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Note

Synthesis and characterization of isocyanide containing rhenium(III) complexes *trans*-[ReCl₃(CNR)(PPh₃)₂] and crystal structure of *trans*-[ReCl₃(CN-t-C₄H₉)(PPh₃)₂]

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Abstract

Isocyanide containing complexes *trans*-[ReCl₃(CNR)(PPh₃)₂] (3) (R = tert-C₄H₉ (3a), c-C₆H₁₁ (3b), C₆H₅ (3c), CH₂C(O)OCH₃ (3d), CH₂CH₂-(*N*-morpholinyl) (3e)) were obtained by reduction of *trans*-[Re(O)Cl₃(PPh₃)₂] with an excess of triphenylphosphane in the presence of the isocyanide or by substitution of the acetonitrile ligand in *trans*-[ReCl₃(NCCH₃)(PPh₃)₂] by the isocyanide ligand. Generally, the substitution reaction starting with Re(III) gives a higher yield. The crystal structure of 3a has been determined by X-ray diffraction methods. 3a crystallizes with one molecule of CH₂Cl₂ per formula unit. Crystals of 3a · CH₂Cl₂ are monoclinic, space group $P2_1/c$ with a = 12.868(3), b = 20.454(7), c = 16.378(9) Å, $\beta = 104.71(4)^\circ$, Z = 4 and $D_0 = 1.58$ g cm⁻³. The structure was solved from 6190 diffraction data $(F_0^2 \ge 3\sigma(F_0^2)]$ collected at -100(2) °C and refined to R = 0.0429 ($R_w = 0.0727$).

Keywords: Crystal structures; Rhenium complexes; Isocyanide complexes

1. Introduction

Neutral rhenium complexes have attracted attention as models for radiotherapeutic agents based on ¹⁸⁶Re. Our interest is centered around the preparation of neutral rhenium complexes, which contain a single 'bifunctional' ligand and thus enable coupling of the complexed metal ion to a biological relevant anchor Re(III) complexes of the type transgroup. $[ReCl_3(CNR)(PPh_3)_2]$ (3) could be useful precursors for the preparation of mixed-ligand complexes [Re(CNR)(L)], in which the coordination sphere consists of a multidentate ligand L and a bifunctional isocyanide ligand CNR. We reported recently on a first example for this approach with the synthesis of trigonal bipyramidal isocyanide-trithiolate complexes from octahedral complexes of type 3 [1]. To date only one derivative of a complex of type 3, trans-[ReCl₃- $(CNCH_3)(PPh_3)_2$, has been described in the literature

0020-1693/95/\$09.50 © 1995 Elsevier Science S.A. All rights reserved SSDI 0020-1693(94)04373-4 [2] and no structural data exist for any complex of this type. In this paper we describe the preparation of a series of complexes *trans*-[ReCl₃(CNR)(PPh₃)₂] (R = tert-C₄H₉ (**3a**), c-C₆H₁₁ (**3b**), C₆H₅ (**3c**), CH₂C(O)-OCH₃ (**3d**), CH₂CH₂-(*N*-morpholinyl) (**3e**) together with the crystal structure of **3a** \cdot CH₂Cl₂.

2. Experimental

2.1. Methods and materials

The isocyanides used in this study were obtained from Alpha Products (for **3a**) and Merck (for **3b** and **3e**). Phenylisocyanide and methyl 2-isocyanoacetate were prepared as described in Refs. [3] and [4], respectively. *Trans*-[Re(O)Cl₃(PPh₃)₂] (1) was synthesized from NH₄[ReO₄] as described by Chatt and Rowe [5]. *Trans*-[ReCl₃(NCCH₃)(PPh₃)₂] (2) was prepared by reduction of 1 with an excess of triphenylphosphane [6]. UV-Vis spectra were recorded on a Carl Zeiss Specord

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M40 spectrometer. IR spectra were measured as KBr pellets on a Carl Zeiss Specord M80. A Bruker WH90 spectrometer was used for all ¹H NMR spectra (solvent CDCl₃). Elemental analyses were performed on a LECO CHNS932 elemental analyzer.

2.2. Synthesis of trans- $[ReCl_3(CNR)(PPh_3)_2]$ (3a-e) from trans- $[ReCl_3(NCCH_3)(PPh_3)_2]$

Similar reaction conditions were employed for the preparation of 3a-e from 2. In a typical reaction 200 mg (0.233 mmol) of 2 were dissolved in 10 ml of dry benzene in a nitrogen atmosphere. 0.350 mmol of the isocyanide was added under nitrogen, the reaction mixture was refluxed for 30 min and the volume was then reduced under nitrogen. This led to the yellow complexes 3. If no precipitation was observed after volume reduction, the reaction mixture was taken to dryness and dissolved in 2 ml of dichloromethane. Crystallization was then induced by addition of 5 ml ethanol. The raw material was washed with diethyl ether and recrystallized from dichloromethane/ethanol to give the yellow, crystalline complexes 3a-e in 70-80% yield. In the case of 3b, however, all attempts of final purification have been unsuccessful up to now. Microanalytical and physical data for the complexes 3a-e are summarized in Table 1.

2.3. Synthesis of trans- $\{ReCl_3[(CNC(CH_3)_3](PPh_3)_2\}$ (3a) from trans- $[Re(O)Cl_3(PPh_3)_2]$

The preparation of complexes of type 3 is also possible in a one-pot synthesis starting with $[Re(O)Cl_3(PPh_3)_2]$ (1). The yield in this reduction-substitution reaction is generally lower (sometimes as low as 3-5%) than for the reaction starting with the Re(III) precursor 2. The best yield (43%) was obtained in the synthesis of 3a. For the preparation of 3a 100 mg (0.120 mmol) of 1 were dissolved in 10 ml of dichloromethane. To this were added 94 mg (0.360 mmol) of triphenylphosphane and 31 μ l (0.300 mmol) of tert-butylisocyanide at room temperature under nitrogen. The reaction mixture was then heated under reflux for 10 min. During this period the color of the solution turned from yellow to dark green and finally to orange. After concentration of the solution and addition of 10 ml of ethanol 51 mg (43%)of yellow crystals of trans-{ReCl₃[(CNC(CH₃)₃]- $(PPh_3)_2$ \cdot CH₂Cl₂ (3a \cdot CH₂Cl₂) precipitated.

2.4. X-ray crystallography

3a crystallized from CH_2Cl_2 /ethanol as the CH_2Cl_2 solvate $3a \cdot CH_2Cl_2$. The crystals are air sensitive (loss of CH_2Cl_2 from the crystals). They were mounted directly in the cold stream (-100(2) °C) of an Enraf-Nonius CAD-4 diffractometer using a modified version of the device proposed by Veith and Bärnighausen [7]. Stan-

Table 1 Analytical and physical data for the complexes 3a-3e

Complex	Formula	Elemental analysis " (%)				M.p.	¹ H NMR (90 MHz, CDCl ₃)			IR (KBr)	UV–Vis ^b	
		С	Н	N	Cl	(°C)	δ (ppm)	Mult.	Int.	Assign.	ν (cm ⁻¹)	Λ_{\max} (nm)
3a · CH₂Cl₂	$C_{42}H_{41}Cl_5NP_2Re$	51.31 (51.20)	4.26 (4.19)	1.49 (1.42)	17.99 (17.99)	191–194	7.89 8.47, 8.72 15.40 5.30	s m m s	9H 18H 12H 2H	C-CH ₃ m, p Ar-H o Ar-H CH ₂ Cl ₂	2144	304 (3.68) 448 (3.35) 455 (3.38)
3b	C43H41Cl3NP2Re	c									2128	455 (3.38)
3c	C43H35Cl3NP2Re	56.10 (56.12)	3.89 (3.83)	1.65 (1.52)	11.35 (11.56)	207–209	3.74 4.65 8.84 14.08 15.63	d t m t m	2H 1H 18H 2H 12H	o CN-Ar-H p CN-Ar-H m, p Ar-H m CN-Ar-H o Ar-H	2104	254 (4.04) 313 (4.04) 462 (3.02)
3d	$C_{40}H_{35}Cl_3NO_2P_2Re$	51.80 (52.44)	3.88 (3.85)	1.60 (1.53)	12.04 (11.61)	184–188	4.25 7.70 8.93 15.65	s s m m	3H 2H 18H 12H	CH ₃ CH ₂ m, p Ar-H o Ar-H	2112	455 (3.31)
3e	$C_{43}H_{42}Cl_3N_2OP_2Re$	53.53 (53.06)	4.45 (4.35)	2.99 (2.88)	11.08 (11.93)	195–200	2.94, 3.94 5.65, 7.35 8.95 15.50	m m m m	4H 4H 18H 12	morpholine- CH_2 ethylene- CH_2 m, p Ar-H o Ar-H	2152	252 (3.37) 303 (3.95) 451 (3.29)

* Calculated values are in parentheses.

^b Values for log ϵ are in parentheses.

^e Elemental analysis remained unsatisfactory.

Table 2Selected crystal and data collection details

Crystal size (mm)	0.45×0.40×0.25
Formula	$C_{42}H_{41}Cl_5NP_2Re$
Formula weight (a.m.u.)	985.21
a (Å)	12.868(3)
$b(\mathbf{A})$	20.454(7)
c (Å)	16.378(9)
β (°)	104.71(4)
$V(Å^3)$	4169(5)
Space group	$P2_1/c$ (No. 14)
Z	4
$D_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$	1.569
$D_{\rm obs}~({\rm g~cm^{-3}})$	1.58
$\mu (\mathrm{cm}^{-1})$	33.8
Radiation, λ (Å)	Μο Κα, 0.71073
Data collection temperature (°C)	-100(2)
2θ Range (°)	$2 \le 2\theta \le 50$
hkl Range	$0 \le h \le 13, \ 0 \le k \le 24, \ -18 \le l \le 18$
Scan type	$\omega - 2\theta$
No. unique data	7340
No. of observed data, $F_o^2 \ge 3\sigma(F_o^2)$	6190
R *	0.0429
R _w *	0.0727
No. variables	446

* $R = \sum \Delta F / \sum F_{o}; R_{w} = [\sum w \Delta F^{2} / \sum F_{o}^{2}]^{1/2}.$

dard centering and autoindexing procedures indicated a monoclinic cell. Intensity data were collected at -100(2) °C. The systematically absent intensities allowed unambiguous assignment of the space group $P2_1/c$. The structure was solved by Patterson methods and refined by full matrix least-squares. An empirical absorption correction [8] was applied to the data before refinement of positional parameters with anisotropic thermal parameters. All hydrogen atoms were added to the model at calculated positions (d(C-H) = 0.95 Å)[9]. Calculations were carried out with the MolEN package of programs [10]. Neutral atomic scattering factors were taken from Ref. [11] and the scattering factors for the non-hydrogen atoms were corrected for anomalous dispersion [12]. Selected data collection and refinement parameters are given in Table 2. Table 3 lists selected bond distances and angles. For additional data concerning the crystal structure determination, see Section 4.

3. Results and discussion

Two different routes (Scheme 1) were employed for the preparation of complexes of type 3. The reduction of 1, carried out under nitrogen, with an excess of triphenylphosphane in the presence of the appropriate isocyanide gave air-stable complexes 3 in moderate yield. However, a higher yield (92%) has been reported for this reaction in the presence of methylisocyanide [2]. Alternatively, complexes 3a-e were obtained in

Table 3 Selected bond distances (Å) and angles (°) for $3a \cdot CH_2Cl_2$

Re-Cl1	2.338(2)	Cl1-Re-Cl2	173.15(6)
Re-Cl2	2.340(2)	Cl1-Re-Cl3	89.56(6)
Re-Cl3	2.426(2)	Cl1-Re-P1	88.28(6)
Re-P1	2.463(2)	Cl1-Re-P2	91.09(6)
Re-P2	2.468(2)	Cl1-ReCl	82.6(2)
Re-C1	2.004(7)	Cl2-ReCl3	97.03(5)
N-C1	1.139(9)	Cl2-Re-P1	89.98(6)
N-C2	1.440(9)	Cl2-Re-P2	90.92(6)
		Cl2-Re-C1	90.8(2)
		Cl3-Re-P1	89.09(6)
		Cl3-Re-P2	88.47(5)
		Cl3-Re-Cl	172.1(2)
		P1-Re-P2	177.49(5)
		P1-Re-C1	91.5(2)
		P2-Re-C1	90.8(2)
		Re-C1N	173.7(6)
		C1-N-C2	170.1(9)

good yield by substitution of the acetonitrile ligand in 2 by an isocyanide ligand. In the reaction of 1, the triphenylphosphane seems to be essential as a reducing agent. If 1 was reacted with an excess of isocyanide in the absence of phosphanes, no Re(III) complexes could be isolated. Instead a blue species formed which decomposed rapidly and was not further investigated.

As expected, the aromatic or β -unsaturated isocyanides used in this study (complexes 3c and 3d) are better π -acceptors than aliphatic saturated ligands (Table 1) [13]. The aliphatic saturated isocyanides appear to act mainly as σ -donors as judged by the IR absorptions



Scheme 1. Synthesis of complexes 3a-e.



Fig. 1. ORTEP drawing of 3a in $3a \cdot CH_2Cl_2$ showing 50% probability thermal ellipsoids and the atomic numbering scheme.

for the N=C bond [14]. The σ -donor capability is even sufficient for binding to Re(V) as observed in {Re(O)Cl₃[CNC(CH₃)₃]₂} [15].

Concerning the ¹H NMR spectra, there are some unexpected low field shifted patterns especially for the aromatic protons (Table 1) in contrast to five-coordinated rhenium(III) isocyanide complexes [1]. This phenomenon of a weak paramagnetism was described for rhenium d⁴ [16] and technetium d⁴ complexes [17]. The largest downfield shift is observed for the *o*-protons in the aryl substituted phosphanes in our complexes as well as in complexes previously described [16,17].

Complex 3a was crystallized as the solvate $3a \cdot CH_2Cl_2$ and characterized by X-ray crystal structure analysis (Fig. 1, Table 3). The structure analysis confirms the proposed *trans*-octahedral geometry. It also reflects the weak π -acceptor qualities of the tert-butylisocyanide, which can be seen in the long Re–Cl (2.004(7) Å) and the short C1–N (1.139(9) Å) distances. Comparable values for an Re(III) complex with methyl 2-isocyanoacetate are 1.905(9) and 1.200(12) Å [1]. However, the latter compound has a trigonal-bipyramidal geometry with coordination number 5. Stronger evidence for the superior π -acceptor qualities of methyl 2-isocyanoacetate compared to tert-butylisocyanide in Re(III) complexes comes from the geometry of the C-N-C angle of the socyanide ligand. This angle is almost linear in $3a \cdot CH_2Cl_2$ (170.1(9)°) while strong backbonding in the methyl 2-isocyanoacetate complex leads to a C-N-C angle of 150.8(9)° [1].

Despite its weak π -acceptor qualities, the tert-butylisocyanide ligand is at least as tightly bound as all other ligands in $3a \cdot CH_2Cl_2$. Even a small *trans* effect is noticeable for the Re-Cl3 bond. Reaction of 3a with a tripodal tetradentate NS₃ ligand leads to substitution of all ligands, but the isocyanide, and formation of a trigonal-bipyramidal complex with the isocyanide in an axial position [1]. This reaction appears to be even more favored with isocyanides which are better π acceptors. Thus complexes of type 3 are superb starting materials for substitution reactions on Re³⁺ ions in which the isocyanide ligand is retained.

4. Supplementary material

A full list of data collection and refinement details, tables of positional parameters for all atoms, all bond distances and angles, anisotropic temperature factors, as well as calculated and observed structure factor amplitudes have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-58462, the names of the authors and the journal citation.

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