Inorganic Chemistry

Article

Unusual Reactivity of the {Re^{V}O}$^{3+}$ Core: Syntheses and Characterization of Novel Rhenium Halide Complexes with *N*-Methyl-*o*-diaminobenzene

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The reactions of 1 or 2 equiv of *N*-methyl-*o*-diaminobenzene with *trans*-[ReOX$_3$(PPh$_3$)$_2$] (X = Cl, Br) in refluxing chloroform gave oxo-free rhenium complexes [Re^{VI}X$_4$(NC$_6$H$_4$NHCH$_3$)(OPPh$_3$)] (X = Cl, **3**; X = Br, **6**), [Re^{V}X$_2$Y-(NC$_6$H$_4$NHCH$_3$)(PPh$_3$)$_2$] (X, Y = Cl, **4**; X = Br, Y = Cl, **7**), [Re^{IV}Cl$_2$(NHC$_6$H$_4$NCH$_3$)$_2$] (**5**), and [Re^{IV}Br$_3$-(NHC$_6$H$_4$NCH$_3$)(PPh$_3$)] (**8**). All complexes were characterized by elemental analysis, ^{1}H NMR and IR spectroscopy, cyclic voltammetry, EPR spectroscopy, and X-ray crystallography. The complexes all display distorted octahedral coordination geometry. For Re(IV) complexes **5** and **8**, the ligands coordinate in the benzosemiquinone diimine form. In Re(VI) complexes **3** and **6** and the Re(V) complexes **4** and **7**, the ligands coordinate in the dianionic monodentate imido form. The EPR spectra of Re(VI) species **3** and **6** in dichloromethane solution at room temperature exhibit the characteristic hyperfine pattern of six lines, with evidence of strong second-order effects. The IR spectra of the complexes are characterized by Re≡N and Re–N stretching bands at ca. 1090 and 540 cm^{-1}, respectively. The Re(IV) and Re(V) complexes display well-resolved NMR spectra, while the Re(VI) complexes exhibit no observable spectra, due to paramagnetism. The cyclic voltammograms of complexes **3** and **6** display Re(VII)/Re(VI) and Re(VI)/Re(V) processes, those of **4** and **7** exhibit Re(VI)/Re(V) and Re(V)/Re(IV) couples, and those of **5** and **8** are characterized by Re(V)/Re(IV) and Re(IV)/Re(III) processes.

Introduction

A major focus of the contemporary interest in the chemistries of the group VII congeners technetium and rhenium reflects the applications of certain isotopes to radiopharmaceutical development.[1,2] ^{99m}Tc-based radiopharmaceuticals continue to provide the mainstay in diagnostic nuclear medicine due to the optimal nuclear properties (γ-emitter, E_{max} = 140 keV, $t_{1/2}$ = 6 h) and ready availability from the ^{99}Mo/^{99m}Tc generator.[3] Furthermore, the radionuclides of rhenium, the group 7 congener of Tc, are β-emitters with properties which make them suitable for radiotherapeutic applications (^{186}Re, E_{max} = 1.07 MeV, $t_{1/2}$ = 90 h; ^{188}Re, E_{max} = 2.12 MeV, $t_{1/2}$ = 17h).[4] Complexes of nonradioactive isotopes of rhenium also serve as model compounds for the chemically related technetium compounds.

The chemistry of the group 7 congeners technetium and rhenium is unusual in that all formal oxidation states between −1 and +7 are represented by stable compounds.[5] The most stable and readily accessible oxidation states are often characterized by chemically robust core structures, which may be exploited as platforms for the development of radiophar-

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(1) (a) Arano, Y. *Ann. Nucl. Med.* **2002**, *16*, 79. (b) Johannsen, B. *Wiss.-Tech. Ber.—Forschungszent. Rossendorf* **2002**, *FZR-340*, 1. (c) Nicolini, M.; Bandoli, G.; Mazzi, U., Eds. *Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine*; New York, 2000; Vol. 5. (d) Jurisson, S. S.; Lyden, J. D. *Chem. Rev.* **1999**, *99*, 2205. (e) Liu, S.; Edwards, O. S. *Chem. Rev.* **1999**, *99*, 2235. (f) Dilworth, J. R.; Parrott, S. J. *Chem. Soc. Rev.* **1998**, *27*, 43. (g) Hom, R. K.; Katzenellenbogen, J. A. *Nucl. Med. Biol.* **1997**, *24*, 485.
(2) (a) Kohlickova, M.; Jedinakova-Krizova, V.; Melichar, F. *Chem. Listy* **2000**, *94*, 151. (b) Volkert, W. A.; Hoffman, T. J. *Chem. Rev.* **1999**, *99*, 2269. (c) Palmedo, H.; Guhlke, S.; Bender, H.; Sartor, J.; Schoeneich, G.; Risse, J.; Grunwalk, F., Jr.; Knapp, F. F.; Biersack, H. J. *Eur. J. Nucl. Med.* **2000**, *27*, 123.
(3) Steigman, I.; Eckelman, W. C. *The Chemistry of Technetium in Medicine*; National Academy Press: Washington, DC, 1992.
(4) Ehrhardt, J.; Ketring, A. R.; Turpin, T. A.; Razavi, M. S.; Vanderheyden, J. L.; Su, F. M.; Feitzberg, A. R. In *Technetium and Rhenium in Chemistry and Nuclear Medicine*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1990; Vol. 3.
(5) Blower, P. J.; Prakash, S. *Perspect. Bioinorg. Chem.* **1999**, *4*, 91.

maceutical reagents.[6] Examples of these cores include the metal oxo unit $\{M^VO\}^{3+}$, the metal nitrido group $\{M^VN\}^{2+}$,[7] the metal hydrazino moiety $\{M(H_xNNR)_n\}^{m+}$,[8,9] and the metal tricarbonyl core $\{M^I(CO)_3\}^+$,[10,11] of which the metal oxo core is the most extensively developed. The $\{MO\}^{3+}$ subunit is stabilized by π-donating alkoxide and thiolate ligands. Consequently, compounds of the $\{M^VO\}^{3+}$ core with N_xS_{4-x} tetradentate ligands with square-pyramidal geometry have been extensively investigated. These include N_4 propyleneamine oxime (PnAO),[12] N_3S triamidomonothiols,[13] N_2S_2 diamidodithiols (DADSs),[14] N_2S_2 monoaminomonoamidodithiols (MAMAs),[15] and diaminodithiols (DADTs),[16] including numerous examples of tripeptides and tetrapeptides appropriately derivatized to act as bifunctional chelators. While the $\{MO\}^{3+}$ core is robust and readily accessible by reduction of the parent MO_4^-, the inevitable formation of multiple isomers with N_xS_{4-x} ligand types[17–21] differing in their pharmacokinetic properties has hindered the widespread

application of such reagents and led to consideration of other ligand sets, as well as core structures. Consequently, the $\{MO\}^{3+}$ core has been investigated with mixed N_xP_y and S_xP_y ligands[22–24] as well as N_4 donor types.[25] Another strategy for the synthesis of neutral complexes with the $\{MO\}^{3+}$ core employs a mixed-ligand set of a tridentate dithiolate of the type $(S–X–S)^{2-}$ (where $X = O$, S, or NR) and a monodentate thiolate, hence the description "3 + 1" mixed-ligand complexes.[26–28] A serious drawback to this approach is the tendency of the 3 + 1 system to undergo further substitution reactions in vivo, presumably to achieve a closed shell,[29] and the lability of the monodentate ligand in the presence of competing ligating functions.

As part of our continuing investigations of the coordination chemistry of the oxorhenium(V) core, we have investigated the chemistry of $\{ReO\}^{3+}$ with efficient chelating ligands which may provide platforms for further derivatization. It is noteworthy that $\{Re^VO\}^{3+}$ is a redox-active moiety which

(6) Banerjee, S. R.; Francesconi, L.; Valliant, J. F.; Babich, J. W.; Zubieta, J. *Nucl. Med. Biol.*, in press.

(7) (a) Bolzati, C.; Boschi, A.; Uccelli, L.; Malogo, E.; Bandoli, G.; Tisato, F.; Refosco, F.; Pasqualini, R.; Duatti, A. *Inorg. Chem.* **1999**, *38*, 4473. (b) Bolzati, C.; Boschi, A.; Uccelli, L.; Tisato, F.; Refosco, F.; Cagnolini, A.; Duatti, A.; Prakash, S.; Bandoli, G.; Vittadini, A. *J. Am. Chem. Soc.* **2002**, *124* (38), 11468 and references therein.

(8) Hirsch-Kuchma, M.; Nicholson, T.; Davison, A.; Jones, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 3189.

(9) Rose, D. J.; Maresca, K. P.; Nicholson, T.; Davison, A.; Jones, A. G.; Babich, J.; Fischman, A.; Graham, W.; DeBord, J. R. D.; Zubieta, J. *Inorg. Chem.* **1998**, *37*, 2701 and references therein.

(10) (a) Waibei, R.; Alberto, R.; Willude, J.; Finnern, R.; Schibli, R.; Stichelberger, A.; Egli, A.; Abram, U.; Mach, J. P.; Pluckthern, A.; Schubiger, P. A. *Nat. Biotechnol.* **1999**, *17*, 897. (b) Egli, A.; Alberto, R.; Tannahill, L.; Schibli, R.; Abram, U.; Schaffland, A.; Waibel, R.; Tourwe, D.; Jeannin, L.; Iterbeke, K.; Schubiger, P. A. *J. Nucl. Med.* **1999**, *40*, 1913. (c) Schibli, R.; LaBelle, R.; Alberto, R.; Garcia-Garayoa, L.; Ortner, K.; Abram, U.; Schubiger, P. A. *Bioconjugate Chem.* **2000**, *11*, 345. (d) Pak, J. K.; Benny, P.; Spingler, B.; Ortner, K.; Alberto, R. *Chemistry* **2003**, *9*, 2053. (e) Alberto, R.; Schbli, R.; Angst, D.; Schubiger, P. A.; Abram, U.; Abram, S.; Kaden, T. L. A. *Transition Met. Chem. (London)* **1997**, *22*, 597. (f) Alberto, R.; Schlibi, R.; Egli, A.; Schubiger, A. P. A. *J. Am. Chem. Soc.* **1998**, *120*, 7987. (g) Alberto, R.; Schlibi, R.; Schubiger, A. P. *J. Am. Chem. Soc.* **1999**, *121*, 6076. (h) Amann, A.; Decristoforo, C.; Ott, I.; Wenger, M.; Bader, D.; Alberto, R.; Putz, G. *Nucl. Med. Biol.* **2001**, *28*, 243. (i) Schibli, R.; Schwartzbach, R.; Alberto, R.; Ortner, K.; Schmalle, H.; Dumas, C.; Egli, A.; Schubiger, P. A. *Bioconjugate Chem.* **2002**, *13*, 750. (j) Alberto, R.; Ortner, K.; Wheatley, N.; Schibli, R.; Schubiger, A. P. *J. Am. Chem. Soc.* **2001**, *123*, 3135.

(11) (a) Stephenson, K. A.; Zubieta, J.; Banerjee, S. R.; Levadala, M. K.; Taggart, L.; Ryan, J.; McFarlane, N.; Boreham, D. R.; Maresca, K. P.; Babich, J. W.; Valliant, J. F. *Bioconjugate Chem.* **2004**, *15*, 128. (b) Banerjee, S. R.; Levadala, M. K.; Lazarova, N.; Wei, L.; Valliant, J. F.; Stephenson, K. A.; Babich, J. W.; Maresca, K. P.; Zubieta, J. *Inorg. Chem.* **2002**, *41*, 6417. (c) Wei, L.; Banerjee, S. R.; Levadala, M. K.; Babich, J. W.; Zubieta, J. *Inorg. Chem. Commun.* **2003**, *6*, 1099.

(12) Papadopoulos, M.; Nock, B.; Maina, T.; Pirmettis, I.; Raptopoulou, C.; Tasiopoulos, A.; Troganis, A.; Kabanos, T.; Terzis, A.; Chiotellis, E. *J. Biol. Inorg. Chem.* **2001**, *6*, 159.

(13) Vanbilloen, H. P.; Bormans, G. M.; DeRoo, M. J.; Verbruggen, A. M. *Nucl. Med. Biol.* **1995**, *22*, 325 and references therein.

(14) Rao, T. N.; Adhikesavalu, D.; Camerman, A.; Fritzberg, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 5798.

(15) Meegalla, S.; Plössl, K.; Kung, M.-P.; Chumpradit, S.; Stevenson, D. A.; Kushner, S. A.; McElgin, W. T.; Mozley, P. D.; Kung, H. F. *J. Med. Chem.* **1997**, *40*, 9 and references therein.

(16) O'Neill, J. P.; Wilson, S. R.; Katzenellenbogen, J. A. *Inorg. Chem.* **1994**, *33*, 319.

(17) (a) Rajagopalan, R.; Grummom, G. D.; Bugaj, J.; Hallemann, L. S.; Webb, E. G.; Marmion, M. E.; Vanderheyden, J.-L.; Srinivasan, A. *Bioconjugate Chem.* **1997**, *8*, 407. (b) Pollak, A.; Roe, D. G.; Pollack, C. M.; Lu, L. F.; Thornback, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 11593.

(18) Numerous examples of peptide-based bifunctional chelators for the $\{Tc^VO\}^{3+}$ core have been described in recent years. Representative examples include (i) MAG$_3$ types (MAG$_3$ = mercaptoacetylglycylglycylglycine) [(a) Liu, S.; Edwards, D. S.; Looby, R. J.; Poirier, M. J.; Rajopadhye, M.; Bourque, J. P.; Carroll, T. R. *Bioconjugate Chem.* **1996**, *7*, 196. (b) Kasina, S.; Sanderson, J. A.; Fitzner, J. N.; Srinivasan, A.; Rao, T. N.; Hobson, L. J.; Reno, J. M.; Axworthy, D. B.; Beaumier, P. L.; Fritzberg, A. R. *Bioconjugate Chem.* **1998**, *9*, 108. (c) Zhu, Z.; Wang, Y.; Zhang, Y.; Liu, G.; Liu, N.; Rusckowski, M.; Hnatowich, D. *J. Nucl. Med. Biol.* **2001**, *28*, 703 and references therein. (d) Van Domselaar, G. H.; Okarvi, S. M.; Fanta, M.; Suresh, M. R.; Wishart, D. S. *J. Labelled Compd. Radiopharm.* **2000**, *43*, 1193], (ii) other cysteine-containing tripeptides and derivatives [(e) Goodbody, A.; Pollak, A. Peptide-chelator conjugates for diagnostic imaging. PCT Int. Appl. 1995; p 22. (f) Pollak, A.; Goodbody, A. E.; Ballinger, J. R.; Duncan, G. S.; Tran, L. L.; Dunn-Dufault, R.; Meghji, K.; Lau, F.; Andrey, T. W. *Nucl. Med. Commun.* **1996**, *17*, 132. (g) Lister-James, J.; Knight, L. C.; Mauer, A. H.; Bush, L. R.; Moyer, B. R.; Dean, R. T. *J. Nucl. Med.* **1996**, *37*, 775. (h) Pearson, D. A.; Lister-James, J.; McBride, W. J.; Wilson, D. M.; Martel, L. J.; Civitello, E. R.; Taylor, J. E.; Moyer, B. R.; Dean, R. T. *J. Med. Chem.* **1996**, *39*, 1361. (i) Wishart, D. S. *Biotechnology (2nd Ed.). 1991– 2001*, *5b*, 325], and (iii) Gly-Ala-Gly-Gly peptide [(j) Ben-Haim, S.; Kahn, D.; Weiner, G.; Madsen, M. T.; Waxman, A. D.; Williams, C. M.; Maguire, R. T. *Nucl. Med. Biol.* **1994**, *21*, 131]. (k) Luyt, L. G.; Hunter, D. H. Technetium-99m labeling of tamoxifen and lysine derivatives using an N2S2 bifunctional chelator: Single isomer radiopharmaceuticals. *Book of Abstracts*, 217th ACS National Meeting, Anaheim, CA, March 21–25, 1999; American Chemical Society: Washington, DC, 1999; NUCL-184.

(19) Zhuang, Z.-P.; Plössl, K.; Kung, M.-P.; Mu, M.; Jung, H. F. *Nucl. Med. Biol.* **1999**, *26*, 217.

(20) Wong, E.; Fauconnier, T.; Bennett, S.; Valliant, J.; Nguyen, T.; Lau, F.; Lu, L. F. L.; Pollak, A.; Bell, R. A.; Thornback, J. R. *Inorg. Chem.* **1997**, *36*, 5799.

(21) Hansen, L.; Hirota, S.; Xu, X.; Taylor, A. T.; Marzilli, L. G. *Inorg. Chem.* **2000**, *39*, 5731 and references therein.

(22) Tisato, F.; Refosco, F.; Ossola, F.; Bolzati, C.; Bandoli, G. *Transition-Met. Chem. (London)* **1997**, *22*, 606 and references therein.

(23) Ossola, F.; Tisato, F.; Refosco, F. *Inorg. Chim. Acta* **2002**, *330*, 17.

(24) Bolzati, C.; Tisato, F.; Refosco, F.; Bandoli, G.; Domella, A. *Inorg. Chem.* **1996**, *35*, 6221.

(25) Kurti, L.; Papagiannopoulou, D.; Papadopoulos, M.; Pirmettis, I.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E.; Harmata, M.; Kuntz, R. R.; Pandurangi, R. S. *Inorg. Chem.* **2003**, *42*, 2960.

(26) Papadopoulos, M.; Pirmettis, I.; Tsoukalas, C.; Nock, B.; Maina, T.; Raptopoulou, C. P.; Pietzsch, H.-J.; Friebe, M.; Spies, H.; Johannsen, B.; Chiotellis, E. *Inorg. Chim. Acta* **1999**, *295*, 1–8.

(27) Siefert, S.; Gupta, A.; Syhre, R.; Spies, H.; Johannsen, B. *Appl. Radiat. Isot.* **2001**, *54*, 637 and references therein.

(28) Syhre, R.; Seifert, S.; Spies, H.; Gupta, A.; Johannsen, B. Stability versus reactivity of "3+1" mixed-ligand technetium-99m complexes in vitro and in vivo. *Eur. J. Nucl. Med.* **1998**, *25* (7), 793–796.

(29) Nock, B.; Maina, T.; Tisato, F.; Papadopoulos, M.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E. *Inorg. Chem.* **2000**, *39*, 2178.

Scheme 1
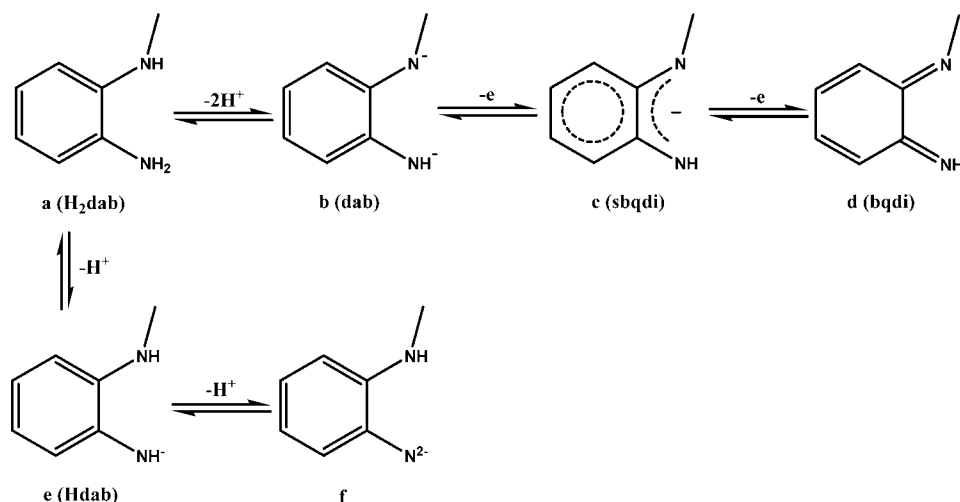
is also chemically reactive as an oxo-transfer unit. This is a significant caveat in the design of radiopharmaceuticals since unexpected and complex reaction chemistry is not at all unusual for the $\{ReO\}^{3+}$ core. This is amply demonstrated in the reactions of oxorhenium(V) species with N-substituted *o*-diaminobenzene undertaken in this study.

o-Diaminobenzene (dab) is a highly delocalized, unsaturated, electron-rich molecule which can serve as a bidentate or monodentate ligand. Scheme 1 summarizes the different forms and oxidation states of the dab derivative *N*-methyl-*o*-diaminobenzene in transition-metal complexes. The reaction of *o*-diaminobenzene and its derivatives with transition metals has been studied extensively, since it leads to complexes with diverse oxidation−reduction processes,[30] and it also provides complexes with unusual structural, magnetic, and chemical properties.[31]

The neutral diaminobenzene bidentate form **a** (H$_2$dab) has been found in the platinum(II) complex [Pt(H$_2$dab)I$_2$],[32] the copper(II) species [Cu(H$_2$dab)$_2$(BF$_4$)$_2$],[33] and the nickel(II) complex [Ni(H$_2$dab)$_2$Cl$_2$].[34] Form **a** can be deprotonated to give the monoimido monoanion form **e** (Hdab) and the 1,2-diamine dianion form **b** (dab). Type **b** has been isolated in (*n*-Bu$_4$N)[Tc^{V}O(dab)$_2$][31a] and in the oxo-free complexes [Re^V(dab)$_2$Cl(PPh$_3$)],[35] [Tc^{VII}(dab)$_3$](TcO$_4$),[31a] and [Re^{VII}-(dab)$_3$][ReO$_4$].[36] Form **e** is observed in *cis*-[Re^{V}O$_2$(Hdab)-(py)$_2$].[37] The **b** form can be oxidized to 1,2-benzosemiquinone diimine monoanionic form **c** (sbqdi), and **c** may be further oxidized to neutral 1,2-benzoquinone diimine form **d** (bqdi).

Form **c** has been found in the complexes of the type [M^{II}(sbqdi)$_2$],[38−40] as well as [Rh^{II}Cl(PPh$_3$)$_2$(sbqdi)],[40] [Co^{III}Cl-(sbqdi)$_2$],[40] [Re^{IV}(sbqdi-OH)$_3$]Cl,[41] [Re^{IV}(sbqdi)$_3$]I,[41] and [Co^{III}(sbqdi)$_2$py]$^+$.[42] The **d** form was isolated in [Fe^{II}(bqdi)-(CN)$_4$]$^{2-}$,[18] [Fe^{II}(bqdi)$_3$](PF$_6$)$_2$,[40] M(bqdi)$_2$ (M = Ni, Co), M(bqdi)$_2$X (M = Co, Fe; X = Cl, I, SCN), [M(bqdi)$_3$](PF$_6$)$_n$ (M = Co, Fe, Ru; n = 1−2),[44] and [Os(bqdi)$_3$][ClO$_4$]$_2$.[45] Finally, form **e** may be further deprotonated to dianionic monodentate imido form **f** which was found in [Re^V(dab-OH)Cl$_3$(PPh$_3$)$_2$] and [Re^V(dab-NO$_2$)Cl$_3$(PPh$_3$)$_2$].[46] In some cases, the ligand can be present as two different forms in a given complex. For example, both **a** and **d** were observed in [Ru(H$_2$dab)(bqdi)$_2$](PF$_6$)$_2$,[47] while both **b** and **d** were observed for [Re^V(dab)$_2$(bqdi)] and [Re^{III}(dab)(bqdi)$_2$].[35]

In this article, we report the syntheses and characterization of Re(IV), Re(V), and Re(VI) complexes with *N*-methyl-*o*-diaminobenzene (H$_2$L). While the oxorhenium(V) starting material [ReOX$_3$(PPh$_3$)$_2$] was used in the preparations, in no case is the $\{ReO\}^{3+}$ core retained in the products. Thus, [Re^{VI}Cl$_4$(*o*-NC$_6$H$_4$NHCH$_3$)(OPPh$_3$)] (**3**), [Re^{IV}Cl$_2$(*o*-NHC$_6$H$_4$NCH$_3$)$_2$](**5**), and [Re^{V}Cl$_3$(*o*-NC$_6$H$_4$NHCH$_3$)(PPh$_3$)$_2$] (**4**) were prepared by the reactions of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with the ligand, while [Re^{VI}Br$_4$(*o*-NC$_6$H$_4$NHCH$_3$)(OPPh$_3$)] (**6**), [Re^{IV}Br$_3$(*o*-NHC$_6$H$_4$NCH$_3$)(PPh$_3$)] (**8**), and [Re^{V}Br$_2$Cl-(*o*-NC$_6$H$_4$NHCH$_3$)(PPh$_3$)$_2$] (**7**) were obtained by the reactions of *trans*-[ReOBr$_3$(PPh$_3$)$_2$] with the ligand.

(30) Carugo, O.; Djinovic, K.; Rizzi, M.; Castellani, C. B. *J. Chem. Soc., Dalton Trans.* **1991**, 1551.
(31) (a) Gerber, T. I. A.; Kemp, H. J.; Bandoli, G.; Dolmella, A.; duPreez, J. G. H. *Inorg. Chim. Acta* **1992**, *202*, 191. (b) Pierport, C. G.; Buchanan, R. M.; *Coord. Chem. Rev.* **1981**, *38*, 45. (c) O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.
(32) Danzeisen, O. F.; Goanta, M.; Rotter, H. W.; Thiele, G. *Inorg. Chim. Acta* **1999**, *287*, 218.
(33) Narayanan, B.; Bhadbhade, M. M. *Acta Crystallogr.* **1996**, *C52*, 3049.
(34) Maxcy, K. R. *Acta Crystallogr.* **2000**, *C56*, e454.
(35) Bandoli, G.; Dolmella, A.; Gerber, T. I. A.; Perils, J.; duPreez, J. G. H. *Inorg. Chim. Acta* **2000**, *303*, 24.
(36) Danopoulos, A. A.; Wong, A. C. C.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1990**, 315.
(37) Bandoli, G.; Dolmella, A.; Gerber, T. I. A.; Luzipo, D.; duPreez, J. G. H. *Inorg. Chim. Acta* **2001**, *325*, 215.
(38) (a) Balch, A. L.; Holm, R. H. *J. Am. Chem. Soc.* **1966**, *88*, 5201. (b) Hale, G. S.; Soderberg, R. H. *Inorg. Chem.* **1968**, *7*, 2300. (c) Chaudhuri, P.; Verani, C. N.; Bull, E.; Bothe, E.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2001**, *123*, 2213.
(39) Peng, S. M.; Peters, K.; Peters, E. M.; Simon, A. *Inorg. Chim. Acta* **1985**, *101*, L35.
(40) Peng, S. M.; Chen, C. T.; Liaw, D. S.; Chen, C. I.; Wang, Y. *Inorg. Chim. Acta* **1985**, *101*, L31.
(41) Gerber, T. I. A.; Luzipo, D.; Mayer, P.; VanBrecht, B. J. A. M.; duPreea, J. G. H. *J. Coord. Chem.* **2003**, *56*, 1049.
(42) Cheng, P. H.; Cheng, H. Y.; Lin, C. C.; Peng, S. M. *Inorg. Chim. Acta* **1990**, *169*, 19.
(43) Christoph, G. G.; Goedken, V. L. *J. Am. Chem. Soc.* **1973**, *95*, 3869.
(44) Warren, L. F. *Inorg. Chem.* **1977**, *16*, 2814.
(45) Ghosh, A. K.; Peng, S. M.; Paul, R. L.; Ward, M. D.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **2001**, 336.
(46) Bandoli, G.; Gerber, T. I. A.; Perils, J.; duPreez, J. G. H. *Inorg. Chim. Acta* **1998**, *278*, 96.
(47) Cheng, H. Y.; Peng, S. M. *Inorg. Chim. Acta* **1990**, *169*, 23.

Experimental Section

Materials. All reagents and organic solvents used in this study are reagent grade and were used without further purification. *trans*-[ReOCl₃(PPh₃)₂] and *trans*-[ReOBr₃(PPh₃)₂] were prepared according to the literature method.[48] Acetonitrile used for electrochemical experiments was dried by being passed through an alumina column just prior to the experiments.

Instruments and Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer; all peak positions are relative to that of TMS. IR spectra were recorded as KBr pellets with a Perkin-Elmer series 1600 FT-IR spectrometer in the region of 400−4000 cm^{-1} with polystyrene as reference. Electrochemical measurements were performed on a BAS potentiostat (model CV-27) equipped with data-collecting and -analyzing capabilities. Dry acetonitrile, deoxygenated under a nitrogen atmosphere, was used as the solvent with 0.1 M tetra-*n*-butylammonium hexafluorophosphate ([NBu₄]PF₆, TBAH) as supporting electrolyte. A three-compartment glass cell, with a platinum bead working electrode, a platinum wire counter electrode, and a silver wire reference electrode, was used for all experiments. Potential values were recorded without junction correction. Ferrocene was used as an internal standard. Under our experimental conditions, with a scan rate of 50 mV/s, the ferrocenium/ferrocene couple occurred at $E_{1/2}$ = +0.465 V with ΔE = 60 mV. Electron paramagnetic resonance spectra were obtained on a Varian E-9 EPR E-line spectrometer. Spectra were referenced to a solid sample of diphenylpicrylhydrazine (DPPH) standard (g = 2.0037). Carbon, hydrogen, and nitrogen analyses were carried out by Oneida Research Services, Whitesboro, NY.

Syntheses of Complexes 1−8. [ReCl₄(PPh₃)₂] (1), [ReCl₄(OPPh₃)₂] (2), and [ReCl₄(NC₆H₄NHCH₃)(OPPh₃)] (3). To a stirred solution of [ReOCl₃(PPh₃)₂] (0.43 g, 0.52 mmol) in 25 mL of chloroform was added H₂L (0.063 g, 0.52 mmol) in 5 mL of chloroform. The solution was refluxed for 3 h, whereupon the color of the reaction mixture changed from yellow-green to dark red. The reaction mixture was then cooled and concentrated under reduced pressure. The residue was loaded onto a silica gel column. Two fractions were obtained from the column. The first dark red fraction was eluted with dichloromethane, while the second dark brown fraction was eluted with CH₃OH/CH₂Cl₂ (4:96). The two fractions were concentrated and carefully layered with hexane. From the first fraction, two different crystalline materials were obtained, large dark red plates and small orange-red blocks which proved to be [ReCl₄(PPh₃)₂] (**1**) and [ReCl₄(OPPh₃)₂] (**2**), respectively. The second fraction gave dark brown plates suitable for X-ray analysis, with the formulation [ReCl₄(NC₆H₄NHCH₃)(OPPh₃)] (**3**).

Data for 1. Yield: 56%. Anal. Calcd (Found) for C₃₆H₃₀Cl₄P₂Re: C, 50.7 (50.91); H, 3.55 (3.61). ^{1}H NMR (δ (ppm), CDCl₃): 7.96 (m, 12H, PPh₃), 7.38 (m, 18H, PPh₃). Cyclic voltammetry: $E_{1/2}$(V/IV) = 0.929 V; E_{pc}(IV/III) = −1.081 V.

Data for 2. Yield: 6%. Anal. Calcd (Found) for C₃₆H₃₀Cl₄O₂P₂Re: C, 48.9 (49.21); H, 3.42 (3.55).

Data for 3. Yield: 22%. Anal. Calcd (Found) for C₂₅H₂₄Cl₄N₂OPRe: C, 41.28 (41.47); H, 3.33 (3.45); N, 3.85 (3.79). ^{1}H NMR (δ (ppm), CDCl₃): 8.17 (br m, PPh₃), 7.45 (br m, PPh₃), 6.56 (br s, bz-dab), 5.95 (br m, bz-dab), 2.44 (br s, CH₃). IR (KBr, ν/cm^{-1}): 1090 (ν(Re=N)). Cyclic voltammetry: E_{pa}(VII/VI) = 1.54 V; $E_{1/2}$(VI/V) = 0.342 V. EPR: g = 2.012.

[ReCl₃(NC₆H₄NHCH₃)(PPh₃)₂] (4) and [ReCl₂(NHC₆H₄NCH₃)₂] (5). A mixture of [ReOCl₃(PPh₃)₂] (0.3 g, 0.36 mmol) and H₂L

(0.088 g, 0.72 mmol) in 25 mL of chloroform was refluxed for 2 h. The yellow-green solution turned dark brown. After being cooled to room temperature, the reaction mixture was concentrated, and the residue was passed through a silica gel column. The red band of complex **4** was obtained using dichloromethane, while the brown band of complex **5** was eluted with CH₃OH/CH₂Cl₂ (2:98). Single crystals of complex **4** (red) and **5** (dark green-blue) suitable for X-ray analysis were obtained by slow diffusion of hexane into solutions of the complexes in dichloromethane.

Data for 4. Yield: 7%. Anal. Calcd (Found) for C₄₃H₃₈Cl₃N₂P₂Re: C, 55.10 (55.22); H, 4.09 (4.27); N, 2.99 (2.88). ^{1}H NMR (δ (ppm), CDCl₃): 7.95 (m, 12H, PPh₃), 7.35 (m, 18H, PPh₃), 6.78 (d, 1H, bz-dab), 6.10 (m, 3H, bz-dab), 2.56 (d, 3H, CH₃). IR (KBr, ν/cm^{-1}): 1093 (ν(Re=N)). Cyclic voltammetry: E_{pa}(VI/V) = 1.346 V; E_{pc}(V/IV) = 0.023 V.

Data for 5. Yield: 58%. Anal. Calcd (Found) for C₁₄H₁₆Cl₂N₄Re: C, 33.80 (33.91); H, 3.24 (3.33); N, 11.26 (11.17). ^{1}H NMR (δ (ppm), CDCl₃): 6.67 (d, 2H, bz-dab), 5.79 (m, 6H, bz-dab), 2.54 (s, 6H, CH₃). IR (KBr, ν/cm^{-1}): 541 (ν(Re−N)). Cyclic voltammetry: $E_{1/2}$(V/IV) = 0.656 V; E_{pc}(IV/III) = −0.345 V.

[ReBr₄(NC₆H₄NHCH₃)(OPPh₃)] (6). Complex **6** was prepared by a procedure similar to that of its chloride analogue, except that the starting material [ReOBr₃(PPh₃)₂] was used instead of [ReOCl₃(PPh₃)₂]. After the reaction mixture was purified by silica gel column chromatography, the dark brown band of complex **6** was obtained using CH₃OH/CH₂Cl₂ (4:96). Yield: 45%. Anal. Calcd (Found) for C₂₅H₂₄Br₄N₂OPRe: C, 33.17 (33.39); H, 2.67 (2.71); N, 3.09 (3.05).). ^{1}H NMR (δ (ppm), CDCl₃): 8.05 (br m, PPh₃), 7.33 (br m, PPh₃), 6.68 (br s, bz-dab), 6.23 (br m, bz-dab), 2.72 (br s, CH₃). IR (KBr, ν/cm^{-1}): 1092 (ν(Re=N)). Cyclic voltammetry: E_{pa}(VII/VI) = 1.503 V; $E_{1/2}$(VI/V) = 0.289 V. EPR: g = 2.006.

[ReBr₂Cl(NC₆H₄NHCH₃)(PPh₃)₂] (7) and [ReBr₃(NHC₆H₄NCH₃)(PPh₃)]·CH₂Cl₂ (8·CH₂Cl₂). To a stirred solution of [ReOBr₃(PPh₃)₂] (0.38 g, 0.39 mmol) in 20 mL of chloroform was added H₂L (0.096 g, 0.78 mmol) in 5 mL of chloroform, whereupon the solution was refluxed for 2 h. The yellow-green reaction mixture changed to dark brown gradually. After the reaction mixture was concentrated, the residue was separated by silica gel column chromatography. A red fraction was obtained using dichloromethane, while a brown fraction was eluted with CH₃OH/CH₂Cl₂ (1:99). After the two fractions were evaporated to dryness, the resulting residues were dissolved in dichloromethane and layered with hexane to form red crystals of complex **7** and brown crystals of complex **8**.

Data for 7. Yield: 6%. Anal. Calcd (Found) for C₄₃H₃₈Br₂ClN₂P₂Re: C, 50.33 (50.57); H, 3.73 (3.85); N, 2.73 (2.59). ^{1}H NMR (δ (ppm), CDCl₃): 7.93 (m, 12H, PPh₃), 7.31 (m, 18H, PPh₃), 6.80 (d, 1H, bz-dab), 6.09 (m, 3H, bz-dab), 2.59 (d, 3H, CH₃). IR (KBr, ν/cm^{-1}): 1090 (ν(Re=N)). Cyclic voltammetry: E_{pa}(VI/V) = 1.297 V; E_{pc}(V/IV) = −0.058 V.

Data for 8. CH₂Cl₂. Yield: 80%. Anal. Calcd (Found) for C₂₅H₂₃Br₃N₂PRe: C, 37.15 (37.23); H, 2.87 (2.95); N, 3.47 (3.29). ^{1}H NMR (δ (ppm), CDCl₃): 7.91 (m, 6H, PPh₃), 7.32 (m, 9H, PPh₃), 6.65 (d, 1H, bz-dab), 5.74 (m, 3H, bz-dab), 2.44 (s, 3H, CH₃). IR (KBr, ν/cm^{-1}): 532 (ν(Re=N)). Cyclic voltammetry: $E_{1/2}$(V/IV) = 0.961 V; E_{pc}(IV/III) = −0.011 V.

X-ray Crystal Structure Determination. The selected crystals of the complexes were studied on a Bruker diffractometer equipped with the SMART CCD system,[49] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data collections were carried out at 90(5) K. The data were corrected for Lorentz polarization

(48) (a) Parshall, G. W. *Inorg. Synth.* **1977**, *17*, 110. (b) Chatt, J.; Row, G. A. *J. Chem. Soc.* **1962**, 4019.

Table 1. Summary of Crystal Data for the Structures of **3**, **5**, **6**, **7**, and **8·CH₂Cl₂**

	3	**5**	**6**	**7**	**8·CH₂Cl₂**
empirical formula	$C_{25}H_{22}Cl_4N_2OPRe$	$C_{14}H_{16}Cl_2N_4Re$	$C_{54}H_{54}Br_8N_4O_2P_2Re$	$C_{43}H_{38}Br_2ClN_2P_2Re$	$C_{26}H_{25}Br_3Cl_2N_2PRe$
fw	725.42	497.41	1864.63	1026.16	893.28
space group	$P2_1/c$	Pbca	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
T, K	90(2)	90(2)	90(2)	90(2)	90(2)
a, Å	12.4511(9)	8.5464(5)	9.8827(8)	10.640(4)	16.2579(10)
b, Å	10.8309(8)	16.6659(10)	15. 6823(13)	12.024(4)	10.2434(7)
c, Å	19.5721(15)	21.5108(12)	20.8230(18)	15.173(5)	18.2100(12)
α, deg	90	90	90.890(2)	93.256(7)	90
β, deg	95.142(2)	90	98.276(2)	92.103(8)	113.9250(10)
γ, deg	90	90	94.656(2)	95.957(7)	90
V, Å³	2628.8(3)	3063.9(3)	3181.9(5)	1925.8(12)	2772.1(3)
Z	4	8	2	2	4
D_{calcd}, g cm⁻³	1.833	2.157	1.946	1.770	2.140
μ, mm⁻¹	5.112	8.279	8.914	5.417	8.978
$R1^a$ (all data)	0.1276	0.0903	0.0856	0.0808	0.0703
$wR2^a$	0.1064	0.0859	0.1748	0.1974	0.1053

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**, **5**, **6**, **7**, and **8·CH₂Cl₂**

3		**5**		**6**		**7**		**8·CH₂Cl₂**	
Re(1)−N(1)	1.711(6)	Re(1)−N(1)	1.982(4)	Re(1)−N(1)	1.704(1)	Re(1)−N(1)	1.719(9)	Re(1)−N(1)	1.973(5)
Re(1)−O(1)	2.044(4)	Re(1)−N(4)	1.991(5)	Re(1)−O(1)	2.057(9)	Re(1)−Cl(1)	2.411(3)	Re(1)−N(2)	1.997(5)
Re(1)−Cl(3)	2.334(2)	Re(1)−N(3)	1.991(4)	Re(1)−Br(3)	2.496(2)	Re(1)−P(2)	2.466(3)	Re(1)−P(1)	2.487(2)
Re(1)−Cl(4)	2.339(2)	Re(1)−N(2)	2.004(5)	Re(1)−Br(4)	2.500(2)	Re(1)−P(1)	2.497(3)	Re(1)−Br(3)	2.5080(6)
Re(1)−Cl(2)	2.360(2)	Re(1)−Cl(1)	2.381(1)	Re(1)−Br(1)	2.507(2)	Re(1)−Br(1)	2.544(2)	Re(1)−Br(1)	2.5183(6)
Re(1)−Cl(1)	2.369(2)	Re(1)−Cl(2)	2.381(1)	Re(1)−Br(2)	2.519(2)	Re(1)−Br(2)	2.546(2)	Re(1)−Br(2)	2.5563(6)
N(1)−Re(1)−O(1)	177.3(2)	N(1)−Re(1)−N(4)	99.6(2)	N(1)−Re(1)−O(1)	177.3(4)	N(1)−Re(1)−Cl(1)	176.3(3)	N(1)−Re(1)−N(2)	77.0(2)
N(1)−Re(1)−Cl(3)	94.5(2)	N(1)−Re(1)−N(3)	175.9(2)	N(1)−Re(1)−Br(3)	95.6(4)	N(1)−Re(1)−P(2)	91.9(3)	N(1)−Re(1)−P(1)	85.3(1)
O(1)−Re(1)−Cl(3)	85.5(1)	N(4)−Re(1)−N(3)	76.5(2)	O(1)−Re(1)−Br(3)	85.4(3)	Cl(1)−Re(1)−P(2)	84.55(9)	N(2)−Re(1)−P(1)	92.6(1)
N(1)−Re(1)−Cl(4)	94.4(2)	N(1)−Re(1)−N(2)	76.4(2)	N(1)−Re(1)−Br(4)	95.5(4)	N(1)−Re(1)−P(1)	91.8(3)	N(1)−Re(1)−Br(3)	95.7(1)
O(1)−Re(1)−Cl(4)	88.3(1)	N(4)−Re(1)−N(2)	94.4(2)	O(1)−Re(1)−Br(4)	87.0(3)	Cl(1)−Re(1)−P(1)	91.64(9)	N(2)−Re(1)−Br(3)	171.6(1)
Cl(3)−Re(1)−Cl(4)	89.56(6)	N(3)−Re(1)−N(2)	105.0(2)	Br(3)−Re(1)−Br(4)	88.3(5)	P(2)−Re(1)−P(1)	175.46(8)	P(1)−Re(1)−Br(3)	90.85(4)
N(1)−Re(1)−Cl(2)	94.1(2)	N(1)−Re(1)−Cl(1)	85.0(1)	N(1)−Re(1)−Br(1)	93.8(4)	N(1)−Re(1)−Br(1)	94.7(3)	N(1)−Re(1)−Br(1)	168.2(1)
O(1)−Re(1)−Cl(2)	83.2(1)	N(4)−Re(1)−Cl(1)	89.8(1)	O(1)−Re(1)−Br(1)	85.2(3)	Cl(1)−Re(1)−Br(1)	84.59(8)	N(2)−Re(1)−Br(1)	94.8(1)
Cl(3)−Re(1)−Cl(2)	90.30(6)	N(3)−Re(1)−Cl(1)	93.7(2)	Br3−Re(1)−Br(1)	170.43(5)	P(2)−Re(1)−Br(1)	92.77(7)	P(1)−Re(1)−Br(1)	86.73(4)
Cl4−Re(1)−Cl(2)	171.51(6)	N(2)−Re(1)−Cl(1)	161.3(1)	Br(4)−Re(1)−Br(1)	89.41(5)	P(1)−Re(1)−Br(1)	84.38(7)	Br(3)−Re(1)−Br(1)	93.09(2)
N(1)−Re(1)−Cl(1)	94.9(2)	N(1)−Re(1)−Cl(2)	98.7(1)	N(1)−Re(1)−Br(2)	91.3(4)	N(1)−Re(1)−Br(2)	91.5(3)	N(1)−Re(1)−Br(2)	95.0(1)
O(1)−Re(1)−Cl(1)	85.2(1)	N(4)−Re(1)−Cl(2)	161.6(1)	O(1)−Re(1)−Br(2)	86.3(3)	Cl(1)−Re(1)−Br(2)	89.44(8)	N(2)−Re(1)−Br(2)	88.6(1)
Cl(3)−Re(1)−Cl(1)	170.63(6)	N(3)−Re(1)−Cl(2)		Br(3)−Re(1)−Br(2)	90.24(5)	P(2)−Re(1)−Br(2)	89.53(7)	P(1)−Re(1)−Br(2)	17 8.78(4)
C(4)−Re(1)−Cl(1)	89.01(6)	N(2)−Re(1)−Cl(2)	91.5(1)	Br4−Re(1)−Br(2)	173.24(6)	P(1)−Re(1)−Br(2)	92.92(7)	Br(3)−Re(1)−Br(2)	87.94(2)
Cl(2)−Re(1)−Cl(1)	89.75(6)	Cl(1)−Re(1)−Cl(2)	90.23(5)	Br(1)−Re(1)−Br(2)	91.01(5)	Br(1)−Re(1)−Br(2)	173.37(5)	Br(1)−Re(1)−Br(2)	93.17(2)

effects, and absorption corrections were made using SADABS.[50] All calculations were performed using SHELXTL.[51] The structures were solved by direct methods, and all of the non-hydrogen atoms were located from the initial solution. After all the non-hydrogen atoms in the structure were located, the model was refined against F^2, initially using isotropic and later anisotropic thermal displacement parameters until the final value of Δ/σ_{max} was less than 0.001. At this point the hydrogen atoms were located from the electron density difference map, and a final cycle of refinements was performed, until the final value of Δ/σ_{max} was again less than 0.001. No anomalies were encountered in the refinement of the structure. The relevant parameters of the crystal data, data collection, structure solution, and refinement are summarized in Table 1, and important bond lengths and bond angles are presented in Table 2. A complete description of the details of the crystallographic methods is given in the Supporting Information.

Results and Discussion

Syntheses. The reaction of *trans*-[ReOCl₃(PPh₃)₂] with 1 equiv of H₂L in refluxing chloroform for 3 h gave complexes

1−3. The different polarities of the three complexes allowed their separation by silica gel column chromatography. Both **1** and **2** were eluted with dichloromethane, while **3** was obtained using a more polar eluant (4:96 methanol/chloroform). Complexes **1** and **2** were separated by recrystallization, forming crystals with different colors and shapes which are readily identified. Complex **1** was the major product whose formulation was proved by elemental analysis and subsequently verified by X-ray crystallography to be [ReCl₄(PPh₃)₂]. The crystal structure of this compound has been published[52−54] in both monoclinic $P2_1/n$ and triclinic $P\bar{1}$ space groups. Curiously, our crystals of [ReCl₄(PPh₃)₂] exhibit a different polymorph (orthorhombic, space group *Aba*2 with $a = 10.964(7)$ Å, $b = 17.121(8)$ Å, $c = 20.43(1)$ Å, and $V = 3834(4)$ Å³). Complex **2** was the minor product with the formula [ReCl₄(OPPh₃)₂] whose crystal structure was published previously by our group.[55] According to

(49) *Smart Software Reference Manual*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.
(50) Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction*; University of Göttingen: Göttingen, Germany, 1996.
(51) Sheldrick, G. M. *SHELXL96: Program for Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1996.
(52) Luo, H. Y.; Orvig, C.; Rettig, S. J. *Acta Crystallogr.* **1996**, *C52*, 1377.
(53) Dziegielewski, J. O.; Machura, B. *Polyhedron* **1996**, *15*, 2813.
(54) Kraudelt, H.; Schilde, U.; Uhlemann, E. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1797.
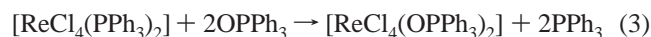
Rouschias and Wilkinson,[56] [ReCl$_4$(PPh$_3$)$_2$] is formed by disproportionation of *trans*-[ReOCl$_3$(PPh$_3$)$_2$], according to eq 1. These authors also mentioned that the estimated yield of

$$3[Re^{V}OCl_3(PPh_3)_2] \rightarrow$$
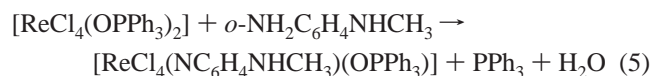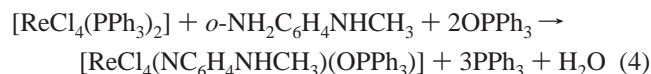$$2[Re^{IV}Cl_4(PPh_3)_2] + Re^{VII}O_3Cl + 2PPh_3 \quad (1)$$
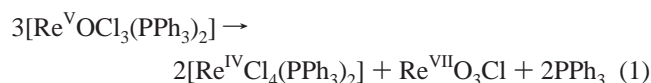
[ReCl$_4$(PPh$_3$)$_2$] often exceeded that implied by eq 1 due to the reduction of the Re(VII) product by the liberated triphenylphosphine to *trans*-[ReOCl$_3$(PPh$_3$)$_2$], as illustrated by eq 2. This observation accounts for the high yield of

$$ReO_3Cl + 2HCl + 3PPh_3 \rightarrow$$
$$[ReOCl_3(PPh_3)_2] + OPPh_3 + H_2O \quad (2)$$
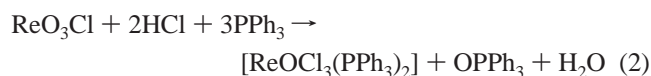
[ReCl$_4$(PPh$_3$)$_2$] observed in this study. Part of the [ReCl$_4$-(PPh$_3$)$_2$] can also undergo substitution with OPPh$_3$ to form complex **2** as a minor product (eq 3). Complex **3** can form

$$[ReCl_4(PPh_3)_2] + 2OPPh_3 \rightarrow [ReCl_4(OPPh_3)_2] + 2PPh_3 \quad (3)$$

from either complex **1** or complex **2** by the following reactions:

$$[ReCl_4(PPh_3)_2] + o\text{-}NH_2C_6H_4NHCH_3 + 2OPPh_3 \rightarrow$$
$$[ReCl_4(NC_6H_4NHCH_3)(OPPh_3)] + 3PPh_3 + H_2O \quad (4)$$

$$[ReCl_4(OPPh_3)_2] + o\text{-}NH_2C_6H_4NHCH_3 \rightarrow$$
$$[ReCl_4(NC_6H_4NHCH_3)(OPPh_3)] + PPh_3 + H_2O \quad (5)$$

In complex **3**, the ligand is in its dianionic, monodentate imido form **f** (see Scheme 1) as proved by the crystal structure (vide infra), so the oxidation state of Re is formally VI. Therefore, during the course of reactions 4 and 5, Re(IV) was oxidized by the ligand to the Re(VI) state.

Complex **6** is the bromide analogue of complex **3** and was prepared by a procedure similar to that for **3**. However, we were unable to isolate the bromide analogues of complexes **1** and **2**.

Complexes **3** and **6** are the first examples of Re(VI) complexes with dab and its derivatives. They are stable both in the solid state and in solution. However, examples of Re(VI) compounds are relatively rare, suggesting the "noninnocent" nature of this ligand.

The reaction of *trans*-[ReOCl$_3$(PPh$_3$)$_2$] with H$_2$L in a 1:2 molar ratio in boiling chloroform gave Re(IV) complex **5** as the major product and Re(V) complex **4** as a minor constituent. The formation of complex **4** is straightforward, as shown in eq 6. Again, the ligand is in its dianionic monodentate imido form **f**, and the coordination geometry is the same as for previously reported Re(V) species.[36,46]
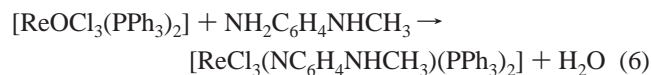
$$[ReOCl_3(PPh_3)_2] + NH_2C_6H_4NHCH_3 \rightarrow$$
$$[ReCl_3(NC_6H_4NHCH_3)(PPh_3)_2] + H_2O \quad (6)$$

Complex **5** is an unusual example of a rhenium(IV) bischloride complex coordinated to two *N*-methyl-dab ligands. From the crystal structure and the electrochemistry study, we confirmed that the ligand is present as sbqdi; consequently, the oxidation state of Re is assigned as IV. From the literature, we found that most Re−dab complexes either exhibit a single ligand to the Re center[36,37,46] or form tris-ligand complexes.[31a,35,36,41] The only example of a Re−dab$_2$ complex has been reported for [Re(dab)$_2$Cl(PPh$_3$)],[36] which is a Re(V) complex with the ligand in its diamine dianionic form **b**. Consequently, complex **5** represents a novel example of a rhenium(IV) bisligand complex with the ligand in its sbqdi form.

We tentatively present the formation of complex **4** according to eq 7. The reaction requires that the ligand be deprotonated to its diamine dianionic form **b** and that **b** be oxidized to sbqdi form **c**, while Re(V) is reduced to Re(IV).

$$[ReOCl_3(PPh_3)_2] + 2NH_2C_6H_4NHCH_3 \rightarrow$$
$$[ReCl_2(NHC_6H_4NCH_3)_2] + H_2O + HCl + 2PPh_3 \quad (7)$$

Attempts to make the bromide analogue of complex **5** following the same reaction procedure were not successful. Surprisingly, when *trans*-[ReOBr$_3$(PPh$_3$)$_2$] was reacted with 2 equiv of the *N*-methyl-*o*-diaminobenzene ligand, **8** was isolated in high yield. The reaction may be rationalized by eq 8.

$$[ReOBr_3(PPh_3)_2] + NH_2C_6H_4NHCH_3 \rightarrow$$
$$[ReBr_3(NHC_6H_4NCH_3)(PPh_3)] + H_2O + PPh_3 \quad (8)$$
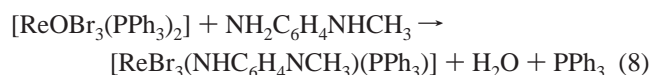
This represents a new rhenium(IV) monoligand complex with the bidentate dab ligand in the sbqdi form. What is also interesting is that the starting material *trans*-[ReOBr$_3$(PPh$_3$)$_2$] exhibits the *mer*-tribromo geometry at the rhenium center, while complex **8** is a *fac*-tribromo species, as confirmed by the X-ray crystal structure analysis. Therefore, the synthesis of complex **8** can be regarded as an example of ligand-induced geometrical rearrangement. This type of rearrangement was also found in our study of *fac*-{ReCl$_3$} core complexes with bifunctional single amino acid derivatives.[61]

Complex **7** was also isolated as a minor product from the above reaction and can be regarded as the bromide analogue of complex **4**. However, the expected product should be the rhenium(V) tribromide complex. Since the reaction was carried out in chloroform and dichloromethane was used for
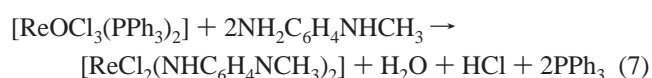
(55) Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *306*, 112.

(56) Rouschias, G.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 465.

(57) Gennari, C.; Colombo, L.; Bertolini, G. *J. Am. Chem. Soc.* **1986**, *108*, 6394.

(58) deLearie, L. A.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 817.

(59) (a) Lahiri, G. K.; Goswami, S.; Falvello, L. R.; Chakravorty, A. *Inorg. Chem.* **1987**, *261*, 3365. (b) Dirghangi, B. K.; Menon, M.; Banerjee, S.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 3595. (c) Banerjee, S.; Dirghangi, B. K.; Menon, M.; Pramanik, A.; Chakrevorty, A. *J. Chem. Soc., Dalton Trans.* **1997**, 2149.

(60) Bhattacharyya, S.; Banerjee, S.; Dirghangi, B. K.; Menon, M.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1999**, 155.

(61) Banerjee, S. R.; Wei, L.; Levadala, M. K.; Lazarova, N.; Golub, V. O.; O'Connor, C. J.; Stephenson, K. A.; Valliant, J. F.; Babich, J. W.; Zubieta, J. *Inorg. Chem.* **2002**, *41*, 5795.

recrystallization, it appears that one of the bromine ligands was replaced by chlorine anion during workup to form complex **7**.

Spectroscopic Properties. The infrared spectra of complexes **3**–**8** exhibit no band in the region 900–1000 cm^{-1} which can be attributed to Re=O stretching modes, indicating the absence of the rhenium(V) oxo group. The IR spectra of complexes **3**, **4**, **6**, and **7** are characterized by an absorption peak around 1090 cm^{-1} which can be assigned to ν(Re=N), while the spectra of complexes **5** and **8** display Re–N stretching bands at 541 and 532 cm^{-1}, respectively. The IR spectra are similar to those of previously reported complexes.[35,37,41,46]

Complexes **4** and **7** are diamagnetic Re(V) species. The proton NMR spectra display doublets at 6.78–6.80 ppm and multiplets in the 6.09–6.10 ppm region which are assigned to the protons of the benzene rings. The peaks at 2.56–2.59 ppm are assigned to the methyl groups. The protons of the PPh$_3$ groups of the complexes appear as two multiplets at 7.93–7.95 and 7.31–7.35 ppm, which integrate for twelve and eighteen protons, respectively, corresponding to two PPh$_3$ groups.

The proton NMR spectra of the Re(VI) complexes **3** and **6** consist of broad, poorly resolved peaks, as expected for d^1 paramagnetic compounds.

Curiously, the proton NMR spectra of complexes **5** and **8** exhibit no obvious paramagnetic shifts and line broadening of the signals, indicating that these compounds are in fact diamagnetic. Similar behavior has been observed for tris-(1,2-benzosemiquinone diimine) complexes of rhenium(IV), [Re^{IV}(sbqdi-OH)$_3$]Cl and [Re^{IV}(sbqdi)$_3$]I,[41] and the tris(3,5-di(*tert*-butyl)benzosemiquinone) complex of chromium(III), [Cr(bsbq)$_3$],[62] and an explanation has been proposed. In addition to the lone pairs of electrons on each nitrogen that are used in bonding, the unpaired electron of each benzosemiquinone diimine ligand is directly involved in the bonding to the Re(IV) ion. Consequently, the intramolecular antiferromagnetic interaction is strong, leading to the observed diamagnetism. The proton signals of the benzene rings of complexes **5** and **8** appear as doublets at 6.65–6.67 ppm and multiplets at 5.74–5.79 ppm. These peaks are located in the high-field region, compared to the proton signals of the benzene ring of the free ligand, which appear as two multiplets at 6.96 and 6.78 ppm. This observation indicates the presence of the benzosemiquinone diimine form of the ligand, suggesting partial loss of aromaticity.

The EPR spectra of the Re(VI) (d^1) complexes **3** and **6** were recorded at room temperature in dichloromethane solution. Figure 1 shows the EPR spectrum of complex **6**, which consists of six well-resolved hyperfine lines due to the $I = 5/2$ nuclei (^{185}Re, 37.07%; ^{187}Re, 62.93%). Spacings between adjacent hyperfine lines are not equal and increase with field strength. The ranges of the variable spacings, arising from second-order effects,[63] are 340–600 G for complex **3** and 360–580 G for complex **6**. The center-field *g* values of complexes **3** and **6** are 2.012 and 2.006, respectively. The solution EPR spectra of the two complexes appear to be relatively unusual for Re(VI) compounds, where
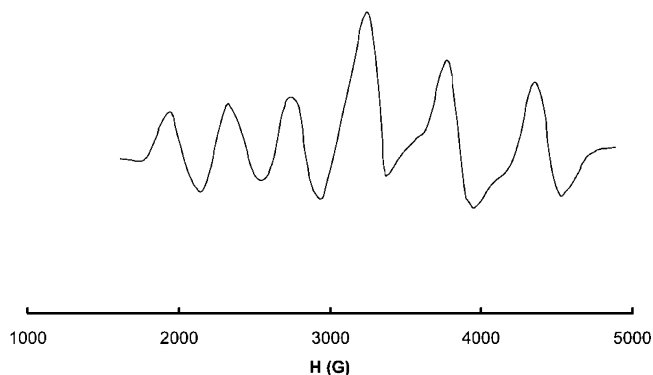

Figure 1. EPR spectrum of complex **6** in CH$_2$Cl$_2$ solution at room temperature. Instrument setting: microwave power, 10 mW; microwave frequency, 9.527 GHz; modulation, 100 kHz; sweep center, 3250 G; sweep time, 120 s.

metal hyperfine coupling generally remains unresolved at room temperature.[57–59] For example, the complexes ReMe$_6$, ReOMe$_4$, and tris(*o*-aminobenzenethiolato)rhenium all show weak, broad, featureless EPR spectra at room temperature.[58,64]

Electrochemistry. The electrochemistry of the complexes was studied in acetonitrile solution under the conditions described in the Experimental Section. The redox behavior is similar to that of the previously reported examples of Re(VII)/Re(VI), Re(VI)/Re(V), Re(V)/Re(IV), and Re(IV)/Re(III) processes.[36,59,60,65–67] The cyclic voltammetry data are summarized in Table 3, and cyclic voltammograms for complexes **5** and **6** are presented in Figure 2.

Complexes **3** and **6** display an irreversible oxidation couple and a reversible reduction couple, which can be assigned to Re(VII)/Re(VI) and Re(VI)/Re(V), respectively. The E_{pa} value of complex **3** is more positive than that of complex **6**, which is consistent with the smaller size and stronger electron-withdrawing power of chlorine anions compared to bromine anions. Complexes **4** and **7** show an irreversible oxidation couple (Re(VI)/Re(V)) and an irreversible reduction couple (Re(V)/Re(IV)). The more positive E_{pa} value and the less negative E_{pc} value of complex **4**, compared to complex **7**, are also related to the better electron acceptor properties of chlorine anions than those of bromine anions. Complexes **1**, **5**, and **8** display a reversible oxidation couple (Re(V)/Re(IV)) and an irreversible reduction couple (Re(IV)/Re(III)).

(62) Buchanan, R. M.; Kessel, S. C.; Downs, H. H.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *100*, 7894.
(63) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonce of Transition Ions*; Clarendon: Oxford, England, 1970; pp 163–178.
(64) (a) Gibson, J. F.; Lack, G. M.; Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1492. (b) Gibson, J. F.; Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1093. (c) Kirmse, R.; Stach, J. *Inorg. Chim. Acta* **1980**, *45*, L251. (d) MaCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. (e) Baldas, J.; Boas, J. F.; Bonnyman, J.; Pilbrow, J. R.; Williams, G. A. *J. Am Chem. Soc.* **1985**, *107*, 1886. (f) Al-Mowali, A. H.; Porte, A. L. *J. Chem. Soc., Dalton Trans.* **1975**, 250. (g) Holloway, J. H.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1975**, 737.
(65) Gardiner, I. M.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3688.
(66) Cerda, M. F.; Obal, G.; Mendez, E.; Zinola, C. F.; Kremer, C.; Martins, M. E.; Luna, A. M. C. *J. Colloid Interface Sci.* **2001**, *236*, 104.
(67) Fung, W. H.; Cheng, W. C.; Eng, S. M.; Che, C. M. *Polyhedron* **1995**, *14*, 1791.

Table 3. Cyclic Voltammetric Formal Potentials for Complexes **1**−**8**

| | E (V) | | | |
complex	Re(VII)/Re(VI)	Re(VI)/Re(V)	Re(V)/Re(IV)	Re(IV)/Re(III)
ReCl$_4$(PPh$_3$)$_2$ (**1**)			0.929 ($E_{1/2}$)^a	−1.081 (E_{pc})^b
ReCl$_2$(NHNCH$_3$C$_6$H$_4$)$_2$ (**5**)			0.656 ($E_{1/2}$)^a	−0.345 (E_{pc})^b
ReBr$_3$(NHNCH$_3$C$_6$H$_4$)(PPh$_3$) (**8**)			0.961 ($E_{1/2}$)^a	−0.011 (E_{pc})^b
ReCl$_3$(NNHCH$_3$C$_6$H$_4$)(PPh$_3$)$_2$ (**4**)		1.346 (E_{pa})^c	0.023 (E_{pc})^b	
ReBr$_2$Cl(NNHCH$_3$C$_6$H$_4$)(PPh$_3$)$_2$ (**7**)		1.297 (E_{pa})^c	−0.058 (E_{pc})^b	
ReCl$_2$(NNH$_2$CH$_3$C$_6$H$_4$)(OPPh$_3$) (**3**)	1.540 (E_{pa})^c	0.342 ($E_{1/2}$)^a		
ReBr$_4$(NNH$_2$CH$_3$C$_6$H$_4$)(OPPh$_3$) (**6**)	1.503 (E_{pa})^c	0.289 ($E_{1/2}$)^a		

^{a} Reversible peak, $E_{1/2} = {}^1/_2(E_{pa} + E_{pc})$, $\Delta E = E_{pa} - E_{pc} \approx 60$ mV. ^{b} Irreversible peak, E_{pc} = cathodic peak potential. ^{c} Irreversible peak, E_{pa} = anodic peak potential.
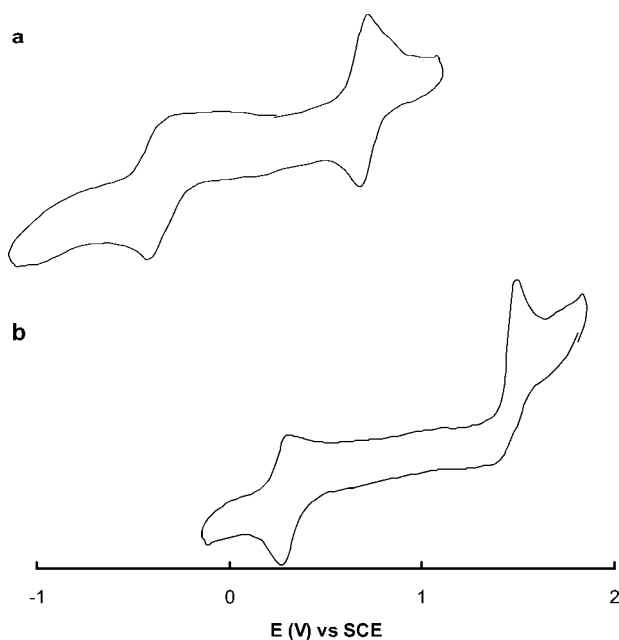
Figure 2. Cyclic voltammograms of complexes **5** and **6** in acetonitrile at a platinum electrode (room temperature, scan rate: 50 mV/s).

Crystallographic Studies. Assignment of metal oxidation states for complexes with dab and its derivatives has always involved some degree of uncertainty and ambiguity due to the potential noninnocent behavior of the ligands toward internal redox reactions with the metal centers. Thus, a given oxidation state of a species may involve any one of a variety of combinations of metal and ligand oxidation states.[36] Consequently, crystal structures of metal complexes derived from noninnocent redox ligands are particularly useful in assigning the formal oxidation states, both of the metals and of the ligands.[30]

The metal−nitrogen bond lengths are often characteristic of a particular oxidation state of the metal, with the carbon−nitrogen and carbon−carbon lengths sensitive to the charge of the ligand.[41] In this work, with the assistance of crystal structure data, we were able to assign the appropriate form of the dab ligand and the formal oxidation states of the rhenium centers.

Complex **3** exhibits distorted octahedral coordination geometry as shown in Figure 3. The equatorial positions are occupied by four chlorine atoms, and the apical positions are occupied by the oxygen atom of the OPPh$_3$ group and the nitrogen atom of the dab ligand. The *trans* angles fall in the range of 170.63(6)−177.3(2)°, showing only
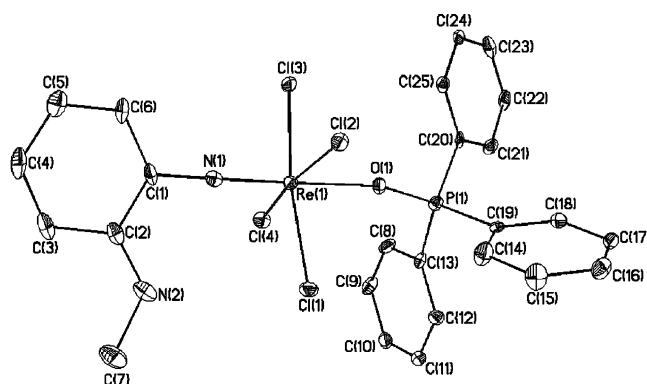
Figure 3. A view of the structure of [ReCl$_4$(NC$_6$H$_4$NHCH$_3$)(OPPh$_3$)] (**3**), showing the atom-labeling scheme and 50% probability ellipsoids.
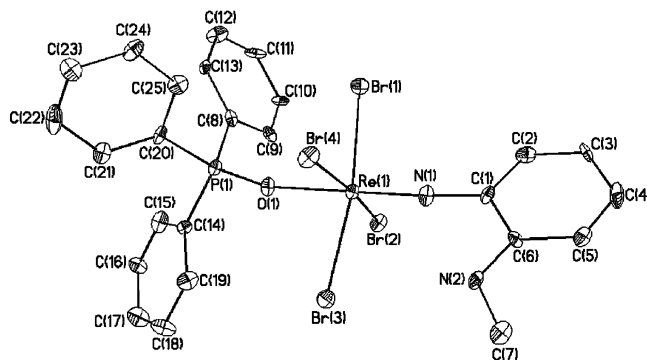
Figure 4. A view of the structure of [ReBr$_4$(NC$_6$H$_4$NHCH$_3$)(OPPh$_3$)] (**6**), showing the atom-labeling scheme and 50% probability ellipsoids.

minor deviations from the idealized octahedral limit. The Re−N(1)−C(1) bond angle (179.0(5)°) shows the linear coordination mode of the ligand unit. The Re−N(1) distance of 1.710(6) Å is typical for a Re−N double bond and agrees with the values found in other octahedral rhenium phenylimido complexes: 1.730(9) Å in [Re{2-N(3-H$_2$N)-C$_6$H$_3$OH}Cl$_3$(PPh$_3$)$_2$],[46] 1.726(6) Å in [Re(NPh)Cl$_3$(PPh$_3$)$_2$]·CH$_2$Cl$_2$,[68] 1.740(6) Å in [Re(NPh)(OEt)(bpy)$_2$]$^{2+}$,[69] and 1.709(8) Å in [Re(NPh)(maltol)$_2$(PPh$_3$)$_2$]$^+$.[70]

Complex **6** is the bromide analogue of complex **3**. As shown in Figure 4, the structure of **6** is similar to that of complex **3**, with the exception that four bromine atoms

(68) Forsellini, E.; Casellato, U.; Graziani, R.; Carletti, M. C.; Magon, L. *Acta Crystallogr.* **1984**, *C40*, 1795.

(69) Bakir, M.; Paulson, S.; Goodson, P.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1127.

(70) Archer, G. M.; Dilworth, J. R.; Jobanputra, P.; Harman, M. E.; Hursthouse, M. B.; Karaulov, A. *Polyhedron* **1991**, *10*, 1539.
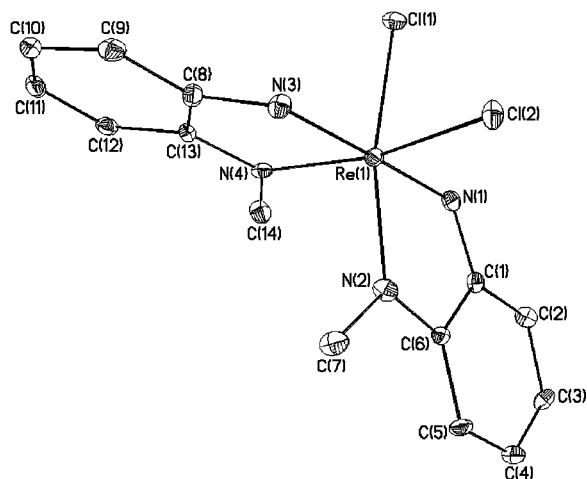
Figure 5. A view of the structure of the [ReCl$_2$(NHC$_6$H$_4$NCH$_3$)$_2$] (**5**), showing the atom-labeling scheme and 50% probability ellipsoids.

Figure 6. Bond lengths of the dab form (A) and bqdi form (B) of the ligand and the observed bond lengths of complex **5**.

replace the chlorine atoms in the equatorial plane. The metrical parameters are similar to those of **6** (Table 2).

Complexes **3** and **6** are unusual Re(VI) complexes with ligands in the dianionic, monodentate imido form **f**. Furthermore, in these two complexes the ligands coordinate *trans* to the OPPh$_3$ group in the axial positions. Other examples of Re with the monodentate imido form of dab derivatives were reported for [Re^{V}Cl$_3$(dab-OH)(PPh$_3$)$_2$][46] and [Re^{V}Cl$_3$-(dab-NO$_2$)(PPh$_3$)$_2$].[36] Both of these are Re(V) complexes, and the monodentate imido ligands occupy the equatorial positions, *cis* to the PPh$_3$ group.

The structure of complex **5** is shown in Figure 5. The rhenium atom is in a distorted octahedral environment with two chlorine atoms in the *cis* orientation, two nitrogen atoms in *trans* positions, and two *cis*-methyl-substituted nitrogen atoms. The most significant angular distortions are associated with the N(1)—Re—N(2) angle of 76.39(19)° and N(4)—Re—N(3) angle of 76.50(19)°, which are a consequence of the formation of the strained five-membered chelate rings. The Re—Cl distances (average 2.3810 Å) are unexceptional. The four Re—N distances are equivalent within experimental error, with an average of 1.992 Å. These distances are shorter than expected single-bond values (2.1–2.3 Å), indicating some π character associated with the bond. This observation is consistent with the sp^2 hybridization of the nitrogen atoms with filled π orbitals perpendicular to the ligand plane to form N → M π bonding. The average Re—N—C bond angle of 118.7(9)° is also consistent with sp^2 hybridization of the nitrogen donor atoms.

The bond distances in the chelating ligands provide an indication of their specific form, i.e., dab (**b**), sbqdi (**c**), or bqdi (**d**) (Scheme 1). Figure 6 illustrates the bond lengths of the dab form (A) and bqdi form (B) of the ligand[72] and the observed bond lengths of complex **5**. The chelating ligands of complex **5** have bond distances intermediate between those of the dab and bqdi forms. For example, the average bond length of the four C—N bonds (1.356 Å) is
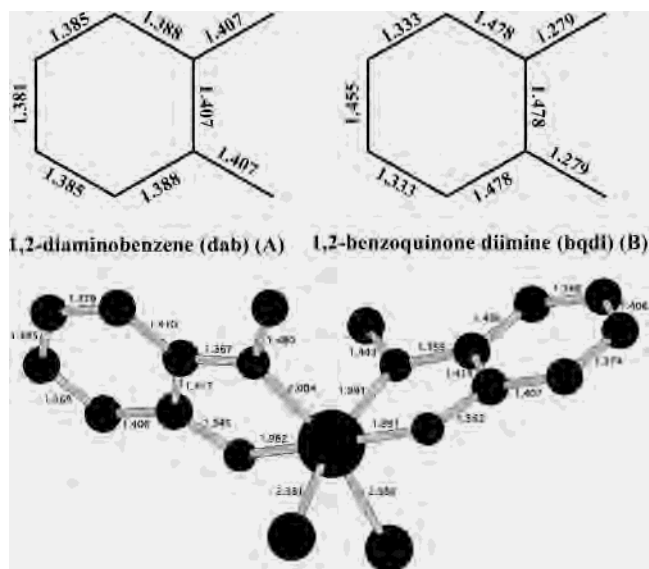
longer than the formal C=N bond length of 1.279(8) Å of the bqdi form and shorter than the average C—N bond length of 1.407(3) Å of the dab form. The value compares well with that of 1.35(1) Å found in [RhCl(PPh$_3$)$_2$(sbqdi)].[40] Similarly, the C—C bond distances in the phenyl rings of complex **5** are also useful indicators. The two chelating ligands have four localized C=C double bonds, C(2)—C(3), C(4)—C(5), C(9)—C(10), and C(11)—C(12), with an average distance of 1.367 Å, which falls between the bond length of the corresponding bonds of the bqdi form (1.333 Å) and the dab form (1.385 Å). The average C—C single-bond distance 1.412(5) Å is longer than the corresponding bond length of the dab form (1.391 Å) and shorter than that of the bqdi form (1.472 Å). However, this value is close to the average bond length of 1.415 Å that was found for these bonds in a number of complexes containing sbqdi ligands.[38c] From the comparison of C—N and C—C bond distances, we conclude that the chelating ligands are in the sbqdi monoanionic form, so the oxidation state of Re is assigned as IV for complex **5**.

The coordination geometry of complex **7** (Figure 7) is distorted octahedral, with *trans* angles in the range 173.35(5)–176.6(3)° showing only minor deviations from the idealized limit. Two *trans*-bromine atoms, a chlorine atom, and a nitrogen atom from the monodentate dab ligand occupy the equatorial plane, while two phosphine atoms from the PPh$_3$ groups define the axial positions. The Re—Br (2.5459(18) Å, 2.5475(16) Å), Re—P (2.467(3) Å, 2.498(3) Å), and Re—Cl (2.413(3) Å) bond distances fall in the expected range. The Re—N bond distance (1.721(9) Å) is typical of double-bond character. The ligand is in the dianionic, monodentate imido form **f**, and the oxidation state of Re is V.

As shown in Figure 8, the distorted octahedral environment of Re in the molecular unit of **8**·CH$_2$Cl$_2$ is defined by three facially bound bromine atoms, two nitrogen donors from the bidentate ligand, and a phosphine atom from the

(71) Taylor, R.; Kennard, O. *Acta Crystallogr.* **1983**, *B39*, 517.
(72) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, 51.
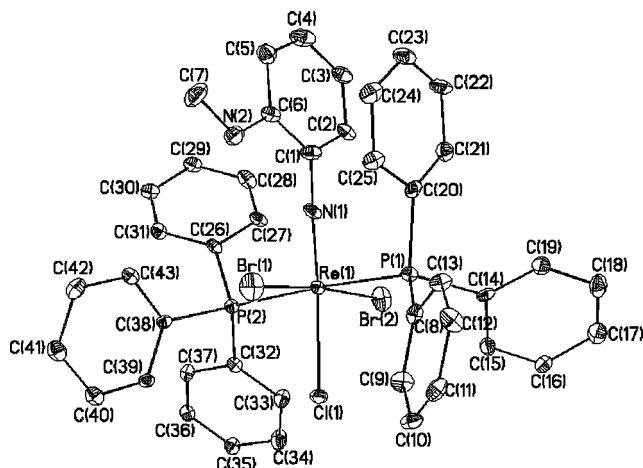
Figure 7. A view of the structure [ReBr$_2$Cl(NC$_6$H$_4$NHCH$_3$)(PPh$_3$)$_2$] (**7**), showing the atom-labeling scheme and 50% probability ellipsoids.
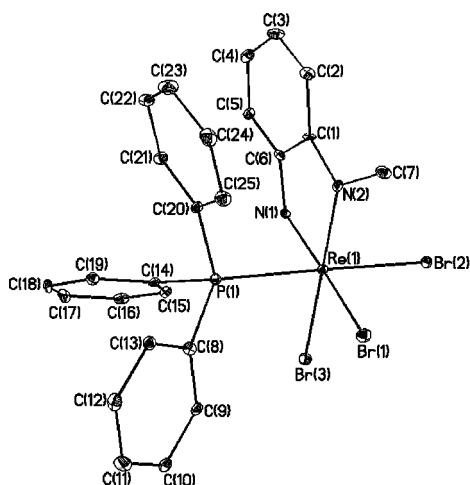
Figure 8. A view of the structure of the complex of [ReBr$_3$(NHC$_6$H$_4$NCH$_3$)-(PPh$_3$)·CH$_2$Cl$_2$ (**8**·CH$_2$Cl$_2$), showing the atom-labeling scheme and 50% probability ellipsoids.

PPh$_3$ group. The Re—Br (2.5183(6)—2.5563(6) Å), and Re—P (2.4873(15) Å) bond lengths are unexceptional. The average Re—N bond length (1.985(5) Å) is somewhat shorter than the typical Re—N single-bond length, and the Re—N—C bond angles (118.1(4)°, 119.2(4)°) are consistent with sp^2 hybridization of the nitrogen donor atoms. Following the

same treatment of the C—N and C—C bond distances as that of complex **5**, we conclude that complex **8** also contains the sbqdi monoanionic form of the ligand, and that the oxidation state of Re is IV.

Conclusions

The reactions of the common rhenium(V) oxo starting materials [ReOX$_3$(PPh$_3$)$_2$] (X = Cl, Br) with *N*-methyl-*o*-diaminobenzene (H$_2$dab) have produced a series of Re(IV), Re(V), and Re(VI) products which are characterized by the absence of a rhenium terminal oxo structural unit. Since the H$_2$dab ligand is noninnocent and redox active, multiple coordination modes are possible as a result of varying degrees of deprotonation and/or oxidation. Thus, in the Re(VI) species [ReX$_4$(NC$_6$H$_4$NHCH$_3$)(OPPh$_3$)] (X = Cl, **3**; Br, **6**) and in the Re(V) compounds [ReX$_2$Y-(NC$_6$H$_4$NHCH$_3$)(PPh$_3$)$_2$] (X = Y = Cl, **4**; X = Br, Y = Cl, **7**), the ligand adopts the imido form **b**. In contrast, Re(IV) species **5** and **8** exhibit the sbqdi monoanionic form of the ligand.

These observations reinforce the extensively documented redox and oxo group reactivity of the {MO}$^{3+}$ core. Consequently, the chemistry of technetium oxo and rhenium oxo compounds with "simple" ligands may be complicated by redox and oxo-group-transfer processes, an observation which raises serious caveats with respect to the coordination chemistry of these cores in radiopharmaceutical development. The continuing difficulties in preparation of monophasic reagents and in characterization at the tracer level of radiopharmaceutical preparations is a non-unexpected consequence of the inherent reactivity of the core.