

Preparations, Characterizations, and Structures of (Biimidazole)dihalobis(triphenylphosphine)rhenium(III) Salts: Strong Ion-Pairing and Acid–Base Properties

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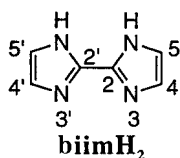
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Two-electron reduction occurs when the Re(V) precursors $\text{ReOX}_3(\text{PPh}_3)_2$ and $\text{ReO}(\text{OEt})\text{X}_2(\text{PPh}_3)_2$ are reacted with biimidazole (biimH_2) in boiling chloroform, affording rhenium(III) cationic complexes of the type *cis,trans*- $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{X}$ with $\text{X} = \text{Cl}, \text{Br},$ and I . Crystal structures are determined for the compounds with the three halogens, as well as for the $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)](\text{benzoate})$ salt. In all cases, the counterion is attached to the complex cation via hydrogen bonding with the N–H groups of coordinated biimidazole. Variable-temperature ^1H NMR spectroscopy shows that a mixture of $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)](\text{benzoate})$ and $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{Cl}$ is in slow exchange below -50°C in CD_2Cl_2 , indicating that ion pairing is retained in solution. Both N–H groups can be deprotonated with sodium methoxide, and their acidities are evaluated from UV–visible spectra. Competition between monodeprotonated $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH})]$ and various carboxylic acids reveals that the acidity of the first N–H proton corresponds to that of acetic acid ($\text{p}K_{\text{a}}(\text{aq}) \sim 4.8$). By a similar competitive reaction between bis-deprotonated $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biim})]^-$ and phenols, the second acidity is estimated to be close to that of phenol ($\text{p}K_{\text{a}}(\text{aq}) \sim 9.8$).

Introduction

Following our studies on the reactivity and optical properties of oxo–rhenium(V) compounds with imidazoles,^{1–3} the 2,2'-biimidazole (biimH_2) ligand attracted our attention as a candidate



for introducing imidazole units into a metal coordination sphere as part of a stabilizing chelate ring. However, since this ligand, once deprotonated, can act as a bis-bidentate bridge, its monomeric complexes could be used as building blocks to prepare polymetallic compounds in which the biimidazole bridge would promote communication between metal centers and eventually lead to systems showing interesting physical or catalytic properties.^{4–7}

In our previous paper on their reactivities with the phosphine-free starting materials ReOCl_4^- and $\text{ReOCl}_3(\text{OPPh}_3)(\text{SMe}_2)$,⁸

biimidazole and its *N,N'*-dimethyl derivative (biimMe_2) were noted to behave differently. $\text{ReOCl}_3(\text{N–N})$ and oxo-bridged $[\{\text{OReCl}_2(\text{N–N})\}_2(\mu\text{-O})]$ complexes were obtained together with other species, but corresponding compounds with both ligands could not be prepared systematically. Synthetic conditions differed, since biimH_2 is extremely insoluble in virtually all solvents whereas biimMe_2 is freely soluble, but these differences cannot be ascribed to solubility alone. The free N–H groups in biimH_2 complexes play a more active role in fixing halides and other anions via hydrogen bonding, while intermediates containing monodentate biimH_2 participating in intramolecular N–H \cdots X interactions are likely involved in halogen displacement from the coordination sphere.

The reactivity patterns observed with phosphine-free precursors do not hold when the reactions are carried out with $\text{ReOCl}_3(\text{PPh}_3)_2$, since the phosphine behaves as an oxygen abstractor and reduces the metal to the Re(III) state. In this paper, we describe the preparations and structures of Re(III) monomers of the type $[\text{ReX}_2(\text{PPh}_3)_2(\text{N–N})]\text{X}$, which allowed us to obtain evidence for systematic ion pairing between biimH_2 and the counteranions and to evaluate the acidity of these N–H groups.

Experimental Section

Reactants and Methods. Reagent grade KReO_4 (99%, Aldrich), PPh_3 (Omega), HI (47%, Anachemia), NaOCH_3 (25% solution in $\text{CH}_3\text{-OH}$, Aldrich), solvents, and other chemicals were used as received. Biimidazole was prepared by the method of Fiesemann et al.⁹ and recrystallized in boiling aqueous NaOH (0.25 M). The starting materials $\text{ReOCl}_3(\text{PPh}_3)_2$,¹⁰ $\text{ReOBr}_3(\text{PPh}_3)_2$,¹¹ and $\text{ReO}(\text{OEt})\text{I}_2(\text{PPh}_3)_2$ ¹² were prepared by following published procedures.

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Table 1. Crystallographic Data

compound	1·CH ₃ OH·CHCl ₃	2·H ₂ O	3·2.5CHCl ₃	4·0.5CH ₂ Cl ₂
empirical formula	C ₄₂ H ₃₆ Cl ₃ N ₄ P ₂ Re·CH ₃ OH·CHCl ₃	C ₄₂ H ₃₆ Br ₃ N ₄ P ₂ Re·H ₂ O	C ₄₂ H ₃₆ I ₃ N ₄ P ₂ Re·2.5CHCl ₃	C ₄₉ H ₄₁ Cl ₂ N ₄ O ₂ P ₂ Re·0.5CH ₂ Cl ₂
fw	1102.66	1102.64	1524.02	1079.82
<i>a</i> , Å	10.410(2)	9.342(2)	10.479(4)	32.4702(2)
<i>b</i> , Å	12.151(2)	35.955(16)	25.791(13)	9.45300(10)
<i>c</i> , Å	18.898(5)	12.825(5)	20.335(8)	30.3331(2)
α, deg	82.277(14)	90	90	90
β, deg	76.19(2)	104.28(2)	108.45(4)	90
γ, deg	82.230(13)	90	90	90
<i>V</i> , Å ³	2287.0(8)	4175(3)	5213(4)	9310.5(1)
<i>Z</i>	2	4	4	8
space group	P1 (No. 2)	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)	Pca2 ₁ (No. 29)
temp, °C	20	20	-50	20
λ(Cu Kα), Å	1.540 56	1.540 56	1.540 56	1.540 56
ρ _{calcd} , g cm ⁻³	1.601	1.754	1.942	1.540
μ, mm ⁻¹	9.31	9.92	23.03	7.55
R1 ^a (<i>I</i> > 2σ(<i>I</i>))	0.0345	0.0398	0.0591	0.0823
wR2 ^b (<i>I</i> > 2σ(<i>I</i>))	0.0920	0.0965	0.1061	0.2085

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

¹H NMR spectra were recorded in CDCl₃ or CD₂Cl₂ at 300 MHz on a Bruker AMX-300 spectrometer or at 400 MHz on a Bruker ARX-400 instrument. Residual solvent signals (CDCl₃ 7.26 ppm, CD₂Cl₂ 5.32 ppm) were used as internal standards, and the chemical shifts are reported with respect to Me₄Si. UV-visible spectra were recorded for CH₂Cl₂ solutions on a Varian Cary 5E UV-vis-NIR spectrometer or on a Varian Cary 100 Bio apparatus. For the determination of pK_a, short-path-length cylindrical cells (type 136, 0.9 or 4.2 mm) from Quaracell were used. Elemental analyses were performed at the Laboratoire d'analyse élémentaire de l'Université de Montréal. Mass spectra were recorded in the FAB⁺ mode for nitrobenzyl alcohol solutions at the Centre Régional de Spectrométrie de Masse de l'Université de Montréal. Magnetic moments were determined at the Laboratoire de Chimie de Coordination du CNRS, Toulouse, France. The measurements were made on the solid samples at 25 °C by the Faraday method, using a Cahn microbalance coupled with a Drusch electromagnet. HgCo(NCS)₄ was used as the standard ($\chi_g = 16.44 \times 10^{-6}$ cgs emu), and corrections were applied for the diamagnetism of the ligands.¹³

Preparative Work. (a) [ReCl₂(PPh₃)₂(biimH₂)]Cl (**1**). ReOCl₃·(PPh₃)₂ (1.01 g; 1.21 mmol) was suspended in 125 mL of boiling chloroform. Biimidazole (0.189 g; 1.41 mmol) and PPh₃ (0.641 g; 2.44 mmol) were then added. The solution became orange-brown immediately, but solid biimidazole had not all dissolved. After 1 h, the solution was dark orange and a very small amount of solid remained in suspension. The solution was filtered while hot and the filtrate evaporated to dryness, leading to a sticky orange solid, to which a minimum amount of chloroform was added. Excess diethyl ether was then added dropwise to precipitate an orange powder that was filtered off and washed with diethyl ether. Yield: 920 mg; 80%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of methanol vapor into a chloroform solution. ¹H NMR (CDCl₃; ppm): δ 12.97 (d, PPh₃ ortho), 8.62 (t, PPh₃ para), 8.47 (t, PPh₃ meta) (³J_{HH} = 7.6 Hz), 0.36 (s, N-H), -0.96 (s, H5), -2.86 (s, H4). ¹H NMR (CD₂Cl₂; ppm): δ 13.07 (d, PPh₃ ortho), 8.66 (t, PPh₃ para), 8.50 (t, PPh₃ meta) (³J_{HH} = 7.6 Hz), 0.65 (s, N-H), -1.18 (s, H5), -3.03 (s, H4). UV-vis (λ (nm) (ε (M⁻¹ cm⁻¹)): 441 sh (2270), 421 (2625), 347 sh (3230). Anal. Calcd for C₄₂H₃₆Cl₃N₄P₂Re·CHCl₃·CH₃OH: C, 47.93; N, 5.08; H, 3.75. Found: C, 47.71; N, 5.11; H, 3.67. MS (FAB⁺; *m/z*): 913 (M)⁺, 912 (M - H)⁺, 651 (M - PPh₃)⁺, 650 (M - H - PPh₃)⁺. μ_{eff} = 1.30 μ_B.

(b) [ReBr₂(PPh₃)₂(biimH₂)]Br (**2**). We used the same method as above starting with ReOBr₃(PPh₃)₂, leading to an impure orange powder. The sample was recrystallized by dissolution in chloroform and

dropwise addition of diethyl ether. Yield: 58%. ¹H NMR (CDCl₃; ppm): δ 13.14 (s, PPh₃ ortho), 8.67 (t, PPh₃ para), 8.45 (t, PPh₃ meta) (³J_{HH} = 7.4 Hz), 0.13 (s, b, N-H), -0.55 (s, H5), -2.95 (s, H4). UV-vis (λ (nm) (ε (M⁻¹ cm⁻¹)): 472 (2510), 422 (2880), 403 sh (2670), 330 sh (5500). Anal. Calcd for C₄₂H₃₆Br₃N₄P₂Re·CHCl₃: C, 42.90; N, 4.65; H, 3.10. Found: C, 42.90; N, 4.65; H, 3.03. MS (FAB⁺; *m/z*): 1001 (M)⁺, 1000 (M - H)⁺, 739 (M - PPh₃)⁺, 738 (M - H - PPh₃)⁺. μ_{eff} = 1.64 μ_B. Crystals of the monohydrate suitable for X-ray work were obtained by slow evaporation of a methanol-diethyl ether solution in open air.

(c) [ReI₂(PPh₃)₂(biimH₂)]I (**3**). ReO(OEt)I₂(PPh₃)₂ (451 mg; 0.44 mmol) was dissolved in 75 mL of boiling chloroform. Biimidazole (70 mg; 0.52 mmol), PPh₃ (231 mg; 0.88 mmol), and 47% HI (0.12 mL; 0.44 mmol) were then added. The solution rapidly became brown-red, and some biimidazole remained in suspension. After 1 h, the dark-red solution was filtered while hot and the filtrate evaporated to dryness. The sticky red solid was then dissolved in a minimum amount of chloroform and precipitated by adding excess diethyl ether dropwise, leading to burgundy-colored microcrystals, which were filtered off and washed with diethyl ether. Yield: 290 mg; 54%. ¹H NMR (CDCl₃; ppm): δ 13.07 (s, PPh₃ ortho), 8.67 (t, PPh₃ para), 8.33 (t, PPh₃ meta) (³J_{HH} = 7.6 Hz), 0.62 (s, H5), 0.53 (s, b, N-H), -3.39 (s, H4). UV-vis (λ (nm) (ε (M⁻¹ cm⁻¹)): 535 (3710), 466 (5260), 441 (5450), 402 (4210), 363 (4240). Anal. Calcd for C₄₂H₃₆I₃N₄P₂Re·0.5CHCl₃: C, 39.71; N, 4.36; H, 2.86. Found: C, 39.70; N, 4.27; H, 2.86. MS (FAB⁺; *m/z*): 1097 (M)⁺, 1096 (M - H)⁺, 835 (M - PPh₃)⁺, 834 (M - H - PPh₃)⁺. μ_{eff} = 1.59 μ_B. Crystals of the 2.5 CHCl₃ solvate suitable for X-ray diffraction were obtained by vapor diffusion of diethyl ether into a chloroform solution.

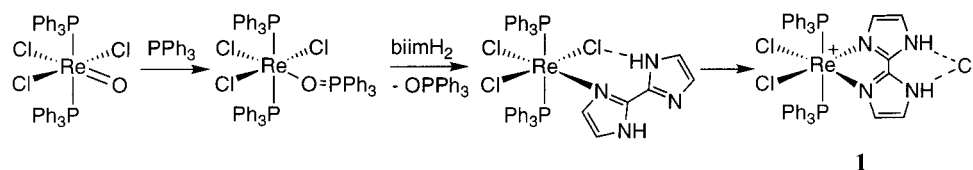
(d) [ReCl₂(PPh₃)₂(biimH₂)](benzoate) (**4**). To a solution of **1** (30 mg; 0.032 mmol) in 8 mL of CH₂Cl₂ was added 1 equiv of NaOCH₃ (1.5 mL of a 0.12% w/v solution), whereupon the solution color changed from orange to brown. One equivalent of benzoic acid was then added (0.7 mL of a 0.046 M solution in CH₂Cl₂), and the color of the solution became orange-red. The solvent was rotovaped to dryness, affording an orange solid. Crystallization by vapor diffusion of pentane into a CH₂Cl₂ solution yielded red crystals suitable for X-ray diffraction. ¹H NMR (CD₂Cl₂; ppm): δ 13.11 (d, PPh₃ ortho), 8.65 (t, PPh₃ para), 8.49 (t, PPh₃ meta) (³J_{HH} = 7.6 Hz), 7.07 (t, PhCOO para), 6.85 (m, PhCOO ortho and meta), -2.13 (s, H5), -3.82 (s, H4).

(e) [ReCl₂(PPh₃)₂(biimH₂)](carboxylate) (**4a**). Samples of salts with other carboxylates for NMR spectroscopy were prepared similarly. For UV-visible and acid-base experiments, the salts were prepared in situ. **1** (~50 mg) was dissolved in 25 mL of CH₂Cl₂ under an argon blanket, and 1 (or 2) equiv of NaOCH₃ (0.12% solution in methanol) was added to deprotonate 1 (or 2) N-H group(s) of coordinated biimH₂. One equivalent of the carboxylic acid or phenol was then added.

Crystallographic Measurements and Structure Determinations. The crystal data for the four compounds are collected in Table 1. Crystals of **1-3** were glued to glass fibers that were then mounted on

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Scheme 1



1

an Enraf-Nonius CAD-4 diffractometer. Preliminary search of an axial photograph yielded a reduced triclinic cell.¹⁴ Monoclinic cells were defined for **2** and **3** on the basis of the Niggli parameters. Laue symmetry was eventually checked from the full data set. All data in the entire sphere were collected for each of the three compounds, corrected for absorption, and averaged¹⁵ to provide the basic four- (**1**) or two-octant (**2** and **3**) data sets. The space group $P2_1/c$ was uniquely defined from the systematic absences for **2** and **3**. The structure of **1** was solved and refined normally in the centric space group $P\bar{1}$.

A crystal of **4** mounted on a glass fiber was studied with a Bruker diffractometer, equipped with a SMART 2K CCD area detector. Graphite-monochromatized Cu $K\alpha$ radiation was generated from a normal-focus sealed tube. The crystal-to-detector distance was 4.908 cm, and the data were collected under the control of SMART software¹⁶ in the 512×512 pixel mode with 4×4 pixel binning. The initial unit cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 9.0° scan in 30 frames over four different parts of the reciprocal space (total of 120 frames).¹⁷ A complete sphere of data were collected, to better than 0.8 Å resolution. Upon completion of data collection, the first 101 frames were re-collected to improve the decay correction analysis. Irregular crystal shape precluded the calculation of an analytical correction for absorption, but a SADABS correction¹⁸ was applied.

The structures were solved by direct methods or Patterson syntheses of SHELXS-86¹⁹ and ΔF syntheses of NRCVAX²⁰ and SHELXL-93.²¹ Unless otherwise stated, non-hydrogen atoms were refined anisotropically with SHELXL-93. Hydrogen atoms were placed in idealized positions and refined isotropically as riding atoms. Their isotropic displacement factors U_{iso} were adjusted 20% (50% for CH_3) above the value for the bonded atom. Further details for each structure determination are provided in the Supporting Information. The VOID routine of PLATON software²² was used to check that no holes large enough to contain solvent molecules remained in the structures.

Results and Discussion

The coordination chemistry of Re(III) is dominated by the diamagnetic Re_2^{6+} core, whose multiple metal-metal bond has been thoroughly studied.²³ Re(III) monomers, which are usually octahedral and paramagnetic, have attracted less attention. Various compounds containing nitrogen-donor ligands have been described, many of which are neutral chloro complexes.^{24–26} A few cationic chloro complexes of bidentate phosphines are known.²⁷

Synthesis of $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{X}$. As mentioned earlier,⁸ the preparative chemistry of biimidazole complexes is hampered by the extremely low solubility of this ligand in virtually all solvents, making it difficult to isolate pure compounds. Nevertheless, good yields of clean $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{X}$ products were obtained when equimolar amounts of biimidazole and the starting Re(V)-oxo complexes $\text{ReOCl}_3(\text{PPh}_3)_2$, $\text{ReOBr}_3(\text{PPh}_3)_2$, and $\text{ReO}(\text{OEt})\text{I}_2(\text{PPh}_3)_2$ were reacted in chloroform in the presence of 2 equiv of PPh_3 . The metal center is reduced to Re(III) by the phosphine via abstraction of the oxo ligand and formation of OPPh_3 .²⁸ The same compounds were obtained in the absence of free PPh_3 , but in lower yields (<25%).

The fact that the yields were tripled by adding excess PPh_3 supports the mechanism of reduction via oxygen abstraction as $\text{O}=\text{PPh}_3$, first proposed by Rouschias and Wilkinson for $\text{ReCl}_3(\text{MeCN})(\text{PPh}_3)_2$ ²⁸ and more recently confirmed for other systems.^{29,30} The sequence of events shown in Scheme 1 can explain the stereochemistry observed for the product. Excess PPh_3 would first add to the oxo ligand to produce a Re(III)-phosphine oxide complex. The good-leaving $\text{O}=\text{PPh}_3$ ligand would then be displaced by an initially monodentate biimH₂ molecule stabilized via an intramolecular N-H...Cl hydrogen bond. Re-Cl bond breaking would finally take place during a concerted process, releasing the chloride ligand and bringing a free N donor into a coordinating position.

Interestingly, under the same conditions, *N,N'*-dimethylated biimidazole gave a complicated mixture shown by NMR spectroscopy to contain various unidentified Re(V) (diamagnetic) and Re(III) (paramagnetic) products. This further supports the assumption presented earlier⁸ that the N-H groups play an active role by quenching the counteranion via two N-H...anion hydrogen bonds and by stabilizing a monodentate biimidazole intermediate. This assumption seems to hold for bromo and iodo compounds, even though hydrogen bonding is weaker.

Spectroscopic Characterization. Despite the fact that the compounds are paramagnetic ($\mu_{\text{eff}} = 1.3–1.6 \mu_{\text{B}}$), their ¹H NMR spectra are remarkably sharp, as shown in Figure 1 for the chloro compound **1**. The PPh_3 protons give rise to a typical pattern identified in other Re(III)- PPh_3 complexes,²⁴ and ³ J_{HH} couplings (~7.5 Hz) are observed. A relatively large downfield shift from the normal diamagnetic position (~7.5 ppm) is found for the ortho protons ($\delta \sim 13$ ppm). The more remote meta and para protons are also displaced downfield, but to a lesser extent ($\delta \sim 8.40$ and ~ 8.65 ppm, respectively). No ¹H-³¹P coupling is observed because of the fast relaxation of phosphorus, which is consistent with the absence of a ³¹P signal. The biimidazole protons are displaced upfield from their diamagnetic values (~7 ppm), but much less than the 1-methylimidazole protons in

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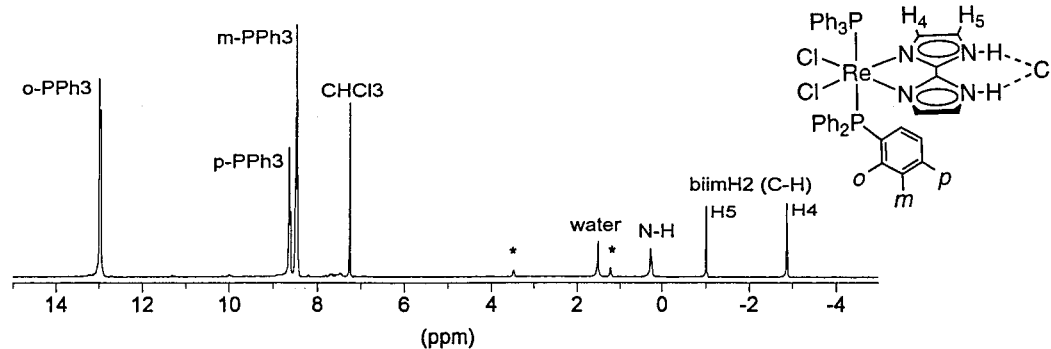


Figure 1. ^1H NMR spectrum of $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{Cl}$ (**1**) in CHCl_3 at room temperature (300 MHz). * = signals of residual diethyl ether.

$\text{ReCl}_3(\text{MeIm})_x(\text{PPh}_3)_{3-x}$ complexes.²⁴ The presence of one N–H and two C–H signals confirms the equivalence of the two rings. The N–H signal is broader, and it is unambiguously identified, since it vanishes upon addition of a few drops of CD_3OD to the solution. The higher-field C–H resonance is tentatively assigned to the proton (H4) next to the coordination site, since it is more displaced than the other from its diamagnetic position and less sensitive to a change in the counterion (see below). Interestingly, **1** and **2** have almost identical spectra, whereas greater differences are noted for **3**, especially for the N–H signal, which now appears slightly upfield from H5. It is difficult to rationalize this behavior, since chemical shifts are affected not only by intramolecular electronic effects but also by the formation of $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]^+\text{X}^-$ ion pairs in solution (see below).

In the FAB^+ mass spectra of **1–3**, the highest m/z peaks are unambiguously assigned to the $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]^+$ parent ion on the basis of the isotopic distributions of $^{35,37}\text{Cl}$, $^{79,81}\text{Br}$, and $^{185,187}\text{Re}$. The pattern for $(\text{M} - \text{H})^+$ is also observed. The next fragment corresponds to the parent ion having lost one phosphine $(\text{M} - \text{PPh}_3)^+$, which suggests that the phosphines are more easily displaced than the halides. The opposite behavior observed for $\text{Re}(\text{V})$ complexes containing bidentate phosphinophenolates reflects the stabilizing effect of the chelate rings in these compounds.^{31,32}

The UV–visible bands observed in spectra of the $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]^+$ species are too strong to correspond to d–d transitions. They likely originate from charge transfer, although they appear at much higher energy than those for the related $[\text{ReCl}_2(\text{PMe}_2\text{Ph})_2(\text{bipyridine})]^+$ species studied by Caspar et al.³³ Weak bands, whose intensity would be consistent with d–d transitions, are observed at higher wavelengths when NaOCH_3 is added to remove the N–H protons: they appear at 560 nm ($\epsilon = 295 \text{ M}^{-1} \text{ cm}^{-1}$) for $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH})]$ and 653 nm ($\epsilon = 325 \text{ M}^{-1} \text{ cm}^{-1}$) for $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biim})]^-$ (see Figure S-3, Supporting Information). It can be reasonably assumed that the shoulder at $\sim 470 \text{ nm}$ for the starting $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]^+$ species originates from the corresponding d–d transition.

Crystallographic Studies on $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{X}$. Crystal structures were determined for the three $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{X}$ compounds ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). An ORTEP drawing of the chloro compound is given in Figure 2, whereas those of the bromo and iodo complexes can be found in the Supporting Information (Figures S-1 and S-2, respectively). Selected

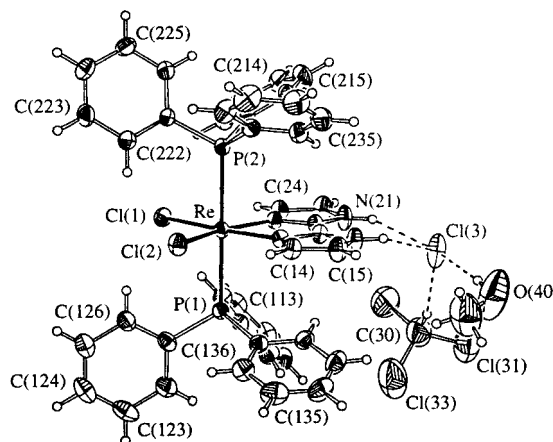


Figure 2. ORTEP drawing of $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{Cl} \cdot \text{CH}_3\text{OH} \cdot \text{CHCl}_3$ (**1**). Ellipsoids correspond to 35% probability, except those for hydrogens, which are shown as spheres of arbitrary size. Dashed lines represent hydrogen bonds. In the phenyl ring numbering scheme, the last digit corresponds to the position around the ring, starting with 1 for the ipso position.

interatomic distances and bond angles are listed in Table 2. In all cases, the unit cell contains a slightly distorted octahedral *cis,trans*- $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]^+$ ion. The same stereochemistry is observed for the neutral $[\text{ReCl}_2(\text{PPh}_3)_2(\text{acac})]$ complex.³⁴ The Re–P bonds are almost collinear ($177.2\text{--}179.2^\circ$), and their angles with the *cis* ligands all lie between 86.5 and 94.1° . The distortion is located mainly in the plane perpendicular to this direction, and it results from the repulsive effect of the halides on one another combined with the bite angle ($\sim 76^\circ$) of biimidazole: this small N–Re–N angle and the absence of bulky α substituents leave space for the halides to move apart ($\text{X–Re–X} = 100\text{--}104^\circ$). In structures of related dichloro compounds,^{25,34–38} a correlation was noted between the Cl–Re–Cl angles and the opposite L–Re–L angles, but the Cl–Re–Cl angles usually remained below 100° . The two *cis* N–Re–X angles are close to 90° for $\text{X} = \text{Br}$ and I , but they differ to a greater extent (87.4 vs 97.3°) for $\text{X} = \text{Cl}$.

In the chloro compound (**1**), the positive charge causes the Re–N ($2.114, 2.129 \text{ \AA}$) and Re–Cl bonds ($2.354, 2.381 \text{ \AA}$) to be shorter than the corresponding bonds (2.133 and 2.390 \AA , respectively) in the *trans* Cl–Re–N unit of the neutral ReCl_3 –

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Table 2. Selected Bond Lengths (Å) and Angles (deg) in the [ReX₂(PPh₃)₂(biimH₂)]X Compounds

	1 (X = Cl)	2 (X = Br)	3 (X = I)
Re–N(13)	2.114(3)	2.118(5)	2.135(11)
Re–N(23)	2.129(3)	2.122(5)	2.137(11)
Re–X(1)	2.3806(12)	2.4927(12)	2.671(2)
Re–X(2)	2.3542(11)	2.5052(9)	2.692(2)
Re–P(1)	2.4761(11)	2.483(2)	2.491(4)
Re–P(2)	2.4664(11)	2.491(2)	2.484(4)
N(11)···X(3)	3.184(4)	3.185(7) ^a	3.487(12)
N(21)···X(3)	3.131(4)	3.489(9) ^a	3.499(13)
C(30)···X(3)	3.547(11)		
O···X(3)	3.206(8)	3.139(11) ^a	
N(13)–Re–N(23)	75.98(13)	75.2(2)	75.7(5)
N(13)–Re–X(1)	173.22(9)	165.76(14)	167.2(3)
N(23)–Re–X(1)	97.30(9)	90.61(15)	91.5(3)
N(13)–Re–X(2)	87.35(10)	90.71(14)	92.2(3)
N(23)–Re–X(2)	163.32(9)	165.83(15)	167.9(3)
X(2)–Re–X(1)	99.38(4)	103.53(3)	100.57(4)
N(13)–Re–P(1)	90.85(10)	92.55(14)	87.8(3)
N(23)–Re–P(1)	90.00(9)	91.46(15)	91.6(3)
N(13)–Re–P(2)	91.00(10)	89.92(14)	91.5(3)
N(23)–Re–P(2)	88.47(9)	90.05(16)	88.7(3)
X(1)–Re–P(1)	89.98(4)	87.05(4)	94.06(10)
X(2)–Re–P(1)	90.22(4)	90.22(5)	86.49(10)
X(1)–Re–P(2)	87.93(4)	90.78(5)	86.67(10)
X(2)–Re–P(2)	91.91(4)	88.84(5)	93.09(10)
P(2)–Re–P(1)	177.24(3)	177.37(6)	179.21(14)
N(11)–H(11)···X(3)	145.2	155.4 ^a	157.7
N(21)–H(21)···X(3)	148.9	145.9 ^a	154.8
X(3)···HOR	166.2 (R = CH ₃)	178.9 (R = H) ^a	
X(3)···HCCl ₃	168.9		

^a With the most populated position (Br(3)) of the disordered Br[−] anion.

(PPh₃)(1-methylimidazole)₂ complex.²⁴ However, the Re–P bonds here are longer (mean 2.471 Å) than that in the latter compound (2.435 Å), as often found when PR₃ groups lie trans to each other.³⁴

In the three halide compounds studied here, the Re–N bonds show no significant dependence on the halogen present. On the other hand, the Re–P bonds in the Cl compound are significantly shorter (by ~0.02 Å) than those in the other two halides, which presumably reflects a greater positive charge on the Re center.

Chelate formation imposes strain in the biimH₂ ligand at the ring junction, as evidenced by the C2'–C2–N3 angles in the chelate rings (~116°) being much smaller than the C2'–C2–N1 angles (~133°). Also, the N lone pairs are not directed exactly along the N–Re bond: the Re–N3–C angles are ~116° inside the chelate ring and ~137° outside.

Free [ReX₂(PPh₃)₂(biimH₂)]⁺ cations likely possess a C₂ axis bisecting the X–Re–X and the N–Re–N angles. This symmetry is not retained in the solid, but the conformations are rather similar in the three salts and departure from idealized C_{2v} symmetry is not extreme. The P–C bonds in one phosphine are approximately above those in the other. One ring in each phosphine (left-hand sides in the figures) is roughly parallel with the P–Re–P direction, and its projection onto the ReN₂X₂ plane is close to the bisector of the X–Re–X angle (X–Re–P–C torsion angles ranging from 40 to 63°). In this way, the phenyl ortho hydrogens remain far enough from the X ligands. In the iodide (3), two other rings related by the approximate C₂ axis, one in each phosphine, are roughly parallel to the ReX₂N₂ plane. Rings C111–C116 and C231–C236 are relatively close to the N11–C15 and N21–C25 five-membered rings of biimidazole, respectively. The inter-ring angles are 8.0 and 10.8°, respectively, whereas the mean distances (~3.29 Å)

indicate some π -stacking interaction. In the bromide (2), ring C211–C216 participates in a similar interaction with ring N11–C15 (inter-ring angle and mean distance of 14.5° and 3.36 Å, respectively), but no phenyl ring is parallel to ring N21–C25. In the chloride (1), departure from parallelism is too large on both sides for stacking to be significant. Therefore, π -stacking plays a less important role than in the previously reported [ReOCl₂(OPPh₃)₂(biimH₂)]⁺ cation, where the PPh₃ part of the OPPh₃ ligand is less constrained.⁸

As shown in Figure 2, the N–H groups in 1 form hydrogen bonds with the chloride counterion Cl3. This same pattern has been found in other Re-biimH₂ complexes.^{8,39} The Cl···N distances (3.13 and 3.18 Å) are in the accepted range (2.91–3.53 Å),⁴⁰ and the N–H···Cl systems do not deviate much from linearity (~147°). In addition to a hydrogen-bonded methanol (O···Cl = 3.21 Å, O–H···Cl = 166°), the environment of Cl[−] includes a CHCl₃ molecule participating in a C–H···Cl interaction, in which the C–H···Cl unit is close to linearity (169°) and the C···Cl separation (3.55 Å) is particularly short. The H···Cl distance (2.59 Å) is near the lower limit of the range reported by Taylor and Kennard for interactions of this type.⁴¹

In the iodide (3) (Figure S-2, Supporting Information), the I[−] counterion is similarly bound to both N–H groups, in the same way as in the [(biimH₂)₂(biimH₃)₂]I₂ unit. Our N···I separations (~3.49 Å) correspond to the shortest contacts observed in this compound.⁴² The presence of two simultaneous interactions reduces the separation appreciably below the typical N···I distance of 3.66 Å proposed by Pimentel for single N–H···I systems.⁴³

The bromide (2) crystallized as the monohydrate. The Br[−] ions and water molecules are both disordered over two sites (the most populated environment of the [ReBr₂(PPh₃)₂(biimH₂)]⁺ cation is shown in Figure S-1, Supporting Information). The N–H···Br[−] hydrogen-bond pattern is less symmetric than that above. In both cases, linearity is retained (N11–H11–Br = 155°, N21–H21–Br = 146°), but the N11···Br separation (3.185 Å) is much below the standard value of 3.37 Å,⁴³ whereas the N21···Br distance is greater (3.489 Å). Lower symmetry apparently results from the location of the water molecule between adjacent Br[−] ions in the chains along the *c* axis in the glide planes.

Crystal Structure of [ReCl₂(PPh₃)₂(biimH₂)](benzoate) (4). Figure 3 shows the ORTEP drawing of the ion pair. The unit cell contains the same Re(III) species as that in the chloride compound (1), and the carboxylate is hydrogen-bonded with biimidazole N–H groups. Because of poor crystal quality due to partial evaporation of lattice CH₂Cl₂ solvent molecules, the individual distances and angles (Table S-1, Supporting Information) have relatively high esd's, but the connectivity and overall structural features are well established.

The asymmetric unit includes two independent molecules, but their stereochemistries and conformations are almost identical and they differ very little from those of the chloride salt (1). The most interesting feature of this structure is the presence two hydrogen bonds between the biimidazole N–H groups and the carboxylate oxygens. These interactions must be particularly strong, since the N–H···O unit is nearly linear (~165°) and

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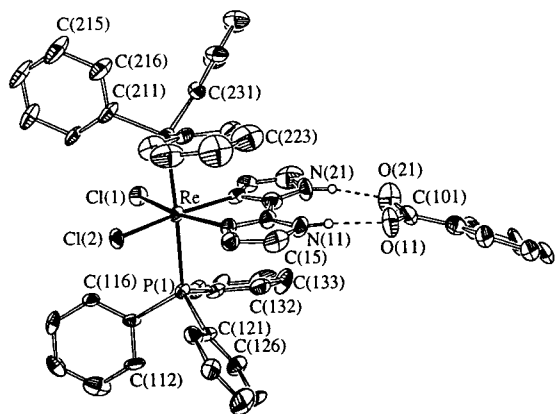


Figure 3. ORTEP drawing of $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)](\text{benzoate})$ (**4**). Hydrogens are omitted for simplicity. Other conditions are as in Figure 2. The second independent molecule in the asymmetric unit has essentially the same structure.

Table 3. Chemical Shifts of the CH Protons of Coordinated biimH₂ in $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]^+$ with Various Counterions, Y⁻ (δ in ppm; CD₂Cl₂)

Y ⁻	H5	H4	pK _a (aq) ⁴⁸
Cl ⁻	-1.18	-3.03	
CF ₃ COO ⁻	-1.27	-3.37	-0.25
CCl ₃ COO ⁻	-1.20	-3.29	0.70
CHCl ₂ COO ⁻	-1.44	-3.44	1.48
CH ₂ ClCOO ⁻	-1.70	-3.59	2.85
C ₆ H ₅ COO ⁻	-2.13	-3.82	4.19
CH ₃ COO ⁻	-3.07	-4.37	4.76

the N \cdots O separation (2.68 Å) is close to the lower limit of the accepted range.⁴⁰ The spectral data discussed below suggest that this association is stable in solution. An acetate ion was similarly associated with $[\text{Fe}(\text{biimH}_2)_2(\text{CH}_3\text{OH})_2]^{2+}$ in the crystal.⁴⁴ In an analogous $[\text{Zn}(\text{biimH}_2)_2(\text{CH}_3\text{OH})_2]^{2+}$ complex recently prepared,⁴⁵ the nitrate counterions were also attached to the N–H groups, but the N \cdots O separation was ~ 0.1 Å greater, since nitrates are poorer hydrogen-bond acceptors than carboxylates.

Ion Pairing in Solution. The above crystal structures obviously establish that ion pairing via hydrogen bonding takes place in the solid state. However, they do not prove that such ion pairs survive in solution. Various experiments were run starting with $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{Cl}$ to cast some light on this point.

The method described for $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)](\text{benzoate})$ (**4**) was used to replace the counterion in **1** and obtain various carboxylates, whose ¹H NMR spectra were obtained in CD₂Cl₂. As shown in Table 3, the chemical shifts of the C–H protons of biimH₂ are very sensitive to the counterion, the signals moving upfield progressively as the counterion becomes more basic.

Other research groups used ¹H NMR spectroscopy to investigate the association between carboxylic acids and 1-methylimidazole⁴⁶ or pyridine.⁴⁷ Their strategies relied mainly on the signals of the protons actually involved in hydrogen bonding, but the adjacent C–H protons were also found to be affected. For 1-methylimidazole/carboxylic acid systems, Tobin et al.⁴⁶ noted an upfield displacement of the imidazole H2 resonance

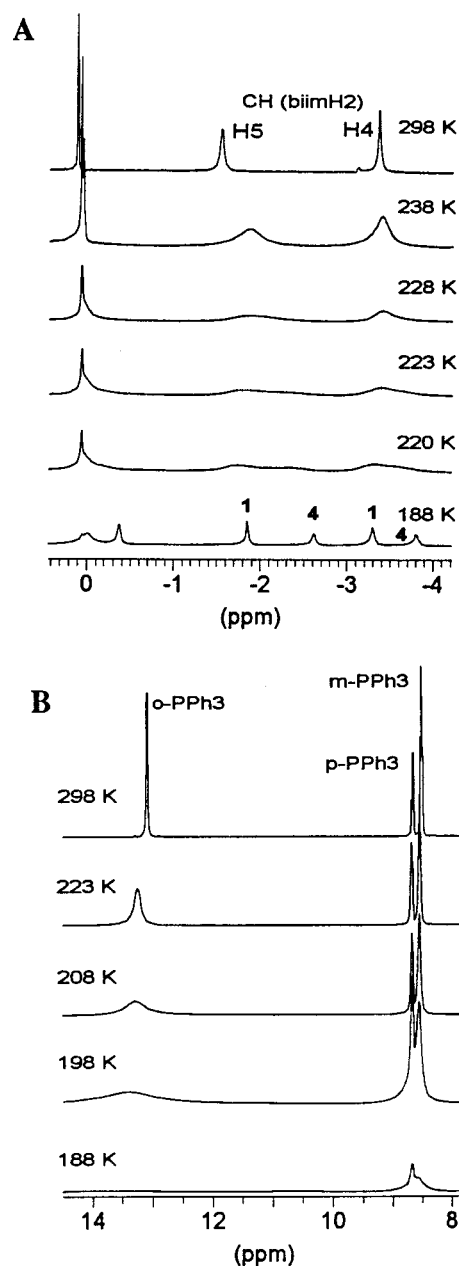


Figure 4. Variable-temperature ¹H NMR spectra of a mixture of **1** and **4**: (A) biimidazole protons; (B) = PPh₃ protons. The 6–8 ppm region (not shown) containing the benzoate resonances is not sensitive to temperature.

as the pK_a(aq) of the carboxylic acid increased. In the present case, the acidic protons cannot be used, since their signals are extremely broad or unobserved. Our displacements for H4 and H5 are very large because they are amplified by paramagnetism. However, the qualitatively similar behavior of these C–H resonances provides further indication that anions and cations do not exist as independent moieties in solution but as hydrogen-bonded ion pairs.

Table 3 also shows that the lower field signal is the more sensitive to the counterion: this is consistent with this signal being assigned to H5, which is closer to the N–H group and thus likely more affected by hydrogen-bonding effects.

A variable-temperature ¹H NMR experiment (Figure 4) performed with a mixture of $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{Cl}$ and $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)](\text{benzoate})$ further supports the presence of stable ion pairs in solution. In separate solutions, these salts show chemical shift differences of 0.95 and 0.79 ppm for H5

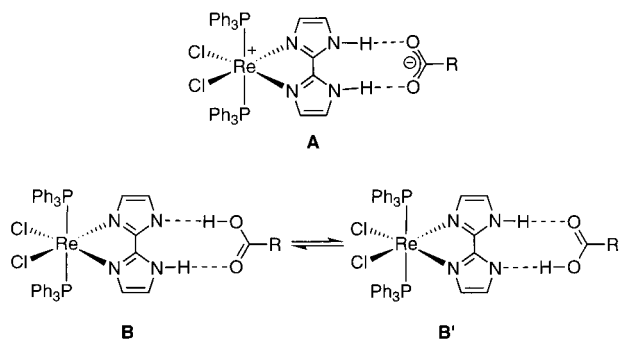
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Chart 1



and H4, respectively, whereas the protons of the more distant phosphine are less affected, a small displacement of 0.04 ppm being observed for the ortho protons only. At room temperature, the mixture shows only one set of biimH₂ signals at averaged positions (Figure 4A) because of fast exchange between the two kinds of ion pairs. When temperature is decreased, these signals broaden progressively as exchange is slowed, and around 225 K, coalescence is observed. Spectra at lower temperature exhibit two sets of biimH₂ signals, showing that the ion pairs survive as two distinct entities for a long time on the NMR time scale.

The PPh₃ signals are also temperature dependent (Figure 4B): the ortho signal at ~13 ppm vanishes in the baseline at 188 K. This was first ascribed to the above exchange process, since the small chemical shift difference ($\Delta\delta = 0.04$ ppm) for the ortho protons should displace coalescence below 225 K. However, even with such a small $\Delta\delta$, the coalescence temperature should not decrease so much. Furthermore, exchange should not broaden the meta and para signals, whose chemical shifts are nearly identical for the two compounds. The observations are better explained by restricted motion of the phosphine (ring rotation about P–C bonds and/or phosphine rotation about the Re–P bond). The fact that the meta/para signals are less broadened than those of the ortho protons could be explained by their greater distance from the enhancing paramagnetic center: the chemical shift differences between inequivalent meta (or para) protons in the restricted species would presumably be smaller than those for the ortho protons. Unfortunately, since spectra could not be obtained below 188 K, this interpretation cannot be confirmed and the possibility remains that broadening might be due to relaxation effects involving coupling to quadrupolar Re nucleus.

Acidity of Coordinated Biimidazole. Association of [ReX₂(PPh₃)₂(biimH₂)]⁺ with halide or carboxylate counterions is clearly established by the above results. However, although the species must be an ion pair for halides, it is not clear whether the carboxylates actually remain ionic (Chart 1A). Indeed, if the conjugated carboxylic acid was less acidic than the first N–H group of the complex, proton transfer would occur and the associated species would actually consist of a carboxylic acid hydrogen-bonded to a neutral, monodeprotonated, [ReX₂(PPh₃)₂(biimH)] species (Chart 1B). X-ray diffraction and NMR spectroscopy cannot discriminate directly between these two possibilities. The two tautomers would exchange rapidly, and the halves of the coordinated biimH[–] ligand would become equivalent on the NMR time scale. Similarly, concerted proton jump in the crystal would introduce dynamic disorder that could not be distinguished from a static state in which the halves of the molecule would be equivalent.

This problem can however be probed by UV–visible spectroscopy, since [ReX₂(PPh₃)₂(biimH₂)]⁺ and its derived species [ReX₂(PPh₃)₂(biimH)] and [ReX₂(PPh₃)₂(biim)][–] show

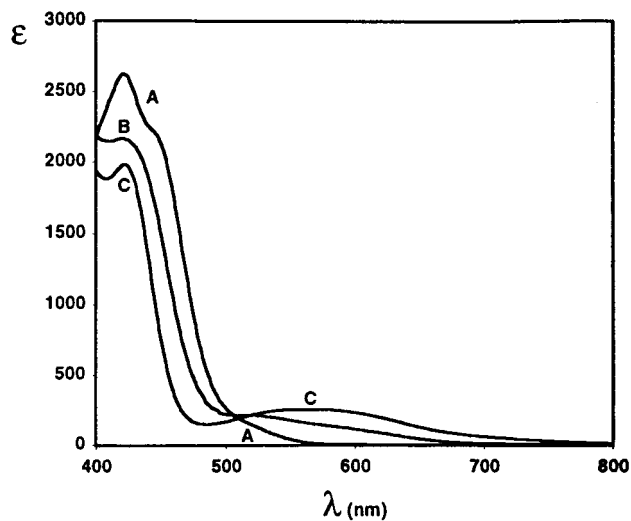
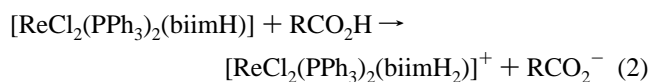
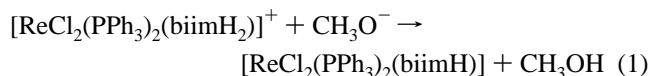


Figure 5. Visible spectra of 0.011 M solutions of [ReCl₂(PPh₃)₂(biimH₂)]⁺ (A), [ReCl₂(PPh₃)₂(biimH)] (C), and a 1:1 [ReCl₂(PPh₃)₂(biimH)]:CH₃COOH mixture (B) in CH₂Cl₂. Cell thickness = 0.09 cm.

different spectra. The study was carried out with the chloro system. The mono- and bisdeprotonated species are generated in solution by adding 1 and 2 equiv of NaOCH₃, respectively. The spectra of the three species are given in the Supporting Information (Figure S-3). The d–d band, probably masked by strong charge-transfer bands of [ReCl₂(PPh₃)₂(biimH₂)]⁺, shifts to higher wavelengths upon deprotonation and becomes well separated from these stronger absorptions.

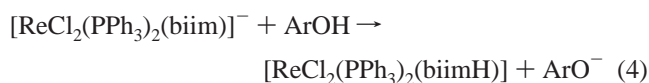
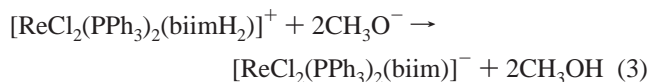
The acidity of the first proton was initially estimated visually via competition reactions with various carboxylic acids. One equivalent of NaOCH₃ was first added to remove an N–H proton (eq 1), whereupon light-orange [ReCl₂(PPh₃)₂(biimH₂)]⁺ became the deep brown neutral species. One equivalent of a carboxylic acid was then added. For the following acids (*pK_a*(aq) for aqueous solution in parentheses),⁴⁸ the initial orange color was regenerated (eq 2), indicating that these acids



dissociate more readily than the first N–H proton: CF₃COOH (–0.25), CCl₃COOH (0.70), CHCl₂COOH (1.48), CH₂ClCOOH (2.85). With (CH₃)₃CCOOH (5.03), the solution remained dark brown and the complex did not reprotonate. For the intermediate acids CH₃COOH (4.76) and C₆H₅COOH (4.19), an excess was needed to recover the initial orange color. Figure 5 shows that the spectrum of the mixture with acetic acid is halfway between those of [ReCl₂(PPh₃)₂(biimH)] and [ReCl₂(PPh₃)₂(biimH₂)]⁺, thereby showing that the first N–H group has the same *pK_a* as acetic acid in CH₂Cl₂.

The same approach was used to evaluate the acidity of the second N–H group. Two equivalents of NaOCH₃ was added to generate the turquoise [ReCl₂(PPh₃)₂(biim)][–] anion, and 1 equiv of a phenol was then added (eqs 3 and 4). With 3-chlorophenol (*pK_a*(aq) = 8.85)⁴⁸ and 3-nitrophenol (8.28), the

(48) *CRC Handbook of Chemistry and Physics*, 75th ed. (Special Student Edition); Lide, D. R., Ed.; Chemical Rubber Co. Press: Boca Raton, FL, 1997.



dark brown color of $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH})]$ reappeared, whereas only partial reprotonation occurred for phenol (9.89) and β -naphthol (9.51). Figure S-4 (Supporting Information) shows that the mixture with phenol contains a 4:3 $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biim})]^- : [\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH})]$ ratio, affording a $\text{p}K_a$ value ~ 0.1 unit below that of phenol. Thus, a difference of ~ 5 units is found between the $\text{p}K_a$'s of the two N–H groups.

Other (biimidazole)metal complexes have been shown to possess moderately acidic protons. For instance, $[\text{Ru}(\text{bipy})_2(\text{biimH}_2)]^{2+}$ and its two deprotonated forms are in equilibrium in MeCN.⁴⁹ Acidity constants not very different from ours were obtained for $[\text{M}(\text{L}-\text{L})_2(\text{biimH}_2)]^{2+}$ complexes of ruthenium and osmium with 2-(phenylazo)pyridine or 2,2'-bipyridine as ancillary ligands.^{50,51} However, since these studies were performed in water–methanol or water–dioxane mixtures, the individual $\text{p}K_a$'s cannot be compared with those obtained here in the aprotic solvent CH_2Cl_2 .⁵²

Conclusion

The particular importance of the N–H groups is evidenced by the ready formation of ion-paired salts with carboxylates. They are undissociated and nonlabile in CH_2Cl_2 , exchange

between $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]\text{Cl}$ and $[\text{ReCl}_2(\text{PPh}_3)_2(\text{biimH}_2)]^-$ (benzoate) being slow on the NMR time scale below -50°C . This association imparts good solubility in solvents of low polarity like benzene, CHCl_3 , and CH_2Cl_2 . Ion pairing is particularly efficient with carboxylates, since the complementary topology of coordinated biimH₂ and carboxylate allows simultaneous formation of two strong N–H \cdots O hydrogen bonds. Structurally similar species can form even when the carboxylic acid is weaker than the N–H proton, in which case association involves complementary N \cdots H–O and N–H \cdots O hydrogen bonds (Chart 1B). By UV–visible spectroscopy, the protonation states of coordinated biimidazoles could be determined in the presence of various carboxylate or phenolate hydrogen-bonding partners. It was established that, in CH_2Cl_2 , both N–H groups can be deprotonated by NaOCH_3 and they have acidities close to those of acetic acid and phenol, respectively. Therefore, $[\text{ReX}_2(\text{PPh}_3)_2(\text{biimH}_2)]^+$ can be deprotonated using only moderately strong bases and these complexes can be regarded as good starting species to develop biimidazole-bridged bimetallic systems.

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Supporting Information Available: Text presenting details of the structure determinations, Table S-1, listing distances and angles in **4**, Figures S-1–S-4 showing ORTEP drawings of **2** and **3** and UV–visible spectra of **1**, **1-H**, **1-2H**, and a 1:1 mixture of **1-2H** and phenol, and X-ray crystallographic files, in CIF format, for **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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