SYNLETT Spotlight 48

Dicobalt Octacarbonyl

Compiled by Stefan Fischer

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

Applications of transition metal chemistry serve as valuable tools for synthetic chemists. An important example is $\text{Co}_2(\text{CO})_8$, a well known reagent of versatile and still increasing utility since its discovery by L. Mond et al. in 1910.¹

The generation of moderately air stable Co-acetylene complexes is the key property of this reagent. These complexes are formed at ambient temperature by stirring solutions of $\text{Co}_2(\text{CO})_8$ and the alkyne (Figure 1). Purification by silica gel chromatography affords the pure products.

Figure 1

The synthesis of $\text{Co}_2(\text{CO})_8$ usually requires high pressures of CO or CO/H_2 depending on the oxidation state of the starting material.² Moreover $\text{Co}_2(\text{CO})_8$ is commercially available from all major suppliers and often no further purification is necessary.

Abstracts

The Pauson–Khand reaction is probably the most widely known process involving $\text{Co}_2(\text{CO})_8$.³ In this reaction cyclopentenones are formed by a cobalt-mediated [2+2+1] cycloaddition of an alkyne, an alkene and CO in a highly convergent manner. The sterically most demanding substituent of the acetylene is incorporated in α -position to the carbonyl group regioselectively. Pauson–Khand reactions were carried out under high pressure and temperature but recent advances allow the use of catalytic amounts of $\text{Co}_2(\text{CO})_8$ under significantly milder reaction conditions.⁴ Thus, in the presence of additives such as N-oxides or primary amines the reaction proceeds at ambient temperature under atmospheric pressure.

Dicobalt hexacarbonyl-stabilized propargyl cations react with a wide variety of nucleophiles. This process is commonly referred to as the Nicholas reaction.⁵ The cation is formed by treatment of a cobalt-complexed propargyl ether with Lewis acids such as $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The liberation of the free alkyne is accomplished oxidatively by cerium ammonium nitrate or *N*-methylmorpholine-*N*-oxide. Approaches towards an enantioselective variation have also been described.⁶

Combinations of Nicholas and Pauson–Khand reactions have been successfully applied in natural product synthesis. A nice example is the synthesis of (+)-epoxydictymene.⁷ The Nicholas reaction served for the closure to the eight-membered ring whereas the two newly formed five-membered rings were formed by a Pauson–Khand reaction.

Complexation of alkynes with $\text{Co}_2(\text{CO})_8$ can also be used to decrease the reactivity of a triple bond. The cobalt complex protects the alkyne from addition reactions such as reductions and hydroborations.⁸ Endiynes are prevented from undergoing undesired Bergman cycloaromatization during synthesis, handling and storage of these sensitive compounds.⁹

The reagent $\text{Co}_2(\text{CO})_8$ is further known to mediate cyclotrimerization of alkynes to benzene derivatives.¹⁰ Bulky substituents, however, cause the formation of cyclopentadienones exclusively.¹¹

In boiling ethereal solution complexes of 1-(1-alkynyl)cyclopropanols rearrange to 2-cyclopenten-1-ones. A catalytic variation, which uses tri(*o*-isopropylphenyl)phosphite as an additive has also been described.¹²

Promoted by $\text{Co}_2(\text{CO})_8$ in acetonitrile 4-isoxazolines are rearranged to 2-acylaziridines in yields up to 92% with varying selectivities.¹³

References

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