Communications

Possible Intermediacy of Hydroxycarbyne Complexes in Carbon Monoxide Reduction†

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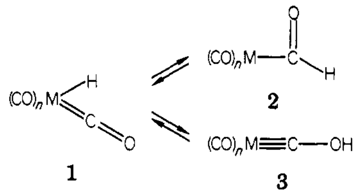
Received April 13, 1982

Summary: Evidence, including thermochemical data, modified extended Hückel calculations, and reactivity and kinetic data, is presented which suggests that hydroxycarbyne complexes may be important intermediates in homogeneous transition-metal-catalyzed carbon monoxide reduction.

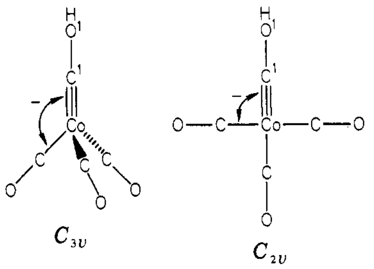
Resurgent interest in the catalytic activation of carbon monoxide[1] has resulted in several reports of apparently homogeneous, transition-metal-catalyzed reductions of this species.[2-5] Despite this progress, considerable uncertainty persists with respect to the mechanism of such reactions. Virtually all the suggested schemes thus far begin with conversion of a metal hydride (1) to a metal formyl complex (2), a step which, in general, appears to be thermodynamically disfavored[6] and therefore, not surprisingly, is lacking in direct experimental support for the catalytically important metals.[7] Several lines of evidence, both theoretical and experimental, lead this author to propose the tautomeric hydroxycarbyne species 3 as an energetically and mechanistically reasonable alternative to 2.



(1)

The energetic feasibility of 3 was at first suggested by electron-counting considerations and "back-of-the-envelope" bond energy calculations. With $HCo(CO)_4$ as the archetypal complex 1, the formyl species $(CO)_3CoCHO$ (2a) possesses a 16-electron count compared to the closed-shell 18-electron total for $(CO)_3CoCOH$ (3a). The enthalpy difference between 2a and 3a is roughly speaking a C–O π bond plus a C–H (sp^2) bond for 2a vs. two Co–C π bonds and an O–H bond for 3a. With use of typical bond energy values from main element compounds[8] and an estimate of 35–40 kcal/mol for π(Co–C),[9] ΔH_f for the hydroxycarbyne $(CO)_3CoCOH$ is found to be about 0–10 kcal/mol more negative than for the formyl derivative, $(CO)_3CoCHO$; that is, 2a and 3a are anticipated to be of comparable stability.

This qualitative conclusion has now been supported by calculations using the modified extended Hückel Theory (MEHT) of Anderson[13] parameterized to give good bond energies. Feder et al.[14] have utilized this type of calculation to compare the molecular electronic energy values and preferred geometries for several prospective intermediates in the cobalt carbonyl catalyzed reduction of carbon monoxide including $HCo(CO)_4$ (1a) and $(CO)_3CoCHO$ (2a). Using a similar methodology at this author's request, Curtiss[15] has calculated relative energies and geometries for pyramidal (C_{3v}) and planar (C_{2v}) forms of the carbyne complex 3a. With the following bond distances fixed O^1–H = 1.09 Å, C^1–O^1 = 1.43 Å, Co–C^1 = 1.82 Å, Co–C = 1.82 Å, and C–O = 1.14 Å, the angles θ optimized to 124° in the C_{3v} structure and 98.6° in the C_{2v} structure. The pyramidal (C_{3v}) geometry was found to be 21 kcal/mol more stable than the planar (C_{2v}) form. Most importantly, relative to the other complexes in the reaction path, *the C_{3v} carbyne complex 3a was found to be 7 kcal/mol more stable than the formyl species 2a* (in its preferred planar geom-



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† Dedicated to the memory of Rowland G. Pettit.

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(9) Although no thermochemical data on carbene or carbyne complexes are available, this value seems reasonable in light of the extremely short M≡CR bond lengths reported,[10] the high ν(M≡CR) and force constants,[10,11] and an estimate of ca. 150 kcal/mol for M≡CR based on $^1/_2$[M≡M[12] + C≡C].

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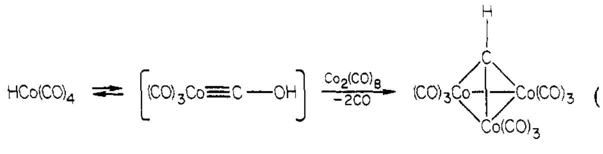
etry) and 15 kcal/mol^{-1} less stable than $HCo(CO)_4$. Although the uncertainty in these calculations could be as high as 10–15 kcal/mol^{-1}, the hydroxycarbyne complex should nevertheless be considered an energetically viable species.

The increasing number of known carbyne complexes including simple methylidyne and alkyl-, amino- and alkoxy-substituted derivatives[10,16] certainly attests to the feasibility of such compounds as reaction intermediates. Although no mononuclear hydroxycarbyne complexes have been reported, interestingly, the cluster hydroxycarbyne (methylidyne) 4 is formed in the reaction of $HCo(CO)_4$ and $Co_2(CO)_8$,[17] a process which may involve capture of the triply bonded carbyne by $Co_2(CO)_8$ (eq 2).[18] Recent reports of low-temperature O-protonation and -alkylation of polynuclear metal carbonyl anions are also noteworthy.[19a–d] In addition, the association of alkali-metal ions with the oxygens of carbonyl ligands for several transition-metal carbonylates[20a–e] adds further credibility to the energetic accessibility of the corresponding O-protonated carbyne derivatives 3.



(2)

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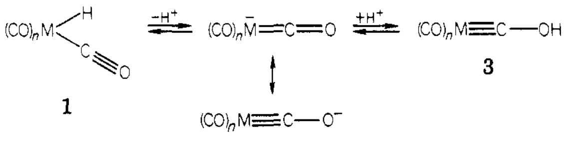
In view of the significant acidity of many metal carbonyl hydrides, formation of a hydroxycarbyne complex from the corresponding metal hydride could proceed analogously to classical keto–enol tautomerism via the metal carbonyl anion (eq 3). Further, just as the enol content of organic carbonyl derivatives increases with increasing substrate acidity,[21] the equilibrium concentration of 3 may parallel the acidity of 1. Indeed, the observation that the most active homogeneous syn gas catalysts (Co, Rh, Ir, Ru) form the most acidic metal hydrides[2e] (i.e., $HCo(CO)_4$,[22] $HRh(CO)_4$,[23] $HIr(CO)_4$,[23] $H_2Ru(CO)_4$[24]) may reflect the importance of the 1 ⇌ 3 preequilibrium in the reduction process.



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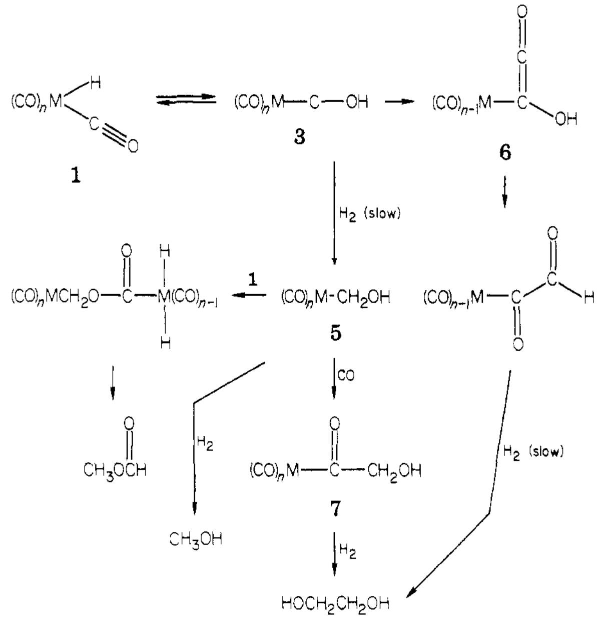

Much of the available kinetic data for the cobalt-[2] and ruthenium-catalyzed[3] CO reduction is equally well accommodated by either formyl or carbyne intermediates. The mechanism shown in Scheme I involving the latter would account for the formation of methanol, methyl formate, and ethylene glycol as primary products, the observed first-order rate dependence on hydrogen pressure, the modest rate acceleration with increasing solvent polarity (for Co[2b,25]), and the inverse deuterium isotope effect (for Co[11,26]). The known hydrogenolysis of carbene complexes[27] and reductive carbonylation of $RCCo_3(CO)_9$ to homologated aldehydes[28] provides precedent for the transformation 3 → 5 → 7. Suggested conversion of hydroxymethyl species 5 to products follows the pathway proposed by previous workers.[2b,d,3b] Homologated products could also arise from carbonylation of 3 via metallo ketene 6, a process which has been observed for isolable carbyne complexes.[29] Methyl formate may result from attack of the hydroxymethyl species 5 on 1 followed by hydrogenolysis.

In view of the calculations and experimental data presented above, hydroxycarbyne complexes should be considered as possible intermediates in the reactions of metal carbonyl hydrides, particularly carbon monoxide reduction. Experiments designed to detect, trap, and/or isolate these species are underway.

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[25] Increasing solvent polarity should favor polar species 3 in the important 1 ⇌ 3 preequilibrium.

[26] The observed isotope effect suggests that the hydrogen atom originally attached to cobalt becomes bound to carbon (to give the formyl) or oxygen (to give the carbyne) in the transition state. See ref 14 for a more complete discussion of the inverse isotope effect.

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Acknowledgment. The assistance of Dr. Larry Curtiss (Argonne National Laboratory) in carrying out the MEHT calculations and helpful discussions with Professor Roald Hoffmann (Cornell) and Dr. James McGinnis (Celanese Research Co.) are gratefully acknowledged. Support from the Alfred P. Sloan Foundation (1980–1982) is greatly appreciated. These ideas were conceived while the author was on sabbatical leave at Celanese Research Co. (Summit, NJ).

Registry No. CO, 630-08-0.

Photochemical Fragmentation of the Cluster $Ru_3(CO)_{12}$: Evidence against Homolytic Bond Cleavage[†]

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Received August 2, 1982

Summary: $Ru(CO)_5$ is the photoproduct when $Ru_3(CO)_{12}$ is photolyzed in octane solution containing 1 M CCl_4 and under a CO atmosphere. Although chlorocarbonylruthenium products are formed eventually, these arise from the facile thermal reaction of $Ru(CO)_5$ with the CCl_4. Quantum yields for $Ru_3(CO)_{12}$ fragmentation are markedly sensitive to the presence of CO but insensitive to that of CCl_4, arguing against proposals of diradical intermediates in this photoreaction.

Photolysis of the trinuclear cluster $Ru_3(CO)_{12}$ in hydrocarbon solutions and in the presence of soft ligands such as CO, ethylene or phosphines has long been known[1] to lead to the fragmentation of the cluster to monomeric species (e.g., eq 1). While this reaction is sufficiently facile

$$Ru_3(CO)_{12} + 3CO \xrightarrow{h\nu} 3Ru(CO)_5 \qquad (1)$$

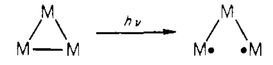
to provide a synthesis pathway for moderate concentrations of mononuclear ruthenium carbonyls in hydrocarbon solutions,[1-4] the photosynthesis procedure is not effective in more polar solvents such as tetrahydrofuran (THF) owing in part to much smaller quantum efficiences (vide infra). Furthermore, although we have found $Ru(CO)_5$ to be the photoproduct under CO at low $Ru_3(CO)_{12}$ concentrations in THF, photolysis at larger $Ru_3(CO)_{12}$ concentrations in this solvent leads to the formation of an uncharacterized, insoluble red material, presumably a polymeric ruthenium carbonyl. These marked effects of the medium on the $Ru_3(CO)_{12}$ photoreactions has stimulated our interest in the quantitative elucidation of the cluster photofragmentation mechanism.

Table I. Disappearance Quantum Yields for the Photolysis of $Ru_3(CO)_{12}$

solvent	conditions	$10^3\phi_d$
octane[c]	1 atm of CO[b]	28 ± 4
octane[d]	1 atm of C_2H_4[b]	51 ± 5
octane[e]	1 atm of Ar[b]	<0.1
CCl_4[f]	1 atm of CO	13 ± 3
CCl_4[f]	1 atm of Ar	0.7 ± 0.1
octane[f]	1 M CCl_4/1 atm of CO	24 ± 4
octane[f]	1 M CCl_4/1 atm of Ar	~0.2
THF[c]	1 atm of CO	3.5 ± 0.7
diglyme[c]	1 atm of CO	0.7 ± 0.1
octane[c]	0.5 M THF/1 atm of CO	1.7 ± 0.1
octane[c]	0.3 M diglyme/1 atm of CO	3.2 ± 0.1

[a] ϕ_d based on the decrease in intensity of the 392-nm absorption band of $Ru_3(CO)_{12}$ given that the products do not absorb light at this wavelength. $[Ru_3(CO)_{12}]$ initial ~5 × 10^{-5} M. $T = 25$ °C λ (irradiation) = 405 nm. The photolysis apparatus and general procedures have been described previously (Hintze, R. E.; Ford, P. C. *J. Am. Chem. Soc.* **1975**, *97*, 2664). [b] Solution prepared by flushing with respective gas, $P = 1$ atm. [c] Product formed is $Ru(CO)_5$. [d] Product formed is $Ru(CO)_4(C_2H_4)$. [e] Product unknown. [f] Products formed are chlorocarbonyls of ruthenium.

The electronic spectrum of $Ru_3(CO)_{12}$ is dominated by a strong absorption band (λ_{max} 392 nm in octane (ϵ_{max} 7.7 × 10^3 L mol^{-1} cm^{-1})) attributed to a transition from an orbital which is bonding with regard to the metal–metal bond framework to one which is antibonding in this regard.[5,6] It has been suggested[3,7] that the photofragmentation resulting from irradiation in this wavelength region may proceed via the cleavage of a single Ru–Ru bond to produce the open chain diradical A (eq 2) in the primary



(2)

A

$$M = Ru(CO)_4$$

photoreaction step. A similar mechanistic proposal has been made for the photofragmentations of $Os_3(CO)_{12}$[8] and of $HMCo_3(CO)_{12}$.[9] Reaction with CCl_4 to give chlorocarbonyl products has been argued as evidence for formation of metal radicals in photoreactions of $Os_3(CO)_{12}$[8] and of numerous dinuclear metal–metal bonded complexes.[7,10] We have shown that 405-nm photolysis of $Ru_3(CO)_{12}$ in CCl_4 solution indeed does lead to formation of chlorocarbonyl ruthenium products; however, the quantum yield for the photofragmentation (ϕ_d) is a factor of 20 larger under CO (1 atm) than under argon (Table I). Even greater differences are seen with the ϕ_d values measured in octane solution with CCl_4 (1 M) added. When this solution is equilibrated with CO (1 atm), ϕ_d is indistinguishable from that value measured in the absence of CCl_4. Under an argon atmosphere, ϕ_d in the octane/1 M CCl_4 solution is 2 orders of magnitude smaller, although apparently somewhat larger than seen in octane solution alone.

Examination of product solution infrared spectra leads to particularly important observations. Photolysis of $Ru_3(CO)_{12}$ in octane/1 M CCl_4 solution under CO (1 atm) for a time period sufficient to cause an 80% decrease of

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[†] Dedicated in memory of Professor Rowland Pettit.

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