

SYNLETT Spotlight 119

Molybdenum Hexacarbonyl [Mo(CO)₆]

Compiled by Marco Marradi

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

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.

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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.¹ Replacement of the carbonyl ligands by both p and s donors affords a large number of different molybde-

num complexes which have found use in organic synthesis. The use of chiral ligands allows high levels of regio- and enantioselectivity to be attained.²

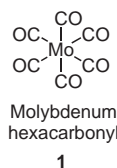
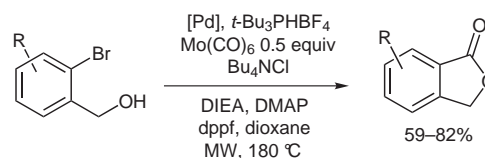


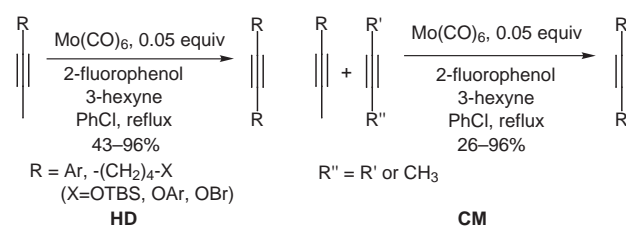
Figure 1

Abstracts

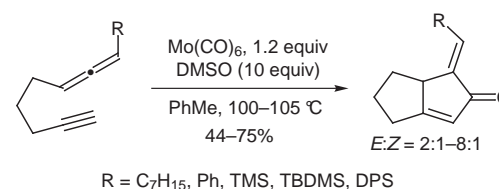
(A) The use of a thermostable catalytic system in combination with Mo(CO)₆ allowed the synthesis of benzofuranones starting from bromobenzyl alcohols.^{3a} Indanones were obtained under similar conditions using *ortho*-bromo(chloro)styrenes.^{3b} A variant was performed by using polymer-supported amines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



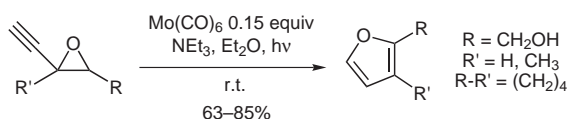
(B) 'Instant' catalysts formed from Mo(CO)₆ and phenols have been developed for alkyne metathesis.^{4a,b} Pre-heating activation of catalytic systems consisting of Mo(CO)₆ and 4-chlorophenol has increased the yields of productive enyne metathesis.^{4c,d} This procedure was used to dimerize *ortho*-alkoxypropynylbenzenes 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).^{4e,f}



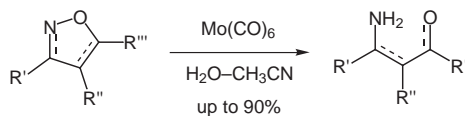
(C) Mo(CO)₆ was reported to effect Pauson–Khand reactions of enynes to afford cyclopentenones.^{5a,b} Chiral alkynyl allenenes afforded enantioenriched α -alkylidene cyclopentenones.^{5c,d} Under the same conditions, functionalized difluoroallenes underwent intramolecular [2+2] cycloaddition to afford *gem*-difluoro bicyclo [4.2.0] systems, instead of the expected Pauson–Khand products.^{5e} A tandem Pauson–Khand reaction of bisyne-bisallenenes to [5.5.5] tetracycles has been reported by Cook, who used a saturated solution of Mo(CO)₆.^{5f}



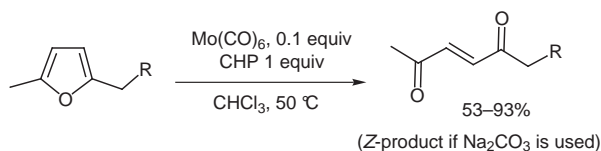
(D) $\text{Mo}(\text{CO})_6$ has catalyzed the cycloisomerization of 1-alkyn-4-ols to 2,3-dihydrofurans and the isomerization of epoxyalkynes to furans.^{6a} Cyclizations of allylphenylethers with skeletal rearrangement to benzopyrans have also been performed.^{6b,c} Friedel–Crafts alkylations have been reported, too.^{6d}



(E) $\text{Mo}(\text{CO})_6$ has been used to reduce the N–O bonds of isoxazoles,^{7a,b} isoxazolines,^{7c–e} isoxazolidines^{7f} and 1,2-oxazines.^{7g,h} Variants employed sub-stoichiometric amounts of $\text{Mo}(\text{CO})_6$ in the presence of NaBH_4 ,^{7h} or a decomplexing work-up on silica gel.⁷ⁱ The selective reduction of azides,^{7k} nitro compounds^{7k} and hydroxylamines⁷ⁱ to amines and deoxygenation of epoxides^{7l} have also been accomplished.



(F) $\text{Mo}(\text{CO})_6$ 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).^{8a} Diones gave peroxypyranones in moderate yields, irrespective of the C=C bond configuration, when *t*-butylhydroperoxide (TBHP) was used.^{8a,b} This indicates that $\text{Mo}(\text{CO})_6$ can be employed not only in reduction processes, but also in oxidations.



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