half-life of hours in solution at 25 °C.[17]) A more probable pathway involves the electron-transfer process shown in Scheme I, similar to the reported reactions of $CpV(CO)_3H^-$ with neutral metal carbonyl complexes.[20] A radical process is also implicated by the fact that CO substitution in $CpRe(CO)_2(NO)^+$ is not normally a rapid reaction.[21,22]

The $HRu(CO)_4^-$ hydride also reacts rapidly with $CpRe(CO)_2(NO)^+$ at 25 °C. Addition of $[CpRe(CO)_2(NO)]PF_6$ to an acetone solution of $PPN[DRu(CO)_4]$ causes rapid disappearance of the ^2H NMR signal at δ -7.77; hydride resonances for CpRe(CO)(NO)D (δ -8.44) and $DRu_3(CO)_{11}^-$ (δ -12.70) are observed to appear. Also evident is the characteristic formyl resonance of CpRe(CO)(NO)(CDO) at δ 16.18.[17,23] The possible stoichiometry of the formyl-producing reaction is given by eq 5.[24]

$$3\ HRu(CO)_4^- + 2\ CpRe(CO)_2(NO)^+ \longrightarrow HRu_3(CO)_{11}^- + 2CpRe(CO)(NO)(CHO) + CO \qquad (5)$$

Of the $CpRe(CO)_2(NO)^+$ converted to the hydride and formyl products, a 20–30% yield of the formyl (based on integrated ^2H NMR peak intensities) is typically observed. The formation pathway of the coproduced rhenium hydride is uncertain. It seems unlikely that all of this product could be formed by decarbonylation of the relatively stable formyl complex.[25] Instead, it appears probable that an electron-transfer process similar to that outlined in Scheme I produces this hydride directly, via a pathway parallel to eq 5.[26] Studies on the details of these processes are continuing.

The hydride cluster $HRu_3(CO)_{11}^-$ is readily formed from H_2 and a ruthenium source in the iodide-promoted catalytic system noted above.[9] Although this cluster appears to be stable under catalytic conditions, it is not improbable that its fragmentation to $HRu(CO)_4^-$ is involved as an initial step in the catalytic sequence.[28]

Intermolecular transfer of hydride from the reactive mononuclear $HRu(CO)_4^-$ species to an electrophilic carbonyl ligand in another complex has now been demonstrated as a feasible step in the CO reduction process by this catalyst system. The facility of this transfer may be responsible for the relatively high catalytic activity of this system.[9,29]

Registry No. $HRu(CO)_4^-$, 77482-04-3; $CpRe(CO)_2(NO)^+$, 45978-17-4; $HRu_3(CO)_{11}^-$, 77482-10-1; CO, 630-08-0.

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(20) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415.

(21) Tam, W.; Lin, G.; Wong, W.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(22) The exchange of carbonyl ligands in $[CpRe(CO)_2(NO]PF_6$ with ^{13}CO (1 atm) is imperceptibly slow at 25 °C in acetone solvent but is greatly accelerated by *catalytic* amounts of $PPN[HRu_3(CO)_{11}]$, consistent with Scheme I.

(23) Experiments using ^{13}CO-enriched $[CpRe(CO)_2(NO)]PF_6$ also showed a doublet ($^1J_{C-D}$ = 23 Hz) accompanying the ^{12}CDO signal.

(24) The same stoichiometry has been observed in other reductions by $HRu(CO)_4^-$. S. G. Shore, private communication.

(25) An experiment was done that indicates that the formyl complex, once formed, is stable under reaction conditions. $[CpRe(CO)_2(NO)]PF_6$ in THF solution was partially converted to CpRe(CO)(NO)(CDO) by reaction with 0.5 equiv of $LiDB(C_2H_5)_3$. The remaining rhenium cation was then allowed to react with $PPN[HRu(CO)_4]$ at 25 °C. Analysis by ^2H showed no change in the amount of CpRe(CO)(NO)(CDO) present after this reaction.

(26) The possibility has not been excluded that electron transfer followed by hydrogen atom transfer[27] to a carbonyl ligand is involved in formyl formation. Selectivity to the formyl and hydride products would then be determined by the relative amounts and reactivities of the two rhenium complexes of eq 2. We have observed, however, that the formyl/hydride selectivity is unaffected by CO pressure over the range 0–3 atm.

(27) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

(28) We do not yet have direct evidence for this cluster fragmentation process, but we have observed that the iron analogue, $PPN[HFe_3(CO)_{11}]$, is completely fragmented in THF solvent under 34 atm of CO at 60 °C. See also: Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1973**, *61*, 365. Although fragmentation of the iron cluster is expected to be much more facile than for the Ru analogue, the pressure employed in the ruthenium-catalyzed reaction (generally above 400 atm[9]) may be sufficient to generate small equilibrium amounts of the mononuclear hydride.

(29) Dombek, B. D. *J. Organomet. Chem.*, in press.

Electrochemical Routes to Paramagnetic Dinuclear and Mononuclear Palladium π Complexes Stabilized by the Pentaphenylcyclopentadienyl Ligand

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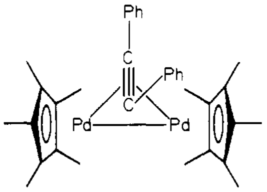
We report an example of the anodic activation of a dinuclear palladium complex to cleavage reactions that give stable mononuclear Pd(II) π complexes. The Pd(II) complexes can in turn be reduced or oxidized in reversible one-electron processes resulting in what appear to be the first persistent paramagnetic Pd(I) or Pd(III) π complexes.

The precursor compound is the diphenylacetylene-bridged dipalladium complex $(\eta^5\text{-}C_5Ph_5)_2Pd_2(\mu\text{-}PhC_2Ph)$,[2] **1**. This compound displays two diffusion-controlled reversible one-electron oxidations ($E°$ = +0.52 and +1.13 V vs. SCE)[3] and a single one-electron reduction ($E°$ = -1.12 V). In CH_2Cl_2 the reduction is fully chemically reversible only at cyclic voltammetry (CV) sweep rates in excess of 200 mV/s, but greater reversibility was observed in THF solutions.[4] Therefore the dimer has a three-step electron-transfer series giving four reasonably stable oxidation states:



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$$\mathbf{1}^{2+} \rightleftharpoons \mathbf{1}^{+} \rightleftharpoons \mathbf{1} \rightleftharpoons \mathbf{1}^{-}$$

Exhaustive anodic oxidation (+0.7 V) of **1** in CH_2Cl_2 at a platinum basket gave an intense green-black solution (n = 0.96 e$^-$); voltammetry at the rotating platinumg electrode (rpe) confirmed the quantitative conversion of **1** to the radical cation $[(\eta^5\text{-}C_5Ph_5)_2Pd_2(\mu\text{-}PhC_2Ph)]^+$, $\mathbf{1}^+$ (Figure 1).

The chemical synthesis of $\mathbf{1}^+$ was readily effected by adding a toluene solution of $AgPF_6$ to an equivalent quantity of **1** in the same solvent. After the solution stirred for 5 min, the black precipitate was removed and extracted with CH_2Cl_2; black microcrystals of $\mathbf{1}^+$ were isolable by hexane addition. The identity of $\mathbf{1}^+$ was confirmed by elemental analysis, by its voltammograms ($E°$ values identical with **1**), and by its frozen solution electron spin resonance spectrum in CH_2Cl_2, which showed one line centered at g = 2.044.

Unlike neutral **1**, the radical cation $\mathbf{1}^+$ is a source of diamagnetic Pd(II) complexes, undergoing cleavage reactions with various ligands [L = PPh_3, L_2 = $Ph_2P(CH_2)_2PPh_2$ (dppe) or cyclooctadiene (cod), etc.] to give $[(\eta^5\text{-}C_5Ph_5)PdL_2][PF_6]$, **2**, according to eq 1. The stoichiometry of the reaction, which also can be

$$2(\mathbf{1}^+) + 4L \rightarrow 2[(\eta^5\text{-}C_5Ph_5)PdL_2]^+ + \mathbf{1} + PhC_2Ph \qquad (1)$$

accomplished by the electrochemical oxidation of **1** in the presence

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(1) (a) University of Bristol; (b) University of Vermont.

(2) Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* **1977**, *99*, 4707.

(3) Data obtained by cyclic voltammetry measurements at a platinum bead electrode in CH_2Cl_2/0.1 M Bu_4NPF_6 electrolyte. Peak separations were typically 70 mV, and i_c/i_a values were unity down to slow sweep rates (ca. 50 mV/s), consistent with a reversible one-electron processes.

(4) In multiple-sweep CV scans or upon bulk cathodic reduction, the solution gives a reversible wave at ca. -0.3 V, which we believe to be due to the pentaphenylcyclopentadienyl anion.

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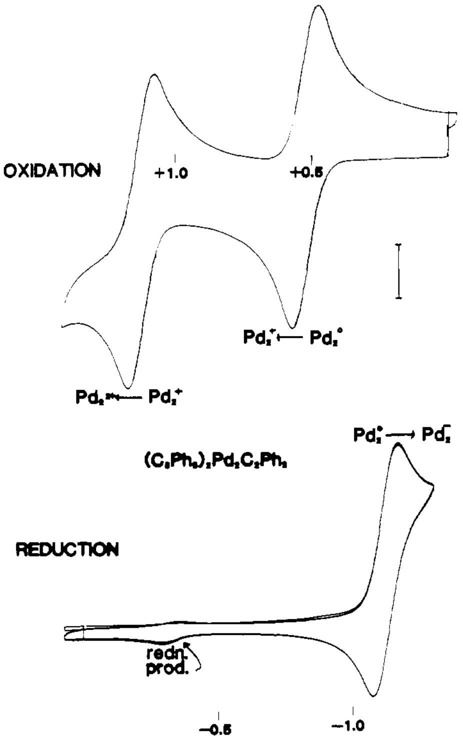

Figure 1. Cyclic voltammograms of 1 in CH_2Cl_2/0.1 M Bu_4NPF_6 at a platinum electrode; scan rate 75 mV s^{-1}. *Y*-axis current marker is 2 μA. Two successive scans are recorded in the reduction curves.

of L, was confirmed by voltammetric experiments at the rpe.

Complex 1^+ also reacts with donor solvents such as tetrahydrofuran, acetone, or acetonitrile to give red-to-purple solutions of solvento-complexes, presumably $[(\eta^5\text{-}C_5Ph_5)Pd(solv)_2]^+$, together with a precipitate of **1**. After filtration, addition of L gave a green solution from which **2** could be isolated after column chromatography on silica.

The Pd(II) complexes **2** can be reduced or oxidized by one electron in what are generally reversible processes[5] to give Pd(I) and Pd(III) π complexes, which have apparently been unknown up to this time.[6] Changing the ligand L_2 in **2** results only in minor changes in the potential of the Pd(II)/Pd(I) couple. $E°$ values for the cod, dppe, and bipyridyl complexes of **2** were −0.47, −0.48, and −0.51 V, respectively, in CH_2Cl_2. This strongly suggests that the LUMO orbital in **2** is predominantly metal in composition and that the assigned change of metal oxidation state in the redox process is a reasonable one. This conclusion is qualitatively supported by ESR measurements. Bulk cathodic reduction of $(\eta^5\text{-}C_5Ph_5)Pd(cod)^+$ in CH_2Cl_2 at −0.6 V (−10 °C) consumed one electron as the solution changed from green to red-orange. Monitoring of the electrolyzed solution with an rpe showed that the precursor cation **2** had been quantitatively reduced to the neutral, formal Pd(I) species $(\eta^5\text{-}C_5Ph_5)Pd(cod)$. The reduced solution exhibited a fluid ESR spectrum in which the central line ($\langle g \rangle = 2.0706$) was flanked by satellites ($\langle a \rangle_{Pd} = 25$ G) arising from ^{105}Pd ($I = {}^5/_2$, 22.2% natural abundance).

Electrochemical oxidations of **2** have been briefly investigated. Oxidation of the cod and bipy complexes were reversible in CH_2Cl_2 ($E° = +1.65$ and +1.18 V, respectively), but the dppe complex oxidized irreversibly. Detailed studies are in progress.

Two effects of the pentaphenylcyclopentadienyl ligand,[7] compared to an unsubstituted Cp ligand, are apparent. One is that the electron-withdrawing ability of the phenyl substituent makes low oxidation states more accessible by raising the potential of the redox couple [the Pd(II)/Pd(I) potential for $(\eta^5\text{-}C_5Ph_5)Pd(cod)^+$ is 270 mV more positive than that of $CpPd(cod)^+$].[8] This is the opposite of the effect seen with the pentamethylcyclopentadienyl ligand, which has the effect of lowering the redox potential (making reductions more difficult).[9] The second effect appears to be greater kinetic stability for the π complexes, regardless of the oxidation state. This is supported by our observation that the reduction and oxidation of $CpPd(cod)^+$ are irreversible under the same conditions[8] in which the C_5Ph_5 analogue gives a stable Pd(I) or Pd(III).

The palladium–cyclopentadienyl π bond is notoriously weak and has been an impediment to development of $CpPdL_n$ chemistry.[10] This does not appear to be the case for $(\eta\text{-}C_5Ph_5)Pd$ compounds, and a study of the reactions, redox and otherwise, of these compounds is underway.

Acknowledgment. This research was generously supported by the National Science Foundation, NATO and the SERC. We also gratefully acknowledge a loan of palladium salts from Johnson Matthey.

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(5) In THF, the first oxidation of **1** is not completely chemically reversible ($E° = +0.71$ V), with $i_c/i_a = 0.83$ at $v = 52$ mV s^{-1}, due to the slow reaction of 1^+ with the solvent.

(6) See, for example: Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. I.

(7) See for the preparation of $(C_5Ph_5)^-$: Zhang, R.; Tsutsui, M.; Bergbreiter, D. E. *J. Organomet. Chem.* **1982**, *229*, 109.

(8) The reduction of $(\eta^5\text{-}C_5H_5)Pd(cod)^+$ is irreversible in nonaqueous solvents except at CV scan rates above 5 V/s ($E° = -0.74$ V). No reversibility was observed for the oxidation of this compound ($E_{pk} = +1.85$ V).

(9) Koelle, U.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 640.

(10) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, 1.

Stereoselective Synthesis of 1,3-Diol Derivatives and Application to the Ansa Bridge of Rifamycin S

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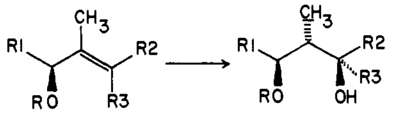
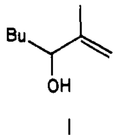
Olefin hydroboration is particularly useful when it can be directed by preexisting chiral centers. Although examples of such controlled hydroboration with cyclic olefins abound,[1] only a few hydroborations have been reported to give serviceable stereochemical control in acyclic systems.[2] We report here that certain classes of acyclic secondary allylic alcohols undergo hydroboration to yield *threo*-1,3-diols with 8->15:1 diastereoselection. The general transformation we have examined is shown in eq. 1.



(1)

To find the system giving the highest stereocontrol, several common hydroborating reagents were examined in various solvents by using alcohols **1**–**3** and their derivatives as substrates. As



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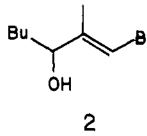

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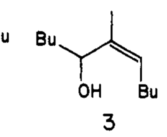

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outlined in the table, the major product was in nearly all ex-

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(1) For example: H. C. Brown, R. Liotta, and L. Brener, *J. Am. Chem. Soc.*, **99**, 3427 (1977); M. H. Gordon, and M. J. T. Robinson, *Tetrahedron Lett.*, 3867 (1968); Y. Senda, S. Kamiayama, and S. Imaizumi, *Tetrahedron*, 33, 2933 (1977).

(2) G. Schmid, T. Fukuyama, K. Akasaka, and Y. Kishi, *J. Am. Chem. Soc.*, **101**, 259 (1979); W. C. Still and K. P. Darst, *ibid.*, **102**, 7385 (1980); W. C. Still and K. R. Shaw, *Tetrahedron Lett.*, **22**, 3725 (1981); K. C. Nicolaou, M. R. Pavia, and S. P. Seitz, *J. Am. Chem. Soc.*, **104**, 2027 (1982); D. A. Evans, J. Bartroli, and T. Godel, *Tetrahedron Lett.*, **23**, 4577 (1982).

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