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Preparation and crystal structure of (2,2'-bibenzimidazole)dihalobis(triphenylphospine)rhenium(III) halides

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Abstract

The reaction of ReOX₃(PPh₃)₂ (where X = Cl, Br) with 2,2'-bibenzimidazole (bibzimH₂) in the presence of excess PPh₃ yields the rhenium(III) cationic complexes [ReX₂(PPh₃)₂(bibzimH₂)]X, in which the phosphines are *trans* to one another, whereas the plane perpendicular to this direction includes the chelating bidentate bibzimH₂ and two *cis* halogen ligands. The third halogen is a halide counter-ion, attached to the complex cation via a pair of N–H···X⁻ hydrogen bonds involving the two N–H groups of bibzimH₂. Crystallographic work on the chloro compound indicates that the departure from octahedral geometry is controlled by the bite of the bibzimH₂ ligand and that the presence of the phenylene groups does not introduce substantial steric hindrance. Despite the fact that the species is paramagnetic, the ¹H NMR spectra were fully assigned.

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Keywords: Rhenium; Benzimidazole; Bibenzimidazole; Crystal structure; Paramagnetic NMR

1. Introduction

In the recent years, our laboratory has become interested in the complexation of 2,2'-biimidazole (biimH₂, Scheme 1) to various metal centers. In the formally neutral form, two nitrogen donors in coplanar rings can adopt a syn orientation leading to chelates similar to those of bipyridine. However, biimH₂ differs from bipyridine by the presence of five-membered rings, which change the bite angle for chelate formation and allow for more conformational freedom about the connecting C2-C2' bond, thereby leading to oligometric or polymeric structures [1–3]. In both cases, the residual N– H bonds generate in the crystal particular hydrogenbond patterns from which supramolecular assemblies can be constructed. Extra structural features appear when biimidazole coordinates in the monoanionic form, since one of the uncoordinated nitrogens is protonated

and the other is not. Hydrogen bonding then takes place with donors, acceptors, or more interestingly, with units containing one of each, including monodeprotonated biimidazolate itself, which gives access to an enlarged variety of patterns for crystal engineering. This versatility is well illustrated by the series of compounds reported by Takodoro et al. [4–7]. Finally, fully deprotonated dianionic biimidazolate can behave as a bis-bidentate/chelating unit like the oxalate dianion and link two metal centers into larger building blocks [8–10] that could be considered in the development of molecular devices [11,12].

In our previous contributions [13,14], we reported that the Re(V) precursors ReOX₃(PPh₃)₂ and Re-O(OEt)X₂(PPh₃)₂ are reduced cleanly by PPh₃ in the presence of biimH₂, giving good yields of the rhenium(III) cationic complexes *cis,trans*-[ReX₂(PPh₃)₂(biimH₂)]X with X = Cl, Br and I. The residual N–H protons of coordinated biimH₂ were found to be moderately acidic and to participate in strong hydrogen-bonding interactions, leading to tight ion pairs with halide or carboxylate counter-ions. By using the smaller phosphine PMe₃, neutral complexes containing monodeprotonated

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biimidazole could be isolated as dimers assembled by a pair of complementary N–H···N hydrogen bonds. This study is being extended here to 2,2-bibenzimidazole (bibzimH₂, Scheme 2), in which the presence of phenylene units opens a number of possibilities for ligand tuning via substitution on the ring. We wish to report the preparation and structural characterization of the compounds $[ReX_2(PPh_3)_2(bibzimH_2)]X$, which show that the extra phenylene rings do not introduce appreciable steric or other undesirable effects and that the chemistry of the Re(III)-biimH₂ systems is applicable to the bulkier bibzimH₂ system.

Scheme 2.

2. Experimental

2.1. Reactants and methods

 $KReO_4$ and all other reactants were obtained from Aldrich and used without further purification. Re- $OCl_3(PPh_3)_2$ [15] and $ReOBr_3(PPh_3)_2$ [16] were prepared by literature methods. Deuterated solvents were purchased from Aldrich or CDN Isotopes.

The NMR spectra were measured with Bruker ARX-400 or AMX-300 spectrometers. For the ¹H spectra, the residual solvent signals (DMSO-d₆, 2.50 ppm; CDCl₃, 7.26 ppm) were used as internal references and the chemical shifts are expressed in ppm versus SiMe₄. Electronic spectra were recorded as CHCl₃ solutions in quartz cells with a UV–Vis–NIR Cary 5E spectrometer. FAB⁺ mass spectra in NBA were measured at the Centre de Spectrométrie de Masse de l'Université de Montréal. Elemental analyses were run at the Laboratoire d'Analyse Élémentaire de l'Université de Montréal.

2.2. Preparation of the ligand

2,2'-Bibenzimidazole was prepared as described by Fieselmann et al. [17]. In our hands, the purification by recrystallization from ethylene glycol was not totally

efficient and an extra purification step was introduced. The yellow solid was dissolved in boiling NaOH, 0.25 M, and refluxed for 2 days. Some insoluble material was filtered off and the dark-brown solution was neutralized with concentrated HCl. The light-violet solid was filtered, transferred into water and refluxed for 1 h to remove any ionic form of the molecule. Finally, the solid was filtered, washed with water, ethanol and diethyl ether, and dried in air. Yield: 24%.

2.3. Preparation of $[ReX_2(PPh_3)_2(bibzimH_2)]X$

A suspension of PPh₃ (0.238 g; 0.91 mmol) and bibzimiH₂ (0.123 g; 0.52 mmol) in 40 mL CHCl₃ is heated to the boiling point, and ReOCl₃(PPh₃)₂ (0.354 g; 0.42 mmol) is added. The lime-green solution darkens quickly and the mixture is refluxed for 2.5 h. It is filtered hot and evaporation of the resulting dark-red solution yields a sticky dark-red material. Upon dropwise addition of diethyl ether, a red powder is obtained, which is filtered and washed with diethyl ether. Crystals of the solvent-free material are obtained by slow diffusion of diethyl ether into a CH₂Cl₂ solution.

2.3.1. $[ReCl_2(PPh_3)_2(bibzimH_2)]Cl$

Yield: 77%. ¹H NMR (CDCl₃): see text. MS FAB⁺ (*m*/*z*): 1014 [M]⁺, 752 [M – PPh₃]⁺, 717 [M – PPh₃ – Cl]⁺. UV–Vis (λ (nm) (ε (M⁻¹ cm⁻¹)): 558 (670), 522 (675), 469 (1350), 434 (1400), 404 (1200), 360 (8700), 341 (8750), 330 (6500). Composition was determined by X-ray diffraction on a crystal picked up in the morphologically homogeneous sample.

2.3.2. $[ReBr_2(PPh_3)_2(bibzimH_2)]Br$

Same as above, from $ReOBr_3(PPh_3)_2$. Yield: 72%. Anal. Calc. for $C_{50}H_{40}Br_3N_4P_2Re$: C, 50.69; H, 3.40; N, 4.73. Found: C, 50.94; H, 3.42; N, 4.72%. ¹H NMR (CDCl₃): see text. MS FAB⁺ (*m*/*z*): 1102 [M]⁺, 843 [M – PPh₃]⁺, 762 [M – PPh₃-Br]⁺.

2.4. X-ray diffraction study

To grow the crystals used for X-ray work, the powder was placed in a vial and covered with acetone, the vial was closed tightly and left at room temperature for a few days. The powder dissolved slowly and reprecipitated as less soluble red blocks of the solvate *cis*-[ReCl₂(PPh₃)₂-(bibzimH₂)]Cl·3(CH₃)₂CO. The X-ray data were collected with a Bruker Smart 2K CCD diffractometer using the graphite-monochromatized Cu K α radiation, as described elsewhere [18]. The data were interpreted with the SHELXTL software [19]. The XPREP procedure [20] was used to apply an absorption correction based on crystal morphology. The non-hydrogen atoms were generally refined anisotropically. The hydrogens were first placed at idealized positions and allowed to ride

Table 1 Crystal data for [ReCl₂(PPh₃)₂(bibzimH₂)]Cl · 3(CH₃)₂CO

Formula	C H CINOPPo
Formula	$C_{591158}C_{131N4}O_{3}\Gamma_{2}Kc$
Formula weight	1225.58
$T(\mathbf{K})$	220(2)
Diffractometer	Bruker Smart CCD 2K
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
a (Å)	14.4209(2)
b (Å)	23.6633(4)
<i>c</i> (Å)	16.7633(2)
β (deg)	94.860(1)
Volume (Å ³)	5699.8(1)
Z	4
$d_{\rm calc}$ (g/cm ³)	1.428
Reflection cell parameters	50 312
Crystal dimensions (mm)	0.16 imes 0.26 imes 0.38
Radiation (λ, \mathbf{A})	Cu Ka (1.54178)
$\mu ({\rm cm}^{-1})$	63.60
Transmission range	0.185-0.361
Reflections measured	68 21 5
Reflections independent	11165 ($R_{int} = 0.07$)
Reflections observed $(I > 2\sigma)$	9843
R^* $(I > 2\sigma)$	0.0555
wR_2^* $(I > 2\sigma)$	0.1582
$S^*(I > 2\sigma)$	1.076
$^{*}R = \sum F_{o} - F_{c} / \sum F_{o} , wR_{2}$	$= \{\sum [w(F_{0}^{2} - F_{c}^{2})^{2}] / \sum w(F_{0}^{2})^{2}\}^{1/2},\$
$S = \{\sum [w(F_{o}^2 - F_{c}^2)^2] / (N_{obs} - N_{part})\}$	$am)\}^{1/2}$.

on the supporting atom. No disorder was detected in the $[\text{ReCl}_2(\text{PPh}_3)_2(\text{bibzimH}_2)]^+$ unit, but the chloride counter-ion and the three acetone molecules of the asymmetric unit were disordered. Each of these acetone sites was modeled with three different sets of positions. The FLAT option was used to keep the molecule planar, whereas constraints were applied on interatomic distances, based on the average data for solvate acetone in the Cambridge Crystallographic Database [21] [C=O, 1.21 Å; C–CH₃, 1.47 Å; O···CH₃, 2.33 Å; CH₃···CH₃, 2.51 Å]. A very small tolerance on the distances had to be applied to stabilize the refinement. The occupancies were first refined with a constraint applied to normalize their sum to unity, then they were rounded off to the nearest 0.05 and fixed (0.60/0.20/0.20) for the rest of the refinement. The chloride ion was described by means of two positions located on each side of the plane through bibzimH₂. These positions were initially refined separately, then simultaneously. The occupancies were refined as above and fixed (0.60/0.40) in the last least-squares

cycles. The final R factor of 0.055 is considered to be satisfactory, considering the severe disorder present in the structure. The crystal data are collected in Table 1.

A data set was also collected on red plates of the solvent-free complex salt, grown by slow diffusion of diethyl ether into a saturated CH₂Cl₂ solution of the raw material. These crystals belong to space group *Pbca*, with a = 11.199, b = 23.455, c = 34.567 Å and Z = 8 molecules per cell. The complex showed the same structure as the Tris–acetone solvate, except for a two-fold orientation disorder around the Re–P bond for one of the PPh₃ ligands. Because of disorder and poor crystal quality, the *R* factor could not be reduced below of 0.12. No further efforts were devoted to this material, since better crystals of the solvate had become available in the meantime.

3. Results and discussion

Good yields of the bromo and chloro complexes $[\text{ReX}_2(\text{PPh}_3)_2(\text{bibzimH}_2)]X$ are obtained by heating $\text{ReOX}_3(\text{PPh}_3)_2$ and bibenzimidazole in CHCl₃ in the presence of excess PPh₃ (Scheme 3). Infrared spectra confirm the presence of PPh₃ and bibzimH₂ in the compounds. A definite proof for the structure is provided by the X-ray diffraction results discussed below. The presence of the $[\text{ReX}_2(\text{PPh}_3)_2(\text{bibzimH}_2)]^+$ ion in the solid is consistent with the FAB⁺ spectra showing the parent-ion pattern with the expected isotopic distribution, together with fragments resulting from the loss of PPh₃ and X. The good solubility in solvents like CH₂Cl₂ and CHCl₃ agrees with the presence of tight ion pairs, as noted for the biimidazole complexes [13]. The compounds were fully characterized by ¹H NMR.

In the free ligand, the two benzimidazole units connected via the C2–C2' bond are symmetry equivalent (Scheme 2). In addition, the N–H protons are involved in a fast tautomeric exchange between the ring N atoms, which renders the H_5/H_8 pair (and H_6/H_7 pair) chemically, but not magnetically, equivalent. Accordingly, only two signals are observed (AA'BB' system, Fig. 1), but they are not first order. The chemical shifts and coupling constants (Table 2) were determined from the method described by Sohar [22].



Scheme 3.



Fig. 1. ¹H NMR signals (DMSO-d₆) of the aromatic protons of free bibenzimidazole.

Table 2 1 H NMR chemical shifts (ppm) and coupling constants (Hz) of bibzimH₂ (DMSO-d₆)

7.66 ppm (m)	
7.29 ppm (m)	
7.9 Hz	
6.5 Hz	
1.3 Hz	
0.0 Hz	
	7.66 ppm (m) 7.29 ppm (m) 7.9 Hz 6.5 Hz 1.3 Hz 0.0 Hz

The low-spin d⁴ center in rhenium(III) monomers is paramagnetic. Despite this fact, the ¹H NMR spectra are relatively clean, integrations are reliable and couplings are often observed. The data for the $bibzimH_2$ complexes are collected in Table 3. The PPh₃ signals appear at the same positions as for the related complexes of biimidazole [13] and they are readily identified from multiplicities and integrations. The ortho protons, close to the metal center, undergo a considerable shift (13.3 ppm) downfield from their normal position (7–8 ppm). Since the Re–N bonds are non-labile, $bibzimH_2$ gives four C–H signals between \sim 7 and \sim 3.7 ppm (Fig. 2). In contrast with those of PPh₃, they are shifted upfield by paramagnetism. The second-order effects noted for the free ligand have now disappeared, since the signals have been shifted considerably. H₅ and H₈ appear as doublets and can be distinguished from H₆ and H_7 , which give pseudo-triplets because of couplings with two adjacent protons. One of the latter protons appears at much higher field (~ 4 ppm) than the other. Semi-empirical PM3 calculations [23] suggest that the

Table 3 1 H NMR data for the [ReX₂(PPh₃)₂(bibzimH₂)]X complexes (in CDCl₃)



Fig. 2. Signals of the coordinated bibenzimidazole protons in the ¹H NMR spectrum (CDCl₃) of $[ReCl_2(PPh_3)_2(bibzimH_2)]Cl]$. The CH₂Cl₂ signal results from residual traces of the recrystallization solvent.

orbitals containing the unpaired electrons are more concentrated on H₆ than on any other proton, whereas its neighbor H₇ is predicted to be the least affected by the unpaired electrons. Accordingly, the higher-field triplet (3.76 (Cl); 4.25 (Br) ppm) is assigned to H₆, whereas the other triplet (7.03 (Cl); 6.71 (Br) ppm) must correspond to H₇. A COSY 2D experiment for [ReBr₂(PPh₃)₂(bibzimH₂)]Br indicates proximity for the protons appearing at 6.22 and 4.25 ppm, respectively. This allows us to assign the doublet at 6.22 ppm to H₅ and the other doublet at 6.01 ppm to H₈. The acidic N–H protons give a broad peak at 4.44 (Cl) or 4.89 (Br) ppm.

3.1. Crystal structures

The [ReCl₂(PPh₃)₂(bibzimH₂)]Cl unit is shown in Fig. 3. The octahedral environment of rhenium(III) includes one non-deprotonated bidentate bibzimH₂ ligand, two phosphines *trans* to one another and two chlorines. The third chlorine is actually the counter ion forming two N-H···Cl⁻ hydrogen bonds with bibzimH₂. Selected interatomic distances and bond angles are compared with those of the biimidazole analog [13] in Table 4.

Most of the departure from octahedral coordination originates from the small bite angle $(76.7(2)^\circ)$ of bibzimH₂, which allows the opposite Re–Cl bonds to move away from each other (Cl(1)–Re–Cl(2) = 96.97(5)°). The Re–P bonds, perpendicular to the ReCl₂N₂ plane, are not exactly collinear (P(1)–Re–P(2) = 175.21(4)°), but

	[ReCl ₂ (PPh ₃) ₂ (bibzimH ₂)]Cl	[ReBr ₂ (PPh ₃) ₂ (bibzimH ₂)]Br
PPh ₃ , H _o	13.31 (d, 12H), ${}^{3}J = 7.0$ Hz	13.32 (d, 12H), ${}^{3}J = 7.1$ Hz
PPh_3, H_p	8.42 (t, 6H), ${}^{3}J = 7.1$ Hz	8.38 (t, 6H), ${}^{3}J = 7.4$ Hz
PPh_3, H_m	8.18 (t, 12H), ${}^{3}J = 7.5$ Hz	8.11 (t, 12H), ${}^{3}J = 7.6$ Hz
bibzim H_2 , H_7	7.03 (t, 2H), ${}^{3}J = 8.0 \text{ Hz}$	6.71 (t, 2H), ${}^{3}J = 8.1$ Hz
bibzimH ₂ , H ₅	6.60 (d, 2H), ${}^{3}J = 8.2$ Hz	6.22 (d, 2H), ${}^{3}J = 8.4$ Hz
bibzim H_2 , H_8	6.38 (d,2H), ${}^{3}J = 8.6$ Hz	6.01 (d, 2H), ${}^{3}J = 8.3$ Hz
bibzimH ₂ , (N)H	4.44 (s broad, 2H)	4.89 (s broad, 2H)
bibzimH ₂ , H ₆	3.76 (t, 2H), ${}^{3}J = 7.7$ Hz	4.25 (t, 2H), ${}^{3}J = 7.7$ Hz



Fig. 3. ORTEP drawing of the [ReCl₂(PPh₃)₂(bibzimH₂)]Cl ion pair. For simplicity, the carbon-bonded hydrogens are omitted.

Table 4

Selected distances (Å) and angles (deg) in the $[ReCl_2(PPh_3)_2(LH_2)]Cl$ compounds

LH ₂	bibzimH ₂	biimH ₂ [13]
Bond lengths		
Re-N(13)	2.127(4)	2.114(3)
Re-N(23)	2.145(4)	2.129(3)
Re-P(1)	2.496(1)	2.476(1)
Re-P(2)	2.494(1)	2.466(1)
Re–Cl(1)	2.360(1)	2.381(1)
Re–Cl(2)	2.369(1)	2.354(1)
Bond angles		
N(13)-Re-N(23)	76.7(2)	76.0(1)
P(1)-Re-P(2)	175.21(4)	177.24(3)
Cl(1)-Re- $Cl(2)$	96.97(5)	99.38(4)
P(1)-Re-N(13)	89.4(1)	90.8(1)
P(1)-Re-N(23)	92.3(1)	90.0(1)
P(1)-Re-Cl (1)	91.51(5)	89.98(4)
P(1)-Re-Cl(2)	88.15(5)	90.22(4)
P(2)-Re-N(13)	88.9(1)	91.0(1)
P(2)-Re-N(23)	91.7(1)	88.5(1)
P(2)-Re-Cl(1)	90.96(5)	87.93(4)
P(2)-Re-Cl(2)	87.48(5)	91.91(4)
Cl(1)-Re-N(13)	169.0(1)	173.2(1)
Cl(1)-Re-N(23)	92.3(1)	97.3(1)
Cl(2)-Re-N(13)	94.0(1)	87.3(1)
Cl(2)-Re-N(23)	170.7(1)	163.3(1)
N(11)-C(12)-C(22)	130.7(5)	133.9(4)
N(13)-C(12)-C(22)	117.0(4)	115.4(4)
N(21)-C(22)-C(12)	128.8(5)	132.5(4)
N(23)-C(22)-C(12)	117.5(4)	117.0(4)
C(12)–N(13)–Re	114.4(3)	116.5(3)
C(14)-N(13)-Re	140.1(4)	137.3(3)
C(22)–N(23)–Re	114.3(3)	115.1(3)
C(24)–N(23)–Re	140.8(3)	138.8(3)

the deviation is small. The Re–N and Re–Cl bond lengths compare well with those of the biimH₂ complex, but the Re–P bonds are ~ 0.02 longer here, probably

because the extra phenylene rings leave less space for the phosphine phenyl rings.

The two benzimidazole halves of the coordinated ligand are coplanar (dihedral angle = $1.7(3)^{\circ}$). As depicted in Fig. 4, ring closure induces in-plane distortions to improve the overlap between the metal orbitals and the ligand σ lone pairs, leading to a large difference between the N₃-C₂-C₂' and N₁-C₂-C₂' angles. In the present bibzimH₂ complex, this difference is somewhat smaller (~117° versus ~130°) than for the biimH₂ complexes (~116° versus ~133°). Thus, the phenylene rings act as bulky α substituents counteracting ligand distortion, which explains that the Cl-Re-Cl angle is smaller here (~97°) than in the biimH₂ analog (~99°).

The N–H groups form hydrogen bonds with the chloride counter-ion (Fig. 3 and Table 5). The N···Cl distances of ~3.06 Å and the N–H···Cl angles (~154°) close to linearity correspond to moderately strong interactions [24]. The reduction of ligand distortion is a favorable factor, since it allows the N···Cl distance and the N–H···Cl angle to be greater than for the biimH₂ complexes (~3.16 Å and ~147°, respectively) [13].

The phosphines are related by an approximate mirror plane. Two phenyl groups of each phosphine are positioned above (or below) the bibzimH₂ ligand, whereas the third phenyl ring is roughly parallel to the Re–P bond and the ortho hydrogen is nested between the two chloro ligands. A similar conformation has been observed for [ReCl₂(PPh₃)₂(biimH₂)]Cl [13]. However, in contrast with the latter case, there are no appreciable π interactions between the phosphine phenyl rings and those of the bibzimH₂, since these rings are not parallel (dihedral angle of 20.5° and 25.0°) and the inter-ring distances are relatively large (3.49 and 3.65 Å).

The ion pairs form columns along the unit cell b direction and the acetone solvent molecules occupy channels between these columns.



Fig. 4. Undistorted biimidazole molecule (left) and distorted coordinated ligand (right).

Table 5								
Geometry c	of the	hydrogen	bonds i	n	ReCl ₂ (I	$PPh_3)_2($	bibzimł	H_2)]Cl

	-		. –
$D - H \cdots A$	D-A (Å)	H–A (Å)	D-H-A (°)
N(11)–H(11)···Cl(31) ^a	3.000(9)	2.18	155.8
$N(21)-H(21)\cdots Cl(31)^{a}$	3.078(8)	2.27	154.3
$N(11)-H(11)\cdots Cl(32)^{a}$	3.128(9)	2.33	152.2
$N(21) – H(21) \cdot \cdot \cdot Cl(32)^a$	3.018(8)	2.21	155.0

^a Occupancies: Cl(31), 0.60; Cl(32), 0.40.

4. Conclusion

This work shows that the extra aromatic rings in $bibzimH_2$ do not preclude the formation of the [Re- $X_2(PPh_3)_2(LH_2)$]X complexes observed with biimidazole and that they introduce only small structural differences due to steric effect. Therefore, this system, with the extra advantage of tunability by substitution on the phenylene unit, could provide a valuable starting point to prepare bimetallic compounds by coordination of an extra metallic center to the external N donors.

5. Supplementary material available

Crystallographic information as a CIF file has been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 215000). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; or e-mail: deposit@ ccdc.cam.ca.uk.

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