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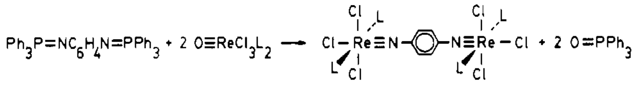
p-Phenylenediimido Complexes of Rhenium(V) and Their Coupling Reactions: Novel Multimetallic Chains

The *p*-phenylenediimido ligand, $[NC_6H_4N]^{4-}$, differs from conventional conjugated difunctional ligands, such as pyrazine, in several important respects. Organoimido ligands in general are excellent π-donors and as such prefer to bind to higher valent metal fragments than do the σ-donor/π-acceptor pyrazine-type ligands. Furthermore, the *p*-phenylenediimido ligand binds to a metal center via robust formal M≡N triple bonds, and thus systems incorporating this bridging ligand are not expected to be prone to dissociation in solution as is often observed in systems bridged by neutral difunctional ligands.[1] We recently reported the preparation of various dimolybdenum *p*-phenylenediimido complexes for which *p*-phenylene diazide was the source of the bridging ligand.[2] We report herein the preparation of various *p*-phenylenediimido complexes of Re(V) via a different method and describe our preliminary results on their coupling reactions to yield novel multimetallic chain compounds.

Reaction of *p*-phenylenebis(triphenylphosphoranimine),[3] $Ph_3P{=}NC_6H_4N{=}PPh_3$, with 2 equiv of $ReOCl_3(PPh_3)_2$[4] in refluxing benzene (4 h; N_2 atmosphere) produces triphenylphosphine oxide and the *p*-phenylenediimido bridged dirhenium species $(Ph_3P)_2Cl_3Re{\equiv}NC_6H_4N{\equiv}ReCl_3(PPh_3)_2$ (**1**), as shown in eq 1.[5]

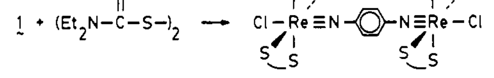


1 (L = PPh_3)

(1)

1 is obtained as an air-stable brown solid that is marginally soluble in common organic solvents. The 400-MHz ^1H NMR spectrum of a $CDCl_3$ solution of **1** features a sharp singlet at δ 6.52 attributable to the four equivalent phenylene protons. The structure shown in eq 1 is consistent with this result and also finds precedent in the structures established by X-ray crystallography for three (arylimido)rhenium(V) complexes of the form $ArN{\equiv}ReCl_3(PR_3)_2$.[6]

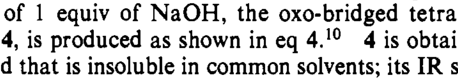
1 reacts with excess tetraethylthiuram disulfide in refluxing benzene (8 h; N_2 atmosphere) to effect the substitution of two chloride ligands and two phosphine ligands at each Re center, forming the tetrakis(diethyldithiocarbamato) species **2**, as shown in eq 2.[7] The assignment of a mutually trans disposition of the chloride ligands in **2** is supported by NMR studies. At 298 K, the ^1H NMR spectrum of **2** in $CDCl_3$ consists of a sharp singlet resonance at δ 7.33 due to the phenylene protons, a triplet at δ 1.38 due to the eight methyl groups, and two well-resolved ABX_3 multiplets at δ 3.86 and 3.71 arising from the diastereotopic methylene protons; this spectrum is invariant as the temperature of the sample is lowered to 233 K. ^{13}C NMR spectra likewise indicate that all four dithiocarbamate ligands remain equivalent throughout the temperature range studied.



(2)

2 ($\widehat{SS} = S_2CNEt_2$)

Treatment of **2** with an excess of sodium ethoxide in refluxing dry ethanol (6 h; N_2 atmosphere) leads to the substitution of the chloride ligands, forming the bright yellow *trans*-bis(ethoxide) complex $(EtO)(Et_2NCS_2)_2Re{\equiv}NC_6H_4N{\equiv}Re(S_2CNEt_2)_2(OEt)$ (**3**), as shown in eq 3.[8] Support for the assignment of a trans geometry in **3** is provided by the structural characterization of a related monomeric *p*-tolylimido complex, $Re(NTol)(S_2CNMe_2)_2(OEt)$.[9] Unlike the other complexes reported herein, **3** is very sensitive to moisture, as will be discussed below.



(3)

3

Complexes **2** and **3** can each undergo coupling reactions leading to the formation of oxo-bridged multimetallic species. Thus, when an acetone solution of **2** is refluxed (1 h; N_2 atmosphere) in the presence of 1 equiv of NaOH, the oxo-bridged tetrarhenium "dimer", **4**, is produced as shown in eq 4.[10] **4** is obtained as a black solid that is insoluble in common solvents; its IR spectrum features a strong absorption at 696 cm^{-1} assignable as an anti-

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(5) Anal. Calcd for $C_{78}H_{64}N_2P_4Cl_6Re_2$: C, 53.89; H, 3.71; N, 1.61. Found: C, 53.83; H, 3.73; N, 1.80. Yield: 69%. ^1H NMR ($CDCl_3$, 298 K): δ 7.70 (br, 36 H, $P(C_6H_5)_3$), 7.22 (br, 24 H, $P(C_6H_5)_3$), 6.52 (s, 4 H, C_6H_4).

(6) (a) $p\text{-}CH_3COC_6H_4N{\equiv}ReCl_3(PEt_2Ph)_2$ and $p\text{-}CH_3OC_6H_4N{\equiv}ReCl_3(PEt_2Ph)_2$: Bright, D.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1099. (b) $C_6H_5N{\equiv}ReCl_3(PPh_3)_2$: Forsellini, E.; Casellato, U.; Graziani, R.; Carletti, M. C.; Magon, L. *Acta Crystallogr.* **1984**, *C40*, 1795.

(7) Anal. Calcd for $C_{26}H_{44}N_6S_8Cl_2Re_2$: C, 27.38; H, 3.89; N, 7.37. Found: C, 27.71; H, 3.80; N, 6.91. Yield: 78%. ^1H NMR ($CDCl_3$, 298 K): δ 7.33 (s, 4 H, C_6H_4), 3.86 (m, 8 H, CH_2), 3.71 (m, 8 H, CH_2), 1.38 (t, 24 H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 211.8 (S_2C), 154.6 (aryl ipso), 124.9 (CH), 45.2 (CH_2), 12.6 (CH_3).

(8) Anal. Calcd for $C_{30}H_{54}N_6O_2S_8Re_2$: C, 31.07; H, 4.69; N, 7.25. Found: C, 30.76; H, 4.53; N, 7.47. Yield: 61%. ^1H NMR ($CDCl_3$, 298 K): δ 7.19 (s, 4 H, C_6H_4), 4.14 (q, 4 H, OCH_2CH_3), 3.75 (q, 16 H, NCH_2CH_3), 1.33 (t, 24 H, NCH_2CH_3), 1.00 (t, 6 H, OCH_2CH_3).

(9) Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 157.

(10) Anal. Calcd for $C_{52}H_{88}N_{12}OS_{16}Cl_2Re_4$: C, 28.06; H, 3.98; N, 7.55; Cl, 3.18. Found: C, 28.46; H, 3.82; N, 7.13; Cl, 3.65. Yield: 83%.

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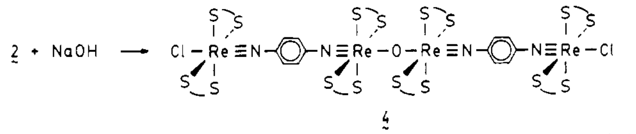
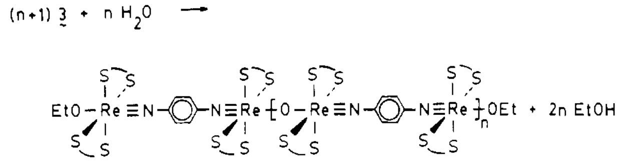


(4)

symmetric ν(Re–O–Re) stretching mode. Similarly, when a CH_2Cl_2 solution of **3** is treated with H_2O, the original yellow color is discharged in favor of deep purple and a black precipitate is formed. This black precipitate is again insoluble in common organic solvents and displays an IR spectrum that retains all of the characteristic dithiocarbamate absorptions of **3** but that also shows a strong broad band at 694 cm^{-1}, assignable as ν(Re–O–Re). Repeating the above experiment with H_2O enriched in both ^{17}O and ^{18}O affords a product displaying additional IR bands at 679 and 660 cm^{-1}; calculated values for ν(Re–^{17}O–Re) and ν(Re–^{18}O–Re) modes are 675 and 658 cm^{-1}, respectively. The hydrolytic coupling reaction of **3** has also been monitored by ^{1}H NMR spectroscopy. When an excess of H_2O is added to a $CDCl_3$ solution of **3**, the peaks due to the rhenium complex disappear as the precipitate forms, while signals due to free ethanol increase in intensity. No intermediates could be observed, and there was no evidence for other decomposition products being formed. Thus, we formulate the coupling reaction as shown in eq 5. Over a 2-h period at 298 K, the amount of ethanol formed corresponded to approximately 80% of the ethoxide ligands originally present in the sample; this result implies an average value of 4 for *n* in eq 5. We have attempted to prepare oligomers of greater solubility by employing a dicyclohexyldithiocarbamate analogue of **3** in the coupling reaction, but the resulting oxo-bridged material (ν(Re–O–Re) = 692 cm^{-1}) was again insoluble.



(5)

This study has demonstrated that, by the proper choice of coligands, phenylenediimido complexes can be used as reactive "monomers" in the construction of novel extended-chain inorganic materials. With proper modifications, such as varying the bridging ligands and tuning of oxidation states, such species may be expected to display novel conducting properties, and we are now pursuing this line of investigation.

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Structure of an L-Tyrosyl-L-histidine–Copper Complex Involving an Axial Copper(II)–Phenol OH Bonding. Implication for Substrate Binding at the Active Site of Tyrosinase

Tyrosinase is a copper-containing monooxygenase that catalyzes the hydroxylation of phenols to catechols (cresolase activity) and the two-electron oxidation of catechols to *o*-quinones (catecholase activity).[1,2] On the basis of the structural similarity of oxytyrosinase to oxyhemocyanin and the associative ligand substitution mechanism, Solomon et al.[1,3-5] proposed the molecular orientations for the hydroxylation and oxidation reactions through systematic chemical and spectroscopic studies. Very recent X-ray crystal structure analyses have revealed the coordination mode of the binuclear copper center in hemocyanin[6] and the O_2^{2-}-bridged binuclear structure of a Cu(II) complex.[7] Although Cu(II)–phenolic substrate interactions are reasonably required for the enzymatic hydroxylation mechanism, it remains unclear whether the phenol group coordinates to the Cu(II) ion in the phenolate (O^-) form or in the protonated (OH) form because of the lack of structural information on Cu(II)–phenol bonding.

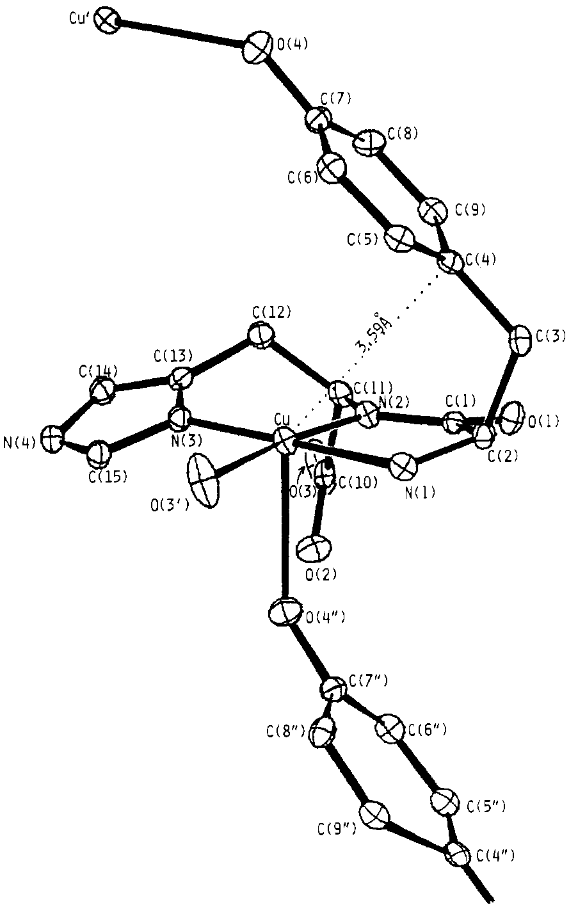

Figure 1. Computer-drawing model for [Cu(Tyr-His)]. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted. The labeling scheme used for the atoms in the molecule is also shown. The atoms with and without primes are related by a screw axis. Selected bond lengths (Å) and angles (deg): Cu–N(1) = 2.022 (4); Cu–N(2) = 1.930 (4); Cu–N(3) = 1.961 (4); Cu–O(3′) = 1.938 (4); Cu–O(4″) = 2.601 (4); N(1)–Cu–N(2) = 83.6 (2); N(1)–Cu–N(3) = 177.0 (2); N(2)–Cu–N(3) = 93.9 (2); O(3′)–Cu–N(1) = 94.7 (1); O(3′)–Cu–N(2) = 174.8 (1); O(3′)–Cu–N(3) = 87.8 (1); O(4″)–Cu–N(1) = 87.8 (1); O(4″)–Cu–N(2) = 89.8 (1); O(4″)–Cu–N(3) = 90.6 (1); O(4″)–Cu–O(3′) = 85.3 (3); Cu–O(4″)–C(7″) = 136.8 (3).

In order to shed light on the tyrosine side chain interactions with Cu(II) bound with nitrogen donors including imidazole, we made an X-ray diffraction study of the copper(II) complex of L-tyrosyl-L-histidine (Tyr-His), [Cu(Tyr-His)] (**1**), as a model

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