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Reactions of Coordinated Molecules. 39. Crystal and Molecular Structure of a Rhena β-Keto Iminato Complex of Boron

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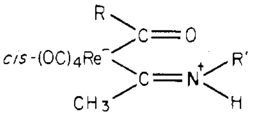
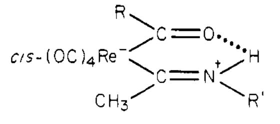
The rhena β-keto iminato complex $[cis\text{-}(OC)_4Re(CH_3CO)(CH_3CNH)]B(Cl)(Ph)$ crystallizes in the triclinic space group $P\bar{1}$ with a = 11.138 (2) Å, b = 12.348 (2) Å, c = 6.823 (2) Å, α = 103.76 (2)°, β = 103.71 (2)°, γ = 103.99 (2)°, V = 840.2 Å^3, and Z = 2. The coordination of the rhena β-keto iminato moiety to boron as a bidentate, chelating ligand is confirmed. Unlike the neutral rhena β-keto iminato compounds that show a localized zwitterionic structure, this rhena β-keto iminato ligand has an apparently delocalized π-electron structure within the rhena chelate ring.

Introduction

In recent years, we have reported the synthesis and characterization of numerous rhena β-keto imines.[2-8] These molecules exist as two geometrical isomers, which are referred to as *inter* or *intra* isomers, **1** and **2**, respectively, depending



1, *inter* isomer

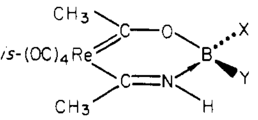


2, *intra* isomer

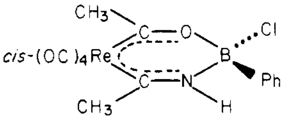
on the type of N–H···O hydrogen bonding observed. The X-ray structures of two rhena β-keto imines as the *inter* isomers revealed a chain network of normal N–H···O hydrogen bonding and, more unexpectedly, a nearly localized zwitterionic electronic structure, as shown in **1**.[2,5] These complexes contain essentially isolated acetyl and iminium ligands coordinated to rhenium instead of the "eneamine" structure observed for organic β-keto imines.

In contrast to the structures of these *inter* isomers, much of our reported spectroscopic data for the *intra* isomers, **2**, indicate that these isomers might have a more delocalized π-electron system throughout the rhena β-keto imine portion of the complex. Presumably, intramolecular hydrogen bonding might facilitate a more delocalized electronic structure. Confirmation of this fact has been quite difficult because nearly all of the *intra* isomers are oils at room temperature.

Recently, we prepared a series of boron complexes having rhena β-keto iminato ligands, **3**, where X and Y are Cl, Br,



3



4

and I, or X = Cl and Y = Ph.[9] An X-ray structural study of this latter complex, **4**, is now reported. This structure reveals that the rhena β-keto iminato moiety does act as a nearly symmetrical bidentate, chelating ligand to boron as do metalla β-diketonato ligands.[10-13] Furthermore, because the B-(Cl)(Ph)$^+$ moiety occupies a coordination position similar to that presumed for the N–H proton in the *intra* isomers **2**, the observed delocalized π-electron structure of **4** tends to support the postulated delocalized structure of the *intra* rhena β-keto imines where intramolecular hydrogen bonding forms a six-membered ring, also.

Table I. Summary of X-ray Crystallographic Data for Complex 4

lattice consts: a = 11.138 (2) Å, b = 12.348 (2) Å, c = 6.823 (2) Å, α = 103.76 (2)°, β = 103.71 (2)°, γ = 103.99 (2)°
radiation: $\lambda(\text{Mo K}\alpha_1)$ = 0.709 26 Å (cell const), $\lambda(\text{Mo K}\alpha)$ = 0.710 10 Å (data colln)
temp: 20 °C
filters: 4-foil Nb for 2θ = 0–11°; 2-foil Nb for 2θ = 11–55°
cryst dimens: 0.6 × 0.3 × 0.3 mm
abs coeff: μ = 75.1 cm^{-1}
transmissn factors: range = 0.0888 to 0.1687; av = 0.1361
abs cor: numerical integration, 8 × 8 × 8 Gaussian grid
diffractometer: four-circle, computer-controlled Picker with Picker FACS-I control software
scan technique: 2θ, step-scan, 13 steps/reflcn
range in 2θ: 1–55°
octants colled: $\pm h, \pm k, \pm l$
no. of reflcns colled: 8365 (3865 indep)
intens loss: 17% over 93 h of exposure
soln: sharpened, origin-removed Patterson map; successive difference maps
final R factors: R = 5.5%;
$R_w = [[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2]^{1/2}$ = 6.2%

Experimental Section

A summary of the principal X-ray crystallographic data is provided in Table I. A pale yellow crystal of **4** was mounted in a glass capillary. A series of precession photographs indicated only $\bar{1}$ symmetry. The assignment of the triclinic space group $P\bar{1}$ is supported by the successful completion of the structure determination. Data collection software for the Picker FACS-I system[14] and the ORABS program[15] used for adsorption corrections have been reported elsewhere. Atomic scattering factors for neutral atoms were those tabulated by Cromer and Mann,[16] and anomalous scattering factors were those given by Cromer and Liberman.[17] The average and maximum shift-to-error ratios for the final refinement cycle were 0.01 and 0.20. A final difference synthesis revealed only relatively large regions of residual electron density that could be assigned to scattering from the rhenium atom. The maximum and minimum electron densities were +3.4 and −3.7 e Å^{-3} located

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Table II. Final Positional Parameters[a] for [*cis*-(OC)$_4$Re(CH$_3$CO)(CH$_3$CNH)]B(Cl)(Ph) (4)

atom[b]	*x*	*y*	*z*
Re	0.07593 (3)	0.22312 (2)	0.31999 (5)
O(1)	0.1273 (9)	0.0010 (6)	0.4151 (15)
O(2)	0.1717 (8)	0.1602 (6)	−0.0718 (13)
O(3)	−0.2093 (7)	0.0791 (7)	0.0354 (16)
O(4)	−0.0142 (8)	0.2827 (6)	0.7215 (12)
O(5)	0.1333 (5)	0.4783 (5)	0.3108 (10)
N	0.3262 (5)	0.4327 (5)	0.5032 (11)
B	0.2790 (9)	0.5042 (8)	0.3736 (17)
Cl	0.3143 (3)	0.4625 (2)	0.1149 (4)
C(1)	0.1095 (9)	0.0821 (8)	0.3761 (16)
C(2)	0.1376 (9)	0.1866 (7)	0.0688 (15)
C(3)	−0.1031 (10)	0.1281 (8)	0.1450 (17)
C(4)	0.0191 (8)	0.2611 (7)	0.5780 (15)
C(5)	0.0454 (7)	0.3800 (7)	0.2744 (13)
C(6)	0.2689 (8)	0.3318 (7)	0.5034 (13)
C(7)	−0.0875 (8)	0.3892 (8)	0.1983 (19)
C(8)	0.3585 (9)	0.2882 (9)	0.6486 (17)
C(9)	0.3457 (8)	0.6413 (7)	0.5002 (15)
C(10)	0.3262 (11)	0.7248 (9)	0.4058 (21)
C(11)	0.3815 (12)	0.8452 (9)	0.5135 (22)
C(12)	0.4587 (13)	0.8824 (9)	0.7181 (22)
C(13)	0.4804 (13)	0.8025 (10)	0.8159 (19)
C(14)	0.4214 (12)	0.6828 (10)	0.7102 (17)
H(71)	−0.133	0.336	0.048
H(72)	−0.141	0.364	0.290
H(73)	−0.082	0.472	0.205
H(81)	0.320 (11)	0.258 (9)	0.750 (18)
H(82)	0.381 (13)	0.213 (11)	0.607 (21)
H(83)	0.444 (12)	0.354 (10)	0.737 (19)
H(9)	0.408	0.467	0.596
H(10)	0.297 (14)	0.707 (12)	0.277 (22)
H(11)	0.364	0.904	0.437
H(12)	0.499	0.969	0.798
H(13)	0.540	0.829	0.969
H(14)	0.440 (10)	0.633 (8)	0.751 (17)

[a] *x*, *y*, and *z* are fractional coordinates with estimated standard deviations in parentheses. Atoms H(9), H(11)–H(13), and H(71)–H(73) were not refined. [b] Hydrogen atom designations involving two digits refer to the hydrogen atom that is bonded to the carbon atom designated by the first digit or by both digits. H(9) refers to the hydrogen atom on N.

1.08 and 1.12 Å, respectively, from the rhenium atom.

The unambiguous location of atoms O(5) and NH was not clearly evident because the NH hydrogen atom was not specifically located in a difference map and intermolecular hydrogen bonding involving this hydrogen atom is not observed. However, the assignment given appears to be preferred to one involving the opposite assignment or a disordered assignment as judged by comparing residual electron densities under both assignments. Also, refinement to convergence under both assignments gave a 0.10% reduction of both *R* factors with the assignment shown.

All hydrogen atoms except H(9), H(11)–H(13), and H(71)–H(73) refined properly. A complete listing of final positional parameters is provided in Table II. The values were used before rounding to calculate the final structure factors. A complete listing of final positional and thermal parameters, least-squares planes data, and a listing of F_o and F_c values are included in the supplementary material.

Structure factor, electron density, and bond distance and angle calculations were performed with the X-RAY 67 programs[18] as implemented and updated on the Vanderbilt DEC-10 computer. Bond distance and angle values are rounded in the usual manner; however, all standard deviations are rounded to the next higher digit.

Results

An ORTEP view of **4** showing the atomic numbering scheme is shown in Figure 1. Final atomic positional parameters are provided in Table II. Selected interatomic distances and angles are presented in Table III.

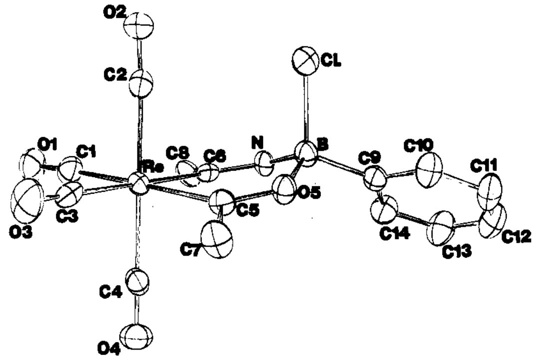

Figure 1. ORTEP view of [*cis*-(OC)$_4$Re(CH$_3$CO)(CH$_3$CNH)]B(Cl)(Ph) (**4**) showing the atomic numbering scheme (thermal ellipsoids at 30% probability). Hydrogen atoms are not shown for clarity.

Table III. Selected Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations for [*cis*-(CO)$_4$Re(CH$_3$CO)(CH$_3$CNH)]B(Cl)(Ph) (4)

	Interatomic Distances		
Re–C(1)	1.97 (2)	C(5)–C(7)	1.49 (2)
Re–C(2)	1.99 (2)	C(6)–C(8)	1.52 (2)
Re–C(3)	1.963 (9)	B–N	1.49 (2)
Re–C(4)	2.00 (2)	B–O(5)	1.51 (2)
Re–C(5)	2.126 (9)	B–Cl	1.88 (2)
Re–C(6)	2.125 (7)	B–C(9)	1.60 (2)
C(1)–O(1)	1.15 (2)	C(9)–C(10)	1.37 (2)
C(2)–O(2)	1.12 (2)	C(10)–C(11)	1.40 (2)
C(3)–O(3)	1.16 (2)	C(11)–C(12)	1.36 (2)
C(4)–O(4)	1.12 (2)	C(12)–C(13)	1.35 (2)
C(5)–O(5)	1.289 (9)	C(13)–C(14)	1.39 (2)
C(6)–N	1.26 (1)	C(14)–C(9)	1.38 (2)
	Interatomic Angles		
C(1)–Re–C(5)	173.3 (4)	Re–C(6)–N	127.6 (7)
C(2)–Re–C(4)	178.4 (4)	Re–C(6)–C(8)	120.9 (6)
C(3)–Re–C(6)	177.5 (5)	C(7)–C(5)–O(5)	110.8 (8)
C(1)–Re–C(2)	88.0 (5)	C(8)–C(6)–N	111.4 (7)
C(1)–Re–C(3)	89.9 (4)	C(5)–O(5)–B	127.9 (8)
C(1)–Re–C(4)	91.5 (5)	C(6)–N–B	129.3 (7)
C(1)–Re–C(6)	92.5 (4)	N–B–Cl	108.3 (7)
C(2)–Re–C(3)	90.6 (5)	N–B–O(5)	113.2 (8)
C(2)–Re–C(5)	93.6 (4)	N–B–C(9)	110.6 (7)
C(2)–Re–C(6)	88.8 (4)	O(5)–B–Cl	104.6 (6)
C(3)–Re–C(4)	91.0 (5)	O(5)–B–C(9)	108.1 (8)
C(3)–Re–C(5)	92.3 (4)	Cl–B–C(9)	112.0 (8)
C(4)–Re–C(5)	86.9 (4)	B–C(9)–C(10)	121.2 (9)
C(4)–Re–C(6)	89.7 (4)	B–C(9)–C(14)	123.0 (1)
C(5)–Re–C(6)	85.4 (3)	C(9)–C(10)–C(11)	122 (2)
Re–C(1)–O(1)	177 (2)	C(10)–C(11)–C(12)	120 (2)
Re–C(2)–O(2)	176.3 (2)	C(11)–C(12)–C(13)	120 (1)
Re–C(3)–O(3)	175 (2)	C(12)–C(13)–C(14)	121 (2)
Re–C(4)–O(4)	179.1 (9)	C(13)–C(14)–C(9)	122 (2)
Re–C(5)–O(5)	127.1 (6)	C(14)–C(9)–C(10)	116.1 (9)
Re–C(5)–C(7)	122.1 (6)		

The structure of the (OC)$_4$Re moiety is as expected for a *cis*-L$_2$Re(CO)$_4$ complex. The average values of the Re–C and C–O distances and the Re–C–O angles for the four terminal CO ligands are 1.98 (2) Å, 1.14 (2) Å, and 177 (2)°. The average value of the three angles defining the principal coordination axes about the Re atom is 177.4 (4)°. The average value of the C–Re–C angles between adjacent ligands is 90.0 (4)°.

The rhena β-keto iminato ligand is bonded to the boron atom as a bidentate, chelating ligand. The structure of this chelate ring is nearly symmetrical within an ca. $\pm 1\sigma$ confidence limit as determined by comparing related pairs of intraring bond distances. Similarly, a plane defined by [Re, B, C(9)] essentially bisects the chelate ring such that the corresponding

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[18] Stewart, J. M. "X-Ray 67 Program System for X-Ray Crystallography for the Univac 1108, CDC 3600/6600, IBM 360/50, 65, 75, IBM 7094", Technical Report TR-67-58; Computer Science Center, University of Maryland: College Park, MD, 1967.

pairs of atoms C(5), C(6) and N, O(5) are both equidistant from this plane to within 0.01 Å.

The average values of the two Re–C(acyl) distances, the C(5)–O(5) and C(6)–N distances, and the N–B and O(5)–B distances are 2.126 (8), 1.28 (1), and 1.50 (2) Å, respectively. The average value of the two C(acyl)–C(methyl) distances are 1.50 (2) Å, which is as expected for a $C(sp^2)$–$C(sp^3)$ single-bond distance. The sum of the angles about each atom C(5), C(6), and C(9) is 360.0 ± 0.3° and thus indicates planar hybridization about these atoms.

The boron atom has a pseudotetrahedral coordination geometry with an average value of 109.5 (7)° for angles between adjacent ligand donor atoms. The B–Cl and B–C(9) distances are 1.88 (2) Å and 1.60 (2) Å, respectively. The geometry of the phenyl group is quite normal. The average values for the intraring C–C distances and internal angles are 1.38 (2) Å and 120 (2)°, respectively. The largest atomic deviation from a plane defined by [C(9), C(10), C(11), C(12), C(13), C(14)] is 0.02 Å for C(14). The sum of the internal angles of the phenyl ring is 721°.

As is evident from Figure 1, the rhena β-keto iminato chelate ring is slightly boat shaped. The [Re, C(5), C(6)] plane and the [B, N, O(5)] plane intersect the [C(5), C(6), O(5), N] plane with obtuse angles of 167.0 and 156.5°, respectively. This type of distortion from planarity for the rhena chelate ring is observed in metalla β-diketonato complexes, also. In $[\mathit{cis}\text{-}(OC)_4\overline{Re(CH_3CO})_2]_2Cu$ (**5**)[19] and $[(\eta\text{-}C_5H_5)(OC)Fe\text{-}(\overline{CH_3CO)(\mathit{i}\text{-}PrC}\underline{O)]B}F_2$,[13] a similar boat-shaped structure for the metalla chelate ring is observed and the values of the corresponding dihedral angles in these structures are 145.1, 142.8° and 156.2, 151.8°, respectively. This ring distortion is caused presumably by internal angle strain within the metalla chelate ring.[13] As observed in these earlier structures, the methyl carbon atoms of **4**, C(7) and C(8), lie slightly below the "basal" plane defined by [C(5), C(6), O(5), N], also. In **4**, the atomic deviation for these methyl carbon atoms is ca. 0.27 Å.

Discussion

The structure of the rhena β-keto iminato chelating ligand of **4** more closely resembles that of a rhena β-diketonato ligand, as in **5**, than that of a rhena β-keto imine, as in **1**. When the chelate-ring structures of **4** and **5** are compared, the significant structural features are as follows: (1) the average Re–C(acyl) distances of **4** and **5** of 2.126 (8) and 2.152 (5) Å, respectively, are quite similar, (2) the average C(6)–N and C(5)–O(5) distance of 1.28 (1) Å in **4** is only slightly longer than the average C(acyl)–O intraring distance of 1.245 (6) Å of **5**, (3) the intraring angles centered at Re of 85.4 (3)° in **4** and 84.1 (2)° in **5** are very similar, and (4) the N···O(5) nonbonding distance in **4** is 2.501 (9) Å, while in **5** the O···O nonbonding distance of 2.783 (4) Å is only 0.28 Å larger.

By contrast, the *inter* isomers of rhena β-keto imines such as **1**, where R is methyl and R′ is Ph[2] or L-$C(CH_3)(H)CO_2Et$,[5] have a localized zwitterionic structure, as shown. The characteristic comparative features of these structures are (1) considerably longer Re–C(acetyl) distances of ca. 2.22 (2) Å and (2) shorter C(acetyl)–O distances of ca. 1.20 (2) Å. For these reasons, complex **4** is described best as having a π-delocalized structure, as shown, like the chelate rings of metalla β-diketonato complexes, rather than a formally localized structure as shown in **3**.

On the basis of a similar degree of anisochronism between the ^1H NMR resonances of the methyl substituents of the (rhena β-keto iminato)B(X)(Y) complexes and those of the methyl substituents of the *intra* isomers of rhena β-keto imines, the rhena ligand structures of these two classes of molecules are presumably very similar and yet significantly different from the localized zwitterionic structures of the rhena β-keto imine *inter* isomers.[3,9] The structural characterization of **4** provides the first example of an essentially delocalized rhena β-keto iminato ligand moiety.

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Registry No. **4**, 80720-94-1.

Supplementary Material Available: Complete listings of final positional and thermal parameters, least-squares planes data, and final observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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