Aminosilanes in Organic Synthesis. Preparation of New Expanded Porphyrin Ligands and Bimetallic Transition-Metal Complexes. Crystal Structure of a Tetrapyrrole Macrocycle Dirhodium Complex

F. H. Carré, R. J. P. Corriu,* Geng Bolin, J. J. E. Moreau,* and C. Vernhet

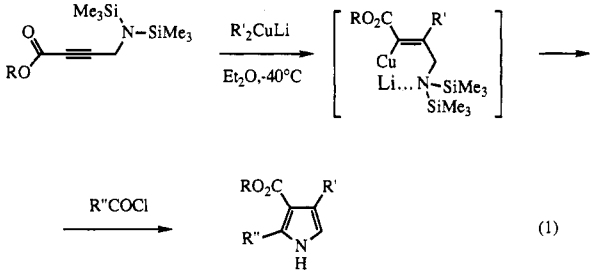
Laboratoire Hétérochimie et Aminoacides, associé au CNRS No. 1097, Département de Chimie Organique Fine, Université de Montpellier II, Sciences et Techniques du Languedoc, 34095 Montpellier Cedex 05, France

Received November 4, 1992

The synthesis of pyrrole *via* carbocupration of γ-amino-α,β-acetylene esters, followed by reaction with acid chlorides, was shown to provide facile routes to new polyheterocyclic compounds and tetrapyrrolic macrocycles. New expanded porphyrins were obtained in two steps from the reaction of diacid dichlorides. The new tetrapyrrole macrocycle formed bimetallic complexes of Pd, Ni, and Rh. The X-ray crystal structure of the dirhodium complex revealed that the two rhodium atoms (Rh···Rh interatomic distance 4.38 Å) lie on the same side of the macrocycle. The latter adopted an overall saddle shape conformation to relieve strain within the molecule.

Introduction

We recently gave illustrative examples showing that bis(trimethylsilyl)amines not only behave as protected primary amino groups but also constitute interesting reagents which follow the formation of carbon–nitrogen bonds.[1-3] Owing to the reactivity of the silicon–nitrogen bond, aminosilanes were shown to offer short synthetic routes to allylic, acetylene, allene, or diene primary amines[2] and also to five-, six-, or seven-membered nitrogen heterocycles.[1,3,4] For example, we reported recently a one-pot synthesis of pyrroles from [bis(trimethylsilyl)amino]-methyl propiolic acid esters upon addition of organocuprate reagents and subsequent reaction with an acid chloride[3] (eq 1). An application of synthetic interest of



(1)

this new pyrrole synthesis was illustrated in a short preparation of bicyclic molecules and an investigation into the mechanism was reported.[3] These pyrroles, unsubstituted in the 5-position, obtained according to eq 1, suggested the possibility of preparing dipyrrolylmethane derivatives. As such they are relevant to the porphyrin field. Porphyrin macrocycles are an important class of compounds owing to their role in biological systems.[5] The design of new porphyrin ligands with specific properties or new structural analogs of porphyrins[6] is an important area of recent work.[6] This work includes the synthesis of homoporphyrins as well as penta- and hexapyrrolic macrocycles. As part of our studies in the use of aminosilanes for the synthesis of nitrogen heterocycles, we decided to investigate the synthesis of di- and polypyrrolic derivatives. We wish to report here facile routes to new polyheterocyclic compounds and tetrapyrrolic macrocycles and to show that the resulting expanded porphyrin can be used as a ligand to form new bimetallic transition-metal complexes. A portion of this has been communicated.[7]

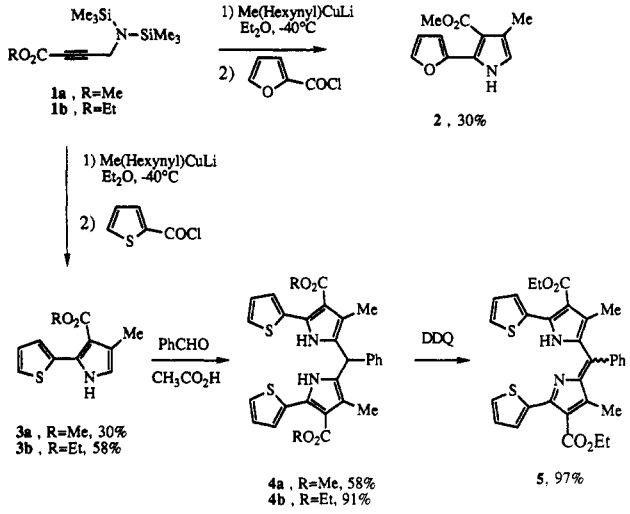
Results and Discussion

Preparation of Polyheterocyclic Derivatives. We first examined the formation of open chain polyheterocylic derivatives which could be of interest as polydentate ligands. The required substituted pyrroles were prepared according to the previously described procedure.[3] As shown in Scheme I, the reaction of methyl(hexylnyl)-cuprate with the methyl or ethyl γ-aminopropiolate **1a** or **1b** was followed by treatment with 2-furyl- or 2-thienyl acid chloride to give the 2-furyl and thienyl pyrroles **2** and **3**, respectively. The resulting bis(heterocyclic) compounds **3a** and **3b** then readily formed dipyrrolylmethane derivatives **4a** and **4b** upon heating with benzaldehyde in acetic acid. The unconjugated compound **4b** was oxidized, upon treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone

(1) Corriu, R. J. P.; Moreau, J. J. E.; Pataud-Sat, M. *J. Org. Chem.* **1990**, *55*, 2878 and references therein.
(2) (a) Corriu, R. J. P.; Huynh, V.; Moreau, J. E. E. *Tetrahedron Lett.* **1984**, *25*, 1887. (b) Corriu, R. J. P.; Huynh, V.; Iqbal, J.; Moreau, J. J. E. *J. Organomet. Chem.* **1984**, *276*, C61. (c) Corriu, R. J. P.; Huynh, V.; Iqbal, J.; Moreau, J. J. E.; Vernhet, C. *Tetrahedron* **1992**, *48*, 6231.
(3) (a) Corriu, R. J. P.; Moreau, J. J. E.; Vernhet, C. *Tetrahedron Lett.* **1987**, *26*, 2963. (b) Corriu, R. J. P.; Bolin, G.; Iqbal, J.; Moreau, J. J. E.; Vernhet, C. *Tetrahedron*, in press.
(4) (a) Corriu, R. J. P.; Bolin, G.; Moreau, J. J. E. *Tetrahedron Lett.* **1991**, *33*, 4121. (b) Corriu, R. J. P.; Bolin, G.; Moreau, J. J. E. *Bull. Soc. Chim. Fr.*, in press.
(5) *The porphrins*; Dolphin, D., Ed.; Academic Press: New York, 1978–79; Vols. 1–7.
(6) (a) Johnson, A. W. In *Porphyrins and Metallo-porphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; p 729. (b) Mashiko, T.; Dolphin, D. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 2, p 813. (c) Sessler, J. L.; Burrell, A. K. *Top. Curr. Chem.* **1991**, *161*, 177 and references therein.
(7) Corriu, R. J. P.; Bolin, G.; Moreau, J. J. E.; Vernhet, C. *J. Chem. Soc., Chem. Commun.* **1991**, 211.

0276-7333/93/2312-2478$04.00/0

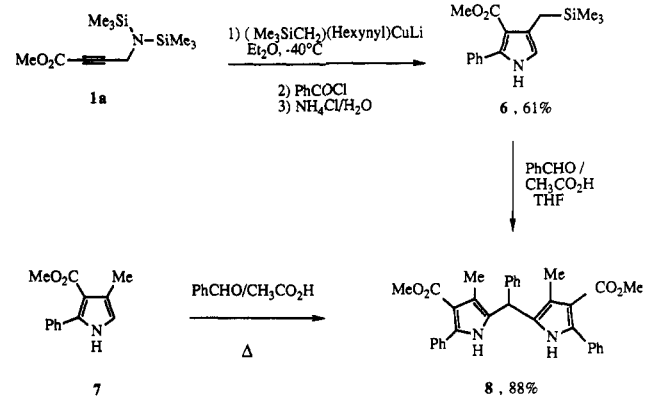
Scheme I. Preparation of Polyheterocyclic Derivatives



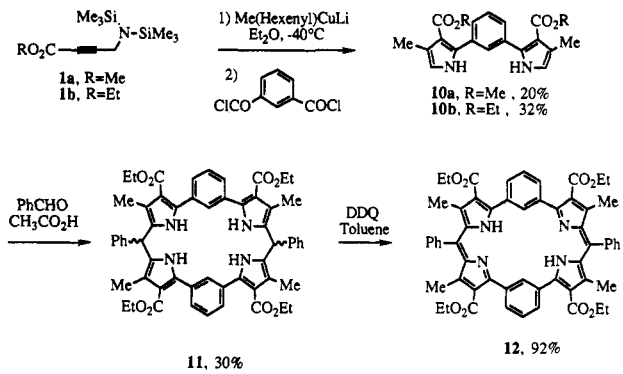
(DDQ), to yield quantitatively the red conjugated derivative **5**. The ^1H and ^{13}C NMR spectra of **5** are consistent with the formation of a single isomer. The stereochemistry of the tetrasubstituted double bond in **5** was not assigned. The reaction in Scheme I offers an access to oligomeric mixed tetraheterocyclic derivatives. Such molecules are of potential interest as metal complex ligands and also for the preparation of molecularly defined conjugated copolymers upon oxidative coupling. Polyheterocyclic polymers can lead to conducting materials upon doping with an electron acceptor.[8]

In order to obtain functionalized dipyrrolylmethanes we examined the possible introduction of a (trimethylsilyl)-methyl substituent. The presence of a trimethylsilyl group in a benzylic-type position should allow further substitution by a variety of electrophilic reagents.[9] As depicted in Scheme II, the reaction of a (trimethylsilyl)cuprate reagent with the acetylene ester **1a** followed by treatment with benzoyl chloride gave the expected silylated pyrrole **6** in a 61% yield. However, the Si–C bond in compound **6** appeared labile. It was readily desilylated to the 2-phenyl-4-methylpyrrole **7** upon acidic treatment. Similarly, the 2-furyl or thienyl analogs of **6** appeared even more labile and were partially desilylated upon workup. From compound **6** the reaction of benzaldehyde failed to give the silylated dipyrrolylmethane. Only the desilylated compound **8** identical to the one produced upon reaction of **7** with benzaldehyde was isolated. It is however worth noting that the presence of the trimethylsilyl group in **6** greatly facilitates the formation of dipyrrolyl methane **8**. Wheras **8** was obtained from **7** and benzaldehyde in refluxing acetic acid, it was formed in THF at 20 °C upon treatment of **6** with 1 equiv of benzaldehyde and 1 equiv

Scheme II. Reactivity of the 4-[(Trimethylsilyl)methyl]pyrrole Derivative 6

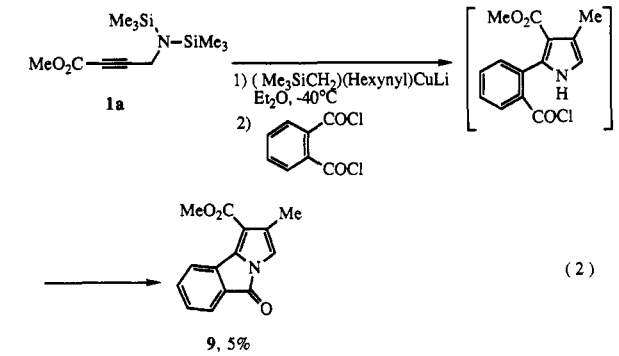


Scheme III. Formation and Cyclization of 1,3-Dipyrrolylbenzene 10



of acetic acid. The trimethylsilyl group in **6** probably provides stabilization of the carbocationic intermediate formed by an electrophilic attack of benzaldehyde at the 5-position of the pyrrole ring. Such a hyperconjugative stabilization would also weaken the Si–C bond and would result in a rapid desilylation.

Formation of Tetrapyrrole Macrocycles. The reactions of **1a** with diacid dichlorides were examined in order to obtain dipyrrole derivatives, having the possibility of cyclizing to the tetrapyrrole macrocycles. Phthaloyl dichloride (eq 2) led to a complex mixture of products



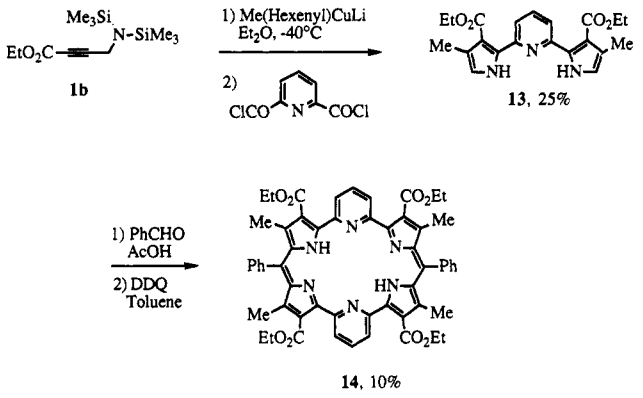
(2)

from which only a low yield of the tricyclic pyrrole **9** was isolated. The initially formed monopyrrolyl intermediate undergoes an intramolecular cyclization to give compound **9**. The use of isophthaloyl dichloride precluded the ring closure to a lactam (Scheme III). From the acetylene esters **1a,b**, the expected 1,3-dipyrrolylbenzenes **10a,b** were isolated although in moderate yields. The reaction of **10b** with benzaldehyde in refluxing acetic acid then allowed isolation of the tetrapyrrole macrocyclic derivatives **11** in

(8) (a) Tourillon, G.; Garnier, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *135*, 173. (b) Kaneto, K.; Khono, Y.; Yoshino, K.; Inuishi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 382. (c) Kobayashi, M.; Chen, J.; Chung, T. C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77. (d) Diaz, A. F.; Kanazawa, K. K.; Gardini, J. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635. (e) Kanazawa, K. K.; Diaz, A. F.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* **1981**, *4*, 119. (f) MacDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, W. S.; Mu, J. L.; Somasiri, N. D. L.; Wu, W.; Yaniger, S. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173.

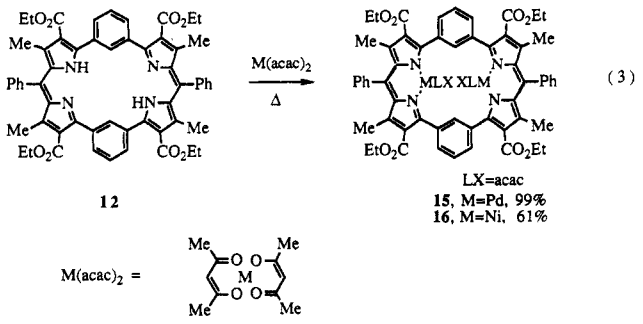
(9) (a) Weber, W. P. *Silicon Reagent for Organic Synthesis*; Spring-Verlag: Berlin, 1983. (b) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, U.K., 1989. (c) Dunoguès, J. *Chem. Tech.* **1982**, *12*, 373. (d) Dunoguès, J. *Ann. Chim. Fr.* **1983**, *8*, 135.

Scheme IV. Formation and Cyclization of 2,6-Dipyrrolylpyridine 13



30% yield. Compound **11** was formed as a mixture of two products, as can be seen from the ^{13}C NMR spectrum of the isolated crystalline compound. These were assigned to a 1/1 mixture of cis and trans isomers according to the configuration of the phenyl-substituted *meso* carbon atoms. Indeed, the mixture of isomers upon heating in toluene in the presence of DDQ was oxidized quantitatively to a single crystalline compound **12**. Analytical and spectroscopic results are fully consistent with the proposed conjugated nonaromatic macrocyclic structure **12**. It also underwent diprotonation upon treatment with acid. A new structural analog of a porphyrin, **17**, was obtained according to Scheme III in 9% overall yield from **1b**. Interestingly, a similar reaction was carried out to form dipyrrolylpyridine. The reaction of 2,6-pyridinedicarboxylic acid dichloride led to a 25% yield of the tris(heterocyclic) compound **13** (Scheme IV). The 2,6-dipyrrolylpyridine **13** was then heated with benzaldehyde in acetic acid and, after oxidation of the crude reaction product with DDQ, afforded the macrocyclic derivative **14** with six nitrogen atoms in the ring in 10% yield. This reaction therefore offers an easy route to expanded tetrapyrrolic macrocycles as well as to macrocycles with more than four heterocyclic subunits.

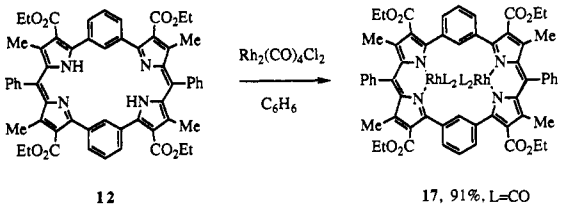
Formation of Transition-Metal Complexes. Expanded porphyrins such as **12** have a great potential as ligands. Indeed, we studied the reaction of **12** to form transition metal complexes. Whereas **12** did not give stable complexes upon heating with metal salts, it was found to act as a binucleating ligand. Palladium salts, which are known to form very stable metalloporphyrins,[10] were reacted with the free ligand **12**. Palladium acetylacetonate gave a stable red complex **15** which was isolated in high yield (eq 3).



(3)

The formation of a bimetallic species containing two palladium atoms was established on the basis of microanalytical data. The infrared and NMR spectra further indicated the formation of a bimetallic complex of the macrocycle. In the latter the two dipyrrolylmethane units of the symmetrical ligand formed independent palladium(II) complexes. The cavity in this 20-membered ring seems too large for the tetracoordination of a single metal atom. To accommodate the square planar coordination of the two palladiums, strain within the molecule is probably relieved by a folding of the ligand.[11] Similarly, the reaction of nickel acetylacetonate gave a bimetallic dinickel complex **16**. **16** exhibited spectroscopic properties similar to those of **15**. From **15** and **16** no crystal suitable for X-ray analysis could be obtained. No indication as to whether the two metal atoms in **15** and **16** lie on the same or opposite side of the macrocyclic plane was obtained.

We then examined the preparation of a rhodium complex of the macrocycle **12**. The reaction of 1 mol of dichlorotetracarbonyldirhodium in benzene also afforded a red bimetallic complex **17** (eq 4). The analytical data are



(4)

consistent with the proposed structure of **17**. The infrared spectrum showed the expected two strong absorptions, consistent with a cis structure of the $Rh(CO)_2$ subunit.[12] ^1H and ^{13}C NMR spectra present signals for chemical shifts similar to those observed in the dipalladium complex **15**. Upon slow cooling, solutions of **17** deposited crystals which allowed X-ray structure determination (see Figures 1–3).

Crystal Structure of 17. Description of the Geometry of the Molecule. The crystal consists of discrete molecules of C_1 symmetry. The atom numbering scheme is defined in Figure 1. The general curvature of the molecule is best seen in Figure 2. Other features, like the orientations of the two *m*-phenylene moieties C51–6 and C71–6 can be observed in the stereoscopic view of Figure 3.

The key point which emerged from the X-ray study is that the two dicarbonylrhodium units are both bound to the same side of the macrocycle, contrary to the dirhodium complex of octaethylporphyrin reported by Takenaka and Sasada[13] and related complexes.[6c,14] The repulsion between the opposite carbonyl groups (1–4 and 2–3) makes the macrocycle adopt an overall saddle shape. It seems this bending may occur easily.

(i) The contact distances between the oxygen atoms of the carbonyl groups [O1···O4, 3.10(1) Å and O2···O3, 3.33(2)

(10) Eisner, V.; Harding, M. J. C. *J. Chem. Soc.* **1964**, 4089.

(11) (a) Ostfeld, D.; Tsutsui, M. *Acc. Chem. Res.* **1974**, *7*, 52. (b) Fleischer, E. B.; Dixon, F. *Bioinorg. Chem.* **1977**, *7*, 129. (c) Bobsein, R. L.; Cash, G.; Peterson, R. *Inorg. Chem.* **1979**, *18*, 3458.

(12) The ratio of intensities of the two strong absorptions is 5/4. A simple calculation gives the angle between the two Rh–CO bonds, 84°. This value is very near the X-ray analysis result (85°). Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988; p 1035. Cotton, F. A.; Lukehart, C. M. *J. Am. Chem. Soc.* **1971**, *93*, 2673.

(13) (a) Takenaka, A.; Sasada, Y.; Omura, T.; Ogoshi, H.; Yoshida, Z. I. *J. Chem. Soc., Chem. Commun.* **1973**, 712. (b) Takenaka, A.; Sasada, Y.; Ogoshi, H.; Omura, T.; Yoshida, Z. I. *Acta Crystallogr.* **1975**, *B31*, 1.

(14) (a) Abeyesekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V.; King, T. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2184. (b) Abeysekera, A. M.; Grigg, R.; Trocha-Grimshaw, J.; Viswanatha, V. *J. Chem. Soc., Perkin Trans 1* **1977**, 36. (c) *Ibid* **1977**, 1395.

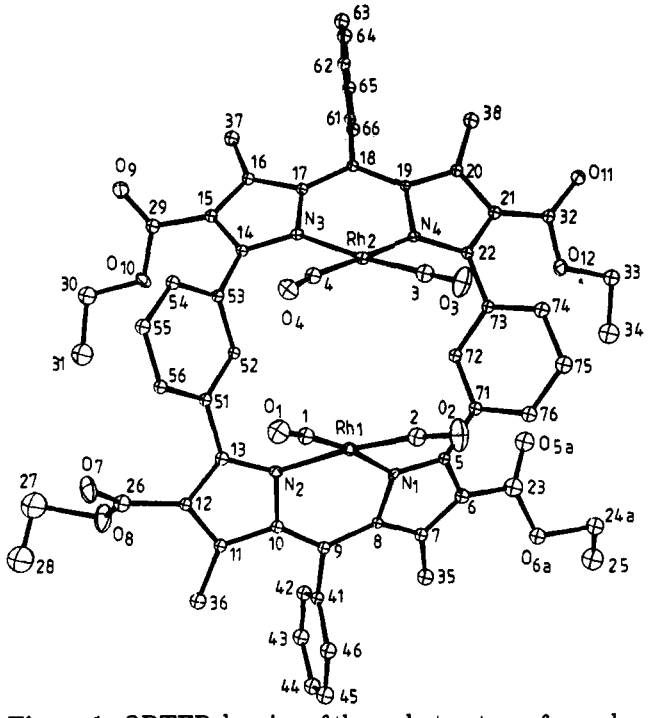


Figure 1. ORTEP drawing of the mol. structure of complex **17**. The ellipsoids and spheres enclose 10% of the electron density. Unaccompanied numbers refer to carbon atoms.

Å] lie in the range of the expected sums of van der Waals radii, 2.9–3.4 Å. (The van der Waals radius of a carbonyl oxygen atom, as estimated by Bondi,[15] is ca. 1.43 to 1.6 or 1.7 Å, depending on whether this radius is measured in a direction parallel or normal to the double bond axis, respectively.)

(ii) Larger interactions of the carbonyl oxygen atoms are also avoided by a slight change of the carbonyls directions out of the two N–Rh–N planes, resulting in an average value of 175° for the angles between the N–Rh bonds and the opposite Rh–CO bonds. In other words, the complex exhibits slightly distorted square planar coordination for the rhodium atoms: their distances out of the C1, C2, N1, N2 and C3, C4, N3, N4 least-squares planes are 0.12 and 0.05 Å, respectively.

(iii) More distorted angles are observed around the four nitrogen atoms: while the pyrrole moieties are fairly planar, the N–Rh bonds are not in the mean plane of the five-membered rings. These deviations are between 9.8 and 27.3°, and the corresponding distances of the Rh atoms out of the rings mean planes range from 0.35 to 0.96 Å.

(iv) Figures 2 and 3 show that the overall bending of the macrocycle is permitted by a concomittant rotation of the *m*-phenylene rings in the opposite direction. For instance, the C51–C13 and C53–C14 bonds, which lie in the plane of the *m*-phenylene ring C51–6 and are not colinear, can contribute to a bending of that part of the macrocycle by as much as an angle of 120°.

Other features of complex **17** are as follows: contrary to the porphyrin nucleus where the four nitrogen atoms are arranged on the apices of a square, the N···N mean distances are of two types, short (2.81 Å) and long (5.63 Å). The short distance is the same as computed from the data published[13] and is comparable with most results concerning porphyrins. Concerning the long N···N distance, it is noteworthy that it is just 2 times the short one.

(15) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

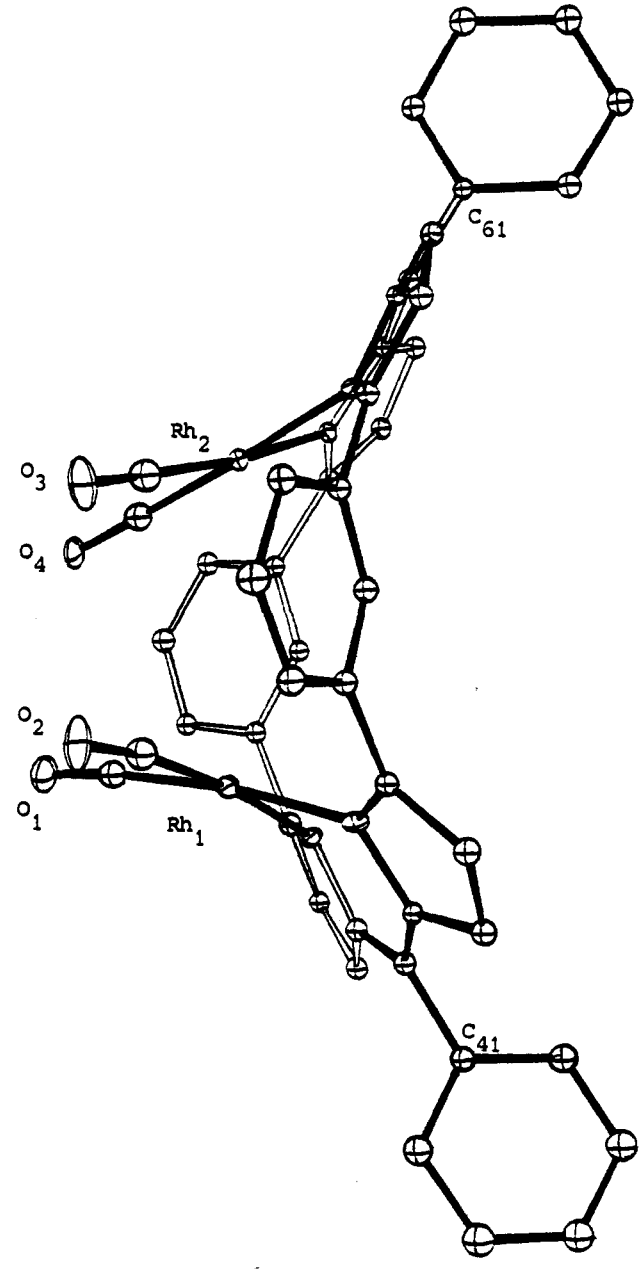


Figure 2. Drawing resulting from a 90° rotation of Figure 1 around an axis passing through the Rh1 and Rh2 atoms.

The dihedral angle between the two coordination planes of the Rh atoms is 41.3°. The Rh1···Rh2 interatomic distance, 4.387(2) Å, rules out any strong interaction between the two transition-metal atoms. Such interactions were found in several rhodium(I) complexes like $[Rh(CO)_2Cl]_2$,[16] Rh···Rh = 3.31 Å, or in the already quoted bis(dicarbonylrhodium)porphyrin:[13] 3.09 Å.

The mean Rh–N bond distance, 2.070(10) Å, and the mean Rh–CO bond distance, 1.854(15) Å, are equal within the experimental errors to the values reported,[13] 2.083 and 1.852 Å, respectively.

Conclusion

The carbocupration of γ-amino-α,β-acetylene esters and subsequent reaction with acid chlorides provide a facile route to polyheterocyclic compounds. The use of diacid

(16) Dahl, L. F.; Martell, C.; Wampler, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 1761.

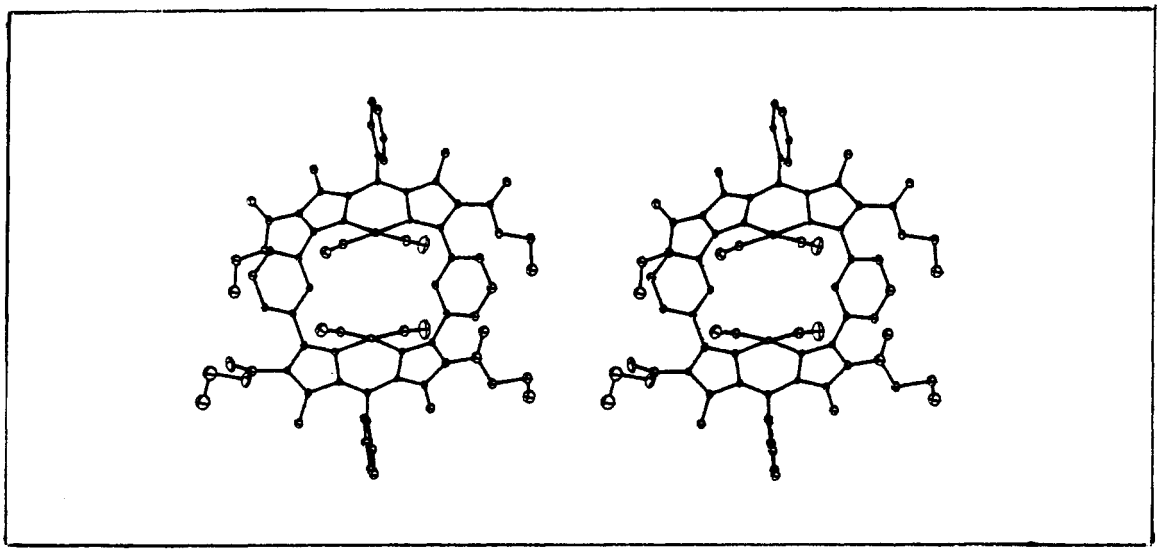


Figure 3. Stereoscopic view of the molecule of complex 17. The general orientation is the same as that for Figure 1.

dichlorides is of interest since it gives a short access to substituted bis(pyrrolyl) derivatives with a free 5-position at the pyrrole rings. A straightforward macrocyclization was obtained *via* dipyrrolylmethane derivatives, formed upon reaction of benzaldehyde with the bis(pyrrolyl)-arenes. The enlarged porphyrin ligand obtained formed bimetallic complexes with transition metals. Interestingly, a dirhodium complex where the two rhodium atoms, with no bonding interaction, lie on the same side of the macrocycle was characterized. It contrasts with a related dirhodium complex of octaethylporphyrin[13] for which the two metal atoms are located above and below the macrocyclic plane. Owing to the presence of a *m*-phenylene spacer between the two dipyrrolyl methane units in the macrocycle **12**, the molecule adopts a saddle shape conformation which allows coordination of the metal atoms on the same side. It seems that the expanded porphyrin **12** is well suited to form such bimetallic complexes.

Experimental Section

General Remarks. All reactions were performed under an atmosphere of nitrogen and using standard vacuum line and Schlenk tube techniques. Melting points were determined using a Gallenkamp apparatus and are uncorrected. Solvents were dried and distilled before use. IR spectra were recorded on a Perkin-Elmer 298 or Perkin-Elmer 1600 FT spectrometer in the form indicated. ^{1}H NMR spectra were recorded on a Bruker AW-60, AW-80, or AC-250 spectrometer. ^{13}C spectra were recorded on a Bruker WP 200 instrument. Chemical shifts are relative to Me_4Si. Mass spectra were obtained on a JEOL-JMS DX 300 instrument. Elemental analyses were carried out by the Service Central de Microanalyse du CNRS. The γ-aminoacetylene esters **1a,b** were prepared as previously described.[2a]

Preparation of Polyheterocyclic Compounds. 2-Furylpyrrole (2). A 2.15 M solution of methyllithium in ether (11.7 mL, 25 mmol) was added at 0 °C to an ether solution of hex-1-yne (2.9 mL, 25 mmol). After 0.5 h, the resulting solution was added to a suspension of CuI (4.75 g, 25 mmol) in 20 mL of ether at 0 °C and stirred for 0.5 h. The bright yellow reaction mixture was cooled to −40 °C, and a new portion of methyllithium (11.7 mL, 25 mmol) was added. After stirring and warming to 0 °C, it was cooled again to −40 °C and 6.5 g (25 mmol) of the ester **1a** was slowly introduced. The mixture was stirred for 2 h, and 2-furyl acid chloride (3.0 mL, 30 mmol) was added. The reaction mixture was slowly warmed to 20 °C, and after 12 h, the crude mixture was hydrolyzed with aqueous NH_4Cl and extracted with ether. The organic layer was collected, washed with water, and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by chromatography (neutral alumina, CH_2Cl_2/Et_2O 9/1) to give 1.55 g of compound **2** (yield, 30%). Mp: 70 °C. ^{1}H NMR ($CDCl_3$): δ 2.14 (3H, s), 3.69 (3H, s), 6.30 (2H, m), 6.85–7.40 (2H, m), 9.03 (1H, bs). IR ($CHCl_3$): 3475, 1710 cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.82. Found: C, 64.48; H, 5.59; N, 6.93.

2-Thienylpyrrole (3a). The reaction was performed as for compound **2** using hex-1-yne (2.3 mL, 20.5 mmol), methyllithium (1.27 M ether solution, 32 mL, 41 mmol), CuI (3.98 g, 20.5 mmol), and acetylene ester **1a** (5.1 g, 20.5 mmol). The reaction with 2-thienylcarbonyl chloride (2.25 mL, 21 mmol) allowed isolation of 1.33 g of 2-thienylpyrrole **3a** (yield, 30%). Mp: 64 °C. ^{1}H NMR ($CDCl_3$): δ 2.25 (3H, s), 3.69 (13H, s), 6.39 (1H, s), 6.80–7.30 (3H, m), 8.90 (1H, vbs). ^{13}C NMR ($CDCl_3$): δ 12.88 (CH_3C=); 50.63 (CH_3O); 111.92, 1178.07, 122.93, 125.89, 126.43, 127.01, 130.47, 134.0 (aromatic carbon atoms); 165.95 (C=O). IR ($CHCl_3$): 3440, 1675 cm^{-1}. Mass spectrum (electron impact): *m/e* 221 (M^+). Exact mass calcd for $C_{11}H_{11}NO_2S$, 221.0510; found, 221.0504.

Compound 3b. As above hex-1-yne (7.2 mL, 66 mmol), 1.9 M methyllithium in ether (70 mL, 132 mmol), CuI (12.6 g, 66 mmol), ester **1b** (18.0 g, 66 mmol), and 2-thienylcarbonyl chloride (7.7 mL, 70 mmol) led to 11.5 g of 2-thienylpyrrole **3b** (yield, 58%). Mp: 75 °C. ^{1}H NMR ($CDCl_3$): δ 1.22 (3H, t), 2.25 (3H, t), 4.17 (2H, q), 6.41 (1H, s), 6.97 (1H, m), 7.22 (2H, m), 8.75 (1H, vbs). ^{13}C NMR ($CDCl_3$): δ 12.67 (CH_3C=); 14.31 (CH_3CH_2O); 59.59 (CH_3CH_2O); 112.31, 116.98, 122.90, 125.79, 126.96, 127.18, 130.34, 133.96 (aromatic carbon atoms); 165.50 (C=O). IR ($CHCl_3$): 3460, 1675 cm^{-1}. Mass spectrum (electron impact): *m/e* 235 (M^+). Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95. Found: C, 61.48; H, 5.79; N, 6.13.

DipyrrolylMethane Derivatives. Compound 4a. 2-Thienylpyrrole **3a** (0.8 g, 3.6 mmol) was dissolved in 10 mL of acetic acid. Then 184 μL (1.8 mmol) of benzaldehyde was added, and the mixture was refluxed for 3 h. After evaporation of the solvent, the residue was extracted with ether, washed with aqueous $NaHCO_3$ and water, and dried over Na_2SO_4. The ether was removed and the residue crystallized from a mixture of CH_2Cl_2/pentane (1/9) to give 0.55 g of dipyrrolylmethane **4a** (yield, 58%). Mp: 201 °C. ^{1}H NMR ($CDCl_3$): δ 2.10 (6H, s), 3.74 (6H, s), 5.59 (1H, s), 6.80–7.50 (11H, m), 7.89 (2H, bs). ^{13}C NMR ($CDCl_3$): δ 10.94 (CH_3C=); 40.16 (CH—C_6H_5); 50.70 (CH_3O); 113.23, 119.29, 126.05, 126.92, 127.01, 127.74, 127.81, 128.26, 128.88, 129.35, 133.69, 139.39 (aromatic carbons); 165.73 (C=O). IR ($CHCl_3$): 3400, 1675 cm^{-1}. Mass spectrum (electron impact): *m/e* 530 (M^+). Anal. Calcd for $C_{29}H_{26}N_2O_4S_2$: C, 65.64; H, 4.94; N, 5.28. Found: C, 65.64; H, 4.72; N, 5.23.

Compound 4b. As for **4a** the reaction of pyrrole **3b** (2.7 g,

11.5 mmol) in 15 mL of acetic acid with benzaldehyde (5.8 μL, 5.75 mmol) gave 2.9 g of dipyrrolylmethane **4b** (yield, 91%). Mp: 166 °C. ^{1}H NMR ($CDCl_3$): δ 1.19 (6H, t), 2.07 (6H, s), 4.12 (4H, q), 5.51 (1H, s), 6.75–7.30 (11H, m), 7.88 (2H, bs). ^{13}C NMR ($CDCl_3$): δ 11.00 (CH_3C=); 14.28 (CH_3CH_2O); 40.14 (CH—C_6H_5); 59.74 (CH_3CH_2O); 113.62, 119.23, 125.97, 126.96, 127.10, 127.71, 127.78, 128.27, 128.72, 129.34, 133.64, 139.45 (aromatic carbon atoms); 165.36 (C=O). IR ($CHCl_3$): 3420, 1685 cm^{-1}. UV (CH_2Cl_2): λ_{max} (ε) 313 (19 380) nm. Mass spectrum (FAB): *m/e* 559 (M + H$^+$). Anal. Calcd for $C_{31}H_{30}N_2O_4S_2$: C, 66.64; H, 5.41; N, 5.01. Found: C, 66.55; H, 5.62; N, 4.72.

Oxidation to Compound 5. To a solution of 0.021 g (0.54 mmol) of DDQ in 10 mL of toluene was added 0.30 g (0.54 mmol) of dipyrrolylmethane **4b**. The mixture was stirred for 4 h. The solvent was evaporated, and the residue was purified by TLC (thin layer chromatography) (silica gel, eluent CH_2Cl_2/MeOH δ 92/8), to give 0.29 g of compound **5** (yield, 97%). Mp: 156 °C. ^{1}H NMR ($CDCl_3$): δ 1.34 (6H, t), 1.59 (6H, s), 4.32 (4H, q), 7.0–7.8 (11H, m), 7.91 (1H, s). ^{13}C NMR ($CDCl_3$): δ 13.64 (CH_3C=); 14.28 (CH_3CH_2O); 60.59 (CH_2O); 113.45, 122.19, 127.81, 128.35, 129.31, 129.45, 136.11, 137.21, 138.48, 144.45, 147.24 (aromatic carbons); 165.91 (C=O). IR ($CHCl_3$): 1690 cm^{-1}. UV and visible spectra (CH_2Cl_2): λ_{max} (ε) 314 (28 680), 534 (29 580) nm. Mass spectrum (electron impact): *m/e* 556 (M$^+$). Anal. Calcd for $C_{31}H_{28}N_2O_4S_2$: C, 66.88; H, 5.07; N, 5.03. Found: C, 66.66; H, 5.15; N, 5.28.

4-[(Trimethylsilyl)methyl]pyrrole Derivatives. Compound 6. The reaction was carried out as for compound **2**, using hex-1-yne (3.5 mL, 30 mmol), 1.05 M methyllithium solution in ether (28.6 mL, 30 mmol), CuI (5.7 g, 30 mmol), 0.69 M [(trimethylsilyl)methyl]lithium solution in THF (43.7 mL, 30 mmol), acetylene ester **1a** (6.9 g, 27 mmol), and benzoyl chloride (3.5 mL, 30 mmol). After purification, 4.7 g of silylpyrrole **6** was isolated (yield, 61%). Mp: 82 °C. ^{1}H NMR ($CDCl_3$): δ 0.05 (9H, s), 2.20 (2H, s), 3.52 (3H, s), 6.20 (1H, s), 7.25 (5H, s), 8.60 (1H, bs). ^{13}C NMR ($CDCl_3$): δ 1.67 (CH_3Si); 15.70 (CH_2Si); 50.30 (CH_3O); 110.55, 115.27, 124.44, 127.71, 127.97, 128.79, 133.26, 137.08 (aromatic carbons); 166.56 (C=O). IR (CCl_4): 3460, 1695, 1260 cm^{-1}. Mass spectrum (FAB): *m/e* 288 (M + H$^+$). Anal. Calcd for $C_{16}H_{21}NO_2Si$: C, 66.86; H, 7.48; N, 5.13. Found: C, 66.53; H, 7.48; N, 5.13.

Dipyrrolylmethane 8. Compound **6** (0.575 g, 2 mmol) was dissolved in THF (10 mL) and cooled to −78 °C. Then 200 μL (2 mmol) of benzaldehyde and 240 μL (4 mmol) of acetic acid were added. The mixture was warmed to 20 °C and stirred for 24 h. After evaporation of the solvent, the residue was extracted with ether, washed with aqueous $NaHCO_3$ and water, and dried. Evaporation of the solvent and chromatographic purification (eluent Et_2O/pentane 3/7) gave 0.41 g of compound **8** (yield, 80%). Mp: 208 °C. ^{1}H NMR ($CDCl_3$): δ 2.11 (6H, s), 3.60 (6H, s), 5.60 (1H, s), 7.28 (5H, s), 7.88 (2H, s). ^{13}C NMR ($CDCl_3$): δ 10.87 (CH_3C=); 40.25 (CH—C_6H_5); 50.62 (CH_3O); 118.90, 127.62, 128.02, 128.15, 128.31, 128.44, 128.86, 129.32, 129.61, 130.75, 132.80, 139.55 (aromatic carbons); 166.42 (C=O). IR ($CHCl_3$): 3430, 1695 cm^{-1}. Mass spectrum (electron impact): *m/e* 518 (M$^+$). Anal. Calcd for $C_{33}H_{30}N_2O_4$: C, 76.43; H, 5.83; N, 5.40. Found: C, 76.60; H, 5.70; N, 5.62. The reaction of pyrrole **7** (1.4 g, 6.5 mmol), prepared as described,[4] dissolved in 10 mL of acetic acid, with 330 μL (3.25 mmol) of benzaldehyde gave, after heating for 3 h at 60 °C, 1.48 g of compound **8** (yield, 88%) with identical characteristics.

Reactions of Diacid Dichloride. Formation of Tetrapyrrole Macrocycles. Formation of Tricyclic Pyrrole 9. The reaction was carried out as for compound **2**, using hex-1-yne (1.8 mL, 16 mmol), methyllithium (0.93 M, 17 mL, 16 mmol, and 0.73 M, 22 mL, 16 mmol), CuI (2.8 g, 15 mmol), and acetylene ester **1b** (4.1 g, 15 mmol) reacted with phthaloyl dichloride (1.3 g, 15 mmol). The crude product was purified by TLC (CH_2Cl_2/Et_2O 95/5), and 0.10 g (yield, 5%) of **9** was obtained after crystallization from methanol. Mp: 113 °C. ^{1}H NMR ($CDCl_3$): δ 1.40 (3H, t), 2.10 (3H, s), 4.28 (2H, q), 6.70 (1H, s), 8.2–8.7 (4H, m). IR (CCl_4): 1760, 1710 cm^{-1}. Mass spectrum (electron impact): *m/e* 255 (M$^+$). Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.37; H, 5.49; N, 5.63.

Preparation of 1,3-Dipyrrolylbenzenes 10a,b. Compound 10a. The reaction was carried out as for compound **2** using hex-1-yne (2.3 mL, 20.5 mmol), 0.87 M methyllithium solution in ether (48 mL, 41 mmol), CuI (3.98 g, 20.5 mmol), acetylene ester **1a** (5.2 g, 20 mmol), and isophthaloyl chloride (2.13 g, 10.2 mmol). The crude product was purified by column chromatography (neutral alumina, Et_2O) to give 0.7 g of 1,3-dipyrrolylbenzene **10a** (yield, 20%). Mp: 189 °C. ^{1}H NMR (DMSO-d_6): δ 2.35 (6H, s), 3.47 (6H, s), 6.42 (2H, s), 6.95–7.80 (4H, m), 10.80 (2H, vbs). ^{13}C NMR (DMSO-d_6): δ 12.37 (CH_3—C=); 50.13 (CH_3); 110.24, 117.51, 120.70, 127.01, 127.98, 128.76, 132.28, 136.35 (aromatic carbons); 165.44 (C=O). IR (DMSO): 3400, 1680 cm^{-1}. Mass spectrum (FAB): *m/e* 353 (M + H$^+$). Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 67.99; H, 5.89; N, 7.54.

Compound 10b. As above using hex-1-yne (16.2 mL, 148 mmol), 1.2 M methyllithium solution in ether (247 mL, 296 mmol), CuI (28.1 g, 148 mmol), acetylene ester **1b** (40 g, 148 mmol), and isophthaloyl chloride (15.0 g, 74 mmol) led to the isolation of 9.0 g of **10b** (yield, 32%). Mp: 195 °C. ^{1}H NMR (acetone-d_6): δ 1.18 (6H, t), 2.28 (6H, s), 4.13 (4H, q), 6.56 (2H, s), 7.40 (4H, m), 9.80 (2H, vbs). ^{13}C NMR (acetone-d_6): δ 12.79 (CH_3C=); 14.54 (CH_3CH_2O); 59.54 (CH_2O); 112.35, 118.20, 122.85, 127.99, 129.41, 120.23, 134.00, 137.83 (aromatic carbons); 166.20 (C=O). IR (C_2H_6O): 3340, 1675 cm^{-1}. Mass spectrum (electron impact): *m/e* 380 (M$^+$). Anal. Calcd for $C_{22}H_{24}N_2O_4$: C, 69.46; H, 6.36; N, 7.36. Found: C, 69.44; H, 6.35; N, 7.27.

Preparation of Macrocycle 12. Dipyrrolylbenzene **10b** (3.3 g, 8.7 mmol) was dissolved in 15 mL of acetic acid solution containing 1 mL (10 mmol) of benzaldehyde. The mixture was heated at 70 °C for 4 h. Then the solvent was evaporated, and the residue was extracted with ether. After washing with aqueous $NaHCO_3$ and then water and drying, 1.22 g of macrocycle **11** was crystallized as a mixture of isomers from a hexane/CH_2Cl_2 (9/1) solution (yield, 30%). Mp: 295 °C. ^{1}H NMR ($CDCl_3$): δ 1.22 (12H, t), 2.14 (12H, s), 4.21 (8H, q), 5.65 (2H, s), 6.90–7.85 (22H, m). ^{13}C NMR ($CDCl_3$): δ 10.77, 11.22 (CH_3—C=); 14.10, 14.24 (CH_3CH_2); 39.04, 39.70 (CH—C_6H_5); 59.59, 59.91 (CH_2O); 113.29, 119.32, 119.64, 124.93, 127.71, 127.85, 128.13, 128.44, 129.31, 129.63, 130.13, 130.64, 132.27, 133.28, 135.79, 139.99, 140.17 (aromatic carbons); 165.70, 165.81 (C=O). IR ($CHCl_3$): 3420, 1685 cm^{-1}. UV (CH_2Cl_2): λ_{max} (ε) 300 (35 980). Mass spectrum (electron impact): *m/e* 936 (M$^+$). Exact mass calcd for $C_{58}H_{56}N_4O_8$, 936.4089; found, 936.4365.

Oxidation to Macrocycle 12. To a solution of DDQ (0.38 g, 1.7 mmol) in 10 mL of toluene was added 0.8 g (0.85 mmol) of compound **12**. The mixture was then stirred for 4 h, and the solvent was removed. Chromatographic purification of the residue (eluent CH_2Cl_2/MeOH 92/8) gave 0.73 g of macrocycle **12** (yield, 92%). Mp: 322 °C dec. ^{1}H NMR ($CDCl_3$): δ 1.05 (12H, t), 1.50 (12H, s), 4.05 (8H, q), 7.20–7.70 (16H, m), 7.90 (2H, s), 14.10 (2H, s, NH exchangable with D_2O). ^{13}C NMR ($CDCl_3$): δ 13.80 (CH_3—C=); 14.27 (CH_3CH_2); 60.34 (CH_2O); 123.28, 127.00, 127.34, 129.15, 129.66, 130.83, 135.02, 137.24, 138.55, 144.94, 145.80, 155.20, 158.06 (aromatic carbons); 165.62 (C=O). IR ($CHCl_3$): 3410, 1705 cm^{-1}. UV and visible spectrum (CH_2Cl_2): λ_{max} (ε): 284 (43 250), 454 (69 700), 487 (31 500). Mass spectrum (electron impact): *m/e* 932 (M$^+$). Exact mass calcd for $C_{58}H_{52}N_4O_8$, 932.3784; found, 932.3763. Anal. Calcd for $C_{58}H_{52}N_4O_8$: C, 74.66; H, 5.62; N, 6.04. Found: C, 74.13; H, 5.59; N, 5.75.

Protonated Form of the Macrocycle 12. A solution of compound **12** (0.102 g, 0.109 mmol) in 20 mL of CH_2Cl_2 was bubbled with dry HCl gas for 7 h. The reaction was followed by TLC. After evaporation of the solvent, the residue was crystallized from CH_2Cl_2 to give 0.1 g of quantitatively protonated macrocycle **12** as dark red crystals. ^{1}H NMR ($CDCl_3$): δ 0.9–1.2 (12H, t), 1.8 (12H, s), 4.0–4.3 (8H, q), 7.2–7.7 (16H, m), 9.1 (2H, s), 13.6 (4H, s). IR (CCl_4): 1725 cm^{-1}. Visible spectrum (C_6H_6): λ_{max} 454 nm. Mass spectrum (FAB positive): *m/e* 933 (M + H$^+$).

Table I. Interatomic Distances (Å) for Complex 17 with Esd's in Parentheses

Rh1–N1	2.056(11)	C43–C44	1.38(2)
Rh1–N2	2.098(10)	C44–C45	1.36(2)
Rh1–C1	1.859(15)	C45–C46	1.42(2)
Rh1–C2	1.840(16)	C46–C41	1.39(2)
C1–O1	1.123(18)	C51–C52	1.40(2)
C2–O2	1.151(20)	C52–C53	1.38(2)
Rh2–N3	2.054(10)	C53–C54	1.39(2)
Rh2–N4	2.071(10)	C54–C55	1.39(2)
Rh2–C3	1.865(16)	C55–C56	1.41(2)
Rh2–C4	1.852(15)	C56–C51	1.40(2)
C3–O3	1.111(20)	C61–C62	1.38(2)
C4–O4	1.125(17)	C62–C63	1.39(2)
		C63–C64	1.41(2)
Rh1···Rh2	4.387(2)	C64–C65	1.36(2)
N1···N2	2.830(14)	C65–C66	1.37(2)
N3···N4	2.790(14)	C66–C61	1.40(2)
N1···N4	5.639(13)	C71–C72	1.37(2)
N2···N3	5.622(13)	C72–C73	1.40(2)
		C73–C74	1.40(2)
N1–C5	1.341(16)	C74–C75	1.42(2)
C71–C5	1.476(17)	C75–C76	1.41(2)
C5–C6	1.412(18)	C76–C71	1.39(2)
C6–C7	1.381(19)		
C7–C8	1.424(18)	C23–C6	1.49(2)
C8–N1	1.416(15)	C23–O5a	1.25(3)
C8–C9	1.422(17)	C23–O6a	1.38(3)
C9–C41	1.486(18)	O6a–C24a	1.62(4)
C9–C10	1.366(17)	C24a–C25	1.23(5)
C10–N2	1.423(15)	C23–O5b	1.30(4)
N2–C13	1.320(16)	C23–O6b	1.20(4)
C13–C51	1.480(18)	O6b–C24b	1.62(5)
C13–C12	1.419(18)	C24b–C25	1.37(5)
C12–C11	1.378(17)	C26–C12	1.48(2)
C11–C10	1.429(18)	C26–O7	1.18(2)
N3–C14	1.359(15)	C26–O8	1.35(2)
C53–C14	1.489(17)	O8–C27	1.73(3)
C14–C15	1.434(17)	C27–C28	1.33(4)
C15–C16	1.385(17)	C29–C15	1.48(2)
C16–C17	1.432(17)	C29–O9	1.20(2)
N3–C17	1.421(15)	C29–O10	1.32(2)
C17–C18	1.406(17)	O10–C30	1.46(2)
C61–C18	1.489(16)	C30–C31	1.45(3)
C18–C19	1.399(16)	C32–C21	1.46(2)
N4–C19	1.422(14)	C32–O11	1.21(2)
C19–C20	1.415(16)	C32–O12	1.32(2)
C20–C21	1.412(17)	O12–C33	1.46(2)
C21–C22	1.436(17)	C33–C34	1.47(2)
C73–C22	1.449(17)	C35–C7	1.51(2)
C22–N4	1.341(16)	C36–C11	1.53(2)
		C37–C16	1.52(2)
C41–C42	1.41(2)	C38–C20	1.54(2)
C42–C43	1.40(2)		

Table II. Main Bond Angles (deg) in the Molecule of Complex 17

N1–Rh1–C1	172.2(5)	N3–Rh2–C3	175.1(5)
N2–Rh1–C2	173.0(6)	N4–Rh2–C4	178.5(5)
N1–Rh1–C2	95.0(6)	N3–Rh2–C4	95.5(5)
N2–Rh1–C1	93.0(5)	N4–Rh2–C3	95.2(6)
N1–Rh1–N2	85.9(4)	N3–Rh2–N4	85.1(4)
C1–Rh1–C2	85.2(7)	C3–Rh2–C4	84.0(7)
Rh1–C1–O1	174.8(1.3)	Rh2–C3–O3	176.0(1.4)
Rh1–C2–O2	172.3(1.5)	Rh2–C4–O4	171.4(1.3)
C71–C5–N1	123.4(1.1)	C53–C14–N3	123.6(1.1)
C5–N1–Rh1	129.6(8)	C14–N3–Rh2	128.0(8)
Rh1–N1–C8	121.7(8)	Rh2–N3–C17	124.3(7)
C5–N1–C8	106.9(1.0)	C14–N3–C17	106.8(1.0)
N1–C8–C9	122.3(1.1)	N3–C17–C18	122.7(1.1)
C8–C9–C10	126.8(1.1)	C17–C18–C19	125.6(1.1)
C9–C10–N2	123.7(1.1)	C18–C19–N4	122.8(1.0)
C10–N2–Rh1	115.5(8)	C19–N4–Rh2	120.1(7)
Rh1–N2–C13	126.1(8)	Rh2–N4–C22	125.7(8)
C10–N2–C13	109.2(1.0)	C19–N4–C22	109.1(9)
N2–C13–C51	120.8(1.1)	N4–C22–C73	122.0(1.1)

Table III. Summary of Crystal Data, Intensity Measurements, and Refinement

formula	$C_{62}H_{50}N_4O_{12}Rh_2$
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.635(3)
b, Å	18.104(5)
c, Å	27.407(12)
β, deg	100.00(3)
vol, Å^3	5685.5
mol wt	1248.9
Z	4
d_{calcd}, g cm^{-3}	1.459
d_{measd}, g cm^{-3}	1.45(2)
cryst size, mm^3	0.70 × 0.45 × 0.40
cryst color	deep red
recryst solv	CH_2Cl_2:hexane, 3:1
mp, °C	312–315 dec
method of data collectn	moving crystal, moving counter
radiatn (graphite monochromated)	Mo Kα
μ, cm^{-1}	6.34
2θ limits, deg	4–42
no. of unique reflectns	5289
no. of obsd reflectns	3420
final no. of variables	349
R	0.052
R_w	0.054
residual electron dens	0.67

Preparation of Dipyrrolylpyridine 13. The reaction was carried out as for compound **2**, using hex-1-yne (16.2 mL, 148 mmol), 1.96 M methyllithium solution in ether (151 mL, 296 mmol), CuI (28.2 g, 148 mmol), and 2,6-pyridinedicarboxylic acid dichloride (15.1 g, 74 mmol). After column chromatography over neutral alumina (eluent CH_2Cl_2) 7.0 g of dipyrrolylpyridine **13** was isolated (yield, 25%). Mp: 150 °C. ^{1}H NMR ($CDCl_3$): δ 11.17 (5H, t), 2.10 (6H, s), 4.07 (4H, q), 6.20 (2H, s), 7.1–7.9 (3H, m), 10.10 (2H, bs). ^{13}C NMR ($CDCl_3$): δ 12.82 (CH_2—C=); 14.37 (CH_3CH_2); 60.05 (CH_2O); 112.89, 117.77, 121.69, 123.43, 134.88, 136.75, 148.93 (aromatic carbons); 166.68 (C=O). IR ($CHCl_3$): 3440, 1685 cm^{-1}. Mass spectrum (electron impact): m/e 381 (M^+). Anal. Calcd for $C_{21}H_{23}N_3O_4$: C, 66.13; H, 6.08; N, 11.02. Found: C, 66.10; H, 6.15; N, 11.02.

Preparation of Macrocyclic Compound 14. Dipyrrolylpyridine **13** (5.5 g, 14.4 mmol) was added to 20 mL of a solution containing 1.5 mL (14.7 mmol) of benzaldehyde in acetic acid. The solution was then stirred for 4 h at 70 °C. The solvent was evaporated and the residue extracted with ether and washed with aqueous $NaHCO_3$. After drying and removal of the solvent, the extract was chromatographed over neutral alumina (eluent CH_2Cl_2) to give 1.0 g of macrocyclic compound as a mixture of isomers (yield, 15%). Mp: 314 °C dec. ^{1}H NMR ($CDCl_3$): δ 1.3 (12H, t), 2.2 (12H, s), 4.28 (8H, q), 5.72 (2H, s), 6.9–7.8 (16H, m), 9.0 (4H, s). IR ($CHCl_3$): 3420, 1690 cm^{-1}. Mass spectrum (electron impact): m/e 938 (M^+). Exact mass calcd for $C_{56}H_{54}N_6O_8$, 938.5009; found, 938.5349.

Oxidation to Macrocycle 14. As for compound **12**, the isomeric mixture (0.5 g, 0.53 mmol) was treated with 0.3 g (1.33 mmol) of DDQ in toluene solution to give 0.158 g of macrocycle **14** (yield, 64%). Mp: 340 °C. ^{1}H NMR ($CDCl_3$): δ 0.98 (12H, t), 1.67 (12H, s), 4.02 (8H, q), 7.1–7.8 (16H, m), 7.92 (2H, s). ^{13}C NMR ($CDCl_3$): δ 11.13 (CH_3—C=); 14.28 (CH_3CH_2); 60.14 (CH_2O); 119.87, 123.74, 127.30, 127.66, 128.40, 128.99, 129.22, 129.90, 133.78, 139.90, 149.30, 150.11 (aromatic carbons); 166.22 (C=O). IR ($CHCl_3$): 3420, 1685 cm^{-1}. Mass spectrum (electron impact): m/e 934 (M^+). Anal. Calcd for $C_{56}H_{50}N_6O_8$: C, 71.93; H, 5.39; N, 8.99. Found: C, 71.59; H, 5.45; N, 9.02.

Formation of Bimetallic Transition-Metal Complexes. Preparation of Dipalladium Complex 15. Macrocyclic ligand **12** (0.21 g, 0.23 mmol) was mixed with 0.29 g (0.95 mmol) of palladium acetylacetonate and 2.0 g of C_6H_5OH. The mixture was heated to reflux for 30 h. The reaction was followed by TLC. After cooling to room temperature, the reaction mixture was dissolved in CH_2Cl_2 (30 mL) and neutralized with aqueous KOH solution. Extracted with ether, the combined organic layer was dried over $MgSO_4$. After evaporation of solvent, the TLC (eluent CH_2Cl_2/Et_2O 96/4) separation and further crystallization from

Table IV. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

atom	x/a	y/b	z/c	U_{iso}	atom	x/a	y/b	z/c	U_{iso}
Rh1	6637.0(1.0)	2032.1(6)	1056.1(4)	*a*	O8	6239(12)	318(8)	−1044(5)	*a*
Rh2	6727.4(9)	4402.8(6)	732.9(4)	*a*	C27	5803(20)	249(14)	−1678(10)	152(4)
N1	8362(9)	1797(5)	1318(4)	*a*	C28	5461(21)	−439(15)	−1611(10)	163(4)
N2	6888(8)	1490(5)	406(4)	*a*	C29	6622(11)	4209(7)	−1324(5)	46(3)
N3	7084(8)	4537(5)	30(4)	*a*	O9	6384(10)	4574(5)	−1693(4)	*a*
N4	8360(8)	4865(5)	963(4)	*a*	O10	6736(8)	3482(5)	−1312(3)	*a*
C1	5036(13)	2115(8)	844(5)	52(3)	C30	6452(15)	3097(9)	−1788(6)	79(3)
C2	6342(13)	2400(8)	1648(6)	66(3)	C31	6405(17)	2317(10)	−1681(7)	112(4)
C3	6339(13)	4360(8)	1365(6)	64(3)	C32	10616(11)	5610(7)	1948(5)	39(3)
C4	5249(13)	4012(8)	533(5)	52(3)	O11	10930(10)	6216(5)	2107(4)	*a*
O1	4060(9)	2117(6)	734(4)	*a*	O12	11106(8)	4993(5)	2139(3)	*a*
O2	6090(10)	2557(9)	2022(5)	*a*	C33	12010(13)	5038(8)	2579(6)	63(3)
O3	6044(10)	4344(8)	1729(4)	*a*	C34	12499(16)	4293(10)	2662(7)	106(4)
O4	4349(8)	3764(5)	474(4)	*a*	C35	10848(13)	427(8)	1621(6)	66(3)
C5	9118(10)	2133(6)	1675(4)	32(3)	C36	7179(12)	−442(8)	−72(5)	60(3)
C6	10090(12)	1674(7)	1838(5)	48(3)	C37	8070(12)	5655(7)	−999(5)	54(3)
C7	9943(11)	1035(7)	1559(5)	42(3)	C38	10100(12)	6643(7)	1033(5)	56(3)
C8	8857(10)	1105(6)	1230(4)	28(3)	C41	8915(11)	−107(7)	839(5)	40(3)
C9	8333(10)	622(7)	846(5)	37(3)	C42	9860(12)	−192(8)	585(5)	56(3)
C10	7422(11)	783(7)	475(5)	37(3)	C43	10456(14)	−862(9)	590(6)	68(3)
C11	6942(11)	363(7)	46(5)	39(3)	C44	10117(14)	−1434(9)	863(6)	68(3)
C12	6207(10)	817(6)	−270(5)	33(3)	C45	9202(14)	−1370(9)	1107(6)	74(3)
C13	6170(11)	1503(7)	−24(5)	41(3)	C46	8571(13)	−700(8)	1099(6)	62(3)
C14	6627(10)	4157(6)	−387(4)	33(3)	C51	5621(11)	2203(7)	−224(5)	35(3)
C15	6910(11)	4517(7)	−817(5)	36(3)	C52	6308(10)	2843(6)	−171(4)	32(3)
C16	7573(11)	5132(7)	−653(5)	36(3)	C53	5867(10)	3495(7)	−387(4)	33(3)
C17	7702(10)	5147(6)	−123(4)	32(3)	C54	4727(11)	3531(7)	−646(5)	40(3)
C18	8378(10)	5627(6)	215(4)	32(3)	C55	4005(12)	2917(7)	−689(5)	47(3)
C19	8699(10)	5505(6)	724(4)	25(2)	C56	4463(11)	2251(7)	−474(5)	37(3)
C20	9496(11)	5896(7)	1081(5)	36(3)	C61	8903(10)	6277(6)	4(4)	30(3)
C21	9731(11)	5460(7)	1514(5)	37(3)	C62	8286(11)	6928(7)	−98(5)	40(3)
C22	8986(10)	4825(6)	1422(5)	33(3)	C63	8777(12)	7535(8)	−293(5)	53(3)
C23	11086(16)	1932(11)	2219(7)	89(4)	C64	9917(12)	7483(8)	−398(5)	55(3)
O5a	11503(17)	2565(11)	2191(8)	93(4)	C65	10512(12)	6839(7)	−308(5)	45(3)
O5b	11089(22)	2533(15)	2476(11)	79(4)	C66	10042(12)	6246(7)	−98(5)	44(3)
O6a	11556(15)	1365(9)	2527(6)	64(3)	C71	8930(11)	2879(7)	1863(5)	39(3)
O6b	11906(27)	1521(19)	2310(13)	114(4)	C72	8932(11)	3478(7)	1555(5)	40(3)
C24a	12507(28)	1657(19)	2989(14)	78(4)	C73	8909(11)	4196(6)	1742(5)	35(3)
C24b	13044(29)	1768(20)	2707(15)	85(4)	C74	8811(11)	4309(8)	2240(5)	51(3)
C25	13240(27)	1168(19)	3011(14)	125(14)	C75	8778(13)	3692(8)	2555(6)	63(3)
C26	5534(13)	643(8)	−766(6)	60(3)	C76	8867(12)	2981(8)	2359(5)	52(3)
O7	4547(10)	767(7)	−934(5)	*a*					

[a] Corresponding atom was refined anisotropically; see the table in the supplementary material.

chloroform afforded 0.3 g of dipalladium complex **15** (yield, 98%) as red crystals. Mp: 250 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.9–1.2 (12H, t), 1.40 (12H, s), 1.50 (12H, s), 3.9–4.2 (8H, q), 4.70 (2H, s), 7.2–7.7 (16H, m), 8.5 (2H, s). ^{13}C NMR ($CDCl_3$): δ 14.28 (CH_3); 14.51 (CH_3); 25.03 (CH_3—C—O); 60.43 (CH_3CH_2O); 100.05 (CH_3—*C*—O); 115.68, 124.90, 126.46, 128.45, 129.38, 129.99, 130.95, 135.71, 136.21, 137.90, 146.19, 150.65, 161.82 (aromatic carbons); 166.01 (*C*=O); 185.11 (O—C—*C*H—C—O). IR (CCl_4): 1700, 1580, 1518, 1495, 1470, 1395, 1288, 1253, 1182, 1120 cm^{-1}. Mass spectrum (FAB positive): *m/e* 1341 (M + H$^+$). UV and visible spectrum (CH_2Cl_2): λ_{max} (ε) 565 (66 700), 503 (117 000), 390 (11 200), 330 (23 700), 292 (38 800) nm. Anal. Calcd for $C_{68}H_{64}N_4O_{12}Pd_2$: C, 60.96; H, 4.81; N, 4.17; Pd, 15.86. Found: C, 61.30; H, 4.88; N, 4.21; Pd, 14.34.

Preparation of Dinickel Compound 16. Macrocyclic ligand **12** (0.25 g, 0.26 mmol) was mixed with 0.5 g (1.96 mmol) of nickel acetylacetonate in 15 mL of benzene. The mixture was then refluxed for 4 days, and the reaction was followed by TLC. After cooling to room temperature, the solvent was removed. Then the preparative TLC separation (eluent CH_2Cl_2/Et_2O 96/4) and crystallization from chloroform gave 0.13 g of dinickel complex **16** (yield, 61%) as red crystals. Mp: 200 °C dec. IR (CCl_4): 1700, 1610, 1528, 1490, 1468, 1385, 1258, 1192, 1125 cm^{-1}. Mass spectrum (FAB positive): *m/e* 1245 (M + H$^+$). UV and visible spectrum (CH_2Cl_2): λ_{max} (ε) 536 (11 200), 480 (257 000), 453 (44 800), 285 (75 300) nm. Anal. Calcd for $C_{68}H_{64}N_4O_{12}Ni_2$: C, 65.52; H, 5.17; N, 4.49. Found: C, 65.88; H, 5.17; N, 4.51.

Preparation of Dirhodium Complex 17. Macrocyclic ligand **12** (0.107 g, 0.115 mmol) was mixed with 0.045 g (0.116 mmol) of dichlorotetracarbonyldirhodium and dissolved in 20 mL of benzene. After 6 h of stirring at room temperature, the solvent was removed. The residue was dissolved in CH_2Cl_2 and purified by preparative TLC (eluent CH_2Cl_2/Et_2O 98/2). The obtained product was further recrystallized in CH_2Cl_2/hexane, affording 0.13 g of dirhodium complex **17** (yield, 91%) as red crystals. Mp: 312–315 °C. ^{1}H NMR ($CDCl_3$): δ 1.05 (12H, t), 1.60 (12H, s), 4.15 (8H, q), 7.4–7.9 (16H, m), 8.45 (2H, s). ^{13}C NMR ($CDCl_3$): δ 14.0 (CH_3); 14.4 (CH_3); 60.3 (CH_2O); 126.8, 129.3, 129.8, 131.8, 133.4, 136.7, 136.8, 137.8, 147.8, 151.0, 163.6 (aromatic carbons); 165.8 (*C*=O); 183.1, 184.5 (*C*≡O) ($J(Rh^{103}–C^{13})$ = 68 Hz). IR (CCl_4): 2080, 2069, 2020, 1996, 1708, 1495, 1275, 1126 cm^{-1}. UV and visible spectrum (CH_2Cl_2): λ_{max} (ε) 555 (2210), 504 (89 800), 410 (3940), 375 (3780), 288 (55 000) nm. Mass spectrum (FAB positive): *m/e* 1249 (M + H$^+$). Anal. Calcd for $C_{62}H_{50}N_4O_{12}Rh_2$: C, 59.63; H, 4.04; N, 4.49. Found: C, 59.94; H, 4.22; N, 4.51.

Crystal Structure of Complex 17. Crystal Preparation. Crystals of complex **17** were grown by slowly cooling to −10 °C a hexane/dichloromethane solution in a nitrogen atmosphere. Dark red elongated blocks were obtained. Preliminary Weissenberg photographs established a monoclinic unit cell with space group $P2_1/c$. A small block was cut from a needle and was sealed inside a Lindeman glass capillary with the [100] direction parallel to the Φ axis of the diffractometer.

X-ray Data Collection. Data were collected on a CAD-4 automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å). Lattice constants (Table III) comes from a least-squares refinement of 25 reflections obtained in the range 15° < 2θ < 22°. The intensities of three standard

reflections were monitored after intervals of 60 min; no significant change of these intensities occurred during data collection. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. Only the reflections having $\sigma(F)/F <$ 0.36 were considered to be observed. The absorption corrections on the F's were neglected.

Structure Determination and Refinement. The structure was solved by the heavy-atom method. A Fourier map phased on the two rhodium atoms revealed only the four nitrogen atoms. Three subsequent Fourier maps and two difference Fourier syntheses led to location of all the remaining oxygen and carbon atoms. At this stage of the determination disorder appeared mainly in two ethyl carboxylate groups and especially in the $C23O_2Et$ group. Different trials to take into account this disorder led to the introduction of two positions (labeled a and b) for the oxygen atoms O5 and O6 and for the atom C24. (It appeared that C25 was better described as a unique isotropic atom.) These were given occupancies of 0.6 and 0.4, respectively; attempts to refine these occupancy factors failed to improve the geometry of the carboxylate group. For the $C26O_2Et$ group disorder seems to occur to a lesser extent since a splitting of the atoms O7 and O8 as described above gave no improvement in the bond distances and angles around atom C26. In the final stages of the refinement, the hydrogen atoms were positioned by calculation (SHELX76 progam) and three isotropic thermal parameters were attributed to these hydrogens according to the groups to which they were attached: CH_2, CH_3, and phenyl rings. No hydrogen atom was positioned for the disordered ethyl groups C24,25 and C27,28. Anisotropic thermal parameters were given to the rhodium atoms, the nitrogen atoms, and the oxygen atoms O1–4 and O7–12. Refinement converged to the final R value of 0.052. Individual bond lengths are listed in Table I, and important bond angles are in Table II. A summary of crystal data, intensity measurements, and refinement is in Table III. The atomic coordinates (non-hydrogen atoms) and isotropic thermal parameters are in Table IV. The anisotropic thermal parameters (non-hydrogen atoms) and the calculated hydrogen atom coordinates are given as supplementary materials (Tables V and VI) along with Table VII (full list of bond angles).

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atoms coordinates, and bond angles (5 pages). Ordering information is given on any current masthead page.

OM9206970