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Isothiocyanato complexes of rhenium

VI. Synthesis, characterization and structures of *cis*-and *trans*-[$ReCl_2(NCS)(Me_2PhP)_3$] [1]

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Abstract

The reaction of [$ReCl_3(Me_2PhP)_3$] with excess KSCN or trimethylsilylisothiocyanate leads to the replacement of only one chloro ligand. Initially, *mer,trans*-[$ReCl_2(NCS)(Me_2PhP)_3$] is formed. The compound crystallizes in the monoclinic space group $P2_1/n$ with a unit cell of dimensions $a = 14.992(2)$, $b = 10.846(1)$, $c = 19.117(6)$ Å, $\beta = 112.89(2)°$, $Z = 4$. The chloro ligands are coordinated in *trans* position to each other. An Re–N bond length of 2.071(4) Å was found for the nitrogen bound NCS^- ligand. *Mer,trans*-[$ReCl_2(NCS)(Me_2PhP)_3$] isomerizes to *mer,cis*-[$ReCl_2(NCS)(Me_2PhP)_3$] at longer reaction periods. The *cis* complex crystallizes in the monoclinic space group $P2_1/n$, $Z = 4$. A unit cell of dimensions $a = 14.824(7)$, $b = 13.158(2)$, $c = 16.212(7)$ Å, $\beta = 112.92(2)°$ was determined for this compound. The rhenium atom is six-coordinate with *cis*-positioned chloro ligands. The Re–N bond distance is shortened by 0.038 Å with respect to *mer,trans*-[$ReCl_2(NCS)(Me_2PhP)_3$]. The coordination geometry of the two isomers of *mer*-[$ReCl_2(NCS)(Me_2PhP)_3$] can be derived from FAB-MS studies. Fragmentation occurs by the loss of complete ligands. It takes place in a strong dependence on the structural *trans* influences of the coordinated ligands. The relative intensities of the main fragments clearly indicate the geometry of the coordination sphere.

Keywords: Rhenium complexes; Isothiocyanate complexes; Crystal structures; Mass spectrometry

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1. Introduction

Recently, we reported about reactions of different rhenium complexes containing chloro ligands with potassium thiocyanate and trimethylsilyl isothiocyanate [1–6]. The halide ligands were fully replaced by isothiocyanate in all hitherto attempted reactions. This occurs independent of the oxidation state of the rhenium centre and its coordination environment. Besides the replacement of Cl^- by NCS^-, a number of secondary reactions could be observed, e.g. the reduction of Re(V) starting materials giving Re(IV) complexes [2,5] or the formation of thionitrosyls by the interaction of Me_3SiNCS with terminal nitrido ligands [3].

In the present paper, we describe the reactions of *mer*-[$ReCl_3(Me_2PhP)_3$] with KSCN and Me_3SiNCS, respectively, which yield Re(III) complexes with mixed chloride/isothiocyanate/phosphine coordination spheres.

2. Experimental

2.1. Synthesis

2.1.1. *Mer-[$ReCl_3(Me_2PhP)_3$]*

This was prepared from [$ReOCl_3(Ph_3P)_2$] and excess Me_2PhP [7]. Me_3SiNCS was purchased commercially (Aldrich).

2.1.2. *Trans-[$ReCl_2(NCS)(Me_2PhP)_3$]*

(a) 213 mg (0.3 mmol) *mer*-[$ReCl_3(Me_2PhP)_3$] were dissolved in 30 ml CH_2Cl_2 and an excess (10 mmol) of Me_3SiNCS was added. The mixture was refluxed for 2 h. After reducing the volume of the solvent in vacuum, 15 ml of methanol were added. Within 2 days orange–red crystals of *trans*-[$ReCl_2(NCS)(Me_2PhP)_3$] deposited which were filtered off and washed with methanol. Yield 204 mg (93% based on Re).

(b) 142 mg (0.2 mmol) *mer*-[$ReCl_3(Me_2PhP)_3$] were dissolved in 20 ml CH_2Cl_2 and a five-fold excess of KSCN in 20 ml methanol was added. The mixture was refluxed for 2 h and the precipitated KCl was removed by filtration. Upon

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[1] For Part V see Ref. [1].

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Table 1
Crystal data collection and structure refinement parameters

	mer,trans-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$]	*mer,cis*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$]
Crystal dimensions (mm)	0.2×0.15×0.1	0.2×0.15×0.1
Formula	$C_{25}H_{33}NP_3SCl_2Re$	$C_{25}H_{33}NP_3SCl_2Re$
Molecular weight	729.64	729.64
Space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/n$
Lattice dimensions		
a (Å)	14.992(2)	14.824(7)
b (Å)	10.846(1)	13.158(2)
c (Å)	19.117(6)	16.212(7)
β (°)	112.89(2)	112.92(2)
V (Å^3), Z	2864, 4	2913, 4
D_{calc} (g cm^{-3})	1.692	1.664
Radiation used, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073
Scan type	$\omega/2\theta$	ω
Absorption coefficient (cm^{-1})	47.40	46.60
Absorption correction	DIFABS	DIFABS
T_{min}	0.814	0.865
T_{max}	1.241	1.128
Range of h, k, l	$-1\rightarrow20, 0\rightarrow15, -26\rightarrow26$	$-20\rightarrow20, -1\rightarrow17, 0\rightarrow22$
Weighting scheme	$1/\sigma_F^2$	$1/\sigma_F^2$
Total unique data	8585	8020
Observed data ($I > 3\sigma(I)$)	6451	4330
No. parameters	299	299
R	0.034	0.041
R_w	0.040	0.048
Measuring temperature (°C)	−50	−65
Programs used	SHELXS-86 [8], SDP [9]	SHELXS-86 [8], SDP [9]

standing overnight, orange–red crystals of *trans*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$] were formed which were filtered off and washed with water and methanol. Yield 204 mg (93% based on Re).

Anal. Found: C, 41.9; H, 5.1; N, 1.9. Calc. for $C_{25}H_{33}NSCl_2P_3Re$: C, 41.2; H, 4.5; N, 1.9%. IR: ν(NCS) 2072 cm^{-1}. FAB$^+$-MS: *m/z* 729 (M^+), 671 [ReCl$_2$(Me$_2$PhP)$_3$]$^+$, 591 [Re(NCS)Cl$_2$(Me$_2$PhP)$_2$]$^+$, 533 [ReCl$_2$(Me$_2$PhP)$_2$]$^+$.

2.1.3. *Cis-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$]*

73 mg (0.1 mmol) *trans*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$] were dissolved in 50 ml CH$_2$Cl$_2$ and an excess of KSCN in methanol was added. The mixture was refluxed for 3 days and reduced in volume. Upon standing overnight, dark red crystals of *cis*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$] deposited which were collected by filtration and washed with methanol. From the mother liquor considerable amounts of the *trans* compound could be recovered. Yield of *cis*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$]: 22 mg (30% based on Re).

Anal. Found: C, 40.7; H, 4.7; N, 1.8. Calc. for $C_{25}H_{33}NSCl_2P_3Re$: C, 41.2; H, 4.5; N, 1.9%. IR: ν(NCS) 2017 cm^{-1}. FAB$^+$-MS: *m/z* 729 (M^+), 671 [ReCl$_2$(Me$_2$PhP)$_3$]$^+$, 591 [Re(NCS)Cl$_2$(Me$_2$PhP)$_2$]$^+$, 533 [ReCl$_2$(Me$_2$PhP)$_2$]$^+$.

2.2. *Physical measurements*

Routine IR spectra were recorded as KBr discs on a Bruker IFS 25. Mass spectra were recorded on a MAT TSQ-70 spectrometer (Finnigan). For the FAB$^+$ measurements xenon was used as primary beam gas. The ion gun was operated at 8 kV and 100 μA (probe temperature 30 °C); nitrobenzylalcohol was used as matrix.

2.3. *X-ray diffraction*

X-ray data were collected on an Enraf-Nonius CAD 4 diffractometer. The unit cell dimensions were determined from the angular settings of 25 high angle reflections. The structures were solved by the heavy-atom Patterson method (SHELXS-86 [8]). Refinement was performed with SDP [9]. All non-hydrogen atoms were located from successive Fourier maps and refined with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions and included in the structure-factor calculations. The final difference Fourier maps showed maximum peaks of 0.923 e Å^{-3} for *trans*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$] and 0.975 e Å^{-3} for *cis*-[ReCl$_2$(NCS)(Me$_2$PhP)$_3$]. Crystal data and more details of the refinements are summarized in Table 1. See also Section 4. Positional parameters are given in Table 2 and Table 3.

3. Results and discussion

Mer-[ReCl$_3$(Me$_2$Ph)$_3$] is a common starting material for the preparation of low-valent rhenium complexes. The synthesis of numerous products with different ligand systems via

Table 2

Fractional positional parameters [a] for *mer,trans*-[$ReCl_2(NCS)(Me_2PhP)_3$]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*
Re	0.31814(1)	0.18682(2)	0.05076(1)	1.861(3)
Cl1	0.18435(9)	0.3194(2)	0.02186(8)	3.18(3)
Cl2	0.44783(9)	0.0507(1)	0.07932(7)	2.74(2)
S1	0.5113(1)	0.5257(2)	0.1976(1)	4.21(4)
P1	0.35916(9)	0.2886(1)	−0.04814(7)	2.18(2)
P2	0.21699(9)	0.0286(1)	−0.03344(7)	2.28(2)
P3	0.2911(1)	0.1366(2)	0.16675(7)	2.66(3)
N1	0.4086(3)	0.3219(5)	0.1182(2)	2.54(9)
C1	0.4512(4)	0.4063(5)	0.1517(3)	2.6(1)
C11	0.4849(4)	0.2617(6)	−0.0335(3)	3.1(1)
C21	0.3533(5)	0.4558(6)	−0.0421(3)	3.5(1)
C31	0.2932(4)	0.2639(6)	−0.1492(3)	2.8(1)
C32	0.1999(4)	0.3127(7)	−0.1831(3)	3.7(1)
C33	0.1460(6)	0.2940(9)	−0.2598(4)	5.4(2)
C34	0.1840(6)	0.2265(8)	−0.3018(4)	5.8(2)
C35	0.2766(5)	0.1795(8)	−0.2692(3)	5.2(2)
C36	0.3320(4)	0.1983(7)	−0.1932(3)	3.7(1)
C41	0.0952(4)	0.0796(7)	−0.0933(3)	3.6(1)
C51	0.2617(5)	−0.0320(6)	−0.1026(3)	3.8(1)
C61	0.1950(4)	−0.1174(5)	0.0056(3)	2.4(1)
C62	0.1048(4)	−0.1488(6)	0.0054(3)	3.0(1)
C63	0.0904(4)	−0.2633(7)	0.0323(4)	3.7(1)
C64	0.1651(5)	−0.3460(6)	0.0602(4)	3.7(1)
C65	0.2553(5)	−0.3162(6)	0.0607(4)	3.7(1)
C66	0.2695(4)	−0.2035(6)	0.0340(3)	3.1(1)
C71	0.1755(4)	0.0690(9)	0.1569(3)	4.5(2)
C81	0.2922(5)	0.2749(7)	0.2202(3)	4.2(1)
C91	0.3802(4)	0.0374(6)	0.2352(3)	2.8(1)
C92	0.3852(5)	−0.0842(7)	0.2170(4)	3.8(1)
C93	0.4521(6)	−0.1653(7)	0.2675(4)	4.8(2)
C94	0.5145(5)	−0.1214(9)	0.3369(4)	5.0(2)
C95	0.5108(6)	−0.0019(9)	0.3555(4)	5.2(2)
C96	0.4449(5)	0.0790(7)	0.3052(4)	4.0(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)a^2\beta_{(1,1)}+b^2\beta_{(2,2)}+c^2\beta_{(3,3)}+ac(\cos\beta)\beta_{(1,3)}$ ($Å^2$).

ligand exchange reactions has been reported [7]. In the course of our systematic studies on NCS^- complexes of rhenium we considered the reaction of this compound with potassium thiocyanate and trimethylsilylisothiocyanate, respectively.

The reactions with both agents result in the ligand exchange of only one chloro ligand by NCS^-. This behaviour is in contrast to the reaction patterns which could be observed earlier for $[ReOCl_4]^-$ [6], [$ReNCl_2(Me_2PhP)_3$] [3], [$ReOCl_3(Ph_3P)_2$] [2] and [$ReNCl_2(Ph_3P)_2$] [4]. All these rhenium complexes react under complete exchange of the halide ligands. In *mer*-[$ReCl_3(Me_2PhP)_3$], however, the exchange of the Cl^- ligand in *trans* position to the phosphine seems to be extremely preferred (presumably by the structural *trans* influence of Me_2PhP). Thus, in the initial step of the reaction only this ligand is replaced by NCS^-. Longer refluxing periods do not result in products with higher isothiocyanate contents, but in the isomerization of *trans,mer*-[$ReCl_2(NCS)(Me_2PhP)_3$] into the *cis* complex. Evidence for species with higher NCS^- contents could only be found in the mass spectrum of *cis*-[$ReCl_2(NCS)(Me_2PhP)_3$], where peaks of very low intensity (2–5% B) could be assigned to the ions $[Re(NCS)_2Cl(Me_2PhP)_2)]^+$ ($m/z=614$) and $[Re(NCS)_2Cl(Me_2PhP)_3)]^+$ ($m/z=752$). Since this result cannot be confirmed by the IR spectrum of the same sample, it cannot be ruled out that the formation of '[$ReCl(NCS)_2$ $(Me_2PhP)_3$]' proceeds only in the FAB matrix during the measurement of the mass spectrum. Similar results are often found during mass spectrometric studies on metal complexes [10].

The title compounds are readily soluble in organic solvents like CH_2Cl_2 or $CHCl_3$ and only sparingly soluble in alcohols. They are indefinitely stable in air as solids as well as in solution. Their IR spectra show intense bands for the ν(NCS) vibrations at 2072 (*trans* isomer) and 2017 (*cis* isomer) cm^{-1}, respectively. Thus, IR spectroscopy can easily be used to check the purity of the compounds.

Crystals of *trans*-[$ReCl_2(NCS)(Me_2PhP)_3$] suitable for an X-ray structure determination could be obtained from CH_2Cl_2/methanol solutions. The compound crystallizes in

Table 3

Fractional positional parameters [a] for *mer,cis*-[$ReCl_2(NCS)(Me_2PhP)_3$]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*
Re	0.25724(2)	0.18522(3)	0.10836(2)	1.999(5)
Cl1	0.3817(2)	0.0928(2)	0.2318(2)	3.37(5)
Cl2	0.1520(2)	0.0437(2)	0.0621(2)	3.25(5)
S1	0.4988(2)	0.4434(3)	0.2165(2)	5.24(8)
P1	0.1843(2)	0.2230(2)	0.2172(2)	2.72(5)
P2	0.1516(2)	0.2969(2)	−0.0059(2)	2.73(5)
P3	0.3309(2)	0.1124(2)	0.0099(2)	2.61(5)
N1	0.3495(4)	0.3058(6)	0.1523(4)	2.6(1)
C1	0.4093(7)	0.3607(8)	0.1777(6)	3.3(2)
C11	0.1969(8)	0.119(1)	0.2939(7)	4.7(3)
C21	0.2474(8)	0.324(1)	0.2933(6)	4.6(2)
C31	0.0534(6)	0.2552(8)	0.1782(6)	2.9(2)
C32	−0.0137(7)	0.184(1)	0.1299(8)	4.3(2)
C33	−0.1135(8)	0.205(1)	0.0974(9)	5.7(3)
C34	−0.1435(8)	0.298(1)	0.1169(9)	5.9(3)
C35	−0.0758(8)	0.369(1)	0.1661(7)	4.5(3)
C36	0.0227(6)	0.3464(8)	0.1973(6)	3.4(2)
C41	0.0349(6)	0.241(1)	−0.0764(7)	4.4(3)
C51	0.1198(9)	0.4151(9)	0.0352(7)	5.0(3)
C61	0.2020(6)	0.3484(8)	−0.0822(6)	2.9(2)
C62	0.1605(7)	0.3340(9)	−0.1741(7)	3.7(2)
C63	0.2031(8)	0.375(1)	−0.2296(7)	4.7(3)
C64	0.2864(7)	0.433(1)	−0.1934(7)	4.1(2)
C65	0.3274(7)	0.4527(8)	−0.1039(7)	3.6(2)
C66	0.2862(7)	0.4113(8)	−0.0475(6)	3.3(2)
C71	0.2452(8)	0.0760(9)	−0.1011(7)	4.3(2)
C81	0.3940(7)	−0.0077(8)	0.0519(7)	3.9(2)
C91	0.4234(5)	0.1877(8)	−0.0104(5)	2.4(2)
C92	0.4215(7)	0.2105(9)	−0.0942(6)	3.6(2)
C93	0.4952(8)	0.268(1)	−0.1036(7)	4.3(2)
C94	0.5709(7)	0.305(1)	−0.0287(7)	4.3(2)
C95	0.5745(7)	0.282(1)	0.0558(7)	4.1(2)
C96	0.5014(7)	0.2218(9)	0.0648(6)	3.5(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)a^2\beta_{(1,1)}+b^2\beta_{(2,2)}+c^2\beta_{(3,3)}+ac(\cos\beta)\beta_{(1,3)}$ ($Å^2$).

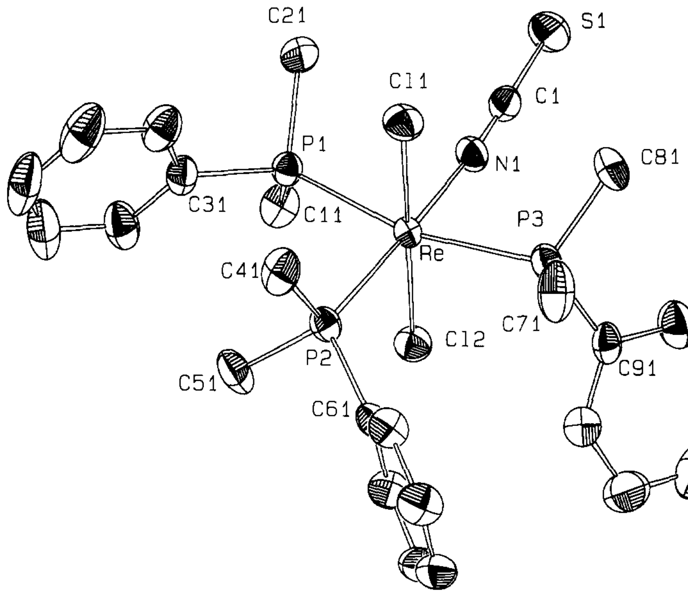

Fig. 1. ORTEP plot [11] of *trans*-$[ReCl_2(NCS)(Me_2PhP)_3]$ along with the atomic numbering scheme (thermal ellipsoids represent 50% of probability).

the monoclinic space group $P2_1/n$ with $Z=4$. The structure consists of neutral, monomeric Re(III) complexes with nitrogen-bonded NCS^- ligands. Fig. 1 shows the molecule together with the atomic numbering scheme. Typical bond lengths and angles are summarized in Table 4. The rhenium atom is octahedrally coordinated with the phosphine ligands in meridional positions. Distortions from the idealized octahedral geometry are evident. The angles P1–Re–P2 and P2–Re–P3 of 94.92(5)° and 99.25(5)°, respectively, are much larger than the N1–Re–P1 (82.1(1)°) and N1–Re–P3 (83.9(1)°) angles. With this, the bonding situation in *trans*-$[ReCl_2(NCS)(Me_2PhP)_3]$ comes close to those in $[ReNCl_2(Me_2PhP)_3]$ [12] and $[ReN(NCS)_2(Me_2PhP)_3]$ [3]. The linear NCS^- ligand (NCS angle 179.0(5)°) is coordinated *trans* to Me_2PhP. Due to the structural *trans* influence of the phosphine the Re–N bond length of 2.071(4) Å is somewhat larger than the equatorial Re–N bond distances in the anion $[ReO(NCS)_5]^{2-}$ (mean value 2.00(1) Å [6]). The bond lengths inside the isothiocyanate ligand together with the Re–N1–C1 angle of 172.7(4)° suggests the preference of the mesomeric form $\mathrm{Re-N{\equiv}C-\underline{\overline{S}}|}$. This is in accordance with the bonding situation in the other structurally characterized isothiocyanato complexes of rhenium [1–6].

Table 4
Selected bond lengths and angles in *trans*- and *cis*-$[ReCl_2(NCS)(Me_2PhP)_3]$ with e.s.d.s

	trans- $[ReCl_2(NCS)(Me_2PhP)_3]$	*cis*- $[ReCl_2(NCS)(Me_2PhP)_3]$
Bond lengths (Å)		
Re–Cl1	2.353(1)	2.451(2)
Re–Cl2	2.331(1)	2.354(2)
Re–P1	2.466(2)	2.451(3)
Re–P2	2.436(1)	2.403(2)
Re–P3	2.465(2)	2.450(3)
Re–N1	2.071(4)	2.032(7)
S1–C1	1.626(6)	1.64(2)
N1–C1	1.157(7)	1.09(1)
Bond angles (°)		
Cl1–Re–Cl2	178.35(5)	93.64(8)
Cl1–Re–P1	91.44(5)	85.13(9)
Cl1–Re–P2	91.18(5)	171.51(8)
Cl1–Re–P3	85.58(5)	87.38(8)
Cl1–Re–N1	90.3(1)	84.8(2)
Cl2–Re–P1	91.69(6)	88.08(9)
Cl2–Re–P2	87.52(4)	94.85(8)
Cl2–Re–P3	93.63(5)	83.81(8)
Cl2–Re–N1	91.0(1)	178.2(3)
P1–Re–P2	94.21(5)	95.39(9)
P1–Re–P3	165.05(5)	168.58(9)
P1–Re–N1	82.1(1)	90.8(2)
P2–Re–P3	99.26(5)	93.30(8)
P2–Re–N1	176.6(2)	86.7(2)
P3–Re–N1	83.9(1)	97.1(2)
Re–N1–C1	172.7(4)	169.8(9)
S1–C1–N1	179.0(5)	180.0(10)

Dark red, X-ray quality crystals of *cis*-$[ReCl_2(NCS)(Me_2PhP)_3]$ are obtained from dichloromethane/methanol solutions. The compound crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$. Typical bond lengths and angles are summarized in Table 4 in comparison to those of the *trans* complex. Fig. 2 contains a plot of the molecular structure together with the atomic numbering scheme. The rhenium atom possesses a distorted octahedral coordination sphere with meridionally coordinated phosphine ligands. The Cl1 atom deviates from the plane which is determined by the three phosphorus atoms and the rhenium atom by 0.575(3) Å. For sterical reasons the angles P1–Re–P2 (95.39(9)°) and P2–Re–P3 ((93.30(8)°) are larger than the angles Cl1–Re–P3 (87.8(8)°) and Cl1–Re–P1 (85.13(9)°). The linear isothiocyanate ligand is situated in *trans* position to Cl2. The Re–N bond length in *cis*-

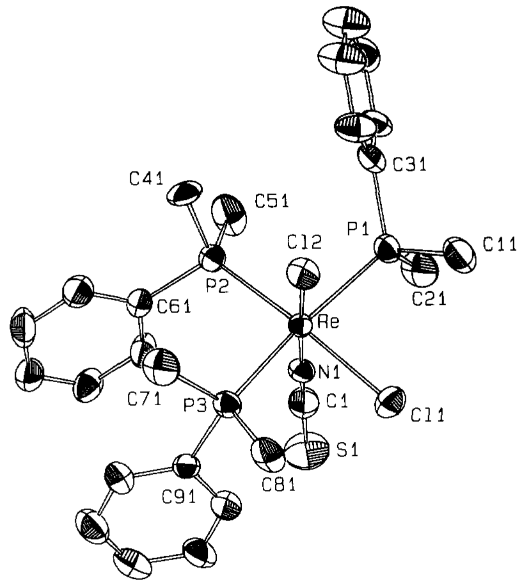

Fig. 2. ORTEP plot [11] of *cis*-$[ReCl_2(NCS)(Me_2PhP)_3]$ along with the atomic numbering scheme (thermal ellipsoids represent 50% of probability).

$[ReCl_2(NCS)(Me_2PhP)_3]$ is larger by 0.03 Å with respect to that in the *trans* isomer.

A comparison of the individual bond distances in the title complexes gives evidence for a structural *trans* influence due to the ligands Me_2PhP and NCS^-. This situation is strongly reflected by the FAB^+ mass spectra of the two isomeric complexes. The spectra of both compounds are characterized by peaks of ions which are formed from the molecular ion at $m/z = 729$ by abstraction of complete ligands ($m/z = 694$ $M^+ - Cl$; $m/z = 671$ $M^+ - NCS$; $m/z = 591$ $M^+ - Me_2PhP$; $m/z = 556$ $M^+ - Cl$, Me_2PhP; $m/z = 533$ $M^+ - NCS$, Me_2PhP). Their relative intensities, however, are strongly dependent on the individual isomer and correspond with the labilization of the corresponding coordination positions by their *trans* ligands. Fig. 3 represents typical FAB^+ mass spectra of *cis*- and *trans*-$[ReCl_2(NCS)(Me_2PhP)_3]$ (the relative intensities are averaged from each 30 individual spectra).

The base peaks of both spectra are those at $m/z = 591$ which relate to $[ReCl_2(NCS)(Me_2PhP)_2]^+$ and the relative intensities of the molecular ions (M^+) are about 90% B. In the course of the mass spectrometric fragmentation ions are formed with high probability by the loss of ligands which are 'prelabilized' by their *trans* ligands. Thus, the fragment at $m/z = 694$ has 50% probability in the spectrum of *cis*-$[ReCl_2(NCS)(Me_2PhP)_3]$ (Cl^- in *trans* position to Me_2PhP) but is of low intensity in that of the *trans* isomer (Cl^- in *trans* position to Cl^-). The same holds true for the fragment at $m/z = 671$ ($M^+ - NCS^-$) which is preferably formed during the fragmentation of *trans*-$[ReCl_2(NCS)(Me_2PhP)_3]$ due to the labilization of isothiocyanate by Me_2PhP. The high formation probability of the ion $[ReCl_2(NCS)(Me_2PhP)_2]^+$ (base peak of both spectra) agrees with the interpretation given above and reflects the situation of two *trans* to each other coordinated phosphine ligands.

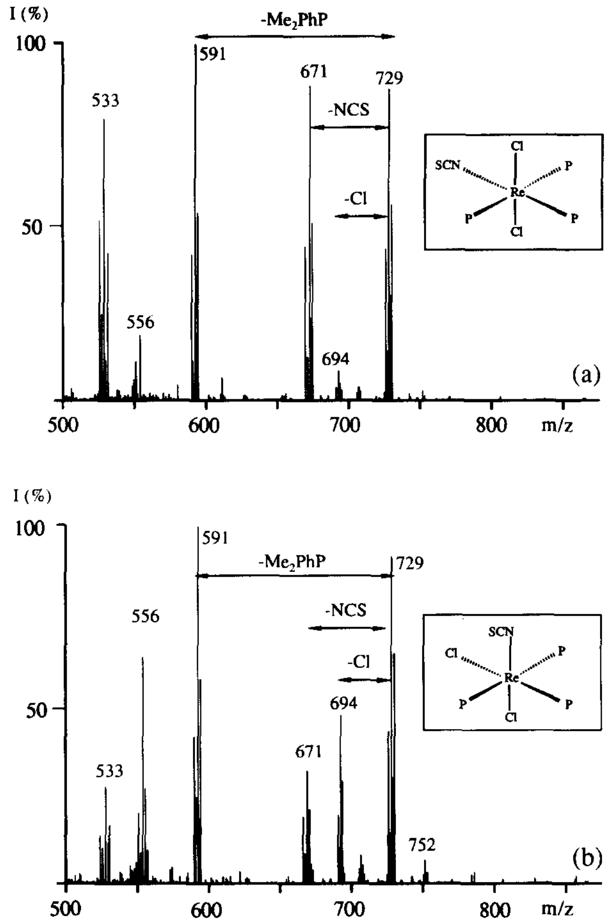

Fig. 3. FAB^+ mass spectra of (a) *trans*- and (b) *cis*-$[ReCl_2(NCS)(Me_2PhP)_3]$ (merged from each 30 individual spectra; matrix: nitrobenzylalcohol).

Summarizing it can be stated, that mass spectrometric fragmentation patterns can be a valuable tool for the estimation of the stereochemistry of complex compounds when ligands with different structural *trans* influences are present in the coordination sphere.

4. Supplementary material

Further details of the crystal structure determinations (F_oF_c lists, full lists of bond lengths and angles, anisotropic thermal parameters and hydrogen atom positions) have been deposited with the Fachinformationszentrum, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, as Supplementary Publication Nos. CSD 57954 (*trans*-$[ReCl_2(NCS)(Me_2PhP)_3]$) and CSD 58158 (*cis*-$[ReCl_2(NCS)(Me_2PhP)_3]$).

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