SYNLETTL

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]

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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.

Abstracts

(A) The use of a thermostable catalytic system in combination with Mo(CO)₆ allowed the synthesis of benzofuranones starting from bromobenzyl alcohols. Indanones were obtained under similar conditions using ortho-bromo(chloro)styrenes. A variant was performed by using polymer-supported amines for the synthesis of amides from aryl halides. A convenient synthesis of α-methylene-γ-butyrolactones from allenyl carbonyls was performed by a DMSO-promoted carbonylation. 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. Pre-heating activation of catalytic systems consisting of Mo(CO)₆ and 4-chlorophenol has increased the yields of productive enyne metathesis. This procedure was used to dimerize ortho-alkoxynpropynylbenzenes and to afford ring-closing alkyne metathesis (RCAM) products from dipropynyls. 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).

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

Figure 1
(D) Mo(CO)₆ has catalyzed the cycloisomerization of 1-alkyn-4-ols to 2,3-dihydrofurans and the isomerization of epoxalkynes to furans.¹⁶ Cyclizations of allylphenylethers with skeletal rearrangement to benzopyrans have also been performed.¹⁶b Friedel–Crafts alkylations have been reported, too.¹⁶d

(E) Mo(CO)₆ has been used to reduce the N–O bonds of isoxazoles,¹⁷a,b isoxazolines,¹⁷c,d and 1,2-oxazines.¹⁷e,f Variants employed sub-stoichiometric amounts of Mo(CO)₆ in the presence of NaBH₄,¹⁷g or a decomplexing work-up on silica gel.¹⁷h The selective reduction of azides,¹⁷i nitro compounds¹⁷j and hydroxylamines¹⁷k to amines and deoxygenation of epoxides¹⁷l have also been accomplished.

(F) Mo(CO)₆ behaved as a catalyst for the mild oxidation of 2,5-dialkylfurans to E or Z (depending on the use of a base) enediones using cumyl hydroperoxide (CHP).¹⁷m Diones gave peroxopyrrolidines in moderate yields, irrespective of the C=C bond configuration, when t-butyldihydroperoxide (TBHP) was used.¹⁷n¹⁷o This indicates that Mo(CO)₆ can be employed not only in reduction processes, but also in oxidations.

References


