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Synthesis of Chiral Molecules Containing Pyridine and 1,3-Pyrimidine Units: Potential Building Blocks for Helicating and Caging Ligands

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Abstract—A simple and efficient method for the synthesis of new chiral polyaza heterocylic structures containing pyridines and 1,3-pyrimidine units has been developed. It is based on the reaction of the appropriate enaminones with optically pure carboxamidine derived from the commercially available (*R*)-(−)-myrtenal.

Interest in selective generation of chiral metal centers in a predetermined configuration has recently increased, especially in the formation of chiral polynuclear coordination species[1] and in the syntheses of chiral helicates.[2] The elegant works of von Zelewsky[3] on the so-called 'chiragen', and by Constable[4] on chiral polypyridines, have demonstrated the utility of the design of enantiopure, well-defined polypyridine ligands in this area. On the other hand, Lehn and co-workers[5] recently used ligands containing pyridines and 1,3-pyrimidine units in the preparation of ordered inorganic architectures. This original work showed the importance of designing new and exciting molecules containing pyridines and 1,3-pyrimidine units.

Results and Discussion

We have already published an efficient procedure for the preparation of polyaza heterocycles containing 1,3-pyrimidine units,[6] which was also applied to the syntheses of functionalized amino acids with metal-binding sites using Nα-Boc-L-arginine as an enantiomerically pure guanidine (Fig. 1).[7,8] In order to develop new chiral chelating molecules for the stereochemical control of coordination complexes, we have decided to extend this straightforward procedure to the preparation of structures with stereogenic centers neighboring the metal-binding sites. In this paper we wish to describe the syntheses of a new family of chiral polydentate ligands containing pyridines and 1,3-pyrimidine units using an optically pure carboxamidine derived from the commercially available (*R*)-(−)-myrtenal.

The general approach that we have used for the preparation of polyaza heterocylic derivatives containing 1,3-pyrimidine units is the condensation of enaminone or bis-enaminone with an appropriate carboxamidine or guanidine under basic conditions.[9] The selected starting material for the syntheses of our chiral (pyrimidyl)pyridines was the pinene-2-carboxamidine **5**. This carboxamidine was chosen not only for its stability (no epimerisation) under reaction conditions, which can be drastic, but also for the solubility of the resulting products in organic solvents. The synthesis of this carboxamidine was achieved using a two-step procedure (Scheme 1). Reaction of (*R*)-(−)-myrtenal with

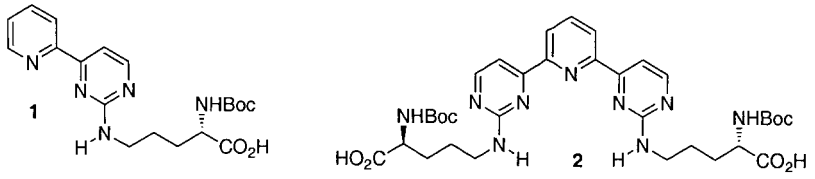

Figure 1. Amino acids with metal-binding sites derived from the Nα-Boc-L-arginine.

Keywords: asymmetric reactions; enamines; amidines; pyrimidines; pyridines; molecular design.

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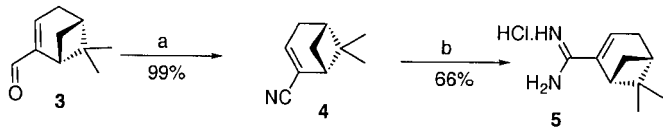
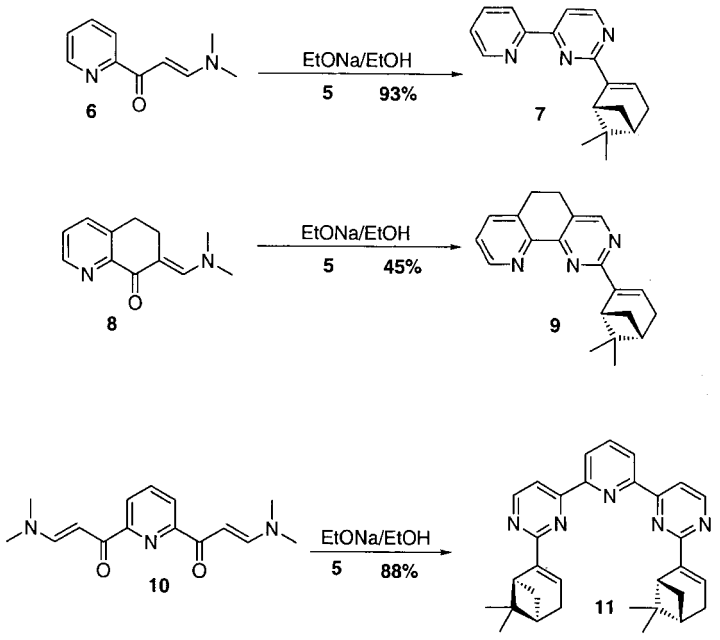


Scheme 1. Syntheses of the 2-pinenecarboxamidine from the (*R*)-myrtenal: (a) $(Me)_2NNH_2$ in toluene 0°C to rt, magnesium monoperoxyphtalate (MMPP) in MeOH at 0°C; (b) $AlMe_3$, NH_4Cl in toluene from 0°C to 80°C.



Scheme 2. Use of the chiral carboxamidine **5** in the preparation of new polyaza compounds.

dimethyl hydrazine followed by oxidation of the resulting hydrazone in situ with magnesium monoperoxyphtalate (MMPP) led to (−)-cyanopinene **4** in quantitative yield.[10] Reaction of **4** with Chloro methyl aluminum amide gave the carboxamidine hydrochloride **5** in 66% yield.[11]

Condensation of **5** with the enaminopyridine **6** in our previous conditions (EtONa/EtOH at 80°C for 16 h) led to 2-(2-pinenyl-4-pyrimidyl)pyridine **7** in 66% yield. The increase of the reaction temperature (from 80 to 100°C) resulted in a spectacular increase of yield of **7** to 93% (Scheme 2). Surprisingly, these excellent conditions gave the annelated (pyrimidyl)pyridine **9**, analogous to **7**, with a moderate yield (45%). However, the reaction of bis-enaminone **10** with **5** led to dipineno-[2′,2″]-2,6-bis-(4′,4″-pyrimidyl)pyridine **11**, in 88% yield. This molecule was crystallized by slow evaporation of dichloromethane solution and its structure was solved by X-ray diffraction. The molecular view of **11** with its atom labeling scheme is shown in Fig. 2.[12] The molecule is built up from a central pyridine ring with two pyrimidine rings in *meta* positions with respect to each other. Each pyrimidine is connected to a chiral (*R*)-pinene group. The whole molecule has a roughly planar conformation except for the pinene moieties. However, the two pyrimidine rings are slightly twisted with respect to the pyridine ring making dihedral angles of −3.2 and 15.5°, respectively. The C atoms of the CH_2 and CMe_2 groups on the pinene fragment are symmetrically distributed with respect to the mean planes defined by the C(141), C(142), C(143), C(144) and C(541), C(542),

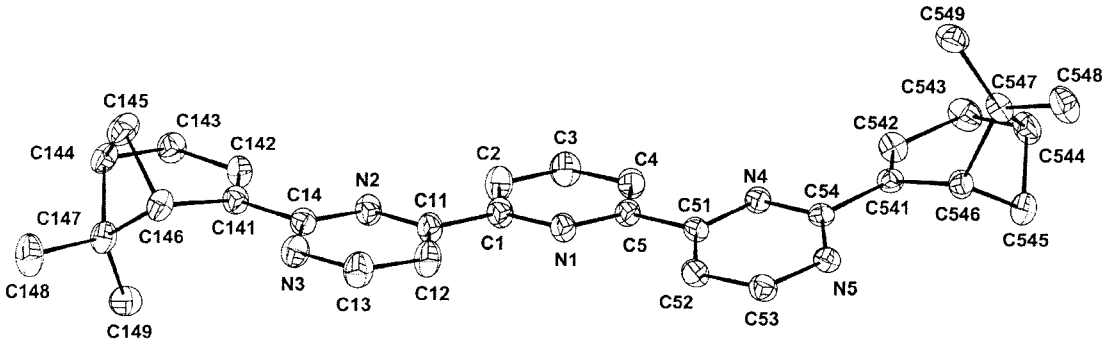


Figure 2. Molecular view of compound **11** with its atom labeling scheme. Ellipsoids are drawn at 50% probability level.

Table 1. Crystal data

Compound	**11**
Formula	$C_{31}H_{33}N_5$
fw(g)	475.64
Shape (color)	Flat needle (colorless)
Size (mm)	0.78, 0.23, 0.08
Space group	$P2_1$
a (Å)	9.615(1)
b (Å)	5.9464(5))
c (Å)	22.674(3)
β (°)	93.60(2)
V (Å^3)	1293.8(3)
Z	2
ρ (calcd) (g cm^{-3})	1.221
μ (MoK$_\alpha$) (cm^{-1})	0.685
Temperature (°K)	160(2)
No. of rflns collected	12651
No. of unique rflns (R_{int})	5033 (0.0376)
R	0.0356
R_w	0.0397
Weighting scheme	Chebyshev
Coefficient. Ar	1.63, −0.074, 1.71, −0.137, 0.421
GOF	1.121

C(543), C(544) (C(145) −1.108 Å, C(147) 1.039 Å; C(545) 1.086 Å, C(547) −1.059 Å) (Table 1). A similar conformation of the pinene fragment was described for the dipineno-[4,5:4″,5″]-fused 2,2′:6′,2″-terpyridine.[12] As observed in related compounds, the nitrogen N(1) of the pyridine ring is *trans* with respect to nitrogen atoms N(2) and N(4) of the pyrimidine rings. Such conformation minimizes electronic repulsion between lone pairs of nitrogen atoms.[6,13]

We have also applied this simple method to the preparation of the unsymmetrical tetradentate ligand **13**. In our precedent work, we have found that the condensation of **10** with the formamidine in 1:2 stoechiometry gave the product derived from the monocondensation, which was isolated in 34% yield.[6] We hoped that the reaction of **10** with 1 molar equivalent of **5** could lead preferentially to the product **12**. As shown in Scheme 3, the condensation of **10** with **5**, in 1:1 stoechiometry gave **12** in 66% yield. The unsymmetrical ligand **13** was then obtained in quantitative yield by reaction of the chiral enaminone **12** with pyridine-2-carboxamidine **6** under standard conditions.

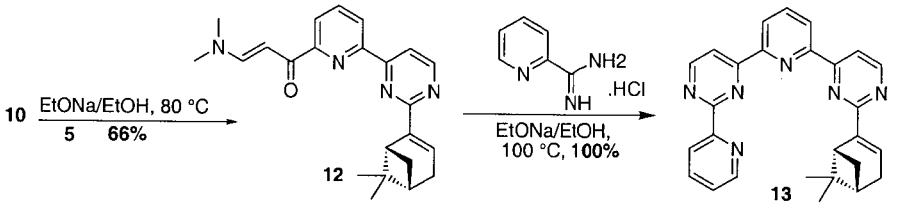
In summary, this extension of our work on the syntheses of polyaza structures containing pyridines and 1,3-pyrimidine units describes an easy way for the preparation of new chiral compounds similar to the chiral polypyridines already reported in the literature. Efforts are already underway for the application of these molecules in the preparation of transition metals complexes with predetermined stereochemistry at the metal center.

Experimental

NMR spectra were recorded on a Bruker AM 250 (250 MHz for ^{1}H and 62.9 MHz for ^{13}C) spectrometer. Optical rotations were measured on Perkin–Elmer 241 MC in our laboratory. DCI mass spectra were recorded with a quadripolar Nermag R 10-10H instrument. Elemental analyses were performed by LCC (Laboratoire de Chimie de Coordination) Microanalytical Service. Column chromatography was performed with Merck silica gel (230–400 mesh). For the preparation of enaminopyridine **6**, enaminoquinoleine **9** and bis-enaminone **10**, see Ref. 6. Dichloromethane and toluene were distilled from calcium hydride, dimethyl formamide from barium oxide and tetrahydrofuran from sodium benzophenone ketyl. All other reagents were used as commercially obtained.

(*R*)-(+)-2-Cyanopinene, 4. A solution of 5.23 g (0.0348 mol) of (*R*)-(−)-Myrtenal and 3.48 g (0.0578 mol) of *N*,*N*-dimethylhydrazine in anhydrous toluene (90 mL) was stirred at room temperature under argon over 2 h. The mixture was cooled to 0°C, at which point methanol (50 mL) and magnesium monoperoxyphtalate (51.07 g, 0.086 mol) were added. The cooled solution was stirred for an additional 15 min. The solution was allowed to warm to room temperature and quenched with $NaHCO_3$ saturated aqueous solution (100 mL), then dichloromethane (80 mL) was added and the layers were separated. The aqueous layer was extracted with dichloromethane (3×100 mL). The organic layers were combined, washed with water (100 mL) and with sodium chloride saturated aqueous solution (100 mL). The organic layer was then dried over Na_2SO_4, filtered and concentrated to give 5.10 g (>99% yield) of **4** as a colorless oil, which was used without further purification. Anal. found: C, 81.63; H, 8.97; N, 9.88. $C_{10}H_{13}N$ (147.22) requires C, 81.59; H, 8.90; N, 9.52; $[\alpha]_D$=+56.8 (c=0.5 $CHCl_3$); δ ^{1}H ($CDCl_3$) 6.50 (s, 3H); 2.30–2.45 (m, 4H); 2.10–2.11 (m, 1H); 1.26 (s, 3H); 1.10–1.20 (d, 1H, J=8 Hz); 0.82 (s, 3H); δ ^{13}C ($CDCl_3$) 142.0, 120.6, 118.2, 44.4, 39.6, 38.0, 32.5, 31.1, 25.5, 20.8; MS (CI,NH_3) m/z (%): 165 (100) [MNH_4^+].

(*R*)-(−)-Pinene-2-carboxamidine, 5. To a cooled suspension of 4.14 g (0.03872 mol) of ammonium chloride in anhydrous toluene (70 mL) at 0°C was added via canula 38.70 mL (0.0774 mol) of $AlMe_3$ (2 M solution in toluene). After stirring for 30 min, the 0°C bath was removed and the mixture was stirred for 30 min more at room temperature. A solution of 5.75 g (0.0378 mol) of **4** in dry toluene (35 mL) was added. The mixture was then placed into an oil bath at 80°C and stirred for an additional 16 h. The reaction was allowed to cool to room temperature, at which time 30 g of silica gel in chloroform (100 mL) was added. The solution



Scheme 3. Preparation of the chiral molecule **13**.

was stirred for 10 min and filtered. The silica gel was washed with methanol/chloroform (200 mL; 1:1) and with methanol (50 mL). The filtrates were concentrated under reduced pressure. The residue was solved in methanol/acetone mixture (50 mL; 1:1) and then filtered. The filtrate was then concentrated to give 5.05 g (66% yield) of **5** as a white solid, mp 230°C. Anal. found: C, 59.87; H, 8.85; N, 13.85. $C_{10}H_{17}ClN_2$ (200.71) requires C, 59.84; H, 8.53; N, 13.96; $[\alpha]_D=-30.80$ (c=0.5 MeOH); δ ^{1}H (CD_3OD) 6.80 (m, 1H); 2.62–2.72 (m, 4H); 2.25–2.28 (m, 1H); 1.49 (s,3H); 1.30 (d, 1H, J=8 Hz); 0.96 (s, 3H); δ ^{13}C (CD_3OD) 167.0, 139.0, 138.9, 43.9, 41.6, 39.3, 33.6, 32.5, 26.2, 21.3; MS (CI, NH_3); m/z (%): 165 (100) [MH^+].

Pinino-2-(4-pyrimidyl)pyridine, 7. To a hot solution of the enaminone **6** 0.176 g (1.01 mmol) in absolute ethanol (5 mL) was added 0.254 g (1.26 mmol) of carboxamidine **5** and 0.065 g (2.8 mmol) of sodium in absolute ethanol (5 mL). The mixture was then stirred at 100°C overnight. The solution was allowed to cool to room temperature and then filtered. The filtrate was concentrated and the crude was purified by flash chromatography (n-C_5H_{12}/AcOEt; 8:2) to give 0.256 g (93% yield) of **7** as a white solid, mp 40°C. Anal. found: C, 77.67; H, 7.21; N, 15.53. $C_{19}H_{19}N_3$ (277.36) requires C, 77.95; H, 6.90; N, 15.15; $[\alpha]_D=-2.40$ (c=0.5 $CHCl_3$); δ ^{1}H ($CDCl_3$) 8.70 (d, 1H, J=5 Hz); 8.65 (dt, 1H, J=5 Hz, 1 Hz); 8.53 (dd, 1H, J=8 Hz, 5 Hz); 8.10 (d, 1H, J=5 Hz); 7.72 (td, 1H, J=8 Hz, 2 Hz); 7.38 (dd, 1H, J=5 Hz, 1 Hz); 7.35 (dd, 1H, J=5 Hz, 1 Hz); 7.17 (m, 1H); 3.5 (td, 1H, J=7.50 Hz, 1.50 Hz); 2.50 (m, 3H); 2.21 (m, 1H); 1.32 (d, 1H, J=8 Hz); 0.87 (s, 3H); δ ^{13}C ($CDCl_3$) 164.2, 162.2, 157.7, 154.4, 149.2, 146.8, 136.8, 130.0, 125.0, 121.6, 114.0, 40.7, 37.8, 32.2, 31.5, 29.6, 26.2, 21.0; MS (CI, NH_3): m/z (%)=295 (100) [MNH_4^+].

Chiral annelated compound, 9. This compound was prepared using the standard conditions by reaction of 0.305 g (1.50 mmol) of **8** with 0.313 g (1.56 mmol) of **5** in the presence of 0.05 g of sodium in absolute ethanol at 100°C for 3 h. After filtration of the mixture, the filtrate was concentrated and the residue was purified by flash chromatography (n-C_5H_{12}/AcOEt; 8:2) to give 0.21 g (45% yield) of **9** as a white powder, mp 138°C; Anal. found: C, 79.39; H, 6.74; N, 14.12. $C_{20}H_{21}N_3$ (303.40) requires C, 79.17; H, 6.98; N, 13.85; $[\alpha]_D=-51.6$ (c=0.5 CHCl3); δ ^{1}H ($CDCl_3$) 8.75 (d, J=5 Hz, 1H); 8.56 (s, 1H); 7.58 (d, J=7 Hz, 1H); 7.31 (d, J=5 Hz, 1H); 7.27 (d, J=5 Hz, 1H); 3.44 (*t*, J=4 Hz, 1H); 2.95 (*t*, J=4 Hz, 2H); 2.51 (t, J=4 Hz, 2H); 2.18 (s, 1H); 1.40 (s, 3H); 1.25 (m, 4H); 0.86 (s, 3H); δ ^{13}C ($CDCl_3$) 164.5; 158.0; 155.9; 150.4; 149.4; 146.3; 135.5; 130.4; 126.8; 124.9; 41.5; 40.7; 37.9; 32.2; 31.6; 29.6; 27.3; 26.3; 23.9; 21.1; MS (CI, NH_3); m/z (%): 321 (100) [MNH_4^+].

Dipinino-[2′,2″]-2,6-bis-(4′,4″-pyrimidyl)pyridine, 11. This compound was prepared by the same protocol as for **7**. Reaction of **10** (0.50 g, 1.83 mmol) in the presence of 4 molar equivalents of **5** and 4 equiv. of sodium gave after purification by crystallization in ethanol 0.76 g (88% yield) of **11** as a white solid, mp 174°C; Anal. found: C, 78.47; H, 6.92; N, 14.56. $C_{31}H_{33}N_5$ (475.27) requires C, 78.30; H, 6.99; N, 14.72); $[\alpha]_D=+5.6$ (c=0.5 $CHCl_3$); δ ^{1}H ($CDCl_3$) 8.84 (d, 2H, J=5 Hz); 8.68 (d, 2H, J=8 Hz); 8.27 (d, J=5 Hz, 2H); 8.07 (t, J=8 Hz, 1H); 3.50 (td, J=8 Hz, 1 Hz, 2H); 2.78–2.60 (m, 2H); 2.23 (m, 2H); 1.47 (s, 3H); 1.32–1.27 (m, 2H); 0.88 (s, 3H); δ ^{13}C ($CDCl_3$) 164.3; 161.9; 157.8; 153.9; 146.7; 137.9; 130.2; 123.0; 114.0; 41.5; 40.6; 37.8; 32.3; 31.4; 29.6; 26.2; 21.0; MS: CI/NH_3; m/z (%): 476 (100) [MH^+].

2-[(*N*,*N*-Dimethylamino)-1-oxo-prop-2-en-1-yl]-6-[pinino-2-(4-pyrimdyl)-pyridine, 12. To a solution of 0.341 g (1.25 mmol) of **10** in hot absolute ethanol (5 mL) was added 0.27 g (1.32 mmol) of **5** and 0.065 g (2.8 mmol) of sodium in absolute ethanol (5 mL). The mixture was stirred at 80°C overnight. The solution was allowed to cool to room temperature and the solvent was removed under reduced pressure. The product was purified by flash chromatography (AcOEt) to give 0.31 g (66% yield) of **12** as a yellow solid, mp 178–179°C; Anal. found: C, 73.62; H, 7.21; N, 14.75. $C_{23}H_{26}N_4O$ (374.5) requires C, 73.77; H, 7.00; N, 14.96; $[\alpha]_D=+68$ (c=0.5 $CHCl_3$); δ ^{1}H ($CDCl_3$) 8.82 (d, J=5.2 Hz, 1H)); 8.75 (d, J=8.9 Hz, 1H); 8.30–8.20 (m, 2H); 8.05–7.96 (m, 2H); 7.20 (m, 1H); 6.64 (d, J=12.6 Hz, 1H); 3.48 (t, J=8.1 Hz, 1H); 3.17 (s, 3H); 3.09 (s, 3H); 2.15 (m, 4H); 1.43 (s, 3H); 1.25 (d, J=8 Hz, 1H); 0.89 (s, 3H); δ ^{13}C ($CDCl_3$) 164.3; 162.2; 157.7; 155.6; 154.7; 152.9; 146.7; 137.7; 130.2; 123.4; 123.3; 114.0; 91.0; 45.1; 41.1; 40.7; 37.8; 37.4; 32.3; 31.5; 26.2; 21.1; MS: CI/NH_3 m/z (%): 375 (100) [MH^+].

Chiral (pyrimidyl)pyridine, 13. This compound was prepared by the same protocol as for **7**. Reaction of 0.30 g (0.8 mmol) of **12** with 1.25 equiv. of the pyridine-2-carboxamidine and 2 equiv. of sodium in absolute ethanol gave 0.50 g of a crude product following removal of ethanol under reduced pressure. This material was then dissolved in dichloromethane and filtered. The filtrate was concentrated to give 0.364 g (>99% yield) of **13** as a white solid, mp 220°C (decomposition); Anal. found: C, 74.45; H, 5.83; N, 19.65. $C_{27}H_{24}N_6$ (432.52) requires C, 74.98; H, 5.59; N, 19.43); $[\alpha]_D=-50$ (c=0.5 $CHCl_3$); δ ^{1}H ($CDCl_3$) 9.14–9.08 (d, J=5 Hz, 2H); 8.97–8.84 (m, 2H); 8.74–8.69 (dd, J=8 Hz, 2 Hz, 2H); 8.52 (d, J=5 Hz, 1H); 8.20 (d, J=5 Hz, 1H); 8.10 (t, J=8 Hz, 1H); 7.95 (td, J=8 Hz, 2 Hz, 2H); 7.42 (ddd, J=8 Hz, 5 Hz, 1 Hz, 1H); 3.54 (t, J=8 Hz, 1H); 2.67–2.49 (m, 3H); 1.50 (s, 2H); 1.33 (d, J=8 Hz, 2H); 0.89 (s, 3H); δ ^{13}C ($CDCl_3$) 164.3; 163.3; 162.9; 161.7; 158.9; 157.8; 154.7; 154.2; 153.3; 150.0; 146.7; 138.1; 136.9; 130.3; 124.9; 123.6; 123.4; 123.3; 116.3; 114.0; 41.5; 40.6; 37.8; 32.3; 31.4; 26.2; 21.0; MS: CI/NH_3 m/z (%): 433 (100) [MH^+].

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References

1. Keene, F. R. *Coord. Chem. Rev.* **1997**, *166*, 121.
2. (a) Mamula, O.; von Zelewsky, A.; Bark, T.; Bernarinelli, G.

Angew. Chem., Int. Ed. Engl. **1999**, *38*, 2945. (b) Bowyer, P. K.; Porter, K. A.; Rae, A. D.; Willis, A. C.; Wild, S. B. *Chem. Commun.* **1998**, 1153. (c) Saalfrank, R. W.; Decker, M.; Hampel, F.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1997**, *130*, 1309. (d) Hayoz, P.; von Zelwsky, A.; Stoeckli-Evans, H. *J. Am. Chem. Soc*. **1993**, *115*, 5111. (e) Evans, D. A.; Worpel, K. A.; Scott, M. *J. Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 430. (f) Modder, J. F.; van Koten, G.; Vrieze, K.; Spek, A. C. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 1698.

3. (a) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 302. (b) von Zelwsky, A.; Mamula O. *J. Chem. Soc. Dalton Trans.* **2000**, 219.

4. (a) Baum, G.; Constable, E. C.; Fenske, D.; Kulke, T. *Chem. Commun.* **1997**, 2043. (b) Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T. *Chem. Commun.* **1999**, 195. (c) Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T. *Chem. Eur. J.* **1999**, *5*, 1862.

5. (a) Hanan, G. S.; Arana, C. R.; Lehn, J.-M.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1122. (b) Hanan, G. S.; Volkmer, D.; Schubert, U. S.; Lehn, J.-M.; Baum, G.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1842. (c) Ohkita, O.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, *5*, 3471.

6. Bejan, E.; Aït-Haddou, H.; Daran, J.-C.; Balavoine, G. G. A. *Synthesis* **1996**, 1012.

7. Bejan, E.; Aït-Haddou, H.; Daran, J.-C.; Balavoine, G. G. A. *Eur. J. Org. Chem.* **1998**, 2907.

8. Aït-Haddou, H.; Bejan, E.; Daran, J.-C.; Balavoine, G. G. A.; Berryer-Penaud, F.; Bonazzola, L.; Smaoui-Chaabouni, H.; Amouyal, E. *J. Chem. Soc. Dalton Trans.* **1999**, 3095.

9. Bejan, E. PhD Thesis, Universite Paris XI, Orsay, France, 1996.

10. Fernandez, R.; Gash, C.; Lassaleta, J.-M.; Liera, J.-M.; Vasquez, J. *Tetrahedron Lett.* **1993**, *34*, 141.

11. Garigipati, R. S. *Tetrahedron Lett.* **1990**, *31*, 1969.

12. X-Ray Structure Determination. Data were collected at 160 K on a Stoe IPDS (Imaging Plate Diffraction System) diffractometer equipped with an Oxford Cryosystems cooler device. The crystal-to-detector distance was 70 mm. The final unit cell parameters were obtained by least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections. The structure was solved by direct methods (SIR97) (see: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115) and refined by least-squares procedures on F_{obs}. H atoms were located on difference Fourier syntheses, but they were introduced in calculation in idealised positions(d(CH)=0.96 Å) and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Least-squares refinements were carried out by minimising the function $\sum w(|F_o|-|F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w=w'[1-\{\Delta F/6\sigma(F_o)\}^2]^2$ where $w'=1/\sum_1^n A_r T_r(x)$ with 5 coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was F_c/F_c(max) (see: Prince, E. *Mathematical Techniques in Crystallography*, Berlin, Springer-Verlag, 1982). Models reached convergence with $R=\sum(\|F_o|-|F_c\|)/(\sum|F_o|)$ and $Rw=[\sum w(|F_o|-|F_c|)^2/\sum w(F_o)^2]^{1/2}$, having values listed in Table 1. The calculations were carried out with the CRYSTALS package programs (see: Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. *CRYSTALS Issue 10*, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1996) running on a Pentium II. The drawing of the molecule was realised with the help of CAMERON (see: Watkin, D. J.; Prout, C. K.; Pearce, L. J. CAMERON, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1996). Full crystal data and details of the structure determination, full listing of interatomic distances and bond angles, fractional atomic coordinates, anisotropic thermal parameters for non hydrogen atoms and atomic coordinates for H atoms have been deposited at the Cambridge Crystallographic Data Center.

13. Ziegler, M.; Monney, V.; Stoeckli-Evans, H.; von Zelewsky, A.; Sasaki, I.; Dupic, G.; Daran, J.-C.; Balavoine, G. G. A. *J. Chem. Soc. Dalton Trans.* **1999**, 667.