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An Alternative Procedure for Preparing Cationic η^4-Diene- Molybdenum Complexes from the Corresponding Allylic Precursors.

Emelie Bjurling and Carl-Magnus Andersson*

Organic Chemistry 1, Chemical Center, Lund University, P.O. Box 124, S-221 00 Lund, Sweden.

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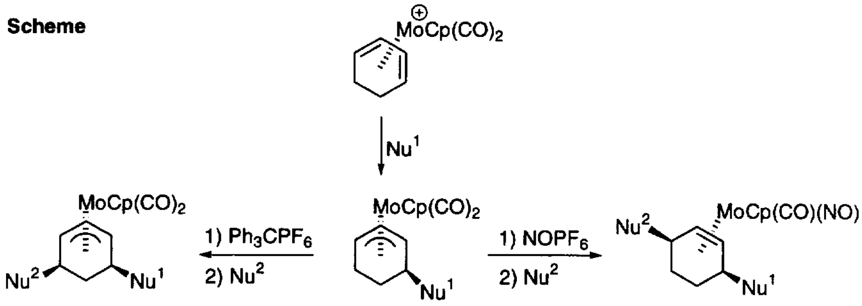
Abstract

In the presence of hexafluoroisopropanol, bromotriphenylmethane effects hydride abstraction from Mo(η^3-allyl)(CO)$_2$Cp providing Mo(η^4-diene)(CO)$_2$CpBr in good yields. © 1999 Elsevier Science Ltd. All rights reserved.

Transition metal π-complexes constitute an invaluable source of electrophiles for carbon-carbon bond forming reactions. While emphasis has been placed on catalytic reactions in recent years, transformations involving isolable organometallic intermediates remain attractive for certain preparative applications [1]. In particular, organometallic strategies in which temporary coordination of the organic ligand to a metal moiety supports sequential metal-assisted reactions are of significance within organic synthesis. An elegant example of such a strategy is the multiple activation/nucleophilic addition reactions involving molybdenum π-complexes (Scheme). This chemistry, largely developed by Faller, Green, Liebeskind and Pearson [2] allows for a very high degree of regio- and stereocontrol during the nucleophilic addition events.

Scheme



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*Fax: + 46 46 222 4119; E-mail: Carl-Magnus.Andersson@orgk1.lu.se

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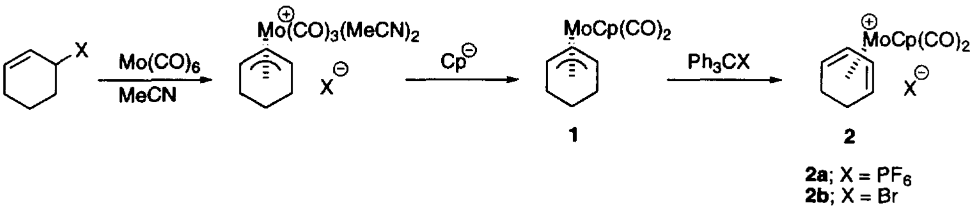
Although cationic complexes of the type Mo(η^4-1,3-diene)(CO)$_2$(η^5-L) are available *via* direct complexation of the diene in certain cases [3], the most general and widely used preparative route [4] utilises displacement of an allylic leaving group with a Mo(0) species (equation 1). The cationic diene complex (**2**) is obtained through hydride abstraction from **1** following the introduction of a η^5-ligand, most commonly as cyclopentadienide ion [5]. Hydride abstraction, of course, remains the only pathway for reactivation of allylic complexes derived from nucleophilic addition (Scheme). Although hydride abstraction using Ph_3CPF_6 or Ph_3CBF_4 has proved to be a reliable route to simple cationic diene complexes, its application to more highly substituted, or labile, precursors has been reported to produce unsatisfactory yields and/or serious side reactions. The trityl salts are highly moisture sensitive, requiring strictly anhydrous conditions to avoid decomposition to triphenylmethanol and acid. Accordingly, several of the published examples of the unsuccessful application of trityl-mediated hydride abstraction have implicated trace acidic impurities as the cause of loss of labile functionalities [6].

Equation 1.



We recently encountered several cases of unsatisfactory hydride abstractions and sought to develop an alternative procedure, involving more convenient and controlled conditions. As an approach to generating the trityl cation *in situ*, we relied upon the ability of the very strongly hydrogen bonding solvent 1,1,1,3,3,3-hexafluoroisopropanol (HFiP) to sustain appreciable concentrations of carbenium ions [7]. This solvent has recently been shown to promote the dissociation of certain halides [8], suggesting its usefulness in replacing expensive and labile, ionic trityl salts with a stable precursor such as bromotriphenylmethane.

Initial experiments were performed to confirm that HFiP did not interfere with hydride abstraction or product isolation in reactions of **1** [5] with trityl hexafluorophosphate. As shown in the Table, the isolated yield [9] of dicarbonyl-η^5-(cyclopentadienyl)-η^4-(cyclohexadiene) molybdenum hexafluorophosphate (**2a**) [5] (entries 1 and 2) was unaffected by the presence of 20% (v/v) of HFiP. More importantly, a similar reaction outcome was observed when Ph_3CPF_6 was replaced by the stable Ph_3CBr under otherwise identical conditions (entry 3). This reaction allowed the isolation of the new bromide **2b** [10], the identity of which was corroborated by its quantitative conversion into **2a** upon treatment with aqueous NH_4PF_6. Neither reaction temperature (entry 4) nor the order of addition of reactants had a profound influence on the

Table: Results from hydride abstractions under various conditions (equation 1).

Entry	Allylic compound	Solvent CH_2Cl_2 / HFiP	Temperature	X in Ph_3CX	Product (Yield, %)[a]
1	**1**	100/0	0 °C	PF_6	**2a** (79)
2	**1**	80/20	0 °C	PF_6	**2a** (83)
3	**1**	80/20	0 °C	Br	**2b** (76)
4	**1**	80/20	rt	Br	**2b** (81)
5	**1**	100/0	0 °C	Br	(0)[b]
6	**1**	80/20 + H_2O[c]	0 °C	Br	**2b** (86)

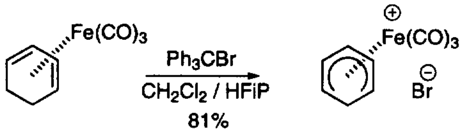
a) Isolated yield. b) This reaction returned a small amount of an unidentified red solid. c) Ten equivalents, relative to bromotriphenylmethane, were added.

reaction outcome. A control experiment (entry 5), omitting HFiP, confirmed its critical role in promoting hydride abstraction by bromotriphenylmethane.

The nucleophilicity of Lewis bases is substantially attenuated in neat HFiP [7] but we were still surprised to find that the presence of 10 equivalents of water did not at all interfere with the hydride abstraction process (entry 6). This result was particularly gratifying in that it indicated that our procedure should be a convenient alternative to the existing methodology. An additional, fortuitous, advantage of our protocol is that the reaction products remain soluble, allowing the monitoring of reaction progress by spectroscopy.

The open dicarbonyl-η^5-(cyclopentadienyl)-η^4-(butadiene) molybdenum bromide was similarly prepared using the Ph_3CBr/HFiP conditions, but, as expected, in a substantially lower yield (20%) [11]. A preliminary experiment also allowed the conversion of tricarbonyl-η^4-(cyclohexadiene)iron [12] into tricarbonyl-η^5-(cyclohexadienyl)iron bromide [13] in good yield (equation 2), suggesting that the present procedure might be generally applicable to the preparation of cationic π-complexes.

Equation 2.



In conclusion, we have shown that certain cationic transition metal π-complexes can be prepared from the neutral precursors of next lower hapticity through the action of bromotriphenylmethane in the presence of hexafluoroisopropanol. We belive that the reaction takes place through *in situ* dissociation of the bromide and subsequent hydride abstraction by trityl cation. The herein reported procedure affords yields comparable to those reported for the traditional conditions, but should provide a convenient alternative since it avoids the use of labile reagent and meticulous drying. Also, our approach might prove useful in cases where fluorine-containing counterions are undesirable, or when acidic impurities derived from trityl salts present complications. Extended studies of Ph_3CBr/HFiP in hydride abstractions will be disclosed in due course.

Acknowledgements

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References and Notes

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[8] Dr. Ola Persson, Lund University, personal communication.

[9] Cationic complexes were isolated by precipitation using degassed diethyl ether or pentane, followed by decantation of the solvent. The product was purified through repeated triturations with diethyl ether.

[10] ^1H-NMR ($CDCl_3$) δ 6.71 (dd, 2H, J = 6.1 and 3.3 Hz), 6.08 (s, 5H, Cp), 5.05 (m, 2H), 2.26 (brd, 2H, J = 13.6 Hz) and 2.04 (brd, 2H, J = 13.6 Hz). IR(KBr): 2000 and 1934 cm^{-1}. HRMS (FAB+): $C_{13}H_{13}MoO_2$ (M+), Found: 298.9963, Calc: 298.9969.

[11] Hydride abstraction from open-chain allyl complexes is complicated by conformational factors as well as competing electrophilic attack on carbon, see: Faller JW, Rosan AM. *J. Am. Chem. Soc.*, **1977**, *99*, 4858.

[12] For a review on iron diene and dienyl complexes, see: Pearson AJ. *Iron Compounds in Organic Synthesis*, Academic, London, 1994.

[13] ^1H-NMR (D_2O) δ 6.92 (t, 1H, J = 6 Hz), 5.63 (t, 2H, J = 6 Hz), 3.98 (t, 2H, J = 6 Hz), 2.68 (dt, 1H, J = 15 and 6 Hz) and 1.67 (d, 1H, J = 15 Hz). IR (KBr): 2108 and 2058 cm-1. HRMS (FAB+): $C_9H_7FeO_3$ (M+), Found: 218.9753, Calc: 218.9744.