Multiple Bonds between Main-Group Elements and Transition Metals, CLXV[1]

Rhenium(V) Oxo Complexes with Bidentate Schiff Bases: Structures and Catalytic Applications

Fritz E. Kühn, Monika U. Rauch, Gerhard M. Lobmaier, Georg R. J. Artus, and Wolfgang A. Herrmann*

Anorganisch-Chemisches Institut der Technischen Universität München,
Lichtenbergstraße 4, D-85747 Garching, Germany

Received January 3, 1997

Keywords: N ligands / O ligands / Rhenium / Structure elucidation / Ligand effects

Reaction of $[NBu_4][ReOCl_4]$ (**1**) with bidentate salicylidene amine ligands (salen = HL) (**2a**–**c**) leads to the formation of monomeric octahedral rhenium(V) compounds of formula $[ReOCl(L)_2]$ (**3a**–**c**). Spectroscopic data indicate asymmetric arrangement of the ligands in the complexes. This is confirmed by the X-ray crystal structures of **3b** and **3c**. Complexes **3a**, **b** have been tested as catalysts for the epoxidation of cyclooctene. No evidence for decomposition of the catalysts is observed during the reaction (as in the case for tri- and tetradentate salen complexes). No undesired byproducts are formed in the catalytic reactions.

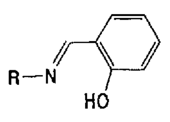
Introduction

One of the first reported catalysts for enantioselective reactions in homogeneous phase contained a chiral Schiff base as ligand[2a,b]. Chiral bis(salicylidene)amine complexes of manganese are known to be efficient catalysts for enantioselective olefin oxidation[2c–i]. Technetium complexes with Schiff base ligands have received particular interest from the use of ^{99m}Tc compounds in nuclear medicine[3]. Because the nuclide ^{186}Re can be used in radiotherapy, rhenium compounds with Schiff-base ligands, which are easily derived from salicylaldehyde and mono- and diamines, have attracted interest[3]. Recently we have shown that some high-valency organorhenium oxides catalyze olefin epoxidation very efficiently[4]. It was also proven that rhenium(V) chloro oxo complexes with tri- and tetradentate Schiff bases are quite effective oxidation catalysts[5]. This led us to examine the catalytic activities and structures of Re(V) complexes with bidentate Schiff base ligands. Very few structures of salen complexes containing the ReOCl fragment have been described in the literature, and the same is true for Tc compounds of this type[6].

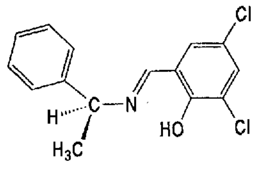
Results and Discussion

The rhenium(V) salen complexes **3a**–**c** were synthesized from $[NBu_4][ReOCl_4]$ (**1**) and the bidentate ligands **2a**–**c** in ethanol solution according to eq. 1. Four equivalents of the ligand had to be used, of which two equivalents served as base to neutralize the two equiv. of HCl released in the substitution reaction. As described for $ReOCl(Mesal)_2$[7], monomeric products of the formula $ReOCl(L)_2$ were formed in good yields. The reaction leading to derivative **3c** had to be performed at room temperature, since enhanced reaction temperatures led to partial or even total decomposition of the freshly formed product, as observed by in situ NMR spectroscopy. Ligand fragments were the only detectable decomposition products in such a case. Another noteworthy difference between **3c** and compounds **3a**, **b** is the significantly higher solubility of **3c** in alcohols. This makes the isolation of **3c** in good yields more difficult (see Experimental Section).

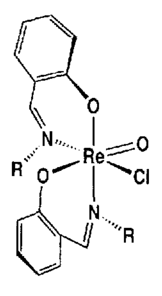
$$\underset{\mathbf{1}}{[NBu_4][ReOCl_4]} + \underset{\mathbf{2a\text{-}c}}{4\,HL} \xrightarrow{EtOH} \underset{\mathbf{3a\text{-}c}}{ReOCl(L)_2} + [NBu_4]Cl + 2\,(HL\bullet HCl) \quad (1)$$



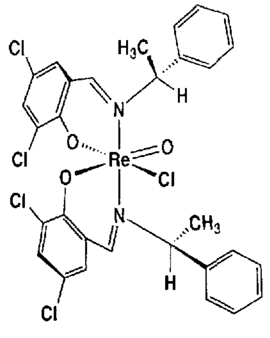
2a,b



2c



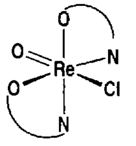
3a (R = C_6H_5)
3b (R = C_6H_{11})

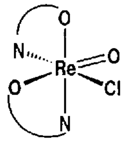


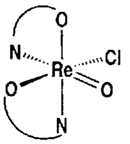
3c

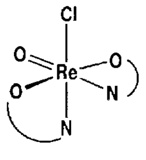
The six possible configurations for metal complexes with two N,O-bidentate Schiff bases are shown by **I**–**VI**. In addition to the four configurations which are also possible for

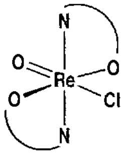
O,N,N,O-tetradentate Schiff bases (**I**–**IV**), two more structure types (**V**,**VI**) with the imino groups in *trans* positions are conceivable. Structure type **I** is known for six-coordinate technetium(V) complexes bearing a chlorine atom in the *trans* position to the Tc=O moiety[8]. Structure type **I** has also been postulated for six-coordinate rhenium(V) complexes with ligands containing less than five carbon atoms in the bridge between the imino groups[9]. An evaluation of the structures of Re(V) complexes available in the Cambridge Structural Data Base reveals that an oxo ligand in this system preferably coordinates *trans* to "hard" ligands (as defined by Pearson[10]) such as aryl- or alkoxy ligands, followed by nitrogen-donor ligands and less preferably coordinates *trans* to soft ligands such as halides or phosphides. It is obvious that the system under investigation in general tries to avoid a *trans* arrangement of an oxo and a chloro ligand. Therefore, structure types **II** and **VI** should be most favorable, and types **I** and **V** most unfavorable. As we have recently shown, tetradentate Re(V) Schiff base complexes with three bridging carbon atoms between the imino groups prefer structure type **II** and not type **I**[5a]. With these results in mind one would expect structure types **II** and **VI** for Re(V) complexes containing two bidentate salen ligands.

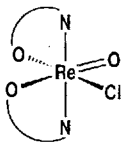

I


II


III


IV


V


VI

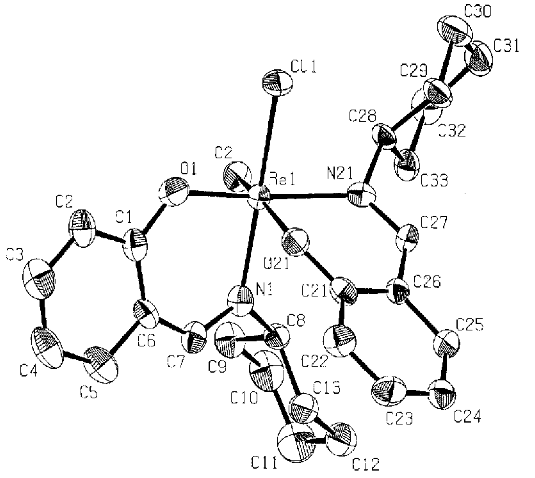


Figure 1. PLATON representation of **3b**. Ellipsoids are at the 50% probability level; hydrogen atoms are omitted for clarity.

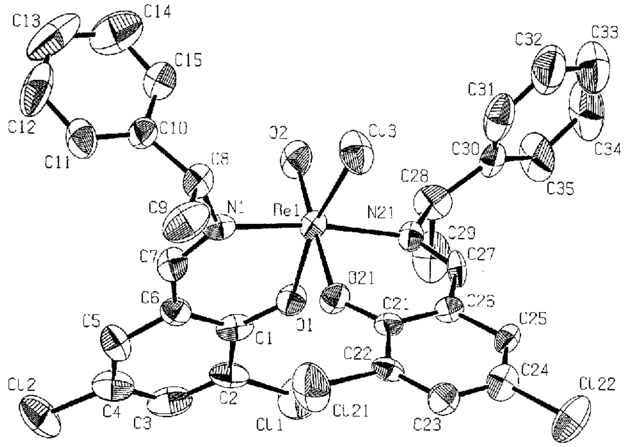


Figure 2. PLATON representation of **3c**. Thermal ellipsoids are at the 50% probability level; hydrogen atoms are omitted for clarity.

The X-ray structures of **3b** and **3c** were determined. Whereas **3b** displays a structure of type **II**, **3c** corresponds to type **VI** (Figures 1 and 2). The latter structure type has not been observed for rhenium(V) salen complexes before.

In each case the phenolate oxygen atom is in a *trans* position to the Re=O moiety. As in the case of the tetradentate ligands, the relatively hard phenoxy donor ligand prefers the *trans* position to the Re=O moiety for electronic reasons. Noteworthy are the structural differences between **3b** and tetradentate complexes of the type ReOCl(L) (L = sal_2en), all type **II** structures. The angles at the Re core do not differ by more than 8° but the Re–N bond distances in **3b** are 0.4 Å longer than in the complexes with tetradentate ligands. This observation cannot be due to inductive effects. It cannot be explained by steric reasons either (because of the larger substituents attached to nitrogen), since the similarly crowded **3c** contains shorter Re–N distances. A more plausible reason for the longer Re–N bond distance in **3b** is that the two salen ligands lack a bridge. In fact, a comparison of tetradentate $ReOCl(sal_2en)$ and bidentate $ReOCl(salen)_2$ complexes shows a clear dependence of the Re–N bond distance on the bridge chain length (Table 1). If **3b**, which lacks a bridge between the salen ligands, is regarded as a standard for comparison, chain lengths of two or three carbon atoms lead to shortening of the Re–N bond distance. Chain lengths of five or more carbon atoms cause elongation of the N–Re bond distances. This is explained by geometric reasons in the first case, and steric hindrance in the latter case. In both cases the Re=O and Re–Cl bond distances are not significantly affected, they are equal, within the error range, for both complex types.

The different ligand arrangements in **3b** and **3c** are very likely due to steric reasons. The steric bulk of the ligands in **3c** is higher than that of the other examined derivatives. Temperature-dependent NMR studies showed that thermodynamic reasons for the formation of the favored observed geometries can be excluded. Both the ^1H- and ^{13}C-NMR signals of **3a** and **3b** do not change in the temperature range between 0°C and 120°C. Compound **3c** is somewhat temperature sensitive and decomposes with ligand elimination and fragmentation at temperatures above 60°C. A ligand rearrangement leading to another structure type is not observed. In **3c** the Re-bonded chloro ligand is *cis* to the Re=O moiety and the N-atoms are *trans* to each other. This ligand arrangement causes helical chirality in the molecule. Selected bond distances and bond angles of compounds **3b** and **3c** are given in Table 2; selected crystallographic data are summarized in Table 3.

Table 1. Chain length and Re–N distance [Å] in complexes of type $ReOCl(L)_n$, $n = 1, 2$

Chain length	Re-N	Structure type	Ref.
8	2.132	**II**	[11a]
5	2.123	**II**	[11b]
0	2.118	**II**	this work
3	2.080	**II**	[5a]
2	2.067	**Va**[a]	[9b]

[a] This compound is dimeric.

Table 2. Selected bond distances [Å] and bond angles [°] of compounds **3b**, **c**

	3b	**3c**
Re1–Cl1/3	2.380(2)	2.386(4)
Re1–O1	1.973(6)	1.985(9)
Re1–O2	1.671(5)	1.683(9)
Re1–O21	1.978(6)	1.953(9)
Re1–N1	2.123(7)	2.09(1)
Re1–N21	2.126(7)	2.087(9)
Cl1/3–Re1–O1	84.7(2)	167.9(3)
Cl1/3–Re1–O2	100.1(2)	92.4(3)
O1–Re1–O2	104.2(3)	98.1(4)
Cl1/3–Re1–O21	92.4(2)	84.5(3)
O1–Re1–O21	85.3(2)	85.1(4)
O2–Re1–O21	164.8(2)	176.9(4)
Cl1/3–Re1–N1	172.8(2)	94.9(3)
O1–Re1–N1	91.0(2)	90.7(4)
O2–Re1–N1	86.6(3)	93.1(4)
O21–Re1–N1	81.4(2)	86.8(3)
Cl1/3–Re1–N21	85.9(2)	85.5(3)
O1–Re1–N21	164.4(2)	87.3(4)
O2–Re1–N21	89.6(3)	95.9(4)
O21–Re1–N21	82.7(2)	84.3(4)
N1–Re1–N21	97.1(2)	170.9(4)

The asymmetric arrangement of the salen ligands in **3a–c** leads to different chemical environments of all protons. Because the ^1H-NMR shifts are somewhat different for the two salen ligands attached to the Re center, a doubled set of signals is observed. The NMR spectra were assigned by means of $^1H-^1H$-COSY experiments. The protons attached to the imino carbon atoms are shifted to higher field in all cases, when compared to those of the free ligands.

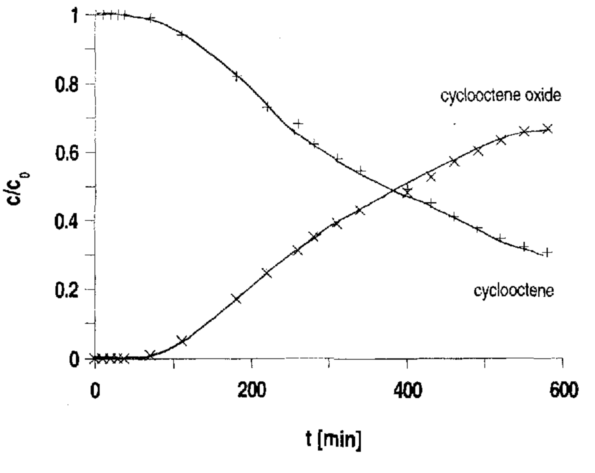
The ligand arrangment is also supported by the IR data of complexes **3a–c**. In all cases two signals are observed for the ν(CH=N) stretching modes, both in the range 1600–1625 cm^{-1}. The ν(Re=O) stretching frequencies are observed in the range 955–960 cm^{-1}.

As with the tetradentate sal_2en ligands[5a], we tested compounds **3a**, **b** as catalysts for olefin oxidation. In a standard reaction, *cis*-cyclooctene was oxidized at 50°C with *tert*-butyl hydroperoxide in $CHCl_3$ in the presence of **3a**, **3b**. Typically, a solution of 9 mmol of *cis*-cyclooctene, and 7.7 mmol dibutyl ether as internal standard and 9 μmol (1 mol%) of the catalyst were used. The oxidant *tert*-butyl hydroperoxide (1 equiv. relative to the olefin) was added at once. The results for the complexes with the bidentate ligands differ significantly from those with the tetra- and tridentate ligands. As in the case of the tetradentate-ligand complexes, an induction period of 30–40 min was needed before catalytic activity was observed. In contrast to tetradentate-ligand complexes, no color change took place and the reaction mixture kept its green color during the whole reaction time. After the reaction cycle, the catalyst could be isolated nearly quantitatively. It was reusable in further experiments, showing no change in its activity. Formation of byproducts was not observed with **3a**, **b** as catalysts, in remarkable contrast to the results with tetradentate Schiff base complexes[5a]. In the latter case, formation of perrhenate took place. The course of the cyclooctene epoxidation with *tert*-butyl hydroperoxide in $CHCl_3$ at 50°C is given in Figure 3.

Table 3. Crystallographic and refinement data for **3b**, **c**

	3b	**3c**
empirical formula	$C_{26}H_{32}ClN_2O_3Re$	$C_{30}H_{24}Cl_5N_2O_3Re$
formula weight [g/mol]	642.21	824.00
crystal color	green	brownish violett
crystal size [mm^3]	0.13 x 0.13 x 0.15	0.13 x 0.15 x 0.15
crystal system	hexagonal	orthorhombic
space group (No.)	$P6_1$ (169)	$P2_12_12_1$ (19)
unit cell dimensions [Å]	$a = 13.409(3)$ $c = 24.525(8)$ $V = 3818.6$ Å^3	$a = 12.155(4)$ $b = 14.949(3)$ $c = 16.899(9)$ $V = 3070.6$ Å^3
ρ_{calc} [g/cm^3]	1.68	1.78
measurement device	IPDS (STOE)	CAD4 (Enraf-Nonius)
F_{000} [e]	1908	1608
Z	6	4
measurement parameters	distance detector crystal: 75 mm (3.1° < 2Θ< 50.2°), 360 images between φ = 0° and φ = 360 °, phi-mode, 2.5 min/image	2.0° < 2Θ < 50.0°ω-scan, max. 60 s, scan width: (1.00 + 0.25 tanΘ)° ± 25%
T [°C]	-50.0(3)	22(2)
measured reflections	48045	6179
unique reflections	4072, $I > 1.0\sigma(I)$	3535, $I > 2.0\sigma(I)$
refined parameters	298	370
absorption correction	not applied	empirical (psi scan data)
R	0.029	0.053
Rw	0.033	0.028
reflections/parameters	13.7	9.6
weighting	$w = 1$	$w = 1/\sigma^2(Fo)$
Flack parameter	0.00	0.005

Figure 3. Catalytic activity of compound **3a** in the oxidation of cyclooctene (see text)



Conclusions

Bidentate Schiff base complexes of the type $ReOCl(L)_2$ form asymmetric structures, with the terminal oxygen ligand *trans* to a phenolate oxygen atom. This result corresponds to what is known for tetradentate Schiff base complexes of Re(V). Two different ligand arrangements have been observed with bidentate salen ligands. The first type is equivalent to the configuration found in complexes with tetradentate ligands. The second type had not been observed before and shows the imino functionalities in a *trans* arrangement with respect to each other. Variable temperature NMR studies indicate that **3a–c** are thermodynamically stable. All the examined Re(V) complexes with two bidentate ligands exhibit catalytic activity in olefin epoxidation and can be reused several times without decomposition.

We are grateful to the *DEGUSSA AG*, the *H. C. Starck GmbH*, the *Deutsche Forschungsgemeinschaft* and the *Stiftung Volkswagenwerk* for generous support of this work. We also thank the referees for perceptive and helpful comments.

Experimental Section

General: All reactions were performed with standard Schlenk techniques in an oxygen-free nitrogen atmosphere. Solvents were dried with standard methods and distilled und N_2. – Infrared spectra: Perkin-Elmer 1600 series FT-IR spectrometer. – ^1H and ^{13}C NMR spectra: at 400 and 100.54 MHz, resp., FT Jeol GX 400. – ^{1}Elemental analyses: the Microanalytical Laboratory of our institute (M. Barth). – Mass spectra: Finnigan MAT 311A and MAT 90 spectrometers. – Tetra-*n*-butyl ammonium tetrachlorooxorhenate(V) was prepared as reported in the literature[12]. Ligands were prepared by mixing the substituted benzaldehydes and amines in a 2:1 stoichiometric ratio and recovering the Schiff base ligands by filtration as yellow solids.

Chlorobis(N-phenyl-salicylideneimine)oxorhenium(V) (**3a**) *and Chlorobis(N-cyclohexyl-salicylideneimine)oxorhenium(V)* (**3b**): 293 mg (0.5 mmol) $[NBu_4][ReOCl_4]$ (**1**) was dissolved in 20 ml ethanol and 2.00 mmol of the ligand **2a** or **b** was added. The reaction mixture was refluxed for three hours and a green precipitate formed during this time. The reaction mixture was then brought to room temperature and the mother liquor filtered off via cannula. The remaining green residue was washed with ethanol and *n*-pentane, then dried under oil pump vacuum.

3a: 250 mg (80%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1610 vst (CH=N), 960 m (Re=O). – ^1H NMR ($CDCl_3$, 20°C) δ = 7.18–7.28, 6.50 (m, 10H, phenyl-*H*), 6.81 (d, 1H, $C^{5'}$-*H*, $^3J_{C5'-H,C4'-H}$ = 8.0 Hz), 6.87 (t, 1H, C^3-*H*, $^3J_{C3-H,C4-H}$ = 8.0 Hz), 7.01 (s, 1H, $C^{7'}$-*H*), 7.09 (t, 1H, $C^{3'}$-*H*, $^3J_{C3'-H,C4'-H}$ = 8.0 Hz), 7.13 (m, 2H, C^5-*H*, $C^{2'}$-*H*), 7.50 (d, 1H, C^2-*H*, $^3J_{C2-H,C3-H}$ = 8.0), 7.65 (t, 1H, C^4-*H*, $^3J_{C4-H,-C5-H}$ = 8.0), 7.74 (s, 1H, C^7-H). – $C_{26}H_{20}ClN_2ReO_3$ (630.11) calcd. C 49.56, H 3.20, N 4.45 Cl 5.63; found C 49.37, H 3.40, N 4.42, Cl 5.84.

3b: Yield: 240 mg (75%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1600, 1622 vst (CH=N), 955 vst (Re=O). – ^1H NMR ($CDCl_3$, 20°C): δ = 0.23–2.74 (m, 10H, cyclohexyl-*H*), 3.57, 4.83 (C^8-*H*, m, 2H) 6.41 (d, 1H, $C^{5'}$-*H*, $^3J_{C5'-H,C4'-H}$ = 8.0 Hz), 6.80 (t, 1H, C^3-*H*, $^3J_{C3-H,C4-H}$ = 7.5 Hz), 6.93 (t, 1H, $C^{3'}$-*H*, $^3J_{C3'-H,C4'-H}$ = 8.0 Hz), 7.06 (t, 1H, $C^{4'}$-*H*), 7.14 (d, 1H, C^5-*H*, $^3J_{C5-H,C4-H}$ = 7.5 Hz), 7.18 (d, 1H, C^2-*H*, $^3J_{C2-H,C3-H}$ = 7.5), 7.40 (d, 1H, $C^{2'}$-*H*, $^3J_{C2'-H,-C3'-H}$ = 8.0), 7.52 (t, 1H, C^4-*H*), 7.47 (s, 1H, $C^{7'}$-*H*), 7.69 (s, 1H, C^7-*H*). – $C_{26}H_{32}ClN_2ReO_3$ (642.20) calcd. C 48.36, H 5.02, N 4.36; found C 48.64, H 5.18, N 4.25.

Chlorobis)[N-(R-(+)-1-phenylethyl)-(3,5-dichlorosalicylidenimine]oxorhenium(V) (**3c**): 293 mg (0.5 mmol) $[NBu_4][ReOCl_4]$ (**1**) was dissolved in 20 ml ethanol and 2.00 mmol of the ligand **2c** was added. The reaction mixture turned green within half an hour and was stirred for an additional week at room temperature. A green precipitate formed during this time. The mother liquor was filtered off via cannula. The residue was washed with 5 ml ethanol, 5 ml diethyl ether and 5 ml *n*-pentane, then dried under oil pump vacuum. The filtered solution was cooled to –20°C; the precipitate that formed after some hours was treated as described above. The green residues were then collected, redissolved in dichloromethane, and layered with an *n*-pentane/diethyl ether solution. After a few days a large amount of green crystals of compound **3c** was formed. Yield: 350 mg (85%). – IR (KBr, cm^{-1}): $\tilde{\nu}$ = 1602 vst, 1615 vst (CH=N), 960 vst (Re=O). – ^1H NMR ($CDCl_3$, 20°C): δ = 2.03 (d, 3H, C^9-*H*, $^3J_{C9-H,C8-H}$ = 7.0 Hz), 2.12 (d, 3H, $C^{9'}$-*H*, $^3J_{C9'-H,C8'-H}$ = 7.0 Hz), 5.70 (dd, 1H, $C^{8'}$-*H*), 6.97 (d, 1H, $C^{5'}$-*H*, $^4J_{C5'-H,C3'-H}$ = 2.5 Hz); 7.07 (dd, 1H, C^8-*H*), 7.06 (d, 1H, $C^{3'}$-H), 7.10 (d, 1H, C^5-*H*, $^4J_{C5-H,C3-H}$ = 2.5 Hz), 7.28 (s, 1H, $C^{7'}$-*H*), 7.35 (m, 1H, C^{13}-*H*), 7.39 (t, 1H, $C^{13'}$-*H*, $^3J_{C13-H,C12-H}$ = 7.5 Hz), 7.41 (m, 2H, C^{12}-*H*), 7.43 (d, 1H, C^3-*H*), 7.46 (m, 2H, $C^{12'}$-*H*), 7.50 (d, 2H, C^{11}-*H*, $^3J_{C11-H,C12-H}$ = 7.0 Hz), 7.72 (d, 2H, $C^{11'}$-*H*, $^3J_{C11'-H,C12'-H}$ = 7.0 Hz), 7.85 (s, 1H, C^7-*H*). – $C_{30}H_{24}Cl_5N_2ReO_3$ (823.98): calcd. C 43.73, H 2.94, N 3.40, Cl 21.51; found C 43.77, H 3.16, N 3.27, Cl 21.79.

X-ray Crystal Structures: All hydrogen atoms in **3b** and **3c** were calculated. All calculations were performed with the program systems listed in ref.[13]. Relevant crystallographic data and structure determination parameters are given in Table 3. For selected interatomic distances and bond angles see Table 2. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-407050 (**3b**) and -407051 (**3c**).

---

[1] Preceding paper of this series: F. E. Kühn, J. Mink, W. A. Herrmann, *Chem. Ber.* **1997**, *130*, 295.

[2] [2a] H. Nozaki, S. Moriuti, H. Takaya, R. Noyori, *Tetrahedron Lett.* **1966**, *43*, 5239. – [2b] H. Nozaki, H. Takaya, S. Moriuti, R. Noyori, *Tetrahedron* **1968**, *24*, 3655. – [2c] W. Zhang, J. L. Loebach, S. R. Wilson, E. N. Jacobsen, *J. Am. Chem. Soc.* **1990**, *112*, 2801. – [2d] E. N. Jacobsen, W. Zhang, A. R. Muci, J. R. Ecker, L. J. Deng, *J. Am. Chem. Soc.* **1991**, *113*, 7063. – [2e] W. Zhang, E. N. Jacobsen, *J. Org. Chem.* **1991**, *56*, 2296. – [2f] E. N. Jacobsen in *Catalytic Assymmetric Synthesis*, I. Ojima, Ed.: Verlag Chemie: New York **1993**. – [2g] S. Chang, R. M. Heid, E. N. Jacobsen, *Tetrahedron Lett.* **1994**, *35*, 669. – [2h] M. Palucki, P. J. Pospisil, W. Zhang, E. N. Jacobson, *J. Am. Chem. Soc.* **1994**, *116*, 9333. – [2i] J. F. Larrow, E. N. Jacobson, *J. Am. Chem. Soc.* **1994**, *116*, 12129.

[3] [3a] E. Deutsch, K. Libson, *Comments Inorg. Chem.* **1984**, *3*, 83. – [3b] M. J. Clarke, L. Podbielsky, *Coord. Chem. Rev.* **1987**, *78*, 253. – [3c] G. L. Griffiths, D. M. Goldenberg, A. Jones, H. Hansen, *J. Bioconjugate Chem.* **1992**, *3*, 91. – [3d] S. Jurisson, D. Berning, W. Jia, D. Ma, *Chem. Rev.* **1993**, *93*, 1137.

[4] [4a] W. A. Herrmann, R. W. Fischer, D. W. Marz, *Angew. Chem.* **1991**, *103*, 1706; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1638. – [4b] W. A. Herrmann, R. W. Fischer, W. Scherer, M. U. Rauch, *Angew. Chem.* **1993**, *105*, 1209; *Angew. Chem. Int. Ed. Engl.* **1993**, *30*, 1157. – [4c] W. A. Herrmann, R. W. Fischer, M. U. Rauch, W. Scherer, *J. Mol. Catal.* **1994**, *86*, 243. – [4d] W. A. Herrmann, J. D. G. Correia, F. E. Kühn, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 168. – [4e] W. A. Herrmann, J. D. G. Correia, M. U. Rauch, G. R. J. Artus, F. E. Kühn, *J. Mol. Catal.* **1997**, in press. – [4f] W. A. Herrmann, F. E. Kühn, M. Mattner, G. R. J. Artus, M. Geisberger, J. D. G. Correia, *J. Organomet. Chem.* **1997**, in press.

[5] [5a] W. A. Herrmann, M. U. Rauch, G. R. J. Artus, *Inorg. Chem.* **1996**, *35*, 1988. – [5b] M. Barz, M. U. Rauch, W. R. Thiel, *J. Chem. Soc., Dalton Trans.*, in press.

[6] [6a] G. Bandoli, U. Mazzi, D. A. Clemente, E. Roncari, *J. Chem. Soc., Dalton Trans.* **1982**, 2455. – [6b] G. Gilli, M. Sacerdoti, V. Bertolasi, R. Rossi, *Acta Crystallogr.* **1982**, *B38*, 100.

[7] A. Marchi, A. Duatti, R. Rossi, L. Magon, U. Mazzi, A. Pasquetto, *Inorg. Chim. Acta* **1984**, *81*, 15.

[8] [8a] G. Bandoli, M. Niccolini, U. Mazzi, F. Refosco, *J. Chem. Soc., Dalton Trans.* **1984**, 2505. – [8b] S. Jurisson, L. F. Lindoy, K. P. Dancey, M. McPartlin, P. A. Tasker, D. K. Uppal, E. Deutsch, *Inorg. Chem.* **1994**, *23*, 227.

[9] [9a] A. R. Middleton, A. F. Masters, G. J. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1979**, 542. – [9b] F. Tissato, F. Refosco, U. Mazzi, G. Bandoli, A. Dolmella, *Inorg. Chim. Acta* **1989**, *164*, 127. – [9c] F. Tisato, F. Refosco, U. Mazzi, G. Bandoli, M. Niccolini, *Inorg. Chim. Acta* **1991**, *189*, 97.

[10] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533.

[11] [11a] H. J. Banbery, F. McQuillan, T. A. Hamor, C. J. Jones, J. A. McCleverty, *J. Chem. Soc., Dalton Trans.* **1989**, 1405. – [11b] H. J. Banbery, F. McQuillan, T. A. Hamor, C. J. Jones, J. A. McCleverty, *Polyhedron*, **1989**, *8*, 559. – [11c] H. J. Banbery, F. McQuillan, T. A. Hamor, C. J. Jones, J. A. McCleverty, *Inorg. Chim. Acta* **1990**, *170*, 23.

[12] R. Alberto, R. Schibli, A. Egli, P. A. Schubinger, W. A. Herrmann, G. R. J. Artus, U. Abram, T. A. Kaden, *J. Organomet. Chem.* **1995**, *492*, 217.

[13] [13a] IPDS Operating system **1994**. – [13b] B. A. Frenz, *SDP*; Enraf-Nonius: Delft, The Netherlands, **1988**. – [13c] G. M. Sheldrick, *SHELXS-86*; Universität Göttingen, Germany, **1986**. – [13d] D. J. Watkin, P. W. Betteridge, J. R. Caruthers, *CRYSTALS User Manual*, Oxford, England, 1986. – [13e] A. L. Spek, PLATON. *Acta Crystallogr.* **1990**, *A46*, C34.

[97002]