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Optically active transition metal compounds 114[1]
The complexes (η^3-$C_{27}H_{33}N_3$)$CuCl_2$ and (η^3-$C_{27}H_{33}N_3$)$M(CO)_3$ (M = Cr, Mo, W) containing the ligand $C_{27}H_{33}N_3$ = *N*,*N*′,*N*″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine

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Abstract

The reaction of *N*,*N*′,*N*″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine (**2**) with anhydrous $CuCl_2$, $(CH_3CN)_3Cr(CO)_3$, (η^6-C_7H_8)$Mo(CO)_3$ and (η^6-C_7H_8)$W(CO)_3$ leads to new chiral complexes, of which (η^3-$C_{27}H_{33}N_3$)$CuCl_2$ (**3**) and η^3-($C_{27}H_{33}N_3$)$CrH(CO)_3$ (**4**) are characterized by X-ray structure analyses. In complex **3** the three nitrogen atoms coordinate in two different ways. Complex **4** crystallizes in a layer-structure and contains chiral cavities. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hexahydrotriazine ligands; Copper; Chromium; Molybdenum; Tungsten; X-ray structure analysis; Chirality

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1. Introduction

N,*N*′,*N*″-Substituted hexahydro-1,3,5-triazines are cyclic ligands containing three nitrogen atoms as coordination sites. In contrast to the 1,4,7-triazacyclonanes, the coordination behavior of these ligands has not been studied in detail. Older publications describe chromium–tricarbonyl complexes characterized only by IR-spectra [2]. Recent publications report on η^3-complexes of hexahydro-1,3,5-triazines with different transition metals [3–8].

N,*N*′,*N*″-Functionalized hexahydro-1,3,5-triazines are easily accessible by reaction of primary amines and formaldehyde. Using optically active amines it is possible to introduce chirality. Here we describe the syntheses and X-ray structure analyses of chiral hexahydro-1,3,5-triazines and their η^3-complexes [9].

2. Synthesis of ligands 1, 2 and X-ray structure of ligand 1

N,*N*′,*N*″-Tris[(S)-1′-methoxycarbonyl-2′-methylpropyl]hexahydro-1,3,5-triazine (**1**) was accessible by reaction of the methyl ester of (S)-valine with formaldehyde [10]. Crystallization from pentane at −30°C gave single crystals, which allowed a X-ray structure analysis (Table 1, Fig. 1). Ligand **2** was synthesized by reaction of (S)-1-phenylethylamine and formaldehyde [11] (Scheme 1).

The structure of **1** shows an axial position of the substituent at N(2). This monoaxial arrangement is the most stable conformation of substituted hexahydrotriazines [12]. Table 2 summarizes bond distances and angles of ligand **1**. With 108.8° [C(1)–N(1)–C(3)], 107.7° [C(1)–N(2)–C(2)] and 110.0° [C(2)–N(3)–C(3)] the angles C–N–C in the hexahydrotriazine ring are smaller than the angles C_{ring}–N–C_{subst} with values of 117.5° [C(1)–N(1)–C(4)], 111.7° [C(2)–N(2)–C(5)] and

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Table 1
Summary of crystal data, data collection and structure refinement[a] for **1**, **3** and **4**

Crystal parameters			
Compound	**1**	**3**	**4**
Formula	$C_{21}H_{39}N_3O_6$	$C_{27}H_{33}N_3Cl_2Cu$	$C_{30}H_{33}N_3O_3Cr \cdot 0.5\ CH_2Cl_2$
Mol. wt.	429.55	534.03	578.07
Color and shape	Colorless, prismatic	Green, needle	Orange, irregular
Size (mm³)	0.35 × 0.60 × 1.2	0.10 × 0.40 × 1.00	0.15 × 0.60 × 0.75
Crystal system	Rhombic	Rhombic	Monoclinic
Space group	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$C2$ (5)
a (Å)	9.094(2)	7.214(3)	18.097(5)
b (Å)	16.365(4)	14.986(9)	10.472(3)
c (Å)	16.766(6)	24.81(1)	15.700(5)
α (°)	90	90	90
β (°)	90	90	99.94(2)
γ (°)	90	90	90
V (Å³)	2495(1)	2682(2)	2931(1)
Z	4	4	4
D_{calc} (g cm^{-3})	—	1.32	1.31
F(000)	936	1116	1212
μ (mm^{-1})	—	1.03	0.52
Data collection			
hkl ranges	0–12, 0–21, −21–21	0–9; 0–17; 0–29	0–25, 0–15, −22–22
2θ range (°)	3.0–52.5	3.0–47.5	3.0–58.0
Total no. of unique reflections	5041	2354	4111
No. of observed reflections ($I > 2.5\sigma(I)$)	2564	1444	3330
No. of reflections and 2θ range (°) for empirical absorption correction	5, 9.0–33.0	5; 11.0–35.0	10; 4.6–46.2
Min; max transmission factors	0.82, 1.00	0.97; 1.00	0.96; 1.00
Data refinement			
No. of LS parameters	272	283	342
Largest shift/e.s.d. in final cycle	0.002	0.008	0.018
$\Delta\rho_{min}$; $\Delta\rho_{max}$ (e Å^{-3})	−0.27, 0.32	−0.48; 0.66	−0.60; 0.70
R^b; R_w^c	0.065, 0.052	0.072; 0.056	0.064; 0.059

[a] Syntex-Nicolet R3 diffractometer, Mo-K_α radiation ($\lambda = 0.71073$ Å), 293 K; graphite crystal monochromator, structure solution by direct methods with SHELXTL PLUS Release 4.2/800 programs.

[b] $R = \Sigma \| F_o - F_c \| / |F_c|$.

[c] $R = \Sigma \| F_o| - |F_c \| w^{1/2} / |F_c| w^{1/2}$, $w = 1/\sigma^2(F_o)$.

118.3° [C(3)–N(3)–C(6)]. Interestingly, the angle at the carbon atom between the two nitrogen atoms with equatorial substituents [N(1)–C(3)–N(3), 107°] is smaller than the angles N(1)–C(1)–N(2) and N(2)–C(2)–N(3) (111.9 and 111.5°, respectively).

3. (η^3-$C_{27}H_{33}N_3$)$CuCl_2$ (3)

On addition of a solution of **2** in ethanol to a solution of anhydrous copper(II) chloride in the same solvent complex dichloro{*N*,*N*′,*N*″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine}copper(II) (**3**) precipitated as a green powder (Scheme 2). The compound is air-stable and can be dissolved in methylene chloride or chloroform. Crystal growth from methylene chloride gave single crystals suitable for a X-ray structure analysis (Fig. 2, Table 1).

The coordination geometry of **3** is a square pyramid. The two chlorine atoms with distances to the metal of 2.24 and 2.17 Å, respectively, and the nitrogen atoms N(1) and N(2) with distances to the metal atom of 2.11 and 2.19 Å (Table 3), respectively, form the basal square plane. With 2.38 Å the distance between copper and the third nitrogen atom N(3) is much larger, N(3) representing the top of the pyramid. This unusual coordination geometry of the hexahydro-1,3,5-triazine ligand has also been observed by Köhn in achiral compounds of this type [4]. The inequivalence of the nitrogen atoms is also obvious from the bond angles in the hexahydrotriazine ring. With 101.5° the angle N(1)–C(19)–N(2) in the basal square plane is much

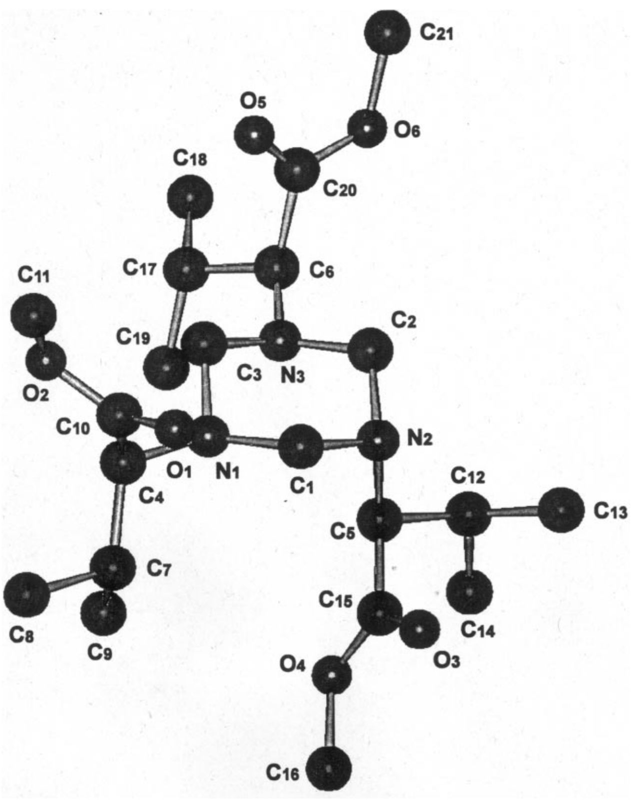


Fig. 1. SCHAKAL plot of the structure of ligand **1** (CSD 408532).

Table 2
Selected bond lengths (Å) and bond angles (°) of ligand **1** and estimated standard deviations in parentheses

N(1)–C(1)	1.476(6)	C(1)–N(1)–C(3)	108.8(3)
N(1)–C(3)	1.458(6)	C(1)–N(1)–C(4)	117.5(3)
N(1)–C(4)	1.459(5)	C(3)–N(1)–C(4)	115.0(3)
N(2)–C(1)	1.447(6)	C(1)–N(2)–C(2)	107.7(4)
N(2)–C(2)	1.459(6)	C(1)–N(2)–C(5)	112.5(3)
N(2)–C(5)	1.478(6)	C(2)–N(2)–C(5)	111.7(4)
N(3)–C(2)	1.448(6)	C(2)–N(3)–C(3)	110.0(3)
N(3)–C(3)	1.453(6)	C(2)–N(3)–C(6)	114.7(3)
N(3)–C(6)	1.457(6)	C(3)–N(3)–C(6)	118.3(4)
O(2)–C(10)	1.294(7)	N(1)–C(1)–N(2)	111.9(3)
O(2)–C(11)	1.437(7)	N(2)–C(2)–N(3)	111.5(3)
		N(1)–C(3)–N(3)	107.2(3)

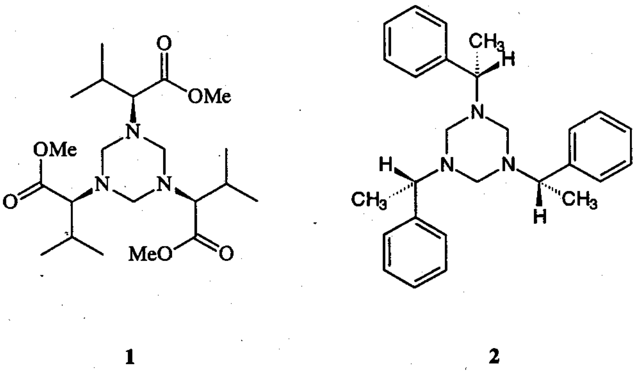
smaller than the other two angles N(2)–C(20)–N(3) = 107.2° and N(3)–C(21)–N(1) = 104.6°, respectively (Table 2). These angles are also smaller than the corresponding angles N_{ring}–C_{ring}–N_{ring} in ligand **1** (107–111°, Table 2). The angles C_{ring}–N_{ring}–C_{ring} in complex **3** are comparable to those in ligand **1**. Because of the hexahydrotriazine ring the bond angles N–Cu–N is small (61.5–64.7°) compared to the angle Cl–Cu–Cl (99.6°).

Phenyl–phenyl interactions were found in the structure of complex **3**. The phenyl rings C(1)–C(6) and C(7)–C(12) show an intramolecular 'parallel displaced' [13] arrangement. An intermolecular interaction leads to a 'T-shaped' structure [13] of phenyl ring C(7)–C(12) and phenyl ring C(13)–C(18) of a neighboring molecule [9].

4. η^3-($C_{27}H_{33}N_3$)M(CO)$_3$, M = Cr, Mo, W (4–6)

The complex tricarbonyl{*N*,*N*′,*N*″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine}chromium (**4**) precipitated as an orange, microcrystalline powder on mixing solutions of trisacetonitrile(tricarbonyl)-chromium and **2** in toluene at room temperature (Scheme 2). Solutions of **4** in methylene chloride were air-sensitive decomposing by formation of a green precipitate. Under nitrogen the solutions were stable for several days and could be chromatographed on silica gel.

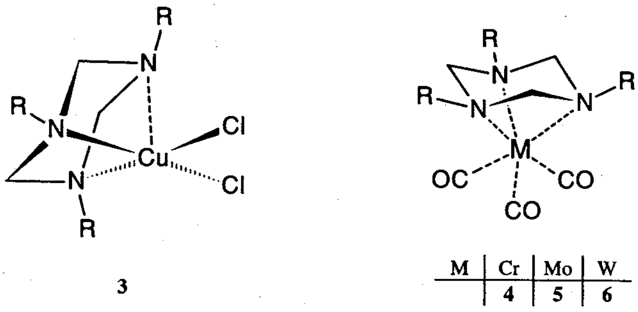
The complexes tricarbonyl{*N*,*N*′,*N*″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine}molybdenum (**5**) and tricarbonyl{*N*,*N*′,*N*″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine}tungsten (**6**) were synthesized by reaction of the corresponding η^6-cycloheptatriene-tricarbonyls with **2** in tetrahydrofuran (Scheme 2). The reaction of trisacetonitrile(tricarbonyl)tungsten and **2** in toluene according to the synthesis of **4** did not give complex **6** [9]. Solutions of compounds **5** and **6** decomposed rapidly on contact with air.



1 **2**

Scheme 1

Scheme 1.



3

Scheme 2: R=(S)-1-phenylethyl

Scheme 2.

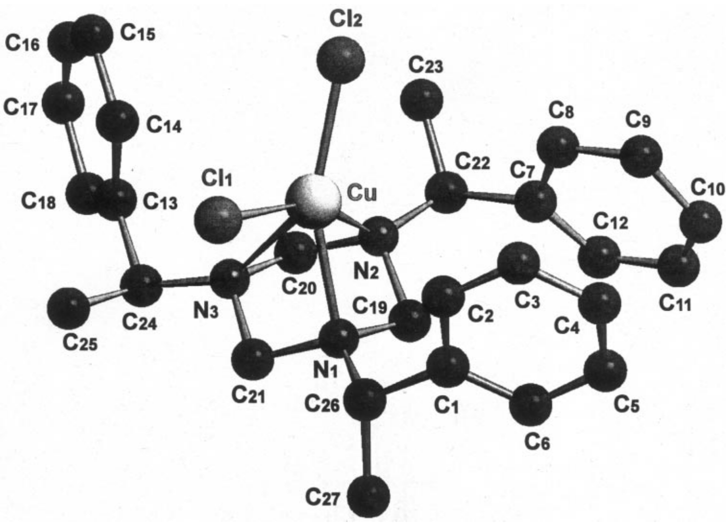


Fig. 2. SCHAKAL plot of the structure of complex **3** (CSD-407301).

The ^{1}H-NMR spectra of complexes **4**–**6** show the typical resonances of ligand **2**. Only the signals of the hydrogen atoms of the CH_2 groups in the hexahydrotriazine ring differ from the ligand spectrum. As the ring inversion is blocked, these hydrogen atoms appear as two doublets. The chemical shifts of the first doublet (Section 5.1) are independent of the central metal ranging from 4.5 to 4.6 ppm in all three complexes. The shifts of the second doublet (Section 5.2) increase in the order **4** (3.13 ppm), **5** (3.35 ppm) and **6** (4.13 ppm).

From a solution of complex **4** (methylene chloride/pentane 1:1) single crystals were grown. These orange, hexagonal flakes reached a diameter of 5 mm and allowed a X-ray structure analysis (Fig. 3, Table 1).

Complex **4** has the three-legged piano stool geometry typical for tricarbonyl complexes. The distances between metal and nitrogen are nearly equal and amount to 2.2 Å (Table 4). With 63° the angles N–Cr–N are comparable to the angle N–Cu–N in complex **2**. The distances Cr–C(CO) are 1.79–1.80 Å. A similar coordination geometry was found for achiral chromium complexes of hexahydro-1,3,5-triazines [3]. An analysis of the angles in the hexahydrotriazine ring shows, that the angles $\mathrm{C_{ring}{-}N_{ring}{-}C_{ring}}$ and $\mathrm{N_{ring}{-}C_{ring}{-}N_{ring}}$ are about 108 and 104°, respectively (Table 4). The angles

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$\mathrm{N_{ring}{-}C_{ring}{-}N_{ring}}$ are smaller than the corresponding angles in ligand **1** (107–111°, Table 2), whereas the angles $\mathrm{C_{ring}{-}N_{ring}{-}C_{ring}}$ are comparable to those in ligand **1** (108–110°).

Table 3
Selected bond lengths (Å) and bond angles (°) of complex **3** and estimated standard deviations in parentheses

Cu(1)–Cl(1)	2.240(5)	Cl(1)–Cu(1)–Cl(2)	99.6(2)
Cu(1)–Cl(2)	2.172(5)	Cl(1)–Cu(1)–N(1)	95.5(3)
Cu(1)–N(1)	2.107(11)	Cl(2)–Cu(1)–N(1)	158.7(3)
Cu(1)–N(2)	2.189(12)	Cl(1)–Cu(1)–N(2)	155.6(3)
Cu(1)–N(3)	2.376(10)	Cl(2)–Cu(1)–N(2)	103.4(3)
		Cl(1)–Cu(1)–N(3)	97.3(3)
C(21)–N(1)–C(26)	116.0(10)	Cl(2)–Cu(1)–N(3)	130.2(3)
C(19)–N(2)–C(20)	109.2(10)	N(1)–Cu(1)–N(2)	64.7(4)
C(20)–N(3)–C(21)	112.4(10)	N(2)–Cu(1)–N(3)	61.5(4)
N(1)–C(19)–N(2)	101.5(10)	N(1)–Cu(1)–N(3)	61.7(4)
N(2)–C(20)–N(3)	107.2(10)	C(19)–N(1)–C(21)	110.1(10)
N(3)–C(21)–N(1)	104.6(10)	C(19)–N(1)–C(26)	115.0(11)

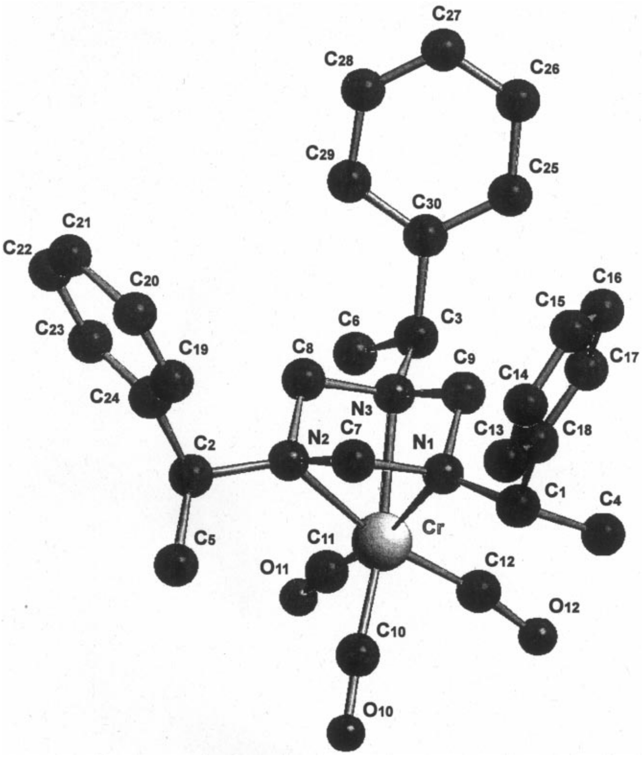

Fig. 3. SCHAKAL plot of the structure of complex **4** (CSD-407900).

Table 4
Selected bond lengths (Å) and bond angles (°) of complex **4** and estimated standard deviations in parentheses

Cr(1)–N(1)	2.185(5)	N(2)–Cr(1)–C(10)	104.4(3)
Cr(1)–N(2)	2.224(5)	N(3)–Cr(1)–C(10)	166.9(3)
Cr(1)–N(3)	2.217(5)	C(10)–Cr(1)–C(11)	83.8(3)
Cr(1)–C(10)	1.803(6)	C(10)–Cr(1)–C(12)	82.6(3)
Cr(1)–C(11)	1.797(7)	C(11)–Cr(1)–C(12)	83.0(3)
Cr(1)–C(12)	1.799(7)	C(7)–N(1)–C(9)	108.4(5)
C(10)–O(10)	1.176(8)	C(7)–N(2)–C(8)	109.5(5)
C(11)–O(11)	1.176(8)	C(8)–N(3)–C(9)	108.3(5)
C(12)–O(12)	1.169(9)	N(1)–C(7)–N(2)	104.2(5)
		N(2)–C(8)–N(3)	104.1(5)
N(1)–Cr(1)–N(2)	63.0(2)	N(1)–C(9)–N(3)	104.1(5)
N(1)–Cr(1)–N(3)	63.6(2)	Cr(1)–C(10)–O(10)	173.6(6)
N(2)–Cr(1)–N(3)	62.9(2)	Cr(1)–C(11)–O(11)	172.4(6)
N(1)–Cr(1)–C(10)	108.7(2)	Cr(1)–C(12)–O(12)	170.9(5)

The packing diagram of complex **4** (Fig. 4) shows a layer-structure. All the phenyl rings of the hexahydrotriazine ligands are oriented to the outsides of the layers (Fig. 4). The distance between two layers is 15.5 Å. As obvious from Fig. 4, this arrangement leads to cavities between two layers, which are covered by six phenyl rings of two chiral hexahydrotriazine ligands. The X-ray analysis showed, that these cavities are partly occupied by disordered methylene chloride molecules. As these cavities are chiral, enantioselective inclusions might be possible on crystallization of small substrates with **4**.

5. Experimental

All complexes were prepared under an atmosphere of dry nitrogen. Solvents were dried and distilled according to standard procedures. IR spectra: Biorad FTS 155 FT-IR and Beckman IR 4240 spectrometer, ^{1}H-NMR spectra: Bruker AC 250 spectrometer (i-TMS), FD mass spectra: Finnigan MAT 112 S instrument, optical rotations: Perkin–Elmer 241 polarimeter, elemental analyses: microanalytical laboratory of the University of Regensburg.

Literature procedures have been used for the syntheses of trisacetonitrile(tricarbonyl)chromium [14], tricarbonyl(η^6-cycloheptatriene)molybdenum [14], tricarbonyl(η^6-cycloheptatriene)tungsten [15] and **2** [11]. More information about the X-ray structure analyses can be obtained at the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen by referring to the CSD-numbers given in Figs. 1–3.

5.1. *N,N′,N″-Tris[(S)-1′-methoxycarbonyl-2′-methylpropyl]hexahydro-1,3,5-triazine (**1**)*

Methyl (S)-valinate hydrochloride (1.0 g, 6 mmol) and NaOH (0.3 g, 6 mmol) were dissolved in water. Benzene (50 ml) and formaldehyde (0.5 ml) were added. After 12 h of stirring at room temperature the organic layer was separated and washed with water. The solvent was evaporated to give an oily residue, which crystallized upon standing for 2 weeks. The pure product was obtained by crystallization from pentane at −30°C. Yield: 440 mg (52%). m.p. 73°C. ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 3.65 (s, 9 H, OCH_3), 3.51 (s, 6 H, N–CH_2–N), 3.13 (d, 3 H, 8.7 Hz, N–CH(C$_3$H$_7$)(COOCH$_3$)), 1.91–2.05 (m, 3 H, CH(CH$_3$)$_2$), 0.97 and 0.84 (2 d, 18 H, 6.7 and 6.6 Hz, CH(CH_3)$_2$). Anal. Found: C, 58.50; H 9.24; N, 9.81. $C_{21}H_{39}CrN_3O_6$ (429.55). Calc.: C, 58.72; H, 9.15; N, 9.78%. MS (FD, CH$_2$Cl$_2$): $m/z = 429.3$ (M). $[\alpha]_D^{20} = -77.3$ ($c = 1$, CH$_2$Cl$_2$).

5.2. *Dichloro{N,N′,N″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine}copper(II) (**3**)*

N,N′,N″-Tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine (**2**) (1.0 g, 2.5 mmol) was dissolved in 10 ml of ethanol and added to a solution of anhydrous copper(II) chloride (0.33 g, 2.45 mmol) in 10 ml of ethanol. The reaction mixture was stirred for 24 h at room temperature. The precipitated green product was recrystallized from CH$_2$Cl$_2$/pentane 1:1 at −30°C. Yield: 0.9 g (70%), m.p. 127°C. Anal. Found: C, 60.50; H 6.20; N, 7.91. $C_{27}H_{33}Cl_2CuN_3$ (534.01). Calc.: C, 60.72; H, 6.23; N, 7.87%.

5.3. *Tricarbonyl{N,N′,N″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-tri azine}chromium (**4**)*

Trisacetonitrile(tricarbonyl)chromium (1.8 g, 7.0 mmol) was suspended in 50 ml of toluene. *N,N′,N″*-Tris[(S)-1′-phenylethyl]hexahydro-1,3,5-triazine (**2**) (2.8 g, 7.0 mmol) was added. After 48 h at room temperature the orange precipitate was filtered off and chromatographed on silica with CH$_2$Cl$_2$. The complex was crystallized from CH$_2$Cl$_2$/pentane 1:1 at −30°C. ^{1}H-NMR spectra and elemental analysis showed, that the crystals contained 0.23 mol CH$_2$Cl$_2$. Yield: 1.9 g (52%), m.p. 100°C (dec.). IR (KBr, cm^{-1}): 3087, 3065, 3032 (=C–H), 2985, 2943, 2839 (–C–H), 1917, 1771, 1747 (C=O). ^{1}H-NMR (CDCl$_3$, 250 MHz): δ 7.16–734 (m, 15 H, phenyl), 4.54 (d, 8.1 Hz, 3 H, N–CH_2–N(a)), 3.70 (q, 7.0 Hz, 3 H, CH), 3.13 (d, 8.1 Hz, 3 H, N–CH_2–N(b)), 1.69 (d, 7.0 Hz, 9 H, CH_3). Anal. Found: C, 65.32; H 6.15; N, 7.35. $C_{30}H_{33}CrN_3O_3$ (535.60) · 0.23 CH$_2$Cl$_2$. Calc.: C, 65.41; H, 6.07; N, 7.57%. MS (FD, CH$_2$Cl$_2$): $m/z = 535$ (M). $[\alpha]_D^{20} = -135.0$ ($c = 1$, CH$_2$Cl$_2$).

5.4. *Tricarbonyl{N,N′,N″-tris[(S)-1′-phenylethyl]hexahydro-1,3,5-tri azine}molybdenum (**5**)*

Tricarbonyl(η^6-cycloheptatriene)molybdenum (0.24 mg, 0.88 mmol) and *N,N′,N″*-tris[(S)-1′-phenyl-ethyl] hexahydro-1,3,5-triazine (**2**) (0.36 mg, 0.90 mmol) were

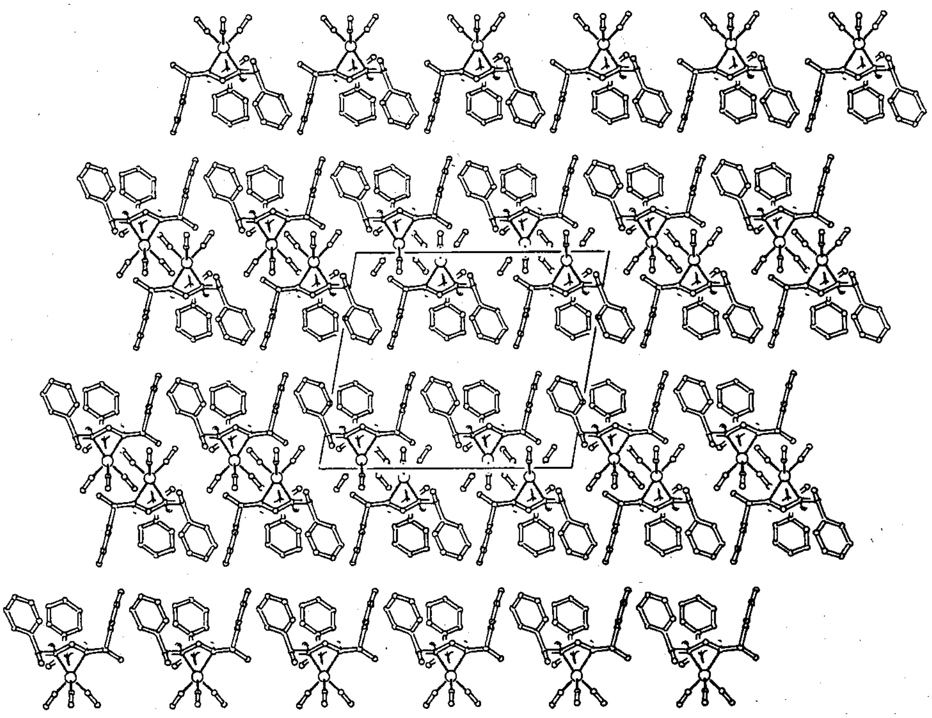

Fig. 4. Packing diagram of complex **4** created by PLUTON. The hydrogen atoms and the disordered methyl chloride have been omitted.

stirred at room temperature in 10 ml of THF for 24 h. The precipitated yellow product was filtered off and washed with pentane. Yield: 0.43 mg (82%). IR (KBr, cm^{-1}): 3060, 3030 (=C–H), 2985, 2920, 2842, 2780 (–C–H), 1920, 1771, 1749 (C=O). ^1H-NMR ($CDCl_3$, 250 MHz): δ 7.20–7.50 (m, 15 H, phenyl), 4.45 (d, 8.2 Hz, 3 H, N–CH_2–N(a)), 3.52 (q, 6.8 Hz, 3 H, CH), 3.35 (d, 8.2 Hz, 3 H, N–CH_2–N(b)), 1.55 (d, 6.8 Hz, 9 H, CH_3). Anal. Found: C, 61.90; H 5.97; N, 7.26. $C_{30}H_{33}MoN_3O_3$ (579.55). Calc.: C, 62.17; H, 5.74; N, 7.25%. MS (FD, CH_2Cl_2): $m/z = 575$ (M, ^{92}Mo).

*5.5. Tricarbonyl{N,N′,N″-tris[(S)-1′-phenylethyl] hexahydro-1,3,5-tri azine}tungsten (**6**)*

Complex **6** was synthesized analogously to complex **5**. The crude product was filtered off and a brown by-product was removed by washing with THF. Yield: 20%. IR (KBr, cm^{-1}): 3060, 3020 (=C–H), 2980, 2930, 2840 (–C–H), 1910, 1765, 1740 (C=O). ^1H-NMR ($CDCl_3$, 250 MHz): δ 7.24–7.44 (m, 15 H, phenyl), 4.62 (d, 8.2 Hz, 3 H, N–CH_2–N(a)), 4.13 (d, 8.2 Hz, 3 H, N–CH_2–N(b)), 3.62 (q, 6.8 Hz, 3 H, CH), 1.60 (d, 6.8 Hz, 9 H, CH_3). $C_{30}H_{33}N_3O_3W$ (667.45). MS (FD, CH_2Cl_2): $m/z = 665.5$ (M, ^{180}W).

References

[1] H. Brunner, P. Faustmann, B. Nuber, J. Organomet. Chem. in press.

[2] A. Lüttringhaus, W. Kullick, Tetrahedron Lett. (1959) 13.

[3] N.L. Armanasco, M.V. Baker, M.R. North, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1997) 1363.

[4] R.D. Köhn, G. Seifert, G. Kociok-Köhn, Chem. Ber. 129 (1996) 1327.

[5] R.D. Köhn, G. Kociok-Köhn, H. Haufe, J. Organomet. Chem. 501 (1995) 303.

[6] R.D. Köhn, G. Kociok-Köhn, Angew. Chem. 106 (1994) 1958; Angew. Chem. Int. Ed. Engl. 33 (1994) 1871.

[7] H. Schuhmann, Z. Naturforsch. 50b (1995) 1038.

[8] M. Haufe, R.D. Köhn, R. Weimann, G. Seifert, D. Zeigan, J. Organomet. Chem. 502 (1996) 121.

[9] A. Winter, Dissertation, Universität Regensburg, 1997.

[10] O. Nakaguchi, T. Oku, H. Takeno, M. Hashimoto, T. Kamiya, Chem. Pharm. Bull. 35 (1987) 3985.

[11] R. Amoroso, G. Cardillo, C. Tomasini, P. Tortoreto, J. Org. Chem. 57 (1992) 1082.

[12] R.A.Y. Jones, A.R. Katritzky, M. Snarey, J. Chem. Soc. B (1970) 135.

[13] P. Hobza, H.L. Selzle, E.W. Schlag, J. Am. Chem. Soc. 116 (1994) 3500.

[14] E.W. Abel, M.A. Bennett, R. Burton, G. Wilkinson, J. Chem. Soc. (1958) 4559.

[15] G.J. Kubas, Inorg. Synth. 27 (1990) 6.