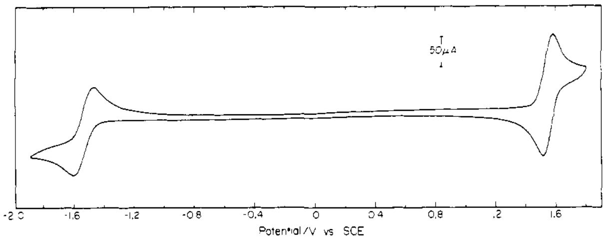

Figure 1. Cyclic voltammogram of 2 mM $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN/0.1 M Bu_4NClO_4 at 25 °C (scan rate 200 mV s^{-1}; Pt-button working, Ag-wire reference, and Pt-wire auxiliary electrodes). The potential was referenced to a ferrocene internal standard and related to the SCE reference using a value of 0.31 V vs. SCE for the $Fc^{+/0}$ couple (Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; p 701).

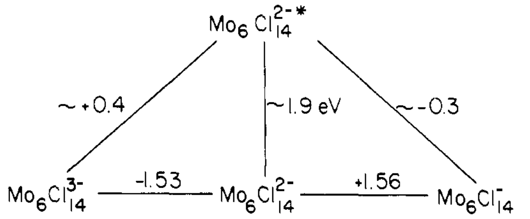

Figure 2. Modified Latimer diagram for $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN (electrode potentials/V vs. SCE).

one-electron oxidation couples.[1-3] The five clusters also exhibit reduction waves at potentials more negative than −1.5 V vs. SCE; for $Mo_6Cl_{14}^{2-}$, a quasi-reversible one-electron wave with a half-wave potential of -1.53 V vs. SCE is attributed to the $Mo_6Cl_{14}^{2-/3-}$ couple (Figure 1).[4] Both oxygen and water must be rigorously excluded in order to obtain a well-defined reduction wave.[5]

A modified Latimer diagram shows that the energy that would be released upon combination of $Mo_6Cl_{14}^{3-}$ and $Mo_6Cl_{14}^{-}$ (3.1 eV) is sufficient to produce one excited cluster ion ($Mo_6Cl_{14}^{2-*}$: $\phi_{em} = 0.19$, $\tau = 0.32$ ms in CH_3CN at 25 °C)[2] (Figure 2). And, indeed, red ECL is observed upon pulsing the potential applied to a Pt working electrode with a square-wave potential program of 1.80 and −1.80 V vs. SCE.[6] The uncorrected ECL spectrum of a stirred acetonitrile solution of $Mo_6Cl_{14}^{2-}$ is identical with the uncorrected emission spectrum produced by steady-state irradiation of $Mo_6Cl_{14}^{2-}$ in CH_3CN (Figure 3). ECL is observed only when the potential applied to the Pt working electrode is stepped into the one-electron oxidation–reduction waves of $Mo_6Cl_{14}^{2-}$, thereby indicating that the effect is attributable to an annihilation reaction between electrogenerated $Mo_6Cl_{14}^{3-}$ and $Mo_6Cl_{14}^{-}$ in which one ground-state ion ($Mo_6Cl_{14}^{2-}$) and one excited ion ($Mo_6Cl_{14}^{2-*}$) are produced.

ECL from inorganic species previously has been limited to mononuclear metal complexes containing chelating aromatic ligands.[7-9] In these complexes, the organic ligands strongly interact with the metal atom, and the excited states possess substantial ligand character. Observation of $Mo_6Cl_{14}^{2-}$ ECL is important in the sense that it opens the way for detailed exploration of the kinetic and mechanistic features of highly exergonic electron-transfer reactions involving symmetric (O_h) all-inorganic species. Further investigations of the ECL properties of these cluster ions should allow key aspects of electron-transfer theories to be evaluated more rigorously than has been possible previously.

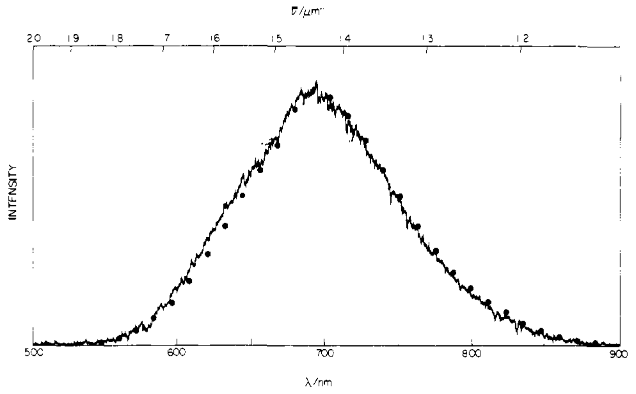

Figure 3. ECL spectrum of $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN at 25 °C using a cyclic square wave at 100 Hz between 1.80 and −1.80 V vs. SCE. Black circles illustrate the luminescence spectrum of $(Bu_4N)_2Mo_6Cl_{14}$ in CH_3CN with 436-nm excitation. Spectra are not corrected for photomultiplier or monochromator response.

Acknowledgment. We thank Dan Buttry for helpful discussions. D.G.N. acknowledges a graduate fellowship (1982–1983) from the Sun Co. This research was supported by National Science Foundation Grant CHE 81-20419.

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[4] Both the oxidation and reduction waves in Figure 1 are observed independently upon scanning anodically and cathodically from the rest potential. This result rules out the possibility that either wave arises from a product derived from oxidation or reduction of $Mo_6Cl_{14}^{2-}$.

[5] All manipulations (including solvent transfers and sample additions) were conducted in a specially designed high-vacuum electrochemical cell with Pt-wire working, Pt-mesh auxiliary, and Ag-wire reference electrodes.

[6] Pulse trains (1–100 Hz) were obtained with a PAR 175 universal programmer. A high-vacuum electrochemical cell was used for all ECL experiments.

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Effect of a CO Ligand on the Reactivity of Co_2^+ toward Alkanes

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Received October 3, 1983

The group 8 atomic transition-metal positive ions activate both C–H and C–C bonds in alkanes in the gas phase.[1-8] Co_2^+, however, is unreactive toward alkanes.[2] We wish to report that addition of a CO ligand to Co_2^+ causes it to efficiently attack C–H bonds in alkanes. Co_2CO^+ reacts with butane according to reaction 1. Reaction 1a accounts for 90% of the total reaction.

$$Co_2CO^+ + n\text{-}C_4H_{10} \rightarrow Co_2COC_4H_6^+ + 2H_2 \qquad (1a)$$

$$Co_2CO^+ + n\text{-}C_4H_{10} \rightarrow Co_2COC_4H_8^+ + H_2 \qquad (1b)$$

The overall rate constant for the reaction, approximately 2×10^{-9} $cm^3\ s^{-1}$, is at least 2 orders of magnitude greater than the greatest possible value for the rate constant for any reaction between Co_2^+ and *n*-butanes.

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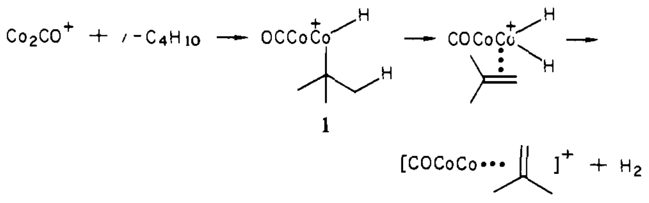
Scheme I



2-Methylpropane behaves in a similar way toward Co_2CO^+ and Co_2^+. Co_2CO^+ readily eliminates H_2 from 2-methylpropane (reaction 2), and Co_2^+ is unreactive. Reaction 2a accounts for

$$Co_2CO^+ + i\text{-}C_4H_{10} \rightarrow Co_2COC_4H_8^+ + H_2 \quad (2a)$$

$$Co_2CO^+ + i\text{-}C_4H_{10} \rightarrow Co_2C_4H_8^+ + H_2 + CO \quad (2b)$$

64% of the overall reaction. The overall rate constant is approximately the same as for reaction 1.

This behavior of Co_2^+ and Co_2CO^+ is markedly different from the behavior of Co^+ and $CoCO^+$. Co^+ reacts with n-butane to form $CoC_2H_4^+$, $CoC_3H_6^+$, and $CoC_4H_8^+$. With 2-methylpropane Co^+ reacts to form $CoC_3H_6^+$ and $CoC_4H_8^+$. $CoCO^+$ reacts with both C_4H_{10} isomers to form only $CoC_4H_{10}^+$.

Co_2^+ and Co_2CO^+ result from electron impact on $Co_2(CO)_8$,[9] and ion cyclotron resonance techniques identify their reactions.[10,11] Under the conditions of the ion cyclotron resonance experiment, only bimolecular gas-phase ion-molecule reactions can give rise to observable ionic products. Double resonance[11] and the pressure dependence of product peak intensities unambiguously identify the reactions. The products of reactions of 2-methylbutane-d_{10} and butane-d_{10} are consistent with the stoichiometries in reactions 1 and 2.

The reactivity of C-H bonds toward Co_2CO^+ is dramatically illustrated by its reaction with i-C_3H_7Br. The H_2 loss channel is 44% of the overall reaction.

$$Co_2CO^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_3H_7Br^+ + CO \quad (3a)$$

$$Co_2CO^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_3H_5Br^+ + H_2 + CO \quad (3b)$$

Furthermore, no HBr loss is observed. This is in contrast to Co_2^+, which breaks i-C_3H_7Br into HBr and C_3H_6 (reaction 4). Similarly,

$$Co_2^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_3H_6^+ + HBr \quad (4a)$$

$$Co_2^+ + i\text{-}C_3H_7Br \rightarrow Co_2HBr^+ + C_3H_6 \quad (4b)$$

Co^+ reacts with i-C_3H_7Br to form only $CoC_3H_6^+$, and $CoCO^+$ reacts with i-C_3H_7Br to form $CoC_3H_6^+$, $CoCOC_3H_6^+$, and $CoC_3H_7Br^+$. The reactions of n-C_3H_7Br are similar to those of i-C_3H_7Br. The same products are formed in somewhat different proportions.

A possible explanation for the effect of a CO ligand on Co_2^+ can be formulated in terms of the mechanism in Scheme I. Metal insertion into C-H and C-C bonds is quite well established as a critical feature of reactions of Fe^+, Co^+, and Ni^+ with alkanes.[1-8] If the formation of **1** is the critical step in the Co_2CO^+ reaction, then a minimal requirement is that the metal insertion is energetically feasible. While the thermochemical stability of **1** is not known, several pertinent bond strengths have been measured. These are $D°(Co^+\text{-}H) = 52 \pm 4$, $D°(Co\text{-}H) = 39 \pm 6$, $D°(Co^+\text{-}CH_3) = 61 \pm 4$, and $D°(Co\text{-}CH_3) = 41 \pm 10$ kcal/mol.[4] A striking feature of these bond strengths is that the bonds to Co^+ are much stronger than the corresponding bonds to Co. This indicates that **1** would be stabilized by concentrating positive charge on the Co that inserts into the C-H bond. The role of the CO ligand in **1** may be exactly that. Metals in zero or negative oxidation states tend to bind carbonyl ligands more strongly than metals in higher oxidation states. A structure such as **1** can strengthen the Co-CO bond as well as the Co-H and Co-R bonds by concentrating positive charge on the Co interacting with the alkane. The effect of a CO ligand on the reactivity of Co_2^+ may thus originate in the ability of the ligand to stabilize an asymmetric distribution of charge between the two Co atoms.

There is very little additional reliable thermochemical data to either support or disprove this hypothesis. Bond strengths between CoH^+ and alkyl radicals or between CoR^+ and H are not known. Essentially no bond strengths involving Co_2^+ are known. It is therefore difficult to address such questions as why C-H bonds add to Co_2CO^+ more readily than C-C bonds, while the opposite is true for Co^+. It is not inconsistent with our hypothesis that Co_2CO^+ reacts somewhat differently than Co^+. Even if one of the Co atoms in Co_2CO^+ carries most of the charge, its electronic environment will still not be identical with a free Co^+ ion.

If the hypothesis that CO activates Co_2^+ by polarizing the charge between the two Co atoms is correct, other ligands should have a similar effect. In particular, ligands that form stable complexes with metals in the zero oxidation state might be expected to have the same effect as CO. It is significant then that the product of (4a) reacts as in reaction 5. The two products

$$Co_2C_3H_6^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_3H_7Br + C_3H_6 \quad (5a)$$

$$Co_2C_3H_6^+ + i\text{-}C_3H_7Br \rightarrow Co_2C_6H_{11}Br^+ + H_2 \quad (5b)$$

of (5) are formed in equal amounts. The elimination of H_2 (channel 5b) indicates that $Co_2C_3H_6^+$ has a reactivity similar to Co_2CO^+. Since propene forms stable complexes with metals in the zero oxidation state, this reactivity of $Co_2C_3H_6^+$ lends support to the hypothetical explanation of the reactivity of Co_2CO^+.

Acknowledgment. The National Science Foundation provided partial support of this work (CHE 8110516).

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(9) Johnson, B. F. G.; Lewis, J.; Williams, J. G.; Wilson, J. M. *J. Chem. Soc. A* **1967**, 341-344. The electron energy was 70 eV, which probably produced Co_2CO^+ ions in a broad distribution of vibrational states. Most electronic excited states and metastable ions should disappear before reaction since the time between collisions is several milliseconds. The large rate constant implies that nearly all the Co_2CO^+ ions are reactive. If the reactions were characteristic of highly excited ions, only a fraction of the ions should react. In addition, Co_2CO^+ can have internal energy no greater than $D(Co_2^+\text{-}CO)$ so it is necessarily always less energetic than Co_2^+. For example, reaction of Co_2^+ with i-C_4H_{10} to give $Co_2C_4H_8^+$, which is not observed, must be more exothermic than (2b) regardless of the internal energy of the Co_2CO^+ reactant in (2b). The reactivity of Co_2CO^+ relative to that of Co_2^+ is thus not the result of internal energy effects.

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Stabilization of 2*H*-Phospholes by Complexation. A Phosphorus-Carbon Double Bond Acting as a Four-Electron Donor

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Received July 25, 1983

We have previously demonstrated[2-5] that the P substituents of tervalent 1*H*-phospholes easily migrate from phosphorus to carbon and yield 2*H*-phospholes. These 2*H*-phospholes are unstable species and spontaneously dimerize. They can be trapped by various reagents but have never been observed as such. Thus, in order to stabilize these species in their monomeric state, we decided to study the same type of migrations in 1*H*-phosphole P complexes. Our basic approach included a preliminary P complexation of phospholyl anion followed by protonation and H migration in the coordination sphere of the metal. In a first attempt, we reacted

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