Generation and reactivity of the dehydrotropylium-$Co_2(CO)_6$ ion†

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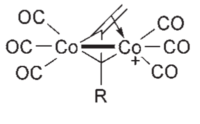
Received (in College Park, MD, USA) 16th July 2008, Accepted 7th August 2008
First published as an Advance Article on the web 17th September 2008
DOI: 10.1039/b812174e

Dehydrotropylium-$Co_2(CO)_6$ ion (2) has been generated by the Lewis acid mediated ionization of alcohol (3); it is attacked by relatively strong nucleophiles ($N > 1$), but undergoes a radical homocoupling in the presence of weak nucleophiles ($N < 1$).

The chemistry of propargyliumdicobalt cations, more commonly known as the Nicholas reaction, has seen widespread use in organic synthesis due a to balance of high stability and sufficient reactivity of the cations, the predictable site selectivity and stereochemical features of the reaction, and the straightforward handling or decomplexation of the precursor and product alkyne complexes.[1] The stability of these cations has normally been interpreted in terms of a fluxional structural represented by **1**, which has found support in spectroscopic and crystallographic studies.[2] Nevertheless, there are important features of the reactivity of these cations that are poorly understood; among these, the most notable is the effect of substituents on cation stability and reactivity.[3] Substitution at the propargylic site has been shown to have a minimal effect on the aforementioned properties. This has significant advantages, in that generation of cations substituted by electron withdrawing groups[4] and in antiaromatic systems[5] is often possible. This feature, however, complicates an in depth understanding of these cations, as by some measures classical standard conjugative and hyperconjugative stabilizing groups actually result in a very slight de-stabilization of the cation.[3b,6] In our own group, solvolysis and allylation reactions have often shown inverted trends in selectivity towards substitution.

Our group has been engaged in the development of a number of methods for the preparation of cycloheptyne-dicobalt systems, many of which are capable of giving precursors to substituted propargyliumdicobalt cations.[7–9] In particular, we believed the study of the nominally aromatic, 'dehydrotropylium' ion **2** would give information regarding strongly stabilizing influences on such cations, and therefore be important to their understanding. This communication reports the preparation and reactivity studies of this cation.



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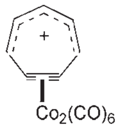

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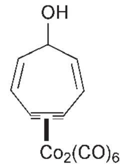

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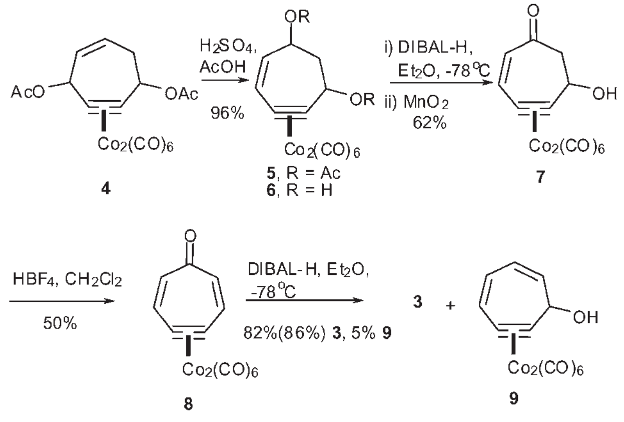
Access to ion **2** comes from precursor alcohol **3**, whose synthesis originated from propargyl diacetate complex **4**, available by ring closing metathesis chemistry.[7] Subjecting **4** to H_2SO_4 treatment in the presence of acetic acid gave rearranged diacetate **5** in excellent yield (96%). Removal of the acetate functions was best accomplished reductively (DIBAL-H), and the resulting diol **6** was oxidized selectively by MnO_2 to give the β-hydroxy ketone **7** (62% yield, 2 steps). Acid induced elimination of the alcohol function afforded the dienone complex **8** in fair yield (50%). Subsequent reduction of **8** gave the dienol **3** (82% yield, 86% based on recovered starting material), with a small amount of rearranged dienynol complex **9** (5% yield) and a small amount of recovered **8** (5% recovery) (Scheme 1).



Scheme 1 Synthesis of cycloheptadienynol complex **3**.

Subjecting alcohol **3** to HBF_4 in Et_2O at −75 °C, or in CH_2Cl_2 followed by precipitation by Et_2O, afforded a solid whose ^1H NMR spectrum (CD_2Cl_2) possessed resonances at δ 8.47 (d, J = 9.5 Hz, 2H), 8.36 (t, J = 9.4 Hz, 1H), and 8.19 ppm (apparent t, J = 9.5 Hz, 2H), but which gradually degraded even at −20 °C. With the limited stability of **2**, we decided to investigate the Nicholas reactions of **3** with nucleophiles of varying strength, particularly as reflected by Mayr's N values,[10] in order to obtain a measure of the electrophilicity

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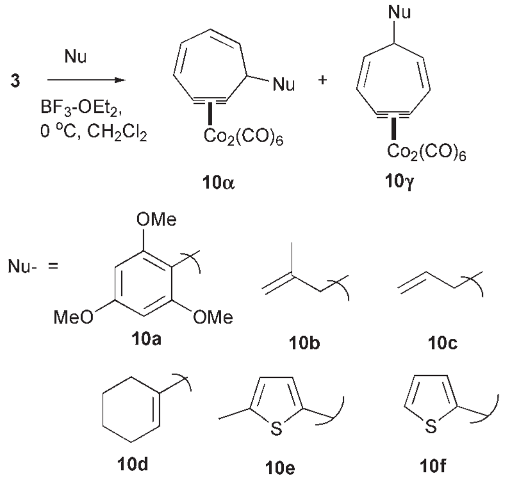
† Electronic supplementary information (ESI) available: Experimental conditions for the preparation of **3**, **10a–e**, and **11**; the spectral data and copies of the ^{13}C NMR spectra of **3**, **10a–e**, **11**. See DOI: 10.1039/b812174e

Table 1 Condensation reactions of **3** with $N > 1$ nucleophiles



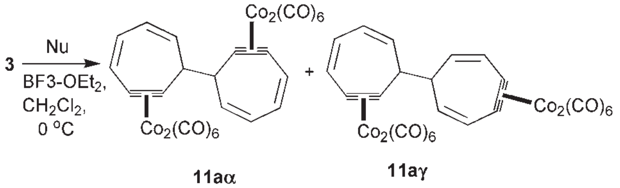
Entry	Nu (N^a)	Compound	Yield (%)	α- : γ-
1	1,3,5-Trimethoxybenzene (3.40)	**10a**	88	100 : 0
2	1,3,5-Trimethoxybenzene (3.40)	**10a**[b]	54	100 : 0
3	2-Methallyltrimethylsilane (4.41)	**10b**	73	67 : 33
4	Allyltrimethylsilane (1.79)	**10c**	70	83 : 17
5	Methylenecyclohexane (1.66)	**10d**	50	91 : 9
6	2-Methylthiophene (1.26)	**10e**	83	100 : 0

[a] Nucleophilicity value. [b] Starting from **9**.

and reactivity pattern of **2** (Table 1). In the presence of BF_3–OEt_2 (3 equiv., 0 °C, CH_2Cl_2), 1,3,5-trimethoxybenzene ($N = 3.40$) reacted rapidly with **3** to give the 7-arylated (α-arylated) dienyne complex **10aα** exclusively in excellent yield; under analogous conditions, rearranged dienynol complex **9** also afforded **10aα** (54% yield). Methallyltrimethylsilane ($N = 4.41$) reacted with **3** similarly to afford mixtures of 7-(α-) and 5-(γ-) methallylated condensation products **10bα** and **10bγ** (73% yield, 2.0 : 1 ratio), while the less nucleophilic allyltrimethylsilane ($N = 1.79$) gave condensation products with an increased proportion of α- attack (70% yield, **10cα** : **10cγ** = 4.9 : 1). Methylenecyclohexane ($N = 1.66$) reacted to give a condensation product mixture containing only a small amount of the γ-product (50% yield, **10dα** : **10dγ** = 10 : 1), while 2-methylthiophenene ($N = 1.26$) gave good condensation yields but no observable γ-product whatsoever (**10eα**, 83% yield). The increasing amounts of conjugated 1,3-dien-5-yne products with decreasing nucleophile N value is reminiscent of the previously reported increased amount of conjugated enyne products with decreasing nucleophilicity in Nicholas reactions of acetoxycycloheptenyne complexes.[11] The apparently inconsistent results with 1,3,5-trimethoxybenzene may be attributed to its demonstrated ability to react reversibly with propargyldicobalt cations.[11]

With nucleophiles less reactive than 2-methylthiophene, the reaction product profiles underwent a distinct change. Condensation products were absent or at most present in trace amounts, and the major isolated products were those of dimerization of cycloheptadienyne unit, as mixtures of α,α- and α,γ-isomers (**11αα** and **11αγ**). In the case of 3-methylanisole ($N = 0.13$), these dimers could be isolated in 26% yield (**11αα** : **11αγ** = 1 : 2.0). For thiophene ($N = -1.01$) the dimers were formed in 34% yield (**11αα** : **11αγ** = 1 : 2.0), and co-eluted with a trace (4%) of the condensation product **10fα**. Most successfully, the use of mesitylene‡ allowed formation of the dimers in 50% yield (**11αα** : **11αγ** = 1 : 2.0) (Table 2).

Table 2 Reactions in the presence of $N < 1$ nucleophile



Entry	Nu (N^a)	Yield (%)[b]	**11αα** : **11αγ**
1	3-Methylanisole (0.13)	26	33 : 67
2	Thiophene (−1.01)	34[c]	33 : 67
3	Mesitylene (< −2.5)	50	33 : 67
4	None	9	33 : 67

[a] Nucleophilicity value. [b] Yield based in all cases on 1 mmol **3** giving a maximum of 0.5 mmol **11**. [c] Isolated with 4% of condensation product **10fα**.

As propargyldicobalt radicals and their dimerization products are known results of the single electron reduction of propargyliumdicobalt cations,[12,13] the isolation of these dimers is attributed to the intermediacy of a cycloheptadienynyldicobalt radical; this process is also reminiscent of nucleophile induced electron transfer of pentadienylirons.[14] Nevertheless, the samples generated for spectroscopic studies of the cation **2**, in the absence of these arenes but in the presence of Et_2O, also contained significant amounts of the dimer **11** (**11αα** : **11αγ** = 1 : 2.0). Furthermore, Lewis acid mediated ionization of alcohol **3** with no added nucleophile present gave some dimer, albeit in lower yield (9%, **11αα** : **11αγ** = 1 : 2.0). As a result, it appears that the electron transfer source may not only be the added arene, but also a second alkynedicobalt unit or the ethereal solvent; both of these types of propargyldicobalt cation to radical mediators have been observed by Melikyan.[12,13] The trace amount of condensation product observed in the thiophene case may be accounted for by a free radical substitution process on thiophene.[15] Dimer **11αα** is isolated as a single diastereomer, which we are assigning as the *syn* diastereomer, based on extensive precedent for its predominance in propargyldicobalt radical dimerization reactions.[12,13,16]

The distinction between the behaviour of the dehydrotropylium-$Co_2(CO)_6$ ion (**2**) and normal hexacarbonylpropargyldicobalt cations is quite striking. With electrophilicity strengths of $E = -1.2$–-2.2,[6,17] propargyl cation-$Co_2(CO)_6$ complexes in general may enter into electrophile–nucleophile reactions with nucleophiles as weak as $N = -4$; conversely, **2** undergoes analogous reactions only with relatively strong ($N > 1$) nucleophiles, and switches to a radical dimerization process in the presence of weaker nucleophiles ($N < 1$). In terms of judging the stability of **2**, however, these results are complex. While the relative slowing of the electrophile–nucleophile combination reactions is consistent with a greater stability, and perhaps aromatic stabilization, of the cation, the ready conversion of such a cation to a radical has been cited as evidence of lowered stability of the cation relative to the radical.[12] Consequently, no definitive statement on the aromatic stabilization of **2** can be made as of yet.

In summary, we have been able to make the precursor alcohol **3** to the dehydrotropylium-$Co_2(CO)_6$ cation (**2**), and to generate the cation itself and observe both electrophilic and electron transfer–radical dimerization reactions. Further studies on comparative reactions of **3** with acyclic analogues, and calculational studies on **2** would shed light on the question of stability/reactivity of this nominally aromatic cation, and will be reported in due course.

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‡ The *N* value is unknown, but based on the values for toluene and *m*-xylene, its estimated *maximum* value is −2.5.

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