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$\begin{array}{l} Re(I)(tricarbonyl)(carboxylate) \ complexes \ with \ the \\ [N,N'-bis(2,4,6-trimethylbenzene)-1,4-diazabutadiene] \ (2,4,6-Me_3G) \\ and \ [N,N'-bis(2,4-dimethylbenzene)-2,3-dimethyl-1,4-diazabutadiene] \\ \ (2,4-Me_2D) \ ligands \ - \ Syntheses \ and \ spectroscopic \ studies. \\ The \ crystal \ structure \ of \ [Re(CO)_3(2,4,6-Me_3G)(OCOCF_3)] \end{array}$

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Abstract

Two new carboxylato complexes, $[Re(CO)_3(DAB)(OCOCF_3)]$ (DAB = substituted aromatic diazabutadiene ligands), were prepared by the reaction of $[Re(CO)_5Cl]$ with the DAB ligands, and the subsequent reaction with AgOCOCF₃ gave the related carboxylate complexes. These new complexes were characterized by FTIR, NMR, UV–Vis spectra and elemental analysis. In both complexes, the Re atom has a distorted octahedral configuration and is coordinated by two carbonyl groups and the diimine group of the organic ligand in the equatorial plane. Octahedral coordination is completed at the axial positions by another carbonyl ligand and a carboxyl O atom of the trifluoroacetate anion. Electrochemical behaviour of the investigated complexes has been studied by cyclic voltammetry. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Rhenium(I) complexes; Diazabutadiene ligand; X-ray crystal structure

1. Introduction

The d⁶ transition metal Re(I), Ru(II), Os(II) or Rh(III) complexes with α -diimine ligands have been the subject of intense investigations [1–4]. Complexes of the type [Re(CO)₃(α -diimine)(X)]^{0/+}, in which X is a halide, bridging ligand, organic donor/acceptor, nitrogen donor or some other monodentate ligand, have been the subject of a large number of studies. Furthermore, this permanently growing interest stems from the ability of these complexes and their reduced form to act as efficient sensitizers for energy and electron transfer processes [5], and as catalysts

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in the selective reduction of CO_2 [6], a process of interest in the conversion and storage of solar energy, and serve as models for natural photosynthesis [7,8]. Control of the excited state resulting from metal-to-ligand charge transfer (MLCT) and the redox properties of these complexes, through structural and electronic modifications in the α -diimine chelate and/or axial ligands, has been proposed as a way to improve the photo- and electrocatalytic properties of these compounds. Therefore, knowledge of the molecular and crystal structure of such complexes is essential for understanding and explaining their properties. Significant research has focused on common chelating ligands such as bipyridine (bpy) and phenanthroline (phen), but the chemistry of the fac-[Re(CO)₃(X)] complexes with other bidentate *a*-diimine ligands remains largely unexplored. Bearing in mind all the above mentioned facts, we decided to pursue studies on the fac-[Re(CO)₃(DAB)(OCOCF₃)]

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complexes in which DAB = [N,N-bis(2,4,6-trimethylbenzene)-1,4-diazabutadiene] (2,4,6-Me₃G), and <math>[N,N-bis(2,4-dimethylbenzene)-2,3-dimethyl-1,4-diazabutadiene] (2,4-Me₂D). To the best of our knowledge, these complexesare the first reported Re(I)(tricarbonyl) carboxylate complexes with aromatic diazabutadiene ligands which werecharacterized by X-ray diffraction analysis, and the complex [Re(CO)₃(2,4-Me₂D)(OCOCF₃)] is the first metalcomplex containing the <math>N,N-bis(2,4-dimethylbenzene)-2,3dimethyl-1,4-diazabutadiene ligand. The crystal structure of [Re(CO)₃(2,4-Me₂D)(OCOCF₃)] has been reported elsewhere [9].

2. Experimental

2.1. General

All chemicals used were reagent grade and were used as received. Solvents used for the reactions were purified by literature methods [10]. The diazabutadiene ligands were prepared according to a modified literature procedure [11]. NMR spectra were obtained on a Bruker Avance DRX500 (500 MHz) spectrometer. The chemical shifts (δ) are reported in part per million (ppm) relative to an internal standard of Me₄Si. The UV-Vis spectra were recorded on a Shimadzu UV-160 spectrophotometer with quartz cells (1 cm path length). Elemental analyses were performed using a Heraeus elemental analyzer. IR spectra were recorded as KBr pellets on a Nicolet Impact 400D spectrophotometer. Electrochemical data were obtained by cyclic voltammetry (CV) with a three-electrode cell containing an Ag/AgCl reference electrode, a Pt wire counter electrode and a Pt working electrode. A Metrohm multipurpose instrument model 757 was used. CV measurements were performed in CH₂Cl₂ with 25 mM of Bu₄NClO₄ (TBAP) as a supporting electrolyte. In all electrochemical experiments, the solutions were purged with Ar gas for at least 5 min.

2.2. X-ray crystallography

Suitable single crystals of [Re(2,4,6-Me₃G)(CO)₃(O- $COCF_3$](1) were obtained by diffusion of *n*-hexane vapour into a CH₂Cl₂ solution at -18 °C. Crystal data and refinement parameters for complex 1 are summarized in Table 1. Intensity data for complex 1 were collected on a Rigaku R-AXIS RAPID image plate diffractometer (λ (Mo K α radiation) = 0.71070 Å) at 295 \pm 2 K. Several scans in the ϕ and ω directions were made to increase the number of redundant reflections, which were averaged over the refinement cycles. An empirical (multi-scan) absorption correction was applied (ABSCOR) [12]. The structure was solved by the direct method (SIR92) [13] and refined by full-matrix least-squares (SHELXL-97) [14]. All calculations were carried out using the WINGX package of the crystallographic programs [15]. The benzene rings were restrained to be flat within a standard deviation of 0.1 Å (FLAT 0.10 instruc-

Table 1	
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Crystal data and structure refinement	t parameters for com	plex 1
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Complex	1
Empirical formula	$C_{25}H_{24}F_3N_2O_5Re$
Formula mass	675.66
Crystal size (mm)	$0.51 \times 0.52 \times 0.62$
Colour	dark-red
Crystal system	monoclinic
Space group	$P2_{1}/c$
θ Range for data collection (°)	$3.0 \leqslant \theta \leqslant 27.5$
a (Å)	8.162(3)
<i>b</i> (Å)	13.581(4)
<i>c</i> (Å)	24.456(9)
β (°)	105.07(2)
$V(Å^3)$	2617.7(16)
Ζ	4
D_{calc} (Mg/m ³)	1.714
$\mu (\mathrm{mm}^{-1})$	4.700
<i>F</i> (000)	1320
Index ranges	$-10 \leqslant h \leqslant 10, -16 \leqslant k \leqslant 17,$
	$-31 \leq l \leq 31$
Number of collected reflections	20168
Number of independent reflections/ R_{int}	5627/0.045
Number of observed reflections $I > 2\sigma(I)$	4644
Number of parameters	331
Goodness-of-fit (GOF)	1.06
R_1 (observed data)	0.0322
wR_2 (all data) ^a	0.0710

^a $w = 1/[\sigma^2(F_o)^2 + (0.0094P)^2 + 8.4642P]$ where $P = (F_o^2 + 2F_c^2)/3$.

tion of SHELXL). The carbon atoms of the benzene rings were refined with distance restraints (SADI 0.002 instruction of SHELXL). All non-hydrogen atoms were refined anisotropically in the F^2 mode. Hydrogen atoms were constrained to idealized geometries and refined isotropically. The riding model was applied for the hydrogen atoms. In addition, the riding methyl hydrogen atoms were allowed to rotate freely during refinement.

2.3. Synthesis

2.3.1. [N,N-bis(2,4,6-trimethylbenzene)-1,4-diazabutadiene] (2,4,6-Me₃G)

To a 500 ml round-bottom flask equipped with a magnetic stir bar was added 250 ml of ethanol and (15.115 g, 111.8 mmol) of 2,4,6-Me₃PhNH₂. Glyoxal (8.406 g, 40 wt% solution, 55.86 mmol) was added to the clear, faint yellow solution, and the resulting yellow solution was stirred at room temperature for 14 h. The solution was filtered and the bright yellow solid thus obtained was washed with cold ethanol and dried in vacuo. IR (KBr, cm⁻¹): v_{max} 1617, 1479 (sym, asym C=N). ¹H NMR (500 MHz, CDCl₃): 2.21 (s, 12H, 2,6-(CH₃)₂); 2.34 (s, 6H, 4-(CH₃)); 6.94 (s, 4H, aromatic hydrogens); 8.15 (s, 2H, iminic hydrogens). ¹³C{¹H} NMR (500 MHz, CDCl₃): 18.68; 21.23; 127.00; 129.42; 134.72; 147.85; 163.94 (¹³C=N). UV–Vis: λ_{max} , ε (nm, M⁻¹ cm⁻¹): 248 (12444); 370 (4445).

2.3.2. [N,N-bis(2,4-dimethylbenzene)-2,3-dimethyl-1,4diazabutadiene] (2,4-Me₂D)

This ligand was prepared by a procedure similar to 2,4,6-Me₃G using (14.4 g, 118.8 mmol) of 2,4-Me₂PhNH₂ and (4.80 g, 55.80 mmol) of diacetyl. The bright yellow solid was washed with cold ethanol and dried in vacuo. IR (KBr, cm⁻¹): v_{max} 1633, 1488 (sym, asym C=N). ¹H NMR (500 MHz, CDCl₃): 2.14 (s, 6H, 2-(CH₃)); 2.17 (s, 6H, 2-(CH₃)); 2.37 (s, 6H, iminic methyls); 6.58–6.60 (d, 2H, aromatic hydrogens); 7.09 (s, 2H, aromatic hydrogens). UV–Vis: λ_{max} , ε (nm, M⁻¹ cm⁻¹): 243 (11360); 345 (3973).

2.3.3. $[Re(CO)_3(2,4,6-Me_3G)(OCOCF_3)]$ (1)

A mixture of $\text{Re}(\text{CO})_5\text{Cl}$ (0.5 mmol, 111 mg) and 2,4,6-Me₃G (0.5 mmol, 146 mg) in 20 ml CH₂Cl₂ and 30 ml of absolute ethanol was heated at reflux for 3 h to give a red-brown solution. The solution was concentrated to half volume and a solution of AgOCOCF₃ (0.5 mmol, 110 mg) in THF was added. The mixture was refluxed for 4 h in the dark. After cooling, the AgCl precipitate was removed by filtration and the crude material was recrystallized from CH₂Cl₂/hexane to give the carboxylate complex 1 as pure dark-red crystals.

Anal. Calc. for C₂₄H₂₄F₃N₂O₅Re: C, 44.44; H, 3.58; N, 4.15. Found; C, 44.45; H, 3.56; N, 4.20%. IR (KBr, cm⁻¹): v_{max} 2031, 1931, 1921 (CO). ¹H NMR (500 MHz, CDCl₃): 2.24 (s, 6H, CH₃); 2.29 (s, 6H, CH₃); 2.38 (s, 6H, CH₃); 7.03 (s, 4H, aromatic hydrogens); 8.79 (s, 2H, iminic hydrogens). UV–Vis: λ_{max} , ε (nm, M⁻¹ cm⁻¹): 239 (13720); 480 (8773).

2.3.4. $[Re(CO)_3(2,4-Me_2D)(OCOCF_3)]$ (2)

This complex was prepared by a procedure similar to 1using 146 mg (0.5 mmol) of 2,4-Me₂D. The crude material recrystallized from CH₂Cl₂/hexane was to give $[Re(CO)_3(2,4-Me_2D)(OCOCF_3)]$ as pure dark-red crystals. Anal. Calc. for C₂₅H₂₄F₃N₂O₅Re: C, 44.44; H, 3.58; N, 4.15. Found; C, 44.46; H, 3.60; N, 4.15%. IR (KBr, cm⁻¹): v_{max} 2023, 1929 (CO). ¹H NMR (500 MHz, CDCl₃): 2.07-2.40 (s, 18H, 6CH₃); 6.7-7.2 (6H, aromatic hydrogens). ${}^{13}C{}^{1}H$ NMR (500 MHz, CDCl₃): 16.76, 17.25, 17.53, 20.16-20.18, 20.30, 20.90-20.94, 119.95-120.04, 120.55, 126.06, 126.62, 127.76, 127.96, 128.35-128.40, 131.90, 131.97, 132.26, 137.61–137.66, 145.73–145.78, 146.12, 176.59–176.80, 195.48. UV–Vis: λ_{max} , ε (nm, $M^{-1} cm^{-1}$): 239 (14386); 430 (9573).

3. Results and discussion

3.1. General characterization

The new *fac*-[Re(CO)₃(DAB)(OCOCF₃)] (DAB = substituted aromatic diazabutadiene ligands) complexes were obtained via substitution reactions, as outlined in Scheme 1. The trifluoroacetateo complexes were synthesized by allowing the in situ reaction of the halide carbonyl with 1





equivalent of AgOCOCF₃ in a mixture of ethanol and THF in the dark. After cooling, the AgCl that formed during the reaction was removed by filtration. The partial removal of the solvent and addition of *n*-hexane resulted in the formation of the corresponding complexes 1 and 2in good yield. These new complexes are stable in the solid state and in solution at room temperature and they were characterized by the usual spectroscopic techniques. The IR spectra of the free ligands exhibit the characteristic bands of the symmetrical and asymmetrical stretching of the imine group at 1617 and 1479 cm^{-1} for 2,4,6-Me₃G and 1633 and 1488 cm⁻¹ for 2,4-Me₂D. The IR spectra of complexes exhibit the characteristic bands in the carbonyl stretching region as a sharp intense band at 2031 and 2023 cm⁻¹ for complexes 1 and 2, respectively, and two lower-energy bands closely spaced at 1936 and 1921 cm^{-1} for complex 1 and 1929 cm⁻¹ for complex 2, typical of Re(I) α -diimine tricarbonyl complexes [16,17]. The nature of the axial ligand in the $[Re(CO)_3(NN)(X)]$ complexes influences, to some extent, the position and the shape of the absorption band in the IR spectra. The π -donor character of the oxygen atom in the trifluoroacetate group increases the $Re \rightarrow CO$ back-bonding, which decreases the energy of v(CO) [18]. The NMR spectra and peak assignments of the ligands and their complexes are presented in Section 2. For complexes 1 and 2, the signal due to the methyl groups in the ortho and para positions of the phenyl ring appears at about 2.24-2.38 and 2.07–2.40 ppm, respectively. The signal due to the iminic methyl in complex 2 appears at about 2.36 ppm. For complex 1, the signal due to the iminic hydrogen appears at about 8.79 ppm. The signal due to the aromatic hydrogens appears at about 7.03 and 7.30 ppm for complex 1 and at about 6.72–7.25 ppm for complex 2. All the signals due to the different hydrogens in the ¹H NMR spectra of complexes 1 and 2 are shifted to the low-field region with respect to the free ligands as a result of ligand coordination. The UV-Vis spectral data of the ligands and their complexes are presented in Table 2. The UV-Vis bands of the ligands are assigned to ligand-centered $\pi \to \pi^*$ and $n \to \pi^*$ transitions [11]. The absorption spectra of the complexes can be interpreted by comparison with other Re(I) complexes with ligands structurally related to those used in this work [19– 21]. The higher energy bands observed in the spectra have been considered as intraligand $\pi \to \pi^*$ transitions, and these are also present for the free ligands in the same spectral regions. The longer wavelength absorption bands show a maximum in the range 400-500 nm. These bands have been assigned partly to metal-to-ligand charge-transfer (MLCT)

Table /

Table 2UV-Vis spectral data of the DAB ligands, and complexes 1 and 2

Compound	Concentration (M)	Solvent	UV–Vis λ_{max} (nm) [ϵ] (M ⁻¹ cm ⁻¹)
2,4,6Me ₃ G	9×10^{-5}	CH_2Cl_2	248 [12444], 370 [4445]
$2,4Me_2D$	1.5×10^{-3}	CH_2Cl_2	243 [11 360], 345 [3973]
Complex 1	7.5×10^{-5}	CH_2Cl_2	239 [13720], 480 [8773]
Complex 2	7.5×10^{-5}	CH_2Cl_2	239 [14386], 430 [9573]



Fig. 1. Cyclic voltammograms of 1 (a) and 2 (b) in CH₂Cl₂ at 293 K (scan

rate, 100 mV/s, $C = 2.5 \times 10^{-4}$ M).

transitions, mixed with a $\pi \to \pi^*$ transition of the Re(DAB) chelate. The electrochemical behaviour of complexes 1 and 2 was examined by means of cyclic voltammetry (CV) in CH₂Cl₂ (Fig. 1). Anodic scans reveal a single reversible oxidation at 1.44 and 1.66 V versus Ag/AgCl for the complexes 1 and 2, respectively. This is assigned to the Re(II)/Re(I) redox couple, which is similar to the anodic peak potential reported for similar systems [22]. Complexes 1 and 2 show quasireversible redox couples with $E_{1/2}$ values of 1.36 and 1.59 V, respectively. The cyclic voltammetry peak-to-peak separations (ΔE_p) of 160 and 130 mV were observed at a scan rate (ν) of 100 mV⁻¹ for complexes 1 and 2, respectively.

3.2. X-ray structure of [Re(CO)₃(2,4,6-Me₃G)(OCOCF₃)] (1)

The molecular structure of 1 is shown in Fig. 2, selected bond lengths and angles are listed in Table 3. The Re atom has a distorted octahedral configuration and is coordinated by two carbonyl groups and the diimine group of the 2,4,6-Me₃G ligand in the equatorial plane. Octahedral coordination is completed at the axial positions by another carbonyl ligand and a carboxyl O atom of the trifluoroacetate anion. The equatorial Re–C distances are 1.909(6) and 1.923(5) Å, respectively. The equatorially disposed N,N'-bidentate chelating 2,4,6-Me₃G ligand forms a ReN₂C₂ five-membered chelate ring and the mean deviation of these atoms from the least-square plane is only 0.0274 Å. In this five-membered chelate ring the



Fig. 2. ORTEP drawing for complex 1. Non-hydrogen atoms are shown as 30% probability ellipsoids.

						-
Selected	bond	distances (A	Å) and	angles	(°) for complex 1	
Table 5						

Complex 1			
Re(1)-N(1)	2.186(4)	C(1)-Re(1)-O(4)	179.7(2)
Re(1) - N(2)	2.160(4)	C(2)-Re(1)-C(3)	88.3(2)
Re(1) - O(4)	2.153(3)	C(3)-Re(1)-N(1)	99.4(2)
Re(1) - C(1)	1.896(6)	N(1)-Re(1)-N(2)	74.1(2)
Re(1)-C(2)	1.909(6)	N(2)-Re(1)-C(2)	98.3(2)
Re(1)-C(3)	1.923(5)		

1 aoie 1					
Parameters	of hydrogen	bonding	interactions	in complex	1

	, , ,		1	
Complex 1	D–H···A	$\begin{array}{c} H \cdots A \\ (\mathring{A}) \end{array}$	D· · ·A (Å)	$\begin{array}{c} D - H \cdots A \\ (^{\circ}) \end{array}$
	C(151)− H(15B)····O(4)	2.44	3.308(8)	150
	$C(6)-H(6)\cdots O(5)^{i}$	2.13	2.940(8)	145
	C(131)-	2.48	3.399(10)	159
	$H(13A) \cdots F(1)^{ii}$			

Symmetry codes: (i) 1 + x, y, z; (ii) 1 - x, -1/2 + y, 1/2 - z.

N(1)-Re(1)-N(2) bite angle is 74.1(2)° and Re-N (N1, N2) bond lengths are 2.186(4) and 2.160(4) Å, respectively. Owing to the steric requirements of the N,N'-bidentate chelating 2,4,6-Me₃G ligand the equatorial bond angles range from 74.1(2)° to 99.4(2)°. The axial C(1)-Re(1)–O(4) bond angle is $179.7(2)^{\circ}$. Due to the π -donor character of the trifluoroacetate ligand, the axial Re-C bond length of 1.896(6) Å is slightly shorter than the corresponding equatorial Re–C distances. The CF₃ group has high thermal motion consistent with some unresolved rotational disorder, as is often found in other trifluoroacetate compounds [9,23,24]. The overall structural similarity of 1 with the previously reported $[Re(CO)_3(2,4-Me_2D)]$ $(OCOCF_3)$ complex [9] reflects the strong tendency of substituted diazabutadiene ligands to enforce a distorted-octahedral geometry at Re. In addition, there are weak intra- and intermolecular C-H···O, as well as intermolecular C-H \cdots F interactions (Table 4) in the crystal lattice of 1.

4. Conclusion

The *fac*-[Re(CO)₃(DAB)(OCOCF₃)] (DAB = 2,4,6-Me₃G, 2,4Me₂D) rhenium(I) complexes have been prepared and characterized by IR, UV–Vis, NMR, electrochemical and X-ray diffraction techniques. Variations in the electronic properties related to rhenium(I), the carbonyl and X ligands, such as electronic transitions, CO stretching and some crystallographic parameters of the complexes, were interpreted on the basis of the DAB and X ligands. It is clear from the data that, by varying the nature of the DAB ligands attached to rhenium, the electronic properties of the *fac*-[Re(CO)₃(DAB)(OCOCF₃)] complexes could be tuned.

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Appendix A. Supplementary material

CCDC 630420 contains the supplementary crystallographic data for 1. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.01.043.

References

 A. Vlcek Jr., J. Heyrovsky, in: V. Balzani (Ed.), Electron Transfer in Chemistry, Part 2, vol. 2, Wiley-VCH Verlag GmbH, Weinheim, 2001, p. 804.

- [2] A.J. Lees, Chem. Rev. 87 (1987) 711.
- [3] A.I. Baba, J.R. Shaw, J.A. Simon, R.P. Thummel, R.H. Schmehl, Coord. Chem. Rev. 171 (1988) 43.
- [4] D.J. Stufkens, A. Vlcek, Coord. Chem. Rev. 171 (1988) 127.
- [5] D.J. Stufkens, Comments Inorg. Chem. 13 (1992) 359.
- [6] (a) J. Hawecker, J.M. Lehn, R. Ziessel, J. Chem. Soc., Chem. Commun (1983) 536;
 (b) B.P. Sullivan, T.J. Meyer, J. Chem. Soc., Chem. Commun. (1984) 1244;
- (c) G. Calzaferri, K. Hadener, J. Li, J. Photochem. Photobiol. A 64 (1992) 259.
- [7] C. Kutal, A.J. Corbin, G. Ferraudi, Organometallics 6 (1987) 553.
- [8] B.P. Sullivan, T.J. Meyer, J. Chem. Soc., Chem. Commun. (1984) 1414, and references therein.
- [9] R. Kia, V. Mirkhani, A. Deák, A. Kálmán, Acta Crystallogr., Sect. E 61 (2005) m566.
- [10] D.D. Perrin, W.L. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, second ed., Pergamon, New York, 1990.
- [11] H. tom Dieck, I.W. Renk, Chem. Ber. 104 (1971) 92.
- [12] T. Higashi, ABSCOR, Rigaku Corporation, Tokyo, Japan, 1995.
- [13] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435.
- [14] G.M. Sheldrick, SHELXL97-Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [15] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837.
- [16] W. Kaim, H.E.A. Kramer, C. Vogler, J. Rieker, J. Organomet. Chem. 367 (1989) 107.
- [17] E. Wolcan, G. Trochia, J. Tocho, O.E. Piro, P. Juliarena, G. Ruiz, M.R. Feliz, J. Chem. Soc., Dalton Trans. (2002) 2194.
- [18] A. Klein, C. Vogler, W. Kaim, Organometallics 15 (1996) 236.
- [19] C.H. Staal, A. Oskam, K. Vrieze, J. Organomet. Chem. 170 (1979) 235.
- [20] R.W. Balk, D.J. Stufkens, A. Oskam, J. Chem. Soc., Dalton Trans. (1981) 1124.
- [21] G.J. Stor, D.J. Stufkens, A. Oskam, Inorg. Chem. 31 (1992) 1318.
- [22] R.N. Dominey, B. Hauser, J. Hubbard, J. Dunham, Inorg. Chem. 30 (1991) 4754.
- [23] V.H. Rodrigues, J.A. Paixao, M.M.R.R. Costa, A. Beja Matos, Acta. Crystallogr., Sect. C 56 (2000) 1053.
- [24] V.H. Rodrigues, J.A. Paixao, M.M.R.R. Costa, A. Beja Matos, Acta. Crystallogr., Sect. C 57 (2001) 417.