SYNLETT Spotlight 119

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

**Molybdenum Hexacarbonyl**

[Mo(CO)₆]

Compiled by Marco Marradi

Marco Marradi took his Degree in Chemistry in 2001 at the University of Florence, where he is currently working on his PhD thesis under the supervision of Prof. A. Goti. His research focuses on the synthesis of chiral nitrones from sugars and their transformation into biologically interesting molecules.

Dipartimento di Chimica Organica “Ugo Schiff”, Università degli Studi di Firenze, Polo Scientifico, via della Lastruccia 13, I-50019 Sesto Fiorentino (FI), Italy
E-mail: marco.marradi@unifi.it

Introduction

Molybdenum hexacarbonyl [Mo(CO)₆] is a stable crystalline solid with an octahedral geometry (Figure 1). It is generally prepared by reductive carbonylation of molybdenum halides, or is obtained from commercial sources. Mo(CO)₆ finds use as catalyst or reagent in several processes, by itself or tuning its reactivity by ligand exchange. Replacement of the carbonyl ligands by both p and s donors affords a large number of different molybdenum complexes which have found use in organic synthesis. The use of chiral ligands allows high levels of regio- and enantioselectivity to be attained.²

Abstracts

(A) The use of a thermostable catalytic system in combination with Mo(CO)₆ allowed the synthesis of benzofuranones starting from bromobenzyl alcohols.³a Indanones were obtained under similar conditions using ortho-bromo(chloro)styrenes.³b A variant was performed by using polymer-supported amines for the synthesis of amides from aryl halides.³c A convenient synthesis of α-methyl-γ-butyrolactones from allenyl carbonyls was performed by a DMSO-promoted carbylation.³d These reactions enlighten the role of Mo(CO)₆ as a source of CO.

(B) ‘Instant’ catalysts formed from Mo(CO)₆ and phenols have been developed for alkyne metathesis.⁴a,b Pre-heating activation of catalytic systems consisting of Mo(CO)₆ and 4-chlorophenol has increased the yields of productive enyne metathesis.⁴a,d This procedure was used to dimerize ortho-alkoxypropynylbenzenes and to afford ring-closing alkyne metathesis (RCAM) products from dipropynyl. The use of 2-fluorophenol in place of 4-chlorophenol led to a more reactive and friendly catalyst, which has been employed not only in RCAM, but also in alkyne homodimerizations (HD) and cross metatheses (CM).⁴e,f

(C) Mo(CO)₆ was reported to effect Pauson–Khand reactions of enynes to afford cyclopentenones.⁵a,b Chiral alkynyl allenes afforded enantioenriched α-alkylidene cyclopentenones.⁵c,d Under the same conditions, functionalized difluoroalenes underwent intramolecular [2+2] cycloaddition to afford gem-difluoro bicyclo[4.2.0] systems, instead of the expected Pauson–Khand products.⁵e A tandem Pauson–Khand reaction of bisyne-bisallenles to [5.5.5.5] tetracycles has been reported by Cook, who used a saturated solution of Mo(CO)₆.⁵f

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(D) Mo(CO)₆ has catalyzed the cycloisomerization of 1-alkyn-4-ols to 2,3-dihydrofurans and the isomerization of epoxalkynes to furans.²⁶ Cyclizations of allylphosphines with skeletal rearrangement to benzopyrans have also been performed.²⁶a Friedel–Crafts alkylations have been reported, too.²⁶d

(E) Mo(CO)₆ has been used to reduce the N–O bonds of isoxazoles, ²⁶b–h isoxazolines, ²⁶i–k and 1,2-oxazines.²⁶j Variants employed sub-stoichiometric amounts of Mo(CO)₆ in the presence of NaBH₄,²⁶i or a decomplexing work-up on silica gel.²⁶j The selective reduction of azides,²⁶k nitro compounds²⁶b and hydroxylamines²⁶h to amines and deoxygenation of epoxides²⁶j have also been accomplished.

(F) Mo(CO)₆ behaved as a catalyst for the mild oxidation of 2,5-diketofurans to E or Z (depending on the use of a base) endones using cumyl hydroperoxide (CHP).²⁶b Diones gave peroxypyrroles in moderate yields, irrespective of the C=C bond configuration, when C=C bond rearrangements have also been performed.²⁶f This indicates that Mo(CO)₆ can be employed not only in reduction processes, but also in oxidations.

References


