Synthesis and Coordination Properties of 6,6′-Dimesityl-2,2′-bipyridine

Michael Schmittel[a,+,*], Andrea Ganz[a], Wolfdieter A. Schenk[b], Michael Hagel[b]

[a] Institut für Organische Chemie der Universität Würzburg,
[b] Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Z. Naturforsch. **54b,** 559–564 (1999); received January 11, 1999

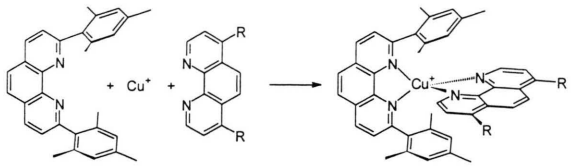
Suzuki Coupling, Copper(I) Complex, X-Ray Data

A synthetic route to 6,6′-dimesityl-2,2′-bipyridine is presented that involves a Suzuki coupling of 6,6′-dibromo-2,2′-bipyridine with mesityl boronic acid. The new sterically crowded ligand is investigated by X-ray analysis and its coordination behavior in the presence of copper(I) is examined.

During the last years, the preparation of large supramolecular structures has become an attractive goal. Many research groups have explored the chances of coordination chemistry since the well-defined geometric situation at individual metal sites facilitates the design of complex architectures [1]. Among others, tetrahedrally coordinating metals, such as copper(I), and rigid chelating ligands, such as phenanthrolines, have been used for the preparation of fascinating structures like helices [1b, 2], catenanes [3], rotaxanes [4] and many others.

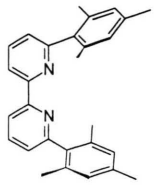
While so far most studies concentrated on bishomoleptic copper(I) complexes as building blocks, we have recently developed a strategy to prepare defined heteroleptic copper(I) bisphenanthroline complexes [5] that allow us to construct molecular boxes in an elegant self-assembly process [6]. The key constituent of our *modus operandi* relies on 2,9-diaryl phenanthrolines, such as **1**, whose sterically crowded aryl groups prevent the formation of the thermodynamically most stable bishomoleptic complex $[Cu(\mathbf{1})_2]^+$, thus rendering the heteroleptic species the most stable one [5].

To further understand the physical organic background of this concept we wished to investigate the properties of the accordingly substituted



1

2,2′-bipyridine **2**. Bipyridine ligands contain an analogous chelating bisimine unit, however display a higher flexibility due to the lacking aromatic bridge [7]. Because of the higher flexibility we expected ligand **2** to exhibit a lower kinetic barrier in the complexation step which could be of importance for the self-repair of supramolecular structures. Herein, we now describe the preparation of **2**, its solid state structure and some investigations concerning its coordination chemistry with copper(I) ions.



2

Results and Discussion

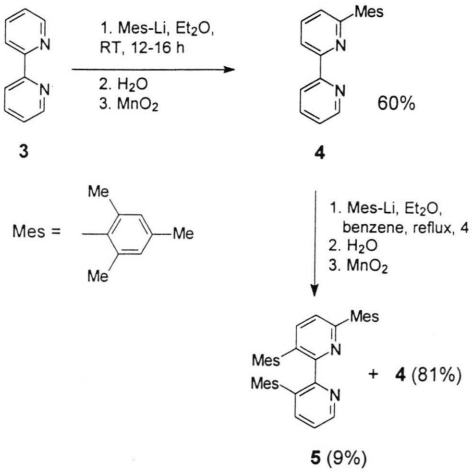
It has been reported for other bipyridine ligands that substitution in 6,6′-positions can be achieved by addition of the appropriate aryllithium compound to the unsubstituted bipyridine **3** followed by oxidation to rearomatize the bipyridine core, in

* Reprint requests to Prof. Dr. M. Schmittel.

+ New address after 01.04.1999: FB 8-OC 1 (Chemie–Biologie), Universität GH Siegen, Adolf-Reichwein-Str., D-57068 Siegen, Germany.
Fax: Int. +49 271 740 32 70
E-mail: schmittel@chemie.uni-siegen.de

0932–0776/99/0400–0559 $06.00

analogy to the preparation of the corresponding phenanthroline ligands [8]. Therefore, we applied similar reaction conditions as in the preparation of ligand **1** [9]. The first substitution step afforded the monosubstituted 6-mesityl-2,2′-bipyridine (**4**) in a yield of 60%, which is comparable to the yield for the preparation of the phenanthroline ligand. In the second step, however, no reaction could be observed under the usual conditions (i.e. room temperature). When heating the mixture to 50–60 °C a trisubstituted product **5** was isolated in 9% yield accompanied by a large amount of unreacted starting material (**4**).



Therefore, to prepare the desired ligand **2** a different synthetic route had to be used. As we could recently prepare sterically crowded biaryl compounds [9] using the Suzuki coupling method [10], we decided to apply this method as well. Hence, 6,6′-dibromo-2,2′-bipyridine (**7**) was prepared by oxidative coupling of 2,6-dibromopyridine (**6**) [11]. Subsequent Suzuki coupling of **7** with mesityl boronic acid (**8**) [12] afforded the new ligand **2** in a yield of 72%.

By crystallization from deuterochloroform at room temperature, suitable crystals of **2** for X-ray analysis were obtained. The X-ray structure shows a transoid, almost planar geometry at the bipyridine moiety as observed for many other bipyridine ligands [13]. The sterically crowded mesityl groups are rotated with respect to the bipyridine skeleton by a dihedral angle of 63° and 64° respectively (Fig. 1, Table 1).

For comparison, the phenyl groups of 6,6′-diphenyl-2,2′-bipyridine are rotated with respect to

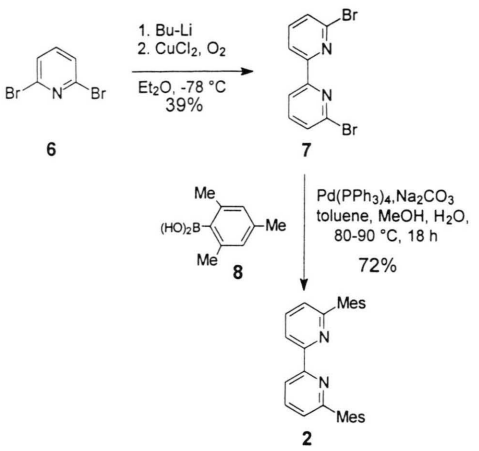


Table I. Selected bond lengths and angles of **2**.

Bond lengths [Å]		Dihedral angles [°]	
N(1)–C(21)	1.346	N(1)–C(25)–C(11)–C(16)	–116.77
N(1)–C(25)	1.365	N(2)–C(31)–C(41)–C(46)	–64.48
N(2)–C(31)	1.324		
N(2)–C(35)	1.335		
C(21)–C(35)	1.490		
C(11)–C(25)	1.478		
C(31)–C(41)	1.505		

the bipyridine skeleton by only 25–30° [14]. Thus, the steric hindrance of the methyl groups in **2** causes the aryl group to be heavily tilted, thereby reducing the conjugation with the bipyridine unit.

To investigate the coordination behavior of **2** we mixed $[Cu(MeCN)_4]BF_4$ with an equimolar amount as well as with an excess of ligand **2** in chloroform or TCE (1,1,2,2-tetrachloroethane). Even after heating these mixtures to 150 °C only the monocoordinated product $[Cu(\mathbf{2})(MeCN)]^+$ was detected (see p. 561).

Thus, even the more flexible bipyridine skeleton can not overcome the steric shielding of the bisimine coordination site exerted by the mesityl groups, therefore preventing the formation of the bishomoleptic complex in an effective manner. These experiments show that **2** matches the profile of steric coordination control [5, 9] which is fundamental to our concept of preparing stable heteroleptic copper(I) complexes. To our knowledge, there has been no report on stable mixed phenanthroline-bipyridine copper(I) complexes, except in cases where the geometrical constraint of one

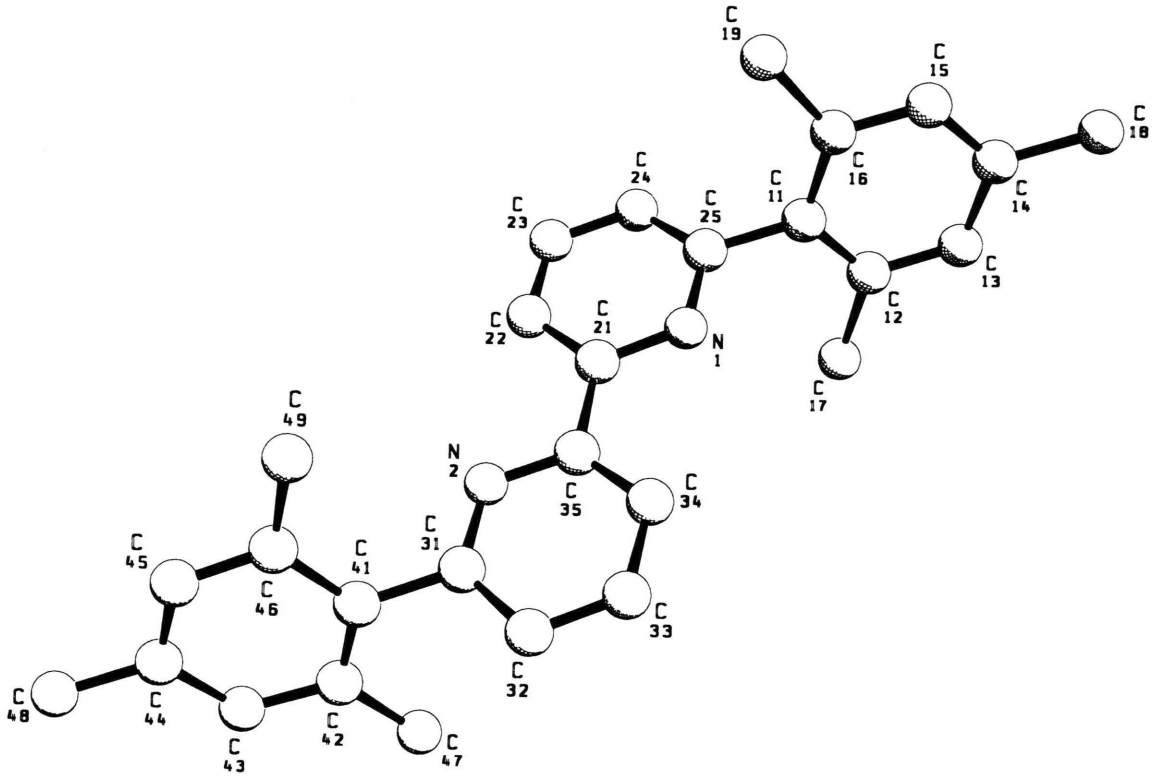
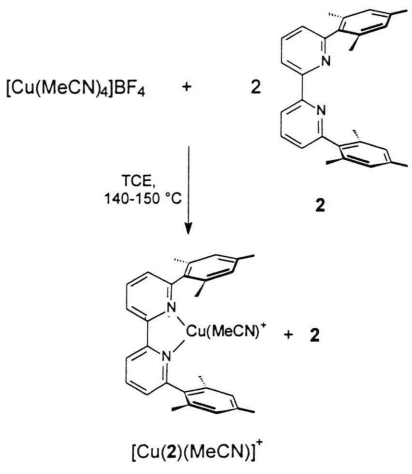
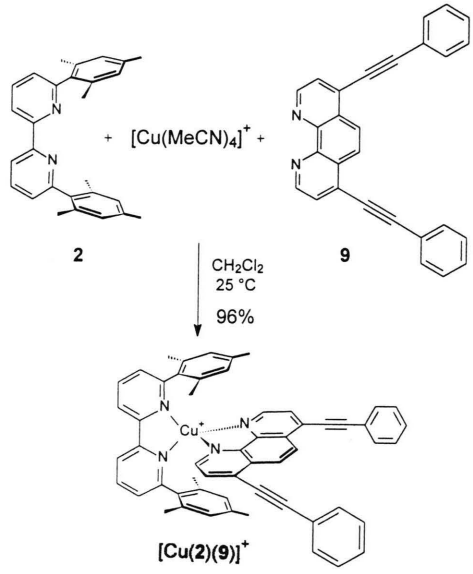


Fig. 1. X-Ray structure (ball stick representation) of **2**.





ligand prevented the formation of a bishomoleptic compound [15]. As a consequence, we can now present the first preparation of an unconstrained mixed phenanthroline-bipyridine copper(I) complex. Reacting ligand **2** with an equimolar amount of $[Cu(MeCN)_4]PF_6$ and the 4,7-disubstituted phenanthroline **9** [16] furnished the new heteroleptic copper(I) complex $[Cu(\mathbf{2})(\mathbf{9})]PF_6$ in a yield of 96%

after purification. It was unambiguously identified on the basis of its spectral and analytical data.

The straightforward preparation of the unconstrained mixed phenanthroline bipyridine copper(I) complex supports the generality of our concept. Future investigations shall explore whether the kinetic barrier of complex dissociation is lower for [Cu(**2**)(**9**)]PF_6 than for [Cu(**1**)(**9**)]PF_6 which could play a major role for the repair of metallosupramolecular architectures spanning several of such coordination sites to yield the thermodynamically most stable structure.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 or AM-250 instruments and calibrated with tetramethylsilane as an internal reference (TMS, δ = 0.0 ppm). IR spectra were recorded on a Perkin-Elmer 1605 series FT-IR-spectrometer. Elemental analyses were measured on a Carlo Erba Elemental Analyzer 1106. Melting points were determined by using a Mettler FP5.0. All reactions were carried out under an inert atmosphere. Solvents were dried using standard methods. Chemicals were purchased and used without further purification.

Failure to prepare **2** *via* **4**

6-(2,4,6-Trimethylphenyl)-2,2′-bipyridine (**4**). Bromomesitylene (3.18 g, 16.0 mmol) was dissolved in diethylether (70 ml) and a 1.6 M solution of *n*-butyllithium in *n*-hexane (16.0 mmol) added at room temperature. After 1 h stirring at room temperature, 2,2′-bipyridine (**3**) (1.00 g, 6.40 mmol) was added and the mixture stirred over night. After hydrolysis with water, the deep orange organic layer was separated and the aqueous layer extracted with dichloromethane (3×50 ml). Manganese dioxide (10.0 g) was added in portions to the combined organic layers and the mixture stirred for 90 min. After addition of magnesium sulfate, the mixture was filtered, concentrated and the brown oily residue purified by column chromatography (silica gel, dichloromethane : methanol = 100:1, R_f = 0.53) affording **2** (1.04 g, 3.80 mmol, 60%) as a yellow solid. IR (KBr) $\tilde{\nu}$ = 3057, 2954, 2857, 1614 (C=C), 1574 (C=C), 1470, 1434, 1378, 783, 754 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ = 2.10 (s, 6H, Me), 2.35 (s, 3H, Me), 6.98 (s, 2H, Mes), 7.26 (dd, ^3J = 7.3 Hz, ^4J = 0.93 Hz, 1H), 7.29 (m, 1H), 7.75 (td, ^3J = 7.9 Hz, ^4J = 1.8 Hz, 1H), 7.87 (t, J = 7.9 Hz, 1H), 8.36 (dd, ^3J = 7.9 Hz, ^4J = 0.9 Hz, 1H), 8.44 (dt, ^3J = 8.2 Hz, ^4J = 0.9 Hz, 1H), 8.68 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.6, 21.2, 108.3, 119.3, 121.9, 124.3, 125.3, 128.9, 136.4, 137.1, 137.5, 137.9, 149.5, 156.4, 156.9, 159.1.

Experiment to prepare **2** *via* **4**: Bromomesitylene (4.46 g, 22.4 mmol) was dissolved in diethylether (100 ml) and a 1.6 M solution of *n*-butyllithium in *n*-hexane (22.4 mmol) was added at room temperature. After 1 h stirring at room temperature, ligand **4** (700 mg, 4.49 mmol) dissolved in benzene (12 ml) was added and the mixture heated to reflux for 4 h. After work-up according to that of **4** the brown oily residue was separated by column chromatography (silica gel, cyclohexane : diethylether = 100:1), furnishing the starting material **4** (997 mg, 3.64 mmol, 81%) and the trisubstituted product **5** (193 mg, 380 μmol). The latter was identified by its characteristic ^1H NMR spectrum. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.11 (s, 18H, Me), 2.36 (m, 9H, Me) , 6.92 (m, 6H, Mes) , 7.20 (d, J = 8.0 Hz, 1H), 7.30 (m, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.76 (m, 1H), 8.65 (m, 1H).

6,6′-Bis(2,4,6-trimethylphenyl)-2,2′-bipyridin (**2**) *by Suzuki coupling*

7 (200 mg, 637 μmol) [11] and tetrakis(triphenylphosphan)palladium(0) (6.00 mg, 5.20 μmol) were dissolved in boiling toluene (40 ml). A solution of **8** (260 mg, 1.59 mmol) [12] in methanol (5 ml) and a 2 M sodium carbonate solution (8 ml) were added and the mixture was heated to reflux for 4 h. After further addition of **8** (100 mg) heating was continued for 3 days. After cooling, the layers were separated and the organic layer washed with a solution of sodium carbonate containing a small amount of ammonia. The aqueous layer was extracted with dichloromethane (2×50 ml) and the organic layers equally washed with the sodium carbonate solution. The combined organic layers were dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (silica gel, dichlormethane : cyclohexane = 3:1; R_f = 0.52) to furnish **2** (182 mg, 465 μmol, 72%) as a colorless solid. M.p. 237–238 °C; IR (KBr) $\tilde{\nu}$ = 2946, 2916, 2851, 1612 (C=C), 1571 (C=C), 1441, 1375, 1150, 1080, 1034, 989, 851, 809, 758 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ = 2.16 (s, 12H, Me), 2.39 (s, 6H, Me), 7.02 (s, 4H, Mes), 7.25 (dd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 2H), 7.84 (t, J = 7.6 Hz, 2H), 8.37 (dd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.5, 21.2, 119.2, 124.7, 128.5, 136.0, 136.9, 137.5, 138.1, 156.3, 159.1.

$C_{28}H_{28}N_2$ (392.5)
Calcd C 85.67 H 7.19 N 7.14%,
Found C 85.36 H 7.21 N 7.13%.

Crystal data of **2**: The structure of **2** was established by an X-ray structural analysis. Crystal data and the details of the procedure are compiled in Table II. The structure was solved by direct methods (SHELXS 96 program) [17] and refined by the block-matrix least-squares method (SHELXL 96 program) [17].

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary material (CSD 410686 a).

Table II. Crystallographic data.

Formula (M_F)	$C_{28}H_{28}N_2$ (392.52)
Space group	$P2_1$
Lattice constants [Å]	a = 6.8785(12)
	b = 15.228(2)
	c = 10.974(2)
	$\alpha = 90°$
	β = 95.701(8)°
	$\gamma = 90°$
Z	2
F(000)	420
Cell volume [Å^3]	1143.9(3)
Temperature	293(2) K
Density [g·cm^{-1}] calc.	1.140
Diffractometer	Enraf-Nonius-CAD4
Radiation	MoKα, Graphite monochromator, λ = 0.71073 Å
Index range	$0 \le h \le 8$
	$-4 \le k \le 18$
	$-11 \le l \le 11$
θ-Range	2.29°–25.95°
Total reflections	3149
Symmetry independent reflections (N)	2925
Parameters (P)	278
N/P	10.52
R-value	$R1$ = 0.0762, $wR2$ = 0.1139
R_ω-value	$R1$ = 0.0408, $wR2$ = 0.0928

Coordination properties of **2**

Reaction of **2** *with copper(I):* $[Cu(MeCN)_4]PF_6$ (5.0 mg, 13 μmol) was dissolved in $CDCl_3$ (0.7 ml) and **2** (10.46 mg, 26 μmol) was added. The yellow solution was examined by NMR spectroscopy and the complex $[Cu(\mathbf{2})(MeCN)]^+$ identified by characteristic chemical shifts, besides uncoordinated **2**. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.98 (s, 15H, Me, $C\underline{H}_3$–CN), 2.32 (s, 6H, Me), 6.95 (s, 4H), 7.54 (d, J = 7.5 Hz, 2H), 8.22 (t, J = 7.8 Hz, 2H), 8.37 (d, J = 7.8 Hz, 2H). When the above reactants were heated in TCE (140–150 °C) for 3 h the subsequent NMR analysis still showed a mixture of $[Cu(\mathbf{2})(MeCN)]^+$: **2** in a ratio of 1:1 and no traces of $[Cu(\mathbf{2})_2]^+$.

Preparation of a heteroleptic complex $[Cu(\mathbf{2})(\mathbf{9})]PF_6$. $[Cu(MeCN)_4]PF_6$ (19.5 mg, 52 μmol) was dissolved in dichloromethane (10 ml) and a solution of **2** (20.0 mg, 52 μmol) and **9** (20.0 mg, 52 μmol) [16] in dichloromethane (10 ml) was added. After stirring the deep violet mixture for 30 min, the solvent was evaporated and the residue purified by column chromatography (silica gel, dichloromethane : methanol = 10 : 1) to afford $[Cu(\mathbf{2})(\mathbf{9})]PF_6$ (49.0 mg, 50 μmol, 96%) as a deep violet solid. M.p. >250 °C; IR (KBr) $\tilde{\nu}$ = 2919, 2828, 2211 (C≡C), 1614 (C=C), 1591 (C=C), 1563 (C=C), 1509, 1463, 1444, 1423, 1377, 821 (P–F), 805, 758, 732, 690 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.52 (s, 6H, [**2**]), 1.72 (s, 12H, [**2**]), 5.89 (s, 4H, [**2**]), 7.47 (d, J = 7.3 Hz, 2H, [**2**]), 7.50 (m, 6H, [**9**]), 7.77 (m, 4H, [**9**]), 7.87 (d, J = 4.9 Hz, 2H, [**9**]), 8.25 (t, J = 7.7 Hz, 2H, [**2**]), 8.42 (s, 2H, [**9**]), 8.48 (d, J = 4.9 Hz, 2H, [**9**]), 8.54 (d, J = 8.2 Hz, 2H, [**2**]); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.6, 20.8, 78.4, 84.3, 101.9, 120.7, 124.9, 126.7, 126.8, 126.9, 128.2, 128.9, 129.9, 130.3, 132.2, 134.8, 137.4, 137.5, 139.1, 142.8, 146.9, 152.2, 158.3.

$C_{56}H_{44}N_4CuPF_6 \cdot 2H_2O$ (1017.53)
Calcd C 66.10 H 4.76 N 5.51%,
Found C 66.56 H 4.89 N 5.46%.

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (Schm 647/5-2, SFB 347) and the Fonds der Chemischen Industrie.

[1] a) E. C. Constable, Progr. Inorg. Chem. **42**, 67 (1994);
b) D. S. Lawrence, T. Jiang, M. Levett, Chem. Rev. **95**, 2229 (1995);
c) A. von Zelewsky, Stereochemistry of Coordination Compounds, Wiley, Chichester (1996).
[2] a) C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. **97**, 2005 (1997);
b) A. Williams, Chem. Eur. J. **3**, 15 (1997).
[3] a) C. O. Dietrich-Buchecker, J. P. Sauvage, Chem. Rev. **87**, 795 (1987);
b) J. S. Lindsey, New J. Chem. **15**, 153 (1991).
[4] F. Zeng, S. C. Zimmerman, Chem. Rev. **97**, 1681 (1997).
[5] M. Schmittel, A. Ganz, Chem. Commun. **1997**, 999.
[6] a) M. Schmittel, C. Michel, A. Ganz, M. Herderich, J. Prakt. Chem. **341**, 228 (1999);
b) M. Schmittel, C. Michel, unpublished results.
[7] S. T. Howard, J. Am. Chem. Soc. **118**, 10269 (1996).
[8] C. O. Dietrich-Buchecker, P. A. Marnot, J. P. Sauvage, Tetrahedron Lett. **23**, 5291 (1982).
[9] M. Schmittel, U. Lüning, M. Meder, A. Ganz, C. Michel, M. Herderich, Heterocycl. Comm. **1997**, 493.
[10] W. J. Thompson, J. Gaudino, J. Org. Chem. **49**, 5237 (1984).
[11] J. E. Parks, B. E. Wagner, R. H. Holm, J. Organomet. Chem. **56**, 53 (1973).
[12] M. F. Hawthorne, J. Org. Chem. **23**, 1579 (1958).
[13] S. T. Howard, J. Am. Chem. Soc. **118**, 10269 (1996).
[14] C. Kaes, M. W. Hosseini, A. DeCian, J. Fischer, Tetrahedron Lett. **38**, 3901 (1997).
[15] H. Sleiman, P. N. W. Baxter, J. M. Lehn, K. Airola, K. Rissanen, Inorg. Chem. **36**, 4734 (1997).
[16] M. Schmittel, A. Ganz, Synlett 710 (1997).
[17] G. M. Sheldrick, Acta Crystallogr. **A46**, 467 (1990)