Preparation and Characterization of Oxorhenium(V) Complexes with 2,2′-Biimidazole: The Strong Affinity of Coordinated Biimidazole for Chloride Ions via N−H···Cl⁻ Hydrogen Bonding

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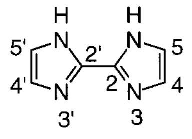
N,*N*′-Dimethylbiimidazole and bipyridine (N−N) react with $ReOCl_3(OPPh_3)(Me_2S)$ to give *mer*-$ReOCl_3$(N−N) compounds. Nonmethylated biimidazole forms a *trans*-O,O $[ReOCl_2(OPPh_3)(biimH_2)]^+$ cation, which is tightly associated with the Cl^- counterion via N−H···Cl^- hydrogen bonding. Hydrolysis of $ReOCl_3(biimMe_2)$ in wet acetone (5% water) leads to the linear oxo-bridged dinuclear species $[\{OReCl_2(biimMe_2)\}_2(\mu\text{-}O)]$ containing chelated $biimMe_2$. Acetone solutions containing only 1% water yield the bent oxo-bridged dinuclear species $[\{OReCl_2\}_2(\mu\text{-}O)(\mu\text{-}biimMe_2)_2]$, where each Re center retains the $ReO_2Cl_2N_2$ coordination but the $biimMe_2$ ligands are bridging. The linear oxo-bridged $[\{OReCl_2(biimH_2)\}_2(\mu\text{-}O)]$ complex obtained with nonmethylated biimidazole includes two Cl^- ions held via N−H···Cl^- hydrogen bonds, leading to a dianionic $[\{OReCl_2(biimH_2\cdots Cl)\}_2(\mu\text{-}O)]^{2-}$ unit in the crystals of the PPh_4^+ salt. The compounds are characterized by IR and NMR spectroscopies, and the structures of $[ReOCl_2(OPPh_3)(biimH_2)]Cl$, $[\{OReCl_2(biimH_2)\}_2(\mu\text{-}O)](PPh_4Cl)_2\cdot 2H_2O$, and $[\{OReCl_2\}_2(\mu\text{-}O)(\mu\text{-}biimMe_2)_2]\cdot$acetone are determined by X-ray diffraction.

Introduction

A number of new oxo−rhenium compounds have been prepared during the past decade. Similarity with Tc imaging agents used in nuclear medicine and potential applications of rhenium compounds in radiotherapy[1] have definitely contributed to this increased activity. However, many other features of the oxo−rhenium core have attracted attention, such as its spectroscopic properties,[2−5] its basicity toward various Lewis acids,[6,7] its influence on ligand distributions in coordination spheres,[8−10] and its roles in oxygen transfer[11−13] and catalytic processes.[14−19]

Our interest in oxo−rhenium complexes with biimidazole stemmed from previous studies on oxo−imidazole systems,[7] whose optical properties were found to differ markedly from those of the corresponding pyridine compounds.[4] This work was extended to biimidazole, whose ability to form chelate rings should improve stability. Moreover, this potentially bridging bis-bidentate ligand, when deprotonated, offers the possibility of generating di- or polynuclear species with interesting properties, since biimidazole is known to favor electron transfer between metal centers[20] and to promote catalytic activity in various metal complexes.[21,22]

The present paper deals with the initial step of this study, namely, the preparation of mononuclear and oxo-bridged dinuclear complexes containing biimidazole ($biimH_2$) and *N*,*N*′-dimethylbiimidazole ($biimMe_2$), in which the ligand participates



$biimH_2$

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(1) Nicolini, M.; Mazzi, U. *Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine 5*; Servizi Grafici Editoriali: Padova, Italy, 1999.

(2) Savoie, C.; Reber, C. *J. Am. Chem. Soc.* **2000**, *122*, 844 and references therein.

(3) Oetliker, U.; Savoie, C.; Stanislas, S.; Reber, C.; Connac, F.; Beauchamp, A. L.; Loiseau, F.; Dartiguenave, M. *J. Chem. Soc., Chem. Commun.* **1998**, 657 and references therein.

(4) Savoie, C.; Reber, C. *Coord. Chem. Rev.* **1998**, *171*, 387 and references therein.

(5) Savoie, C.; Reber, C.; Bélanger, S.; Beauchamp, A. L. *Inorg. Chem.* **1995**, *34*, 3851.

(6) Doerrer, L. H.; Galsworthy, J. R.; Green, M. L.; Leech, M. A. *J. Chem. Soc., Dalton Trans.* **1998**, 2483.

(7) Bélanger, S.; Beauchamp, A. L. *Inorg. Chem.* **1996**, *35*, 7836; **1997**, *36*, 3640.

(8) van Bommel, K. J. C.; Verboom, W.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. *Inorg. Chem.* **1998**, *37*, 4197.

(9) Hahn, F. E.; Imhof, L.; Lügger, T. *Inorg. Chim. Acta* **1998**, *269*, 347.

(10) Fortin, S.; Beauchamp, A. L. *Inorg. Chim. Acta* **1998**, *279*, 159.

(11) Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862.

(12) Bryan, J. C.; Stenkamp, R. E.; Tulip, T. H.; Mayer, J. M. *Inorg. Chem.* **1987**, *26*, 2283.

(13) Seymore, S. B.; Brown, S. N. *Inorg. Chem.* **2000**, *39*, 325.

(14) Kühn, F. E.; Rauch, M. U.; Lobmaier, G. M.; Artus, G. R. J.; Herrmann, W. A. *Chem. Ber.* **1997**, *130*, 1427.

(15) Gunaratne, H. Q. N.; McKervey, M. A.; Feutren, S.; Finlay, J.; Boyd, J. *Tetrahedron Lett.* **1998**, *39*, 5655.

(16) Finlay, J.; McKervey, M. A.; Gunaratne, H. Q. N. *Tetrahedron Lett.* **1998**, *39*, 5651.

(17) Arterburn, J. B.; Perry, M. C.; Nelson, S. L.; Dible, B. R.; Holguin, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 9309.

(18) Arterburn, J. B.; Nelson, S. L. *J. Org. Chem.* **1996**, *61*, 2260.

(19) Jung, J.-H.; Albright, T. A.; Hoffmann, D. M.; Lee, T. R. *J. Chem. Soc., Dalton Trans.* **1999**, 4487.

(20) Carmona, D.; Ferrer, J.; Mendoza, A.; Lahoz, F. J.; Oro, L. A.; Viguri, F.; Reyes, J. *Organometallics* **1995**, *14*, 2066 and references therein.

(21) Esteruelas, M. A.; Garcia, M. P.; Lopez, A. M.; Oro, L. A. *Organometallics* **1991**, *10*, 127. Esteruelas, M. A.; Garcia, M. P.; Lopez, A. M.; Oro, L. A. *Organometallics* **1992**, *11*, 702.

(22) Garcia, M. P.; Lopez, A. M.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Chem. Commun.* **1988**, 793.

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in a single bidentate interaction. Compounds with pyridine have been known for some time,[10,23,24] but systems with imidazole and its derivatives have been described only recently.[25−28]

The chemistry described here reveals interesting ligating features of the biimidazole framework. First, it can either behave as a chelating agent or adopt a syn-bridging role in oxo-bridged dinuclear compounds. Second, N-methylation of biimidazole introduces drastic changes in reactivity because halide ion association with coordinated biimidazole by hydrogen bonding via the N−H groups is a significant stabilizing factor.

Experimental Section

Reactants and Methods. Reagent grade $KReO_4$, 2,2′-bipyridine (Aldrich), solvents, and other chemicals were used as received. Deuterated solvents were purchased from CDN Isotopes. ^1H NMR spectra were recorded at 300 MHz on a Bruker AMX-300 spectrometer or at 400 MHz on a Bruker ARX-400 instrument. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on the latter instrument at 101 and 162 MHz, respectively. Residual solvent signals were used as internal references,[29] and the chemical shifts are reported vs Me_4Si for the ^1H and ^{13}C spectra. H_3PO_4 was used as the external standard ($\delta = 0$) for the ^{31}P spectra. Solid-state CP-MAS ^{13}C NMR spectra were recorded at 75.5 MHz on a Bruker Avance DSX-300 instrument, glycine being used as the external standard (δ(carboxyl) = 176.0 ppm). IR spectra were generally recorded for samples in KBr pellets on a Perkin-Elmer 1750 FTIR spectrophotometer. Elemental analyses were performed at the Laboratoire d'analyse élémentaire de l'Université de Montréal.

Preparative Work. Biimidazole was prepared according to Fieselmann et al.[30] and recrystallized in boiling aqueous NaOH (0.25 M). *N,N*′-Dimethylbiimidazole was prepared according to Melloni et al.[31] The starting materials $ReOCl_3(OPPh_3)(Me_2S)$ (**1**) and $(Bu_4N)[ReOCl_4]$ (**2**) were prepared by following published procedures.[32,33]

$ReOCl_3$(bpy). A pure yellow-green sample of the mer isomer was obtained from **1** by the method of Bryan et al.[12] ^1H NMR (DMSO-d_6; ppm): δ 9.08 (d, 1H, $J = 8$ Hz), 8.69 (d, 1H, $J = 8$ Hz), 8.57 (d, 1H, $J = 6$ Hz), 8.35 (t, 1H, $J = 8$ Hz), 8.28 (d, 1H, $J = 6$ Hz), 8.01(t, 1H, $J = 6$ Hz), 7.87 (t, 1H, $J = 8$ Hz), 7.58 (t, 1H, $J = 6$ Hz).

The method of Chakravorti[34] gave a 3:2 fac:mer mixture. ^1H NMR signals of the fac isomer (DMSO-d_6; ppm): δ 9.22 (d, 2H, $J = 7.6$ Hz), 8.90 (d, 2H, $J = 7.6$ Hz), 8.55 (dt, 2H, $J = 6$ and 1.5 Hz), ∼8.0 (2H, overlapping with a signal of the mer isomer).

$ReOCl_3(biimH_2)$ (3). Biimidazole (20 mg; 0.15 mmol) was slowly added to a yellow solution of **2** (57 mg; 0.10 mmol) in CH_2Cl_2 (15 mL), and the resulting mixture became bright yellow-green. After 10 min, the reaction was stopped, the mixture was filtered, and the solvent was evaporated to near dryness, but no precipitate appeared. Complete removal of the solvent afforded a green oily residue whose ^1H NMR spectrum indicated a 3:2 mixture of the mer and fac isomers. ^1H NMR ($CDCl_3$; ppm): δ 14.67 (s, N−H, fac), 13.89 and 13.58 (s, N−H, mer), 7.86 and 7.47 (s, C−H, fac), 7.22, 7.05, 6.99, and 6.74 (s, C−H, mer). IR (CH_2Cl_2 solution; sample between NaCl plates; cm^{-1}): 982, ν(Re═O). All attempts to remove the Bu_4NCl produced and to separate the isomers failed.

In one case, moist PPh_4Cl was added to the residue dissolved in CH_2Cl_2 solution to favor precipitation. No precipitate formed spontaneously, but vapor diffusion of diethyl ether into this solution produced a small amount of blue crystals (**4**). An X-ray diffraction study of a specimen from this crystallographically homogeneous sample showed the composition to be $[\{OReCl_2(biimH_2)\}_2O](PPh_4Cl)_2 \cdot 2H_2O$.

$[ReOCl_2(OPPh_3)(biimH_2)]Cl$ (5). A suspension of **1** (496 mg; 0.76 mmol) in $CHCl_3$ was heated to reflux, and biimidazole (15 mg, 1.14 mmol) was added in small portions. A grass-green solution was rapidly obtained, and a small amount of solid remained. The mixture was refluxed for 10 min, cooled in an ice bath, and filtered to remove a small amount of brown solid. The filtrate was evaporated to dryness, the oily residue was dissolved in a minimum amount of acetone, and diethyl ether was added dropwise until the solution became slightly cloudy. A drop of acetone was added to obtain a clear solution, which was allowed to stand while a pale green solid slowly appeared. After a few hours, the mixture was filtered, and the solid was washed with small portions of a 1:4 acetone:diethyl ether mixture. Yield: 208 mg (38%). ^1H NMR ($CDCl_3$; ppm): δ 14.76 (s, 2H, N−H), 7.80 (s, 2H, H4 or H5), 7.61 (t, 3H, $^3J_{HH} = 7.4$ Hz, PPh_3 para), 7.44 (td, 6H, $^3J_{HH} = 7.8$ Hz, $^4J_{HP} = 3.4$ Hz, PPh_3 meta), 7.30 (s, 2H, H5 or H4), 7.21 (dd, 6H, $^3J_{HH} = 8.0$ Hz, $^3J_{HP} = 13.1$ Hz, PPh_3 ortho). ^{13}C NMR ($CDCl_3$; ppm): δ 147.3 (s, C2), 134.0 (d, $^4J_{CP} = 3.1$ Hz, PPh_3 para), 132.5 (s, C4 or C5), 132.3 (d, $^3J_{CP} = 11.5$ Hz, PPh_3 ortho), 129.2 (d, $^3J_{CP} = 13.4$ Hz, PPh_3 meta), 125.6 (d, $^1J_{CP} = 110.7$ Hz, PPh_3 ipso), 120.0 (s, C5 or C4). ^{31}P NMR ($CDCl_3$; ppm): δ 46.1. IR (KBr; cm^{-1}): 1000, ν(Re═O). Anal. Calcd for $C_{24}H_{21}Cl_3N_4O_2PRe$: C, 39.98; N, 7.77; H, 2.94. Found: C, 39.91; N, 7.87; H, 2.92.

***mer*-$ReOCl_3(biimMe_2)$ (6).** $biimMe_2$ (52 mg; 0.31 mmol) and **1** (200 mg; 0.31 mmol) were suspended in THF under argon, and the mixture was stirred for 1 h at room temperature. The color changed rapidly from light green to yellow-green. The yellow-green solid was filtered off and washed successively with THF and diethyl ether. Yield: 111 mg (76%). ^1H NMR (DMSO-d_6; ppm): δ 7.69 (d, 1H, $J \approx 1.4$ Hz), 7.25 (d, 1H, $J \approx 1.4$ Hz), 7.19 (d, 1H, $J \approx 1.4$ Hz), 6.99 (d, 1H, $J \approx 1.4$ Hz), 4.61 (s, 3H), 4.41 (s, 3H). ^{13}C NMR (DMSO-d_6; ppm): δ 136.9 and 133.9 (C2, C2′), 128.5, 128.4, 128.0, and 127.8 (C4, C4′, C5, C5′), 37.3 and 37.1 (N−CH_3). ^{13}C CP-MAS (ppm): δ 138.9 and 135.4 (C2, C2′), 129.4 (br, C4, C4′, C5, C5′), 40.8 (N−CH_3). IR (KBr; cm^{-1}): 985 (vs), ν(Re═O). Anal. Calcd for $C_8H_{10}Cl_3N_4ORe$: C, 20.41; N, 11.90; H, 2.14. Found: C, 20.56; N, 11.46; H, 2.08. The ^1H NMR spectrum indicated that the sample contained a small amount (<5%) of the fac isomer, which could be responsible for a weak ν(Re═O) IR band at 970 cm^{-1}. Recrystallizing the crude product in boiling acetone reduced the amount of the fac isomer to <3%.

$[\{OReCl_2(biimMe_2)\}_2(\mu\text{-}O)]$ (7). Compound **6** (250 mg; 0.53 mmol) was stirred in 50 mL of acetone containing 5% water for 17 h at room temperature. The green solid was filtered off and washed successively with acetone and diethyl ether. Yield: 18 mg (77%). IR (KBr; cm^{-1}): 980 (m), ν(Re═O); 700−740 (br, vs), ν(Re−O−Re); 1700 (m), ν(C═O) (acetone). ^{13}C CP-MAS (ppm): δ 144.4 (C2, C2′), 136.0, 134.2, and 128.5 (C4, C4′, C5, C5′), 37.4 (N−CH_3), 211.5 and 33.0 (acetone). Solution spectra could not be obtained because of the very low solubility of **7** in common organic solvents. Anal. Calcd for $C_{16}H_{20}Cl_4N_8O_3Re_2 \cdot 0.5C_3H_6O$: C, 22.96; N, 12.24; H, 2.53. Found: C, 22.78; N, 12.30; H, 2.45.

$[\{OReCl_2\}_2(\mu\text{-}O)(\mu\text{-}biimMe_2)_2]$ (8). **6** (52 mg; 0.11 mmol) was refluxed for 17 h in 10 mL of acetone containing 1% water. A light-blue solid was filtered off and washed successively with acetone and diethyl ether. Yield: 30 mg (62%). IR (KBr; cm^{-1}): 972 (w), ν(Re═O); 1700 (s), ν(C═O) (acetone). ^{13}C CP-MAS (ppm): δ 136.0 (C2, C2′), 132.0, 128.7, 126.4, 125.5, and 124.1 (C4, C4′, C5, C5′), 38.6 and 34.8 (N−CH_3), 211.5 and 33.0 (acetone). Anal. Calcd for $C_{16}H_{20}Cl_4N_8O_3Re_2 \cdot C_3H_6O$: C, 24.16; N, 11.86; H, 2.77. Found: C, 23.89; N, 11.88; H, 2.64. Overnight pumping did not remove lattice acetone. The same compound was obtained in lower yield when the reaction was run at room temperature for 5 days.

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(23) Johnson, N. P.; Taha, F. I. M.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2614.

(24) Chakravorti, M. C. *J. Indian. Chem. Soc.* **1970**, *47*, 844.

(25) Pearson, C.; Beauchamp, A. L. *Acta Crystallogr.* **1994**, *C50*, 42.

(26) Alessio, E.; Hansen, L.; Iwamoto, M.; Marzilli, L. G. *J. Am. Chem. Soc.* **1996**, *118*, 7593.

(27) Hansen, L.; Alessio, E.; Iwamoto, M.; Marzilli, P. A.; Marzilli, L. G. *Inorg. Chim. Acta* **1995**, *240*, 413.

(28) Alessio, E.; Zangrando, E.; Iengo, E.; Macchi, M.; Marzilli, P. A.; Marzilli, L. G. *Inorg. Chem.* **2000**, *39*, 294.

(29) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

(30) Fieselmann, B. F.; Hendrickson, D. N.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2078.

(31) Melloni, P.; Dradi, E.; Logemann, W.; de Carneri, I. D.; Trane, F. *J. Med. Chem.* **1972**, *15*, 926.

(32) Grove, D. E.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1224.

(33) Alberto, R.; Schibli, R.; Egli, A.; Schubiger, P. A.; Herrmann, W. A.; Artus, G.; Abram, U.; Kaden, T. A. *J. Organomet. Chem.* **1995**, *462*, 217.

(34) Chakravorti, M. C. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1991.

Table 1. Crystallographic Data

	5	**4**	**8**·acetone
formula	$C_{24}H_{21}Cl_3N_4O_2PRe$	$C_{60}H_{56}Cl_6N_8O_5P_2Re_2$	$C_{19}H_{26}Cl_4N_8O_4Re_2$
fw	720.98	1616.23	944.70
a, Å	9.370(3)	10.323(3)	9.802(3)
b, Å	9.573(3)	11.794(3)	10.022(3)
c, Å	16.394(5)	13.548(4)	15.188(4)
α, deg	86.46(2)	86.22(2)	72.56(2)
β, deg	80.57(2)	83.63(2)	82.77(2)
γ, deg	68.69(3)	71.64(2)	89.47(2)
V, Å^3	1351.5(7)	1555.0(8)	1411.5(7)
Z	2	1	2
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
temp, °C	20	20	20
λ, Å	1.540 56 (Cu Kα)	1.540 56 (Cu Kα)	1.540 56 (Cu Kα)
ρ_{calcd}, g cm^{-3}	1.772	1.726	2.223
crystal size, mm	0.51 × 0.38 × 0.08	0.41 × 0.22 × 0.20	0.31 × 0.08 × 0.07
μ, mm^{-1}	12.09	10.57	19.77
transm coeff	0.455−0.044	0.292−0.102	0.373−0.121
ranges of *h*, *k*, and *l*	$-10 \leq h \leq 11$	$-12 \leq h \leq 12$	$-11 \leq h\ 11$
	$-11 \leq k \leq 11$	$-14 \leq k \leq 14$	$-12 \leq k \leq 0$
	$-19 \leq l \leq 19$	$-16 \leq l \leq 16$	$-18 \leq l \leq 18$
$R1^a$ ($I > 2\sigma(I)$)	0.0293	0.0554	0.0370
w$R2^b$ ($I > 2\sigma(I)$)	0.0816	0.1547	0.0942
S^c	1.121	1.080	1.088

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

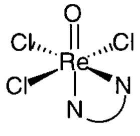
Upon refluxing in methanol for 24 h, **7** partially converted to **8**. When the turquoise solid mixture of **7** and **8** obtained by filtration was stirred in DMSO, **8** dissolved (more readily than the above acetone solvate) and insoluble **7** was removed by filtration. ^{1}H and ^{13}C NMR spectra of **8** were recorded on DMSO-d_6 solutions so obtained. ^{1}H NMR (DMSO-d_6; ppm): δ 7.82 (s, 2H), 7.69 (s, 2H), 7.48 (s, 2H), 7.17 (s, 2H), 3.70 (s, 6H), 3.66 (s, 6H). ^{13}C NMR (DMSO-d_6; ppm): δ 136.8 (C2), 135.5 (C2′ and C4/C4′), 132.4 (C4′/C4), 124.2 and 123.2 (C5, C5′), 35.2 and 34.4 (N−CH_3).

Crystallographic Measurements and Structure Determinations. Bright-green crystals of **5** suitable for X-ray diffraction work were obtained from an acetone−diethyl ether mixture. Blue crystals of **4** were grown as described above. Blue crystals of **8** were obtained when **6** dissolved in acetone was left in a freezer (−15 °C) for 2 weeks. The crystals were glued onto glass fibers and mounted on an Enraf-Nonius CAD-4 diffractometer. In each case, low-angle spots in an axial photograph led to a reduced triclinic cell,[35] for which no higher symmetry was detected. A half-sphere of data were collected for **8**, and whole spheres were collected for **4** and **5**. These data were corrected for absorption and averaged[36] to provide basic four-octant data sets.

The structures were solved by direct methods using SHELXS-86[37] and Δ*F* syntheses of NRCVAX[38] and SHELXL-93.[39] They refined normally in the centric space group $P\bar{1}$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined as riding atoms with the following distances: C−H 0.93 (sp^2 C) or 0.96 Å (methyl), N−H 0.86 Å, O−H 0.83 Å (H_2O). Their isotropic temperature factors were adjusted to 20% (sp^2 C and N) or 50% (methyl and water) above the value for the supporting atom. The VOID routine of the PLATON software[40] was used to check that no holes large enough to contain solvent molecules remained in the structure. Crystal data for the three compounds are collected in Table 1.

Results and Discussion

Monooxo Compounds with Bipyridine. To define preparative strategies for biimidazole compounds, methods used for the related ligand bipyridine were tested first. Bryan et al.[12] reported that bipyridine reacts cleanly with $ReOCl_3(OPPh_3)(SMe_2)$ (**1**) to give high yields of a $ReOCl_3$(bpy) compound. However, the stereochemistry was not specified. We repeated this experiment and isolated the expected yellow-green compound. The presence of a single species was indicated by ^{1}H NMR spectroscopy. Eight signals of equal intensity were observed, indicating that the two rings of bipyridine are inequivalent and the complex must be the mer isomer (**A**). This was further confirmed by preliminary X-ray diffraction results. The crystals[41] were all twinned and the *R* factor could not be reduced below 15%, but these results unambiguously established that the composition and ligand arrangement about the Re center correspond to *mer*-$ReOCl_3$(bpy). Thus, since the starting $ReOCl_3(OPPh_3)(SMe_2)$ complex is the *trans*-O,O isomer,[42] the reaction can be regarded as a simple displacement of the good leaving ligands SMe_2 and $OPPh_3$ without rearrangement. In the recently described $[ReOMe_2(bpy)]BF_4$ and $ReOClMe_2$(bpy) complexes,[22] bipyridine is also coordinated with an N donor trans to the oxo group.



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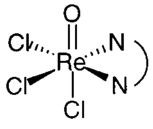

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Chakravorti[34] isolated a $ReOCl_3$(bpy) material when a mixture of Re_2O_7 and bipyridine in HCl−ethanol was reduced with H_3PO_2. We obtained a yellow-green solid by this method starting with $HReO_4$ or $KReO_4$. The ^{1}H NMR spectra included the

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(35) *CAD-4 Software*, Version 5.0; Enraf-Nonius: Delft, The Netherlands, 1989.

(36) Ahmed, F. R.; Hall, S. R.; Pippy, M. E.; Huber, C. P. NRC Crystallographic Computer Programs for the IBM/360: Accession Nos. 133−147. *J. Appl. Crystallogr.* **1973**, *6*, 309.

(37) Sheldrick, G. M. *SHELXS-86*: *Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1990.

(38) Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

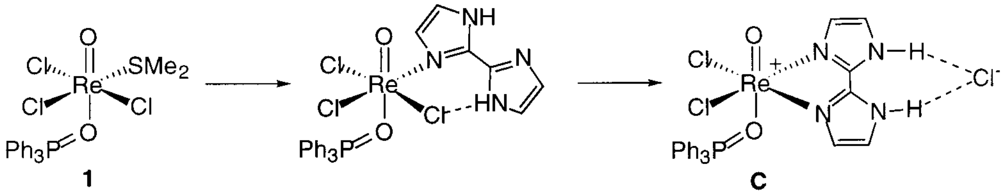
(39) Sheldrick, G. M. *SHELXL-93*: *Program for the Refinement of Crystal Structures* (*Beta Test 03*); University of Göttingen: Göttingen, Germany, 1993.

(40) Spek, A. L. *PLATON*: *Molecular Geometry Program*; University of Utrecht: Utrecht, The Netherlands, July 1995.

(41) Crystal data for the green crystals isolated from the reaction of $ReOCl_3(OPPh_3)(SMe_2)$ and bpy in boiling acetonitrile: orthorhombic, *Fdd*2; $a = 12.627(4)$, $b = 21.300(7)$, $c = 28.927(15)$ Å.

(42) Abu-Omar, M. M.; Khan, S. I. *Inorg. Chem.* **1998**, *37*, 4979.

Scheme 1



signals of the mer isomer (40%), together with another set of four signals (60%) for a species in which the two rings of bipyridine are equivalent. By adding bipyridine to the NMR tube, we verified that these signals were not due to the free ligand. This new species is undoubtedly the fac isomer (**B**). All attempts to separate these two isomers by fractional crystallization failed, and chromatographic methods were ruled out by poor solubility. When a solution of this mixture in DMSO was left at room temperature, decomposition occurred (faster for the fac isomer) and the free ligand appeared.

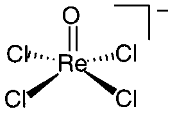
Wilkinson's group reported the preparation of a brown bipyridine compound from $ReOCl_3(PPh_3)(OPPh_3)$,[43] but in our hands, this method yielded a black material that was not further investigated.

Monooxo Compounds with Biimidazoles. Since the procedure of Bryan et al.[12] yielded the pure *mer*-$ReOCl_3$(bpy) isomer, it was used for the reactions with the biimidazole ligands, and it gave satisfactory results.

$biimMe_2$ reacts with $ReOCl_3(OPPh_3)(SMe_2)$, giving a yellow-green material whose microanalysis corresponds to $ReOCl_3(biimMe_2)$. The presence of a Re=O group is evidenced by the strong IR band at 985 cm^{-1}, in the normal range.[34,44] The featureless ^{31}P NMR spectrum indicates that $OPPh_3$ has been totally displaced. In the ^{1}H NMR spectrum of the species in DMSO-d_6, four doublets in the aromatic region (7.0−7.7 ppm) and two methyl singlets of triple intensity at 4.4−4.6 ppm show that the two rings are inequivalent. This same conclusion is reached from the ^{13}C spectra. Thus, $biimMe_2$ reacts according to the same pattern as bipyridine, giving the same mer isomer (**A**). However, in this case, the crude product contains a small amount (<5%) of another species (^{1}H NMR signals at 8.11 and 8.05 ppm for ring protons and at 4.44 ppm for the methyl group), probably the fac isomer (**B**), in which the two imidazole rings are equivalent. Besides the strong ν(Re=O) band at 985 cm^{-1}, the IR spectrum shows a weak signal at 970 cm^{-1} assigned to the fac isomer. Recrystallization leads to the essentially pure mer isomer.

Reacting $biimH_2$ and $ReOCl_3(OPPh_3)(SMe_2)$ for a few minutes in hot $CHCl_3$ leads to a light-green solid showing a ^{31}P NMR signal at 46 ppm for coordinated $OPPh_3$ and a strong IR band for the Re=O group at 1000 cm^{-1}, a frequency ∼20 cm^{-1} higher than those found for other compounds containing the O=Re−$OPPh_3$ moiety.[32,43] ^{1}H NMR signals are found for $biimH_2$ and $OPPh_3$ between 7 and 8 ppm. A set of three signals (1:2:2 intensity ratio) is assigned to the aromatic protons of $OPPh_3$, couplings to ^{31}P being identified by ^{31}P decoupling. The ortho protons appear as a doublet of doublets, due to coupling with ^{31}P (13.1 Hz) and the meta protons (8.0 Hz), whereas the meta protons show couplings with both the ortho and para protons (7.8 Hz) and with ^{31}P (3.4 Hz). The weaker triplet at 7.61 ppm (7.4 Hz) originates from the para protons. The two rings of coordinated $biimH_2$ are equivalent since a single set of resonances is present: a broad N−H singlet at 14.76 ppm and sharp singlets at 7.80 and 7.30 ppm for the C−H protons. Ring equivalence is also indicated by the ^{13}C NMR spectrum. The $OPPh_3$ carbons were unambiguously assigned from $^{1}H-^{13}C$ 2D and DEPT experiments. The ipso carbon exhibits a very strong $^{13}C-^{31}P$ coupling ($^{1}J_{CP}$ = 111 Hz), whereas ortho, meta, and para carbons also couple to ^{31}P with constants of 11.4, 13.5, and 3.1 Hz, respectively.

X-ray work (see below) shows that the crystal contains the $[ReOCl_2(OPPh_3)(biimH_2)]^+$ cation (**C**, Scheme 1), in which the $OPPh_3$ ligand remains trans to the Re=O bond, whereas $biimH_2$ has displaced an adjacent Cl atom and the SMe_2 ligand. The Cl^- counterion is not independent of the complex cation, since it is strongly hydrogen-bonded to the two N−H groups. Thus, SMe_2 is displaced first, as noted by Hansen et al.,[27] producing an intermediate with biimidazole coordinated in a monodentate manner (Scheme 1). In the case of $biimMe_2$, the following step would be the displacement of the next best leaving group, namely, $OPPh_3$, to give the neutral mer complex (**A**). In contrast, the monodentate intermediate with $biimH_2$ is likely stabilized by an intramolecular N−H···Cl hydrogen bond, which apparently enhances the capability of the Cl ligand to leave the coordination sphere.



D

Attempts to obtain $ReOCl_3(biimH_2)$ from $ReOCl_3(OPPh_3)(SMe_2)$ by using higher temperatures or longer reaction times invariably led to decomposition with precipitation of the insoluble $biimH_2$ ligand. Therefore, $[ReOCl_4]^-$ (**D**) was tried as a starting species, since an empty coordination site is already available and a single chlorine atom has to be substituted. When the Bu_4N^+ salt of $[ReOCl_4]^-$ was used, an oily material was obtained and shown by ^{1}H NMR to contain both the mer and the fac isomers (3:2 ratio), despite the fact that initial attack at the empty site across the Re=O bond was hoped to favor the mer isomer. The ν(Re=O) band at 982 cm^{-1} is broader than usual because both isomers are present. It proved to be impossible to separate the two isomers and to remove the Bu_4NCl salt produced. This may be related to the tendency of Cl^- to strongly associate with N−H groups in the $[ReOCl_2(OPPh_3)(biimH_2)]Cl$ compound mentioned above and in an oxo-bridged dinuclear compound to be described below. Since such ion pairing was recently shown to survive in halogenated solvents for related Re(III)−$biimH_2$ complexes,[45] high solubility of $ReOCl_3(biimH_2)$ may be ascribed to the formation of a $[ReOCl_3(biimH_2)\cdots Cl]^-$ adduct that cannot be precipitated with Bu_4N^+. This association probably accounts for the slow exchange of the N−H protons, which give clear signals at 14.67 ppm (fac) and at 13.89 and 13.58 ppm (mer). Dry PPh_4Cl was

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[43] Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 993.

[44] Jezowska-Trzebiatowska, B.; Hanuza, J.; Baluka, M. *Spectrochim. Acta* **1971**, *27A*, 1753.

[45] Fortin, S.; Beauchamp, A. L. *Inorg. Chem.*, submitted for publication.

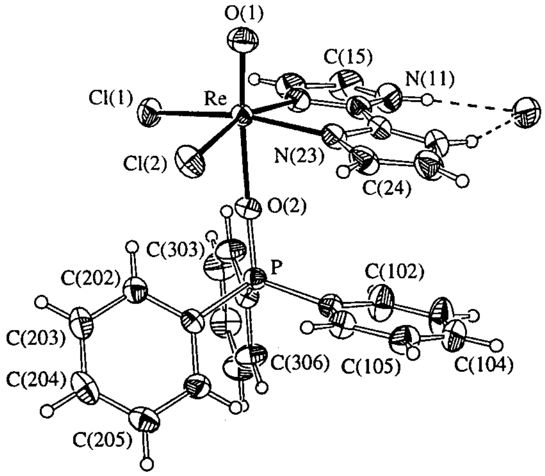


Figure 1. ORTEP drawing of [ReOCl$_2$(OPPh$_3$)(biimH$_2$)]Cl (**5**). Ellipsoids correspond to 40% probability. Dashed lines represent hydrogen bonds with the chloride ion.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **5**

Re−O(1)	1.640(3)	Re−O(2)	2.105(3)
Re−N(23)	2.084(3)	Re−N(13)	2.107(3)
Re−Cl(1)	2.3478(13)	Re−Cl(2)	2.3518(12)
P−O(2)	1.509(3)	N(11)−Cl(3)	3.067(5)
N(21)−Cl(3)	3.112(5)		

O(1)−Re−O(2)	175.74(14)	O(2)−Re−Cl(2)	85.73(8)
O(1)−Re−N(13)	96.0(2)	N(13)−Re−Cl(1)	93.30(10)
O(1)−Re−N(23)	95.0(2)	N(13)−Re−Cl(2)	164.28(10)
O(1)−Re−Cl(1)	98.18(14)	N(13)−Re−N(23)	78.42(14)
O(1)−Re−Cl(2)	97.55(13)	N(23)−Re−Cl(1)	165.12(10)
O(2)−Re−N(23)	82.09(13)	N(23)−Re−Cl(2)	92.49(10)
O(2)−Re−N(13)	80.38(12)	Cl(1)−Re−Cl(2)	92.60(5)
O(2)−Re−Cl(1)	84.35(9)	Re−O(2)−P	163.4(2)
Re−N(13)−C(12)	113.5(3)	Re−N(23)−C(22)	114.3(3)
Re−N(13)−C(14)	139.8(4)	Re−N(23)−C(24)	138.5(3)
N(11)−C(12)−C(22)	132.4(4)	N(21)−C(22)−C(12)	132.7(4)
N(13)−C(12)−C(22)	116.8(4)	N(23)−C(22)−C(12)	116.8(4)
N(11)−H(11)−Cl(3)	153	N(21)−H(21)−Cl(3)	151

added to induce crystallization, and a solid was isolated. The N−H protons appear at the same positions as above for the two isomers of ReOCl$_3$(biimH$_2$). The C−H resonances are partially masked by the strong peaks of PPh$_4^+$, whose integrations indicate that free PPh$_4$Cl has coprecipitated.

Crystal Structure of 5. The unit cell contains the structural unit shown in Figure 1, which consists of a distorted octahedral [ReOCl$_2$(OPPh$_3$)(biimH$_2$)]$^+$ cation and a Cl$^-$ counterion hydrogen-bonded to the N−H groups of biimH$_2$. The OPPh$_3$ ligand lies trans to the oxo ligand along the axial direction, whereas the chelating bidentate biimH$_2$ ligand and two cis Cl atoms occupy the equatorial plane. Selected distances and angles are listed in Table 2.

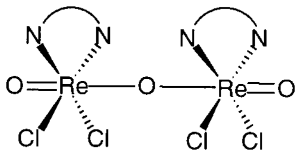
As often observed in monooxo systems, the equatorial ligands are displaced away from the Re═O group: the L−Re−O(P) angles are in the 80−86° range and the O═Re−L angles lie between 95 and 98°, the chlorines being slightly more displaced than the nitrogen donors, as noted for ReOCl$_3$(OPPh$_3$)(Me$_3$-benzimidazole).[27] The small bite angle (78.4(1)°) of biimH$_2$, similar to those found in other Re compounds,[45,46] leaves more space for the other equatorial ligands and leads to cis angles greater than those in the benzimidazole complex. The O═Re−O moiety does not deviate greatly from linearity (175.7(1)°), but the phosphine oxide is tilted away from this direction (Re−O−P = 163.4(2)°). This angle is within the range 160−165° [27,42,47,48] reported for related compounds. In the present case, the ligand is so oriented that the C(101)−C(106) phenyl ring is approximately parallel to biimidazole (dihedral angle = 8.6(4)°) and participates in π-stacking interactions with the N(21)−C(25) ring (inter-ring distance ~ 3.7 Å).

The Re═O distance (1.640(3) Å) lies at the short end of the range found for monooxo complexes (1.63−1.71 Å)[49] and is consistent with a triple-bond character.[50] The Re−Cl and Re−N distances are normal, whereas the Re−O(P) distance (2.105(3) Å) is at the upper limit of the range (2.07−2.10 Å) reported for other O═Re−OPPh$_3$ complexes.[27,42,47,48]

The biimH$_2$ ligand undergoes severe distortion upon chelation, since ring closure requires that the N donors move together. The geometry of the individual rings is not appreciably affected,[51,52] but strain develops at ring junction: the intra-ring N3−C2−C2′ angles (117°) are reduced by 8°, whereas the external N1−C2−C2′ angles increase (133°). Furthermore, the metal is not coordinated exactly along the lone-pair direction: the Re−N3−C2 angles in the chelate ring (114°) differ considerably from the Re−N3−C4 angles outside (139°). Although the two independent imidazole rings remain individually planar, the molecule is bent slightly about the C2−C2′ bond, leading to a dihedral angle of 6.7(4)° between these rings. The metal atom lies within 0.05 Å from the imidazole planes.

The Cl$^-$ counterion forms strong hydrogen bonds with the two N−H groups of coordinated biimH$_2$. The Cl···N distances (N(11)−Cl(3) = 3.067(5), N(21)−Cl(3) = 3.112(5) Å) are in the accepted range (2.91−3.53 Å),[53] and the hydrogen bonds do not deviate much from linearity (N−H−Cl ~ 151°). The rest of the environment of Cl$^-$ consists of weaker normal van der Waals contacts. Therefore, the structure is best described as a tight [ReOCl$_2$(OPPh$_3$)(biimH$_2$)]$^+$···Cl$^-$ ion pair, and considering the high solubility of this ionic compound in CHCl$_3$, CH$_2$Cl$_2$, and acetone, this ion pair probably survives in solution, as recently observed for related biimH$_2$ compounds.[45]

Oxo-Bridged Dinuclear Compounds. Wilkinson et al.[23] first prepared Re$_2$O$_3$Cl$_4$(bpy)$_2$ from ReCl$_5$ and bpy in acetone. Guest and Lock[54] obtained the same material by refluxing ReOCl$_3$(bpy) in ethanol. The stereochemistry was postulated to be that of the Re$_2$O$_3$Cl$_4$(py)$_4$ analogue, that is, to consist of a linear O═Re−O−Re═O backbone with perpendicular *cis*-dichloro−bipyridine planes (**E**). In our hands, hydrolysis of ReOCl$_3$(bpy) in wet acetone afforded a green solid, whose ^{1}H NMR spectrum showed a single set of bpy signals, consistent with the above assumption.



E

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(46) Bélanger, S.; Beauchamp, A. L. *Acta Crystallogr.* **1999**, *C55*, 517.

(47) Bryan, J. C.; Perry, M. C.; Arterburn, J. B. *Acta Crystallogr.* **1998**, *C54*, 1607.

(48) Rose, D. J.; Maresca, K. P.; Kettler, P. B.; Chang, Y. D.; Soghomomian, V.; Chen, Q.; Abrams, M. J.; Larsen, S. K.; Zubieta, J. *Inorg. Chem.* **1996**, *35*, 3548.

(49) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454.

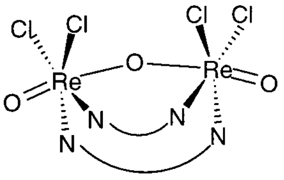
(50) Nugent, W. A.; Mayer, J. M. *Metal-ligand Multiple Bonds*; John Wiley & Sons: New York, 1987.

(51) Cromer, D. T.; Ryan, R. R.; Storm, C. B. *Acta Crystallogr.* **1987**, *C43*, 1435.

Hydrolysis of $ReOCl_3(biimMe_2)$ is not so simple. Refluxing in acetone containing 5% water yields a green material (**7**), which likely corresponds to the oxo-bridged bipyridine analogue. Its IR spectrum is typical of such oxo-bridged dimers:[10] a medium absorption at ~975 cm^{-1} attributed to the terminal oxo stretch and a very strong and broad band at ~700 cm^{-1} for the Re−O−Re stretch. Our frequency is slightly higher, but the shape is identical with the one described by Cotton et al.[55] for *cis,cis*-$Re_2O_3Cl_4(py)_4$. Lattice acetone gives rise to a medium C═O stretching band at 1700 cm^{-1}. Solution NMR spectra could not be obtained because of the poor solubility of **7** in all common solvents, but the simplicity of the ^{13}C CP-MAS spectrum is consistent with the relatively high symmetry expected for a $[\{OReCl_2(biimMe_2)\}_2(\mu\text{-}O)]$ species.

When $ReOCl_3(biimMe_2)$ is refluxed in acetone containing less water (1%), a different light-blue compound (**8**) is obtained, whose microanalysis corresponds to the same stoichiometry as above. Besides the absorptions due to $biimMe_2$, this material shows a Re═O band, weaker than above, at 972 cm^{-1}, but no Re−O−Re absorption in the 700−740 cm^{-1} range. The intensity of the acetone band at 1700 cm^{-1} is approximately twice as high as that for **7**, in agreement with elemental analysis. In DMSO-d_6, four ^1H NMR signals are observed for C−H protons and two for the methyl groups of $biimMe_2$. Coupling constants ($^3J_{HH}$) of 1.6 Hz are found for the aromatic signals. These data are consistent with two types of imidazole rings. The ^{13}C results lead to the same conclusion.

The crystallographic work described hereafter shows that the latter compound contains the O═Re−O−Re═O backbone and *cis*-$ReCl_2N_2$ planes perpendicular to this direction, but this time, the biimidazole ligands are bridging the two Re centers (**F**).



F

This $[\{OReCl_2\}_2(\mu\text{-}O)(\mu\text{-}biimMe_2)_2]$ species possesses a 2-fold axis through the bridging oxo ligand, making the two $biimMe_2$ ligands equivalent, in agreement with the NMR data.

Compound **8** seems to be the thermodynamic compound, since refluxing the chelate complex **7** in methanol leads to **8** instead of the expected oxo−methoxo compound ReO(OMe)-Cl_2(N−N).[10]

Hydrolysis experiments were not run on the nonmethylated complex $ReOCl_3(biimH_2)$ because it had been obtained only as an oily mixture of the mer and fac isomers. However, an oxo-bridged species was isolated when recrystallization of the $ReOCl_3(biimH_2)$ mixture was attempted in the presence of moist PPh_4Cl. Since the structure of **5** indicated a high affinity of Cl^- for the N−H groups of coordinated $biimH_2$, we hoped a $[ReOCl_3(biimH_2)\cdots Cl]^-$ adduct could form and precipitate as the PPh_4^+ salt. Chloride association with N−H groups indeed occurred, but the water introduced with PPh_4Cl converted $ReOCl_3(biimH_2)$ to an oxo-bridged dinuclear compound containing chelating $biimH_2$, which was isolated as the bisadduct $(PPh_4)_2[\{OReCl_2(biimH_2)\cdots Cl\}_2(\mu\text{-}O)]\cdot 2H_2O$.

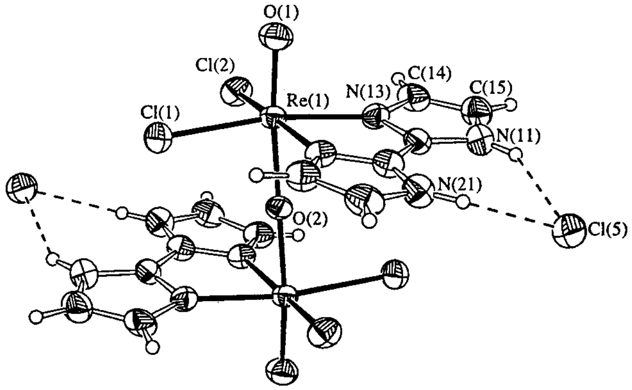


Figure 2. ORTEP drawing of the $[\{OReCl_2(biimH_2\cdots Cl)\}_2O]^{2-}$ units in **4**. The bridging O(2) atom lies on a crystallographic inversion center. The PPh_4^+ ions and lattice water molecules are not shown. Ellipsoids correspond to 40% probability. Dashed lines represent hydrogen bonds with the chloride ions.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **4**

Re(1)−O(1)	1.693(5)	Re(1)−O(2)	1.9047(6)
Re(1)−N(13)	2.109(6)	Re(1)−N(23)	2.138(6)
Re(1)−Cl(1)	2.408(2)	Re(1)−Cl(2)	2.386(2)
O(1)−Re(1)−O(2)	173.6(2)	O(2)−Re(1)−Cl(2)	89.21(5)
O(1)−Re(1)−N(13)	92.1(3)	N(13)−Re(1)−N(23)	77.2(2)
O(1)−Re(1)−N(23)	91.1(3)	N(13)−Re(1)−Cl(1)	170.1(2)
O(1)−Re(1)−Cl(1)	95.2(2)	N(13)−Re(1)−Cl(2)	96.0(2)
O(1)−Re(1)−Cl(2)	95.7(2)	N(23)−Re(1)−Cl(1)	96.1(2)
O(2)−Re(1)−N(13)	83.2(2)	N(23)−Re(1)−Cl(2)	170.5(2)
O(2)−Re(1)−N(23)	83.5(2)	Cl(2)−Re(1)−Cl(1)	89.86(7)
O(2)−Re(1)−Cl(1)	88.93(5)	Re(1)−O(2)−Re(2)	180.0
Re−N(13)−C(12)	115.0(5)	Re−N(23)−C(22)	113.1(5)
Re−N(13)−C(14)	139.0(5)	Re−N(23)−C(24)	139.6(5)
N(13)−C(12)−C(22)	116.7(6)	N(23)−C(22)−C(12)	117.5(6)
N(11)−C(12)−C(22)	131.6(7)	N(21)−C(22)−C(12)	131.4(7)

Crystal Structure of 4. This compound contains the oxo-bridged dinuclear species $[\{OReCl_2(biimH_2)\}_2(\mu\text{-}O)]$ with a linear O═Re−O−Re═O backbone (Figure 2) similar to those of the $[\{OReCl_2(py)_2\}_2(\mu\text{-}O)]$ compound studied by Lock and Turner[56] and related systems. The unit cell also contains two Cl^- and two PPh_4^+ ions per dinuclear molecule. As observed above, a Cl^- ion is hydrogen-bonded to the N−H groups of each $biimH_2$ ligand. Therefore, the structure is best described as the bis-PPh_4^+ salt of the tightly associated $[\{OReCl_2(biimH_2\cdots Cl)\}_2(\mu\text{-}O)]^{2-}$ unit. Selected distances and angles are listed in Table 3.

Deviation from linearity in the O═Re−O−Re═O backbone is small. The halves of the molecule are related by a crystallographic inversion center. Therefore, the Re−O−Re angle is exactly 180° and the two O−Re═O angles are equal (173.6-(2)°). As usual, the donor atoms in the $ReCl_2N_2$ plane are repelled by the Re═O group, but the deviation from 90° is ~3° less here than in the monomeric complex **5**. The Re═O and Re−O distances of 1.693(5) and 1.905(1) Å are typical of this backbone.[10,25,56]

The particularities of chelated biimidazole mentioned above are observed here as well: bite angle of 77.2(2)°, strain at ring junction (intra-ring N3−C2−C2′ angles ~15° greater than external N1−C2−C2′ angles), and coordination off the lone-pair direction (Re−N3−C2 angles in the chelate ring ~15°

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(52) Therrien, B.; Beauchamp, A. L. *Acta Crystallogr.* **1999**, *C55*, IUC9900054.

(53) Stout, G. H.; Jensen, L. H. *X-ray Structure Determination*: *A Practical Guide*; Macmillan: New York, 1968.

(54) Guest, A.; Lock, C. J. L. *Can. J. Chem.* **1971**, *49*, 603.

(55) Cotton, F. A.; Robinson, W. R.; Walton, R. A. *Inorg. Chem.* **1967**, *6*, 223.

(56) Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1978**, *56*, 179.

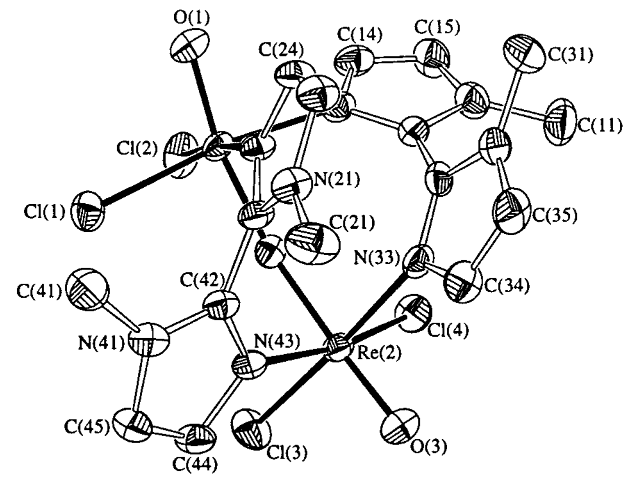

Figure 3. ORTEP drawing of the [{OReCl$_2$}$_2$(μ-O)(μ-biimMe$_2$)$_2$] molecule (**8**) in the acetone solvate. Ellipsoids correspond to 40% probability. Hydrogens are omitted for clarity.

greater than the Re−N3−C4 angles outside). The two imidazole rings show a dihedral angle of 6.8°, and the Re atom is only 0.104 and 0.039 Å out of the imidazole planes.

In contrast to the case of [{OReCl$_2$(py)$_2$}$_2$(μ-O)][10,56] and related systems with monodentate N ligands,[25,28] the biimH$_2$ ligand must be perpendicular to the backbone. The halves of the molecule being related by a crystallographic inversion center at the central μ-oxo ligand, the two biimidazole ligands are on opposite sides and show no stacking interactions. The distances of the Cl atoms of one unit to the biimidazole plane in the other unit are 3.70 (Cl(1)) and 3.64 Å (Cl(2)), that is, roughly equal to the sum of the van der Waals radii.[57]

The strong affinity of the Cl$^-$ anion for the N−H groups of coordinated biimH$_2$ has been noted above and elsewhere.[45,46] The chloride ion is attached to biimidazole through two moderately strong hydrogen bonds: N(11)···Cl(5) = 3.216(8) Å; N(21)···Cl(5) = 3.040(7) Å; N−H−Cl angle ~153°. The lattice also includes one water molecule per Cl$^-$ ion, which is hydrogen-bonded to this anion (O(4)···Cl(5) = 3.149(8) Å; O−H−Cl = 169°) and to a coordinated Cl atom (O(4)···Cl(1) = 3.279(9) Å; O−H−Cl = 179°). PPh$_4^+$ simply acts as a counterion without particular interactions with the rest of the structure.

Crystal Structure of 8. The molecule (Figure 3) contains an O═Re−O−Re═O backbone, and an equatorial set of Cl$_2$N$_2$ donors is found about each Re atom. In contrast with **4**, the two biimMe$_2$ ligands are bridging and the O═Re−O−Re═O unit is bent at the center. Selected distances and angles are given in Table 4.

The rhenium−oxygen bonds do not differ greatly from those found in **4**, but the Re−Cl bonds are, on average, ~0.020 Å shorter, whereas the Re−N bonds are ~0.020 Å longer. Departure from linearity in the O═Re−O−Re═O backbone is unusually large: the central Re−O−Re unit is bent to 162.6(3)° and the O═Re−O angles average 167.1°. On the other hand, the cis angles in the ReCl$_2$N$_2$ planes are close to ideality (88.7−91.5°): the N−Re−N angle, which was imposed (77°) by the chelate ring in **4** and **5**, has now returned to the normal ~91° value, without introducing appreciable changes in the Cl−Re−Cl angles (~90.2°). A general displacement of the cis ligands away from the Re═O bond is noted, as usual: the O═Re−L$_{cis}$ angles are, on average, ~6° greater than the corresponding L$_{cis}$−Re−O angles. Thus, by trading a chelating for a bridging role, the biimidazole units introduce some strain in the dimer, especially in the backbone. However, from the standpoint of the biimidazole moiety, coordination takes place more "naturally": the Re−N−C angles inside and outside the chelate ring now differ by only ~4°, and they are close to those observed for imidazole or benzimidazole dioxo complexes.[4,58] Similarly, strain at the ring junction is reduced: the internal and external angles at C2 differ by only ~6.3°. However, less energy-costly distortions appear elsewhere. The two imidazole rings in the ligands are not coplanar: rotation about the C2−C2′ bonds generates a dihedral angle of ~62°. The two ReCl$_2$N$_2$ units are rotated by ~50° from the eclipsed conformation, which allows the bridging biimidazoles to interact by π stacking via rings N(21)−C(25) and N(31)−C(35): these planes are almost parallel (dihedral angle = 11.3(5)°), and the distance between the ring centers is 3.3 Å.

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compound **8**

Re(1)−O(1)	1.685(5)	Re(2)−O(3)	1.681(6)
Re(1)−O(2)	1.894(5)	Re(2)−O(2)	1.897(5)
Re(1)−N(13)	2.144(7)	Re(2)−N(33)	2.131(6)
Re(1)−N(23)	2.127(6)	Re(2)−N(43)	2.170(6)
Re(1)−Cl(1)	2.373(2)	Re(2)−Cl(3)	2.370(2)
Re(1)−Cl(2)	2.389(2)	Re(2)−Cl(4)	2.372(2)
O(1)−Re(1)−O(2)	168.2(2)	O(3)−Re(2)−O(2)	166.0(2)
O(1)−Re(1)−N(13)	90.0(3)	O(3)−Re(2)−N(33)	86.3(3)
O(1)−Re(1)−N(23)	87.5(2)	O(3)−Re(2)−N(43)	90.0(3)
O(1)−Re(1)−Cl(1)	98.3(2)	O(3)−Re(2)−Cl(3)	97.4(2)
O(1)−Re(1)−Cl(2)	96.8(2)	O(3)−Re(2)−Cl(4)	98.9(2)
O(2)−Re(1)−N(13)	81.1(2)	O(2)−Re(2)−N(33)	83.9(2)
O(2)−Re(1)−N(23)	84.7(2)	O(2)−Re(2)−N(43)	80.3(2)
O(2)−Re(1)−Cl(1)	90.5(2)	O(2)−Re(2)−Cl(3)	92.6(2)
O(2)−Re(1)−Cl(2)	91.1(2)	O(2)−Re(2)−Cl(4)	90.8(2)
N(23)−Re(1)−N(13)	90.3(2)	N(33)−Re(2)−N(43)	91.5(2)
N(23)−Re(1)−Cl(1)	88.8(2)	N(33)−Re(2)−Cl(4)	88.7(2)
N(13)−Re(1)−Cl(2)	90.0(2)	N(43)−Re(2)−Cl(3)	89.3(2)
Cl(1)−Re(1)−Cl(2)	90.36(8)	Cl(3)−Re(2)−Cl(4)	89.98(8)
Cl(1)−Re(1)−N(13)	171.6(2)	Cl(3)−Re(2)−N(33)	176.3(2)
Cl(2)−Re(1)−N(23)	175.7(2)	Cl(4)−Re(2)−N(43)	171.0(2)
Re(1)−O(2)−Re(2)	162.6(3)		
Re−N(13)−C(12)	128.5(5)	Re−N(33)−C(32)	131.1(5)
Re−N(13)−C(14)	126.0(5)	Re−N(33)−C(34)	123.7(5)
Re−N(23)−C(22)	129.6(5)	Re−N(43)−C(42)	129.3(5)
Re−N(23)−C(24)	123.5(5)	Re−N(43)−C(44)	123.7(5)
N(11)−C(12)−C(32)	120.3(7)	N(31)−C(32)−C(12)	122.1(7)
N(13)−C(12)−C(32)	129.4(7)	N(33)−C(32)−C(12)	128.0(7)
N(21)−C(22)−C(42)	122.7(7)	N(41)−C(42)−C(22)	122.1(7)
N(23)−C(22)−C(42)	128.6(6)	N(43)−C(42)−C(22)	128.4(7)
N(11)−C(12)−C(32)−N(31)	56.2(11)		
N(13)−C(12)−C(32)−N(33)	65.3(12)		
N(23)−C(22)−C(42)−N(43)	64.3(12)		
N(21)−C(22)−C(42)−N(41)	60.9(10)		

Structural Differences between the biimH$_2$ and bpy Ligands. Although ReOCl$_3$(N−N) and [{OReCl$_2$(N−N)}$_2$(μ-O)] compounds are formed by both biimidazole and bipyridine, these two ligands exhibit major structural differences due to the sizes of their respective aromatic rings. In idealized bipyridine, the lone-pair directions meet at ~2.8 Å from the N donors, which is not drastically greater than a normal Re−N distance (~2.10 Å). A chelate ring can form with minimal distortion: the C−C−N angles at the ring junction remain close to 120° (θ ~ 116°, θ' ~ 124°), and the metal lies only 3−4° off the lone-pair direction (ϕ ~ 116°, ϕ' ~ 124°), whereas the small bite angle β (~75°) is accommodated readily in an

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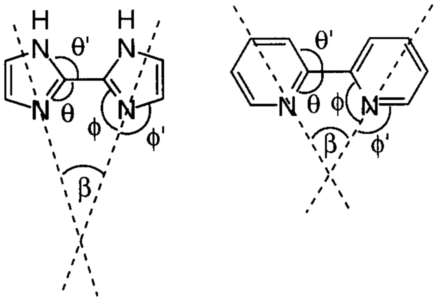
(57) Huheey, J. E.; Keiter, R. L.; Keiter, E. A. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; p 292.

(58) Bélanger, S.; Fortin, S.; Beauchamp, A. L. *Can. J. Chem.* **1997**, *75*, 37.



octahedral environment.[59] For an idealized biimidazole unit, the lone-pair directions converge at a much greater distance (4.9 Å), so that severe distortion is required to close the ring. In the structures above and that of $[\{\mathrm{ORe(biimH_2)_2}\}_2(\mu\text{-O})]\mathrm{Cl_4}$,[46] the intra-ring angles θ at the connecting C2−C2′ bonds have reduced from 125 to 117° to bring the N donors closer. Furthermore, the Re−N vector deviates by 13° from the lone-pair direction ($\phi \sim 115°$, $\phi' \sim 140°$). However, in the case of methylated biimidazole, which normally exists as the anti conformer[52] but is forced into a syn arrangement in the chelate, distortion moves the methyl groups apart, thereby reducing steric hindrance.

In contrast to bipyridine, $\mathrm{biimMe_2}$ forms two isomeric oxo-bridged dinuclear compounds: the standard single-bridge $[\{\mathrm{OReCl_2(biimMe_2)}\}_2(\mu\text{-O})]$ molecule (**E**), containing chelated $\mathrm{biimMe_2}$, and the triple-bridge $[\{\mathrm{OReCl_2}\}_2(\mu\text{-O})(\mu\text{-biimMe_2})_2]$ species (**F**), in which both $\mathrm{biimMe_2}$ ligands are bridging. The latter is apparently the more stable, since it forms instead of the expected alkoxo compound $\mathrm{ReO(OMe)Cl_2(biimMe_2)}$ when the single-bridge complex is refluxed in methanol. By comparing structures **4** and **8**, we note that the distortions pointed out earlier for chelated biimidazole are appreciably reduced when the ligand is bridging: the differences between the angles inside and outside the chelate rings are now only 5° at N3 and 6° at C2. In bridging $\mathrm{biimMe_2}$, the rings are no longer coplanar, which suggests that breaking the resonance between the two aromatic systems is not energy costly.

Concluding Remarks

Synthetic work with nonmethylated biimidazole ($\mathrm{biimH_2}$) is hampered by the very low solubility of this ligand, which can be ascribed to extended stacking interactions and efficient N−H···N hydrogen bonding in the crystal.[51] Unreacted ligand is difficult to remove; compounds initially formed tend to decompose when the reaction is pursued or redissolution is attempted for purification. On the other hand, short reaction times lead to $[\mathrm{ReOCl_2(OPPh_3)(biimH_2)}]\mathrm{Cl}$, in which strong ion pairing is observed to take place via $\mathrm{N{-}H\cdots Cl^-}$ hydrogen bonding. Chloride association also allows isolation of the oxo-bridged complex $[\{\mathrm{OReCl_2(biimH_2)}\}_2(\mu\text{-O})]$ as the bis-$\mathrm{PPh_4Cl}$ adduct, which is best described as the $\mathrm{PPh_4^+}$ salt of the $[\{\mathrm{OReCl_2(biimH_2\cdots Cl)}\}_2(\mu\text{-O})]^{2-}$ unit. This type of interaction seems to exist whenever halide ions are present[45,46,60] and apparently has an important, although yet unpredictable, role. We believe the solubility of $\mathrm{ReOCl_3(biimH_2)}$, much higher than that of $\mathrm{ReOCl_3(biimMe_2)}$, is due to an associated $[\mathrm{ReOCl_3(biimH_2\cdots Cl)}]^-$ species that cannot be precipitated by $\mathrm{Bu_4N^+}$. Therefore, the strong tendency of coordinated $\mathrm{biimH_2}$ to form hydrogen bonds should be taken into account in devising strategies for preparing clean materials.

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Supporting Information Available: X-ray crystallographic files in CIF format for **4**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(59) Based on nine crystal structures of Re−bipyridine compounds. *Cambridge Structural Database*, Version 5.18; Cambridge University: Cambridge, England (accessed Oct 1999).

(60) Bélanger, S.; Beauchamp, A. L. *Acta Crystallogr.* **1996**, *C52*, 2588.