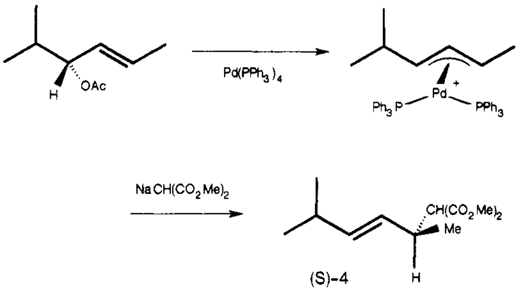
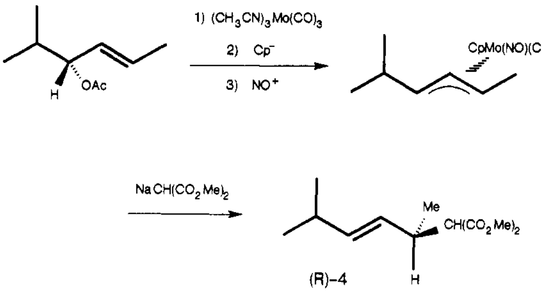
to the metal), resulting in an inversion at the site of nucleophilic addition. Thus, a chiral allyl acetate should experience a net inversion of the stereochemistry relative to the chiral center during the stoichiometric molybdenum allyl alkylation.

To demonstrate this net-inversion mechanism, we prepared a sample of dimethyl [(*E*)-5-methyl-3-hexen-2-yl]malonate (4) by addition of sodiomalonate to **3**-BF_4,[12] followed by decomplexation of the η^2-olefin formed. The stereochemistry of the molybdenum-mediated allyl alkylation was compared to that of the palladium-catalyzed alkylation[14] where the overall process is known to proceed through a double-inversion mechanism for stabilized carbanions.[15] The relative configuration of the addition products was determined by using a chiral shift reagent and observing the separation of the diastereomeric methyl ester singlets. The experiment demonstrates that starting with the same enantiomer of a chiral allyl acetate, the stoichiometric molybdenum-mediated alkylation results in addition products that have the *opposite* configuration of those obtained through the palladium-catalyzed alkylation. This shows that indeed the alkylation products of the stoichiometric molybdenum system experience a net inversion of configuration of the stereochemistry of the starting allyl acetate. By virtue of the retention during the oxidative addition step of chiral allyl acetates, the stoichiometric molybdenum system provides a route to asymmetrically allylated products where inversion of the stereochemistry of the chiral center is desired.





A number of molybdenum and tungsten catalysts also promote allylic alkylation, and it appears that moderately high net retention is observed in the products. As $(MeCN)_3Mo(CO)_3$ is similar to many of the catalysts, particularly in regard to the feature that several readily displaceable ligands are present, the results above suggest that oxidative addition of allylic acetates may well occur with retention in the catalytic cycle. Thus, these results imply that whereas net retention is a consequence of double inversion with palladium catalysis, net retention may be a consequence of double retention in many of the molybdenum-catalyzed reactions reported thus far.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. 1, 114581-58-7; 2, 114581-59-8; (*S*)-3, 114672-91-2; (*R*)-3, 114581-61-2; (*R*)-4, 114581-62-3; (*S*)-5, 114581-63-4; Cp^-, 12127-83-2; (*R*),(*E*)-$(CH_3)_2CHCH(OH)CH{=}CHCH_3$, 92283-72-2; NO^+, 14452-93-8; $(CH_3CN)_2Mo(CO)_2(OAc)$(5-methyl-2-4-η^3-hexenyl), 114594-71-7; $NaCH(CO_2Me)_2$, 18424-76-5; (*R*),(*E*)-$(CH_3)_2CHCH(OAc)CH{=}CHCH_3$, 114613-28-4; $Mo(CO)_6$, 13939-06-5; L-(+)-diisopropyl tartrate, 2217-15-4.

Supplementary Material Available: Discussion of absolute configuration X-ray crystal structure determination of (+)-1 and tables of data parameters, atomic positions, bond lengths and angles, calculated hydrogen positions, thermal parameters, and Bijvoet pair intensity comparisons (10 pages); a listing of calculated and observed structure factors (17 pages). Ordering information is given on any current masthead page.

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[12] Replacement of CO by NO^+ produces a new stereogenic center at Mo and, therefore, two diastereomers of 3, [CpMo(NO)(CO)(5-methyl-2–4-η^3-hexenyl)]$^+$, in a 48:52 ratio. The (*S*)-3 diastereomer, which contains the 2(*S*),4(*R*)-(5-methyl-2–4-η^3-hexenyl) ligand, yields addition of nucleophiles exclusively to the methyl-substituted terminus of the allyl.[13] Addition of sodiomalonate to a diastereomeric mixture of 3-BF_4 results in a mixture of regioisomers, where the nucleophile has added to different ends of the η^3-allyl group yielding 48% (*R*)-4 and 52% (*S*)-5 after decomplexation. A sample of pure (*R*)-4 can be isolated via preparative TLC (silica, $CHCl_3$). The relative configuration of (*S*)-5 was determined by using a chiral NMR shift reagent and observing the separation of the diastereomeric methyl ester singlets. These results were compared to those from a sample of (*R*)-5 prepared by using $Mo(CO)_6$ as the allyl alkylation catalyst where the catalytic cycle proceeds through a net-retention mechanism.[6a]

[13] (a) The regiochemistry of the addition is controlled by the relative position of the NO group. The separation of diastereomers and the ability of the NO to override the steric directing effect of the *i*-Pr group will be discussed in a forthcoming full paper.[13b] (b) Faller, J. W.; Linebarrier, D.; Lambert, C., manuscript in preparation.

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Unusually Long-lived Cobalt(II) and Cobalt(I) Species Identified during Electrochemical Reduction of Neopentyl B_{12} Costa-Type Models

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Summary: Unusually long-lived complexes, which are formally in cobalt(II) and cobalt(I) oxidation states, are identified spectrally and electrochemically during the cathodic reduction in acetonitrile of a Costa-type organocobalt(III) B_{12} model with a particularly bulky alkyl axial ligand, namely, neopentyl. The solution behavior is different from that reported for other similar complexes in that intermolecular alkyl transfer processes are essentially prevented by the bulky neopentyl axial ligand.

The electrochemistry of organocobalt compounds[1-11] related to coenzyme B_{12} and methyl B_{12} has had a major role in defining the chemical properties of cobalamins.[12-14] Systematic studies of the cathodic behavior of organocobalt B_{12} models, $[H_2OCo((DO)(DOH)pn)R]ClO_4$ (R = an axial alkyl group and (DO)(DOH)pn = the $N^2,N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime) uninegative equatorial ligand), have been particularly important. However, in these Costa-type models, intermolecular alkyl transfer is facile, and reasonably long-lived $Co^{II}R$ species are observed only in the presence of added N-donor heterocyclic ligands. Unstable $Co^{I}R$ species have been observed,[10,13] but not in Costa-type models.

We report here definitive electrochemical studies, supported by OTTLE (optically transparent thin-layer electrode) measurements, which establish the essentially reversible formation of long-lived, formally Co(II) and Co(I) species on reduction of $[H_2OCo((DO)(DOH)pn)$neo-Pent$]ClO_4$ (**1**); neo-Pent = neopentyl) in acetonitrile. The bulk of the neopentyl group prevents intermolecular alkyl transfer, even in the absence of added N-donor ligands.

The cyclic voltammogram of **1** (Figure 1) reveals two sequential cathodic–anodic peak systems; the first and second peaks are quasi-reversible and reversible charge-transfer processes, respectively.[17,18] Coulometric tests at potentials (referenced vs ferrocene, Fc) of the more cathodic peak revealed that 2 mol of electrons/mol of **1** are consumed in the overall reduction process. Voltammetric curves recorded on the electrolyzed solution starting at the electrolysis potential showed the same system of peaks as the initial solution. Exhaustive reoxidation at the potentials of peak B involved the consumption of 2 mol of electrons/mol of original **1**, and the voltammograms recorded on the reoxidized solution exactly reproduced that reported in Figure 1.

Additional information could be gained by spectroelectrochemical measurements performed with an OTTLE cell, using a diode-array spectrometer. Spectra were recorded in the range 350–820 nm, either under potentiometric conditions (i.e., the potential was stepped at a selected value while the spectra were recorded until no significant change was found between two subsequent runs (300–500 s)) or during a slow scan rate potential sweep (0.2–0.3 mV s^{-1}) (i.e., one spectrum every 10 mV). The spectrum of an exhaustively reduced solution (g, Figure 2)) has two sharp bands at λ_{max} = 632 (strong) and 424 nm (weak). Spectra recorded at intermediate potentials reveal a band with λ_{max} = 806 nm. The absorbances at these three λ_{max} as a function of the potential in the forward (cathodic) and backward (anodic) scans are shown in Figure 3. While the plots for λ_{max} = 424 and 632 nm plateau at the most negative potentials, the plot for 806 nm exhibits a maximum and then returns to zero just at potentials corresponding to the plateau of the two other plots. In addition, the ratio between the intensities at 424 and 632 nm remains constant. The mirror image relationship between the two halves of Figure 3 confirms the

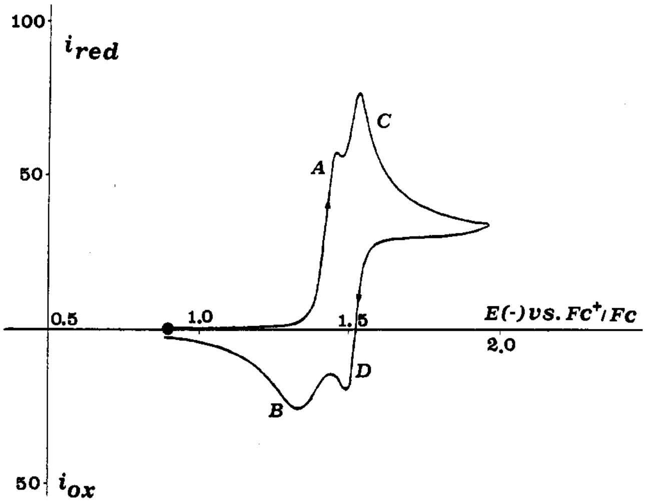

Figure 1. Cyclic voltammetric curve recorded on a 2.5 mM $[H_2OCo^{III}(DO)((DOH)pn)$neo-Pent$]ClO_4$, 0.1 M tetraethylammonium perchlorate, acetonitrile solution (platinum working electrode; 0.1 V s^{-1} potential scan rate; −17 °C starting temperature; ●, starting potential for the initially cathodic scan; E is expressed in volts and i in μA).

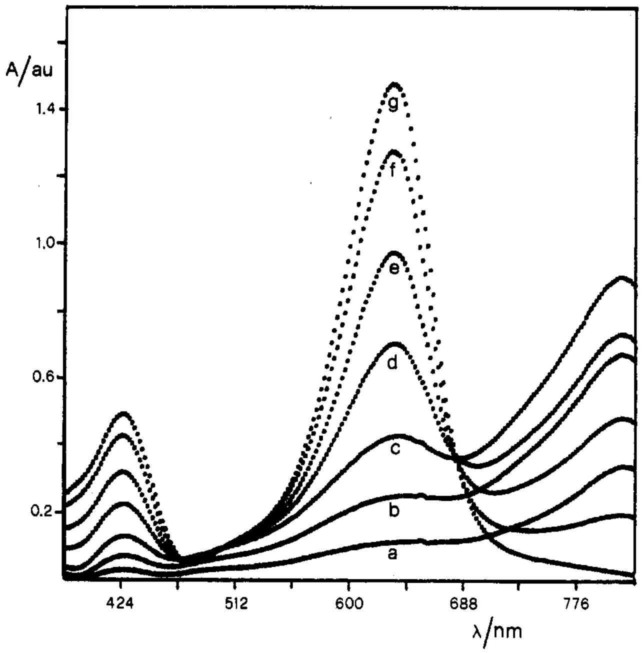

Figure 2. Spectra recorded on an OTTLE cell at 0 °C during a cathodic potential sweep. Potential values: a, −1.020 V; b, −1.060 V; c, −1.100 V; d, −1.150 V; e, −1.180 V; f, −1.210 V; g, −1.450 V vs SCE.

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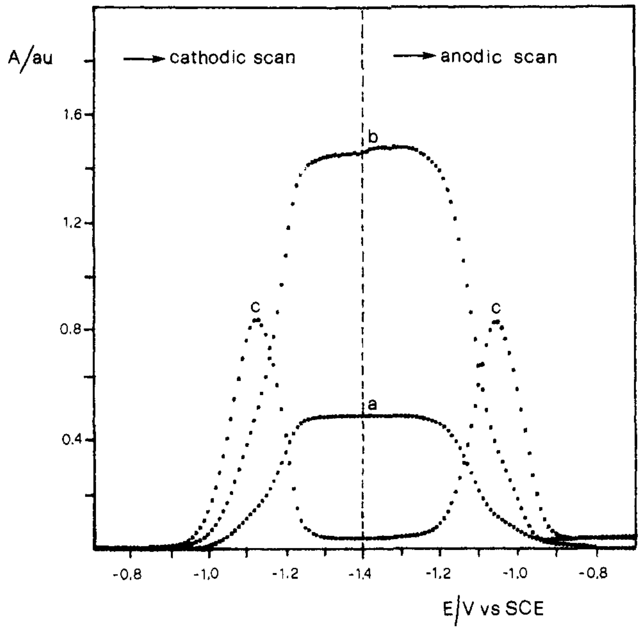

Figure 3. Plot of the absorbances at 424 (a), 632 (b), and 806 (c) nm as a function of the potential.

reversibility of the chemical processes involved. Analogous plots (not shown) of potentiostatic experiments at potentials corresponding to the rising portion of the less cathodic peak (A, Figure 1) show three S-shaped curves, which implies that the species responsible for the 806-nm peak does not undergo any chemical reaction and is stable over a limited potential range.

The whole of the voltammetric, bulk electrolysis and OTTLE data is consistent with the occurrence of two subsequent uncomplicated one-electron charge transfers.[19,20] The intermediate formally Co(II) (806-nm band) and the final formally Co(I) (424- and 632-nm bands) species are chemically stable, unlike all previously studied similar complexes. Cyclic voltammetric curves and absorbance-potential plots allow an approximate evaluation of $E^{r}_{1/2}$ (a good approximation of the standard potential[21]) for the Co(III)/Co(II) couple and a more precise estimation of this parameter for the Co(II)/Co(I) couple, referenced vs Fc, as follows:[22]

$$[\mathrm{LCo^{III}neo\text{-}Pent}]^{+} + e^{-} \leftrightarrow \text{“}\mathrm{LCo^{II}neo\text{-}Pent}\text{”}$$

$$E^{r}_{1/2} \approx -1.39 \text{ V at } -17\ {}^\circ\mathrm{C}$$

$$\text{“}\mathrm{LCo^{II}neo\text{-}Pent}\text{”} + e^{-} \leftrightarrow [\text{“}\mathrm{LCo^{I}neo\text{-}Pent}\text{”}]^{-}$$

$$E^{r}_{1/2} \approx -1.51 \text{ V at } -17\ {}^\circ\mathrm{C}$$

where L includes ligands other than neopentyl, i.e., (DO)(DOH)pn and the possible axial water or solvent molecules. As suggested previously for much less well-behaved systems,[10,13] the neopentyl group may have migrated onto the equatorial ligand in the reduced species,[23] hence the quotes. Uncertainty over the location of the R group in such species has persisted for years,[13] and further study of the sterically hindered, well-behaved organocobalt species discovered here offers some promise for the resolution of this issue.

Acknowledgment. L.G.M. thanks the NIH (GM 29225) for support.

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[23] Although our focus is not mechanism, the reversible character of the II/I couple and the quasi-reversible III/II couple suggest that the intramolecular transfer occurs in the III/II step.

Generation and Reactivity of a Triosmium Carbon Radical. Hydrogen Abstraction, Arene Addition, and the Formation of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$, a Dialkylidyne, Diketone Complex

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Received March 18, 1988

Summary: Photolyzing a mixture of $Re_2(CO)_{10}$ and $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ under CO (~2 atm) is a convenient method of generating the radical $H_3Os_3(CO)_9(\mu_3\text{-}C^{\bullet})$. This species abstracts hydrogen from cyclohexane and toluene and adds to benzene. In deuteriated hydrocarbons $H_3Os_3(CO)_9(\mu_3\text{-}CD)$ is produced, but in cyclohexane-d_{12} a diketone complex, $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$, also is formed.

Current interest focuses on the nature and reactivity of exposed carbon atoms in peripheral metal carbide clusters.[1-4] Observed reactivities have indicated that low-coordinate carbon atoms, especially μ_4-C, will be most reactive, perhaps best modeling carbon species on metal surfaces. To date no μ_3-C clusters have been isolated, although calculations suggest that such species may be accessible.[4] One class of μ_3-C clusters consists of the carbon radicals generated from stable μ_3-CX compounds. Such radicals have been proposed as intermediates in some reactions of $Co_3(CO)_9(\mu_3\text{-}CY)$ clusters[5] as well as in the reduction of $H_3Ru_3(CO)_9(\mu_3\text{-}CBr)$ by $(n\text{-}Bu)_3SnH$.[6] We wish to report a convenient method for the generation of the $H_3Os_3(CO)_9(\mu_3\text{-}C^{\bullet})$ radical along with preliminary studies of its reactivity. We also report the formation and characterization of $[H_3Os_3(CO)_9(\mu_3\text{-}CCO)]_2$, a novel dimeric diketone cluster.

Interconversion of triosmium methylidyne and halomethylidyne clusters proceeds cleanly and under mild conditions (eq 1),[7,8] using reagents precedented by organic alkyl radical reactions.[9] It is reasonable to propose that

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[8] Heating $H_3Os_3(CO)_9(\mu_3\text{-}CH)$ at 45 °C in CO-saturated CCl_4 or $BrCCl_3$, with excess t-BuOCl, gives $H_3Os_3(CO)_9(\mu_3\text{-}CX)$ (X = Cl or Br), respectively, in ~90% yield after TLC on fluorescent silica (pentane). The reverse reaction is accomplished by heating $H_3Os_3(CO)_9(\mu_3\text{-}CBr)$ with excess $n\text{-}Bu_3SnH$ in heptane under CO at 60 °C (85%).

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