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Carbon−Carbon σ-Bond Transfer Hydrogenation with DMF Catalyzed by Cobalt Porphyrins

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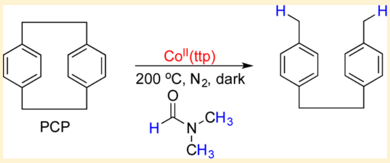
Supporting Information

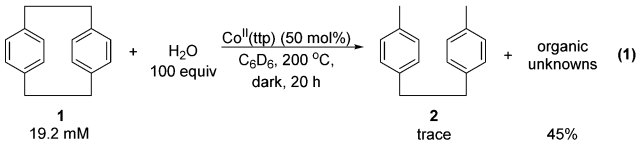
ABSTRACT: Cobalt porphyrins were found to catalyze the transfer hydrogenation of the carbon−carbon σ bond of [2.2]paracyclophane (PCP) with the solvent DMF serving as the hydrogenating agent. Successful trapping experiments with benzene solvent and the kinetic isotope effect (4.9) suggested the presence of benzyl radical intermediates in undergoing hydrogen atom transfer from DMF as the rate-limiting step. The rate law was established by initial rate measurements to be rate = $k_{obs}[Co^{II}(ttp)][PCP]$.



Catalytic carbon−carbon bond activation (CCCA) is the key chemical transformation in hydrocracking, turning crude oil into petroleum.[1] CCCA holds the potential to convert heavy polymeric residues and biomass into lighter, economically valuable chemicals.[2] Despite the usefulness of CCCA, examples with transition-metal complexes in homogeneous media remain limited.[3] The small number of literature reports on CCCA reflects the inertness of the C−C σ bond relative to the C−H bond.[4] CCCA with transition-metal complexes in homogeneous media mainly employs strategies such as chelation assistance,[5] ring strain relief,[6] and carbonyl functionality[7] to generate organometallic intermediates, followed by subsequent rearrangement of the carbon skeleton[8] or M−C σ-bond hydrogenation with H_2[9] to complete the catalytic cycle.

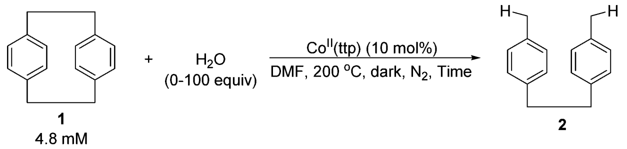
Our group has been interested in carbon−carbon bond activation (CCA) of organic substrates and has reported several stoichiometric examples.[10] Recently, we have developed rhodium and iridium metalloporphyrin (M(por), M = Rh, Ir) catalyzed C−C σ-bond hydrogenation of [2.2]paracyclophane (**1**) with water as the hydrogenating agent.[11] In light of these successes, we wish to extend the catalysis to a much less reactive but more easily accessible and cheaper cobalt porphyrin catalyst. Co(II) porphyrin is expected to have a lower reactivity than the corresponding rhodium and iridium porphyrin analogues since (1) Co−C bonds are generally weaker[12] and (2) Co^{II}(por) metalloporphyrin radical has a lower SOMO energy level.[13] As a result of low reactivity, CCA by cobalt complexes remains scarce in the literature.[14] Stoichiometric CCA with cobalt complexes includes ring expansion of allyl or cyclopentadienyl with alkyne to give seven-membered ring cobalt complexes[15] and C−CN bond cleavage via oxidative addition with electron-rich Co(I) complexes.[16] Catalytic CCA was recently reported for the cleavage of secondary and tertiary benzyl alcohols bearing a pyridinyl directing group.[17] Here, we report our success on Co(II) porphyrin catalyzed C−C σ-bond transfer hydrogenation of PCP in DMF solvent as the transfer hydrogenating agent.

Initially, we envisioned that Co^{II}(ttp) (ttp = 5,10,15,20-tetratolylporphyrinato dianion) could react with PCP similarly to the rhodium and iridium analogues. A 50 mol % catalyst loading was used to compensate the expected low reactivity of Co^{II}(ttp). Unfortunately, only a trace amount of the hydrogenation product 4,4′-dimethylbibenzyl (**2**) was formed together with other unknown organic products when the reaction was carried out in benzene-d_6 solvent (eq 1).



We suspected that the hydrolysis of Co^{II}(ttp) benzyl intermediates was slow in nonpolar benzene solvent; the more polar solvent DMF to facilitate hydrolysis of intermediates was then examined with 10 mol % catalyst, as in the case of rhodium and iridium analogues.[11] To our delight, **2** was obtained selectively in DMF in a good yield of 81% (Table 1, entry 2). In order to promote hydrogenation, we then

Table 1. Water Loading Effect



			yield (%)		
entry	H_2O (equiv)	time (days)	**1**	**2**	**1** + **2**
1	0	6	6	86	92
2	100	15	17	81	99

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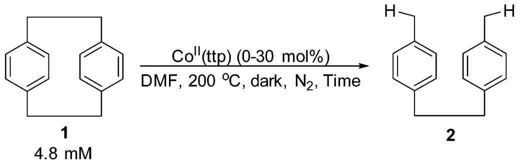
investigated the water loading effect. To our surprise, catalytic hydrogenation of **1** proceeded at a faster rate in the absence of water to give an 86% yield of **2** in 6 days (Table 1, entry 1).[18]

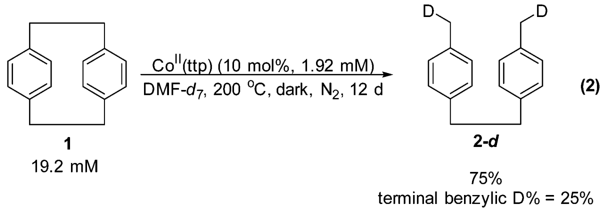
We then investigated the effect of catalyst loading in DMF without H_2O added. A control experiment showed no background reaction in the absence of catalyst (Table 2, entry 1). Increased Co^{II}(ttp) loading from 10 to 20 mol % enhanced the product yield from 86% to 95% and shortened the reaction time from 6 to 3 days (Table 2, entries 2 and 3). A higher loading of 30 mol % gave a faster hydrogenation but slightly lower yield of 73% (Table 2, entry 4).

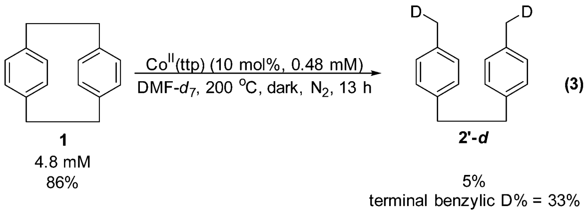
Table 2. Co^{II}(ttp) Catalyst Loading Effect

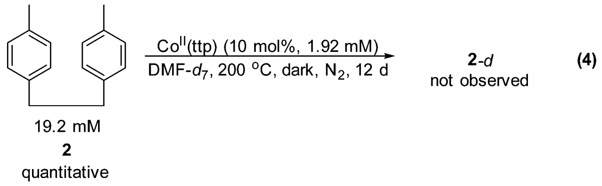


entry	Co^{II}(ttp) (mol %)	time (days)	yield (%)		
			1	2	1 + 2
1	0	5	99	0	99
2	10	6	6	86	92
3	20	3	0	95	95
4	30	2	0	73	73

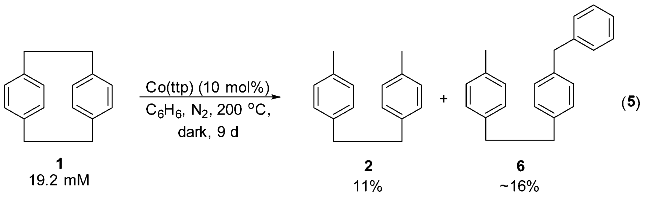
To establish the hydrogen source for the hydrogenation, deuterium labeling experiments were conducted. Hydrogenations with both full and partial conversion conducted in deuterated DMF (DMF-d_7)[19] gave the deuterated product **2-*d*** and **2'-*d*** in 75% and 5% yield and deuterium incorporation on terminal benzylic positions in 25% and 33% yields, respectively, as measured by ^{1}H NMR (eqs 2 and 3).[20] Deuterium incorporation on unreacted PCP was not observed; thus, no prior C−H activation and exchange on **1** occurred before CCA. A control experiment also indicated no deuterium exchange between **2** and DMF-d_7 (eq 4). These experiments confirmed that the solvent DMF served as the hydrogenating agent. Indeed, DMF has been used as a hydrogen atom transfer agent for radical reactions.[21]







On the basis of our reported bimetalloradical activation of PCP with Rh porphyrin[11a] and on the well-known metalloradical chemistry of Co(II) porphyrin, we attempted to trap radical intermediates, most likely benzyl radicals, that may exist in the catalysis. TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) failed to yield any trapping products, likely due to the known thermal instability of TEMPO-Bn at temperatures higher than 93 °C.[22] The benzyl radical intermediate was then successfully trapped by radical substitution of benzene solvent as **6** (eq 5).[23] The poor mass balance observed was attributed to the Co^{II}(ttp) end-capped oligomerization of **1**.[24]



To gain mechanistic insight into Co^{II}(ttp)-catalyzed transfer hydrogenation of PCP in DMF, kinetic studies by initial rate measurements were conducted with at least a 10-fold excess of [PCP] over [Co^{II}(ttp)]. Conversion of PCP to **2** was monitored by GC-MS ([Co^{II}(ttp)] = 0.060−0.48 mM, [PCP] = 1.2−9.6 mM, and T = (180−205) ± 0.2 °C). The initial rate of formation of hydrogenation product **2** increased linearly with [Co^{II}(ttp)] and [PCP], respectively (Figure 1), giving a pseudo-first-order kinetic plot for both species and an overall second-order reaction represented by rate = k_{obs}[Co^{II}(ttp)][PCP].

The temperature-dependent rates constants measured at (180−205) ± 0.2 °C yielded the following values for the activation parameters: $\Delta H^\ddagger = +26.9 \pm 2.3$ kcal mol^{-1}, $\Delta S^\ddagger = -12 \pm 5$ cal mol^{-1} K^{-1}, and $\Delta G^\ddagger = +32.5 \pm 3.3$ kcal mol^{-1}

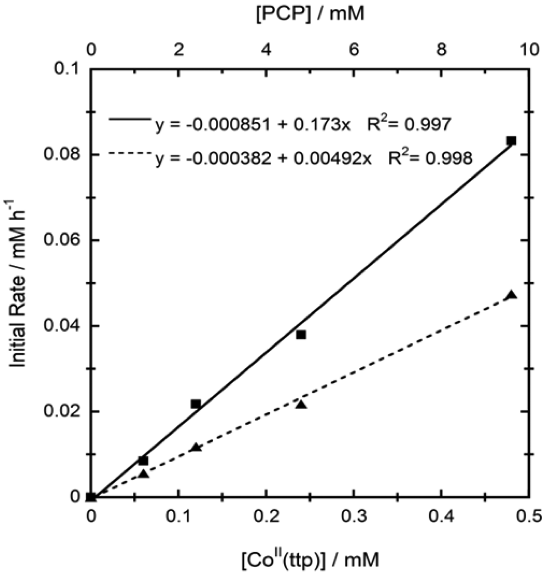


Figure 1. Plots of the initial rate of formation of [**2**] at 200 °C: (■) against [Co^{II}(ttp)] = 0.060−0.48 mM with [PCP] = 4.8 mM; (▲) against [PCP] = 1.2−9.6 mM with [Co^{II}(ttp)] = 0.12 mM.

(Figure 2).[25] The small but negative $\Delta S^{\ddagger}$ suggests an associative transition state.

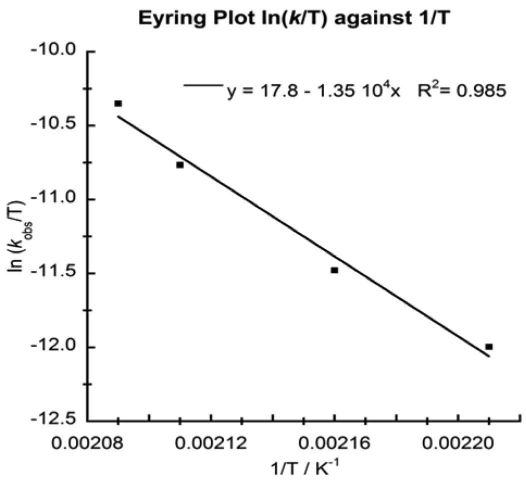
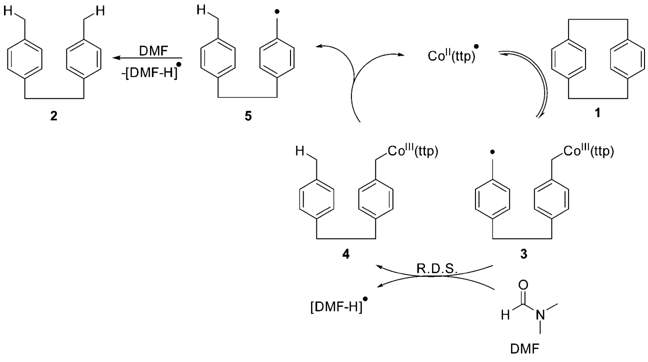


Figure 2. Eyring plot for determination of activation parameters ($[Co^{II}(ttp)]$ = 0.48 mM, [PCP] = 4.8 mM) at 180−205 °C.

Further mechanistic insight into the transition state came from kinetic isotope effect (KIE) studies. The initial rates of catalysis in DMF and DMF-d_7 were measured separately from two parallel reactions to be k_H = 0.083 mM h^{-1} and k_D = 0.017 mM h^{-1}, respectively ($[Co^{II}(ttp)]$ = 0.48 mM, [PCP] = 4.80 mM at 200 °C). The KIE (k_H/k_D) was then determined to be 4.9. The KIE from a competition experiment with equimolar amounts of DMF-d_0 and DMF-d_7 was determined to 6.5. Both values point to a rate-limiting hydrogen atom transfer step of the benzyl radical intermediate with the DMF molecule in a linear transition state.

On the basis of the above results and our current understanding of metalloporphyrin-based CCA of PCP,[11] Scheme 1 illustrates the proposed catalytic cycle for $Co^{II}(ttp)$-catalyzed C−C σ-bond transfer hydrogenation of PCP with DMF. Initially, the C−C σ-bond cleavage of **1** with $Co^{II}(ttp)$ gives the benzyl radical intermediate **3**.[26] **3** then undergoes hydrogen atom transfer (HAT) from the solvent DMF to give **4**. Fast homolysis of the weak Co−C bond at 200 °C[27] yields another benzyl radical intermediate **5** and regenerates $Co^{II}(ttp)$ for further catalysis. Finally, **5** undergoes a second HAT from DMF to afford the hydrogenation product **2**.

Scheme 1. Proposed Catalytic Cycle



In summary, the carbon−carbon σ-bond transfer hydrogenation of [2.2]paracyclophane with DMF catalyzed by cobalt porphyrin was achieved. The metalloradical Co(II) porphyrin attacks the C−C σ-bond of PCP, and the resultant benzyl radical abstracts a hydrogen atom from DMF to give the hydrogenation product.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Experimental procedures and NMR and MS spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(18) The amount of residual water in DMF used was 0.2% (≤23 equiv with respect to **1**).

(19) The amount of residual water in DMF-d_7 used was 0.1% (≤12 equiv with respect to 4.80 mM of **1** and ≤ 2.9 equiv with respect to 19.2 mM of **1**).

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(24) Co^{II}(ttp) end-capped oligomers were detected by MALDI-TOF MS. See Figure S11 and Tables S9 and S10 in the Supporting Information for structural assignment and mass spectral interpretation.

(25) Computed activation parameters for the thermolysis of PCP at 188 °C are $\Delta H^{\ddagger} = +37.7 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = +2.7 \pm 1.1$ cal mol^{-1} K^{-1}, and $\Delta G^{\ddagger} = +36.5 \pm 0.5$ kcal mol^{-1}. Roth, W. R.; Hopf, H.; de Meijere, A.; Hunold, F.; Börner, S.; Neumann, M.; Wasser, T.; Szurowski, J.; Mlynek, C. *Liebigs Ann.* **1996**, *1996*, 2141−2154.

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