www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 599 (2000) 308–312

Note

Synthesis and X-ray structures of manganese(I) and rhenium(I) formato complexes, *fac*-$(CO)_3$(dppp)M–OC(H)O

Miyoshia T. Williams [a], Christopher McEachin [a], Thomas M. Becker [b], Douglas M. Ho [c], Santosh K. Mandal [a,*]

[a] *Department of Chemistry, Morgan State University, Baltimore, MD 21251, USA*
[b] *Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221, USA*
[c] *Department of Chemistry, Princeton University, Princeton, NJ 08544, USA*

Received 18 October 1999; received in revised form 7 December 1999

Abstract

The mononuclear manganese(I) and rhenium(I) formato complexes, *fac*-$(CO)_3$(dppp)M–OC(H)O (M = Mn, **1**; M = Re, **2**), have been prepared from *fac*-$(CO)_3$(dppp)MH and formic acid, and their X-ray structures determined. Compounds **1** and **2** are unusual in that the formato ligands are bound in a terminal, monodentate fashion. For Mn, only multinuclear complexes containing bridging formato ligands have been characterized previously by X-ray diffraction. The M–O bond lengths and M–O–C bond angles are 2.043(2) Å and 124.2(2)°, respectively for **1** and 2.167(3) Å and 122.3(3)°, respectively for **2**. Compounds **1** and **2** can also be decarboxylated at elevated temperatures with quantitative recovery of *fac*-$(CO)_3$(dppp)MH. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Synthesis; Manganese; Rhenium; Formato complexes; X-ray structure

---

1. Introduction

Metallocarboxylic acids (M–CO_2H) and their isomeric monodentate formato complexes (M–OC(H)O) have been proposed as intermediates in the water–gas shift reaction [1]. Formato complexes have also been implicated in the metal-catalyzed reduction of CO_2 to HCO_2^- [2], CO_2–H_2 reactions [3], isomerization of methyl formate to acetic acid [4], decarboxylation of formic acid [5], and transfer hydrogenations [6]. The synthesis and reactivity of metallocarboxylic acid and formato complexes are therefore of key interest to the above and related processes. The synthesis and reactivity of the metallocarboxylic acids *fac*-$(CO)_3$(dppe)$ReCO_2H$ and *fac*-$(CO)_3$(dppp)$ReCO_2H$ have been reported earlier [7]. We have now completed complementary studies on the isomeric formato systems, and describe herein the synthesis, structural and reaction chemistry of *fac*-$(CO)_3$(dppp)Mn–OC(H)O (**1**) and *fac*-$(CO)_3$(dppp)Re–OC(H)O (**2**).

2. Results and discussion

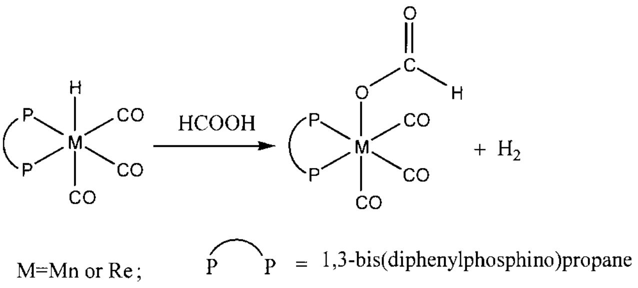
2.1. Synthesis of the manganese formato complex 1 and rhenium formato complex 2

Formato complexes can be prepared from a variety of starting materials, e.g. carbon dioxide [8], simple formate salts [1], or from formic acid itself [9]. Since the manganese(I) and rhenium(I) hydrido complexes *fac*-$(CO)_3$(dppp)MH were readily available [10], the synthesis of **1** and **2** by the insertion of CO_2 into the M–H bond was first attempted. Unfortunately, the formato complexes were not obtained. The latter formic acid route was therefore attempted next and found to give the desired products (Eq. (1)):

---

* Corresponding author. Fax: + 1-410-3193778.
E-mail address: smandal@morgan.edu (S.K. Mandal)

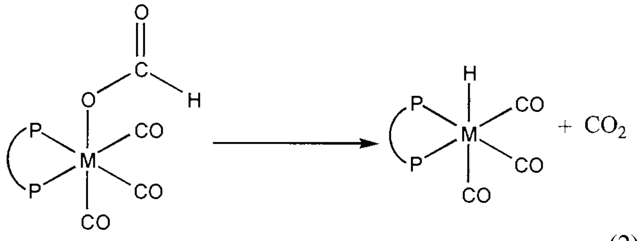
0022-328X/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(99)00743-3



(1)

2.2. Decarboxylations of **1** and **2**

Complexes **1** and **2** were converted to the corresponding hydrides at their melting temperatures. Also when **1** or **2** was heated to 110°C in toluene-d_8, the corresponding hydrides were obtained (Eq. (2)).



(2)

The decarboxylation mechanism of formato complexes have been reported by many research groups. It has been suggested to proceed via β elimination of the hydrogen atom to the metal center, followed by formation of a metal hydride species. This mechanism requires a vacant coordination site on the metal. For example, (η^5-C_5H_5)Fe(CO)$_2$OC(H)O was found to decarboxylate with CO dissociation [1]. However, the rhenium formate, (η^5-C_5H_5)Re(NO)(PPh$_3$)OC(H)O was found to decarboxylate without PPh$_3$ dissociation [11]. We did not study the decarboxylation mechanism at this time. Attempts to decarboxylate and transform **1** and **2** to metallocarboxylates were unsuccessful.

2.3. Spectral studies

The IR and NMR spectral data for **1** and **2** are given in Section 3. Three strong IR bands observed between 2033 and 1898 cm^{-1} are consistent with the presence of a *facial* M(CO)$_3$ functional group in these compounds. A medium-intensity band observed in the 1630–1610 cm^{-1} region is attributable to the C=O group of a formate anion. The formate ^{1}H- and ^{13}C-NMR resonances occur as triplets at roughly 8.4 and 169.0 ppm, respectively. These observations are consistent with the presence of discrete (dppp)M(η^1-O_2CH) moieties, the formate ^{1}H and ^{13}C triplet signals being the result of coupling with the two phosphorus atoms of the dppp ligand. The ^{13}C resonances for the terminal carbonyl ligands occur as a broad signal centered at 215.8 ppm for **1**, and as two triplets at 194.3 (axial, CO) and 190.7 ppm (equatorial, 2CO) for **2**.

2.4. X-ray structures of **1** and **2**

A molecular plot and selected distances and angles for **1** are provided in Fig. 1 and Table 2, respectively. The Mn atom is octahedrally coordinated to three carbonyl ligands in a facial arrangement, a bidentate

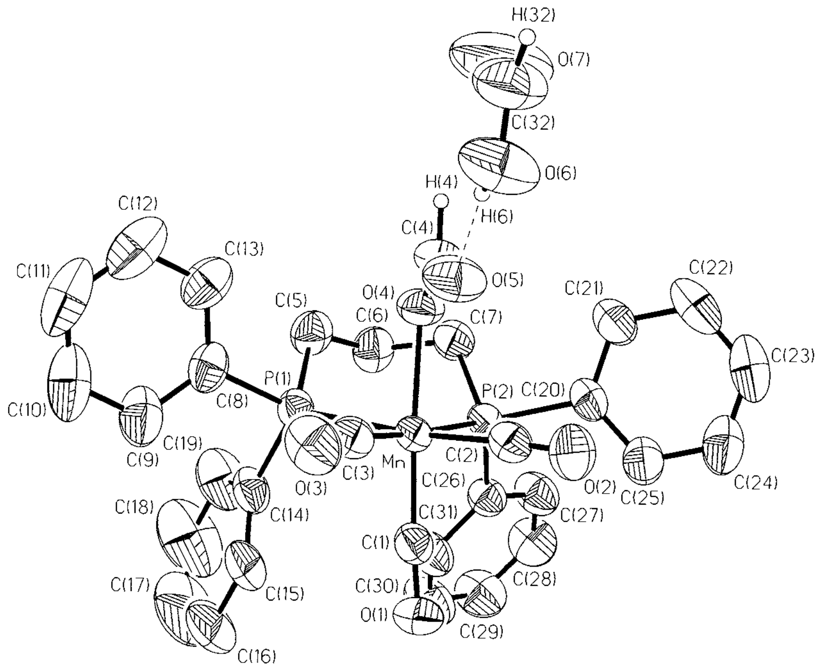


Fig. 1. A thermal ellipsoid plot of compound **1**.

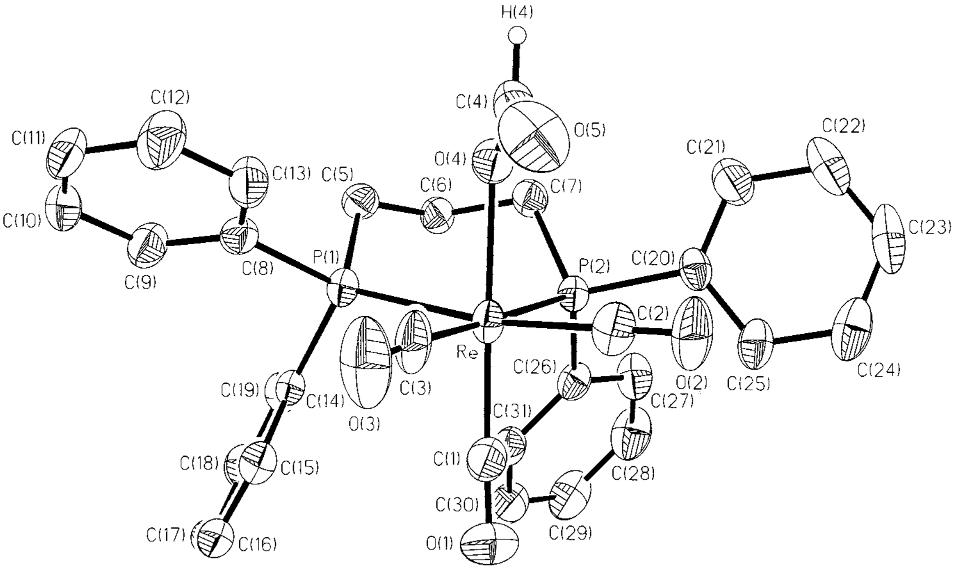


Fig. 2. A thermal ellipsoid plot of compound **2**.

dppp, and a monodentate formate anion. The equatorial Mn–CO bonds are 0.05 Å longer than the axial Mn–CO bond, consistent with dppp having a greater *trans* influence than formate. The formate ligand is bound to the Mn atom in a *syn* conformation with the O(4)–C(4)–O(5) plane symmetrically bisecting the equatorial $Mn(CO)_2$ moiety. The C(2)–Mn–O(4)–C(4)–O(5) and C(3)–Mn–O(4)–C(4)–O(5) torsion angles are −44.3(2) and 44.9(2)°, respectively. The Mn–O(4) bond is 2.043(2) Å and is comparable to distances of 2.020–2.042 Å reported for manganese carboxylato complexes [12] and *fac*-$(CO)_3$(dppe)$MnOC(O)OCH_3$ [13]. A molecular plot and selected bond distances and angles for **2** are provided in Fig. 2 and Table 2, respectively. The Re coordination geometry is analogous to that described above for the Mn derivative, e.g. the equatorial Re–CO bonds are 0.04 Å longer than the axial Re–CO bond, the C(2)–Re–O(4)–C(4)–O(5) and C(3)–Re–O(4)–C(4)–O(5) torsion angles are −45.3(3) and 44.4(3)°, respectively, and the Re–O(4) bond is 2.167(3) Å. The latter Re–O(4) distance is comparable to values of 2.127(3)–2.230(10) Å observed in related carboxylato [14] and carbonato bridged complexes [15]. The Re–O(4) bond is 0.124 Å longer than the Mn–O(4) bond in excellent agreement with an expectation value of 0.13 Å based on the difference in the Re and Mn covalent radii.

The most interesting feature in **1** and **2** is the metal–formate binding mode. To our knowledge, **1** is the first example of a monomeric manganese complex confirmed crystallographically to contain a terminally bound formato ligand. Compound **2** is equally uncommon. The only other rhenium example is *fac*-$(CO)_3$(bipy)Re–OC(H)O [16]. It is interesting to note that the axial formate and one of the equatorial carbonyls are eclipsed with respect to each other in this bipy analogue, in contrast to the staggered geometry found in **1** and **2**. Finally, we mention that crystals of **1** also contain formic acid molecules of crystallization. One formic acid molecule is hydrogen bonded to each formate O(5) atom in the lattice with O(6)–H(6), H(6)···O(5), O(6)···O(5), and O(6)–H(6)···O(5) being 0.92(2), 1.71(4), 2.579(3) Å, and 156(4)°, respectively. Crystals of **2** did not contain formic acid.

3. Experimental

All manipulations were carried out under a nitrogen atmosphere. Reagent grade chemicals were used without further purification. Formic acid (96%) was obtained from Aldrich Chemical Company, Inc. IR spectra were recorded on a Perkin–Elmer 1600 series FTIR instrument. NMR spectra were recorded on a Bruker AC 250 (250.133 MHz, ^1H; 62.896 MHz, ^{13}C) spectrometer. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Microanalyses were conducted by Quantitative Technologies Inc.

*3.1. Synthesis of the manganese formato complex **1** and rhenium formato complex **2***

To 0.73–0.91 mmol of *fac*-$M(CO)_3$(dppp)H (M = Mn; Re) [10] dissolved in about 50 cm^3 of dichloromethane was added formic acid (0.15–0.17 cm^3, 3.98–4.51 mmol) and the solutions were stirred for 1 h. The excess acid was removed by extraction with water. The dichloromethane solution was concentrated and mixed with hexane. The resultant mixture was cooled at −5°C. Pure crystalline formato complexes **1** and **2** were collected by filtration. Data for **1**: yield, 88%; m.p. 153–155°C with decomposition. IR (cm^{-1}, CH_2Cl_2): ν(C≡O) 2027 vs, 1960 s, 1906 s, and ν(C=O) 1617 m. ^{1}H-NMR (δ, $CDCl_3$): 8.53 (t, 2 Hz, 1H, O=C–H), 7.49–7.31 (m, 20H, C_6H_5), 2.86–2.21 (m, 6H, $CH_2CH_2CH_2$). ^{13}C-NMR (δ, $CDCl_3$): 215.8 (s, br, CO), 169.2 (t, 6 Hz, C=O), 135.8–128.6 (m, C_6H_5), 24.9 (t, 11 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 18.7 (18.7, s, $CH_2\mathit{C}H_2CH_2$). Anal. Found: C, 61.5; H, 4.6. $C_{31}H_{27}MnO_5P_2$ Anal. Calc.: C, 62.4; H, 4.6%. The elemental analysis done on a crushed sample that had been evacuated to remove any traces of dichloromethane, hexanes or formic acid, indicates that **1** slowly decomposes. Data for **2**: yield: 93%; m.p. 185–188°C with decomposition. IR (cm^{-1}, CH_2Cl_2): ν(C≡O) 2033 vs, 1954 s, 1898 s, and ν(C=O) 1625 m. ^{1}H-NMR (δ, $CDCl_3$): 8.19 (t, 2 Hz, O=C–H), 7.50–7.29 (m, 20H, C_6H_5), 2.94–2.28 (m, 6H, $CH_2CH_2CH_2$). ^{13}C-NMR (δ, $CDCl_3$): 194.3 (t, 6 Hz, C≡O), 190.7 (t, 24 Hz, 2 C≡O), 168.9 (t, 6 Hz, C=O), 136.1–126.57 (m, C_6H_5), 24.6 (t, 15 Hz, $\mathit{C}H_2CH_2\mathit{C}H_2$), 19.3 (18.7, s, $CH_2\mathit{C}H_2CH_2$). Anal. Found: C, 50.8; H, 3.7. $C_{31}H_{27}O_5P_2Re$ Anal. Calc.: C, 51.2; H, 3.7%.

Table 1
Summary of crystal data for *fac*-Mn(CO)$_3$(dppp)OC(H)O·HC(O)OH (**1**) and *fac*-(CO)$_3$(dppp)Re–OC(H)O

	1	**2**
Color and habit	Yellow prism	Colorless plate
Crystal size (mm)	$0.50 \times 0.50 \times 0.50$	$0.07 \times 0.13 \times 0.15$
Chemical formula	$C_{32}H_{29}MnO_7P_2$	$C_{31}H_{27}O_5P_2Re$
a (Å)	9.5216(6)	17.8435(3)
b (Å)	10.2134(5)	16.5212(2)
c (Å)	16.9567(8)	19.8756(3)
α (°)	90.503(4)	90
β (°)	94.807(5)	90
γ (°)	106.774(4)	90
V (Å^3)	1572.3(2)	5859.2(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	*Pbca* (no. 61)
Z	2	8
Diffractometer	Siemens P4	Nonius Kappa CCD
μ(Mo–K$_\alpha$) (mm^{-1})	0.566	4.295
Scan mode, θ_{max} (°)	ω, 25.00	ω, 27.53
Completeness (%)	100	99.9
Limiting indices	$0 \le h \le 11$, $-12 \le k \le 11$, $-20 \le l \le 20$	$0 \le h \le 23$, $0 \le k \le 21$, $0 \le l \le 25$
Absorption correction	None	Gaussian
Reflections collected	5906	54 230
Reflections merged (R_{int})	5540 (0.0197)	6747 (0.0801)
Reflections observed	4044; $I > 2\sigma(I)$	4593; $I > 2\sigma(I)$
Variables	382	352
R (all) [a]	0.0356 (0.0549)	0.0314 (0.0652)
R_w (all) [a]	0.0849 (0.0908)	0.0566 (0.0658)
Goodness-of-fit (all)	1.042 (0.940)	1.073 (1.018)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2

[a] Definitions of R and R_w: R: $\Sigma||F_o|-|F_c||/\Sigma|F_o|$, R_w: $[\Sigma w_i(|F_o|^2-|F_c|^2)^2/\Sigma w_i|F_o^2|^2]^{1/2}$.

3.2. Decarboxylations of 1 and 2

About 0.015 mmol of **1** or **2** was dissolved in 0.500 cm^3 of toluene-d_8 at 110°C and the reaction was monitored by ^{31}P-NMR. After 2 h, the only product from **1** or **2** was the corresponding hydride. No evidence of free dppp ligand was observed. Also when heated to their melting points, the formato complexes **1** and **2** lose CO_2 and are converted quantitatively to their corresponding hydrides. The decarboxylations occur slowly at lower temperatures without melting.

3.3. X-ray crystal structure of *fac-Mn(CO)$_3$(dppp)OC(H)O·HC(O)OH* (1)

Crystals of **1** were grown from CH_2Cl_2–hexane at −5°C. Data were collected on a Siemens P4 diffractometer at 298(2) K and corrected for decay and Lorentz-polarization effects, but not for absorption or extinction. The structure was solved by heavy atom methods and refined by full-matrix least-squares on F^2 using SHELXTL. The non-hydrogen atoms were refined anisotropically and the hydrogens were included with a riding model and isotropic displacement coefficients $U(H) = 1.2U(C)$ except where noted below and the weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. The formic acid hydrogen atom H(6) was assigned an isotropic displacement coefficient $U(H) = 1.5U(O)$, and its coordinates were free to vary. Convergence gave $R = 0.0356$ for 4044 reflections with $I > 2\sigma(I)$. Additional crystallographic data and results are summarized in Table 1.

3.4. X-ray crystal structure of *fac-Re(CO)$_3$(dppp)OC(H)O* (2)

Crystals of **2** were grown from CH_2Cl_2–hexane at −5°C. Data were collected on a Nonius Kappa CCD diffractometer at 200(2) K and corrected for Lorentz-polarization and absorption effects, but not for extinction. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned isotropic displacement coefficient $U(H) = 1.2U(C)$ and were allowed to ride on their respective carbons. The

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

1		**2**	
Bond lengths			
Mn–C(1)	1.779(2)	Re–C(1)	1.898(5)
Mn–C(2)	1.826(3)	Re–C(2)	1.943(4)
Mn–C(3)	1.833(3)	Re–C(3)	1.940(5)
Mn–O(4)	2.043(2)	Re–O(4)	2.167(3)
Mn–P(1)	2.3666(7)	Re–P(1)	2.4699(10)
Mn–P(2)	2.3517(7)	Re–P(2)	2.4570(10)
C(4)–O(4)	1.271(3)	C(4)–O(4)	1.277(5)
C(4)–O(5)	1.223(3)	C(4)–O(5)	1.219(5)
O(6)–H(6)	0.92(4)		
H(6)···O(5)	1.71(4)		
O(6)···O(5)	2.579(3)		
Bond angles			
C(3)–Mn–P(2)	176.43(7)	C(3)–Re–P(2)	178.4(2)
C(2)–Mn–P(1)	173.92(7)	C(2)–Re–P(1)	171.51(13)
C(2)–Mn–O(4)	92.03(9)	C(2)–Re–O(4)	90.45(14)
C(3)–Mn–O(4)	94.14(9)	C(3)–Re–O(4)	96.9(2)
O(1)–C(1)–Mn	173.7(2)	O(1)–C(1)–Re	176.6(4)
O(2)–C(2)–Mn	176.1(2)	O(2)–C(2)–Re	179.5(4)
O(3)–C(3)–Mn	175.8(2)	O(3)–C(3)–Re	175.6(5)
C(4)–O(4)–Mn	124.2(2)	C(4)–O(4)–Re	122.3(3)
O(5)–C(4)–O(4)	126.5(2)	O(5)–C(4)–O(4)	126.8(5)
O(6)–H(6)···O(5)	156(4)		

weighting scheme employed was $w = 1/(\sigma^2(F_o^2 + (0.0246P)^2 + 3.8979P]$, where, $P = (F_o^2 + 2F_c^2)/3$. Convergence gave $R = 0.0314$ for 4593 reflections with $I > 2\sigma(I)$. Additional crystallographic data and results are summarized in Table 1.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 135153 for compound **1**, CCDC no. 135154 for compound **2**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] D.J. Darensbourg, M.B. Fischer, R.E. Schmidt Jr., B.J. Baldwin, J. Am. Chem. Soc. 103 (1981) 1298.

[2] R.P.A. Sneeden, in: G. Wilkinson, F.G.A. Stone, E. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon, New York, 1982, p. 225.

[3] K. Klier, Adv. Catal. 31 (1982) 243. For the evidence of formation of surface-bound formates, see: J.M. Basset, A. Choplin, A. Theolier, Nouv. J. Chim. 9 (1985) 655.

[4] R.L. Pruett, R.T. Kacmarcik, Organometallics 1 (1982) 1693.

[5] R.J. Madix, Adv. Catal. 29 (1980) 1.

[6] R. Bar, Y. Sasson, J. Blum, J. Mol. Catal. 16 (1982) 175.

[7] S.K. Mandal, D.M. Ho, M. Orchin, J. Organomet. Chem. 439 (1992) 53.

[8] (a) M.K. Whittlesey, R.N. Perutz, M.H. Moore, Organometallics 15 (1996) 5166. (b) D.L. Allen, M.L.H. Green, J.A. Bandy, J. Chem. Soc. Dalton Trans. (1990) 541. (c) P. Kundel, H. Berke, J. Organomet. Chem. 339 (1988) 297. (d) B.P. Sullivan, T.J. Meyer, J. Chem. Soc. Chem. Commun. (1984) 1244. (e) A. Immirzi, A. Musco, Inorg. Chim. Acta 22 (1977) L35.

[9] (a) J.H. Merrifield, J.M. Fernandez, W.E. Buhro, J.A. Gladysz, Inorg. Chem. 23 (1984) 4022. (b) C.C. Tso, A.R. Cutler, Inorg. Chem. 29 (1990) 471. (c) C. Pomp, K. Wieghardt, B. Nuber, J. Weiss, Inorg. Chem. 27 (1988) 3789.

[10] S.K. Mandal, J. Feldman, M. Orchin, J. Coord. Chem. 33 (1994) 219.

[11] J.H. Merrifield, J.A. Gladysz, Organometallics 2 (1983) 782.

[12] (a) W.A. Herrmann, I. Schweizer, P.S. Skell, M. Ziegler, K. Weidenhammer, B. Nuber, Chem. Ber. 112 (1979) 2423. (b) F.A. Cotton, D.J. Darrensbourg, B.W.S. Kolthammer, Inorg. Chem. 20 (1981) 1287.

[13] S.K. Mandal, D.M. Ho, M. Orchin, Organometallics 12 (1993) 1714.

[14] G. La Monica, S. Cenini, E. Forni, M. Manassero, V.G. Albano, J. Organomet. Chem. 112 (1976) 297.

[15] S.K. Mandal, D.M. Ho, G.Q. Li, M. Orchin, Polyhedron 17 (1998) 607.

[16] J. Guilhem, C. Pascard, J-M. Lehn, R. Ziessel, J. Chem. Soc. Dalton Trans. (1989) 1449.