in a reduced dimensional space around the double helix. It is notable here that, based on the ΔG values for these reactions, the calculated rates from Marcus theory indicate that the electron transfer between these pairs should be diffusion-controlled.[9] An additional explanation that may account at least in part for our findings lies in the involvement of the π-framework of the nucleotides in mediating long-range electron transfer through the extended range of donor–acceptor electronic coupling. Some combination of long-range electron transfer and diffusion is possible.

In conclusion, binding to DNA assists the electron transfer between the metal-centered donor–acceptor pairs. The increases in rate in the presence of DNA illustrate that reactions at macromolecular surfaces may be faster than those in the bulk homogeneous phase. These systems can provide models for the diffusion of molecules bound on biological macromolecular surfaces, for protein diffusion along DNA helices, and in considering effects of medium, orientation and diffusion on electron transfer on macromolecular surfaces. Detailed experiments are in progress to sort out the different mechanisms possible and also to determine the effective diffusion rates small molecules experience in the vicinity of DNA.

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Catecholate Complexes of High Oxidation State Metal Ions. Synthesis and Characterization of Tris(3,5-di-*tert*-butylcatecholato)rhenium(VI)

Lynn A. deLearie and Cortlandt G. Pierpont*

Department of Chemistry and Biochemistry
University of Colorado, Boulder, Colorado 80309

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Catecholate ligands bond with transition-metal ions as strong π-donors and stabilize metal ions in high oxidation states.[1] Complexes of high oxidation state rhenium ions usually contain oxo or nitrido ligands, and examples of rhenium(VI) compounds without strong π-donor ligands are limited to the reactive fluoride and methyl complexes ReL_6 and ReL_8^{2-}, L = F, CH_3.[2] Neutral, trigonal-prismatic tris(1,2-dithiolene) and tris(1,2-thioamido) complexes of rhenium are known but metal–ligand delocalization complicates assignment of formal charge.[3,4] In this paper we describe the synthesis and characterization of a neutral tris(catecholato)rhenium(VI) complex which is isoelectronic with the 1,2-dithiolene complexes but exists with a charge-localized electronic structure.

Reactions between metal carbonyl complexes and *o*-benzoquinones under either thermal or photochemical conditions serve as convenient synthetic routes to simple binary metal–quinone complexes.[5] Metal–carbonyl complexes containing semiquinone ligands which may appear as intermediates in these reactions have been formed by using a monochromatic light source. Wan has reported formation of substituted semiquinone carbonyl complexes of manganese and rhenium by irradiation at 310 nm to form the metal tetracarbonyl radical, (1).[6,7] In a similar reaction carried out by using a polychromatic light source, we observed that the tetrameric 3,5-di-*tert*-butylsemiquinone complex of manganese(II) could be formed, (2).[8] Apparently, this results from photoexcitation of both the metal carbonyl and the semiquinone carbonyl complex products formed during the reaction. In similar chemistry, irradiation of a solution containing $Re_2(CO)_{10}$ and 3,5-di-*tert*-butyl-1,2-benzoquinone in toluene or anisole produces $Re(DBCat)_3$ as a dark purple crystalline product in nearly quantitative yield. The product obtained by using a polychromatic light source shows no carbonyl bands in the infrared, and a parent ion in the mass spectrum consistent with the monomeric tris(quinone)rhenium formulation.[9] The results of a crystallographic molecular structure determination confirm the monomeric structure of the complex (Figure 1)[10] and show that the molecule

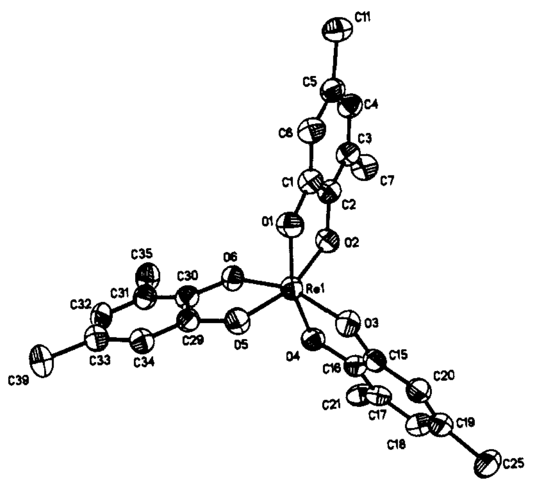


Figure 1. ORTEP plot of $Re(DBCat)_3$. Methyl carbon atoms of the *tert*-butyl groups have been omitted for clarity. The "twist angle" between triangular faces defined by chelating oxygen atoms is 37.9°.

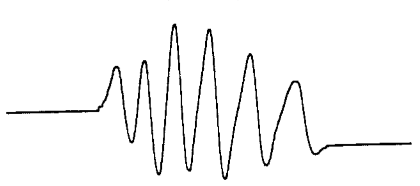
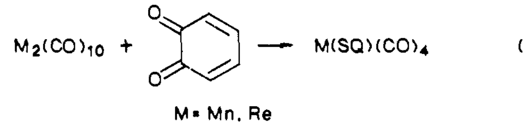
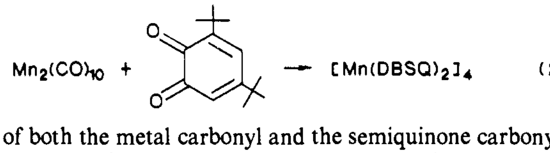


Figure 2. Isotropic EPR spectrum of $Re(DBCat)_3$ recorded in CH_2Cl_2 solution at room temperature. The horizontal coordinate of the figure is in units of gauss.





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[9] Mass spectrum: parent ions at m/z of 848 (^{187}Re) and 846 (^{185}Re). UV–visible: 273 (16000 M^{-1} cm^{-1}), 492 (20000 M^{-1} cm^{-1}), shoulder 590 nm.

[10] Monoclinic, $P2_1/n$, $a = 15.880$ (3) Å, $b = 15.897$ (3) Å, $c = 16.450$ (3) Å, $\beta = 93.53$ (2)°, $V = 4145$ (1) Å^3 at 296 K $D_{calcd} = 1.358$ g cm^{-3}, $D_{exptl} = 1.34$ (2) g cm^{-3}, $Z = 4$, $R = 0.039$, $R_w = 0.042$ for 5711 observed reflections ($F > 6\sigma(F)$).

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has an octahedral coordination geometry in contradistinction with the sulfur-donor analogues. Carbon-oxygen bond lengths of the ligands average to 1.353 (6) Å, a value associated with localized catecholate ligands.[5a] Rhenium-oxygen bond lengths average to 1.932 (4) Å, a value shorter than other reported Re-O lengths to all but oxo ligands by more than 0.05 Å. For comparison, Herrmann has recently reported Re-O lengths of 1.99 (1) Å for the Re(V) complex $(\eta^5\text{-}C_5Me_5)Re(Cl_4Cat)_2$.[11] As a d^1, Re(VI) complex, $Re(DBCat)_3$ has a solid-state magnetic moment of 1.18 (1) μ_B, showing the pronounced effect of spin-orbit coupling, and a uniquely simple solution EPR spectrum (Figure 2). The isotropic spectrum recorded at room temperature in dichloromethane solution consists of six lines due to the $I = {}^5/_2$ ^{185}Re and ^{187}Re isotopes. Spacing between lines shows evidence of a strong second-order effect. Correction for this effect gave isotropic $\langle g \rangle$ and A values of 2.010 and 0.002 cm^{-1}. Other Re(VI) complexes show only a broad signal in solution at room temperature with no resolved hyperfine in cases where a signal can be observed.[12] Cyclic voltammetry on $Re(DBCat)_3$ shows a reversible, one-electron reduction to the Re(V) species, $Re(DBCat)_3^-$, at −0.656 V (vs. Fc^+/Fc), and a reversible oxidation at +0.594 V.[13] Oxidation may occur either at one ligand to give the species $Re(DBSQ)(DBCat)_2^+$ with mixed-charge quinone ligands or at the metal to give the Re(VII) complex $Re(DBCat)_3^+$.

Charge distribution within the metal catecholate or, more generally, the metal quinone chelate ring is determined by the relative energies of metal and quinone electronic levels. Effects which change this order result in transfer of charge between quinone and metal. One particular effect is related to the position of the metal in the group and valence d-orbital energy. Neutral bis- and tris(quinone) complexes of first-row metals contain semiquinone ligands, while related complexes prepared with metals of the second and third transition series contain catecholates with higher oxidation state metal ions. For example, complexes of chromium are of the form tris(semiquinone)chromium(III), while molybdenum analogues are tris(catecholate)molybdenum(VI) species.[1a,14,15] Differences in form and charge distribution between $[Mn(DBSQ)_2]_4$ and $Re(DBCat)_3$ further illustrate this property.

The most striking property of $Re(DBCat)_3$ is its unreactivity. The molybdenum analogue reacts with trace quantities of oxygen to give oxomolybdenum species and benzoquinone.[14] No such sensitivity to oxygen or to trace quantities of water contained in solvents has been noted for $Re(DBCat)_3$. In fact, Herrmann has prepared $(\eta^5\text{-}C_5Me_5)Re(Cl_4Cat)_2$ by displacement of oxo ligands from $(\eta^5\text{-}C_5Me_5)ReO_2$ with tetrachloro-1,2-benzoquinone.[11] This behavior is unusual for a high oxidation state metal ion and appears facilitated by the strong π-donor bonding of the catecholate ligands.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for tris(3,5-di-*tert*-butylcatecholato)-rhenium(VI) (2 pages); observed and calculated structure factors for tris(3,5-di-*tert*-butylcatecholato)rhenium(VI) (34 pages). Ordering information is given on any current masthead page.

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Asymmetric Electrophilic Amination: Synthesis of α-Amino and α-Hydrazino Acids with High Optical Purity

Cesare Gennari,* Lino Colombo, and Giorgio Bertolini

Dipartimento di Chimica Organica e Industriale
dell'Università, Centro C.N.R. Sostanze
Organiche Naturali, 20133 Milano, Italy

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The *E* silyl ketene acetal derived from (1*R*,2*S*)-*N*-methylephedrine propionate (**1**) (R = Me) was recently shown to be a very useful reagent for the $TiCl_4$-mediated asymmetric synthesis of anti α-methyl-β-hydroxy esters.[1,2] Asymmetric electrophilic formylation ($TiCl_4$, $HC(OMe)_3$) proved also to be quite successful.[3] Here we report that asymmetric electrophilic amination ($TiCl_4$, *t*-BuOOCN=NCOO-*t*-Bu (DTBAD)) can be achieved using this reagent and that this process fulfills the following requirements: (a) enantiomeric excesses in the range 78-91%; (b) reasonably good chemical yields; (c) both enantiomers of the chiral auxiliary are inexpensive, commercially available materials;[4] (d) the chiral auxiliary can be recycled; (e) the absolute configuration of the reaction products is easily predictable. By this route natural, rare,[5] and unnatural α-amino acids **4** can be easily prepared[6] (Scheme I). α-Hydrazino acids **3**, which are intermediates in the synthetic sequence (Scheme I), are very interesting compounds because of their biological properties and as building blocks for modified peptides,[7] cephalosporins, and penicillins.[8,9]

N-Methylephedrine (1*R*,2*S*) was treated with RCOCl in CH_2Cl_2 to give the corresponding esters (100%). LDA enolization (THF, −78 °C) and Me_3SiCl trapping (−78 °C) gave the silyl ketene acetals **1** (95%; $E/Z \geqslant 95{:}5$), which were worked up by evaporation without water quenching. Slow addition of 1 mol equiv of the silyl ketene acetals in methylene chloride to 1 mol equiv of the $TiCl_4$-di-*tert*-butyl azadicarboxylate (DTBAD) complex[10] at −80 °C in CH_2Cl_2 gave fair to good overall yields[11,12]

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(11) The only by-products were the unreacted ephedrine ester and di-*tert*-butyl hydrazinodicarboxylate, which was probably generated by diimide reduction of DTBAD. Diimide was generated by acidic decomposition of DTBAD (−2 (2-methylpropene), $-2CO_2$).

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