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Sodium methylthiolate as an efficient deprotecting agent for dicobalt hexacarbonyl complexes of acetylenes

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Abstract

Various dicobalt hexacarbonyl acetylene complexes were efficiently converted to the unprotected acetylene by the reaction of two molar equivalents of sodium methylthiolate. Yields and reaction times depend upon the choice of solvent. DMF proved to be the most efficient solvent, with the reaction proceeding at >80% conversion in 5 minutes at room temperature. © 1999 Elsevier Science Ltd. All rights reserved.

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The palladium cross-coupling reaction has quickly emerged as the standard to generate aryl–acetylene bonds.[1] With an efficient method to construct these bonds, a plethora of acetylene based materials has recently appeared in the literature.[2–6] Some examples include non-linear-optical materials, self-assembling systems, enediyne antibiotic mimics, linear-carbon polymers, and extended π systems to study energy transfer mechanisms.[2–6] As the use of alkyne chemistry has gained prominence in organic synthesis, methods to efficiently mask and unmask the reactive acetylene moiety have been developed. Acetylenes are typically protected as a dicobalt hexacarbonyl complex, allowing one to perform chemistry that would otherwise transform the acetylene.[7] Jones et al. have recently published an extensive study on the decomplexation of a series of enediyne dicobalt hexacarbonyl complexes.[4]

In an attempt to prepare 2,2′-dihydroxytolane (**2**), the dicobalt hexacarbonyl complex **1** was prepared and treated with two molar equivalents of sodium methylthiolate (SMT) in DMF at room temperature (Fig. 1).[8–10] This led to the clean conversion of **1** into a single product after five minutes, as evidenced by TLC analysis. After workup and isolation, the product was identified as the uncomplexed acetylene **3**, produced in quantitative yield (Table 1, entry 1). With this result in hand, the same transformation was attempted with one molar equivalent of SMT. Analysis of the reaction mixture showed a 1:1 mixture of the unreacted dicobalt complex **1** and the acetylene **3**. However, addition of a second equivalent of SMT resulted in complete conversion to **3** (entry 2).

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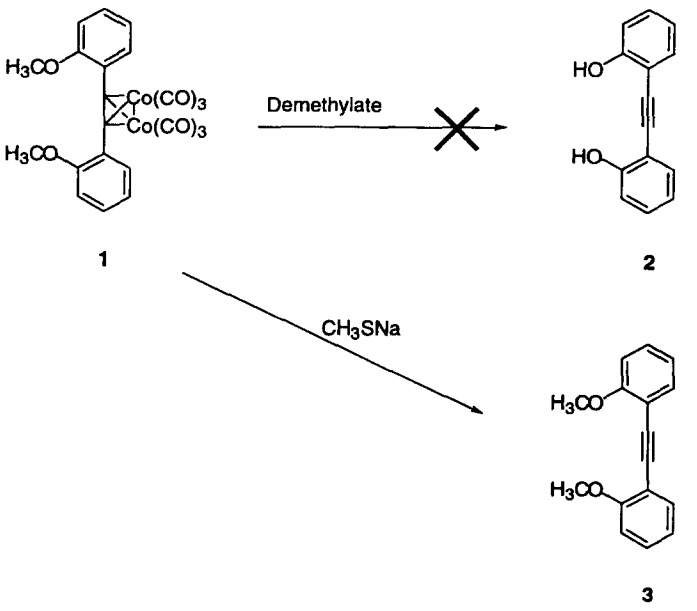


Figure 1.

Solvent selection proves critical for the efficient conversion of **4** to **5**. Methanol proved to be slightly slower than DMF and the use of THF resulted in no reaction (entries 4, 5). Greater than five molar equivalents of SMT were needed when acetonitrile was chosen as the solvent and reaction times increased greatly, probably due to the low solubility of SMT in acetonitrile (entry 6).

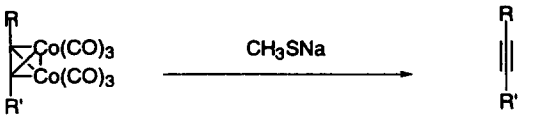
Diarylacetylene complexes with either electron donating or withdrawing groups can be easily converted to the acetylene by this method (entries 1, 8). In addition, dialkylacetylene dicobalt complexes are efficiently converted to the acetylene **5** under these conditions (entry 9). For example, 3-hexyne is easily prepared from the dicobalt complex **4**.

In summary, a highly efficient and mild method for the conversion of dicobalt hexacarbonyl complexes **4** to the acetylenes **5** with two molar equivalents of SMT has been reported. This approach offers advantages over other popular methods for the deprotection of the complexes: the reaction is mild, a large excess of the deprotecting agent is not needed, and the reaction is completed in a matter of minutes. Studies are currently underway to investigate the mechanism of this transformation.

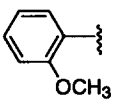
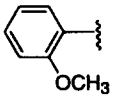
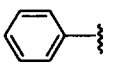
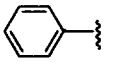
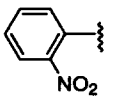
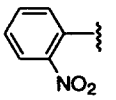
1. Typical experimental procedure for the conversion of 4 to 5

Under an atmosphere of N_2, a 50 mL round bottom flask, outfitted with a magnetic stir bar, is charged with 1.0 mmol of the corresponding dicobalt hexacarbonyl complex **4** in 15 mL anhydrous DMF. Sodium methylthiolate (2.0 mmol) was added and the mixture was stirred at room temperature for five minute. After this period, 25 mL of H_2O is added, and this solution is extracted with three 25 mL portions of CH_2Cl_2. The combined organic extracts are washed with H_2O, brine, and dried over Na_2SO_4. After filtration and evaporation of the solvent, the residue is chromatographed on silica with 1:1 CH_2Cl_2:hexanes to isolate the acetylene **7**. 3-Hexyne was purified by distillation. All compounds gave spectral data consistent with that reported in the literature.

Table 1



4 5

Entry	eq. SMT	R	R'	solvent	T(°C)	Time(min)	% yield
1	2			DMF	25	5	>99
2	1			DMF	25	5	50
3	2			DMF	-30	5	>99
4	2			MeOH	25	20	97
5	5			THF	25	180	nr
6	5			CH_3CN	25	45	87
7	2			DMF	25	5	>99
8	2			DMF	25	5	>99
9	2	C_2H_5—	C_2H_5—	DMF	25	5	83[a]

[a]purified by distillation

Acknowledgements

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