Table II. Calculated and Observed Ratios of Radicals Consumed by Reactions 12 and 10

concn, μM					
$(NH_3)_5$-Co(mbpy)$^{4+}$			$(A_0 - A_\infty)/A_0$	R	
initial	final	CO_2^-		obsd[a]	calcd[b]
10	1	9	0.53	17	18
20	6	14	0.61	3.7	4.6
30	13	17	0.71	1.4	2.5
200	196	4	1.0		

[a] Ratio of concentrations of radicals consumed by reactions 12 and 10 from $(A_0 - A_\infty)(A_0)^{-1}$. [b] $k_3[(NH_3)_5Co(mbpy^\bullet)^{3+}]^2/k_2[(NH_3)_5Co(mpby^\bullet)^{3+}][(NH_3)_5Co(mbpy)^{4+}]$.

with $k_1 = (8.7 \pm 0.8) \times 10^2$ s^{-1} and $k_2 = (5.4 \pm 0.5) \times 10^7$ M^{-1} s^{-1} (Figure 1). These rate constants are associated with reactions 10 and 11, respectively, and are specific cases of eq 3 and 2. The

$$(NH_3)_5Co^{III}(mbpy^\bullet)^{3+} + (NH_3)_5Co^{III}(mbpy)^{4+} \rightarrow (NH_3)_5Co^{III}(mbpy)^{4+} + (NH_3)_5Co^{II}(mbpy)^{3+} \quad k_2 \quad (10)$$

$$(NH_3)_5Co^{III}(mbpy^\bullet)^{3+} \rightarrow (NH_3)_5Co^{II}(mbpy)^{3+} \quad k_1 \quad (11)$$

species $(NH_3)_5Co^{II}(mbpy^\bullet)^{2+}$ and $(NH_3)_5Co^{II}(mbpy)^{3+}$ would be expected to dissociate into constituents although this might be in the 100-μs to 1-ms region.[14] The free ligand radical mbpy$^\bullet$ cannot be easily distinguished spectrally from the coordinated ligand radical. We attempted to determine k_1 unequivocally by examining the behavior of the transient generated by using equivalent amounts (10 μM) of $(NH_3)_5Co^{III}(mbpy)^{4+}$ and $^\bullet CO_2^-$ and thus setting up the condition of $(NH_3)_5Co^{III}(mbpy^\bullet)^{3+}$ as the sole cobalt species in solution after the pulse. The surprising result was that the decay of the transient was now second-order (up to 85% reaction; Figure 2) and the loss of radical signal at 600 nm was only 50 ± 5% (Figure 2). This was ascribed to the disproportionation reaction (12); compare (4).[12] The value of $2k_3$ =

$$2(NH_3)_5Co^{III}(mbpy^\bullet)^{3+} \rightarrow (NH_3)_5Co^{III}(mbpy)^{4+} + (NH_3)_5Co^{II}(mbpy^\bullet)^{2+} \quad 2k_3 \quad (12)$$

$(2.4 \pm 0.2) \times 10^8$ M^{-1} s^{-1} is slightly larger than that of k_2, and this may be ascribed to a decrease in charge repulsion. Toward the end of the decay, where cobalt(III) radical concentration is quite small (1–2 μM), there is a *slight* deviation from the expected second-order plot and a first-order reaction (eq 11) appears to remain (Figure 2), giving a value of $k_1 = 5.4 \times 10^2$ s^{-1}. We believe that the value of k_1 from Figure 1 is more accurate than that obtained from the tail end of the decay curve of Figure 2, and we have used that in Table I. In the system conditions when both reactions 10 and 12 were operative, we made no attempt to analyze kinetically. The relative absorbances remaining at the completion of the reaction could however be shown to correlate reasonably well those expected on the basis of the relative rates of the competing reactions (Table II).

The three modes of decay of the cobalt(III)–radical complex are thus observed with the 1-methyl-4,4′-bipyridinium ion ligand. The associated rate constants are similar to those observed with related complexes (Table I). With our system, second-order reactions of the complexed radical tend to overshadow the first-order intramolecular process. This is very unusual for cobalt(III)–ammine radicals. The slowness of the intramolecular electron transfer in our system may reside in the large distance of the unpaired electron from the cobalt center.[4] In addition, the redox potential of the *N*-methylbipyridinium cation is less than −0.9 V,[15] which is much lower than that for *p*-nitrobenzoate (−0.40 V). This will lead to a faster intermolecular rate of reaction of the derived radical (e.g. with $Co(NH_3)_6^{3+}$ [16]) and of the cobalt(III) complex. The complex $(NH_3)_5Co(mpby)^{4+}$ is an excellent (intermolecular) oxidizing agent.[12]

The reaction also of the ruthenium analogue $(NH_3)_5Ru^{III}(mbpy)^{4+}$ (50–150 μM) with $^\bullet CO_2^-$ was studied at pH 6.2. The reaction was second-order with $k = (1.1 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}, much larger than for the cobalt(III) reaction. The product was stable, and the absorption characteristics (a broad maximum at 570–600 nm, $\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}) were very similar to those of $(NH_3)_5Ru^{II}(mbpy)^{3+}$ ($\epsilon^{max}_{580nm} = 1.4 \times 10^4$ M^{-1} cm^{-1}). No intermediate with an absorbance around 400 nm was observed, and so either the radical intermediate $(NH_3)_5Ru^{III}(mbpy^\bullet)^{3+}$ was not formed or, more likely, the intramolecular electron transfer to form the Ru(II) product occurred very fast ($k > 10^6$ s^{-1}). A much more rapid intramolecular electron process would be anticipated for ruthenium(III).[17] The very slow intramolecular electron transfer of $(NH_3)_5Co^{III}(mbpy^\bullet)^{3+}$ compared with that of the ruthenium analogue may be attributed to the poor overlap of the π-orbital of the viologen radical with the σ-orbital (e_g) of the Co(III) center.[18] The acceptor orbital of the Ru(III) center is a π-orbital (t_{2g}), which matches the donor orbital of the viologen radical.

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A Soluble Alkoxyzinc Hydride, $[HZnOC(CH_3)_3]_4$. Synthesis and Reactions with Copper(I) Alkoxides

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Methanol is a major commercial chemical, consistently ranking among the top 25 chemicals produced in the United States each year.[1] Several methanol synthesis catalysts are currently in use, but the majority are based on copper and zinc oxide as essential components. It has been proposed that the reaction of CO and H_2 over such catalysts involves the interaction of a copper carbonyl with a zinc hydride.[2,3]

Several groups have been involved in the synthesis of model compounds containing CO bonded to copper or hydrogen bonded to zinc. Copper (I) compounds, such as $[(CH_3)_3COCu(CO)]_4$,[4] have been synthesized and characterized. Ashby and Goel reported the synthesis of $HZnO(C_6H_{11})$ from ZnH_2 and cyclohexanol, but this compound was not isolated in pure form, due to its insolubility in many common solvents.[5] Caulton et al. described the synthesis of $HZnO(CH_2)_2NMe_2$, but full details about its characterization have not yet been reported.[6]

As part of a study of model compounds for methanol synthesis catalysts, we report the synthesis and characterization of a tetrameric alkoxyzinc hydride, $[(CH_3)_3COZnH]_4$, and some of its reactions with $[(CH_3)_3COCu(PPh_3)]_4$ and $[(CH_3)_3COCu(CO)]_4$.

Experimental Section

Most synthesis and working oprations were carried out under a dry argon atmosphere.[7] Some operations involving air-sensitive materials

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were carried out in a Vacuum Atmospheres Corp. drybox under prepurified nitrogen. Melting points were observed in capillaries sealed under vacuum. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN. Hydride analysis was carried out by hydrolyzing samples and collecting the hydrogen gas evolved with a Toepler pump.[8] A Mattson Polaris IR-10410 spectrometer was used to record infrared spectra.[9] Gas chromatograms were recorded on a Hewlett-Packard 5880A gas chromatograph with a 25-m cross-linked methylsilicone capillary column, a flame ionization detector, and a 5880A Level 4 terminal. Mass spectra were obtained by fast bombardment (FAB) on a Kratos MS890MS spectrometer. Proton nuclear magnetic resonance (NMR) spectra were obtained by using a Varian XL-200 spectrometer, using residual ^1H peaks in deuterated solvents to calibrate the spectra.

All solvents were reagent grade and were distilled under argon from solutions of sodium benzophenone ketyl. The ZnH_2 was prepared by a modified published procedure,[10] employing centrifugation rather than filtration to collect the product. The alkoxides $[(CH_3)_3COCu(CO)]_4$[4] and $[(CH_3)_3COCu(PPh_3)]_4$[11] were prepared by published procedures. The *tert*-butyl alcohol (Fisher) was dried over molecular sieves before use.

Synthesis of $[HZnOC(CH_3)_3]_4$ (1). Dropwise addition of 4.0 mL (0.043 mol) of $(CH_3)_3COH$ to a rapidly stirred slurry of 3.25 g (0.048 mol) of ZnH_2 in 150 mL of THF in a heavy-walled 250-mL centrifuge bottle, capped with a septum and connected to a source of argon[7] by means of a septum, caused immediate evolution of gas. The cloudy white suspension was heated to 50 °C in an oil bath and stirred, magnetically, for 24 h, during which time it became gray. An IR spectrum of the supernatant solution showed the reaction to be complete as judged by the absence of the ν(OH) band of the alcohol. The slurry was transferred by cannula and filtered through a Celite-covered, fritted glass filter, into a Schlenk reaction vessel (SRV).[7] The volume of the pale yellow filtrate was reduced to 10 mL by trap to trap vacuum distillation (TTVD), and the filtrate was then cooled slowly to −32 °C over a period of 24 h. The supernatant liquid was removed through a cannula, and the clear, colorless crystals were washed twice with 10 mL of hexanes at −78 °C. When dried under vacuum the crystals turned white and opaque and weighed 4.04 g (68%); mp 165–167 °C dec. The supernatant liquid and washings were combined, reduced in volume, and cooled slowly to −32 °C to obtain a second crop of 1.41 g (24%; total yield, 92%).

A 0.1585 g (1.136 mmol) sample of the compound produced 2.81 × 10^{-3} mL (1.148 mmol) of H_2 gas at STP when hydrolyzed with water. Anal. Calcd for $C_4H_{10}OZn$: Zn, 46.86; C, 34.47; H, 7.23. Found: Zn, 47.79; C, 34.07; H, 6.88. ^1H NMR (C_6D_6): δ 4.56 (1 H, ZnH), 1.48 (9 H, $C(CH_3)_3$). IR ν(Zn–H) (hexane): 1810 cm^{-1} (m).

Attempted Reaction of 1 and $[(CH_3)_3COCu]_4$ with CO and H_2. In a dry box, a solution of 0.336 g (0.602 mmol) of **1** in 20 mL of THF and a solution of 0.341 g (0.624 mmol) of $[(CH_3)_3COCu]_4$ in 20 mL of THF were poured into a 300-mL stainless-steel high-pressure reaction vessel, which was then sealed. The vessel was placed in a rocking autoclave (Am. Instrument. Co.) under flow of N_2, purged with H_2, and filled with 51 atm of H_2 and 17 atm of CO. The vessel was heated to 160–170 °C, shaken for 144 h, and then allowed to cool. the dark brown solid suspension was transferred to an SRV by cannula and the volatiles, collected by TTVD, were shown by GC analysis to contain *t*-BuOH, but no MeOH.

Reaction of 1 with $[(CH_3)_3COCu(PPh_3)]_4$. To an 80-mL SRV containing 0.164 g (0.103 mmol) of $[(CH_3)_3COCu(PPh_3)]_4$ were added 0.057 g (0.103 mmol) of **1** and 10 mL of benzene-d_6. The solution changed from pale yellow to clear orange immediately and then slowly darkened as a solid formed. After 24 h, the solution was filtered through a "fine" frit, leaving a tan solid that was washed twice with 5 mL of benzene-d_6. The copper colored filtrate and washings were taken to dryness by TTVD, and 5 mL of THF was added to dissolve the resulting orange solid. This was followed by the slow addition of 3 mL of hexanes, and after the mixture was allowed to stand for 3 h at room temperature, a small quantity of fine, bright red crystals formed. The supernatant liquid was removed by cannula, and the crystals were washed with 5 mL of hexanes and dried under vacuum; mp 145–147 °C dec [lit.[12] mp ($[HCuPPh_3]_6$·DMF) 111 °C dec]. A mass spectrum (FAB) showed an ion at *m/e* 326 ($[C_{18}H_{16}CuP]^+$), but the total signal was so weak that no other fragments could be identified or distinguished. ^1H NMR (C_6D_6): broad peak centered at δ 3.6, along with aromatic protons. lit.[6] ^1H NMR ($[HCuP(tol)_3]_6$): δ 3.5 (broad).

Reaction of 1 with $[(CH_3)_3COCu(CO)]_4$. To 0.480 g (0.731 mmol) of $[(CH_3)_3COCu(CO)]_4$ and 0.405 g (0.726 mmol) of **1** in a 100-mL SRV was added 30 mL of THF. The solution was stirred, causing a gradual color change from pale yellow to brownish red and the evolution of CO (IR ν(CO): 2143 cm^{-1}). An IR spectrum of the solution after 48 h showed only a weak band in the CO stretching region. The dark red solution was filtered, leaving a reddish black solid on the frit and a copper-colored solid on the reaction vessel walls. The former solid was insoluble in benzene and toluene, and an IR spectrum (KBr) of the solid was identical with that of *tert*-butyl alcohol without the ν(OH). This spectrum was also similar to the spectra of the starting materials, although the reaction product showed only a very weak ν(CO) and no ν(ZnH). Anal. Found: C, 21.66; H, 4.51; Zn, 25.7; Cu, 27.3.

Results and Discussion

Following the method of Ashby and Goel,[5] we combined ZnH_2 with various alcohols, desiring to obtain a soluble alkoxyzinc hydride. Ethanol and isobutyl alcohol gave insoluble products whereas bis(2-methoxyethoxy)ethanol produced a soluble product that we were unable to crystallize. With *tert*-butyl alcohol, however, a soluble crystalline product, **1**, formed. In searching for a procedure to produce the largest yield of **1**, we found that the reaction temperature was of pivotal importance because of the thermal instability of ZnH_2. At room temperature, the reaction was slow, and much of the ZnH_2 decomposed before it could react with the alcohol. When the mixture was heated to reflux, the reaction proceeded more quickly, but the decomposition of ZnH_2 occurred more rapidly also. A temperature of 45–50 °C gave the best yields and minimized the ZnH_2 decomposition.

The chemical shift of δ 4.56 in the ^1H NMR spectrum for the hydride in **1** is similar to the observed range of δ 3.6–4.6 for a series of alkylzinc hydrides,[13] and to the chemical shift of δ 4.20 for $HZnO(CH_2)_2NMe_2$.[6] The peak in the IR spectrum of **1** at 1810 cm^{-1} is similar to the peak at 1780 cm^{-1} observed for CyZnH.[5]

A FAB mass spectrum of **1** revealed that the compound is a tetramer, $[(CH_3)_3COZnH]_4$. The molecular ion showed the correct isotope pattern (*m/e* 552, 554, 556, 558, 560) for $\{C_{16}H_{38}O_4Zn_4\}^+$, produced by the loss of two hydrogens from the parent molecule. The loss of hydrogen during FAB mass spectroscopy has been reported for a series of rhenium dihydride complexes,[14] and for $[(\eta^5\text{-}C_5Me_5Ir)_4H]_4(BF_4)_2$.[15]

With a view toward the formation of homogeneous catalysts for methanol synthesis, a mixture of **1** with $[(CH_3)_3COCu]_4$ in THF was treated with H_2 and CO at 170 °C and 68 atm. The GC analysis of the volatile components of this reaction mixture showed the presence of only *tert*-butyl alcohol along with the THF; no methanol was observed.

When THF solutions of **1** and $[(CH_3)_3COCu(CO)]_4$ were mixed at room temperature, there was an immediate evolution of gas, followed by a rapid color change from pale yellow to deep red. If the reaction solution was filtered immediately after the color change occurred, no solid could be collected, and an IR spectrum of the solution showed the presence of both starting materials. From repeated trials of this reaction, however, it was found that an insoluble solid would form in this solution upon

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standing, with a simultaneous decrease in the strength of the δ(Zn-H) and ν(CO) bands in the IR spectra. These spectra and the elemental analysis suggest the *tert*-butoxy groups remained intact in the solid. This evidence, along with the presence of metallic copper on the walls of the reaction vessel, implicates a reduction of the Cu(I) species with the simultaneous release of carbon monoxide.

Because Tsuda et al.[11] had shown that PPh_3 would displace CO from $[(CH_3)_3COCu(CO)]_4$, we thought that the phosphine complex might not dissociate when combined with the alkoxyzinc hydride. Hydride transfer had been reported between $[(CH_3)_3COCu(PPh_3)]_4$ and $HZnO(CH_2)_2NMe_2$.[6] The reddish orange copper compound produced from **1** and $[(CH_3)_3COCu(PPh_3)]_4$ showed the presence of a hydride and a PPh_3 in the ^1H NMR spectrum. If similar hydride transfer from zinc to copper were to have happened with **1** and $[(CH_3)_3COCu(CO)]_4$, CO would be displaced and the resulting alkoxycopper hydride might undergo an internal redox reaction giving the observed copper metal and *tert*-butyl alcohol.

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Registry No. **1**, 119656-28-9; $[(CH_3)_3COCu(PPh_3)]_4$, 79811-70-4; $[(CH_3)_3COCu]_4$, 60842-00-4; $[HCuPPh_3]_6$, 33636-93-0; $[(CH_3)_3COCu(CO)]_4$, 85479-93-2.

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Crystal Symmetry Governing the Metallic vs Semiconducting Properties of Cesium Molybdenum Bronzes Cs_xMoO_3 ($x \cong 0.25, 0.33$)

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Alkali-metal molybdenum oxides have three well-characterized phases:[1] blue bronzes $A_{0.3}MoO_3$,[2] purple bronzes $A_{0.9}Mo_6O_{17}$,[3] and red bronzes $A_{0.33}MoO_3$.[4] At room temperature, the blue and purple bronzes are metals while the red bronzes are semiconductors. Recent band electronic structure studies[5,6] have shown that the red bronzes $A_{0.33}MoO_3$ (A = Li, K, Rb, Cs, Tl) are regular semiconductors, which have a band gap as a consequence of the O-Mo···O bond alternations in their crystal structures. Cesium molybdenum bronze $Cs_{0.25}MoO_3$[7] does not belong to any of these molybdenum bronze classes but is closely related in structure to the red bronze $Cs_{0.33}MoO_3$.[4a] However, our band structure calculations[8] predict $Cs_{0.25}MoO_3$ to be a pseudo-one-dimensional metal. In this note, we report how and why the two cesium bronzes $Cs_{0.33}MoO_3$ and $Cs_{0.25}MoO_3$ differ in their electronic structures concerning the metallic vs semiconducting properties.

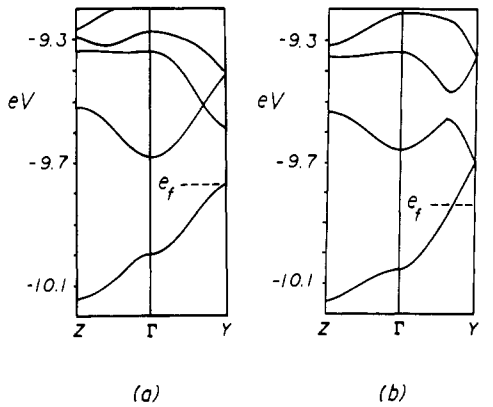

Figure 1. Bottom portion of the t_{2g}-block bands calculated for (a) the Mo_6O_{18} layer **4a** of $Cs_{0.33}MoO_3$ and (b) the Mo_6O_{18} layer **4b** of $Cs_{0.25}MoO_3$. The wave vectors Γ, Y, and Z are defined as $\Gamma = (0, 0)$, $Y = (b^*/2, 0)$, and $Z = (0, c^*/2)$, where the reciprocal vectors b^* and c^* are related to the repeat vectors of the Mo_6O_{18} layer defined in **1** and **4**.

The crystal structures of $Cs_{0.33}MoO_3$ and $Cs_{0.25}MoO_3$ may be constructed by beginning with the Mo_2O_9 chain **1**, which is made up of corner-shared MoO_6 octahedra. The Mo_6O_{24} chains **2a** and **2b** are obtained by adding extra MoO_6 octahedra (i.e., the

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