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Evidence for Formation of a Co–H Bond from $(H_2O)_2Co(dmgBF_2)_2$ under H_2: Application to Radical Cyclizations

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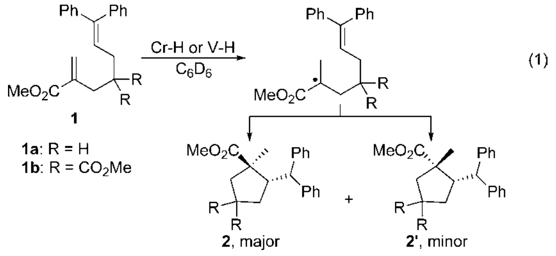
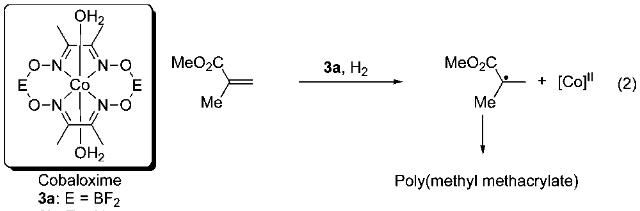
Ⓢ *Supporting Information*

ABSTRACT: Under H_2, the radical cyclization of appropriate dienes can be catalyzed by cobaloximes. H• can be abstracted from an intermediate (presumably a cobalt hydride) by trityl radicals (Ar_3C•) or by TEMPO. The rate-determining step in these reactions is the uptake of H_2, which is second order in cobalt and first order in hydrogen; the third-order rate constant is 106(3) $M^{-2}{\cdot}s^{-1}$.

Hydrogen atom (H•) transfer (HAT) from transition-metal hydrides to unsaturated organic molecules is a key step in many reactions, in particular hydrogenation and hydroformylation.[1] Our group has measured the rate constants for HAT from $CpCr(CO)_3H$ and $HV(CO)_4(P{-}P)$ to various olefins[2] and used these reactions to carry out radical cyclizations (eq 1).[2c,3] With $CpCr(CO)_3H$, the reaction is catalytic, as $CpCr(CO)_3H$ is regenerated from $CpCr(CO)_3$• with H_2,[4] but HAT is relatively slow. With $HV(CO)_4(P{-}P)$, HAT is faster, but cyclizations can be effected only stoichiometrically because the V–H bond is too weak for •$V(CO)_4(P{-}P)$ to cleave H_2. Both the Cr and V hydrides are air-sensitive and thermally unstable.

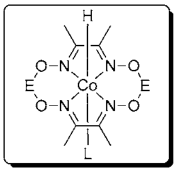


The possibility that Co complexes might catalyze the generation of radicals from H_2 was suggested by the 2006 report[5] that the macrocyclic Co^{II} complex $(H_2O)_2Co(dmgBF_2)_2$ (**3a**) (dmg = dimethylglyoximato) could initiate the polymerization of acrylates under H_2 gas (eq 2). Such "cobaloximes" are air- and moisture-stable solids that are widely accepted as models for vitamin B_{12}. Indeed, van der Donk has shown that vitamin B_{12} itself can catalyze radical cyclizations with Ti^{III} as the stoichiometric reductant,[6] and Carreira has shown that photolysis of cobaloxime complexes generates a catalyst for the cyclization of unsaturated alkyl iodides.[7] A Co^{III} hydride is probably formed in all three of these reactions: in eq 2 from H_2, in the van der Donk chemistry by protonation of the Co^{I} vitamin B_{12} anion, and in the Carreira chemistry from an alkyl–Co^{III} intermediate.



Cobaloxime
3a: E = BF_2
3b: E = H

Cobaloxime hydrides **4**, and the hydrides of similar tetraazamacrocycle complexes, have been proposed as intermediates in the operation of Co catalysts for H_2 evolution. Important recent work in this area has come from Gray,[8] Peters,[8d,9] Eisenberg,[10] Fontecave,[11] Sun,[11b,12] Alberto,[13] Bakac,[14] and Tiede.[15]



Hydridocobaloxime **4**
4a: E = BF_2
4b: E = H
L = Solvent or Base

Often cobaloxime hydrides are thermodynamically unstable, such as **4b** (L = py).[16] There have been suggestions[17] that hydride **4b** (L = PBu_3), originally reported to be formed from $ClCo(dmgH)_2(PBu_3)$ and $NaBH_4$,[18] was mischaracterized and that the original procedure actually gives a Co^{II} monomer in equilibrium with its dimer;[17] however, a report of the preparation of the PBu_3 hydride has just appeared,[19] albeit with a ^1H NMR spectrum that differs from that originally reported.[18] The pK_a of the PBu_3 hydride **4b** was estimated in the original report as 10.5 from "phase-distribution measurements" between $MeOH/H_2O$ and hexane.[18]

Schrauzer and co-workers reported a reaction between cobaloxime **3b** and H_2,[20] and there were subsequent studies of the kinetics of H_2 uptake by **3b** in the presence of various acceptors, including Schiff bases,[21] the dmgH ligand itself,[22] and styrene.[23] However, no spectroscopic data were reported for the $dmgBF_2$ hydridocobaloxime **4a** with L = H_2O until 2010, when Szajna-Fuller and Bakac assigned a peak at 608 nm to **4a** in water.[14] (This peak is close to, but less intense than, the peak at 610 nm assigned to $[Co^{I}(dmgBF_2)_2]^{-}$.[14])

We therefore set out to trap cobaloxime hydride **4a** from the reaction of cobaloxime **3a** with H_2. We began by trying tris(*p*-

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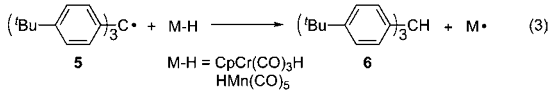
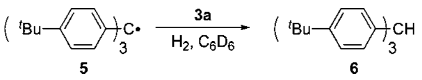
tert-butylphenyl)methyl radical (**5**), which is monomeric in solution (head-to-tail dimerization is prevented by its *p-tert*-butyl substituents[24]) and known to be effective at H• abstraction from transition metals (eq 3).[25] The reactions of **5** are easily monitored by watching the disappearance of its UV−vis signal (λ_{max} = 526 nm) or the appearance of the ^{1}H NMR signal of the product, tris(*p-tert*-butylphenyl)methane (**6**).



(3)

Indeed, **5** was converted to **6** in the presence of **3a** and H_2 (eq 4). No **6** was observed unless both **3a** and H_2 were present.



(4)

Cobaloxime **3a** *catalyzes* the reaction between trityl radical **5** and H_2, presumably via cobalt hydride **4a**. When eq 4 was monitored by NMR spectroscopy under constant H_2 pressure, the rate of formation of **6** did not change with time (Figure 1); the reaction is thus *zeroth order* in **5**.

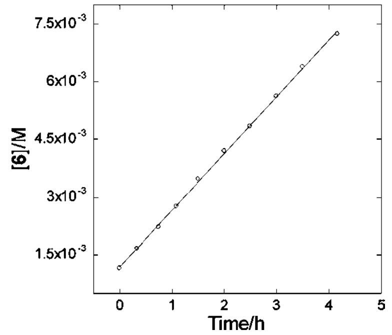


Figure 1. Cobaloxime-mediated formation of **6** from **5** under 2.4 atm H_2 in C_6D_6 at 295 K (eq 4). [**3a**] = 7.60 × 10^{-4} M and $[\mathbf{5}]_0$ = 1.02 × 10^{-2} M.

We confirmed this conclusion by showing that the rate d[**6**]/d*t* was independent of the initial concentration of **5** (Figure S17 in the Supporting Information). We then studied reaction 4 at various H_2 pressures and various **3a** concentrations. During a given reaction, [H_2] remained constant because it was present in substantial excess, and [**3a**] remained constant because it was regenerated. The reaction proved to be first order in H_2 (Figure 2a) and second order in cobalt (Figure 2b). These results suggest efficient trapping of hydride **4a** by $Ar_3C\bullet$ **5** and rate-limiting activation of H_2 by **3a**, that is, the rate law in eq 5, which is the same as the rate law reported earlier for catalysis of H_2 uptake by **3b**.[16,22b,d,23]

$$\frac{d[Ar_3CH]}{dt} = k[(H_2O)_2Co(dmgBF_2)_2]^2[H_2] \qquad (5)$$

This rate law suggests the mechanism in Scheme 1 with large k_2 and small k_1. From Figure 2a and the value of $[\mathbf{3a}]^2$ we obtain a k_1 value of 108(7) $M^{-2}s^{-1}$ (Figure S7), and from Figure 2b and the value of [H_2] we obtain a k_1 value of 104(3) $M^{-2}s^{-1}$ (Figure S13), implying that k_1 is 106(3) $M^{-2}s^{-1}$ at 295 K.[26] The first step, eq 6 in Scheme 1, is analogous to those for the activation of H_2 by other metalloradicals, such as $\bullet Co(CN)_5^{3-}$ (Halpern),[27] •Rh(TMP) (Wayland),[28] $\bullet Cr(CO)_3Cp^*$ (Hoff),[29] $\bullet Cr(CO)_3Cp$ (Franz),[4b] and $\bullet W(CO)_2(NHC)Cp$ (Bullock).[30]

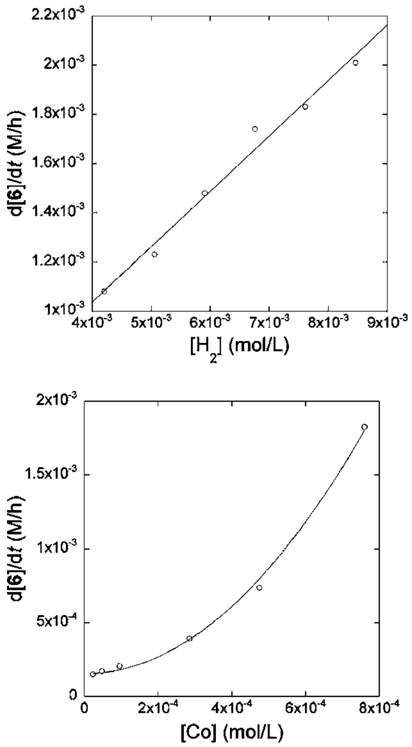
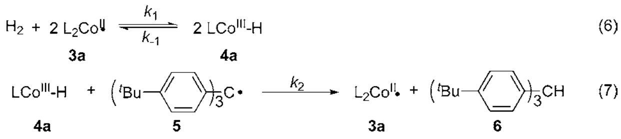
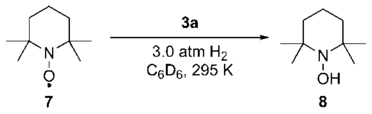


Figure 2. (a) Rate d[**6**]/d*t* of eq 4 vs [H_2]. (b) Rate d[**6**]/d*t* of eq 4 vs [**3a**]. All rates were measured at 295 K in C_6D_6.

Scheme 1. Mechanism of Cobaloxime-Mediated Formation of 6 from 5

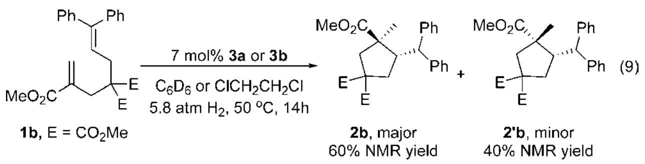


Of course the value of k_1 should be independent of the nature as well as the concentration of the trapping radical. We therefore replaced **5** by 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO, **7**), giving eq 8. We examined the rate of eq 8 with [**3a**] = 7.60 × 10^{-4} M and P_{H_2} = 3.0 atm (Figure S16). With [**7**] = 0.116 M, the rate d[**8**]/d*t* was found to be 1.82(2) × 10^{-3} Mh^{-1}, implying a k_1 value of 115(1) $M^{-2}s^{-1}$, almost the same as that found with various concentrations of **5** (Figure S18). This result is consistent with the mechanism in Scheme 1.[31]



(8)

It seemed likely that the apparent cobalt hydride intermediate **4a** would also donate H• to a cyclization substrate such as **1**, so we tried the cobaloximes **3a** and **3b** under H_2 as catalysts for the cyclization of **1b**. With substrate **1b**, we saw quantitative cyclization to **2b** and **2′b** (eq 9), the same result (with the same diastereomer ratio) obtained earlier with the Cr and V hydrides.[3]



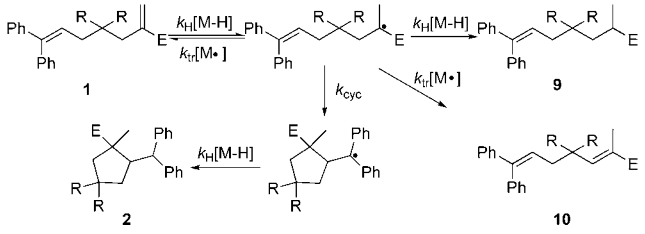
1b, E = CO$_2$Me

2b, major 60% NMR yield

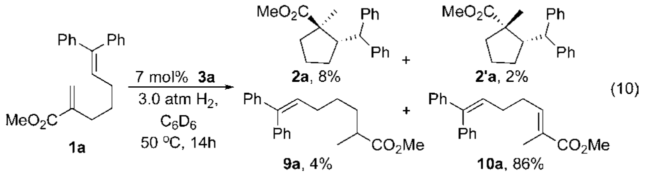
2′b, minor 40% NMR yield

We then considered what advantages cobaloximes might offer over our previous catalysts. *If* the reaction of cobaloxime **3a** with H$_2$ is slower than the reaction of the resulting hydride **4a** with our cyclization substrates, the resting state of our catalyst will be Co$^{\rm II}$, and the concentration of its hydride **4a** will remain low during the cyclization. The increase in [M•]/[M−H] will change the distribution of byproducts (typically **9** and **10** in Scheme 2) that accompany cyclization. Hydrogenation to **9** requires an additional M−H, while isomerization to **10** requires only M• (here Co$^{\rm II}$). Thus, the cobalt catalyst should give less hydrogenation to **9** and more isomerization to **10**.

Scheme 2. How Byproducts Are Formed during Cyclization Reactions

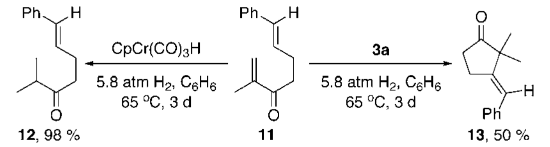


Indeed, with substrate **1a** and cobalt catalyst **3a**, *isomerization to **10a** is the prevailing reaction* (eq 10). Only traces of the cyclization products **2a** and **2′a** and the hydrogenation product **9a** are observed.

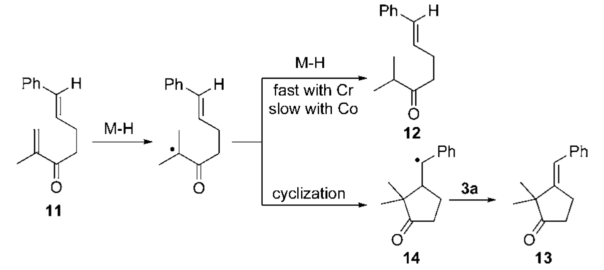


However, with the enone substrate **11**,[32] the use of the cobalt catalyst is advantageous. The structure of **11** eliminates isomerization as a possibility. The Cr catalyst results almost exclusively in hydrogenation to give **12**, but the Co catalyst *gives substantial cyclization*, albeit to the unhydrogenated product **13** (Scheme 3). Presumably **13** results from removal of H• from the cyclized radical **14** by Co$^{\rm II}$ (Scheme 4). The phenyl substituent in **11** directs the cyclization to a five-membered ring[33] instead of the six-membered ring reported for the parent radical.[34] The Co catalyst does give some hydrogenation (the remaining 50% of substrate **11** is converted to **12**).

Scheme 3. Comparison of Cr and Co Catalysts for Cyclization of 11



Scheme 4. Mechanism for the Formation of 12 and 13 from 11



Cobaloxime **3a** thus catalyzes the cyclization of **11** without net hydrogen uptake, although the presence of H$_2$ is required (**3a** has no effect on **11** in the absence of H$_2$). Our kinetics studies show that **3a** and H$_2$ generate an intermediate (presumably hydride **4a**) that can transfer H·. Both of our catalysts for cyclization, CpCr(CO)$_3$H and **3a**, avoid the need for a heavy atom in the substrate as well as the need for a tin reagent.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, spectroscopic data, and kinetic procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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