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Preliminary communication

A CONVENIENT, ONE-STEP SYNTHESIS OF THE CATIONIC η^3-ALLYLMOLYBDENUM COMPLEX $[(\eta^5\text{-}C_5H_5)_2Mo(\eta^3\text{-}C_3H_5)]^+[p\text{-}CH_3C_6H_4SO_3]^-$

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Summary

$[(\eta^5\text{-}C_5H_5)_2Mo(\eta^3\text{-}C_3H_5)]^+$ $[p\text{-}CH_3C_6H_4SO_3]$ is conveniently synthesized by the reaction of $(\eta^5\text{-}C_5H_5)_2MoH_2$ with allyl alcohol in the presence of *p*-toluene sulfonic acid, the mechanism of which is explained by the electrophilic cleavage of the allyl–O bond of the coordinated allyl alcohol.

The cationic η-allyl complex of molybdenum(IV), $[Cp_2Mo(\eta^3\text{-}C_3H_5)]^+$ (Cp = η^5-C_5H_5) was shown to have an interesting reactivity towards nucleophiles such as $NaBH_4$ giving molybdenacyclobutane derivatives [1], which are important in elucidating the mechanism of metal-catalyzed olefin metathesis reactions [1,2]. Although studies on the complex in this respect have developed fairly extensively, the rest of its chemistry has been left unclarified. This may be due in part to the rather tedious method of preparation of the cationic allyl complex which, using Cp_2MoH_2 (I) as the starting material, includes the isolation of very reactive molybdenum-lithium, -aluminum, or -magnesium clusters [1,3]. Here we show that the cationic allyl complex $[Cp_2Mo(\eta^3\text{-}C_3H_5)]^+[p\text{-}CH_3C_6H_4SO_3]^-$ (II) can be readily obtained by a one-step reaction starting from I.

On stirring a solution of I with a large excess of allyl alcohol in the presence of one equivalent of *p*-toluenesulfonic acid monohydrate (TsOH), at room temperature for 5 h under vacuum, the color of the solution changed from yellow into green and finally into red. Evaporation of the unreacted allyl alcohol from the solution left a brown powder which was recrystallized from EtOH to give orange crystals of II in 81% yield. Recrystallization from EtOH gave an analytically pure sample of II * in

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* II: ^{1}H NMR $[(CD_3)_2SO]$ δ (ppm): 5.47 (5H, s, Cp), 5.23 (5H, s, Cp), 4.15 [1H, tt, $J(H_cH_{syn})$ 9.5 Hz, $J(H_cH_{anti})$ 14.5 Hz, H_c], 3.43 [2H, dd, J 9.5 Hz, $J(H_{syn}H_{anti})$ 3.3 Hz, H_{syn}], 2.08 (2H, dd, J 14.5 Hz, J 3.3 Hz, H_{anti}). Resonances due to the TsO protons are omitted. Found: C, 54.88; H, 5.28; S, 7.19. $C_{20}H_{22}O_3SMo$ calcd.: C, 54.79; H, 5.06; S, 7.31%.

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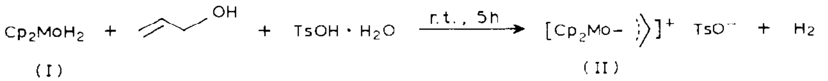
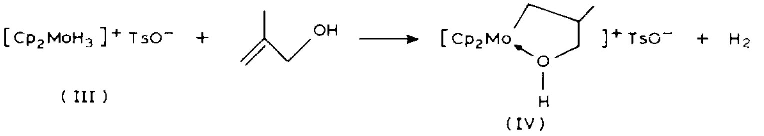
62% yield. The reaction was accompanied by evolution of H_2 in an amount equivalent to that of II.

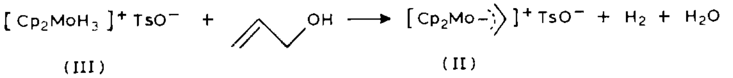

(1)

Use of TsOH in an amount precisely equivalent to that of the dihydride (I) is essential since an uncharacterized light-green compound was obtained instead of II when more than one equivalent of TsOH was employed. When I was heated at 50°C in allyl alcohol in the absence of TsOH no reaction took place.

Recently, we reported the preparation of the cationic trihydridomolybdenum(VI) complex $[Cp_2MoH_3]^+$ TsO^- (III) by the reaction of I with TsOH in Et_2O and the reaction of III with substituted allylic alcohols such as β-methallyl alcohol giving the γ-hydroxyalkyl complex (IV) [4,5].


(2)

When allyl alcohol was allowed to react with cation III at 50°C, the cationic allyl complex II instead of the γ-hydroxyalkyl complex, was obtained in 47% yield. This result indicates that the reaction shown in eq. 1 involves initial formation of the trihydrido cation III, which then reacts with allyl alcohol giving II.


(3)

Complex II was also obtained by a reaction similar to eq. 3 using allyl ethyl ether, diallyl ether (in tetrahydrofuran solution), or allyl acetate (in EtOH solution) in place of allyl alcohol. The reactivities of diallyl ether and allyl acetate were much lower than those of the other two. Allyl cyanide, allyl chloride, and allyl phenyl ether did not give allyl complex II. The observed order of reactivities of CH_2=$CHCH_2Z$ in reaction 3 was opposite to the reported tendencies for the palladium(0)-assisted cleavage of the C–Z bond of allylic compounds in which the oxidative addition to metal(0) was assumed to take place [6].

The reaction of allyl alcohol with the trideuterido analogue of III, $[Cp_2MoD_3]^+[TsO]^-$ (III-d_3) *, gave the η-allyl complex II, in which no deuterium incorporated was observed as deduced from its ^1H NMR spectrum.

These findings exclude the possibility of the mechanisms involving either direct oxidative addition of the allylic compound accompanied by allyl–O bond cleavage or olefin insertion into the metal–hydrogen bond giving an alkylmolybdenum intermediate, although both mechanisms have been previously proposed for the metal-assisted allyl–O cleavage with nickel(0), and palladium(0) [6,7], and cobalt, rhodium and ruthenium hydrides [8], respectively. In the present system, trihydrido cation III formed initially may release hydrogen to give the reactive monohydrido

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* Trideuterido cation (III-d_3) was prepared by treating III with EtOD at room temperature for 22 h and was used in situ for the subsequent reaction with allyl alcohol.

cation $[Cp_2MoH]^+TsO^-$ which has been known to be in equilibrium with its neutral isomer, $[Cp_2Mo(H)OTs]$ [4]. TsOH in these intermediates may be replaced with allyl alcohol to give a molybdenum(II) intermediate in which allyl alcohol is coordinated through its π electrons. The coordinated allylic ligand may be electrophilically attacked at the oxygen atom by the TsOH liberated to give II. The latter process was reported for the formation of cationic η-allyliron complexes by acidolysis of the coordinated allyl ethers [9].

The convenient, one-step synthesis of the η-allylmolybdenum complex via electrophilic cleavage of the allyl–O bond of allyl alcohol, in which the labile properties of the TsO group as a ligand seem to play an important role, may contribute to further development of the chemistry of η-allyl complexes especially with reference to metal mediated catalytic allylation [10].

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