Transition-Metal Complexes of (1S,2S,3R)-3-Hydroxycamphorsultam

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Complexes of (1S,2S,3R)-3-hydroxycamphorsultam (Chemical Abstracts Service name (1aS,3aS,7R)-8,8-dimethyl-7-hydroxy-1,1a,4,5,6,7-hexahydro-3H-3a,6-methano-2,1-benzisothiazole 2,2-dioxide) with the transition metals Fe-(III), Cu(II), Co(II), and Re(III) have been prepared and characterized by elemental microanalysis, NMR, and IR, and their electrochemical properties have been studied by cyclic voltammetry and controlled potential electrolysis. The X-ray structure of the copper complex [{CuCl}₂(-L′)₂], which crystallizes in the monoclinic space group *I*2 with *a* = 13.9777(8), *b* = 7.2778(3), *c* = 19.891(1) Å, *β* = 91.96(4), *Z* = 4, *V* = 2020(2) Å³ (*R* = 0.027 and *R*ₓ = 0.029), shows that it is a dimeric oxygen bridged compound with a Cu⋯Cu distance of 2.989(4) Å, containing a hydrogen bond between one oxygen of the sulfonamide group and a triethylammonium ion, which is formed from triethylamine used to deprotonate the chiral ligand.

Introduction

Enantiomerically pure camphor is a convenient chiral pool source for the production of chiral compounds, as it contains a rigid but easy to modify skeleton. Thus, it has served as starting material in the enantioselective synthesis of steroids[1-4] and terpenes.[5-8] Many derivatives of camphor have served as chiral auxiliaries and catalysts.[9] For enantioselective reactions of carbanions, cycloadditions, and related reactions, Oppolzer has introduced the very successful camphorsultam (I).[10,11] Recently, we have prepared (1S,2S,3R)-3-hydroxycamphorsultam (II) ((1aS,3aS,7R)-8,8-dimethyl-7-hydroxy-1,1a,4,5,6,7-hexahydro-3H-3a,6-methano-2,1-benzisothiazole 2,2-dioxide) and used it as a ligand for aluminum, titanium, and tin to prepare chiral Lewis acids for enantioselective catalysis of Diels–Alder and ene reactions.[12,13] To gain more insight in the coordination behavior of this ligand and its connection with possible catalytic activity, we have prepared complexes with some transition metals and studied their structure by NMR, IR, electrochemistry, and X-ray structure analysis.

Experimental Section

All experiments were carried out under nitrogen, using dried and distilled solvents. Ligand II (1S,2S,3R)-3-hydroxycamphorsultam) was prepared as previously described.[12] IR spectra were measured with a Perkin-Elmer 683 instrument, and NMR spectra with a Bruker AM 360

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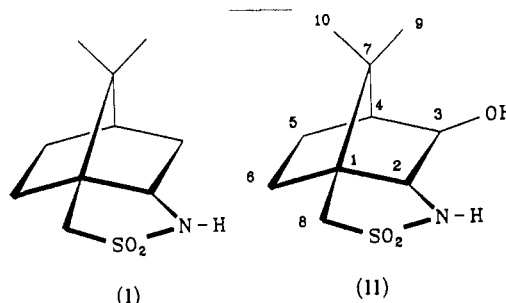(13) Ketter, A.; Herrmann, R. *Z. Naturforsch., Sect. B* 1990, *45*, 1684.

Figure 1. Oppolzer's sultam (I) and ligand (II) with numbering of atoms for NMR.

(360.134 MHz for ¹H, 90.556 MHz for ¹³C) and a Varian 300 (299.949 MHz for ¹H). Cyclic voltammetry and controlled potential electrolysis were performed with a Hi-Tek waveform generator PPRI and a Hi-Tek potentiostat DT2101, in 0.2 M NBu₄BF₄ in acetonitrile, THF, or dichloromethane, respectively. Ferrocene was used as internal reference.

Crystallographic Data Collection and Refinement of the Structure. A green needle of III of approximately 1.00 × 0.15 × 0.15 mm was mounted in a glass capillary under nitrogen. Data were collected with an Enraf Nonius Turbo CAD4 diffractometer, equipped with a rotating anode (50 kV, 90 mA), using graphite monochromated Mo Kα radiation. A total of 7719 diffracted intensities were measured by the ω/2θ scan mode in the 1.5 < θ < 25° range in the region −h to +h, −k to 0, −l to +l. From these reflections, 3361 did not show net intensities above the average background. Three standard reflections were monitored during data collection, but no decay or instrumental instability was detected. Lorentz and polarization corrections were applied. An empirical absorption correction was used[14] (minimum transmission factor 0.938, maximum 0.999). From the 1927 unique reflections, 1876 with *F*₀ > 3σ*F*₀ were used for solution and refinement of the structure. The position of the copper atom was obtained by a tridimensional Patterson synthesis. The remaining non-hydrogen atoms were obtained by difference Fourier synthesis. Hydrogens were inserted at idealized positions and isotropic thermal motion parameters allowed to refine. The hydrogen atom attached to the nitrogen atom of the NHEt₃ molecule was located in the density map. Full-matrix least-squares refinement including anisotropic thermal displacement parameters for the non-hydrogen atoms converged to *R* = 0.027 and *R*ₓ = 0.029. A unit weighting scheme was used. A Hamilton test was performed showing this to be the true enantiomeric configuration. The *R* values obtained refining both the "true" structure and the "inverted" one were the above mentioned and *R* = 0.031, *R*ₓ = 0.033. Also Flack's

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Table I. Structure and Properties of the Complexes III–VI(L′ = L(NEt$_3$H); L = Double Deprotonated Ligand II)

| | compound | yield (%) | color | microanalysis | | | | | | IR data in KBr (cm^{-1}) | |
| | | | | calcd (%) | | | found (%) | | | | |
				C	H	N	C	H	N	ν_{NH}	ν_{SO_2}
III	[{CuCl}$_2$(μ-L′)$_2$]	80	green	44.5	7.2	6.5	44.6	7.2	6.7	2670 (m), 2490 (s)	1225 (s), 1210 (s)
IV	[(FeCl$_2$(THF)}$_2$(μ-L′)$_2$]	40	yellow-green	45.3	7.4	5.3	45.9	7.2	5.8	2670 (m), 2495 (s)	1250 (w)
V	[{CoCl(H$_2$O)}$_2$(μ-L′)$_2$]	50	blue	42.8	6.8	6.4	43.3	7.4	6.3	2670 (m), 2493 (s)	1255 (s), 1245 (s)
VI	[{Re(OMe)$_2$(NEt$_3$)}$_2$(μ-L′)$_2$]	70	colorless	43.2	7.6	6.3	43.2	7.1	6.3	2600 – 2670 (m), 2498 (s)	1285 (s)

parameter refined to 0.004(17) with the coordinates of the true structure. Scattering factors were taken from ref 15.

All calculations were carried out on a MicroVax 3400 at Instituto Superior Técnico, using SHELX76,[16] PARST[17] (calculation of geometric data), and ORTEP[18] (illustrations).

Preparation of the Compounds. 1. Copper Complex (III). To a solution of CuCl$_2$·2H$_2$O (230 mg, 1.35 mmol) in 20 mL of methanol, 0.5 mL (3.61 mmol) of triethylamine and 300 mg (1.30 mmol) of ligand II were added. The mixture was stirred at room temperature for 6 h. The suspension was filtered, and 12 mL of diethyl ether was added to the solution. The precipitated crystals were filtered off and dried under vacuum.

^{13}C NMR (the chemical shifts of the free ligand II are given in parentheses; for the numbering of the atoms in II, see Figure 1): C$_1$ 80.4 (56.8); C$_2$ 152.5 (67.4); C$_3$ –7.6 (75.4); C$_4$ 89.0 (50.4); C$_5$ 32.5 (30.7); C$_6$ 28.6 (23.8); C$_7$ 42.2 (47.5); C$_8$ 86.5 (51.3); C$_9$ and C$_{10}$ 17.4, 21.3 (21.2, 22.1); NEt$_3$ 9.2, 48.1.

2. Iron Complex (IV). To a solution of 280 mg (1.21 mmol) of ligand II in 5 mL of THF, 0.65 mL (4.69 mmol) of triethylamine was added. A solution of anhydrous FeCl$_2$ (150 mg, 1.18 mmol) in 5 mL of THF was added and the mixture stirred at room temperature for 2 days. A stream of dry air was bubbled through the slurry for 20 min. The suspension was filtered and the precipitate washed with 4 mL of diethyl ether and dried under vacuum.

3. Cobalt Complex (V). To a mixture of 970 mg (4.08 mmol) of CoCl$_2$·6H$_2$O and 950 mg (4.11 mmol) of ligand II, THF (30 mL) was added. To the stirred suspension, triethylamine (1.00 mL, 7.21 mmol) was added and the mixture refluxed for 2 h. The solution was concentrated until a blue precipitate appeared. It was filtered off and dried under vacuum.

4. Rhenium Complex (VI). To a mixture of [ReOCl$_3$(PPh$_3$)$_2$] (500 mg, 0.60 mmol) and 300 mg (1.30 mmol) of ligand II, 40 mL of methanol and 1.00 mL (7.21 mmol) of triethylamine were added. After refluxing for 1 h, the solution was concentrated to ~20 mL, and 26 mL of diethyl ether was added. The colorless precipitate (PPh$_3$O) was filtered off and the solution concentrated until a precipitate appeared. After filtration, it was washed with diethyl ether (10 mL) and dried under vacuum.

Results and Discussion

Synthesis of the Compounds. The reactions between the metal salts (FeCl$_2$, CoCl$_2$, CuCl$_2$, and [ReOCl$_3$(PPh$_3$)$_2$]) and the ligand II were carried out at room temperature, in methanol or THF. In ligand II, two atoms can *a priori* be expected to act as donor atoms for coordination to metals: the oxygen of the hydroxy group and the nitrogen of the sulfonamide group. This means that II should behave as a bidentate ligand. The SO$_2$ group of sulfonamides is generally not sufficiently electron rich to be able to coordinate to the above metal sites. The nitrogen in sulfonamides is a poor donor due to the electron-withdrawing SO$_2$ group, and it seems to participate in coordination on metal centers (which are not especially activated like the Lewis acids TiCl$_4$ and AlCl$_3$[12]) only after deprotonation.[19,20] Thus, the reactions have been carried out in the presence of triethylamine, to assist coordination of the nitrogen by deprotonation. It should be noted that the free

Table II. Crystallographic Data for Compound III

chemical formula	C$_{32}$H$_{56}$Cl$_2$Cu$_2$N$_4$O$_6$S$_2$	a/Å	13.9778(8)
formula weight	854.12	b/Å	7.2778(3)
space group	*I*2 (No. 5)	c/Å	19.891(1)
Mo(Kα)/Å	λ = 0.71069	β/deg	91.96(4)
ρ_{obs}/g cm^{-3}	1.41	V/Å^3	2020(2)
μ(Mo Kα)/cm^{-1}	13.72	Z	4
		T/°C	ambient
		$R(F_o)^a$	0.027
		$R_w(F_o)^b$	0.029

^{a} $R(F_o) = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_w(F_o) = \{\sum w(|F_o| - |F_c|)^2/w\sum|F_o|^2\}^{1/2}$.

ligand does not react with triethylamine under the same reaction conditions, which implies that deprotonation occurs only if both metal and base are present in solution. The products contain metal and ligand in the ratio 1:1 and, depending on the metal, one or two molecules of triethylamine (as such or as triethylammonium ion). They are stable at room temperature, but decompose in air, or on standing in solution, and can be recrystallized only with difficulty. The product obtained from FeCl$_2$ in THF is easier to isolate in pure form as Fe(III) complex and therefore is oxidized with dry air. The properties of the products are listed in Table I. In the reaction with CuCl$_2$, crystals suitable for X-ray structure analysis were obtained.

X-ray Structure of Complex (III). The copper complex III [{CuCl}$_2$(μ-L′)$_2$] (C$_{32}$H$_{56}$Cl$_2$Cu$_2$N$_4$O$_6$S$_2$, M = 854.12) crystallizes in the monoclinic space group *I*2 with a = 13.9777(8), b = 7.2778(3), c = 19.891(1) Å, β = 91.96(4)°, V = 2020(2) Å^3 (by least-squares refinement of the setting angles of 25 automatically centered reflections in the range 13 < θ < 20°, λ = 0.71069 Å), Z = 4, D_c = 1.41g·cm^{-3}, $F(000)$ = 904, μ(Mo Kα) = 13.27 cm^{-1}. The molecular crystal data are displayed in Table II.

The molecular structure consists of an oxo-bridged dinuclear copper unit which contains a 2-fold axis. The chiral ligand is deprotonated at oxygen and nitrogen, and links two copper atoms by asymmetric oxygen bridges (distances Cu–O 1.938(5) Å and 1.907(3) Å , Cu···Cu 2.989(4) Å). The copper atoms have a distorted square planar coordination sphere, with the nitrogen of the chiral ligand forming a five-membered chelate (bond angle O–Cu–N 83.8(2)°) and a residual chlorine atom (bond angles N–Cu–Cl 101.4(2)° , Cl–Cu–O 174.1(1)° , O–Cu–O 77.4(2)°). The deviation from ideal square planar geometry is shown by the puckering angles defined as the angles between the planes containing the bridging oxygens and one copper atom (165.4°) and between the plains formed by the two copper atoms and one of the bridging oxygens (161.9°). The values for both the distances and the angles correspond well to that found in similar dinuclear copper complexes with chelating N–O ligands, e.g. refs 21 and 22. The chiral ligand itself does not show noteworthy deviations from the geometry expected for the rigid carbon skeleton of the free ligand. Very similar distances and angles have been found in (camphorsulfonyl)oxaziridine[23] and (camphorlactonesulfonyl)-oxaziridine,[24] as far as the carbon skeleton is concerned. The

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Table III. Fractional Atomic Coordinates (×10^4) of Compound III

	x	y	z	B_{eq} (Å^2)^a
Cu	-81.3(3)	-2500	-751.1(2)	2.75(1)
Cl	-1259(1)	-2536(3)	-1532(1)	3.70(3)
S	1316(1)	-2061(2)	-1998(1)	2.73(3)
O(2)	874(2)	-306(6)	-2141(2)	4.07(10)
O(3)	1185(2)	-3351(6)	-2542(2)	4.66(11)
C(8)	2593(3)	-1791(8)	-1836(2)	3.36(12)
C(1)	2730(3)	-2187(9)	-1084(2)	3.36(13)
C(6)	3616(3)	-3278(10)	-836(3)	4.89(18)
C(5)	3520(3)	-3176(12)	-62(3)	6.20(26)
C(4)	2646(3)	-1866(10)	30(2)	4.84(20)
C(7)	2717(3)	-567(9)	-574(3)	4.02(14)
C(9)	1896(4)	815(9)	-661(3)	4.73(17)
C(10)	3643(4)	605(12)	-566(3)	6.39(24)
N(1)	1025(2)	-2821(7)	-1290(2)	3.09(10)
C(2)	1878(3)	-3421(8)	-901(2)	3.17(12)
C(3)	1773(3)	-3106(9)	-136(2)	3.85(15)
O(1)	860(2)	-2312(8)	-16(1)	3.94(10)
N(2)	-4197(3)	-3342(7)	-2680(2)	3.47(11)
C(11)	-3726(4)	-2623(12)	-3301(3)	4.98(15)
C(12)	-4410(5)	-2335(14)	-3881(3)	6.32(20)
C(21)	-4785(3)	-1900(8)	-2346(3)	3.99(12)
C(22)	-4194(5)	-518(9)	-1944(3)	4.92(18)
C(31)	-3504(4)	-4297(10)	-2215(3)	5.01(17)
C(32)	-3977(5)	-5280(11)	-1659(3)	5.83(21)

^{a} $B_{eq} = 8\pi^2(^1/_3(U_{11} + U_{22} + U_{33} + 2 \cos \beta U_{13})$.

Table IV. Selected Bond Lengths (Å) and Angles (deg) of Compound III

|			
Cu–Cu^a	2.989(4)	O(1)–Cu^a	1.907(5)
Cl–Cu	2.225(3)	N(1)–Cu	1.923(5)
O(1)–Cu	1.938(5)	O(2)–S	1.442(5)
O(3)–S	1.440(5)	C(8)–S	1.813(6)
N(1)–S	1.579(5)	H–N(2)	0.846(49)
N(1)–Cu–Cl	101.4(2)	O(1)–Cu–Cl	174.1(1)
Cl–Cu–O(1)^a	97.6(2)	O(1)–Cu–O(1)^a	77.4(2)
N1–Cu–O(1)^a	160.7(2)	Cu–O(1)–Cu^a	102.0(2)
O(1)–Cu–N(1)	83.8(2)	O(3)–S–O(2)	112.7(3)
C(8)–S–O(2)	110.6(3)	C(8)–S–O(3)	107.7(3)
N(1)–S–O(2)	111.4(3)	N(1)–S–O(3)	114.3(3)
N(1)–S–C(8)	99.3(3)	C(1)–C(8)–S	104.1(4)
C(3)–O(1)–Cu	115.6(4)	S–N(1)–Cu	133.6(2)
C(2)–N(1)–Cu	113.4(3)	C(2)–N(1)–S	110.2(3)
N(1)–C(2)–C(1)	108.8(5)	C(3)–C(2)–C(1)	104.2(5)
C(3)–C(2)–N(1)	111.8(4)	O(1)–C(3)–C(2)	109.8(4)

^{a} –x, y, –z.

bond lengths of the sulfonamide substructure compare well with those observed in other sulfonamide complexes (C–S 1.813(6) Å, S–O 1.440(5) and 1.442(5) Å, S–N 1.579(5) Å), but the N–Cu distance is relatively short (1.923(5) Å), compared with 2.028 Å.[19] A striking difference to the S–N single bonds found in the oxaziridines (bond lengths of 1.739 and 1.743 Å in the (camphorlactonesulfonyl)oxaziridine[24]) and in complexes containing the N–S–N unit[25] (1.691 and 1.706 Å) is observed in III (1.579(5) Å) and other sulfonamide complexes of copper (1.576(4) Å);[19] this corresponds to a S=N double bond (e.g., 1.513 and 1.527 Å in bis[di-*tert*-butyl(thiophosphinyl)]sulfur diimide[26]). Accordingly, the nitrogen atom has an almost planar array of the ligands. A possible explanation refers to extensive charge delocalization in the sulfonamide subunit.[19] A complete list of atomic coordinates is given in Table III and selected bond lengths and angles are given in Table IV. The structure is depicted in Figure 2.

Of particular interest is the triethylammonium ion included in the crystal. Its position relative to the complex is such that the hydrogen of the N–H bond points in the direction of the *endo*-oxygen of the SO$_2$ group (O^2 in Figure 2). We interpret this as

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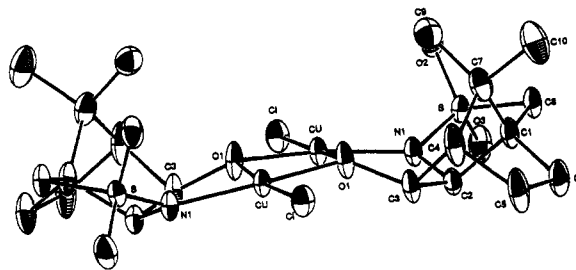
Figure 2. Molecular drawing of compound III showing atomic labeling scheme.

a N–H···O hydrogen bond (distances N···O 2.756 Å, N–H 0.846(49) Å, O···H 1.990 Å, angle O–H–N 150.0°). The distances of the hydrogen to other potential donor atoms are much greater and indicate that there is no interaction (N_{sultam}···H 3.78 Å, S···H 3.27 Å, $O_{SO_2(exo)}$···H (O^3 in Figure 2) 3.89 Å, Cl···H 4.39 Å). Such asymmetric hydrogen bonds have been observed in other dinuclear copper complexes as well.[22] On the other hand, the formation of a hydrogen bond from an ammonium ion to an oxygen atom with no pronounced donating properties is unexpected, but its stabilizing effect on the (formally negatively charged) copper(II) complex gives a rationale for the ready inclusion of an ammonium ion in the crystal.

IR Spectra of the Complexes. The IR spectra of the complexes have been determined in KBr pellets and show the complete disappearance of the typical strong and sharp sulfonamide bands (ν_{NH}) at 3315 and 3355 cm^{-1} observed in the free ligand II. As can be seen in Table I, the ν_{SO_2} vibrations (in II: 1310 (vs), 1055 (s) cm^{-1}) are considerably changed in the complexes; a shift to lower frequencies is observed for the asymmetric stretching of the SO$_2$ groups. Bands in the region of 2500–2700 cm^{-1} can be attributed to ν_{NH} of the triethylammonium ion; free triethylammonium hydrochloride has bands at 2680 and 2495 cm^{-1}. This means that a molecule of ligand II is always accompanied by a triethylammonium ion, in all the complexes (III–VI), and suggests a similar arrangement of both moieties, like that observed in the copper complex III. We will therefore use L' as abbreviation for the ligand L(NEt$_3$H) formed by addition of triethylammonium to double deprotonated II (=L) and formulate all complexes as dimeric.

Solution Properties of the Complexes. The solubility of the complexes III–VI varies much, depending on the metal; solvents with high coordination ability can lead to complete decomposition. On the other hand, the cobalt complex (V) decomposes on attempted dissolution in chloroform or dichloromethane; it immediately changes its color to pink. Thus, different solvents had to be employed for obtaining NMR spectra and electrochemical data. The copper(II) complex (III), the iron(III) complex (IV), and the cobalt(II) complex (V) are paramagnetic and therefore more difficult to analyze by NMR. By COSY, it was, however, possible to assign most of the ^{1}H NMR signals, except where severe signal overlap occurred. The results are shown in Table V. In the case of the copper complex (III), a ^{13}C NMR spectrum could be obtained and assigned by polarization transfer experiments and comparison of isotropic shifts and line widths of the signals; for nonaromatic ligands in Cu(II) complexes, the spin density is localized at the metal and therefore allows such assignments.[27]

In the diamagnetic rhenium complex (VI), the chemical shifts and coupling constants are almost the same as in the free ligand; greater deviations are observed only for the hydrogens at the carbon atoms 2 and 3 directly linked to the nitrogen and oxygen donor atoms ($\Delta\delta \leq 0.3$ ppm) (for the numbering of atoms in the chiral ligand used in Table V, see Figure 1). A typical observation is the nonequivalency of the two hydrogen atoms on C$_8$

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Table V. ¹H NMR Data of the Compounds II–VI[a]

compd	2	3	4	5	6	8	9, 10	others
II[b]	3.44 (dd, $J = 7.2$ Hz, $J = 9.3$ Hz)	4.25 (dd, $J = 4,4$ Hz, $J = 7.2$ Hz)	1.95 (d, $J = 4.4$ Hz)	1.15 (m, *endo*); 1.90 (m, *exo*)	1.30 (m, *endo*); 1.85 (m, *exo*)	3.20 (s)	0.90 (*anti*); 1.29 (*syn*)	3.09 (d, $J = 4.4$ Hz, OH); 4.96 (d, $J = 9.3$ Hz, NH)
III[b,d]	4.86	6.31		0.5–1.8 (5H)[e]		3.72	1.10; ~1.45[e]	1.45; 3.13 (NEt₃); 9.66 (NH)
IV[b,d]	~4.50[e]	~4.65[e]	2.15	0.9–1.6 (4H)[e]		3.61	1.01; ~1.40[e]	1.40; 3.25 (NEt₃); 1.97; 4.65 (THF)
V[c,d]	3.78	4.67	2.30	1.3–1.9 (4H)[e]		3.55; 3.60[e]	1.35; 1.73	1.57; 3.60[e] (NEt₃); 2.48 (H₂O)
VI[b]	3.63 (d, $J = 7.5$ Hz)	4.53 (d, $J = 7.5$ Hz)	2.13 (d, $J = 6.4$ Hz)	1.13 (m, 2H); 1.75 (m, 2H)		3.18 (d, 1H, $J = 14.6$ Hz); ~3.1 (1H)[e]	0.55; 0.73	1.35 (tr, 18H); 3.12 (qu, 12 H, $J = 7.4$ Hz)

[a] For the numbering of atoms in the chiral ligand, see Figure 1. [b] In CDCl₃. [c] In acetone-d_6. [d] Paramagnetic; all signals are broad and without structure. [e] Overlap with other signals.

Table VI. Cyclic Voltammetry Data for the Compounds II–VI, Potentials Quoted Relative to sce

compound	solvent	reductions [E_p (V)]	oxidations [E_p (V)]
II	CH₂Cl₂	–1.58	
III	CH₂Cl₂	–1.13	1.01
IV	THF	–0.09,[a] –0.95	1.03
V	CH₃CN	–1.04	1.03
VI	CH₃CN	–0.92	0.56;[a] 1.04

[a] Reversible ($E_{1/2}$ quoted).

(neighboring the SO₂ group) which appear as two distinct doublets with a coupling constant of 12–15 Hz in different complexes, while they are degenerate in the free ligand (singlet). This behavior was first observed in aluminum and titanium complexes of II,[12] and can be attributed to restricted rotations due to chelate formation. A small quantity (~10%) of free ligand can be detected in the NMR spectra of all the complexes after some time, which we think is due to decomposition by a kind of acid/base equilibrium. The observation of this equilibrium explains the difficulties in recrystallizing the complexes, as there is not only a partial liberation of free ligand but also a stoichiometric quantity of triethylammonium ion drawn away from coordinated II which further destabilizes the complexes. The cobalt complex (V) is most sensitive toward solvents; even in acetone, it decomposes after about 30 min, and the ¹³C NMR spectrum shows only free ligand, but no signals of the complex.

The electrochemical behavior of the free ligand II and the complexes III–VI was studied by cyclic voltammetry at a platinum electrode using 0.2 M solutions of NBu₄BF₄ in the appropriate solvent (acetonitrile for V and THF for IV, as these complexes are not sufficiently stable in dichloromethane used for the other complexes). The potentials are quoted relative to standard calomel electrode (sce) and were measured with ferrocene as internal standard ($E^{ox}_{1/2}$ = 0.545 V) (see Table VI).

In spite of the different metals present in the complexes, III–VI display an irreversible oxidation wave at potentials of 1.01–1.04 V, which we attribute to the oxidation of triethylamine (free triethylamine is oxidized at 1.11 V under the same conditions). The cationic character of the triethylammonium salt is obviously reduced considerably by hydrogen bonding, which accounts for the lower oxidation potential. The free ligand II does not show any oxidations within the potential limits observed. At the Re-(III) center in VI, a reversible oxidation wave at $E^{ox}_{1/2}$ = 0.56 V is observed which we attribute to the Re(III) → Re(IV) process. Upon oxidation at a potential above that of the triethylamine, this wave loses its reversibility, a fact which points to fast decomposition of the complex after the second electron transfer process. This is probably due to proton loss of the triethylammonium ion. No oxidation processes based on the metal sites could be detected in the complexes III–V, which is due to the relatively high oxidation state of the metal. Irreversible reduction of all the complexes occurred within a potential range of –0.92 to –1.13 V. The free ligand II shows an irreversible reduction too, but at much lower potential (E_p = –1.58 V), which we assign to the reduction of the sulfonamide group. The corresponding reduction process in the complexes III–VI is shifted to lower potentials as a consequence of coordination to the metal centers and could therefore not be detected within the limit of the potential. To get further insight in the nature of the irreversible reductions in the complexes III and IV, controlled potential electrolysis was performed at the corresponding cathodic waves. In the case of the copper complex (III), a one-electron reduction process was observed, in agreement with the formation of a mixed valence Cu(I)–Cu(II) species. Cyclic voltammetry performed on the electrolyzed solution shows a new reversible reduction wave at $E_{1/2}$ = –0.71 V, but the new species could not be isolated from the solution after electrolysis. In the iron(III) complex (IV), two reduction waves are observed. The first corresponds to a reversible electron transfer process occurring at ($E^{red}_{1/2}$ = –0.09 V) and is

attributed to the formation of a mixed valence Fe(II)-Fe(III) species. The other is an irreversible reduction process occurring at lower potential ($E^{red}_{1/2}$ = -0.95 V) which is believed to correspond to the formation of the Fe(II)-Fe(II) dimer. Controlled potential electrolysis of the Re(III) complex (VI) shows that four electrons per mole are involved in the reduction process in agreement with the generation of a Re(I) species. Mixed valence species have been identified through electrochemical studies to be formed, upon electron transfer, in dimeric copper complexes[28,29] and other metal sites.[30]

Conclusion

As ligand II has been successfully employed for the synthesis of chiral Lewis acids with aluminum and titanium, the question arises if the new complexes could have applications in synthesis. Due to the presence of the triethylammonium ion and the acid/base equilibrium discussed above, their use as chiral Lewis acids does not seem promising, and we found that III does indeed not catalyze Diels-Alder reactions. On the other hand, dinuclear

copper(II) complexes have been found to act as oxidation catalysts, e.g. for the oxidation of phosphines, sulfides, and alkenes. However, catalytic activity has been observed only in compounds where the Cu···Cu distance exceeds a limit of about 3 Å,[31] while the value found in III is only 2.989 Å. In preliminary experiments on oxidations of sulfides and triphenylphosphine with molecular oxygen, III did not show any catalytic activity. The potential of the other complexes for catalysis still remains to be explored.

Supplementary Material Available: Tables listing full crystallographic data, atomic displacement parameters, hydrogen atomic coordinates, bond lengths and angles, hydrogen angles, and a figure showing in detail the hydrogen bond interaction described in the text (9 pages). Ordering information is given on any current masthead page.

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