Tridentate Coordination Mode of *N*,*N*′-Dimethyl-2,11-diaza[3.3](2,6)pyridinophane in a Tricarbonylmolybdenum(0) Complex

Harald Kelm and Hans-Jörg Krüger*

Institut für Anorganische und Angewandte Chemie der Universität Hamburg,
Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany
Fax: (internat.) + 49(0)40/4123-2893
E-mail: krueger@xray.chemie.uni-hamburg.de

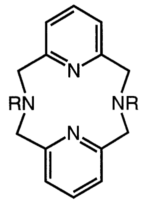
Received May 20, 1998

Keywords: Carbonyl complexes / Coordination modes / Fluxionality / Macrocyclic ligands / N ligands

Tridentate coordination of the potentially tetradentate ligand *N*,*N*′-dimethyl-2,11-diaza[3.3](2,6)pyridinophane ($L–N_4Me_2$) has been structurally established in the tricarbonylmolybdenum(0) complex $[Mo(L–N_4Me_2)(CO)_3]$. The fluxional behavior of the coordinated tetraazamacrocyclic ligand is demonstrated by a variable-temperature ^1H-NMR study. The relevance of the tridentate coordination mode of the ligand is discussed with respect to its intermediacy in the reaction mechanism for the formation of *cis* octahedral metal complexes containing tetradentate 2,11-diaza[3.3](2,6)pyridinophane derivatives as ligands.

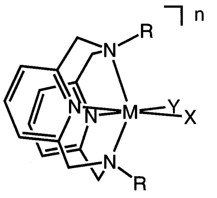
Introduction

The macrocyclic ligand 2,11-diaza[3.3](2,6)pyridinophane ($L-N_4R_2$) disposes of four potential nitrogen donor atoms for the complexation of metal ions. Due to its small ring size, the tetraazamacrocycle generally forms *cis* octahedral coordination geometries (**1**) with all nitrogen donor atoms bound to the metal ions.[1][2] With iron(II), iron(III), and cobalt(II) ions, eight-coordination has been observed in complexes of the composition $[M(L-N_4H_2)_2]^{n+}$ (**2**), in which both diazapyridinophane units act as tetradentate ligands.[3][4] In contrast, the nickel(II) ion in the complex $[Ni(L-N_4H_2)_2]^{2+}$ (**3**) is coordinated to all nitrogen donor atoms of one of the tetraazamacrocyclic ligands and to one each of the pyridine and amine nitrogen atoms of the second ligand.[4] Thus, in octahedral metal complexes only the tetra- and bidentate coordination modes have been structurally established with 2,11-diaza[3.3](2,6)pyridinophane ligands. Because we are interested in the general coordination chemistry of this type of ligand, we decided to explore the possibility of a tridentate coordination of the diazapyridinophane ligands in octahedral metal complexes. It is known that tricarbonylmolybdenum(0) fragments can sustain the tridentate coordination mode with the tetraazamacrocycles **4**−**7** which possess 12-, 14-, 15-, and 16-membered rings.[5][6] In one instance a structure analysis has been reported.[5] Tridentate coordination may, however, be more difficult to achieve with the macrocyclic ligand $L-N_4R_2$, since this type of ligand is, relative to the tetraazamacrocycles **4**−**7**, significantly more rigid due to the presence of two pyridine units in the ring and therefore has considerably fewer degrees of conformational freedom. The initial results of a study directed towards the feasibility of the tridentate coordination of 2,11-diaza[3.3](2,6)pyridinophane ligands are described here.

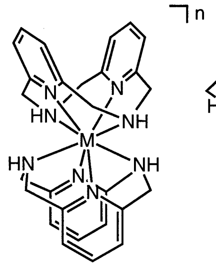


$L–N_4R_2$

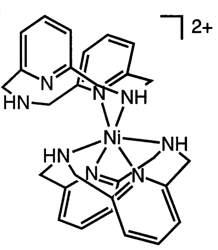
R = H: $L–N_4H_2$
R = Me: $L–N_4Me_2$
R = *t*-Bu: $L–N_4t$-Bu_2



1



2

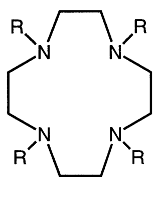


3

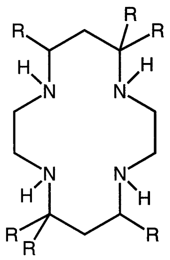
M = Fe^{II}, Co^{II}, n = 2+
Fe^{III}, n = 3+

Results and Discussion

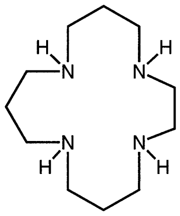
The reaction of the ligand $L-N_4Me_2$ with an equivalent amount of $[Mo(CO)_6]$ in refluxing toluene yields a dark red complex whose elemental analysis is consistent with its formulation as $[Mo(L-N_4Me_2)(CO)_3]$ (**8**). The IR spectrum of the compound is dominated by a very intense, narrow ($\Delta\nu_{1/2}$ = 30 cm^{-1}) band at 1893 cm^{-1} and an equally intense, rather broad ($\Delta\nu_{1/2}$ = 60 cm^{-1}) band at 1762 cm^{-1}; these bands are assigned to the two CO stretching vibrations (A_1 and E) expected for a *fac*-$Mo(CO)_3$ fragment with a local C_{3v}-symmetry. The ν(CO) frequencies for the



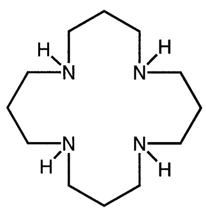
4
R = H or Me



5
R = H or Me



6

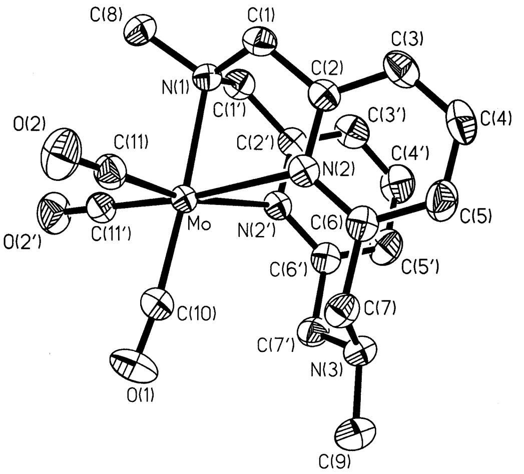


7

terminally bound carbonyl ligands lie in the same range as those observed for other octahedral tricarbonylmolybdenum(0) complexes with C_3N_3 coordination environments.[6][7][8] The relatively low energy of these ν(CO) frequencies, indicating strong π-back bondings between the metal and the carbon atoms, is attributed to the presence of strong σ-only donors with no or rather weak π-acceptor capabilities, such as amines and pyridines.

A perspective view of the structure of **8** is presented in Figure 1. The molecule possesses crystallographically imposed C_s symmetry. The most noteworthy structural aspect of complex **8** is the finding that the potentially tetradentate ligand $L{-}N_4Me_2$ acts only as a tridentate ligand here. Thus, the somewhat distorted octahedral coordination environment around the molybdenum atom is composed of three carbonyl ligands occupying one face of the octahedron and three nitrogen donor atoms of the macrocyclic ligand coordinated to the opposite face. By maintaining a *syn* chair-boat conformation, $L{-}N_4Me_2$ is bound to the metal ion only through the two pyridine and one of the amine nitrogen atoms. In contrast to previously discussed octahedral complexes where the tetraazamacrocyclic ligand is bound to a metal ion in a tetradentate fashion,[1][2] here the bond from the metal ion to the amine nitrogen atom ($Mo{-}N_{amine}$ bond, 2.306 Å) is considerably shorter than that to the pyridine nitrogen atoms ($Mo{-}N_{py}$ bond, 2.342 Å). Overall the lengths of the $Mo^0{-}N$ bonds are similar to those observed in other six-coordinate molybdenum complexes with the same ligand donor set (2.242−2.407 Å with the mean at 2.314 Å).[5][8][9][10] Presumably due to steric interactions between the methylene protons next to the uncoordinated amine nitrogen atom and the axial carbonyl ligand [containing C(10) and O(1)], the coordination of the macrocycle to the metal ion is considerably distorted, as demonstrated, for example, by the rather small N−Mo−N angles of 68.7° and 75.5°. In agreement with the rather low ν(CO) frequencies, the Mo−C bond lengths of 1.933 and 1.943 Å indicate substantial Mo=C double bond character.[9] These bond lengths fall into the general range observed for Mo−CO bonds in complexes with an octahedral MoC_3N_3 coordination sphere (1.898−1.952 Å with the mean at 1.923 Å).[5][8][9][10]

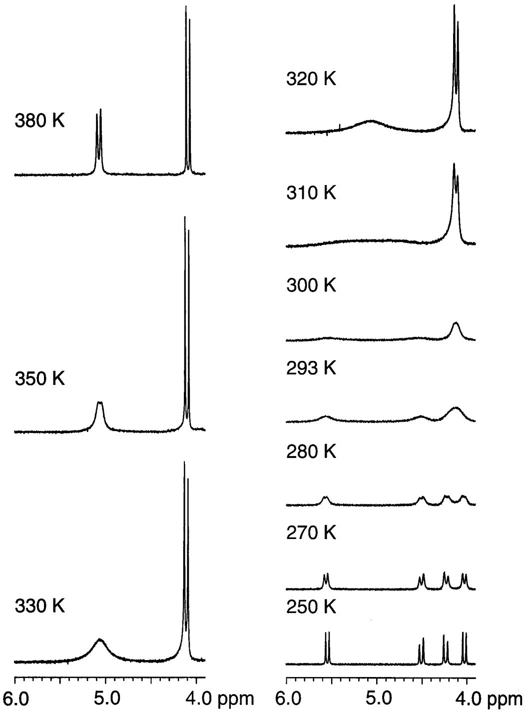
Figure 1. Perspective view of the structure of $[Mo(L{-}N_4Me_2)(CO)_3]$ showing thermal ellipsoids at 50% probability and the atom-numbering scheme; the primed and unprimed atoms are related by a mirror plane[a]



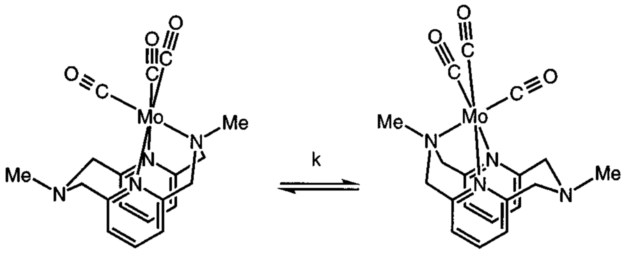
[a] Selected bond lengths [Å] and angles [°]: Mo−N(1) 2.306(3), Mo−N(2) 2.342(2), Mo−C(10) 1.943(4), Mo−C(11) 1.933(3), C(10)−O(1) 1.167(5), C(11)−O(2) 1.172(3); C(10)−Mo−C(11) 83.4(1), C(11)−Mo−C(11′) 88.0(2), N(1)−Mo−N(2) 75.49(8), N(1)−Mo−C(11) 94.3(1), N(1)−Mo−C(10) 176.7(1), N(2)−Mo−N(2′) 68.7(1), N(2)−Mo−C(10) 107.2(1), N(2)−Mo−C(11) 100.9(1), N(2)−Mo−C(11′) 166.79(9).

In solution, fluxional behavior is observed for the coordinated macrocyclic ligand by a variable-temperature ^{1}H-NMR study. Thus, at low temperatures (240 K), the methylene proton signals appear as two well separated AB systems in the ^{1}H-NMR spectrum (Figure 2). The first AB system occurs at $\delta = 4.02$ and 5.51 with a coupling constant $J_{AB} = 14$ Hz and the second at $\delta = 4.23$ and 4.51 with $J_{AB} = 15$ Hz. Raising the temperature causes the two AB systems to be replaced by a new AB system at $\delta = 4.1$ and 5.1 with $J_{AB} = 15$ Hz by coalescence of the signals at $\delta = 4.02$ and 4.23 and those at $\delta = 4.51$ and 5.51. In a similar way, the two signals corresponding to the protons of two methyl groups which are found at $\delta = 2.50$ and 3.23 at low temperatures coalesce to a singlet at $\delta = 2.9$. In analogy, the slightly different signals attributed to the 3-pyridine and 5-pyridine protons appear at higher temperatures as one signal. The dynamic NMR study clearly demonstrates that, when the complex is dissolved, an intramolecular substitution reaction takes place in which, as depicted in Scheme 1, the uncoordinated amine nitrogen donor replaces the bound one. Simulations of the NMR subspectra corresponding to the methylene protons at different temperatures yield the reaction velocities k for this process at each temperature; at room temperature, k and the free activation energy $\Delta G^{\neq}$ were determined to be 286 s^{-1} and 59.0 kJ mol^{-1}, respectively. From a plot of ln(*k/T*) vs 1/*T*, the free activation parameters $\Delta H^{\neq} = 58.1$ kJ mol^{-1} and $\Delta S^{\neq} = -3.14$ J K^{-1} mol^{-1} were obtained. Since the experimental error in determining the value of the entropy of activation by NMR spectroscopy is inherently quite large, this rather small value for the entropy of activation prohibits its use in a discussion of the possible mechanism of the reaction. The reaction mechanism is currently being investigated with a series of tricarbonyl metal complexes $[M(L{-}N_4R_2)(CO)_3]$ (where M = Cr^0, Mo^0, or W^0 and R = H, Me, or *t*Bu). Preliminary results of this kinetic study suggest that the reaction proceeds either by an associative or an associative interchange mechanism.

Figure 2. ^{1}H-NMR signals of the methylene protons of $[Mo(L{-}N_4Me_2)(CO)_3]$ in deuterated dimethylformamide at different temperatures (360 MHz)



Scheme 1



The tridentate coordination mode of the ligand $L{-}N_4Me_2$ has only been observed here because the tricarbonylmolybdenum(0) fragment is quite stable. Since adequate π-back-bonding from the metal ion to the carbonyl ligands is required to stabilize the molybdenum(0) atom, the presence of only two carbonyl ligands is apparently not sufficient to stabilize a molybdenum(0) atom if it is coordinated to four relatively strong σ-donors, such as amines or pyridines, with no or only rather weak π-acceptor capabilities. Therefore, the molybdenum(0) atom prefers the coordination of three carbonyl ligands and forfeits ligation of one of the four possible nitrogen donors of the macrocyclic ligands. However, it is interesting to point out that for all diamagnetic *cis* octahedral metal complexes investigated thus far the NMR spectra demonstrate that the tetraazamacrocycle, once coordinated as tetradentate ligand, stays bound to the metal ion through all its nitrogen donor atoms.

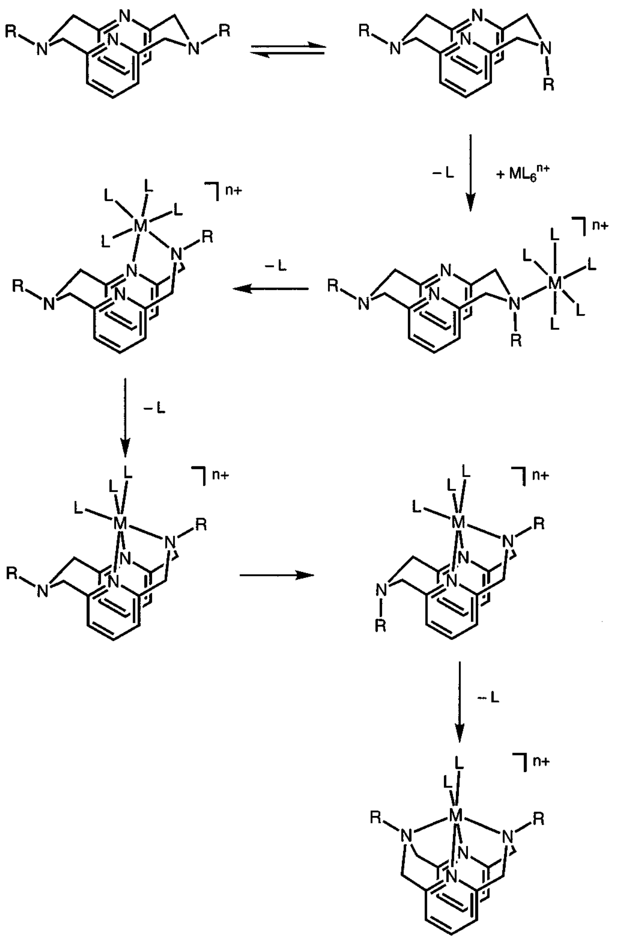
The structures of the complexes **3** and **8** provide some quite interesting insights into mechanistic aspects of the coordination of octahedral metal ions by diazapyridinophane ligands. Thus, the bidentate and tridentate coordination modes of the tetraazamacrocyclic ligands observed in these complexes can be viewed as intermediates in the formation of tetradentate chelation of the ligand. As uncoordinated macrocycle the dialkyl-substituted diazapyridinophane is present as *syn* chair-chair conformer. The reaction sequence depicted in Figure 3 starts with the coordination of just one nitrogen atom, most likely one of the amine nitrogen donors since these can be approached by the metal ion more easily because of steric considerations. Next, by changing the chair-chair conformation of the ligand to a boat-chair conformation, bidentate chelation over one amine and one pyridine nitrogen atom occurs, similar to that found in **3**. The macrocyclic ring slides further over the metal ion, and the second pyridine nitrogen atom forms a bond to the metal ion, yielding a facial coordination of the ligand like that observed in **8**. By converting the chair-boat conformation to a boat-boat conformation, the last amine nitrogen donor atom is then able to interact with the metal ion and, thus, tetradentate chelation of the ligand is completed.

Conclusion

Tridentate coordination has been structurally established for the ligand $L{-}N_4Me_2$ in a tricarbonylmolybdenum(0) complex. In solution, an intramolecular rearrangement of the ligand occurs where the uncoordinated amine nitrogen atom replaces the coordinated one at the molybdenum atom. In general, 2,11-diaza[3.3](2,6)pyridinophanes display a decisive tendency to form preferentially *cis* octahedral complexes; only in very specific cases, e.g. when the other ligands in the complex are very strongly bound as in $[Mo(L{-}N_4Me_2)(CO)_3]$ or when no further coordination sites are available in the octahedral complex as in $[Ni(L{-}N_4H_2)_2]^{2+}$, do these ligands relinquish tetradentate chelation and become tri- or bidentate chelators. Similar bi- and tridentate coordination modes of the macrocyclic ligand are proposed to occur in the intermediates in formation of *cis* octahedral complexes.

We thank the *Deutsche Forschungsgemeinschaft* for financial support.

Figure 3. Possible mechanism for the formation of octahedral metal complexes by reaction of hydrated metal ions (L = H_2O) with ligands of the type $L-N_4R_2$



Experimental Section

Physical Methods: ^{1}H-NMR: Bruker AM 360, TMS as internal standard. The spectra of the dynamic NMR study were simulated using the program geNMR Version 3.4, IvorySoft, 1993. – UV/Vis: Varian Cary 5 E. – IR: Perkin-Elmer 1720 FT-IR.

Preparation of the Ligand: The tetraazamacrocyclic ligand $L-N_4Me_2$ was synthesized according to already published procedures, employing some slight modifications.[11]

$[Mo(L-N_4Me_2)(CO)_3]$ (**8**): A solution of $[Mo(CO)_6]$ (134 mg, 0.5 mmol) and $L-N_4Me_2$ (134 mg, 0.5 mmol) in toluene (30 ml) was refluxed for 5 h under anaerobic conditions. The resulting red precipitate was collected by filtration, washed with toluene, and dried. Recrystallization by diffusion of ether into a solution of the solid in dimethylformamide (40 ml) afforded analytically pure product (127 mg, 57% yield) as a dark red crystalline material. – $C_{19}H_{20}N_4MoO_3$ (448.33): calcd. C 50.90, H 12.50, N 4.50; found C 50.72, H 12.45, N 4.57. – UV/Vis (dimethylformamide): λ_{max} (ε_M) = 407 (3090) and 315 (3610) nm. – IR (KBr): $\tilde{\nu}$ = 2933, 2898, 2766, 1893, 1762, 1604, 1570, 1464, 1449, 1431, 1374, 1163, 1093, 1020, 976, 819, 765 cm^{-1} (strong bands only).

Crystal Structure Analysis: Slow mixing by diffusion of two layers consisting of hexane and a solution of $[Mo(L-N_4Me_2)(CO)_3]$ in dimethylformamide afforded single crystals. Formula $C_{19}H_{20}N_4MoO_3$; M_r 448.33 g mol^{-1}; crystal dimensions 0.25 × 0.4 × 0.4 mm; crystal system monoclinic; space group $P2_1/m$ (No. 11); $Z = 2$; cell dimensions: $a = 9.371(3)$, $b = 11.780(3)$, $c = 9.551(2)$ Å, $\beta = 118.96(2)°$; $V = 922.5(4)$ Å^3; $\rho_{calcd.} = 1.614$ g cm^{-3}; $F(000) = 456$; graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å); $\mu = 7.39$ cm^{-1}; $T = 293$ K; Hilger & Watts diffractometer; ω-2Θ scans in the range $4.90° \le 2\Theta \le 55.10°$; 2167 unique reflections [1994 reflections with $F_o > 4\,\sigma(F_o)$]; 136 variables; GooF on F^2 [$F_o > 4\,\sigma(F_o)$] = 1.181; R [$F_o > 4\,\sigma(F_o)$] = 3.11% with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; wR^2 [$F_o > 4\,\sigma(F_o)$] = 7.05% with $wR^2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$; largest peak (hole) = 0.58 (–0.92) e Å^{-3}. The positions of the non-hydrogen atoms were determined by SHELXS 86[12] and by Fourier difference maps using the program SHELXL-93.[12] The structural parameters were refined with the program SHELXL-93, using F^2 of all symmetry-independent reflections except those with very negative F^2 values. All non-hydrogen atoms were refined anisotropically. The complex is bisected by a crystallographical mirror plane passing through the molybdenum ion, one of the carbonyl ligands, the two amine nitrogen atoms, and the carbon atoms of the two methyl groups. Hydrogen atoms were assigned idealized locations and their isotropic temperature factors were refined.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101671. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

---

[1] [1a] H.-J. Krüger, *Chem. Ber.* **1995**, *128*, 531–539. – [1b] W. O. Koch, H.-J. Krüger, *Angew. Chem.* **1995**, *107*, 2928–2931; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2671–2674. – [1c] H. Kelm, H.-J. Krüger, *Inorg. Chem.* **1996**, *35*, 3533–3540. – [1d] W. O. Koch, V. Schünemann, M. Gerdan, A. X. Trautwein, H.-J. Krüger, *Chem. Eur. J.* **1998**, *4*, 686–691. – [1e] W. O. Koch, V. Schünemann, M. Gerdan, A. X. Trautwein, H.-J. Krüger, *Chem. Eur. J.* **1998**, *4*, 1255–1265.

[2] [2a] F. R. Fronczek, A. Mamo, S. Pappalardo, *Inorg. Chem.* **1989**, *28*, 1419–1422. – [2b] H. Sakaba, C. Kabuto, H. Horino, M. Arai, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1822–1824. – [2c] C.-M. Che, Z.-Y. Li, K.-Y. Wong, C.-K. Poon, T. C. W. Mak, S.-M. Peng, *Polyhedron* **1994**, *13*, 771–776.

[3] W. O. Koch, A. Barbieri, M. Grodzicki, V. Schünemann, A. X. Trautwein, H.-J. Krüger, *Angew. Chem.* **1996**, *108*, 484–486; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 422–424.

[4] W. O. Koch, J. T. Kaiser, H.-J. Krüger, *J. Chem. Soc., Chem. Commun.* **1997**, 2237–2238.

[5] R. W. Hay, I. Fraser, G. Ferguson, *J. Chem. Soc., Dalton Trans.* **1989**, 2183–2186.

[6] V. Patinec, J.-J. Yaouanc, J. C. Clément, H. Handel, H. des Abbayes, M. M. Kubicki, *J. Organomet. Chem.* **1995**, *494*, 215–222.

[7] [7a] E. W. Abel, M. A. Bennett, G. Wilkinson, *J. Chem. Soc.* **1959**, 2323–2327. – [7b] L. W. Houk, G. R. Dobson, *J. Chem. Soc. A* **1966**, 317–319.

[8] G. Haselhorst, S. Stoetzel, A. Strassburger, W. Walz, K. Wieghardt, B. Nuber, *J. Chem. Soc., Dalton Trans.* **1993**, 83–90.

[9] F. A. Cotton, R.M. Wing, *Inorg. Chem.* **1965**, *4*, 314–317.

[10] [10a] S. E. Anslow, K. S. Chong, S. J. Rettig, A. Storr, J. Trotter, *Can. J. Chem.* **1981**, *59*, 3123–3135. – [10b] C. P. Marabella, J. H. Enemark, *J. Organomet. Chem.* **1982**, *226*, 57–62. – [10c] T. J. Desmond, F. J. Lalor, G. Ferguson, M. Parvez, *J. Organomet. Chem.* **1984**, *277*, 91–97. – [10d] R. A. Howie, G. P. McQuillan, *J. Chem. Soc., Dalton Trans.* **1986**, 759–764. – [10e] S. P. van Kouwenberg, E. H. Wong, G. R. Weisman, E. J. Gabe, F. L. Lee, P. Jackson, *Polyhedron* **1989**, *8*, 2333–2338. – [10f] T. M. Bockman, J. K. Kochi, *New J. Chem.* **1992**, *16*, 39–49. – [10g] K.-B. Shiu, J. Y. Lee, Y. Wang, M.-C. Cheng, S.-L. Wang, F.-

L. Liao, *J. Organomet. Chem.* **1993**, *453*, 211−219. – [10h] A. Chandrasekaran, S. S. Krishnamurthy, M. Nethaji, *J. Chem. Soc., Dalton Trans.* **1994**, 63−68.

[11] [11a] B. Alpha, E. Anklam, R. Deschenaux, J.-M. Lehn, M. Pietraskiewicz, *Helv. Chim. Acta* **1988**, *71*, 1042−1052. – [11b] F. Bottino, M. Di Grazia, P. Finocchiaro, F. R. Fronczek, A. Mamo, S. Pappalardo, *J. Org. Chem.* **1988**, *53*, 3521−3529.

[12] G. M. Sheldrick, *SHELXS-86: Crystal Structure Solution Program*, Göttingen, **1986**; G. M. Sheldrick in *Crystallographic Computing 3* (Eds.: G. M. Sheldrick, C. Krüger, R. Goddard) Oxford University Press, **1985**, pp. 175; G. M. Sheldrick, *SHELXL-93: Crystal Structure Refinement Program*, Göttingen, **1993**.

[98157]