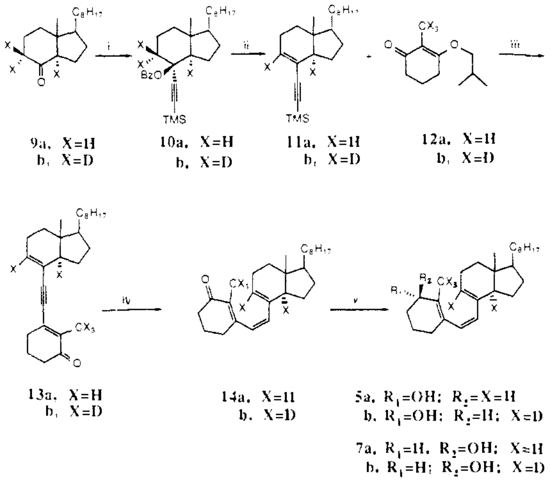
Table II. Activation Parameters[a] for the Previtamin D → Vitamin D Transformation

substrate	E_A[b]	log A[c]	$\Delta G^{\ddagger}$[b]	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[d]
5a (1*S*)	18.8 (±0.07)	8.5 (±0.03)	25.9 (±0.1)	18.1 (±0.1)	−22.2 (±0.1)
7a (1*R*)	19.1 (±0.5)	8.6 (±0.2)	26.1 (±0.7)	18.4 (±0.5)	−21.7 (±0.6)
previtamin D_3[e]	19.1 (±0.5)	8.5 (±0.2)	26.3 (±0.7)	18.4 (±0.5)	−22.2 (±0.6)

[a] At 80.0 °C. The rate constants were determined over the temperature range, 60.55–87.70 °C (±0.05 °C). [b] kcal/mol. [c] A in s^{-1}. [d] cal/mol K. [e] Data at 80.0 °C from ref 3a.

Scheme III[a]



[a] 1. TMS–CC–TMS/MeLi, LiBr, THF; 2. Benzoyl chloride (neat), −78 °C to RT, room temperature (**10a**, 91%; **10b**, 86%); (ii) FVP, quartz tube with quartz chips, 480 °C, N_2 flow, 5 mmHg vacuum (**11a**, 51%; **11b**, 40%); (iii) MeLi/LiBr/THF; **12**; HOAc/H_2O (**13a**, 71%; **13b**, 79%); (iv) Lindlar catalyst, quinoline, benzene (**14a**, 89%; **14b**, 88%); (v) $NaBH_4$, $CeCl_3$, methanol (**5a**, 49%; **7a**, 33%; **5b**, 36%; **7b**, 28%).

solutions of the previtamins in isooctane (10^{-3} molar) were prepared, and aliquots were introduced into capillary reaction vessels, which were then sealed and stored at −80 °C. No detectable isomerization or decomposition of previtamin was noticed for samples handled in this manner. For the kinetic measurements, each sample during heating was removed at appropriate time intervals and was immediately cooled to −80 °C and later analyzed by analytical HPLC (10% ethyl acetate in hexanes, Waters Radial-Pak; calibrated silica cartridge column, UV detection at 254 nm). Peak areas were integrated by using the cut and weigh method. The weights obtained were transformed into concentrations by using the measured extinction coefficient at 254 nm for each of the species: **5a** or **5b**, ϵ = 8900; **6a** or **6b**, ϵ = 16 300; **7a** or **7b**, ϵ = 8200; **8a** or **8b**, ϵ = 16 800. A plot of ln [fraction of starting material remaining] versus time [s] (followed to a low 20–30% conversion) afforded a straight line with slope $-k$ representing the first-order rate constant. In one study, the product composition determined by ^1H NMR integration (C-18 angular methyl group) proved identical (within ± 3%) with that determined by the HPLC integration method.

The kinetic isotope effect data and activation parameters for **5** and **7** are summarized in Tables I and II, respectively. The activation parameters for **5a** and **7a**, both of which bear C_1–OH groups, are very similar to those previously reported for isomerization of the parent previtamin D_3, which bears a C_3–OH group. However, the isomerization of **5** and **7** to their corresponding vitamin D forms occurs with a primary kinetic isotope effect, k_H/k_D, of ~6, nearly an order of magnitude smaller than that reported for previtamin D_3. The k_H/k_D value of ~6 (80 °C) reported in this study is thus not particularly unusual in magnitude and only modestly larger than the values 2.6–4.0 (at 98.6 °C) recently reported by this laboratory for a [1,7]-sigmatropic shift in a different heptatriene system.[8] The parent previtamin D_3 isomerization (**2** → **3**) for which the large k_H/k_D of ~45 was reported clearly needs to be reevaluated.[9]

Acknowledgment. This study was supported by NIH Grant DK-16595. Dr. Menso Rappoldt of Duphar, B.V. (Weesp, The Netherlands), generously provided starting materials. K.J.M. acknowledges receipt of a President's and N. T. Coleman undergraduate research awards. We are especially grateful to H. Y. Elnagar, Dr. G.-Y. Shen, and Dr. A. Palenzuela of this laboratory for valuable input.

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(9) During the review of this manuscript, Professors Y. Mazur and M. Sheves have kindly informed us that the k_H value (1.2×10^{-3} s^{-1} at 80 °C) utilized in their computation of k_H/k_D (ref 5) is in error. We believe the k_H value reported in ref 3a would have been more appropriate.

Dissociative versus Molecular Chemisorption of Nitric Oxide on Small Bare Cationic Cobalt Clusters in the Gas Phase

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The surface chemistry of nitric oxide (NO) has been the focus of intense study due, in part, to its importance in environmental concerns.[1] These investigations have emphasized the characterization of the molecular structure of NO on surfaces,[2] dynamics of dissociation,[3] factors (substrate geometry, presence of other adsorbates, temperature, etc.) affecting dissociation or activation,[4] and reaction with other adsorbates.[5] Of relevance to these studies is the investigation of small metal cluster ions in the gas phase.[6] Techniques have been developed that allow both the size of the cluster and the presence of adatoms or molecules to be controlled and their effects on reactivity monitored. As an example we recently reported that Co_2NO^+ undergoes oxide transfer to CO, process 1, whereas $Co_2(CO)NO^+$, Co_3NO^+, and Co_4NO^+ are unreactive with CO.[7]

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$$Co_2NO^+ + CO \rightarrow Co_2N^+ + CO_2 \qquad (1)$$

A fundamental question in such studies concerns the structure of these Co_xNO^+ clusters (molecular nitric oxide versus dissociated nitride–oxide). Such information is required before processes such as 1 can be understood at the molecular level. Nitric oxide readily dissociates on a number of clean metal surfaces[3,8] including a Co(0001) surface[9] at low coverages with molecular chemisorption favored at higher coverages. In addition, the formation of metal cluster nitrides from transition-metal cluster–nitrosyl–carbonyl complexes is facile,[10] and stable oxide–nitride–carbonyl metal clusters have been characterized.[11]

In this report we investigate the structure of NO on Co_x^+ (x = 2–4) by studying displacement reactions with $^{18}O_2$. Preadsorption of $^{18}O_2$ has been employed for investigating NO adsorption on a Pt(111) surface where thermal desorption yielded both NO^{16} and NO^{18}.[12] The dissociative adsorption of H_2 on gaseous neutral Co and Nb clusters,[13] Fe clusters,[14] and cationic Nb clusters[15] has been inferred.

All experiments were performed on a Nicolet FTMS-1000 Fourier transform mass spectrometer[16] equipped with a 5.08 cm cubic trapping cell and a 3.0 T superconducting magnet.[17] $Co_x(NO)^+$ ions were generated by first allowing fragment ions formed from electron impact on $Co(CO)_3NO$ to react with $Co(CO)_3NO$.[18] Next, collisional activation (CA)[19,20] was used to remove unwanted ligands, as exemplified by processes 2–4, followed by isolation of the desired ion by swept double resonance ejection techniques.[16]

$$Co_2(CO)_3NO^+ \xrightarrow{CA} Co_2NO^+ + 3CO \qquad (2)$$

$$Co_3(CO)_2(NO)_2^+ \xrightarrow{CA} Co_3NO^+ + 2CO + NO \qquad (3)$$

$$Co_4(CO)NO^+ \xrightarrow{CA} Co_4NO^+ + CO \qquad (4)$$

lowed by isolation of the desired ion by swept double resonance ejection techniques.[16] Argon was used as the target for collisional activation (CA) at a pressure of ~1 × 10^{-5} Torr and also served to collisionally cool the Co_xNO^+ ions prior to study. The pressure of dioxygen was <5 × 10^{-8} Torr to ensure that the clusters were thermalized prior to reaction with dioxygen. $^{18}O_2$ was obtained from MSD Isotopes with >98 atom% purity.

Dioxygen reacts with all three Co_xNO^+ ions by reaction 5, exclusively, yielding the corresponding dioxide clusters.[21,22] Both

$$Co_xNO^+ + O_2 \rightarrow Co_x(O)_2^+ + NO \qquad (5)$$

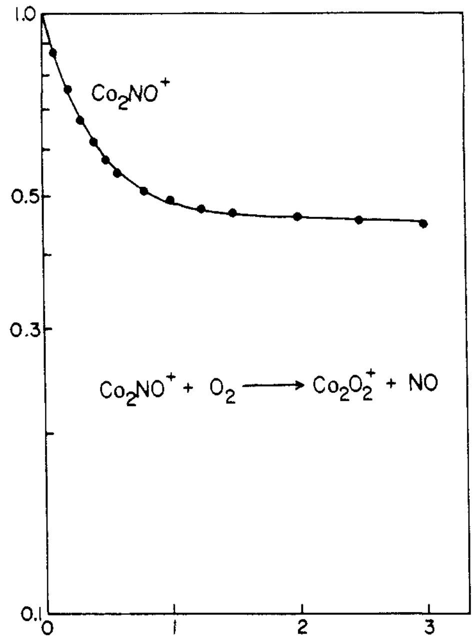

Figure 1. Temporal variation of Co_2NO^+ abundance, formed in reaction 2, when trapped in the presence of 1.9 × 10^{-7} Torr O_2.

Co_3NO^+ and Co_4NO^+ react by pseudo-first-order kinetics with a rate constant for Co_3NO^+ of 6.4 ± 1.3 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Langevin[23] collision rate = 5.6 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}). However only 55% of Co_2NO^+ reacts with dioxygen, as illustrated in Figure 1, suggesting at least two distinct Co_2NO^+ structures, one of which is reactive with dioxygen. Reactions of $^{18}O_2$ with these Co_xNO^+ species are summarized in reactions 6–10. Absence of oxygen scrambling, process 6, strongly suggests that the reactive form of Co_2NO^+ consists of molecular nitric oxide bound to Co_2^+.

$$Co_2NO^+ + {}^{18}O_2 \longrightarrow Co_2({}^{18}O)_2^+ + NO \qquad (6)$$

$$Co_3NO^+ + {}^{18}O_2 \xrightarrow{24\%} Co_3({}^{18}O)_2^+ + NO^{16}O \qquad (7)$$

$$\phantom{Co_3NO^+ + {}^{18}O_2} \xrightarrow{76\%} Co_3{}^{18}(O)({}^{16}O)^+ + N^{18}O \qquad (8)$$

$$Co_4NO^+ + {}^{18}O_2 \xrightarrow{37\%} Co_4({}^{18}O)_2^+ + N^{16}O \qquad (9)$$

$$\phantom{Co_4NO^+ + {}^{18}O_2} \xrightarrow{63\%} Co_4({}^{18}O)({}^{16}O)^+ + N^{18}O \qquad (10)$$

The unreactive portion of Co_2NO^+ may consist of NO dissociatively attached to Co_2^+ or to different bonding modes of NO to Co_2^+[24] that are unreactive with dioxygen. Both Co_3NO^+ and Co_4NO^+ yield substantial scrambling with $^{18}O_2$, reactions 7–10. This scrambling can be rationalized by invoking initial dissociative attachment of dioxygen to a cluster–nitrido–oxide species generating a trioxide–nitrido intermediate which subsequently eliminates nitric oxide as either $N^{18}O$ or $N^{16}O$. If both Co_3NO^+ and Co_4NO^+ consisted of molecular nitric oxide clusters, then little or no scrambling would be expected. A statistical distribution of label in the ionic products would yield a 2:1 ratio of $Co_x({}^{18}O)({}^{16}O)^+$:$Co_x({}^{18}O)_2^+$. For Co_3NO^+ the ratio observed is 3.2:1 with $Co_3({}^{18}O)({}^{16}O)^+$, the scrambled product, *favored* over the

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(17) A complete description of the instrument will appear in a later publication.

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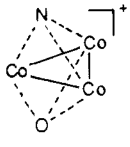
statistical distribution of label. For Co_4NO^+ the ratio of $Co_4(^{18}O)(^{16}O)^+$:$Co_4(^{18}O)_2$ is 1.7:1.

The isotopic distribution for Co_3NO^+ may have consequences rooted in the geometry of the $Co_3(N)(O)^+$ species where the nitride and oxide reside in positions above and below a triangular Co_3 nucleus **1**.[25] In such a configuration, the preferential elmination of $N^{18}O$ upon reaction with $^{18}O_2$ can easily be envisioned.



1

The above results clearly show that nitric oxide undergoes dissociative chemisorption on Co_3^+ and Co_4^+ in analogy with surface chemistry.[8,9] The effect additional NO and CO ligands have on dissociative chemisorption of nitric oxide on these small cobalt clusters is currently under investigation as well as their reactivity. These results will yield information on the molecular level for reactions of relevance to both surface chemistry and catalysis. In addition we are also probing the nature of the unreactive portion of Co_2NO^+ (with dioxygen) and studying a variety of other cluster-nitric oxide complexes. These limited results demonstrate that nitric oxide has a rich and varied chemistry with small gas-phase transition-metal cluster ions just as it has on metal surfaces and organometallic clusters.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Carbon-Carbon Bond Activation via β-Alkyl Elimination. Reversible Branching of 1,4-Pentadienes Catalyzed by Scandocene Hydride Derivatives

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Received August 26, 1987

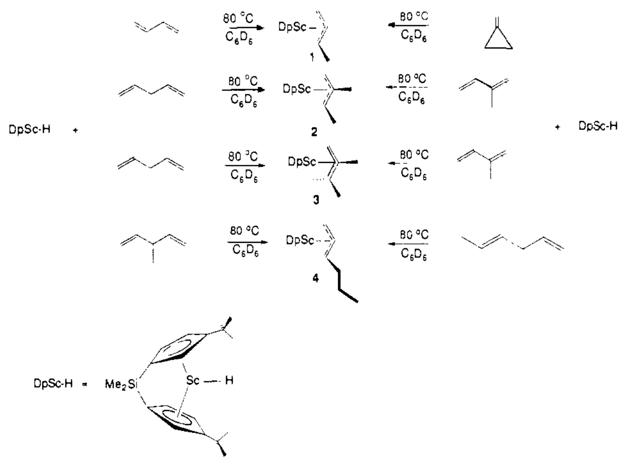
Although impressive advances have recently been made in activating the carbon-hydrogen bonds of hydrocarbons,[1] the activation of carbon-carbon bonds by soluble transition-metal complexes remains one of the most prominent challenges in organometallic chemistry. Since classical approaches to hydrocarbon rearrangements involve acid-promoted carbocation chemistry, we have explored the possibility that highly Lewis acidic, early transition-metal alkyls and hydrides could effect C-C bond-forming or -breaking processes for simple hydrocarbons. We report herein that a scandocene hydride complex catalyzes the reversible branching and cyclization of 1,4-pentadienes. The key feature responsible for this unusual reactivity is reversible olefin insertion/β-alkyl elimination.

Permethylscandocene alkyls, $(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R$, rapidly polymerize ethylene but undergo preferential σ bond metathesis with α olefins (eq 1).[2] Unfavorable steric interactions between the

$$(\eta^5\text{-}C_5Me_5)_2Sc\text{-}R + CH_2{=}CHR' \rightarrow (\eta^5\text{-}C_5Me_5)_2Sc\text{-}CH{=}CHR' + R\text{-}H \quad (1)$$

olefin substituent and an $(\eta^5\text{-}C_5Me_5)$ ligand appear to prevent coordination of the olefin π bond, so that attack at a vinylic C-H bond occurs to the exclusion of insertion. We have therefore prepared some less sterically hindered scandocene derivatives, including $[Me_2Si(\eta^5\text{-}C_5H_3CMe_3)_2]Sc\text{-}R$, "DpSc-R", (R = H, alkyl, etc.) (Scheme I). The starting material, $(DpSc\text{-}Cl)_n$,[3] is obtained in ca. 55% yield via treatment of $ScCl_3\cdot(THF)_3$ (THF = tetrahydrofuran) with $Li_2[Me_2Si(C_5H_3CMe_3)_2]$ in toluene. The trimethylsilylmethyl derivative, $DpSc\text{-}CH_2SiMe_3$, is prepared (60%) by treatment of $(DpSc\text{-}Cl)_n$ with trimethylsilyllithium. The dimeric hydride derivative $(DpSc\text{-}H)_2$[4] is obtained (quantitatively, ^1H NMR; isolated 70%) by hydrogenolysis of $DpSc\text{-}CH_2SiMe_3$.

Scheme I



Butadiene, 1,4-pentadiene, 2-methyl-1,4-pentadiene, and 3-methyl-1,4-pentadiene react with $(DpSc\text{-}H)_2$ (most likely via the monomer, DpSc-H) to afford the allyl derivatives **1**, **2**, **3**, and **4** (Scheme I), which were independently prepared by treating $(DpSc\text{-}H)_2$ with methylenecyclopropane isoprene, 2,3-dimethylbutadiene, and 1,4-hexadiene.[5] We tentatively interpret these results according to the mechanisms shown in Schemes II and III. Addition of the 1,4-pentadienes to the Sc-H bond of DpSc-H, followed by intramolecular olefin insertion affords cyclopropylmethyl- or cyclobutylmethylscandium intermediates. The methyl branch is introduced (or removed) by β-alkyl elimination in the alternative sense. β-H elimination and readdition to DpSc-H subsequently yields the stable allyl compound in each case.

Both cyclopropylmethyl and cyclobutylmethyl intermediates are required to accommodate all of the observed rearrangements. The symmetry for **5c**, **6a**, and **6b** precludes skeletal rearrangement, since β-alkyl elimination may occur by only one pathway, namely

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[3] Of the two possible isomeric forms (*meso* and *d,l*), these procedures afford only *meso*. See Supplementary Material for ^1H and ^{13}C NMR data and elemental analyses.

[4] Calcd for $C_{20}H_{31}SiSc$: C, 69.73; H, 9.07. Found: C, 69.80; H, 8.98. ^1H NMR (benzene-d_6, 90 MHz) δ 0.21 (s, 3 H), 0.82 (s, 3 H), 1.21 (s, 18 H), 6.27 (m, 2 H), 6.67 (m, 2 H), 7.33 (M, 2 H) (Sc-*H* not located, presumably due to ^{45}Sc quadrupolar broadening). MW (ebulliometry) = 717. Calcd for dimer 688.

[5] On the basis of the discussion which follows, branching of 1,4-hexadiene would be expected if addition of DpSc-H to the internal double bond occurs faster than isomerization to 2,4-hexadiene. However, monitoring the formation of **4** reveals that DpSc-H rapidly catalyzes isomerization of 1,4-hexadiene to 2,4-hexadiene (^{13}C and ^1H NMR), presumably via $[CH_3CH(DpSc)CH_2CH{=}CHCH_3]$. Formation of **4** from reaction of 2,4-hexadiene with DpSc-H occurs much more slowly. See footnote 13.

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