

Note

Synthesis and X-ray structures of manganese(I) and rhenium(I) formate 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) formate 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 formate ligands are bound in a terminal, monodentate fashion. For Mn, only multinuclear complexes containing bridging formate 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; Formate complexes; X-ray structure

1. Introduction

Metallo-carboxylic acids (M–CO₂H) and their isomeric monodentate formate complexes (M–OC(H)O) have been proposed as intermediates in the water–gas shift reaction [1]. Formate complexes have also been implicated in the metal-catalyzed reduction of CO₂ to HCO₂[–] [2], CO₂–H₂ reactions [3], isomerization of methyl formate to acetic acid [4], decarboxylation of formic acid [5], and transfer hydrogenations [6]. The synthesis and reactivity of metallo-carboxylic acid and formate complexes are therefore of key interest to the above and related processes. The synthesis and reactivity of the metallo-carboxylic acids *fac*-(CO)₃(dppe)ReCO₂H and *fac*-(CO)₃(dppp)ReCO₂H have been reported earlier [7]. We have now completed complementary studies on the isomeric formate sys-

tems, 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**).

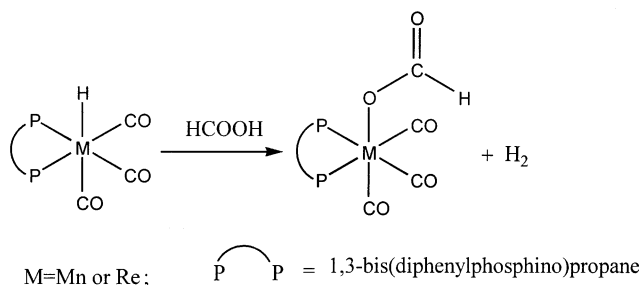
2. Results and discussion

2.1. Synthesis of the manganese formate complex **1** and rhenium formate complex **2**

Formate 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 CO₂ into the M–H bond was first attempted. Unfortunately, the formate 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.

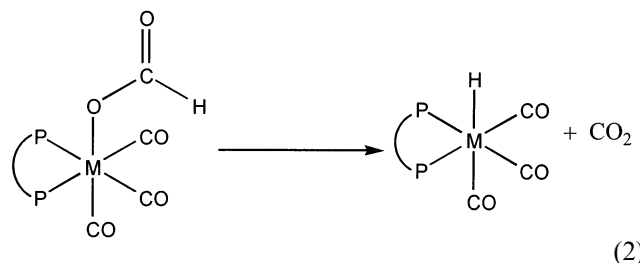
E-mail address: smandal@morgan.edu (S.K. Mandal)



(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 formate 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, $(\eta^5-C_5H_5)Fe(CO)_2OC(H)O$ was found to decarboxylate with CO dissociation [1]. However, the rhenium formate, $(\eta^5-C_5H_5)Re(NO)(PPh_3)OC(H)O$ 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 1H - 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 $(dppp)M(\eta^1-O_2CH)$ moieties, the formate 1H 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

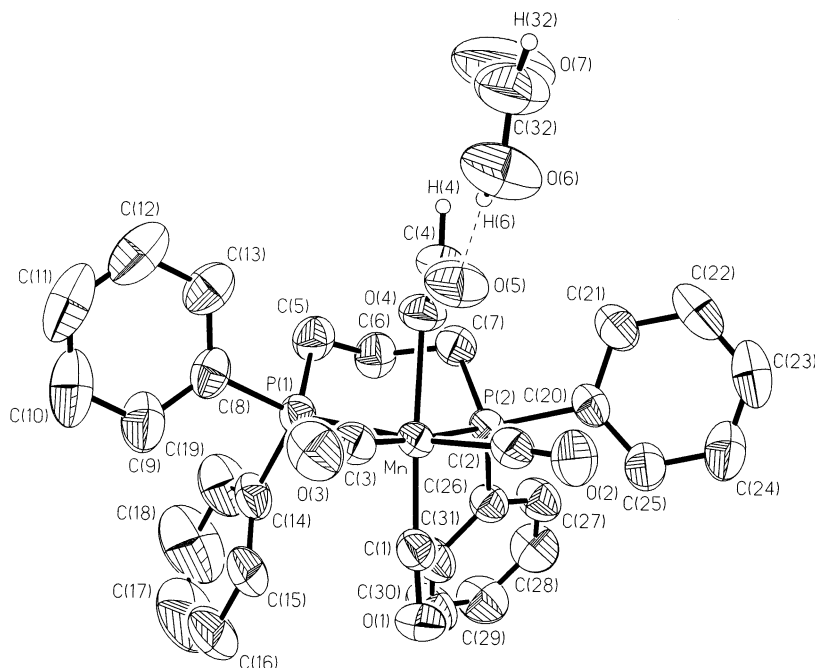


Fig. 1. A thermal ellipsoid plot of compound **1**.

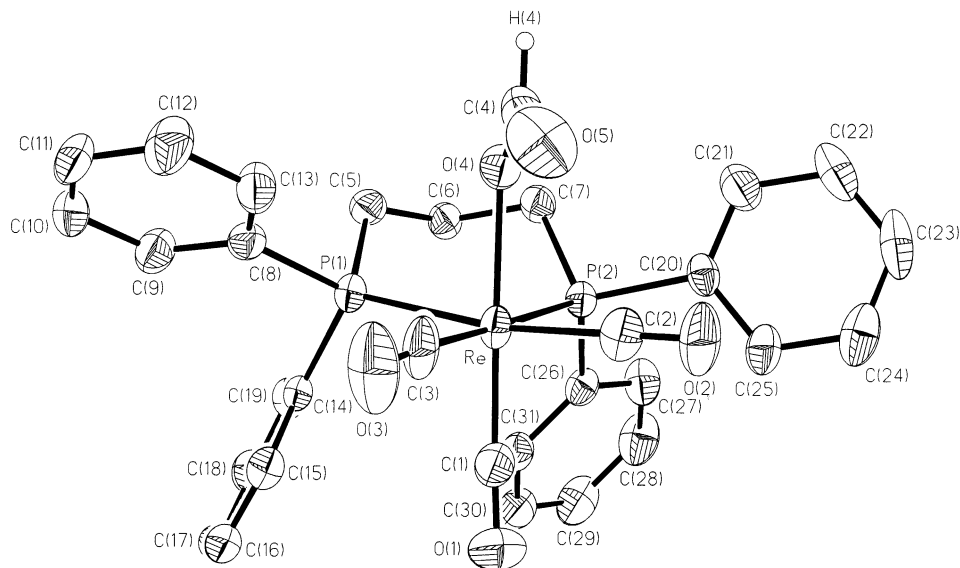


Fig. 2. A thermal ellipsoid plot of compound **2**.

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)OCH₃ [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 formate 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 car-

bonyls 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, ¹³C) 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 formate complex **1** and rhenium formate complex **2**

To 0.73–0.91 mmol of *fac*-M(CO)₃(dppp)H (M = Mn; Re) [10] dissolved in about 50 cm³ of dichloromethane was added formic acid (0.15–0.17 cm³, 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 formate complexes **1**

and **2** were collected by filtration. Data for **1**: yield, 88%; m.p. 153–155°C with decomposition. IR (cm⁻¹, CH₂Cl₂): $\nu(\text{C}\equiv\text{O})$ 2027 vs, 1960 s, 1906 s, and $\nu(\text{C}=\text{O})$ 1617 m. ¹H-NMR (δ , CDCl₃): 8.53 (t, 2 Hz, 1H, O=C–H), 7.49–7.31 (m, 20H, C₆H₅), 2.86–2.21 (m, 6H, CH₂CH₂CH₂). ¹³C-NMR (δ , CDCl₃): 215.8 (s, br, CO), 169.2 (t, 6 Hz, C=O), 135.8–128.6 (m, C₆H₅), 24.9 (t, 11 Hz, CH₂CH₂CH₂), 18.7 (18.7, s, CH₂CH₂CH₂). Anal. Found: C, 61.5; H, 4.6. C₃₁H₂₇MnO₅P₂ 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:

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 × 0.50 × 0.50	0.07 × 0.13 × 0.15
Chemical formula	C ₃₂ H ₂₉ MnO ₇ P ₂	C ₃₁ H ₂₇ O ₅ P ₂ Re
<i>a</i> (Å)	9.5216(6)	17.8435(3)
<i>b</i> (Å)	10.2134(5)	16.5212(2)
<i>c</i> (Å)	16.9567(8)	19.8756(3)
α (°)	90.503(4)	90
β (°)	94.807(5)	90
γ (°)	106.774(4)	90
<i>V</i> (Å ³)	1572.3(2)	5859.2(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>Pbca</i> (no. 61)
<i>Z</i>	2	8
Diffractionmeter	Siemens P4	Nonius Kappa CCD
μ (Mo–K α) (mm ⁻¹)	0.566	4.295
Scan mode, θ_{max} (°)	ω , 25.00	ω , 27.53
Completeness (%)	100	99.9
Limiting indices	0 ≤ <i>h</i> ≤ 11, –12 ≤ <i>k</i> ≤ 11, –20 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 23, 0 ≤ <i>k</i> ≤ 21, 0 ≤ <i>l</i> ≤ 25
Absorption correction	None	Gaussian
Reflections collected	5906	54 230
Reflections merged (<i>R</i> _{int})	5540 (0.0197)	6747 (0.0801)
Reflections observed	4044; <i>I</i> > 2σ(<i>I</i>)	4593; <i>I</i> > 2σ(<i>I</i>)
Variables	382	352
<i>R</i> (all) ^a	0.0356 (0.0549)	0.0314 (0.0652)
<i>R</i> _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 <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²

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

93%; m.p. 185–188°C with decomposition. IR (cm⁻¹, CH₂Cl₂): $\nu(\text{C}\equiv\text{O})$ 2033 vs, 1954 s, 1898 s, and $\nu(\text{C}=\text{O})$ 1625 m. ¹H-NMR (δ , CDCl₃): 8.19 (t, 2 Hz, O=C–H), 7.50–7.29 (m, 20H, C₆H₅), 2.94–2.28 (m, 6H, CH₂CH₂CH₂). ¹³C-NMR (δ , CDCl₃): 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, C₆H₅), 24.6 (t, 15 Hz, CH₂CH₂CH₂), 19.3 (18.7, s, CH₂CH₂CH₂). Anal. Found: C, 50.8; H, 3.7. C₃₁H₂₇O₅P₂Re Anal. Calc.: C, 51.2; H, 3.7%.

3.2. Decarboxylations of **1** and **2**

About 0.015 mmol of **1** or **2** was dissolved in 0.500 cm³ of toluene-*d*₈ at 110°C and the reaction was monitored by ³¹P-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 CO₂ 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 CH₂Cl₂–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) = 1.2*U*(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) = 1.5*U*(O), and its coordinates were free to vary. Convergence gave *R* = 0.0356 for 4044 reflections with *I* > 2σ(*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 CH₂Cl₂–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) = 1.2*U*(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	
<i>Bond lengths</i>			
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)		
<i>Bond angles</i>			
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. Sneed, 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. Wiegardt, 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. Darensbourg, 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.