Journal of Organometallic Chemistry, 438 (1992) 117–130
Elsevier Sequoia S.A., Lausanne
JOM 22810

Novel concepts in directed biaryl synthesis

XV *. Chiral rhenium complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R,R\text{-lactone }**)]^+BF_4^-$ of lactone-bridged biaryls as ligands: synthesis, structure, and stereochemical properties ***

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(Received April 13, 1992)

Abstract

The preparation is reported of the first series of (racemic) chiral rhenium complexes with "axially prostereogenic" biaryl lactone ligands, which are potential substrates for atropisomer-selective biaryl syntheses. NMR spectroscopy reveals the presence of both helimeric forms of the twisted biaryllactone ligand for the more hindered representatives (R = Me, Et), whereas the less hindered compounds (R = H, OMe) show rapid interconversion of the two helimeric diastereomers. In the crystal, by contrast, one of the complexes (R = OMe) occurs as only one of the two possible diastereomers, as shown by an X-ray diffraction study.

Introduction

Lactone-type bridged biaryls like **1** [2] have proved to be most useful intermediates in the regio- and stereoselective synthesis of stereochemically homogeneous biaryls [3–5]: although already containing a biaryl axis, they have drastically lowered atropisomerization barriers, compared with the final target molecules (*e.g.* **2**). In consequence, they are not separable into stable atropisomers (*e.g.* for R = H, OCH_3, CH_3, *etc.*) but "axially prostereogenic" [6]. We have found that,

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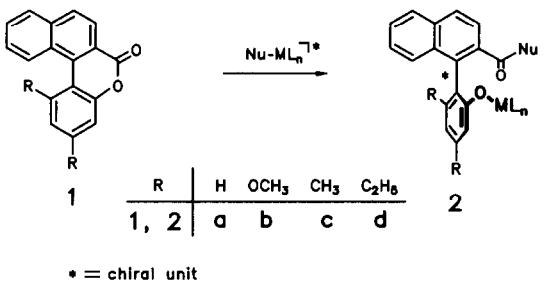
* For Part XIV, see ref. 1.

** *R,R*-lactone = 1,3-Di-R-6*H*-benzo[*b*]naphtho[1,2-d]pyran-6-one.

*** Dedicated to Professor Ekkehard Winterfeldt on the occasion of his 60th birthday.



Scheme 1. The directed ring opening of "axially prostereogenic" [5] biaryl lactones, with simultaneous asymmetric induction at the axis.

using metalated *O*-, *N*- and *H*-nucleophiles [6–10], they can very efficiently be atropisomer-selectively ring-opened (*e.g.* to give **2**). This stereoselective "twisting process" of biaryl axes may be performed by internal or external asymmetric induction, and has already been applied to several natural product syntheses [5–7].

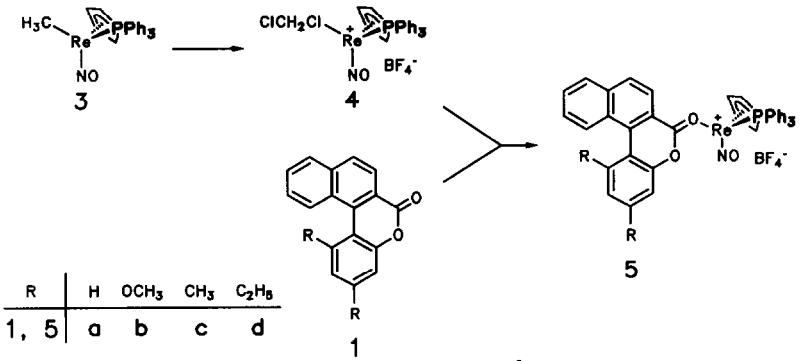
Besides ring opening reactions of achiral lactones with chiral metalated (*i.e.* formally anionic) nucleophiles, Lewis acid catalysed reactions with non-charged chiral nucleophiles, or, better still, with cheap achiral nucleophiles after coordination of the lactones to a chiral Lewis acid, would also be highly attractive. In this paper, we report on the preparation of (still racemic) chiral biaryl lactone rhenium complexes **5a–d**, using the well known [11–13] complex fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$, which has been shown by the elegant work of Gladysz *et al.* to coordinate to a broad variety of organic Lewis bases [14–18] and to control the reduction of ketone and aldehyde complexes in a very stereoselective manner [15,16,19]. Furthermore, structural features of these lactone complexes, as evident from spectroscopic properties and from an X-ray structure analysis of one of the compounds, are described.

Preparation of the lactone complexes

The synthesis of the required rhenium-reagent, the (still racemic) labile dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**4**), was performed, as previously described [13], by reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**3**) with $HBF_4 \cdot OEt_2$ in dichloromethane at $-80°C$. After immediate addition of 1.0–1.6 equiv. of the corresponding biaryl lactone **1** and warming to room temperature within 5 h, the rhenium complexes **5** were isolated in 81–92% yield as bright red powders by precipitation with ether and subsequent washing with ether and pentane. The use of higher quantities of the crystalline lactones **1** requires more extensive washing and can lead to reduced yields. The complexes **5** are generally well soluble in CH_2Cl_2 and $CHCl_3$ and practically insoluble in ether, toluene and pentane.

Spectroscopic properties

The complexes **5a–d** were characterized unambiguously by IR and NMR spectroscopy (^1H, ^1H-^1H-COSY, ^{13}C, ^{13}C-^1H-COSY, $^{31}P\{^1H\}$) (see Table 1), as well as by elemental analysis.



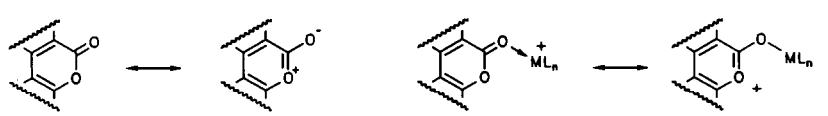
Scheme 2. Generation of the racemic complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R,R\text{-lactone})]^+ BF_4^-$ (**5**) with a helicene-like biaryl lactone ligand. *

The IR data (ν(NO) 1685–1700 cm^{-1}) hint at σ-coordination, as expected [14,17,20] from the electronic properties of the lactone ligand. Furthermore, the absorption wavenumber of the complexes (ν(CO) 1560–1570 cm^{-1}) is distinctly lower than that for the free lactone **1** (ν(CO) 1700–1710 cm^{-1}). This may be attributed to the interaction of the HOMO *d* orbital of the rhenium with the π^* orbital of the C=O group [17] and the resulting enhancement of the electron density in the π^* orbital, which leads to a lower strength of the C=O double bond in II, compared with that in the free ligand I (*cf.* Scheme 3).

It is noteworthy that this shift of *ca.* 140 cm^{-1} is clearly higher than for the comparable 2*H*-pyran-2-one- and 4*H*-pyran-4-one-complexes ($\Delta\nu$(CO) = 31–48 cm^{-1}) [14], and this may be due to the aromatic system of the biaryl lactone. A similar effect is also observed for the ketone complexes of acetone (ν(CO) = 1622 cm^{-1}) and acetophenone (ν(CO) = 1554 cm^{-1}) [17].

A further characteristic feature of the complexes **5** is the distinct lowfield shift of the signal of the C=O carbon atom in the ^{13}C spectrum (170–172 ppm) compared with that from the free lactone **1** (160–162 ppm), a first indication of the desired enhanced reactivity of the carbonyl group towards nucleophiles.

Interestingly, a peak doubling for the ^1H resonance signals of the cyclopentadienyl ligand and the alkyl group at C-1 is observed for **5c** and **5d**, the complexes with the sterically more hindered, alkyl substituted lactone ligands **1c** and **1d**. The same phenomenon is observed for the corresponding ^{31}P resonance signal for the



Scheme 3. Electronic structures of the free lactones I and the corresponding metal complexes II.

* In this paper, racemic material was used throughout. For reasons of clarity, only the enantiomers with *R*-configuration (for **3** *S*) at the metal center are shown.

Table 1

Spectroscopic data of the complexes **5a–d** (for numbering of the atoms, see Fig. 1)

	IR (cm^{-1})	^{31}P NMR, δ	^{1}H NMR, δ	^{13}C NMR, δ
5a	1685vs ν(NO) 1605m ν(C=C) 1560s ν(C=O)	19.04	5.71 (s, 5H, C_5H_5) 7.22–7.45 (m, 15H, $P(C_6H_5)_3$), 7.88 (m_c, 1H, 2-*H*), 7.55–7.85 (m, 4H, 3-*H*, 4-*H*, 10-*H*, 11-*H*), 7.89 (d, $^3J_{7-8}$ = 8.67 Hz, 1H, 7-*H*), 8.06–8.10 (m, 2H, 8-H, 9-H), 8.65 (m_c, 1H, 1-*H*), 8.90 (m_c, 1H, 12-*H*)	92.38 (C_5H_5), 117.42 (12c-C), 118.99 (6a-C), 127.59 (12b-C), 118.55, 123.21, 127.08, 128.03, 128.70 and 128.93 (2-C, 3-C, 4-C, 7-C, 9-C and 11-C), 129.30 (d, ^3J(P–C) = 10.7 Hz, *m*-C), 129.79, 131.12, 131.34, 131.72,(1-C, 8-C, 10-C, 12-C); 131.64 (*p*-C), 131.78 (d, ^1J(P–C) = 54.93 Hz, *i*-C), 133.90 (d, ^2J(P–C) = 10.7 Hz, *o*-C), 135.04, 138.08 (8a-C, 12a-C), 150.31 (4a-C), 171.89 (6-C)
5b	1690vs ν(NO) 1610m ν(C=C) 1560s ν(C=O)	19.03	3.90 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 5.67 (s, 5H, C_5H_5), 6.73 (d, $^4J_{4-2}$ = 2.4 Hz, 1H, 4-*H*), 6.94 (d, $^4J_{2-4}$ = 2.4 Hz, 1H, 2-*H*), 7.23–7.35 (m, 15H, $P(C_6H_5)_3$), 7.62 (ddd, $^3J_{11-12}$ = 8.4 Hz, $^3J_{11-10}$ = 7.0 Hz, $^4J_{11-9}$ = 1.4 Hz, 1H, 11-*H*), 7.69 (d, $^3J_{7-8}$ = 8.6 Hz, 1H, 7-*H*), 7.75 (ddd, $^3J_{10-9}$ = 7.9 Hz, $^3J_{10-11}$ = 7.0 Hz, $^3J_{10-12}$ = 1.2 Hz, 1H, 10-*H*), 7.91 (d, $^3J_{8-7}$ = 8.6 Hz, 1H, 8-*H*), 7.96 (dd, $^3J_{9-10}$ = 7.9 Hz, $^4J_{9-11}$ = 1.4 Hz, 9-*H*), 8.04 (dd, $^3J_{12-11}$ = 8.4 Hz, $^4J_{12-10}$ = 1.2 Hz, 12-*H*)	55.86 (OCH_3), 56.58 (OCH_3), 92.29 (C_5H_5), 94.24, 98.03 (2-C, 4-C), 102.95 (12c-C), 116.51 (6a-C), 122.38 (7-C), 125.65 (11-C) 127.32 (12b-C), 127.99 (9-C) 129.25 (d, ^3J(P–C) = 10.9 Hz, *m*-C), 129.70 (8-C), 130.89 (10-C), 131.20 (12-C), 131.61 (*p*-C) 131.85 (d, ^1J(P–C) = 56.2 Hz, *i*-C), 133.90 (d, ^2J(P–C) = 10.9 Hz, *o*-C), 136.07, 137.61 (8a-C, 12a-C), 152.71, 158.20, 163.57 (1-C, 3-C, 4a-C), 171.85 (6-C)

5c	1700vs ν(NO) 1600m ν(C=C) 1560s ν(C=O)	18.46/19.59	2.27/2.31 (s/s, 3H, 1-CH_3 [37/63]), 2.57 (s, 3H, 3-CH_3), 5.66/5.67 (s/s, 5H, C_5H_5 [63/37]), 7.05–7.62 (m, 17H, 2-*H*, 4-*H*, P(C_6H_5)$_3$), 7.64–7.81 (m, 2H, 10-*H*, 11-*H*), 7.84 (d, $^3J_{7-8}$ = 8.8 Hz, 1H, 7-*H*9, 7.91–8.09 (m, 3H, 8-*H*, 9-*H*, 12-*H*)	21.54 (CH_3), 23.87 (CH_3), 92.35 (C_5H_5), [114.78–142.46, 29 signals found instead of 23 expected, of those the following could be unambiguously assigned: 129.27 (m, *m*-C), 131.61 (*p*-C), 133.90 (d, ^2J(P–C) = 10.8 Hz, *o*-C)], 151.01 (4a-C), 171.72 (6-C)
5d	1690vs, ν(NO) 1610m ν(C=C) 1570s ν(C=O)	18.63/19.40	0.89/1.01 (t/t, ^3J = 7.4 Hz, 3H, 1-CH_2CH_3 [44/56]), 1.38/1.39 (t/t, ^3J = 7.6 Hz, 3H, 3-CH_2CH_3 [44/56]), 2.57 (m_c, 1H, 1-CH*H*CH_3), 2.92 (m, 3H, 1-C*H*HCH_3, 1-CH_2CH_3), 5.66/5.69 (s, s, 5H, C_5H_5 [56/44]), 7.10–7.59 (m, 17H, 2-*H*, 4-*H*, P(C_6H_5)$_3$), 7.64–7.82 (m, 2H, 10-*H*, 11-*H*), 7.79/7.85 (d/d, $^3J_{7-8}$ = 8.6 Hz, 1H, 7-H [56/44]), 7.98–8.07 (m, 3H, 8-*H*, 9-*H*, 12-*H*)	13.39/13.48 (1-CH_2CH_3), 14.39 (3-CH_2CH_3), 27.22, 27.46 (1-CH_2CH_3, 3-CH_2CH_3), 90.10 (C_5H_5), [111.60–147.27, 29 signals found instead of 23 expected, of those the following could be unambiguously assigned: 127.43 (m, *m*-C), 129.77 (*p*-C), 132.07 (d,^2J(P–C) = 10.7 Hz, *o*-C)], 148.82 (4a-C), 170.01 (6-C)

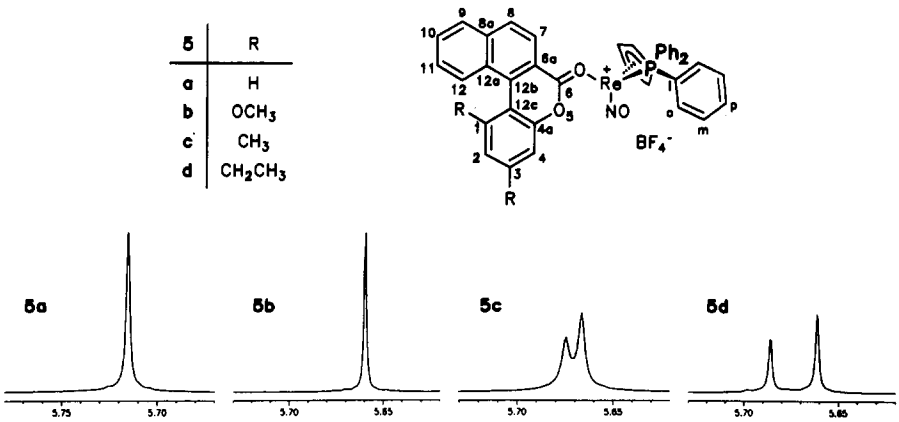


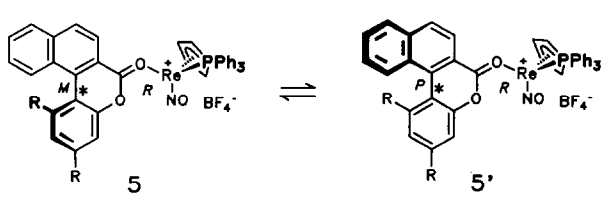
Fig. 1. ^{1}H NMR signals of the cyclopentadienyl ligand of the lactone complexes **5a–d**.

PPh_3 ligand and for several ^{13}C NMR signals (*e.g.* 1-alkyl or *o*-C, *m*-C of the triphenylphosphine group).

This spectroscopic behavior does not arise from a ^{1}H-^{31}P coupling (^{31}P{^{1}H}) or from the eventual occurrence of *E/Z* coordination isomers [18], since these should be observed for all four complexes prepared. Also an equilibrium of π/σ-coordination of the ligand can be excluded from the IR spectrum (no ν(NO) above 1700 cm^{-1} [20]). The peak doubling is rather due to the presence of two diastereomeric species, arising from a hindered rotation about the biaryl linkage, leading to conformationally more or less stable atropisomers or helimers **5** and **5'**, the interconversion rate for which is slow for the complexes **5c** and **d**, compared with that for **5a** and **b**, on the NMR time scale. This is in agreement with the fact that the peak splitting, *e.g.* in proton NMR, is strongest for **5d**, the most hindered example, and is most distinct near the stereogenic elements, the stereocentre (*e.g.* for the cyclopentadienyl ligand) and especially the axis (*e.g.* for 1-alkyl), whereas it is no longer observed for the remote para substituents at C-3. Furthermore, the peak ratio (where determinable) is constant (63:37 for **5c** and 56:44 for **5d**).

Structure in the crystal

For a further structural confirmation, we carried out an X-ray diffraction study with a monoclinic crystal of **5b**, obtained by diffusion of ether into a solution of the complex in dichloromethane, and the structure determined is shown in Fig. 2.



Scheme 4. Interconversion of the helimeric structure of the lactone ligand.

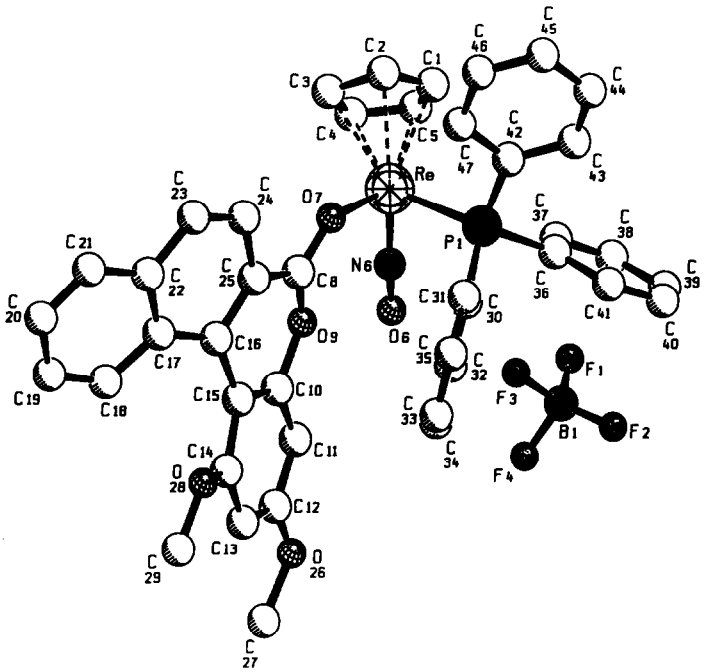


Fig. 2. Structure of **5b** in the crystal.

Crystallographic data, atomic parameters, bond lengths, and bond angles are summarized in Tables 2–5 (see Experimental section).

In the crystal, **5b** occurs as a racemate, but as only one of the two possible helimeric diastereomers (and its enantiomer) (*i.e.* of the two racemic diastereomers, *RP/SM* and *RM/SP*, only the latter is found). The conformation at the C=O double bond is unambiguously established as *Z* and the σ-coordination deduced above is confirmed. The N6–Re–O7–C8 array is nearly planar, as shown by the dihedral angle of only 6°, an even smaller torsion angle than that for the corresponding rhenium complex with acetophenone (9°) or γ-butyrolactone (12°) as ligands [14,17]. The Re–O7 bond length (211.2 pm) is slightly longer than in the mentioned acetophenone complex (208.0 pm) [17], but shorter than that in the comparable γ-butyrolactone complex (213.7 pm) [14]. These structural properties of the complex had been expected from consideration of the position of the HOMO *d* orbital of the rhenium atom [14,17].

A comparison of the exocyclic C8–O7 bond length of **5b** (125.4 pm) with that of the free lactone **1b** (120.5 pm) [2] shows that the carbonyl bond is lengthened, and thus weakened, by the coordination to the rhenium. At the same time, the endocyclic O9–C8 bond is significantly shorter in the complex (131.6 pm) than in the free lactone (137.1 pm), demonstrating its greater π-character arising from the electron donating ability of the endocyclic oxygen. As expected (*cf.* Scheme 3), this leads to a slight planarization of the heterocyclic pyranone ring, as recognized by the dihedral angle C14–C15–C16–C17 of the "inner spiral loop", which is smaller for the rhenium complexed lactone **5b** (27.94°) compared with the corresponding torsion angle in the free ligand (32.22°) [2]. This also becomes apparent upon

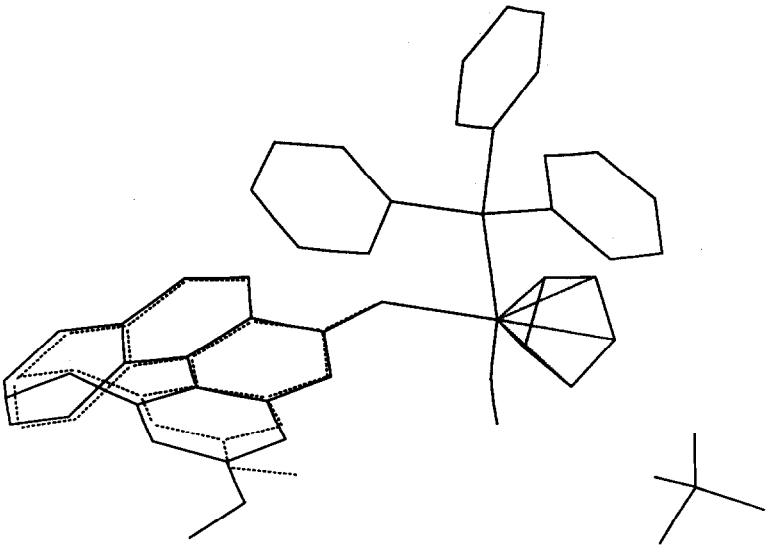


Fig. 3. Superimposed view of the structures of the rhenium complex **5b** (———) and the free lactone ligand **1b** (· · · · · ·) matched in respect of the six pyranone ring atoms.

superposition of the structures of the free and the coordinated lactones, which shows **1b** to be more twisted than **5b** (see Fig. 3).

Studies of these compounds in solution by DNMR and EXAFS [21,22] spectroscopy, the preparation of the correspondingly enantiomerically pure complexes and investigation of the stereoselectivity of their reactivity towards nucleophiles, is in progress. As Fig. 2 shows, a nucleophilic attack on the coordinated carbonyl function should occur from only one side (the *si*-face for the enantiomer drawn in Fig. 2), since the other side (here the *re*-face) is markedly shielded by the bulky triphenylphosphine ligand.

Experimental section

General

All reactions were performed under dry argon by Schlenk tube techniques with dry glassware.

Spectroscopic data (see Table 1)

IR spectra were recorded on a Perkin–Elmer 1420 spectrophotometer. ^{1}H and ^{13}C spectra were recorded on a Bruker WM 400 spectrometer and are referenced to internal $CHDCl_2$ (^{1}H, δ 5.32 ppm; ^{13}C, δ 53.80 ppm). ^{31}P NMR data were recorded on an AMX 400 Bruker spectrometer and are referenced to external H_3PO_4. Melting points were determined by DTA and are corrected. Elemental analyses were performed by the microanalytical laboratory of the Inorganic Institute of the University of Würzburg.

Solvents and reagents were purified as follows: CH_2Cl_2 and CD_2Cl_2 were distilled from P_2O_5, ether and pentane were distilled from sodium, and $HBF_4 \cdot OEt_2$ was used as purchased from Aldrich.

Preparation of (R,S)-*[(η^5-C_5H_5)Re(NO)(PPh_3)(H,H-lactone)]$^+BF_4^-$ (**5a**)*

A solution of (*R,S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**3**; 180 mg, 0.32 mmol) [11] in 15 ml CH_2Cl_2 in a Schlenk flask containing a stirring bar was cooled to −80°C and 56 μl of $HBF_4 \cdot OEt_2$ (34 mg, 0.39 mmol) were added, followed immediately by 87 mg (0.36 mmol) of a solution of **1a** in 15 ml of CH_2Cl_2. The dark red solution was allowed to warm up to room temperature during 5 h, the solvent removed under oil pump vacuum at room temperature and the crude solid residue dissolved in a minimum of CH_2Cl_2. The product was precipitated by slow addition of ether with rapid stirring. The red solid was filtered off and washed with ether until no **1a** was detectable in the filtrate. The solid was subsequently washed once with pentane (10 ml) and then dried under vacuum at room temperature to give 230 mg (0.26 mmol, 81%) of **5a** as an orange-red powder; m.p. (dec) 148°C. Anal. Found: C, 54.26; H, 3.20; N, 1.74. $C_{40}H_{30}BF_4NO_3PRe$ calc.: C, 54.80; H, 3.45; N, 1.60%.

Preparation of (R,S)-*[(η^5-C_5H_5)Re(NO)(PPh_3)(OCH_3, OCH_3-lactone)]$^+BF_4^-$ (**5b**)*

Use of 210 mg (0.38 mmol) of complex (*R,S*)-**3**, 138 mg (0.45 mmol) of lactone **1b** and 64 μl (40 mg, 0.45 mmol) of $HBF_4 \cdot OEt_2$ in a procedure similar to that described for **1a**, gave 290 mg (0.31 mmol, 82%) of **5b** as a bright red powder; m.p. (dec) 162°C. Anal. Found: C, 53.61; H, 3.66; N, 1.54. $C_{42}H_{34}BF_4NO_5PRe$ calc.: C, 53.85; H, 3.66; N, 1.49%.

Preparation of (R,S)-*[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3, CH_3-lactone)]$^+BF_4^-$ (**5c**)*

The rhenium lactone complex **5c** was obtained from 270 mg (0.48 mmol) of (*R,S*)-**3**, 217 mg (0.79 mmol) lactone **1c** and 84 μl (51 mg, 0.58 mmol) of $HBF_4 \cdot OEt_2$ by a procedure similar to that used for **5a**. Work up gave 380 mg (0.42 mmol, 87%) of **5c** as a dark red powder; m.p. (dec) 170°C. Anal. Found: C, 55.53; H, 4.07; N, 1.54. $C_{42}H_{34}BF_4NO_3PRe$ calc.: C, 55.76; H, 3.79; N, 1.55%.

Preparation of (R,S)-*[(η^5-C_5H_5)Re(NO)(PPh_3)(C_2H_5, C_2H_5-lactone)]$^+BF_4^-$ (**5d**)*

Use of 130 mg (0.23 mmol) of complex (*R,S*)-**3**, 70 mg (0.23 mmol) of diethyllactone **1d** and 37 μl (22 mg, 0.26 mmol) of $HBF_4 \cdot OEt_2$ in the procedure described for **5a**, gave 200 mg (0.22 mmol, 92%) of **5d** as a red powder; m.p. (dec) 170°C. Anal. Found: C, 56.39; H, 4.11; N, 1.53. $C_{44}H_{38}BF_4NO_3PRe$ calc.: C, 56.66; H, 4.11; N, 1.50%.

X-Ray crystallographic study of ***5b***

Suitable crystals were grown by diffusion of ether into a solution of **5b** in dichloromethane. Measurement of diffraction intensities was performed on a Stoe Stadi 4 diffractometer by using Mo-K_α radiation (0.7107 Å). Cell parameters were determined by least-squares refinement of 25 reflections. The structure was solved with Siemens SHELXTL PLUS package using direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen positions were calculated using a riding model and were considered fixed with isotropic U_{eq} in all refinements. The final residual values R and R_w and other crystal data are given in Table 2. Further details of the structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-56042, the names of the authors, and the journal citation.

Table 2

Summary of crystallographic data for the complex **5b**

Empirical formula	$C_{42}H_{34}BF_4NO_5PRe$
Molecular mass	936.72
a (pm)	2219.2(3)
b (pm)	1435.5(3)
c (pm)	2568.4(5)
β (deg)	113.02(1)
V (pm^3)	$7583.0(8)\times10^6$
Z	8
d (calc.) (g cm^{-3})	1.641
Crystal system	Monoclinic
Space group	$C2/c$
Crystal size (mm)	$0.25\times0.45\times0.15$
θ range (deg)	1.75–25.0
Recip. latt. segment	$h = -26$–19
	$k = 0$–17
	$l = 0$–30
No. reflections measd.	7059
No. unique reflections	6604
No. reflections $F > 3\sigma(F)$	4745
Linear abs. coeff. (mm^{-1})	3.35
Abs. correction	Geometrical
F_o/parameter ratio	9.57
R, R_w	0.048, 0.035
Largest positive difference peak (e Å^{-3})	1.26
Largest negative difference peak (e Å^{-3})	0.98

Table 3

Atomic parameters ($\times10^4$) and equivalent isotropic displacement parameters (pm$^2\times10^{-1}$)

Atom	x	y	z	U_{eq} [a]
Re	1543(1)	7973(1)	1219(1)	42(1)
C1	1957(13)	9378(15)	1424(7)	147(11)
C2	1361(16)	9497(10)	1266(13)	148(17)
C3	1066(7)	9249(13)	734(12)	138(11)
C4	1581(17)	8982(11)	576(7)	141(13)
C5	2110(11)	9095(14)	1023(16)	165(17)
P1	1998(1)	7480(2)	2178(1)	43(1)
N6	1814(3)	6992(6)	973(3)	55(3)
O6	2051(3)	6391(5)	782(3)	86(4)
O7	642(3)	7524(4)	1231(2)	48(3)
C8	324(5)	6785(6)	1063(3)	48(4)
O9	597(3)	6135(4)	869(2)	46(3)
C10	342(4)	5229(6)	764(3)	45(4)
C11	743(4)	4587(6)	660(3)	50(4)
C12	533(5)	3674(7)	583(4)	55(5)
C13	−44(4)	3422(6)	656(3)	52(4)
C14	−423(4)	4083(6)	763(4)	50(4)
C15	−271(4)	5045(6)	774(3)	42(4)
C16	−674(4)	5831(5)	811(3)	40(4)
C17	−1363(4)	5861(5)	615(3)	41(4)
C18	−1772(4)	5194(6)	228(3)	43(4)

Table 3 (continued)

Atom	x	y	z	U_{eq} [a]
C19	−2427(4)	5253(7)	27(4)	51(4)
C20	−2734(4)	5979(7)	186(4)	63(5)
C21	−2371(4)	6650(7)	534(4)	61(5)
C22	−1676(4)	6627(6)	738(3)	49(4)
C23	−1299(4)	7405(6)	1039(4)	57(4)
C24	−645(4)	7443(6)	1170(3)	52(4)
C25	−337(4)	6656(6)	1040(3)	42(4)
O26	930(3)	3077(5)	457(3)	75(3)
C27	705(5)	2169(7)	275(4)	78(5)
O28	−932(3)	3879(4)	907(3)	61(3)
C29	−1186(5)	2974(7)	807(4)	90(6)
C30	1618(4)	6445(6)	2337(3)	46(4)
C31	1259(6)	6477(7)	2661(5)	91(7)
C32	972(6)	5694(8)	2763(5)	116(9)
C33	1010(5)	4880(8)	2524(5)	81(6)
C34	1349(5)	4826(7)	2185(4)	70(5)
C35	1657(5)	5604(6)	2087(4)	60(5)
C36	2882(4)	7193(6)	2435(3)	49(4)
C37	3223(4)	7389(6)	2110(4)	62(5)
C38	3887(5)	7191(8)	2311(4)	87(6)
C39	4191(5)	6791(7)	2827(5)	85(6)
C40	3843(5)	6584(7)	3146(4)	73(5)
C41	3193(5)	6767(6)	2959(4)	64(5)
C42	1902(4)	8355(6)	2659(3)	45(4)
C43	2411(5)	8611(6)	3157(3)	54(4)
C44	2302(5)	9273(7)	3486(4)	76(6)
C45	1708(6)	9703(7)	3341(5)	76(6)
C46	1205(6)	9456(7)	2863(5)	78(6)
C47	1291(5)	8782(7)	2505(4)	72(5)
B1	4513(6)	5307(11)	972(6)	72(7)
F1	4825(3)	5936(5)	782(3)	100(4)
F2	4819(4)	5006(7)	1470(3)	177(5)
F3	3913(4)	5681(6)	862(4)	185(7)
F4	4325(5)	4599(5)	616(4)	187(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4

Bond lengths (pm)

Re–C1	219.3(22)	Re–C2	223.6(16)
Re–C3	223.7(19)	Re–C4	223.1(21)
Re–C5	222.0(29)	Re–P1	239.0(2)
Re–N6	174.6(8)	Re–O7	211.2(6)
C1–C2	123.3(44)	C1–C5	127.8(48)
C2–C3	132.1(39)	C3–C4	140.8(44)
C4–C5	129.4(35)	P1–C30	183.2(9)
P1–C36	185.4(9)	P1–C42	183.8(9)
N6–O6	121.1(12)	O7–C8	125.4(10)
C8–O9	131.6(12)	C8–C25	145.6(14)
O9–C10	140.2(10)	C10–C11	137.9(13)

Table 4 (continued)

C10–C15	139.5(14)	C11–C12	137.9(13)
C12–C13	141.1(15)	C12–O26	135.6(13)
C13–C14	136.7(14)	C14–C15	141.9(13)
C14–O28	135.3(13)	C15–C16	146.6(13)
C16–C17	141.2(12)	C16–C25	140.2(11)
C17–C18	142.5(10)	C17–C22	140.1(13)
C18–C19	134.3(12)	C19–C20	139.1(15)
C20–C21	135.0(12)	C21–C22	142.2(13)
C22–C23	142.9(12)	C23–C24	135.8(13)
C24–C25	142.6(13)	O26–C27	141.0(12)
O28–C29	140.1(12)	C30–C31	136.5(18)
C30–C35	138.7(13)	C31–C32	136.7(18)
C32–C33	134.0(18)	C33–C34	136.1(19)
C34–C35	138.4(15)	C36–C37	136.3(15)
C36–C41	139.8(12)	C37–C38	138.5(14)
C38–C39	136.4(15)	C39–C40	136.6(19)
C40–C41	135.4(15)	C42–C43	139.2(10)
C42–C47	139.6(14)	C43–C44	135.8(15)
C44–C45	136.8(17)	C45–C46	135.0(14)
C46–C47	140.5(16)	B1–F1	134.3(18)
B1–F2	127.2(16)	B1–F3	135.8(17)
B1–F4	132.5(17)		

Table 5

Bond angles (deg)

C1–Re–C2	32.3(11)	C1–Re–C3	56.3(7)
C2–Re–C3	34.3(10)	C1–Re–C4	56.6(6)
C2–Re–C4	57.7(12)	C3–Re–C4	36.7(11)
C1–Re–C5	33.6(12)	C2–Re–C5	55.5(13)
C3–Re–C5	57.6(7)	C4–Re–C5	33.8(11)
C1–Re–P1	93.1(4)	C2–Re–P1	104.2(8)
C3–Re–P1	137.7(7)	C4–Re–P1	147.3(6)
C5–Re–P1	113.9(8)	C1–Re–N6	131.1(8)
C2–Re–N6	154.7(11)	C3–Re–N6	127.6(8)
C4–Re–N6	97.6(7)	C5–Re–N6	101.2(9)
P1–Re–N6	94.2(2)	C1–Re–O7	125.9(8)
C2–Re–O7	96.1(10)	C3–Re–O7	90.9(5)
C4–Re–O7	121.4(9)	C5–Re–O7	148.1(6)
P1–Re–O7	85.0(1)	N6–Re–O7	102.8(3)
Re–C1–C2	75.7(13)	Re–C1–C5	74.3(14)
C2–C1–C5	111.4(22)	Re–C2–C1	71.9(13)
Re–C2–C3	72.9(11)	C1–C2–C3	109.8(31)
Re–C3–C2	72.8(12)	Re–C3–C4	71.4(10)
C2–C3–C4	104.3(21)	Re–C4–C3	71.9(15)
Re–C4–C5	72.6(16)	C3–C4–C5	105.2(24)
Re–C5–C1	72.0(19)	Re–C5–C4	73.5(16)
C1–C5–C4	109.2(28)	Re–P1–C30	115.4(2)
Re–P1–C36	113.3(3)	C30–P1–C36	104.8(4)
Re–P1–C42	112.7(3)	C30–P1–C42	102.6(4)
C36–P1–C42	107.2(4)	Re–N6–O6	171.5(8)
Re–O7–C8	131.4(6)	O7–C8–O9	116.8(9)

Table 5 (continued)

O7–C8–C25	123.0(9)	O9–C8–C25	120.1(7)
C8–O9–C10	121.3(8)	O9–C10–C11	114.5(8)
O9–C10–C15	119.7(8)	C11–C10–C15	125.8(8)
C10–C11–C12	117.1(9)	C11–C12–C13	119.8(10)
C11–C12–O26	114.9(9)	C13–C12–O26	125.3(8)
C12–C13–C14	120.7(8)	C13–C14–C15	121.3(9)
C13–C14–O28	123.6(8)	C15–C14–O28	114.9(9)
C10–C15–C14	114.1(8)	C10–C15–C16	118.6(8)
C14–C15–C16	127.2(9)	C15–C16–C17	127.1(7)
C15–C16–C25	116.1(8)	C17–C16–C25	116.7(8)
C16–C17–C18	122.3(8)	C16–C17–C22	120.3(7)
C18–C17–C22	116.8(7)	C17–C18–C19	121.6(8)
C18–C19–C20	120.9(8)	C19–C20–C21	119.9(9)
C20–C21–C22	120.5(9)	C17–C22–C21	119.7(8)
C17–C22–C23	120.1(8)	C21–C22–C23	120.1(9)
C22–C23–C24	120.5(9)	C23–C24–C25	118.3(8)
C8–C25–C16	119.2(8)	C8–C25–C24'	117.1(7)
C16–C25–C24	122.9(8)	C12–O26–C27	119.1(8)
C14–O28–C29	118.0(8)	P1–C30–C31	122.7(7)
P1–C30–C35	118.9(8)	C31–C30–C35	118.2(9)
C30–C31–C32	121.2(11)	C31–C32–C33	120.7(14)
C32–C33–C34	119.8(12)	C33–C34–C35	120.6(10)
C30–C35–C34	119.5(11)	P1–C36–C37	119.9(6)
P1–C36–C41	119.8(8)	C37–C36–C41	120.3(8)
C36–C37–C38	119.5(8)	C37–C38–C39	120.0(12)
C38–C39–C40	120.1(10)	C39–C40–C41	121.1(9)
C36–C41–C40	119.0(11)	P1–C42–C43	122.8(7)
P1–C42–C47	117.6(6)	C43–C42–C47	119.6(9)
C42–C43–C44	119.1(9)	C43–C44–C45	122.2(9)
C44–C45–C46	119.7(11)	C45–C46–C47	120.5(11)
C42–C47–C46	118.9(8)	F1–B1–F2	116.7(10)
F1–B1–F3	105.2(12)	F2–B1–F3	116.0(15)
F1–B1–F4	109.1(14)	F2–B1–F4	109.9(13)
F3–B1–F4	98.2(10)		

Acknowledgements

We thank R. Schedl (DTA), C.P. Kneis (elemental analysis), E. Ruckdeschel, Dr. D. Scheutzow and Dr. W. Buchner (NMR) for support. Generous financial support of this work by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich No. 347, Selective Reactions of Metal-Activated Molecules) and the Fonds der Chemischen Industrie is gratefully acknowledged.

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