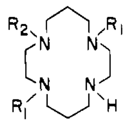
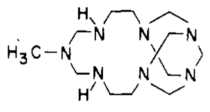


$R_1 = CH_2CH_2C(O)NH_2$
$R_2 = CH_2CH_2C{\equiv}N$

2



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of Korea. We thank Chee-Hun Kwak for technical assistance.

Registry No. $[Ni(A)]Cl_2{\cdot}2H_2O$, 119413-95-5; $H_2N(CH_2)_2NH(CH_2)_2NH_2$, 111-40-0; CH_2O, 50-00-0; $[Ni(A)](ClO_4)_2$, 119478-59-0; $[Ni(B)](ClO_4)_2$, 119413-97-7; $H_2N(CH_2)_2NH(CH_2)_3NH_2$, 13531-52-7; $[Ni(A)](PF_6)_2$, 119478-60-3; $[Ni(B)](PF_6)_2$, 119413-98-8; $[Ni(A)(NCS)_2]$, 119413-99-9; $[Ni(B)(NCS)_2]$, 119414-00-5.

Supplementary Material Available: Tables SI–SIV, listing crystal data and data collection parameters, anisotropic thermal parameters, atomic coordinates and thermal parameters of the hydrogen atoms, and bond lengths and angles involving the hydrogen atoms (4 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Reduction by $^{\bullet}CO_2$ of (1-Methyl-4,4′-bipyridinium)pentaamminecobalt(III) Perchlorate and Kinetic Behavior of the Transient Radical in Aqueous Solution

K. Tsukahara[1] and Ralph G. Wilkins*

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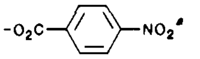
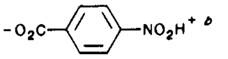
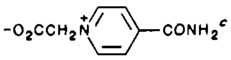
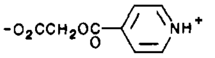
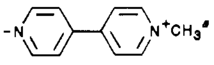
The subject of electron transfer within molecules is an intriguing and much studied topic. A wide variety of systems have been examined including binuclear metal complexes,[2] extended organics,[3] and metalloproteins.[2,4] Cobalt(III) complexes containing reducible aromatic ligands, L, have been much utilized for studying the modes of electron transfer. Typical examples are shown in Table I.[5-7] A popular approach is to effect very rapid *one-electron* reduction of the cobalt complex by using a deficiency of a vigorous reducing agent, usually e_{aq}^- or $^{\bullet}CO_2^-$ generated by pulse radiolysis. A definite amount of reduction is at the ligand center (reaction 1). The loss of the radical center can be easily monitored

$$\mathrm{Co^{III}{-}L} \xrightarrow[{}^{\bullet}\mathrm{CO_2^-}]{e_{aq}^-\text{ or}} \mathrm{Co^{III}{-}L^{\bullet-}} \qquad (1)$$

spectrally. In the systems so far examined (Table I) decay of the coordinated radical ligand usually occurs by an intramolecular electron transfer (eq 2) leading to the cobalt(II) species. This

$$\mathrm{Co^{III}{-}L^{\bullet-}} \rightarrow \mathrm{Co^{II}{-}L} \quad k_1 \qquad (2)$$

Table I. Rate Constants for Decay of $Co(NH_3)_5(L^{\bullet-})^{n+}$ at 23–25 °C

–L	k_1, s^{-1}	k_2, M^{-1} s^{-1}	$2k_3$, M^{-1} s^{-1}	ref
	2.6×10^3			7
	5		1.5×10^8	7
	$\leq 2.0 \times 10^4$	1.5×10^9		5
	2.0×10^4	$\leq 6 \times 10^6$		5
	2.5×10^3			6
 mbpy	8.7×10^2	5.4×10^7	2.4×10^8	*d*

[a] pH 7. [b] 1 M $HClO_4$. [c] pH 4.5–5.5. [d] This work.

is indicated by the observation of first-order loss of radical signal, with the rate constant k_1 being independent of the concentration of radical complex (i.e. dose of reductant radical used) and of Co^{III}–L complex used (in excess). Only rarely[5] is the first-order loss of $Co^{III}{-}L^{\bullet-}$ directly dependent on the concentration of Co^{III}–L present, and this is interpreted in terms of reaction 3. Sometimes

$$\mathrm{Co^{III}{-}L^{\bullet-} + Co^{III}{-}L \rightarrow Co^{III}{-}L + Co^{II}{-}L} \quad k_2 \qquad (3)$$

the loss of $Co^{III}{-}L^{\bullet-}$ is second-order,[7] and this is attributed to a disproportionation in acid (eq 4). In all cases (2)–(4), the cobalt(II) product is expected to rapidly dissociate to constituents.

$$\mathrm{2Co^{III}{-}L{\cdot}H \rightarrow Co^{III}{-}L + Co^{II}{-}LH_2} \quad 2k_3 \qquad (4)$$

The presence of (3) makes it difficult to determine the value of k_1 (which is a small intercept on a k_{obs} vs $[Co^{III}{-}L]$ plot). The occurrence of (4) is usually attended by mixed first- and second-order kinetics, since as the concentration of $Co^{III}{-}L^{\bullet-}$ is reduced, the importance of (4) is superseded by process 2 and k_1 results from the (first-order) end of the decay.

In a continuation of our interest in viologen radicals,[8] we have studied the reduction of the complex $(NH_3)_5Co(mbpy)^{4+}$ ($mbpy^+$ = 1-methyl-4,4′-bipyridinium cation; see Table I) by $^{\bullet}CO_2^-$, observed the coordinated bipyridinyl radical intermediate $(NH_3)_5Co(mbpy^{\bullet})^{3+}$, and noted the three modes of decay outlined above (Table I).

Experimental Section

Materials. 1-Methyl-4,4′-bipyridinium perchlorate and (1-Methyl-4,4′-bipyridinium)pentaamminecobalt(III) perchlorate were prepared as described in the literature[9] with slight modifications. The crude cobalt(III) product in solution was added to a column of CM-Sephadex C25 (Na^+ form). The column was washed with sodium perchlorate solutions (0.1–0.5 M), and $mbpy^+$, Co^{2+}, and $Co(NH_3)_5OS(CH_3)_2^{3+}$ were eluted. An orange fraction was eluted with 0.5–0.6 M sodium perchlorate solution. The first portion contained $Co(NH_3)_6^{3+}$, and the second portion, which was collected, was evaporated to a small volume. Ethanol addition caused deposition of pink crystals, which were recrystallized twice from water. Anal. Calcd for $[(NH_3)_5Co(mbpy)](ClO_4)_4{\cdot}H_2O$: C, 18.07; H, 3.86; N, 13.41. Found: C, 18.19; H, 3.71; N, 13.43. $\epsilon^{max}_{250nm} = 2.16 \times 10^4$, $\epsilon^{max}_{275nm} = 1.75 \times 10^4$, $\epsilon^{sh}_{340nm} \sim 95$, and $\epsilon^{max}_{475nm} = 69.1$ M^{-1} cm^{-1} in water. (1-Methyl-4,4′-bipyridinium)pentaammineruthenium(III) complex was prepared by adding several pieces of zinc amalgam to 1.0 g of $[Ru(NH_3)_5Cl]Cl_2$ suspended in 30 mL of water for 45 min in argon, with gentle stirring. The resulting solution was added to an argon-degassed solution of [mbpy]Cl (0.85 g in 10 mL of water). After 30 min the blue solution was cooled in ice and filtered. A 0.3-mL portion of 50% sulfuric acid and then 0.46 g of potassium peroxydisulfate were added with stirring. The orange solution after 15

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(2) (a) Isied, S. S. *Prog. Inorg. Chem.* **1984**, *32*, 443. (b) Haim, A. *Pure Appl. Chem.* **1983**, *55*, 89.
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min was filtered and evaporated to a small volume, addition of solid NH_4PF_6 to which precipitated a yellow product (1.5 g, 55%). This was recrystallized from very dilute acid (H_2SO_4) and washed with ethanol and ether. Anal. Calcd for $[(NH_3)_5Ru(mbpy)](PF_6)_2(SO_4)\cdot 2H_2O$: C, 16.95; H, 3.88; N, 12.58; S, 4.11. Found: C, 16.68; H, 3.79; N, 12.52; S, 4.03. $\epsilon^{max}_{247nm} = 1.35 \times 10^4$, $\epsilon^{max}_{275nm} = 1.24 \times 10^4$, and $\epsilon^{sh}_{300nm} = 1.0 \times 10^4$ M^{-1} cm^{-1} in water. Reduction with excess sodium ascorbate produced the corresponding Ru(II)cation, $\epsilon^{max}_{582nm} = 1.44 \times 10^4$ M^{-1} cm^{-1} in water. Cyclic voltammetry in 0.05 M aqueous KCl solution showed a reversible one-electron redox potential at 0.43 V (vs NHE), using a Pt electrode. A CN Van de Graaff electron accelerator at the Center for Fast Kinetics Research was used as an electron source. Pulses of 100-ns duration were delivered to samples in a quartz cell (1-cm optical path length), and absorptions of species were monitored by using a conventional xenon lamp or tungsten lamp, monochromator, and photomultiplier. The signals were digitized by a Biomation 8100 transient recorder and analyzed by using an on-line PDP 11/70 minicomputer. The radiolysis of water by ionizing radiation can be described by eq 5

$$H_2O \rightarrow e_{aq}^-\ (2.65),\ OH\ (2.65),\ H\ (0.60),\ H_2O_2\ (0.75),\ H_2(0.45),\ H_3O^+ \quad (5)$$

with *G* values (the number of product molecules formed by the absorption of 100 eV in solution) in parenthesis. In the presence of 0.1 M formate and saturated N_2O solutions at pH ~7, CO_2^- radicals are produced (eq 6–8).[5] The concentrations of reducing radical ($^\bullet CO_2^-$) generated were

$$e_{aq}^- + N_2O \rightarrow N_2 + OH \qquad k = 8.7 \times 10^9\ M^{-1}\ s^{-1} \quad (6)$$

$$OH + HCO_2^- \rightarrow {}^\bullet CO_2^- + H_2O \qquad k = 3.0 \times 10^9\ M^{-1}\ s^{-1} \quad (7)$$

$$H + HCO_2^- \rightarrow {}^\bullet CO_2^- + H_2 \qquad k = 1.8 \times 10^8\ M^{-1}\ s^{-1} \quad (8)$$

3–17 μM and were determined by methyl viologen radical production in separate experiments ($\epsilon_{600nm} = 1.4 \times 10^4$ M^{-1} cm^{-1}). The rate constant values were independent of the wavelength of observation, which was usually at 600 nm. The uncertainties were assessed from their average deviations. Each observed rate constant is an average of three to five runs. All data were obtained at pH 7.2 ± 0.2 at 25 ± 1 °C and *I* = 0.1 M ($NaHCO_2$).

Results and Discussion

The second-order rate constant for reaction 9 of $(NH_3)_5Co(mbpy)^{4+}$ with $^\bullet CO_2^-$ is (2.4 ± 0.6) × 10^9 M^{-1} s^{-1}, a typical value

$$(NH_3)_5Co^{III}(mbpy)^{4+} + {}^\bullet CO_2^- \rightarrow (NH_3)_5Co^{III}(mbpy^\bullet)^{3+} + CO_2 \quad (9)$$

for these types of reduction.[5,7] The spectrum of the product after 37 μs was recorded by using 50 μM cobalt(III) and 9.3 μM $^\bullet CO_2^-$. In this time the $^\bullet CO_2^-$ reaction is completed and decay has barely commenced (see below). The transient shows maxima at 380 nm ($\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}) and 580 nm ($\epsilon = 6.5 \times 10^3$ M^{-1} cm^{-1}).[10] Reaction of the free ligand $mbpy^+$ (100 μM) with $^\bullet CO_2^-$ (9.3 μM) is complete within 20 μs. The spectral characteristics of the product $mbpy^\bullet$ ($\epsilon^{max}_{380nm} = 1.7 \times 10^4$ M^{-1} cm^{-1} and $\epsilon^{max}_{590nm} = 7.4 \times 10^3$ M^{-1} cm^{-1}) compared with those of the coordinated ligand radical indicate that ≥90% of $^\bullet CO_2^-$ has attacked the $mbpy^+$ center in the cobalt(III) complex, since in general there is a strong similarity in values of λ_{max} and ϵ for free and $(NH_3)_5Co$-coordinated pyridinyl radicals.[6,7,10] The radical $mbpy^\bullet$ is stable in solution for at least 400 ms, but the cobalt(III)-coordinated radical decays in times ranging from 0.5 to 10 ms depending on the concentration of cobalt(III) complex pulsed. Previous attempts to observe $(NH_3)_5Co(mbpy^\bullet)^{3+}$ using $^*Ru(bpy)_3^{2+}$[9] and MV^+[12] as reducing agents were unsuccessful. The inability to detect a transient may arise from interference by the back-reaction in the photochemical reaction[9] or from the fact that the MV^+ reaction was in 1.0 M H^+[12] and not in neutral solution (our conditions). It is perhaps significant that no transient was observed[13] when even $(NH_3)_5COOCOC_6H_4NO_2^{2+}$ was reacted with $^*Ru(bpy)_3^{2+}$. A relatively stable radical ($k = 2.6 \times 10^3$ s^{-1}) is well established with the *p*-nitrobenzoate-coordinated system.

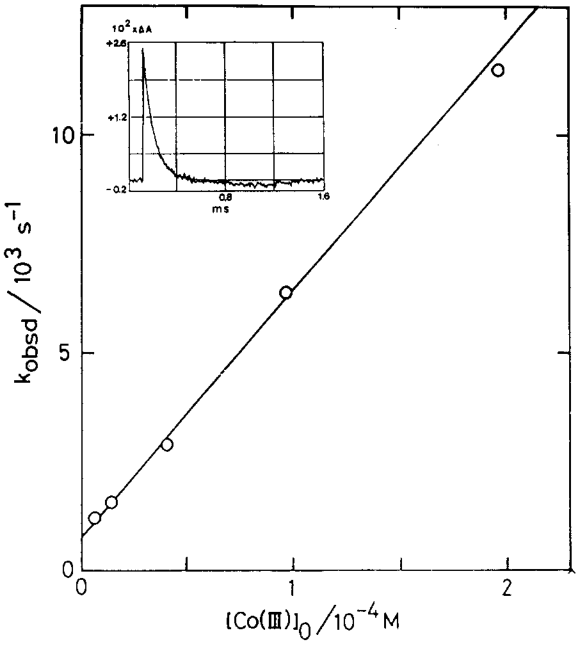

Figure 1. Plot of $k_{obsd}/10^3$ s^{-1} versus concentration of $(NH_3)_5Co(mbpy)^{4+}$ for the first-order loss of $(NH_3)_5Co^{III}(mbpy^\bullet)^{3+}$ at 600 nm. The two lowest values are from initial rate data. Inset: typical decay curve (200 μM Co(III) complex, 4 μM $^\bullet CO_2^-$, smooth line first-order, $k = 1.15 \times 10^4$ s^{-1}). All data are at pH 7.2 and 25 ± 1 °C, and absorbance changes (×10^2; 1-cm cell) are at 600 nm.

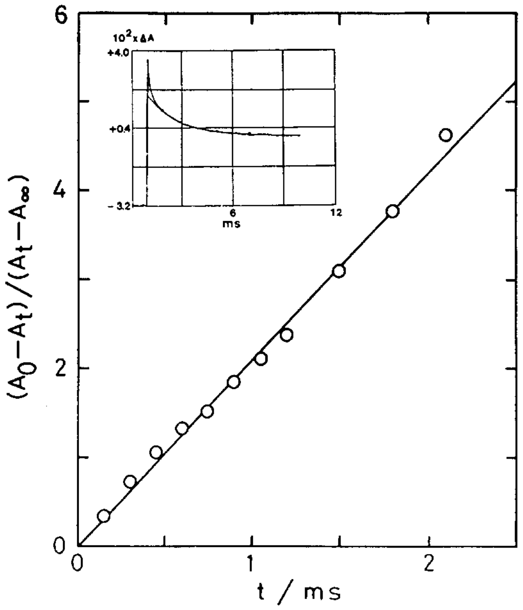

Figure 2. Second-order plot up to 2 ms of decay data. Absorbance changes (×10^2; 1 cm cell) are at 600 nm. Inset: decay of $(NH_3)_5Co(mbpy^\bullet)^{3+}$ at pH 7.2 and 25 ± 1 °C (10 μM cobalt(III) complex, 9 μM$^\bullet CO_2^-$; upper line experimental data merging into lower line first-order loss, $k = 5.4 \times 10^2$ s^{-1}).

Decay Kinetics of $(NH_3)_5Co(mbpy^\bullet)^{3+}$. At the highest concentrations of cobalt(III) complex subjected to $^\bullet CO_2^-$ attack (50–200 μM initial concentrations), the loss of $(NH_3)_2Co(mbpy^\bullet)^{3+}$ (3–9 μM) is *complete* and excellent first-order (Figure 1). The first-order rate constant k_{obsd} is dependent on $(NH_3)_5Co(mbpy)^{4+}$ concentration:

$$k_{obsd} = k_1 + k_2[(NH_3)_5Co(mbpy)^{4+}]$$

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(10) The ϵ values are calculated on the basis of 100% reduction at the viologen center. This is not unreasonable if one recalls that the reduction of $Co(NH_3)_6^{3+}$ by $^\bullet CO_2^-$ is (1.1 ± 0.3) × 10^8 M^{-1} s^{-1} at pH 6.9,[11] which must be at the cobalt(III) center, and is some 10-fold slower than $^\bullet CO_2^-$ reduction of the viologen complex.

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

concn, μM					
$(NH_3)_5$-$Co(mbpy)^{4+}$				R	
initial	final	CO_2^-	$(A_0 - A_\infty)/A_0$	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.

Acknowledgment. We are grateful to the National Science Foundation for a grant to support this work. The pulse radiolysis experiments were carried out at the Center for Fast Kinetics Research, The University of Texas, Austin TX 78712. The center is supported jointly by the Biotechnology Branch of the Division of Research Resources of the NIH (Grant RR 00886) and by The University of Texas, Austin.

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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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