trying to introduce four electrons by a further increase of the cathodic potential led to decomposition of the dimer and recovery of the starting monomer. This could be easily monitored by spectroelectrochemistry (appearance of the characteristic broad Soret band of the monomeric porphyrin: see Supporting Information). For dimer **28** ("enaminothioaldehyde dimer"), the redox splitting on the oxidation side was increased to 140 mV. For all compounds derived from enamine **5**, an additional oxidation step (at ca. 1.20 V) was found at the limit of the potential range and might be attributed to the oxidation of the amine. On the reduction side, four independent one electron steps were observed, but with loss of the reversibility, even for the first reduction step, and decomplexation.

For the cis dimers **26** and **28**, built from the enaminoaldehyde and enaminothioaldehyde monomers, it seems that the peculiar coordination geometry (intermediate between square planar and tetrahedral) around the Pd(II) connecting ion leads to much less stable dimers. The high cathodic potential generally needed to reduce the Pd(II) square planar complexes prevented destruction of the other dimers since Pd(II) was not reduced within the electrochemical range studied. In the last two examples, dimers **26** and **28**, these potentials are less cathodic, since the coordination geometry destabilize the +2 state compared with a square planar coordination. Thus, within the range of potentials studied, reduction of the connecting Pd(II) can occur and decomposition of the dimeric structures leads to the porphyrin monomers.

The electrochemistry of all palladium(II)-linked dimers, for all new chelates used in this study, showed that this kind of connection induces strong interactions between the two

individual porphyrin rings. The redox splitting values found (110−190 mV), which reflect the extent of the interactions, compare well with the splitting values found in covalently linked conjugated dimers. With the notable exception of the triply fused dimers described by Otsuka et al.,[5i] where the two porphyrins are connected without any spacer, thus presenting splitting values up to 400 mV, all other covalently linked conjugated dimers (phenyl, acetylenic, or olefinic links) show redox splitting values in the same range (from 0 to 260 mV). A *trans*-ethene or ethynyl *meso*−*meso* linkage between two porphyrins leads to values respectively equal to 100 and 260 mV.[2b] Therefore, the simple metal ion connection between two porphyrins bearing chelating sites leads to redox splitting values close to the best results reached with covalently linked dimers.

## Conclusion

We have been able to show that the metal ion link between two porphyrinic chromophores bearing chelating sites at their periphery can be generalized to other chelates and is not restricted to the initially described enaminoketone functionalized porphyrins.[9] All porphyrin dimers prepared present strong interactions between the individual rings in the ground state. However, while the sentence "two rings is better than one", which D. Arnold[3] used as title for his review on porphyrin oligomers, is still valid, in covalently connected oligomers as well as in multiporphyrins connected by metal ions, one should be aware that this last approach, although flexible and easy to carry out, brings its own specific problems. In this article, we describe two such events: on one hand the cis−trans isomerism is illustrated by the sensitivity of isoelectronic chelates to steric factors, on the other, the complexation of the chelate may have unexpected effects on the overall electronic properties of the oligomers, if the complexation modifies the monomeric chromophore itself. Preparation of higher oligomers (built from porphyrins bearing two chelating sites) with the new insights taken from this study is in progress. The replacement of the oxygen atom in enaminoketones for sulfur presents at least three major advantages: a higher stability of the metal ion connection, monomeric chromophores with a very low band gap (close to near infrared for bis(enaminothioketones)[29]), and an increase of the interactions between each porphyrin.

## Experimental Section

**General Procedures.** UV−visible spectra: Hewlett-Packard 8453 ($CH_2Cl_2$). NMR ($CDCl_3$ at 25 °C unless otherwise stated, $\delta$ (ppm) vs TMS): Bruker AC 300, AM 400, and ARX 500. COSY $^1H-^1H$ NMR have been run on all compounds. Elemental analyses were performed at the Service de Microanalyse, Université Louis Pasteur, Strasbourg, France. Chromatographic separations were obtained using Merck 9385 silica gel or Merck 1097 alumina. All monomeric porphyrins gave correct masses (Finnigan TSQ 700, EI, 12 eV), and all dimers gave correct molecular mass peaks (FAB or MALDI−TOF).

**Preparation of 2-Nitro-*meso*-tetraarylporphyrins.** To a warm chloroform solution (40−45 °C) of the copper or nickel tetraaryl porphyrin (1.5 mmol in 600 mL) were added a solution of lithium nitrate in acetic acid (1.72 g, 25 mmol in 100 mL) and acetic anhydride (95 mL, 1 mol). The advancement of the reaction was carefully monitored by silica gel TLC, and after completion of the nitration (approximatively 1.5 h), the reaction mixture was neutralized with an aqueous $NaHCO_3$ solution, washed three times with water, and the solvent evaporated. After crystallization (dichloromethane/methanol) the known copper or nickel 2-nitro-*meso*-tetraarylporphyrins[15,16] were obtained in 90 to 95% yields (aryl = phenyl, *p*-tolyl, and 3,5-di-*tert*-butyl-phenyl).

**Nickel Enaminoporphyrins 5, 6, and 7.** A degassed solution of nickel 2-nitro-*meso*-tetraarylporphyrin (0.55 mmol) in 1,2-dichlorobenzene (3 mL) and triethyl phosphite (0.5 mL, 2.9 mmol) was heated under argon at 155 °C during 3 h. After cooling, the reaction mixture was poured on a silica gel column (eluent hexane/dichloromethane). The green nickel enaminoporphyrins **5**, **6**, or **7** were obtained in 70−75% yield after crystallization from dichloromethane/methanol.

**5 (Ar = Phenyl).** $^1H$ NMR: $\delta$ = 9.45, 8.83 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.64, 8.58 (2s, 2 + 2H, pyrrole), 8.01 (s, 1H, pyrrole), 8.91 (dd, 1H, $J$ = 7.5 and 1 Hz, cyclized phenyl), 7.96−8.04 (m, 6H, $H_{ortho}$), 7.60−7.73 (m, 12H, $9H_{meta+para}$ + 3H cyclized phenyl), 9.20 (broad s, 1H, NH). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 426 ($\epsilon$ = 71 500), 554 (6100), 598 (8700), 628 (15 200). Anal. Calcd for $NiC_{44}N_5H_{27}$: C, 77.22; H, 3.98; N, 10.23. Found: C, 76.87; H, 4.19; N, 9.99.

**7 (Ar = 3,5-Di-*tert*-butyl-phenyl).** $^1H$ NMR: $\delta$ = 9.35, 8.83 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.68, 8.65 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.63, 8.59 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.04 (s, 1H, pyrrole), 8.83 (d, 1H, $J$ = 2 Hz, cyclized phenyl), 7.81 (d, 1H, $J$ = 2 Hz, cyclized phenyl), 7.88, 7.86, 7.84 (3d, 3 × 2H, $J$ = 2 Hz, $H_{ortho}$), 7.72, 7.70, 7.67 (3t, 3 × 1H, $J$ = 2 Hz, $H_{para}$), 9.55 (broad s, 1H, NH), 1.89, 1.57 (2s, 2 × 9H, *tert*-Bu), 1.49, 1.47, 1.46 (3s, 3 × 18H, *tert*-Bu). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 424 ($\epsilon$ = 76 300), 446 (69 500 sh), 602 (11 500 sh), 634 (18 200). Anal. Calcd (%) for $NiC_{76}N_5H_{91}\cdot H_2O$: C, 79.29; H, 8.14; N, 6.08. Found: C, 79.44; H, 8.41; N, 5.98.

**Nickel Enaminoaldehydes 8, 9, and 10.** To a solution of the nickel enaminoporphyrin **5** (or **6** or **7**) in dichloromethane (0.44 mmol in 50 mL) were added dimethylformamide (2.5 mL, 32 mmol) and phosphorus oxychloride (2.5 mL, 27 mmol). The rapid consumption of the starting material was followed by silica gel TLC, and after approximatively 10−15 min, the reaction was quenched with a saturated aqueous solution of sodium acetate. The organic phase was then washed with water (3 × 200 mL) and dried on sodium sulfate. After evaporation and crystallization from chloroform/methanol, the green nickel enaminoaldehyde **8** (or **9** or **10**) was obtained in 90% (or 85 or 87%) yield.

**8 (Ar = Phenyl).** $^1H$ NMR: $\delta$ = 9.35, 8.79 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.61, 8.59 (AB, 2H, $J$ = 5.1 Hz, pyrrole), 8.51, 8.53 (AB, 2H, $J$ = 4.8 Hz, pyrrole), 8.96 (dd, 1H, $J$ = 7.2 and 1.5 Hz, cyclized phenyl), 8.04 (dd, 1H, $J$ = 7.2 and 1.5 Hz, cyclized phenyl), 7.92−8.01 (m, 6H, $H_{ortho}$), 7.62−7.82 (m, 11H, $9H_{meta+para}$ + 2H cyclized phenyl), 12.51 (broad s, 1H, NH), 9.09 (s, 1H, CHO). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 446 ($\epsilon$ = 122 000), 560 (10 000), 626 (18 400). Anal. Calcd for $NiC_{45}N_5H_{27}O\cdot{}^1/_2CHCl_3$: C, 70.78; H, 3.59; N, 9.07. Found: C, 71.09; H, 3.68; N, 9.11.

**10 (Ar = 3,5-Di-*tert*-butylphenyl).** $^1H$ NMR: $\delta$ = 9.27, 8.80 (2d, 1 + 1H, $J$ = 5.0 Hz, pyrrole), 8.72, 8.65 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.57, 8.53 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.87 (d, 1H, $J$ = 1.8 Hz, cyclized phenyl), 8.04 (d, 1H, $J$ = 1.8 Hz, cyclized phenyl), 7.83, 7.81, 7.80 (3d, 6H, $H_{ortho}$), 7.73, 7.69, 7.66 (3t, 3H, $H_{para}$), 13.36 (broad s, 1H, NH), 8.91 (s, 1H, CHO), 1.97, 1.58 (2s,

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9+9H, *tert*-Bu), 1.47, 1.44, 1.43 (3s, 3 × 18H, *tert*-Bu). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 454 ($\epsilon$ = 114 000), 564 (10 000), 608 (12 600), 634 (21 000). Anal. Calcd for $NiC_{77}N_5H_{91}O$: C, 79.64; H, 7.90; N, 6.03. Found: C, 79.61; H, 8.05; N, 5.92.

**Nickel Enaminothioaldehyde 11.** A degassed benzene (50 mL) solution of nickel enaminoaldehyde **8** (150 mg, 0.21 mmol) and Lawesson's reagent (100 mg, 0.25 mmol) was heated under argon at 75 °C for 10 min. After cooling, the solution was poured on a short silica gel column and eluted with dichloromethane/hexane 1/1. Crystallization from dichloromethane/methanol afforded nickel enaminothioaldehyde **11** in 78% yield.

**11 (Ar = phenyl).** $^1$H NMR: $\delta$ = 9.31, 8.77 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.55, 8.48 (2d, 2H, $J$ = 5.1 Hz, pyrrole), 8.47, 8.49 (AB, 2H, $J$ = 5.1 Hz, pyrrole), 8.94 (dd, 1H, $J$ = 7.2 and 1.5 Hz, cyclized phenyl), 8.11 (dd, 1H, $J$ = 7.2 and 1.5 Hz, cyclized phenyl), 7.84 (m, 2H, cyclized phenyl), 7.89−7.98 (m, 6H, $H_{ortho}$), 7.61−7.74 (m, 9H, $H_{meta+para}$), 15.41 (broad s, 1H, NH), 10.37 (s, 1H, CHS). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 422 ($\epsilon$ = 61 000), 470 (118 000), 568 (9300), 598 (9700), 650 (22 300). Anal. Calcd for $NiC_{45}N_5H_{27}S\cdot{}^1/_2H_2O$: C, 73.29; H, 3.83; N, 9.50; S, 4.35. Found: C, 73.41; H, 3.72; N, 9.48; S, 4.41.

**Nickel Enaminothiocetone 12.** A solution of nickel enaminocetone **2** (273 mg, 0.26 mmol) and Lawesson's reagent (152 mg, 2.66 mmol) in benzene (150 mL) was heated under reflux until consumption of all starting material (approximatively 2 h). After evaporation of the solvent, the residue was chromatographed on a silica gel column (eluent: dichloromethane/hexane 1/1). After crystallization from dichloromethane/methanol, the green nickel enaminothioketone **12** was isolated in 97% yield (270 mg, 254 mmol).

**12.** $^1$H NMR: $\delta$ = 9.14, 8.70 (2d, 1 + 1H, $J$ = 5.0 Hz, pyrrole), 8.45, 8.30 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.42, 8.32 (2d, 1 + 1H, $J$ = 4.9 Hz, pyrrole), 9.12 (dd, 1H, $J$ = 8.1 and ∼1 Hz, cyclized phenyl), 8.14 (dd, 1H, $J$ = 8.1 and ∼1 Hz, cyclized phenyl), 7.74 (ddd, 1H, $J$ = 8.1, 8.1 and ∼1 Hz, cyclized phenyl). 7.53 (ddd, 1H, $J$ = 8.1, 8.1 and ∼1 Hz, cyclized phenyl), 7.80, 7.69, 7.67 (3t, 3 × 1H, $J$ = 1.8 Hz, $H_{para}$), 7.60−7.80 (broad, 6H, $H_{ortho}$), 12.18, 6.21 (broad. 1 + 1H, N−H), 1.46, 1.44, 1.43 (3s, 3 × 18H, *tert*-Bu). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 390 ($\epsilon$ = 51 000), 428 (59 000), 473 (46 000 sh), 496 (81 000), 654 (14 500 sh), 692 (22 000). Anal. Calcd for $NiC_{69}N_5H_{75}S$: C, 77.81; H, 7.10; N, 6.57. Found: C, 77.91; H, 7.11; N, 6.25.

**Nickel Ketoporphyrins 15 and 16.** The ketoporphyrin free bases were prepared according to the procedure described by Ishkov[19] and were metalated overnight in refluxing toluene in the presence of nickel(II) acetylacetonate. The raw material was purified by chromatography (short silica gel column, eluent dichloromethane) and crystallized from dichloromethane/methanol. Nickel ketoporphyrins **15** and **16** were isolated in 90% and 85% yield.

**15 (Ar = Phenyl).** $^1$H NMR (300 MHz, $CDCl_3$, 45 °C): $\delta$ = 8.89, 8.48 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.17, 8.07, 8.01, 7.98 (4d, 4 × 1H, $J$ = 4.8 Hz, pyrrole), 8.50 (s, 1H, additional ring), 8.46 (dd, 1H, $J$ = 7.5 and ∼1 Hz, cyclized phenyl), 8.15 (dd, 1H, $J$ = 7.5 and ∼1 Hz, cyclized phenyl), 7.50−7.93 (m, 17H, $6H_{ortho}$ + $9H_{meta+para}$ + 2H cyclized phenyl). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 406 ($\epsilon$ = 66 000), 462 (32600), 490 (34300), 657 (12000 sh), 720 (17000). Anal. Calcd for $NiC_{45}N_4H_{26}O\cdot{}^1/_2H_2O$: C, 76.51; H, 3.85; N, 7.93. Found: C, 76.78; H, 3.77; N, 8.02.

**16** (Ar = *p*-tolyl): $^1$H NMR: $\delta$ = 8.83, 8.47 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.17, 8.04 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.08, 7.97 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.40 (s, 1H, additional ring), 8.34 (d, 1H, $J$ = 8.4 Hz, cyclized phenyl), 7.91 (d, 1H, $J$ = 1.1 Hz, cyclized phenyl), 7.62 (dd, 1H, $J$ = 8.4 and 1.1 Hz, cyclized phenyl), 7.74 (d, 2H, $J$ = 7.7 Hz, tolyl), 7.69 (d, 2H, $J$ = 7.7 Hz, tolyl), 7.50 (d, 2H, $J$ = 7.7 Hz, tolyl), 7.35−7.47 (3d, 3 × 2H, tolyl), 2.60 (2s, 3+3H, Me), 2.58 (s, 3H, Me), 2.57 (s, 3H, Me). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 410 ($\epsilon$ = 70 300), 464 (32 200), 494 (33100), 666 (12500 sh), 716 (18700). Anal. Calcd for $NiC_{49}N_4H_{34}O\cdot H_2O$: C, 76.26; H, 4.70; N, 7.26. Found: C, 76.25; H, 4.33; N, 7.19.

**Nickel Enaminoketoporphyrins 17 and 18.** A solution of nickel ketoporphyrin **15** (or **16**) (0.057 mmol), sodium hydroxide (0.2 g, 5 mmol) and 4-amino-4*H*-1,2,4-triazole (160 mg, 1.9 mmol) in a mixture of toluene and ethanol (50 and 5 mL) was heated under reflux for 5 h. After cooling, trifluoroacetic acid (1 mL, 13 mmol) was added and the solution refluxed for an additional hour. The reaction medium was concentrated on a rotary evaporator and dichloromethane (150 mL) added. The organic phase was then washed three times with water and dried with sodium sulfate. Chromatography on silica gel (eluent: dichloromethane/ethyl acetate from 0 to 10%) and crystallization from dichloromethane/methanol afforded green nickel enaminoketone **17** (or **18**) in 61% (or 83%) yield.

**17 (Ar = Phenyl).** $^1$H NMR (300 MHz, $CDCl_3$, 45 °C): $\delta$ = 8.89, 8.51 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.28, 8.22, 8.16, 8.10 (4d, 4 × 1H, $J$ = 4.8 Hz, pyrrole), 8.36 (dd, 1H, $J$ = 8.0 and ∼1 Hz, cyclized phenyl), 7.95 (dd, 1H, $J$ = 7.7 and ∼1 Hz, cyclized phenyl), 7.72 (ddd, 1H, $J$ = 7.8, 7.8 and ∼1 Hz, cyclized phenyl). 7.45 (ddd, 1H, $J$ = 7.8, 7.8 and ∼1 Hz, cyclized phenyl), 7.80−7.93 and 7.54−7.78 (m, 15H, *meso* phenyl). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 414 ($\epsilon$ = 51 000), 450 (52 000), 476 (64 000), 624 (12 000 sh), 650 (15 000 sh), 678 (23 000). Anal. Calcd for $NiC_{45}N_5H_{27}O\cdot H_2O$: C, 73.99; H, 4.00; N, 9.59. Found: C, 74.23; H, 3.76; N, 9.61.

**18 (Ar = *p*-Tolyl).** $^1$H NMR: $\delta$ = 8.90, 8.57 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.29, 8.21 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.25, 8.11 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.27 (d, 1H, cyclized phenyl), ∼7.76 (d, 1H, cyclized phenyl), 7.60 (dd, 1H, cyclized phenyl), 7.70−7.82 (m, 4H, tolyl), 7.54−7.65 (m, 2H, tolyl), 7.37−7.50 (m, 6H, tolyl), 2.60 (2s, 3 + 3H, Me), 2.58 (s, 3H, Me), 2.52 (s, 3H, Me). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 416 ($\epsilon$ = 54 800), 452 (54 000), 480 (69 600), 622 (12 600 sh), 654 (18 900 sh), 678 (26 400). Anal Calcd for $NiC_{49}N_5H_{35}O\cdot H_2O$: C, 74.82; H, 4.74; N, 8.90. Found: C, 75.02; H, 4.50; N, 8.84.

**Palladium Dimer 26.** To a solution of nickel enaminoaldehyde **8** (40 mg, 0.056 mmol) in 1,2-dichloroethane (30 mL) was added dropwise (1.5 h of addition) at 60 °C under argon a solution of palladium(II) acetate (8 mg, 0.035 mmol) in 1,2-dichloroethane (15 mL). The advancement of the reaction was followed by silica gel TLC (eluent: hexane/dichloromethane 1/1). After 18 h, the solvent was evaporated and the residue chromatographed on a silica gel column (eluent: tetrachloromethane/dichloromethane from 4/1 to 1/1). After crystallization from dichloromethane/methanol, dimer **26** was obtained in 75% yield. Alternatively, when the reaction was stopped after 30−40% conversion, rapid evaporation of the solvent followed by rapid chromatography on a silica gel column (same conditions as before) and evaporation of the elution solvents afforded a solid containing 90−95% of the trans isomer **24** (or **25** in the case of the *p*-tolyl derivative). See Supporting Information for the NMR characterization of this unstable isomer.

**24 (Trans, Ar = Phenyl).** $^1$H NMR (300 MHz, $C_2D_2Cl_4$, 45 °C): $\delta$ = 9.30, 8.75 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 8.61, 8.49 (2d, 2 + 2H, $J$ = 5.1 Hz, pyrrole), 8.42, 8.37 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 8.85 (dd, 2H, $J$ = 7.8 and 1.2 Hz, cyclized phenyl), 8.72 (dd, 2H, $J$ = 7.8 and 1.2 Hz, cyclized phenyl), 8.04 (m, 8H, $H_{ortho}$), 7.93 (m, 4H, $H_{ortho}$), 7.82 (m, 8H, cyclized phenyl +

$H_{meta+para}$), 7.73 (m, 8H, cyclized phenyl + $H_{meta+para}$), 7.67 (m, 6H, $H_{meta+para}$), 7.35 (s, 2H, CHO).

**26 (Cis, Ar = Phenyl).** $^1$H NMR (500 MHz, $C_2D_2Cl_4$, 65 °C): $\delta$ = 9.20, 8.85 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 8.59, 8.53 (2d, 2 + 2H, $J$ = 5.1 Hz, pyrrole), 8.47, 8.40 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 8.44 (dd, 2H, $J$ = 7.8 and 1.2 Hz, cyclized phenyl), 7.71 (dd, 2H, $J$ = 7.8 and 1.2 Hz, cyclized phenyl), 7.42 (ddd, 2H, $J$ = 7.8, 7.6, and 1.2 Hz, cyclized phenyl), 6.69 (ddd, 2H, $J$ = 7.8, 7.6, and 1.2 Hz, cyclized phenyl), 8.09 (broad m, 8H, $H_{ortho}$), 7.96 (broad m, 4H, $H_{ortho}$), 7.84, 7.76, 7.67 (3m, 3 × 6H, $H_{meta+para}$), 7.78 (s, 2H, CHO). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 415 ($\epsilon$ = 84 000 sh), 450 (139 000 sh), 478 (196 000), 560 (25 400), 622 (21 000), 668 (38 300). Anal. Calcd for $PdNi_2C_{90}N_{10}H_{52}O_2 \cdot H_2O$: C, 69.86; H, 3.52; N, 9.05. Found: C, 70.01; H, 3.53; N, 8.82.

**Palladium(II) Dimers 22 (or 23) and Palladium(II) Metalated 20 (or 21).** To a solution of palladium(II)acetylacetonate (150 mg, 0.492 mmol) in chloroform (25 mL) heated at 60 °C was added dropwise (addition over 8 h) a solution of nickel porphyrin **17** (or **18**) (40 mg, 0.056 mmol) in chloroform (15 mL). The solvent was evaporated, and the solid residue was taken up in a mixture of dichloromethane/hexane 1/1. The less soluble dimer **22** (or **23**) was isolated by filtration in 77% (or 75%) yield. The filtrate was concentrated and chromatographed on silica gel (eluent: dichloromethane/hexane 1/1 to dichloromethane). The metalated monomer **20** (or **21**) was obtained, after crystallization from dichloromethane/methanol, in 16% (or 15%) yield.

**22 (Ar = Phenyl).** $^1$H NMR (300 MHz, $C_2D_2Cl_4$, 75 °C): $\delta$ = 9.19, 8.72 (2d, 2 + 2H, $J$ = 5.1 Hz, pyrrole), 8.49, 8.38 (2d, 2 + 2H, $J$ = 5.0 Hz, pyrrole), 8.47, 8.30 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 8.37 (broad dd, 2H, cyclized phenyl), 8.26 (broad dd, 2H, cyclized phenyl), 7.86 (broad ddd, 2H, cyclized phenyl). 7.71 (broad ddd, 2H, cyclized phenyl), 7.95−8.10, 7.80−7.92 and 7.62−7.78 (m, 30H, *meso* phenyl), 7.35 (broad s, 2H, NH). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 416 ($\epsilon$ = 60 000), 450 (93 000 sh), 472 (127 000 sh), 486 (136 000), 608 (25 000), 640 (27 000), 662 (31 000). Anal. Calcd for $PdNi_2C_{90}N_{10}H_{52}O_2 \cdot CH_3OH$: C, 70.01; H, 3.62; N, 8.97. Found: C, 70.02; H, 3.52; N, 8.65.

**23 (Ar = *p*-Tolyl).** $^1$H NMR (500 MHz, $C_2D_2Cl_4$, 80 °C): $\delta$ = 9.23, 8.78 (2d, 2 + 2H, $J$ = 5.2 Hz, pyrrole), 8.51, 8.40 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 8.50, 8.40 (2d, 2 + 2H, $J$ = 4.5 Hz, pyrrole), 8.16 (d, 2H, $J$ = 7.6 Hz, cyclized phenyl), 7.99 (d, 2H, $J$ ~ 1 Hz, cyclized phenyl), 7.66 (dd, 2H, $J$ = 7.6 and 1 Hz, cyclized phenyl), 7.86, 7.91, and 7.92 (3d, 3 × 4H, $J$ = 7.7 Hz, tolyl), 7.49, 7.52, and 7.69 (3d, 3 × 4H, $J$ = 7.7 Hz, tolyl), 2.64, 2.65, 2.67, and 2.84 (4s, 4 × 6H, Me). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 418 ($\epsilon$ = 56 000), 486 (129 000), 610 (28 400), 664 (35 300). Anal. Calcd for $PdNi_2C_{98}N_{10}H_{68}O_2 \cdot 2H_2O$: C, 70.17; H, 4.33; N, 8.35. Found: C, 70.27; H, 4.06; N, 8.28.

**20 (Ar = Phenyl).** $^1$H NMR (300 MHz, $CDCl_3$, 45 °C): $\delta$ = 9.09, 8.65 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.41, 8.29 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.37, 8.35 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), ~8.20 (broad dd, 1H, cyclized phenyl), ~8.10 (broad dd, 1H, cyclized phenyl), ~7.69 (broad ddd, 1H, cyclized phenyl). ~7.40 (broad ddd, 1H, cyclized phenyl), 7.58−7.96 (m, 15H, *meso* phenyl), ~7.40 (broad s, 1H, NH), 5.43 (s, 1H, acac), 2.10, 2.09 (2s, 3 + 3H, Me acac). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 412 ($\epsilon$ = 38 400), 446 (62 000 sh), 466 (85 000 sh), 606 (11 000), 636 (14 000), 658 (19 200). Anal. Calcd for $PdNiC_{50}N_5H_{33}O_3 \cdot H_2O$: C, 64.23; H, 3.77; N, 7.49. Found: C, 64.10; H, 3.48; N, 7.43.

**21 (Ar = *p*-Tolyl).** $^1$H NMR (300 MHz, $CDCl_3$, 45 °C): $\delta$ = 9.08, 8.66 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.43, 8.29 (2d, 1 + 1H, $J$ = 4.8 Hz, pyrrole), 8.39, 8.34 (2d, 1 + 1H, $J$ = 5.1 Hz, pyrrole), 8.11 (d, 1H, $J$ = 8.0 Hz, cyclized phenyl), 7.93 (d, 1H, $J$ = 1 Hz, cyclized phenyl), 7.55 (dd, 1H, $J$ = 8.0 and 1.0 Hz, cyclized phenyl), 7.78 (2d, 2 + 2H, $J$ = 7.7 Hz, *meso*-aryl), 7.69 (d, 2H, $J$ = 7.7 Hz, *meso*-aryl), 7.43 (2d, 2 + 2H, $J$ = 7.7 Hz, *meso*-aryl), 7.42 (d, 2H, $J$ = 7.7 Hz, *meso*-aryl), 7.39 (s, 1H, NH), 5.45 (s, 1H, acac), 2.55, 2.58, 2.59, and 2.61 (4s, 4 × 3H, Me tolyl), 2.11, 2.09 (2s, 3 + 3H, Me acac). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 414 ($\epsilon$ = 39 600), 470 (93 300), 606 (11 400), 658 (21 800). Anal. Calcd for $PdNiC_{54}N_5H_{41}O_3 \cdot {}^1/_2H_2O$: C, 66.04; H, 4.31; N, 7.13. Found: C, 66.00; H, 4.17; N, 7.04.

**Palladium Dimer 19.** To a degassed solution of nickel enaminothioketone **12** (30 mg, 0.028 mmol) in chloroform (15 mL) was added dropwise at 50 °C a solution of palladium(II) acetate (4 mg, 0.018 mmol) in chloroform (10 mL). After consumption of all starting material, the solvent was evaporated and dimer **19** isolated by crystallization from dichloromethane/methanol in 89% yield (28 mg, 0.0125 mmol).

**19**: $^1$H NMR (300 MHz, $CDCl_3$, 40 °C): $\delta$ = 9.03, 8.61 (2d, 2 + 2H, $J$ = 5.0 Hz, pyrrole), 8.35, 8.04 (2d, 2 + 2H, $J$ = 5.1 Hz, pyrrole), 8.26, 8.16 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 9.32 (dd, 2H, $J$ = 7.8 and ~1 Hz, cyclized phenyl), 8.38 (dd, 2H, $J$ = 7.8 and ~1 Hz, cyclized phenyl), 7.89 (ddd, 2H, $J$ = 7.8, 7.8 and ~1 Hz, cyclized phenyl). 7.80 (ddd, 2H, $J$ = 7.8, 7.8 and ~1 Hz, cyclized phenyl), 8.27, 7.69, 7.65 (3t, 3 × 2H, $J$ = 1.8 Hz, $H_{para}$), 7.60−7.90 (broad m, 12H, $H_{ortho}$), 8.49 (broad s, 2H, N−H), 1.57, 1.48, 1.43 (3s, 3 × 36H, *tert*-Bu). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 396 ($\epsilon$ = 71 000), 450 (94 000), 524 (124 000), 654 (30 000), 682 (29 400), 732 (30 000). Anal. Calcd for $PdNi_2C_{138}N_{10}H_{148}S_2 \cdot 3H_2O$: C, 72.42; H, 6.78; N, 6.12. Found: C, 72.44; H, 6.68; N, 5.81.

**Palladium Dimer 28.** To a solution of nickel enaminothioaldehyde **11** (72 mg, 0.1 mmol) in dichloromethane (30 mL) was added dropwise (1.5 h of addition) at 60 °C under argon a solution of palladium(II) acetate (12 mg, 0.053 mmol) in dichloromethane (15 mL). The advancement of the reaction was followed by silica gel TLC (eluent: hexane/dichloromethane 1/1). The solvent was evaporated and the residue chromatographed on a silica gel column (eluent: hexane/dichloromethane from 3/1 to 1/1). After crystallization from chloroform/methanol, dimer **28** was obtained in 77% yield.

**28.** $^1$H NMR (400 MHz, $C_2D_2Cl_4$, 85 °C): $\delta$ = 9.07, 8.80 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 8.52, 8.48 (2d, 2 + 2H, $J$ = 5.1 Hz, pyrrole), 8.40, 8.37 (2d, 2 + 2H, $J$ = 4.8 Hz, pyrrole), 8.38 (dd, 2H, $J$ = 7.8 and 1.2 Hz, cyclized phenyl), 7.95 (dd, 2H, $J$ = 7.8 and 1.2 Hz, cyclized phenyl), 7.29 (ddd, 2H, $J$ = 7.8, 7.6, and 1.2 Hz, cyclized phenyl), 6.14 (ddd, 1H, $J$ = 7.8, 7.6, and 1.2 Hz, cyclized phenyl), 7.94−8.08 (m, 12H, $H_{ortho}$), 7.67, 7.76, 7.85 (3m, 3 × 6H, $H_{meta+para}$), 8.18 (s, 2H, CHS). UV−vis ($CH_2Cl_2$): $\lambda_{max}$ = 432 ($\epsilon$ = 120 000), 506 (146 000), 572 (24 000), 628 (17 800), 714 (27 600). Anal. Calcd for $PdNi_2C_{90}N_{10}H_{52}S_2 \cdot {}^1/_2CHCl_3$: C, 67.05; H, 3.26; N, 8.64. Found: C, 67.20; H, 3.25 N, 8.63.

**Electrochemical Studies.** Dichloromethane was purchased spectroscopic grade from Merck, dried over molecular sieves (4 Å), and stored under argon prior to use. $NBu_4PF_6$ was purchased electrochemical grade from Fluka and used as received. The electrochemical experiments were carried out at room temperature in dichloromethane containing 0.1 M $NBu_4PF_6$ in a classical three-electrode cell. The working electrode was either a glassy carbon disk electrode (3 mm diameter) or a platinum disk electrode (2 mm diameter) used either in motionless mode for cyclic voltammetry (CV: 10 mV·s$^{-1}$ to 10 V·s$^{-1}$) or as rotating disk electrode for rotating disk voltammetry (RDV). The electrochemical cell was connected to a computerized multipurpose electrochemical device, AUTOLAB (Eco Chemie BV−Utrecht, The Netherlands), driven

by GPES software running on a personal computer. All potentials are referenced to the ferrocene/ferrocenium ($Fc/Fc^+$) couple used as an internal standard. The auxiliary electrode was a Pt wire, and a Pt wire was also used as a pseudo-reference electrode. The accessible potentials ranged from +1.2 to −2.4 V vs $Fc/Fc^+$ in dichloromethane.

**Crystal Data for Nickel Enaminoporphyrin 5.** $C_{44}H_{27}N_5Ni \cdot CH_2Cl_2$, $M = 769.38$, triclinic, space group $P\bar{1}$, $a = 10.2958(2)$ Å, $b = 10.5646(3)$ Å, $c = 16.7828(5)$ Å, $\alpha = 102.178(5)°$, $\beta = 92.441(5)°$, $\gamma = 97.380(5)°$, $V = 1765.04(8)$ Å$^3$, $Z = 2$, and $D_c = 1.45$ g cm$^{-3}$. A total of 13 037 $\pm h \pm k + l$ reflections were collected on a green crystal of dimensions 0.10 × 0.08 × 0.08 mm$^3$, using a KappaCCD diffractometer, graphite-monochromated Mo Kα, $2.5 < \theta < 29.10°$, and temperature 173 K. A total of 6790 unique reflections having $I > 3\sigma(I)$ were used to determine and refine the structure. Final results: $R = 0.068$, $R_w = 0.086$, GOF = 1.248, and largest peak in final difference = 0.907 e Å$^{-3}$.

**Crystal Data for Nickel Enaminoaldehyde 8.** $2(C_{45}H_{27}N_5NiO) \cdot CH_2Cl_2 \cdot H_2O$, $M = 1527.87$, monoclinic, space group $P12_1/c1$, $a = 22.5313(3)$ Å, $b = 9.6798(2)$ Å, $c = 17.6195(6)$ Å, $\beta = 107.796(5)°$, $V = 3658.9(2)$ Å$^3$, $Z = 2$, and $D_c = 1.39$ g cm$^{-3}$. A total of 16 565 $\pm h \pm k + l$ reflections was collected on a crystal of dimensions 0.25 × 0.04 × 0.02 mm$^3$, using a KappaCCD diffractometer, graphite-monochromated Mo Kα, $2.5 < \theta < 29.13°$, and temperature 173 K. A total of 5232 unique reflections having $I > 3\sigma(I)$ were used to determine and refine the structure. Final results: $R = 0.052$, $R_w = 0.070$, GOF = 1.039, and largest peak in final difference = 1.183 e Å$^{-3}$.

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**Supporting Information Available:** X-ray data for compounds **5** and **8** (CIF file), text giving the NMR data for the tolyl derivatives **6**, **9**, and **25** (relevant NOE correlations from the ROESY spectrum of **25**, demonstrating that **25** is the trans isomer), and figures giving the electronic spectra of monomer **8** and dimer **26**, electronic spectra of dimer **26** before and during electrolysis, MALDI−TOF spectra of dimers **23** and **28**, and X-ray structures of enamine **5** and enaminoaldehyde **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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