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Syntheses and Optical and Electrochemical Properties of Porphyrin Dimers Linked by Metal Ions

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Abstract: The preparation, isolation, and characterization of several new peripherally functionalized monomeric porphyrins and metalloporphyrins and of porphyrin dimers are described. These dimers are obtained by linking with metal ions two monomeric porphyrins bearing at their periphery an enaminoketone chelate fully conjugated with the aromatic ring. Porphyrin dimers linked by metal ions display large interactions in the ground state as evidenced by their electronic spectra and their electrochemical behavior. Compared to the monomeric analogue, these dimers show absorption spectra with intensified red-shifted Q-bands and their first oxidation potentials are substantially lowered and split into two distinct redox steps.

Introduction

Tetrapyrrolic macrocycles, such as porphyrins, and their metal complexes are involved in many biological processes, namely, molecular catalysis, electron transfer, binding or transport of small molecules, light harvesting, and photosynthesis. Model systems for these biological systems have been developed by numerous research groups.[1] However, the development of efficient syntheses of the appropriate tetrapyrrolic macrocycles still remains a major problem. Recently, the potential use of porphyrins or oligoporphyrins as new molecular materials has also led to an increase of the synthetic efforts toward artificial porphyrin assemblies.[2] The building of larger arrays (covalently linked porphyrin oligomers) presents an even greater synthetic challenge.[3] These syntheses have culminated in the preparation of a linear array of 128 porphyrins[4] or a molecular bandana made of 21 covalently linked porphyrins.[5] Keeping in mind the potential use of these systems as new materials, the efficiency of the syntheses (less than 1% for the 21-mer) has to be improved markedly before practical applications might be considered.

For many potential applications, interactions between the linked porphyrins are necessary. With the notable exceptions of acetylenic or ethylenic linkages,[6] single connections between two porphyrinic rings do not lead to substantial interactions in the ground state. Therefore, multiply linked systems have been prepared in which the properties of the assembly are no longer

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(1) (a) Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds; Academic Press: Boston, MA, 2000; Vol. 6, p 1. (b) Sanders, J. K. M. in ref 1a: Vol. 3, p 347. (c) Fukuzumi, S. in ref 1a: Vol. 8, p 115. (d) Gust, D.; Moore, T. A.in ref 1a: Vol. 8, p 153. (e) Barbe, J.-M.; Guilard, R.in ref 1a: Vol. 3, p 211. (f) Chou, J.-H.; Kosal, M. E.; Nalwa, H. S.; Rakow, N. A.; Suslick, K. S.in ref 1a: Vol. 6, p 43.

(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. Osuka, A.; Shimidzu, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 135. Nakano, A.; Osuka, A.; Yamazaki, I.; Yamazaki, T.; Nishimura, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3023. Nakano, A.; Yamazaki, T.; Nishimura, Y.; Yamazaki, I.; Osuka, A. *Chem. Eur. J.* **2000**, *6*, 3254. Kim, Y. H.; Jeong, D. H.; Kim, D.; Jeoung, S. C.; Cho, H. S.; Kim, S. K.; Aratani, N.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 76. Khoury, R. G.; Jaquinod, L.; Smith, K. M. *Chem. Commun.* **1997**, 1057. Khoury, R. G.; Jaquinod, L.; Nurco, D. J.; Pandey, R. K.; Senge, M. O.; Smith, K. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2496. Dubowchik, C. M.; Hamilton, A. D. *J. Chem. Soc. Chem. Commun.* **1986**, 1391. Dubowchik, C. M.; Hamilton, A. D. *J. Chem. Soc. Chem. Commun.* **1987**, 293. Arnold, D. P.; Hartnell, R. G. *Tetrahedron*, **2001**, *57*, 1335. Arnold, D.; Johnson, A. W.; Winter, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1643. Blake, I. M.; Rees, L. H.; Claridge, T. D. W.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1818. Anderson, H. L.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1400. Anderson, S.; Anderson, H. L.; Sanders, J. K. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2247. Mak, C. C.; Pomeranc, D.; Montalti, M.; Prodi, L.; Sanders, J. K. M. *Chem. Commun.* **1999**, 1083. Mak, C. C.; Bampos, N.; Sanders, J. K. M. *Chem. Commun.* **1999**, 1085. Sessler, J. L.; Capuano, V. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1134. Wennerstrom, O.; Ericson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett.* **1989**, *30*, 1129. Hammel, D.; Erk, P.; Schuler, B.; Heinze, J.; Mullen, K. *Adv. Mater.* **1992**, *4*, 737. Ponomarev, G. V.; Borovkov, V. V.; Sugiura, K.; Sakata, Y.; Shul′ga, A. M. *Tetrahedron Lett.* **1993**, *34*, 2153. Li, F.; Yang, S. I.; Ciringh, Y.; Seth, J.; Martin, C. H., III; Singh, D. L.; Kim, D.; Birge, R. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **1998**, *120*, 10001. Prathapan, S.; Johnson, T. E.; Lindsey, J. S. *J. Am. Chem. Soc.* **1993**, *115*, 7519. Belcher, W. J.; Burrell, A. K.; Campbell, W. M.; Officer, D. L.; Reid, D. C. W.; Wild, K. Y. *Tetrahedron*, **1999**, *55*, 2401. Burrell, A. K.; Officer, D. L. *Synlett* **1998**, 1297. Milgrom, L. R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2535. Beavington, R.; Burn, P. L. *J. Chem. Soc., Perkin Trans. 1* **2000**, 605 and 1231. Duggan, S. A.; Fallon, G.; Langford, S. J.; Lau, V.-L.; Satchell, J. F.; Paddon-Row, M. N. *J. Org. Chem.* **2001**, *66*, 4419. Norsten, T.; Branda, N. *Chem. Commun.* **1998**, 1258. Susumu, K.; Shimidzu, T.; Tanaka, K.; Segawa, H. *Tetrahedron Lett.* **1996**, *37*, 8399. Mongin, O.; Gossauer, A. *Tetrahedron* **1997**, *53*, 6835.

(4) (a) Aratani, N.; Osuka, A.; Kim, Y. H.; Jeong, D. H.; Kim, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1458. (b) Kim, Y. H.; Jeong, D. H.; Kim, D.; Jeoung, S. C.; Cho, H. S.; Kim, S. K.; Aratani, N.; Osuka, A. *J. Am. Chem. Soc.* **2001**, *123*, 76.

(5) Sugiura, K.-i.; Tanaka, H.; Matsumoto, T.; Kawai, T.; Sakata, Y. *Chem. Lett.*, **1999**, 1193.

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the simple sum of the properties of each porphyrin: these additional properties might lead to molecular materials for new applications.[7] However, the syntheses of multiply linked porphyrin oligomers becomes even more tedious than those of singly connected porphyrin oligomers.

On the other hand, one might use noncovalent bonds to build greater assemblies. Hydrogen bonds,[8] catenation of rings,[1a] metal-linked sandwich structures,[9] or coordination of porphyrin peripheral groups to metals have been used to build finite or infinite assemblies.[10] Linking the macrocycles through coordination bonds offers additional variations, with each metal center presenting specific properties: oxidation levels, coordination numbers, and geometries. However, most examples deal with porphyrins bearing *meso*-pyridinyl groups, since the wide coordination spectrum of the pyridine group allows large assemblies to be built. Due to noncoplanarity between the *meso*-pyridines and the porphyrin ring, one does not expect much information to be transmitted through the coordinated metal.

A porphyrin bearing a peripheral coordinating site, preferably with chelating properties and coplanar with the macrocycle, would combine the efficiency of the covalent approach in terms of porphyrin−porphyrin interaction and the modularity of the connection of porphyrins via metal coordination. In addition, since the formation of coordination bonds might be considered as a reversible reaction in many cases, if the different components of the assembly (metalloporphyrin as ligands and metal ions as connectors) are carefully chosen, one might reach the ideal case of a purely thermodynamically driven reaction whose yields should be very high. In these systems, the possibility of modulating the properties of the macrocycle through the internal coordination site still remains.

This approach has been successfully illustrated in the porphyrazin series: one or two chelating sites positioned on phenyl groups of benzoporphyrazin molecules have been used to obtain di- or trinuclear complexes with significant magnetic interactions between the different metal ions through the aromatic rings.[11]

We already briefly described the use of metal coordination to connect two porphyrins, leading to dimers with strong interactions between the two macrocycles as demonstrated by UV−visible spectroscopy and preliminary electrochemical experiments.[12] In this article, we present the synthesis of porphyrins bearing a peripheral enaminoketone moiety fully conjugated with the macrocyclic π-system, a set of related reactions, and the coordination properties of enaminoketoporphyrin ligands and demonstrate that strong porphyrin−porphyrin interactions can be detected spectroscopically and electrochemically when two such ligands are connected by a metal.

Preparation of Enaminoketones

Preparation of Ketones 1 and 2. The usual route to ketone **1** requires first the formylation of a metalloporphyrin under Vilsmeier−Haack conditions followed by acid-catalyzed cyclization of the aldehyde and demetalation of the porphyrin.[13] The cyclization reaction was usually run under the oxidative conditions described by Ishkov and Zhilina,[14] to optimize the conversion to the ketone. Demetalation had to be done carefully to avoid a second cyclization previously described by Dolphin and co-workers for *meso*-tetraanisylporphyrins.[15] The overall yield of this sequence is fair (∼50−60%; Scheme 1).

To improve the solubility of the porphyrinic oligomers we wished to prepare ketone **2**. However, specific achievement of such a substitution pattern of the *meso*-aryl groups, as well as

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(6) See, for example: (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) Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science*, **1994**, *264*, 1105. (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.

(7) (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) Sugiura, K.-i.; Matsumoto, T.; Ohkouchi, S.; Naitoh, Y.; Kawai, T.; Takai, Y.; Ushiroda, K.; Sakata, Y. *Chem. Commun.* **1999**, 1957.

(8) Drain, C. M.; Fischer, R.; Nolen, E. G.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 243. Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704. Drain, C. M.; Russell, K. C.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1996**, 337. Tamiaki, H. *Coord. Chem. Rev.* **1996**, *148*, 183. Tamiaki, H.; Miyatake, T.; Tanikaga, R.; Holzwarth, A. R.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 772. Jesorka, A.; Balaban, T. S.; Holzwarth, A. R.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2861. Bhyrappa, P.; Wilson, S. R.; Suslick, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 8492. Kobayashi, K.; Koyanagi, M.; Endo, K.; Masuda, H.; Aoyama, Y. *Chem. Eur. J.* **1998**, *4*, 417. Ikeda, C.; Nagahara, N.; Motegi, E.; Yoshioka, N.; Inoue, H. *Chem. Commun.* **1999**, 1759. Nagata, N.; Kugimiya, S.-i.; Kobuke, Y. *J. Chem. Soc., Chem. Commun.* **2000**, 1389. Goldberg, I. *Chem. Eur. J.* **2000**, *6*, 3863. Kosal, M. E.; Suslick, K. S. *J. Solid State Chem.* **2000**, *152*, 87. Drain, C. M.; Shi, X.; Milic, T.; Nifiatis, F. *J. Chem. Soc., Chem. Commun.* **2001**, 287.

(9) 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. III3, p 245.

(10) 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 ref 1a: Vol. 3, p 347. Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3606. Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727. Drain, C. M.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1994**, 2313. Hunter, C. A.; Sarson, L. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 359. Chi, X.; Guerin, A. J.; Haycock, R. A.; Hunter, C. A.; Sarson, L. D. *J. Chem. Soc., Chem. Commun.* **1995**, 2567. Harriman, A.; Odobel, F.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 9461. Crossley, M. J.; Burn, P. L.; Langford, S. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 1921. Yuan, H.; Thomas, L.; Woo, L. K. *Inorg. Chem.* **1996**, *35*, 2808. Hunter, C. A.; Hyde, R. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1936. Stang, P. J.; Fan, J.; Olenyuk, B. *J. Chem. Soc., Chem. Commun.* **1997**, 1453. Slone, R. V.; Hupp, J. T. *Inorg. Chem.* **1997**, *36*, 5422. Huck, W. T. S.; Rohrer, A.; Ailkumar, A. T.; Fokkens, R. H.; Nibbering, N. M. M.; Veggel, F. C. J. M. v.; Reinhoudt, D. N. *New J. Chem.* **1998**, *22*, 165. Drain, C. M.; Nifiatis, F.; Vasenko, A.; Batteas, J. D. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2344. Fan, J.; Whiteford, J. A.; Olenyuk, B.; Levin, M. D.; Stang, P. J.; Fleischer, E. B. *J. Am. Chem. Soc.* **1999**, *121*, 2741. Okumura, A.; Funatsu, K.; Sasaki, Y.; Imamura, T. *Chem. Lett.* **1999**, 779. Darling, S. L.; Mak, C. C.; Bampos, N.; Feeder, N.; Teat, S. J.; Sanders, J. K. M. *New J. Chem.* **1999**, *23*, 359. Vannelli, T. A.; Karpishin, T. B. *Inorg. Chem.* **1999**, *38*, 2246. Haycock, R. A.; Hunter, C. A.; James, D. A.; Michelsen, U.; Sutton, L. R. *Org. Lett.* **2000**, *2*, 2435. Michelsen, U.; Hunter, C. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 764. Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Barigelletti, F.; Flamigni, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1292. Rucareanu, S.; Mongin, O.; Schuwey, A.; Hoyler, N.; Gossauer, A.; Amrein, W.; Hediger, H.-U. *J. Org. Chem.* **2001**, *66*, 4973. Fujita, N.; Biradha, K.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1718.

(11) (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.

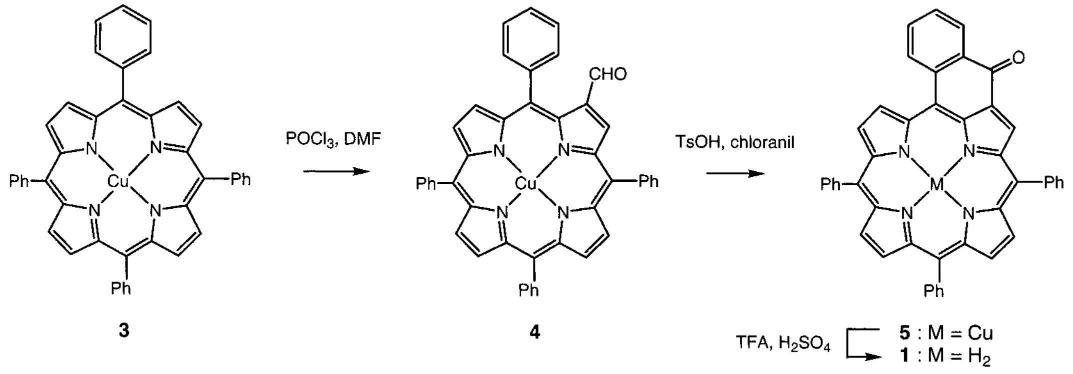
(12) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2001**, 91.

(13) (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.

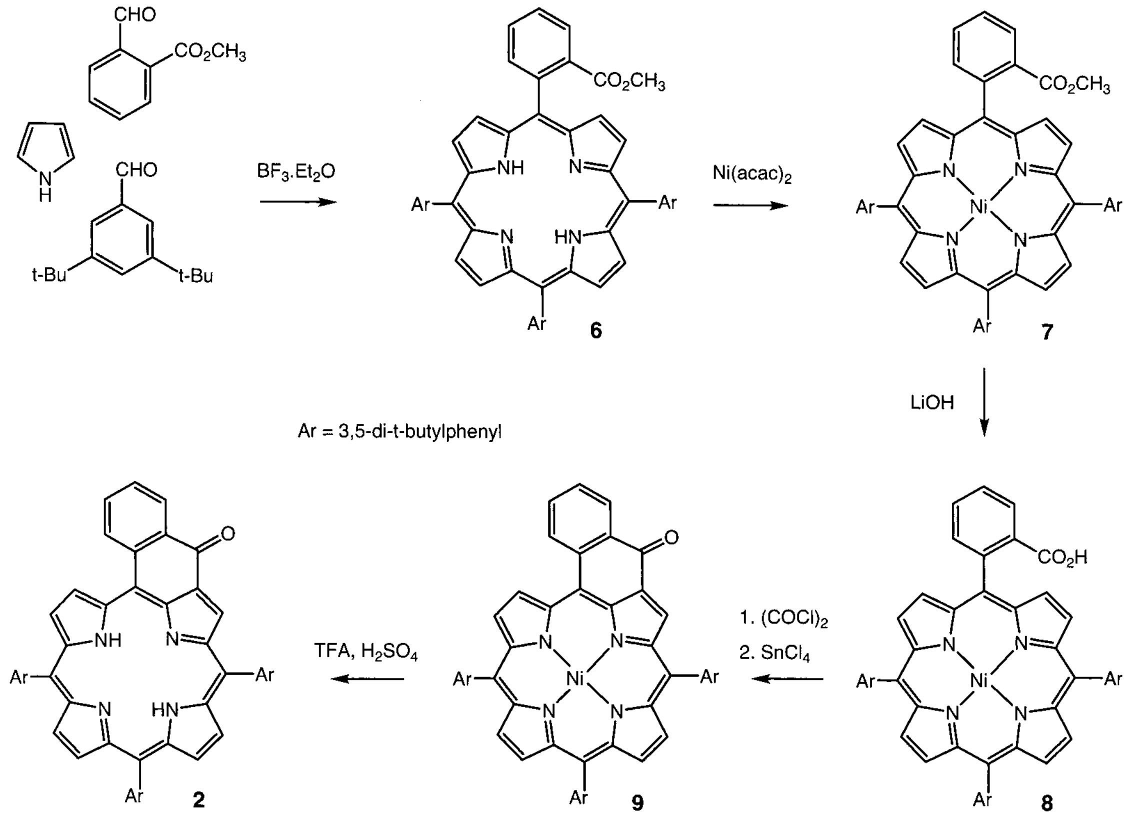
(14) Ishkov, Y. V.; Zhilina, Z. I. *Zh. Org. Khim.* **1995**, *31*, 136.

(15) Barloy, L.; Dolphin, D.; Dupré, D.; Wijesekera, T. P. *J. Org. Chem.* **1994**, *59*, 7976.

Scheme 1



Scheme 2



regiospecific formylation, is out of reach. Also, the use of symmetrical *meso*-tetra-di-*tert*-butylphenyporphyrin would end in an unwanted highly hindered coordination site. Last but not the least, the efficiency of the formylation route is limited by the fact that, under more drastic conditions, mixtures of polyformylporphyrins are obtained, thus limiting the scope of the reaction to the preparation of monoketones. The Friedel–Crafts reaction offered an alternative, provided that the appropriate groups could be positioned on a *meso*-phenyl group such that they could subsequently be cyclized onto a pyrrolic carbon (Scheme 2).

Porphyrin **6** was obtained under Lindsey's conditions[16] and isolated by chromatography from the mixture of esters. Hydrolysis of the ester group (LiOH in dioxane/water) and treatment of carboxylic acid **8** with oxalyl chloride in refluxing benzene gave the acid chloride, which was used as such. The Friedel–Crafts reaction proceeded in good yield when the acid chloride was treated with SnCl$_4$ in benzene to give ketone **9** (80–90% yield). The extension of this reaction sequence to obtain diketones from diesters will be presented elsewhere.

Amination of Ketones 1 and 2 and Related Reactions. The amination of ketones **1** or **2** is an easy reaction that occurred upon treatment with various nitrogen nucleophiles bearing a potential leaving group (Scheme 3) (only products due to 1,4-addition were observed):[17] hydroxylamine, hydrazine, tosylhydrazine, and hydroxylamine *O*-sulfonic acid. This last compound is the choice reagent, giving enaminoketones **10** and **17** in excellent yields (85–90%).

The NMR and UV–visible data for enaminoketone **10** are fully consistent with the proposed structure and very similar to

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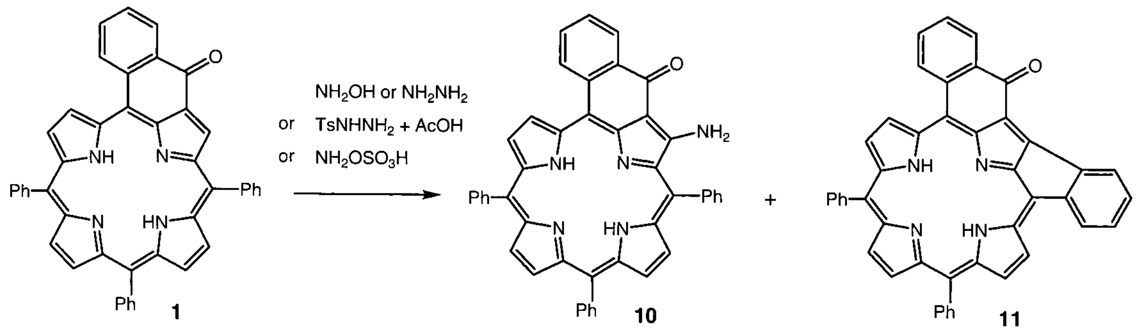
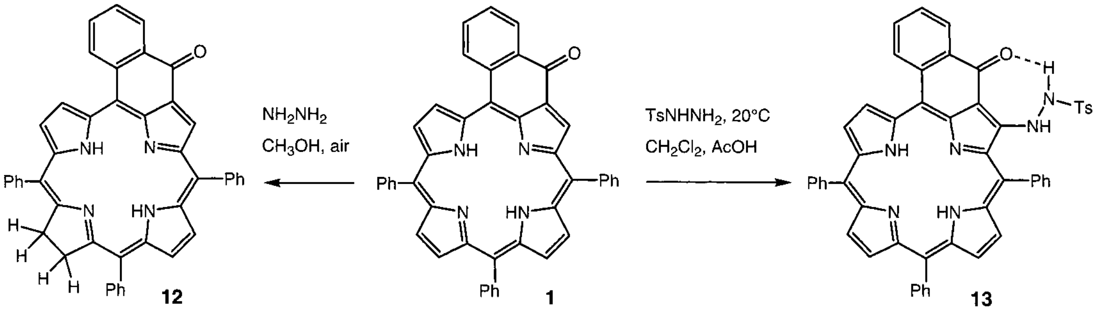
[16] Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827. Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864. Lindsey, J. S. in ref 1a: Vol. 1, p 45.

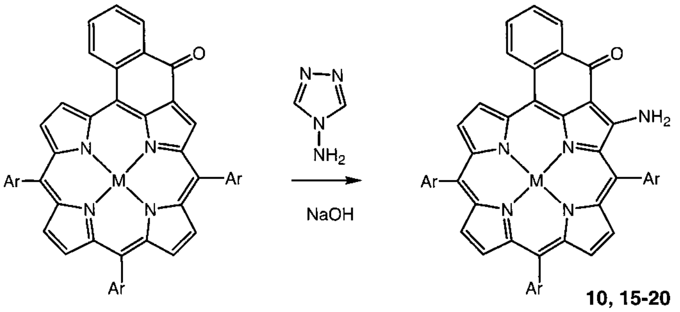
[17] Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Tetrahedron Lett.* **2001**, *42*, 2103.

Scheme 3



Scheme 4





10, 15-20

	M	Ar
10	H₂	Ph
15	Cu	Ph
16	Ni	Ph
17	H₂	3,5-di-t-butylPh
18	Cu	3,5-di-t-butylPh
19	Ni	3,5-di-t-butylPh
20	Pd	3,5-di-t-butylPh

that of ketone **1**, except for two NMR signals due to the NH_2 group instead of a pyrrolic singlet. These signals are far apart (9.0 and 5.48 ppm), suggesting that one proton ($\delta = 9.0$ ppm) is strongly hydrogen-bonded to the carbonyl oxygen atom, while the other one is shielded by the vicinal phenyl ring.

Small variations of the reaction conditions allowed us to illustrate the versatile reactivity of ketone **1** (Scheme 4). Replacement of AcOH by CH_3OH in the reaction of hydrazine resulted in the clean formation of chlorin **12**, arising from the reduction of a pyrrole double bond. Air oxidation of hydrazine to diimide was clearly the source of the reducing agent. As expected,[18] the pyrrole that was reduced is opposite to the functionalized one.

When run at room temperature rather than in refluxing CH_2Cl_2, the reaction with tosylhydrazine gave substituted tosylhydrazine **13** (see below for structural data for **13**). In this case, air oxidation—disfavored in a refluxing solvent—may occur faster than the elimination of tosylamide.

In addition to the products described above, all reactions run in acidic solutions, including the plain demetalation of ketone **1**, produced the same byproduct, namely, a doubly cyclized ketone **11** (already described by Dolphin et al.[15] for *meso*-anisyl-substituted porphyrins). The X-ray structure of the pyridinozinc complex of **11** has been solved.[17]

The amination reaction described above is limited to the free base porphyrins, and metal complexes do not react at all even under forcing conditions. 4-Amino-4*H*-1,2,4-triazole has been used as an amination reagent for pyridines and activated benzene rings in the presence of a strong base (t-BuOK).[19] We found that ketones **1** and **2** were aminated in high yield by this reagent, using NaOH as the base, and also that the reaction could be extended to the corresponding nickel, copper, and palladium complexes.

Crystal Structures of Monomeric Porphyrins. We could not obtain crystals of the aminoketones, either as free bases or as metal complexes, suitable for X-ray structure determination. However, related compounds possessing an additional ring gave suitable crystals and two corresponding structures were solved. A first structure determination, albeit of low resolution, was published for the copper complex of ketone **1** in 1980.[13a] During the course of this work, we determined the structure of chlorin **14**[14] (Figure 1) and tosylhydrazine **13**.

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(18) Crossley, M. J.; Burn, P. L.; Chew, S. S.; Cuttance, F. B.; Newsom, I. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1564.

(19) (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.

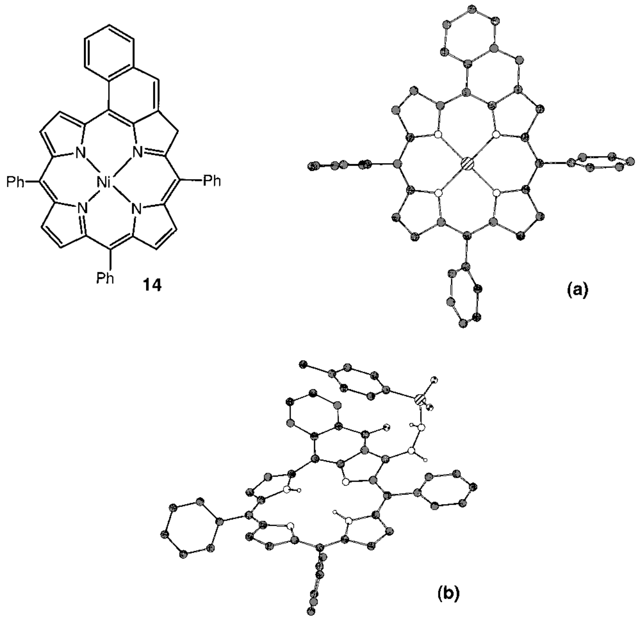


Figure 1. X-ray structures of (a) nickel chlorin **14** and (b) hydrazine **13** (all hydrogen atoms omitted except H−N).

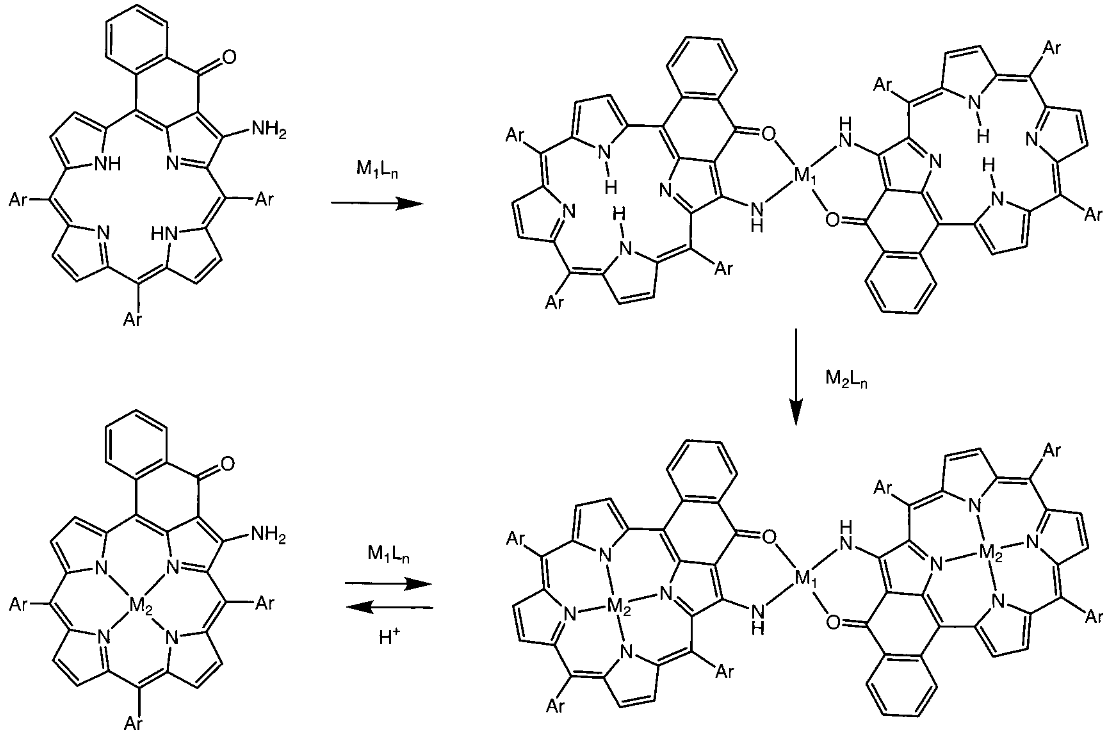
In addition to specific features, the two structures have in common a six-membered ring fused to the porphyrin at a meso- and a β-position. The major effect of this ring is to bring into the porphyrin plane the *meso*-phenyl to which it is bound and to enforce a close contact between one hydrogen of this phenyl and one of the closest noncyclized pyrrole rings (H−H = 2.127 Å in **13**, and 2.222 Å in **14**). A useful consequence of this proximity is a strong deshielding effect on the hydrogen of this last pyrrole, a NMR touchstone for cyclization.

The structure of tosylhydrazine **13** confirmed the stacking of the side chain and the porphyrin ring, which was suggested by the large NMR upfield shift of the tosyl signals (δ = 7.37 (ortho to SO_2 group), 5.94 (meta to SO_2 group), and 1.12 ppm for the aryl and methyl protons, respectively). This stacking is favored by the formation of a seven-membered ring including a hydrogen bond (O···H = 1.617 Å) between the NH vicinal to the tosyl group and the carbonyl oxygen. The general shape of the porphyrin ring of **13** and **14** is that of a saddle.

Preparation of Porphyrin Dimers. Dimers were assembled by several routes, either by exhaustive metalation of all sites of an enaminoketone free base, by coordination of two molecules of a metalloenaminoketone on a selected metal ion, or by selective coordination of a metal ion to the external sites of two enaminoketone free bases, followed by the metalation of the internal sites.

The most complex situation was observed upon direct metalation of enaminoketone free bases (Scheme 5). Reaction of **10** with 1 equiv of $Ni(acac)_2$ rapidly gave an insoluble dark material, believed to be the product of external coordination of two free bases and one nickel ion. Prolonged heating resulted in the formation of the porphyrin internal complex **16**. In the more soluble di-*tert*-butylphenyl series, the same sequence of reactions could be followed in solution, but the instability of the initial dimer (two free bases connected by one nickel ion) precluded its isolation. It was later observed that, although stable as solids, dimers connected by metals such as nickel, copper, or zinc decompose quantitatively upon attempted chromatography, or upon standing as dilute solutions. Actually, the simplest route for preparing **16** or **19** takes advantage of this unstability: heating enaminoketones **10** or **17** with an excess nickel acetylacetonate gave the fully metalated dimers which, in turn, were cleaved with acetic acid to give monomeric **16** or **19**. In the case of palladium, the internal metalation is much slower and the stability of the externally metalated dimer **26** (di-*tert*-

Scheme 5 [a]



[a] In order, meso group ($M_2/M_1/M_2$). **21**: Ph (Ni/Ni/Ni). **22**: Ph (Ni/Cu/Ni). **23**: Ph (Ni/Pd/Ni). **24**: Ph (Cu/Pd/Cu). **25**: Ph (Cu/Cu/Cu). **26**: 3,5-di-*tert*-butylphenyl (H_2/Pd/H_2). **27**: 3,5-di-*tert*-butylphenyl (Cu/Pd/Cu). **28**: 3,5-di-*tert*-butylphenyl (Pd/Pd/Pd). **29**: 3,5-di-*tert*-butylphenyl (Zn/Pd/Zn).

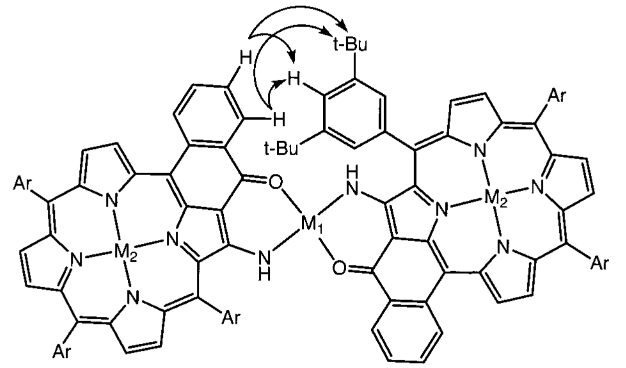


Figure 2. Relevant ROESY cross signals observed for **26**: M_1, Pd; M_2, H_2.

butylphenyl series) is sufficient to allow its isolation. Further heating slowly gave the internal metalation product and exhaustive metalation allowed the one-pot preparation of trimetallic dimer **28**.

Much simpler procedures were followed to specifically prepare dimers from previously metalated enaminoketones. Dimers were obtained by treating these monomeric metal complexes (M = Ni, Cu, Pd) with 0.5 equivalent of the corresponding metal derivative $M(OAc)_2$ (M = Cu, Pd) or $Ni(acac)_2$. On the other hand, the palladium complex **26** could be quantitatively metalated with zinc in the internal sites to give **29**, without cleaving the porphyrin-palladium-porphyrin connections.

None of the dimers yielded crystals suitable for a X-ray structure determination. For N−O ligands, and in particular for enaminoketones, it is known that in the solid state the square planar metal complexes were found with the trans geometry (centrosymmetric). In solution, the cis form might be present if the nitrogen is substituted with an H-atom.[20] No conclusions could be drawn from the electronic spectra, due to the presence of the strong bands of the porphyrins. The ^1H NMR spectra of the diamagnetic dimers showed that these compounds are present as one isomer. Whether the isomer is cis or trans could not be determined from the NMR spectra because of the high symmetry (center or plane of symmetry for respectively the trans and cis isomers) of these dimers.

However, $^1H-^1H$ COSY coupled with NOESY experiments unambiguously allowed structural determination. HH ROESY cross signals (see Figure 2, **26**) were observed between two protons of the cyclized phenyl and the para proton and the *tert*-butyl protons of a *meso*-aryl group belonging to the other porphyrin. We think that the cis isomer was never observed due to the proximity of the bulky *meso*-aryl group close to the N−H group. We assume that the paramagnetic dimers should have the same geometries as the diamagnetic ones.

Reaction of the nickelenaminoketones **16** or **19** with $Pd(acac)_2$ in excess led to **30** and **31** (see Scheme 6) along with traces of dimers. In this case, both nickelporphyrins are complexed at the periphery with a Pd(acac) fragment.

Electronic Spectra and Electrochemical Behavior. The electronic interactions between two connected porphyrin rings might be estimated from their electronic spectra. For covalent linkages, it is known that a 1,4-butadiynylene bridge allows electronic interactions (efficient π-overlap) whereas for a phenylene bridge (orthogonal to the porphyrin plane) only electrostatic interactions have been observed.[21] As a consequence, the modifications of the chromophore are more important for planar conjugated systems, in particular, for multiply covalently linked porphyrins.

Scheme 6

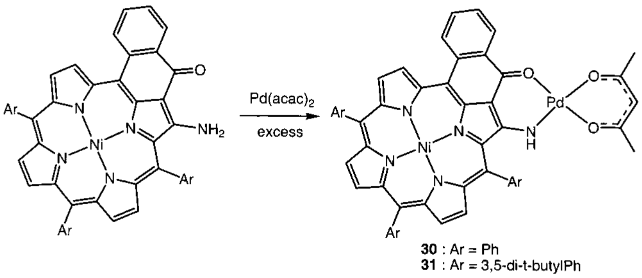


Table 1. Electronic Spectra: Lowest Energy Band for Monomers and Dimers

	λ_{max} (ϵ)	Δ*E* (eV)
monomer		
H_2 **10**	709 (7000)	1.75
Cu **15**	656 (25 000)	1.89
Ni **16**	649 (18 600)	1.91
H_2 **17**	711 (85 00)	1.74
Cu **18**	656 (30 500)	1.89
Ni **19**	650 (20 700)	1.90
Pd **20**	634 (31 600)	1.95
dimer		
Ni/Ni/Ni **21**	700 (32 800)	1.77
Ni/Cu/Ni **22**	677 (30 800)	1.83
Ni/Pd/Ni **23**	696 (47 100)	1.78
Cu/Pd/Cu **24**	696 (45 100)	1.78
Cu/Cu/Cu **25**	678 (59 600)	1.82
H_2/Pd/H_2 **26**	730 (39 000)	1.69
Cu/Pd/Cu **27**	696 (69 000)	1.78
Pd/Pd/Pd **28**	676 (79 400)	1.83
Zn/Pd/Zn **29**	696 (75 400)	1.78
Ni/Pd **30**	686 (25 200)	1.80
Ni/Pd **31**	686 (26 000)	1.80

These new porphyrin dimers all showed similar electronic spectra indicative of the interaction introduced between the two aromatic rings through the connecting metal. The lowest energy absorption bands for metalloporphyrin monomers were found between 634 and 656 nm, whereas for the dimers they were located between 676 and 700 nm (see Table 1 and Figure 3). A similar red-shift is observed for the two porphyrin bases linked by palladium(II). In addition to the bathochromic shift, the molar extinction coefficient value ϵ increases for the lowest energy band. For example, nickel complex **16** absorbs at 649 nm (ϵ = 18 600) and the dimer Ni/Pd/Ni **23** at 696 nm (ϵ = 47 100).

These effects are clearly a consequence of two cumulative factors. The coordination of a metal complex to the external site leads to a bathochromic shift of 37 nm (compare **16** and **30** in Table 1). Adding a second porphyrin leads to a further wavelength and extinction coefficient increase of the lowest energy band (compare **30** and **23** in Table 1). These effects have already been discussed for a nickel porphyrazine dimer.[11c] The distance between the two nickel ions in a dimer can be estimated quite precisely to be 14 Å from an X-ray structure of a related

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(20) See, for example: (a) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241. (b) Maverick, A. W.; Fronczek, F. R.; Martone, D. P.; Bradbury, J. R. *J. Coord. Chem.* **1989**, *20*, 149 and references therein.

(21) (a) Ribo, J. M.; Bofill, J. M.; Crusats, J.; Rubires, R. *Chem. Eur. J.* **2001**, *7*, 2733. (b) Piet, J. J.; Taylor, P. N.; Wegewijs, B. R.; Anderson, H. L.; Osuka, A.; Warman, J. *J. Phys. Chem. B* **2001**, *105*, 97 and references therein.

Table 2. Cyclic Voltammetry Data for Monomers and Dimers[a]

compound	E_{red3}	E_{red2}	E_{red1}	E_{Ox1}	E_{ox2}	E_{ox3}	$E_{ox1} - E_{red1}$
Cu **15**		−1.76(1)	−1.38(1)	0.46(1)	0.76(1)		1.84
Ni **16**		−1.63(1)	−1.26(1)	0.60(1)	0.95(1)		1.86
H_2 **17**		−1.65(1)	−1.36(1)	0.46(1)	0.72(1)		1.82
Cu **18**		−1.85(1)	−1.51(1)	0.39(1)	0.71(1)		1.90
Ni **19**[b]		−1.80(1)	−1.44(1)	0.45(1)	0.79(1)		1.89
Pd **20**			−1.45(1)	0.46(1)			1.91
Ni/Ni/Ni **21**	−1.90(1)	−1.80(1)	−1.37(2)	0.32(1)	0.48(1)	0.67(2)	1.69
Ni/Cu/Ni[b] **22**	−2.25(2)	−1.74(2)	−1.22(1)	0.30(1)	0.47(1)	0.82(2)	1.52
Ni/Pd/Ni **23**	−1.94(1)	−1.86(1)	−1.45(2)	0.32(1)	0.48(1)	0.82(2)	1.77
Cu/Pd/Cu **24**			−1.50(2)	0.29(1)	0.45(1)	0.75(2)	1.79
H_2/Pd/H_2 **26**			−1.50(2)	0.32(1)	0.45(1)	0.65(2)	1.82
Cu/Pd/Cu **27**			−1.52(2)	0.26(1)	0.42(1)	0.72(2)	1.78
Pd/Pd/Pd **28**	−2.10(1)	−1.90(1)	−1.48(2)	0.34(1)	0.50(1)	0.50(1)	1.82

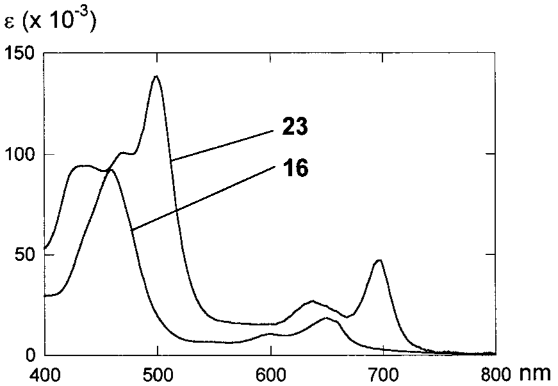

Figure 3. Comparison of the electronic spectra of monomer **16** (nickel enaminoketone) and dimer **23** (Ni/Pd/Ni).

compound.[22] Therefore, excitonic coupling alone cannot account for the large shift observed.[23] Since the metal fragment is coplanar with the porphyrin and the chelate fully conjugated with the macrocycle, the complexation has an effect similar to the addition of at least one fused benzene ring. The controversial concept of metalloaromaticity,[24a] first introduced by Calvin as early as 1945 for copper(acac)$_2$,[24b] might be invoked to explain the stability of our complexes and the optical properties displayed after anchoring a Pd(acac) fragment or a second porphyrin.

The electrochemical behavior of these porphyrins was studied by cyclic voltammetry and linear sweep voltammetry. All monomeric compounds, except palladium complex **20**, gave two well-defined one-electron reversible oxidation steps as well as two well-defined one-electron reversible reduction steps whose redox potentials are summarized in Table 2 and illustrated in Figure 4 for nickel complex **16**. In the case of **20**, only the first oxidation and the first reduction steps gave well-defined signals, whereas the second steps gave spreadout signals due to electrode inhibition. Compared to unfunctionalized metalloporphyrins, these compounds are easier to oxidize whereas their reductions occur at rather similar potentials. The potential difference between the first oxidation and the first reduction is equal to 1.85 ± 0.05 V. These values are much smaller than the ones reported for unfunctionalized porphyrins (2.25 ± 0.15 V)[25] and are in good agreement with the red shifts observed in the visible spectra of these compounds ($\lambda = 634-656$ nm/1.89−1.95 eV).

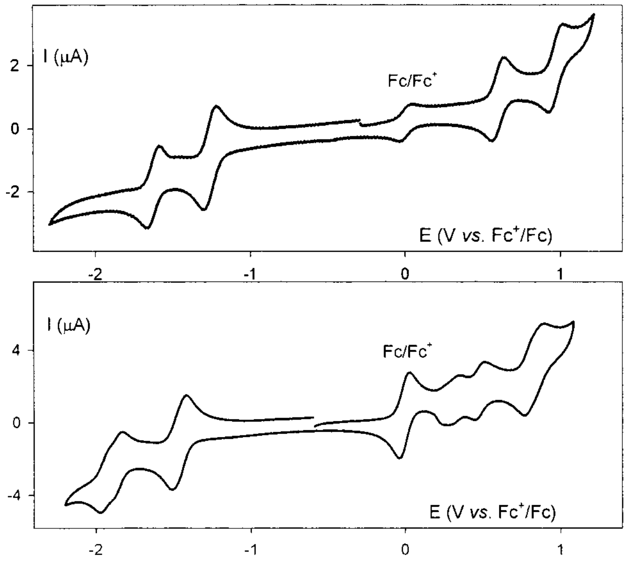

Figure 4. Cyclic voltammetry of monomer **16** (nickel enaminoketone) (top) and dimer **23** (Ni/Pd/Ni) (bottom). For experimental conditions, see Table 2.

With the exception of **22**, all dimeric species showed rather similar electrochemical behavior in CH_2Cl_2, illustrated in Figure 4 by the cyclic voltammetry of dimer **23**. The redox potentials of all compounds studied are summarized in Table 2. All electron transfers are chemically reversible. The first reduction step involves two overlapping one-electron steps on two almost independent redox centers,[26] whereas the second peak corresponds to the overlap of two one-electron transfers separated by 80−200 mV. The first two oxidation steps each involve one electron, whereas the third oxidation step shows the characteristics of two overlapping one-electron transfers separated by 40−60 mV. The oxidation yielded ligand-centered radical cations. These radical cations should be mainly localized near the external coordination site, since the region of the aromatic ring substituted by heteroatoms is the most susceptible site of the first electron removal. This leads to the lowering of the first oxidation potentials and to the rather large potential split (130−170 mV) observed between the first two one-electron oxidations.

"Significant redox splitting is a hallmark of strongly interacting ground-state redox centers and indicates that the resultant

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(22) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J. *Chem. Commun.* **2002**, 266.

(23) Kasha, M.; Rawls, H. R.; Ashraf El-Bayoumi, M. *Pure Appl. Chem.* **1965**, *11*, 371.

(24) (a) Masui, H. *Coord. Chem. Rev.* **2001**, *219−221*, 957 and references therein. (b) Calvin, M.; Wilson, K. W. *J. Am. Chem. Soc.* **1945**, *67*, 2003.

(25) Kadish, K. M.; Royal, G.; Van Caemelbecke, E.; Gueletti, L. in ref 1a: Vol. 9, p 1.

(26) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

charge ... is considerably delocalized over both porphyrin centers" was stated by Therien.[6f] To quantify more precisely the importance of the delocalization, compared to covalently linked dimers already known, one might compare the redox splitting values found in the metal-linked dimers with values reported in the literature. These interactions are extremely variable and the splitting values range from 0 to 0.44 V, depending on the type of connection used, where the connections were made, and how many connections were placed between the two porphyrins. For example, a butadiynyl β-pyrrole-linked dimer showed no splitting,[6f] whereas the same spacer between two meso positions gave a splitting value of 0.12 V. A simple *trans*-ethene or ethynyl meso−meso linkage gave respectively 0.1 or 0.26 V.[2b] Of course, the highest splitting values were reported for the triply fused dimers described by Osuka et al. since the distance between the two porphyrins is minimized (no spacer at all) and three connections were created. For this kind of dimer, the splitting values range from 0.25 to 0.44 V.[7i] We found redox splitting values in the range 0.13−0.17 V for metal-linked dimers, and thus the strength of the porphyrin-porphyrin interaction for this new type of connection might be placed between one double and one triple bond.

The potential difference between the first oxidation and the first reduction for the dimers is lowered to 1.69−1.82 V and correlates well with the HOMO−LUMO gap estimated from the electronic spectra (see Table 1). This correlation is a good confirmation that the first oxidation and reduction processes are located on the aromatic rings and are not metal-centered.

In the case of dimer **22**, an additional one-electron reduction is observed before reduction of the porphyrin cores. This step probably corresponds to the one-electron reduction of the linking copper(II) and therefore leads to a large cathodic shift of the two porphyrin reduction steps. It is known that cyclic voltammetry studies of the copper(II) complexes of simple enaminoketone ligands gave fully irreversible (electrochemically and chemically) waves upon reduction, at potentials around −1.5 V.[27] In our case, a reversible one-electron reduction (on the cyclic voltammetry time scale) was observed. However, coulometric reduction of dimer **22** in a spectroelectrochemical cell rapidly showed that the dimeric structure was lost. After consumption of more than one electron per dimer, the monomeric nickel enaminoketone **10** was recovered quantitatively and identified by UV−visible spectroscopy and NMR. For this compound, the potential difference ($E_{\text{ox1}} - E_{\text{red1}}$) taken from electrochemical data ($\Delta E = 1.52$ V) and the optical gap estimated from the electronic spectrum ($\Delta E = 1.83$ eV) are different, because the first reduction step is metal-centered.

Spectroelectrochemical investigations were carried out on dimer **23** and its precursor **16** (see Supporting Information). During the first reduction as well as during the first oxidation, **16** showed UV−visible spectral evolution with well-defined isosbestic points. The generated spectra are characteristic of the radical anion and the radical cation, which confirm ligand-centered electron transfers. Indeed, the Soret band decreased whereas low-energy bands, at 788 and 850 nm for the reduction and at 696, 782, and 850 nm for the oxidation, were observed.[28] Electrolysis of dimer **23** on the plateau potential (at −1.55 V) of the first reduction gave UV−visible spectral evolution with well-defined isosbectic points. The generated species showed typical absorption bands at 708, 762, and 813 nm, characteristic of radical anions.[28] After electrolysis, the initial spectrum could be recovered quantitatively by reoxidation. Oxidation on the plateau potential of the first step (at 0.40 V) as well as for the second step (at 0.58 V) gave UV−visible spectral evolution with a decrease of the absorbance in the Soret bands and new absorption bands at lower energy around 780 nm (probably radical cations).[28] Again, the initial spectrum could be recovered by stepwise reduction, demonstrating the stability of the dimeric structure during coulometric experiments.

Conclusion and Perspectives

The straightforward synthesis of porphyrins bearing external enaminoketone coordination sites allows the preparation of new dimers linked by metal ions. The efficient porphyrin−porphyrin interaction is a consequence of the planar nature of the linkages and is illustrated by their electronic spectra and their electrochemical data. Since these new compounds allow the coordination of metal ions internally and externally, we have also started the preparation of trimetallic dimers containing magnetically active metals (Cu, Mn, V, etc.). Preliminary results show that magnetic interactions are also observed between the metals coordinated inside and outside the porphyrins.[29]

The synthesis of bisenaminoketoporphyrins where two external coordination sites are located in divergent directions has been achieved recently. These compounds allow the preparation of higher oligomers, with even larger interactions between the different porphyrin moieties.[22]

Last, but not the least, the new ligands and the trimetallic dimers described in this article are very easy to prepare and the syntheses may be scaled up. The use of coordination bonds to build porphyrin oligomers seems to be a very suitable route from a synthetic point of view and represents a possible alternative to the covalent approach. The number of possibilities offered by transition metals in terms of coordination geometry opens up the synthesis of oligomers with variable shape and dimensions.

Experimental Section

General Information. UV−visible spectra were obtained on the Hewlett-Packard 8453 (CH_2Cl_2). NMR ($CDCl_3$ data were obtained at 298 K unless otherwise stated (δ (ppm) vs TMS) with Bruker AC 300, AM 400, and ARX 500 instruments. 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 1076 alumina. All monomeric porphyrins gave correct masses (Finnigan TSQ 700, EI, 12 eV), and the dimers gave molecular mass peaks (FAB, Micromass Autospec).

Preparation of Ketone 1. This standard procedure combines steps from several sources.[13−15] To a suspension of copper *meso*-tetraphenylporphyrin **3** (CuTPP, 3.2 g, 4.7 mmol) in 1,2-dichloroethane (500 mL) was added dry DMF (26 mL) and $POCl_3$ (20 mL). The mixture was brought to reflux for 17 h and then poured into a solution of NaOAc (250 g) in water (1 L). After 1 h, the organic phase was decanted, washed with water (4 × 1 L), dried (Na_2SO_4), and concentrated to 100

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(27) For simple bis(β-ketoenamine) complexes, it is known that copper complexes are easier to reduce than the corresponding nickel or palladium complexes by 800−1000 mV. See, for example: (a) Cinquantini, A.; Seeber, R.; Cini, R.; Zanello, P. *J. Electroanal. Chem.* **1982**, *134*, 65. (b) Bradbury, J. R.; Hampton, J. L.; Martone, D. P.; Maverick, A. W. *Inorg. Chem.* **1989**, *28*, 2392.

(28) Kadish, K. M.; Van Caemelbecke, E.; Royal, G. in ref 1a: Vol. 8, p 3.

(29) Richeter, S.; Jeandon, C.; Ruppert, R.; Callot, H. J.; Sutter, J.-P., unpublished results.

mL. Addition of methanol induced the crystallization of copper 2-formylTPP **4** (3.08 g, 92%). Copper 2-formylTPP **4** (3.08 g) was added to a solution of TsOH·H$_2$O (0.64 g) and chloranil (2.15 g) in 1,2-dichloroethane (175 mL) and benzene (2.5 mL). After 1.5 h at reflux, the organic phase was washed with saturated aqueous NaHCO$_3$ and water and dried (Na$_2$SO$_4$). Chromatography on alumina (500 mL, 1,2-dichloroethane) gave copper complex **5** as a green fraction which was concentrated and crystallized in CH$_2$Cl$_2$/MeOH (1.74 g, 57%). Demetalation was performed in a TFA (84 mL)/H$_2$SO$_4$ (16 mL) mixture for 0.5 h. The acidic solution was poured slowly on ice, neutralized with saturated aqueous NaHCO$_3$, extracted with CH$_2$Cl$_2$ (100 mL), washed with water, and dried (Na$_2$SO$_4$). Crystallization from CH$_2$Cl$_2$/MeOH gave the free base **1**[13b] (1.5 g, 96%).

***Meso*-tris(3,5-di-*tert*-butylphenyl)-mono-*ortho*-carbomethoxyphenylporphyrin 6.** To a solution of methyl 2-formylbenzoate (246 mg, 1.5 mmol), 3,5-di-*tert*-butylbenzaldehyde (981 mg, 4.49 mmol), and pyrrole (402 mg, 6 mmol) in CH$_2$Cl$_2$ (750 mL, freshly distilled over calcium hydride), kept under argon, was added BF$_3$·Et$_2$O (0.5 mL, 3.95 mmol). After 2 h in the dark, chloranil (1.5 g, 6.1 mmol) was added and the solution refluxed for 1 h. Filtration through a bed of alumina and evaporation of the solvent gave a residue which was chromatographed (silica gel, 500 mL, hexane). Hexane followed by increasing CH$_2$Cl$_2$ in hexane eluted *meso*-tetra-3,5-di-*tert*-butylphenylporphyrin (190 mg, 12%), monoester **6** (251 mg, 17%), crystallized from CH$_2$Cl$_2$/MeOH, followed by polyesters which will be described elsewhere. For **6**. ^{1}H NMR: $\delta = 8.88$ (s, 4H, pyrrole), 8.84, 8.65 (2d AB, 2 + 2H, $J = 4.8$ Hz, pyrrole), 8.40 (dd, 1H, $J = 7.4$ and 1.8 Hz, benzoate H), 8.18 (dd, 1H, $J = 7.0$ and 1.6 Hz, benzoate H), 7.9−7.8 (m, 2H, benzoate H), 8.13, 8.08, 8.05, 8.03 (4dd, 2 + 1 + 1 + 2H, $J = \sim 1.6$ Hz, Ar H$_{\text{ortho}}$), 7.78 (3 superimposed dd, 3H, $J = \sim 1.6$ Hz, Ar H$_{\text{para}}$), 2.79 (s, 3 H, OCH$_3$), 1.54, 1.52, 1.51 (3s, 18 + 18 + 18H, *tert*-butyl), −2.60 (br s, 2H, NH); UV−visible: $\lambda_{\max} = 422$ ($\epsilon = 500\,000$), 518 (18 700), 554 (9900), 594 (5600), 648 (5000) nm. Elemental Anal. Calcd (%) for C$_{70}$H$_{80}$N$_4$O$_2$: C, 83.29; H, 7.99; N, 5.55. Found: C, 83.40; H, 8.03; N, 5.35.

Ketone 9. Ester **6** (388 mg, 0.384 mmol) was dissolved in toluene (110 mL). Addition of nickel(II) acetylacetonate (200 mg, 0.78 mmol) and heating (100 °C, 24 h) gave a red solution. Evaporation and chromatography (silica gel, 150 mL, CH$_2$Cl$_2$) gave the nickel complex **7**, which could be used as such afterward. To a solution of ester **7** (410 mg, 0.385 mmol) in dioxane (225 mL) were added LiOH·H$_2$O (6 g, 0.143 mol) and water (25 mL). The mixture was refluxed for 24 h. The solvents were evaporated, and toluene (20 mL) was added and evaporated. The resulting solid was put on top of a silica gel column (200 mL, CH$_2$Cl$_2$/hexane 1:1). The same solvent eluted the untransformed ester (73 mg), while CH$_2$Cl$_2$ + 1% AcOH eluted acid **8** (310 mg, crude product), used as such for the next step after evaporation of the solvent. To the solid crude acid **8** was added benzene (200 mL) and oxalyl chloride (6 mL). The mixture was stirred at room temperature for 2 h. Distillation of 20 mL of solvent, to remove excess reagent, was followed by addition of SnCl$_4$ (4 mL). After 1 h at room temperature, CH$_2$Cl$_2$ (200 mL) was added, and the solution was neutralized with aqueous NaOH. The organic phase was washed four times with water, dried (Na$_2$SO$_4$), and evaporated. Chromatography (silica gel, 400 mL, hexane/CH$_2$Cl$_2$ 1:1) gave a green fraction. Crystallization from CH$_2$Cl$_2$/MeOH afforded ketone **9** (357 mg, 87%). ^{1}H NMR: $\delta = 9.25$, 8.70 (2d, 1 + 1H, $J = 5.1$ Hz, pyrrole), 9.15 (s, 1H, pyrrole), 8.53, 8.52, 8.45, 8.41 (4d, 1 + 1 + 1 + 1H, $J = 5.0$ Hz, pyrrole), 8.47 (dd, 1H, $J = 7.0$ and 1 Hz, cyclized Ph), 8.01 (dd, 1H, $J = 7.7$ and 1 Hz, cyclized Ph), 7.70 (ddd, 1H, $J = 7.7$, 7.0, and 1 Hz, cyclized Ph), 7.59 (ddd, 1H, $J = 7.7$, 7.0, and 1 Hz, cyclized Ph), 7.76, 7.74, 7.72 (3d, 2 + 2 + 2H, $J = 1.7$ Hz, Ar H$_{\text{ortho}}$), 7.70, 7.67 (2 superimposed t + t, 2 + 1H, $J = 1.7$ Hz, Ar H$_{\text{para}}$), 1.47, 1.45, 1.44 (3s, 18 + 18 + 18H, *tert*-butyl). UV−visible: $\lambda_{\max} = 322$ ($\epsilon = 27\,300$), 382 (40 000), 465 (125 500), 649 (18 600) nm. Elemental Anal. Calcd (%) for C$_{69}$H$_{74}$N$_4$ONi: C, 80.15; H, 7.21; N, 5.42. Found: C, 80.18; H, 7.33; N, 5.13.

Demetalation of Ketone 9. Nickel complex **9** (254 mg, 0.246 mmol) was dissolved in a TFA (18 mL)/H$_2$SO$_4$ (3 mL) mixture and the solution kept at room temperature for 45 min. It was then poured on ice, diluted with CH$_2$Cl$_2$ (150 mL), neutralized with saturated aqueous NaHCO$_3$, washed with water, dried (Na$_2$SO$_4$), and evaporated. Chromatography of the residue on alumina (150 mL) and elution with CH$_2$Cl$_2$ gave free base **2**, which was crystallized from CH$_2$Cl$_2$/MeOH (232 mg, 97%). ^{1}H NMR: $\delta = 9.33$, 8.66 (2d, 1 + 1H, $J = 4.9$ Hz, pyrrole), 9.25 (s, 1H, pyrrole), 8.59, 8.60 (2d, 1 + 1H, $J = 4.5$ Hz, pyrrole), 8.53, 8.57 (2d, 1 + 1H, $J = 5$ Hz, pyrrole), 8.52 (dd, 1H, $J = 8.3$ and 1.3 Hz, cyclized Ph), 8.44 (dd, 1H, $J = 7.8$ and ∼1 Hz, cyclized Ph), 7.80 (ddd, 1H, $J = 8.3$, 7.8, and 1.3 Hz, cyclized Ph), 7.50 (ddd, 1H, $J = 8.3$, 7.8, and ∼1 Hz, cyclized Ph), 7.98, 7.94, 7.92 (3d, 2 + 2 + 2H, $J = 1.8$ Hz, Ar H$_{\text{ortho}}$), 7.79, 7.75 (2 superimposed t + t, 2 + 1H, $J = 1.8$ Hz, Ar H$_{\text{para}}$), 1.53, 1.51, 1.49 (3s, 18 + 18 + 18H, *tert*-butyl), −0.45 (br s, 2H, N−H). UV−visible: $\lambda_{\max} = 332$ ($\epsilon = 34\,000$), 394 (49 600), 466 (135 200), 581 (7600), 644 (11 200), 746 (13 800) nm. Elemental Anal. Calcd (%) for C$_{69}$H$_{76}$N$_4$O: C, 84.79; H, 7.84; N, 5.73. Found: C, 84.86; H, 8.10; N, 5.53.

Reaction of Ketone 1 with Tosylhydrazine. A solution of ketone **1** (50 mg, 0.078 mmol) and tosylhydrazine (62 mg, 4.25 equiv) in AcOH (5 mL) and CH$_2$Cl$_2$ (10 mL) was brought to reflux for 72 h. The solution was washed with saturated aqueous NaHCO$_3$ and water and dried (Na$_2$SO$_4$). The residue was chromatographed (silica gel, 80 mL, CH$_2$Cl$_2$) to give some starting material followed by enaminoketone **10** (21 mg, 41%, crystallized from CH$_2$Cl$_2$/MeOH). ^{1}H NMR: $\delta = 9.39$, 8.71 (2d, 1 + 1H, $J = 4.9$ Hz, pyrrole), 8.56, 8.50, 8.43, 8.30 (4 d, 1 + 1 + 1 + 1H, $J = 4.6$ Hz, pyrrole), 8.63 (dd, 1H, $J = 7.7$ and 1.5 Hz, cyclized phenyl), 8.60 (dd, 1H, $J = 7.8$ and ∼1 Hz, cyclized phenyl), 7.84 (ddd, 1H, $J = 7.7$, 7.8, and 1.5 Hz, cyclized phenyl), 7.59 (ddd, 1H, $J = 7.7$, 7.8, and ∼1 Hz, cyclized phenyl), 8.0−8.14 (m, 9H, phenyl), 7.34−7.85 (m, 6H, phenyl), 9.0 (br s, 1H, NH), 5.48 (br s, 1H, NH), −0.8 (br, 2H, NH). UV−visible: $\lambda_{\max} = 451$ ($\epsilon = 102\,000$), 568 (9000), 614 (20 000), 709 (7000). Elemental Anal. Calcd (%) for C$_{45}$H$_{29}$N$_5$O: C, 82.42; H, 4.46; N, 10.68. Found: C, 82.62; H, 4.38; N, 10.42.

A solution of ketone **1** (30 mg, 0.047 mmol) and tosylhydrazine (35 mg, 4 equiv) in AcOH (20 mL) and CHCl$_3$ (5 mL) was kept under air at 20 °C for 72 h. The solution was diluted with CH$_2$Cl$_2$, washed with saturated aqueous NaHCO$_3$ and water, and dried (Na$_2$SO$_4$). The residue was chromatographed (silica gel, 80 mL, CH$_2$Cl$_2$) to give some starting material followed by tosylhydrazinoporphyrin **13** (20 mg, 52%, crystallized from CH$_2$Cl$_2$/MeOH). ^{1}H NMR: $\delta = 9.30$, 8.71 (2d, 1 + 1H, $J = 5.0$ Hz, pyrrole), 8.58, 8.30 (2d, 1 + 1H, $J = 5.0$ Hz, pyrrole), 8.49, 8.43 (2d, 1 + 1H, $J = 4.6$ Hz, pyrrole), 8.53 (dd, 1H, $J = 7.8$ and 1.3 Hz, cyclized Ph), 8.28 (br dd, 1H, $J = 8.5$ and ∼1 Hz, cyclized Ph), 7.83 (ddd, 1H, $J = 8.5$, 7.8, and 1.3 Hz, cyclized phenyl), 7.56 (ddd, 1H, $J = 8.5$, 7.8 and ∼1 Hz, cyclized Ph), 8.15−7.9, 7.85−7.65 (2m, 15H, phenyl), 7.37, 5.94 (2d, 2 + 2H, $J = 8.0$ Hz, tosyl), 1.12 (s, 3H, tosyl), 12.25 (d, 1H, $J = 6.7$ Hz, NH), 7.52 (d, 1H, $J = 6.7$ Hz, NH), − 1 (very br, 2H, NH). UV−visble: $\lambda_{\max} = 376$ ($\epsilon = 57\,100$), 400 (59 600), 474 (78 000), 578 (8500), 630 (13 400), 728 (7200) nm. Elemental Anal. Calcd (%) for C$_{52}$H$_{36}$N$_6$O$_3$S: C, 75.71; H, 4.40; N, 10.19. Found: C, 75.64; H, 4.35; N, 10.25.

Reaction of Ketone 1 with Hydroxylamine. To a solution of ketone **1** (40 mg, 0.062 mmol) in CHCl$_3$ (10 mL) and AcOH (10 mL) was added NH$_2$OH·HCl (35 mg, 0.5 mmol) and NaOAc (200 mg). The solution was heated at 50 °C for 96 h and then washed with saturated aqueous NaHCO$_3$ and dried (Na$_2$SO$_4$). Chromatography (silica gel, 80 mL, CH$_2$Cl$_2$) gave recovered starting material (17 mg) and enaminoketone **10** (16 mg, 40%, crystallized from CHCl$_3$/MeOH).

Reaction of Ketone 1 with Hydrazine. A solution of ketone **1** (20 mg, 0.031 mmol) in MeOH (4 mL) and CH$_2$Cl$_2$ (12 mL) was treated with NH$_2$NH$_2$·H$_2$O (0.2 mL, 4.1 mmol). After 120 h, the solution was evaporated to dryness. Chromatography (silica gel, 100 mL, CH_2Cl_2) gave successively recovered starting material (5 mg) and chlorin **12** (11 mg, 55%, crystallized from CH_2Cl_2/MeOH). ^{1}H NMR: δ = 9.08, 8.24 (2d, 1 + 1H, J = 4.5 Hz, pyrrole), 8.79 (s, 1H, pyrrole), 7.95, 7.80 (2d, 1 + 1H, J = 5.1 Hz, pyrrole), 8.43 (d, 1H, J = 7.8 Hz, cyclized phenyl), 8.26 (d, 1H, J = 7.5 Hz, cyclized phenyl), 7.9, 7.7, and 7.5 (3m, 16H), 7.45 (t, 1H, J = 7.5 Hz, cyclized phenyl), 3.87 (narrow m, 4H, reduced pyrrole), −0.6 (very br, 2H, NH). UV−visible: λ_{max} = 344 (ϵ = 41 800), 476 (136 000), 504 (39 400), 644 (7700), 702 (11 500) nm. Elemental Anal. Calcd for (%) $C_{45}H_{30}N_4O\cdot1.5H_2O$: C, 80.70; H, 4.97; N, 8.36. Found: C, 80.76; H, 4.66; N, 8.33.

When the same reaction was run with AcOH replacing MeOH, enaminoketone **10** (3 mg) and ketone **11** (8 mg) were produced.

Reaction of Ketones 1 and 2 with Hydroxylamine *O*-Sulfonic Acid. To a solution of ketone **1** (250 mg, 0.39 mmol) in CH_2Cl_2 (60 mL) was added hydroxylamine O-sulfonic acid (400 mg, 3.5 mmol), NaOAc (300 mg, 3.7 mmol), and AcOH (60 mL). The mixture was brought to reflux for 24 h and then treated with a large excess saturated aqueous $NaHCO_3$, washed twice with water, and dried (Na_2SO_4). Chromatography (silica gel, 300 mL, CH_2Cl_2) gave enaminoketone **10** (228 mg, 87%, crystallized from CH_2Cl_2/MeOH). Enaminoketone **17** was obtained similarly from **2** in 89% yield.

Reaction of Ketones 1, 2 and Their Metal Complexes with 4-Amino-4*H*-1,2,4-triazole. To a solution of a ketone or its metal complex (0.06 mmol) in toluene (40 mL) were added ethanol (4 mL), 4-amino-4*H*-1,2,4-triazole (60 mg, 0.7 mmol), and NaOH (300 mg). The solution was brought to reflux for 1 h, cooled, washed with water, and dried (Na_2SO_4). Filtration on a short silica gel column and elution with CH_2Cl_2 gave the enaminoketone, which was crystallized from CH_2Cl_2/MeOH.

Copper Complex 15 of Enaminoketone 10. The reaction starting from the enaminoketone free base **10** is very slow, due to the formation of rather stable external metalation products. For this reason, **15** was prepared by amination of the known ketone **5** with 4-amino-4*H*-1,2,4-triazole in 88% yield. UV−visible: λ_{max} = 400 (ϵ = 28 400), 462 (129 400), 602 (10 700), 656 (25 000) nm. Elemental Anal. Calcd (%) for $C_{45}H_{27}N_5OCu$: C, 75.35; H, 3.79; N, 9.76. Found: C, 75.64; H, 3.59; N, 9.47.

Nickel Complex 16 of Enaminoketone 10. To a solution of enaminoketone **10** (50 mg, 0.076 mmol) in toluene (25 mL) was added $Ni(acac)_2$ (20 mg, 0.078 mmol). The solution was heated at 80 °C for 24 h. Evaporation of the solvent gave a residue, which was dissolved in CH_2Cl_2 (50 mL) and AcOH (50 mL) and then stirred for 30 min at room temperature. The solution was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and filtered through a silica gel column (100 mL, CH_2Cl_2). The dark green product **16** (49 mg, 90%) was crystallized from CH_2Cl_2/MeOH. ^{1}H NMR: δ = 9.21, 8.70 (2d, 1 + 1H, J = 5.1 Hz, pyrrole), 8.46, 8.31 (2d, 1 + 1H, J = 5.0 Hz, pyrrole), 8.40, 8.29 (2d, 1 + 1H, J = 4.9 Hz, pyrrole), 8.55 (dd, 1H, J = 8.0 and 1 Hz, cyclized phenyl), 8.13 (dd, 1H, J = 8.2 and 1 Hz, cyclized phenyl), 7.75 (ddd, 1H, J = 8.2, 8.0, and 1 Hz, cyclized phenyl), 7.53 (ddd, 1H, J = 8.2, 8.0 and 1 Hz, cyclized phenyl), 7.6−7.9 (m, 15H, phenyl). UV−visible: λ_{max} = 458 (ϵ = 92 000), 599 (10 800), 649 (18 600) nm. Elemental Anal. Calcd (%) for $C_{45}H_{27}N_5ONi$: C, 75.87; H, 3.82; N, 9.83. Found: C, 75.68; H, 3.72; N, 9.67.

Enaminoketone 17. This compound was obtained in 89% yield (same procedure as for **10**) from ketone **2** and hydroxylamine-*O*-sulfonic acid. ^{1}H NMR: δ = 9.40, 8.74 (2d, 1 + 1H, J = 5 Hz, pyrrole H), 8.62, 8.37 (2d, 1 + 1H, J = 4.8 Hz, pyrrole H), 8.47, 8.54 (2d, 1 + 1H, J = 4.6 Hz, pyrrole H), 8.66 (dd, 1H, J = ∼8.0 and 1.5 Hz, cyclized Ph), 8.65 (dd, 1H, J = ∼8.0 and 1.5 Hz, cyclized Ph), 7.84 (ddd, 1H, J = ∼8.0, 8.0, and 1.5 Hz, cyclized Ph), 7.59 (ddd, 1H, J = ∼8.0, 8.0, and 1.5 Hz, cyclized Ph), 7.99, 7.95, 7.85 (3d, 2 + 2 + 2H, J = 1.8 Hz, Ar H_{ortho}), 7.88, 7.77, 7.74 (3t, 1 + 1 + 1H, J = 1.8 Hz, Ar H_{para}), 9.0, 5.45 (2 br s, 1 + 1H, NH), 1.2−1.75 (group of s, 54H, *tert*-butyl), −0.75 (br s, 2H, NH). UV−visible: λ_{max} = 315 (ϵ = 28 200), 371 (46 200), 394 (47 300), 456 (107 800), 571 (9100), 617 (21 500), 711 (8500) nm. Elemental Anal. Calcd (%) for $C_{69}H_{77}N_5O$: C, 83.51; H, 7.82; N, 7.06. Found: C, 83.43; H, 7.94; N, 6.80.

Copper Complex 18 of Enaminoketone 17. Compound **18** was prepared by amination of copper ketone **5** with 4-amino-4*H*-1,2,4-triazole in 87% yield. UV−visible: λ_{max} = 380 (ϵ = 34 000), 400 (36 300), 464 (153 700), 602 (12 700), 656 (30 500) nm. Elemental Anal. Calcd (%) for $C_{69}H_{75}N_5OCu$: C, 78.63; H, 7.17; N, 6.64. Found: C, 78.73; H, 7.39; N, 6.50.

Nickel Complex 19 of Enaminoketone 17. To a solution of enaminoketone **17** (35 mg, 0.035 mmol) in toluene (30 mL) was added $Ni(acac)_2$ (80 mg, ∼10 equiv). The solution was heated at 80 °C for 24 h. Evaporation of the solvent gave a residue, which was dissolved in CH_2Cl_2 (50 mL) and AcOH (50 mL), and then stirred for 30 min at room temperature. The solution was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and filtered through a silica gel column (100 mL, CH_2Cl_2). The dark green product (34 mg, 92%) was crystallized from CH_2Cl_2/MeOH. ^{1}H NMR: δ = 9.19, 8.73 (2d, 1 + 1H, J = 5 Hz, pyrrole), 8.49, 8.35 (2d, 1 + 1H, J = 4.9 Hz, pyrrole), 8.48, 8.39 (2d, 1 + 1H, J = 4.8 Hz, pyrrole), 8.56 (dd, 1H, J = 7.8 and ∼1 Hz, cyclized Ph), 8.17 (dd, 1H, J = 8.0 and ∼1 Hz, cyclized Ph), 7.75 (ddd, 1H, J = 8.0, 7.8, and ∼1 Hz, cyclized Ph), 7.51 (ddd, 1H, J = 8.0, 7.8, and ∼1 Hz, cyclized Ph), 7.8−7.6 (m, 9H, Ar H), 5.3 (very br, 1H, N−H), 1.46, 1.43, 1.26 (3s, 18 + 18 + 18H, *tert*-butyl). UV−visible: λ_{max} = 370 (ϵ = 27 700), 399 (28 400), 462 (99 400), 600 (10 800), 650 (20 700) nm. Elemental Anal. Calcd (%) for $C_{69}H_{75}N_5ONi$: C, 79.00; H, 7.21; N, 6.68. Found: C, 79.16; H, 7.38; N, 6.50.

Palladium Complex 20 of Enaminoketone 17. To a solution of ketone **1** (24 mg, 0.037 mmol) in toluene (50 mL) was added $Pd(OAc)_2$ (20 mg, 0.089 mmol). The solution was heated under reflux for 6 h and then evaporated. The palladium complex of ketone **1** was obtained in 82% yield, after crystallization of the solid residue from CH_2Cl_2/MeOH. The amination of this metalated ketone with 4-amino-4*H*-1,2,4-triazole gave palladium complex **20** in 77% yield. ^{1}H NMR: δ = 9.38, 8.77 (2d, 1 + 1H, J = 5.0 Hz, pyrrole), 8.58, 8.56, 8.52, 8.35 (4d, 1 + 1 + 1 + 1 H, J = 4.9 Hz, pyrrole), 8.77 (dd, 1H, J = 7.5 and ∼1 Hz, cyclized Ph), 8.17 (dd, 1H, J = 8.0 and ∼1 Hz, cyclized Ph), 7.75 (ddd, 1H, J = 8.0, 7.5, and ∼1 Hz, cyclized Ph), 7.51 (ddd, 1H, J = 8.0, 7.5 and ∼1 Hz, cyclized Ph), 7.95, 7.90, 7.83 (3d, 2 + 2 + 2H, J = 1.8 Hz, Ar H_{ortho}), 7.87, 7.76, 7.73 (3t, 1 + 1 + 1H, J = 1.8 Hz, Ar H_{para}), 5.4 (very br, 1H, N−H), 1.52, 1.48, 1.47 (3s, 18 + 18 + 18H, *tert*-butyl). UV−visible: λ_{max} = 370 (ϵ = 29 700), 398 (31 000), 468 (117 500), 584 (14 000), 634 (31 600) nm. Elemental Anal. Calcd (%) for $C_{69}H_{75}N_5OPd\cdot H_2O$: C, 74.34; H, 6.96; N, 6.28. Found: C, 74.11; H, 6.69; N, 6.16.

Dimer 21. Treatment of a solution of nickel enaminoketone **16** (25 mg, 0.035 mmol) in toluene (10 mL) with $Ni(acac)_2$ (5 mg, 0.018 mmol) at 40 °C for a few minutes gave a brown solution. Evaporation of toluene and crystallization of the residue from CH_2Cl_2.MeOH gave dark brown crystals of dimer **21** (22 mg, 85%). ^{1}H NMR: δ = 8.98, 8.58 (2d, 2 + 2H, J = 4.9 Hz, pyrrole), 8.43, 8.28, 8.14, 8.01 (4d, 2 + 2 + 2 + 2H, J = 4.8 Hz, pyrrole), 8.30 (dd, 2H, J = 8.8 and ∼1 Hz, cyclized Ph), 8.05 (dd, 2H, J = 8.8 and ∼1 Hz, cyclized Ph), 7.62 (ddd, 2H, J = 8.8, 8.8, and ∼1 Hz, cyclized Ph), 7.94 (ddd, 2H, J = 8.8, 8.8, and ∼1 Hz, cyclized Ph), 7.95−7.85 and 7.7−7.6 (2m, 30H, Ar H), 6.00 (s, 2H, NH). UV−visible: λ_{max} = 441 (ϵ = 99 500), 468 (98 000), 504 (125 900), 645 (26 200), 700 (32 800) nm. Elemental Anal. Calcd (%) for $C_{90}H_{52}N_{10}O_2Ni_3$: C, 72.96; H, 3.54; N, 9.45. Found: C, 73.16; H, 3.42; N, 9.14.

Dimer 22. To a solution of nickel enaminoketone **10** (25 mg, 0.035 mmol) in toluene (10 mL) was added $Cu(OAc)_2\cdot H_2O$ (4 mg, 0.02 mmol), and the mixture was heated under reflux for 24 h. Evaporation of toluene and crystallization of the residue from CH_2Cl_2/MeOH gave dark green crystals of dimer **22** (20 mg, 75%). UV−visible: λ_{max} =

416 (ϵ = 55 800), 468 (90 200), 489 (105 700), 640 (21 700), 677 (30 800) nm. Satisfactory analytical data could not be obtained for **22**.

Dimer 23. To a solution of nickel enaminoketone **16** (25 mg, 0.035 mmol) in toluene (20 mL) was added $Pd(OAc)_2$ (4 mg, 0.018 mmol). After 24 h at 80 °C and evaporation of the solvent, dimer **23** was crystallized from CH_2Cl_2/MeOH (23 mg, 86%). ^1H NMR ($CDCl_3$, 318 K): δ = 8.93, 8.52 (2d, 2 + 2H, J = 4.7 Hz, pyrrole), 8.28, 8.27, 8.15, 8.02 (4d, 2 + 2 + 2 + 2H, J = 4.8 Hz, pyrrole), 8.50, 8.24, 8.05, 7.77 (br dd and ddd, 2 + 2 + 2 + 2H, cyclized Ph), 7.60−7.93 (m, 30H, phenyl), 7.52 (s, 2H, N−H). UV−visible: λ_{max} = 439 (ϵ = 81 100), 470 (100 200), 500 (137 900), 638 (26 900), 696 (47 100) nm. Elemental Anal. Calcd (%) for $C_{90}H_{52}N_{10}O_2Ni_2Pd.CH_3OH$: C, 70.01; H, 3.62; N, 8.97. Found: C, 69.81; H, 3.76; N, 8.73.

Dimer 24. This compound was obtained in 83% yield (same procedure as for **23**) from copper enaminoketone **15** and $Pd(OAc)_2$. UV−visible: λ_{max} = 378 (ϵ = 43 200), 422 (63 500), 496 (132 700), 636 (27 300), 656 (29 000), 696 (45 100) nm. Elemental Anal. Calcd (%) for $C_{90}H_{52}N_{10}O_2Cu_2Pd$: C, 70.24; H, 3.41; N, 9.1. Found: C, 70.24; H, 3.19; N, 9.06.

Dimer 25. The compound was obtained in 73% yield (same procedure as for **22**) from copper enaminoketone **15** and $Cu(OAc)_2{\cdot}H_2O$. UV−visible: λ_{max} = 372 (ϵ = 59 000), 414 (80 500), 486 (270 000), 626 (28 500), 678 (59 600) nm. Elemental Anal. Calcd (%) for $C_{90}H_{52}N_{10}O_2Cu_3{\cdot}H_2O$: C, 71.39; H, 3.59; N, 9.25. Found: C, 71.51; H, 3.62; N, 9.27.

Dimer 26. To a solution of enaminoketone **17** (42 mg, 0.0423 mmol) in toluene (30 mL) was added $Pd(OAc)_2$ (5 mg, ~0.5 equiv). After 24 h at 80 °C and evaporation of the solvent, the residue was chromatographed (silica gel, 100 mL). Elution with increasing ratios of CH_2Cl_2 in hexane gave the product as a green solid (28 mg, 63%, crystallized from CH_2Cl_2/MeOH). ^1H NMR: δ = 9.38, 8.71 (2d, 2 + 2H, J = 4.9 Hz, pyrrole), 8.56, 8.10 (2d, 2 + 2H, J = 4.9 Hz, pyrrole), 8.44, 8.41 (2d, 2 + 2H, J = 4.5 Hz, pyrrole), 8.89 (dd, 2H, J = 7.8 and ~1 Hz, cyclized Ph), 8.59 (dd, 2H, J = 7.9 and ~1 Hz, cyclized Ph), 8.03 (ddd, 2H, J = 7.9, 7.8 and ~1 Hz, cyclized Ph), 7.94 (ddd, 2H, J = 7.9, 7.8 and ~1 Hz, cyclized Ph), 8.06, 8.01, 7.94 (3d, 4 + 4 + 4H, J = 1.7 Hz, Ar H_{ortho}), 8.26, 7.77, 7.72 (3t, 2 + 2 + 2H, J = 1.7 Hz, Ar H_{para}), 8.30 (s, 2H, NH), −0.2 (br s, 4H, NH), 1.61, 1.54, 1.49 (3s, 36 + 36 + 36H, *tert*-butyl). UV−visible: λ_{max} = 375 (ϵ = 84 900), 429 (119 000), 475 (119 200), 507 (181 700), 588 (31 500), 639 (34 300), 660 (25 300), 730 (39 000) nm. Elemental Anal. Calcd (%) for $C_{138}H_{152}N_{10}O_2Pd.2CH_3OH$: C, 78.09; H, 7.49; N, 6.50. Found: C, 77.84; H, 7.40; N, 6.44.

Dimer 27. This compound was obtained in 84% yield (same procedure as for **23**) from copper enaminoketone **18** and $Pd(OAc)_2$. UV−visible: λ_{max} = 378 (ϵ = 58 900), 424 (93 300), 496 (238 700), 636 (30 600), 664 (34 900), 696 (69 000) nm. Elemental Anal. Calcd (%) for $C_{138}H_{148}N_{10}O_2Cu_2Pd$: C, 74.92; H, 6.74; N, 6.33. Found: C, 75.06; H, 6.71; N, 6.17.

Dimer 28. To a solution of enaminoketone **17** (60 mg, 0.061 mmol) in toluene (60 mL) was added $Pd(OAc)_2$ (14 mg, 0.062 mmol). After 48 h at 110 °C and evaporation of the solvent, the residue was chromatographed (silica gel, 100 mL). Elution with increasing ratios of CH_2Cl_2 in hexane gave dimer **28** (16 mg, 23%, crystallized from CH_2Cl_2/MeOH). Alternatively, **28** might be prepared by reacting **20** with 0.5 equiv of $Pd(OAc)_2$ in refluxing toluene for 24 h. ^1H NMR: δ = 9.31, 8.70 (2d, 2 + 2H, J = 4.8 Hz, pyrrole), 8.45, 7.97 (2d, 2 + 2H, J = 5.0 Hz, pyrrole), 8.44, 8.38 (2d, 2 + 2H, J = 4.8 Hz, pyrrole), 8.78 (dd, 2H, J = 8.0 and ~1 Hz, cyclized Ph), 8.58 (dd, 2H, J = 7.8 and 1.6 Hz, cyclized Ph), 8.01 (ddd, 2H, J = 8.0, 7.8, and ~1 Hz, cyclized Ph), 7.93 (ddd, 2H, J = 7.8, 8.0, and 1.6 Hz, cyclized Ph), 8.00, 7.94, 7.88 (3d, 4 + 4 + 4H, J = 1.7 Hz, Ar H_{ortho}), 8.19, 7.75, 7.71 (3t, 2 + 2 + 2H, J = 1.7 Hz, Ar H_{para}), 8.19 (br s, 2H, NH), 1.59, 1.53, 1.47 (3s, 36 + 36 + 36H, *tert*-butyl). UV−visible: λ_{max} = 368 (ϵ = 67 600), 424 (118 100), 468 (114 700), 500 (246 500), 620 (35 600), 636 (35 600), 676 (79 400) nm. Elemental Anal. Calcd (%) for $C_{138}H_{148}N_{10}O_2Pd_3$: C, 72.13; H, 6.49; N, 6.10. Found: C, 72.19; H, 6.46; N, 6.01.

Dimer 29. This compound was prepared (85% from CH_2Cl_2-MeOH) by metalation of **26** ($Zn(OAc)_2{\cdot}2\ H_2O$ in CH_2Cl_2/MeOH) or by metallating the internal site of the enaminoketone with $Zn(OAc)_2{\cdot}2\ H_2O$ (external zinc complex is highly unstable) and treating the product with $Pd(OAc)_2$. ^1H NMR: δ = 9.36, 8.70 (2d, 2 + 2H, J = 4.7 Hz, pyrrole), 8.51, 7.99 (2d, 2 + 2H, J = 4.6 Hz, pyrrole), 8.48, 8.42 (2d, 2 + 2H, J = 4.5 Hz, pyrrole), 8.88 (dd, 2H, J = 7.7 and ~1 Hz, cyclized Ph), 8.59 (dd, 2H, J = 7.4 and ~1.5 Hz, cyclized Ph), 8.02 (ddd, 2H, J = 7.7, 7.4, and ~1 Hz, cyclized Ph), 7.93 (ddd, 2H, J = 7.7, 7.4, and ~1.5 Hz, cyclized Ph), 8.05, 7.99, 7.93 (3d, 4 + 4 + 4H, J = 1.7 Hz, Ar H_{ortho}), 8.26, 7.76, 7.72 (3t, 2 + 2 + 2H, J = 1.7 Hz, Ar H_{para}), 8.20 (s, 2H, NH), 1.61, 1.54, 1.49 (3s, 36 + 36 + 36H, *tert*-butyl). UV−visible: λ_{max} = 378 (ϵ = 75 800), 428 (100 800), 500 (245 800), 634 (31 100), 674 (53 700), 696 (75 400) nm. Elemental Anal. Calcd (%) for $C_{138}H_{148}N_{10}O_2Zn_2Pd$: C, 74.8; H, 6.73; N, 6.32. Found: C, 75.08; H, 6.55; N, 6.06.

Compound 30. To a solution of $Pd(acac)_2$ (250 mg, 0.822 mmol) in $CHCl_3$ (25 mL) at 50 °C was added dropwise during 8 h a solution of **16** (40 mg, 0.056 mmol) in $CHCl_3$ (25 mL). After chromatography (silica gel, 100 mL, toluene) and crystallization from CH_2Cl_2/MeOH, **30** was obtained in 35% yield. ^1H NMR: δ = 9.03, 8.58 (2d, 1 + 1H, J = 5.0 Hz, pyrrole), 8.30, 8.16 (2d, 1 + 1H, 4.9 Hz, pyrrole), 8.28, 8.14 (2d, 1 + 1H, 4.8 Hz, pyrrole), 8.75 (dd, 1H, J = 7.5 and ~1 Hz, cyclized Ph), 8.26 (dd, 1H, J = 7.8 and ~1 Hz, cyclized Ph), 7.50 (ddd, 1H, J = 7.8, 7.5 and ~1 Hz, cyclized Ph), 7.59−7.90 (m, 16 H, 15H phenyl + 1H cyclized Ph), 6.32 (s large, 1H, N−H), 5.45 (s, 1H, Hacac), 2.02, 2.19 (2s, 3 + 3H, acac Me). UV−visible: λ_{max} = 420 (ϵ = 49 300), 458 (57 400 sh), 484 (81 400), 640 (12 900), 686 (25 200) nm. Elemental Anal. Calcd (%) for $C_{50}H_{33}N_5O_3NiPd.CH_3OH$: C, 64.55; H, 3.93; N, 7.38. Found: C, 64.71; H, 3.81; N, 7.30.

Compound 31. This compound was obtained in 64% yield from **19** and $Pd(acac)_2$ using the same procedure as for **30**. ^1H NMR: δ = 9.06, 8.63 (2d, 1 + 1H, J = 5.0 Hz, pyrrole), 8.39, 8.24 (2d, 1 + 1H, J = 4.9 Hz, pyrrole), 8.30, 8.18 (2d, 1 + 1H, J = 4.8 Hz, pyrrole), 8.78 (dd, 1H, J = 7.5 and ~1 Hz, cyclized Ph), 8.33 (dd, 1H, J = 7.8 and ~1 Hz, cyclized Ph), 7.78 (ddd, 1H, J = 7.8, 7.5, and ~1 Hz, cyclized Ph), 7.54 (ddd, 1H, J = 7.8, 7.5, and ~1 Hz, cyclized Ph), 7.71−7.74 (3d, 2 + 2 + 2H, J = 1.8 Hz, Ar H_{ortho}), 7.61, 7.64, 7.66 (3t, 1 + 1 + 1H, J = 1.8 Hz, Ar H_{para}), 6.34 (s large, 1H, N−H), 5.43 (s, 1H, Hacac), 2.01, 2.18 (2s, 3 + 3H, acac Me), 1.42, 1.43, 1.46 (3s, 18 + 18 + 18H, *tert*-butyl). UV−visible: λ_{max} = 420 (ϵ = 47 600), 458 (58 300 sh), 484 (79 800), 640 (13 000) nm, 686 (26000). Elemental Anal. Calcd (%) for $C_{74}H_{81}N_5O_3NiPd$: C, 70.90; H, 6.51; N, 5.59. Found: C, 70.74; H, 6.50; N, 5.34.

Electrochemical Experiments; Dichloromethane (Merck, spectroscopic grade) was dried over molecular sieves (4 Å) and stored under argon. Tetrabutylammonium hexafluorophosphate (NBu_4PF_6; Fluka, electrochemical grade) was used as received. The electrochemical experiments were carried out at room temperature in CH_2Cl_2 containing 0.1 M NBu_4PF_6 in a classical three-electrode cell. The working electrode was either a platinum (Pt, 2-mm diameter) or a glassy carbon disk (GC, 3-mm diameter). The auxiliary and the pseudoreference electrode were Pt wires. All potentials were referenced to the ferricinium/ferrocene (Fc^+/Fc) couple used as an internal standard. The electrochemical cell was connected to a computerized multipurpose electrochemical device Autolab (Eco Chemie BV, Utrecht, The Netherlands) driven by a GPES software running on a personal computer.

Crystal Data and Data Collection. Crystal data for **14**: $C_{45}H_{28}N_4Ni{\cdot}CH_2Cl_2$ M = 768.39, monoclinic, space group $C12/c1$; a = 17.995(1) Å, b = 12.345(1) Å, c = 32.486(1) Å, β = 104.558(5)°, V = 6985(1) Å^3, Z = 8, D_c = 1.46 g·cm^{-3}. A total of 12 577 $\pm h \pm k$+l reflections was collected on a dark blue crystal of dimensions 0.15 × 0.13 × 0.10 mm^3, using a KappaCCD diffractometer, graphite-monochromated Mo Kα, 2.5 < θ < 20.83, temperature 173 K. A total of 2663 unique reflections having $I > 3\sigma(I)$ were used to determine and refine the structure. Final results: $R = 0.054$, Rw = 0.070, GOF = 1.118, and largest peak in final difference, 0.334 e·Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC-172526.

Crystal Data for 13: $C_{52}H_{36}N_6O_3S$, $M = 824.97$, monoclinic, space group $P12_1/c1$; $a = 16.2410(6)$ Å, $b = 15.0840(4)$ Å, $c = 16.6350(7)$ Å, $\beta = 94.516(2)°$, $V = 4062.6(4)$ Å^3, $Z = 4$, $D_c = 1.35$ g·cm^{-3}. A total of 31 367 $\pm h \pm k +$l reflections was collected on a dark red crystal of dimensions 0.22 × 0.20 × 0.04 mm^3, using a KappaCCD diffractometer, graphite monochromated Mo Kα, $2.5 < \theta < 32.44$, temperature 293 K. A total of 4857 unique reflections having $I > 3\sigma(I)$ were used to determine and refine the structure. Final results: $R = 0.052$, Rw = 0.075, GOF = 1.431, and largest peak in final difference, 0.215 e·Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication CCDC-172527. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Rd., Cambridge CB21EZ, U.K. (E-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: X-ray structures of **11** (as pyridinozinc complex), **13**, and **14**, spectroelectrochemical investigations of **16** and **23** (electronic spectra of **16** after first reduction and first oxidation and of dimer **23** after first reduction and after first and second oxidation step). This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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