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SELECTIVE REDUCTION OF ORGANIC HALIDES AND α-DIKETONES BY $MoH_2(\eta\text{-}C_5H_5)_2$

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Summary

A systematic study of reaction of organic halides with MoH_2Cp_2 (Cp = $\eta^5\text{-}C_5H_5$) was performed and the results were compared with those of WH_2Cp_2, $MoH_4(dppe)_2$ (dppe = 1,2-bis(diphenylphosphino)ethane), and $FeH_2(dppe)_2$. Among many organic halides, $\mathrm{Ph}\overline{\mathrm{CH{-}CBr_2{-}CH_2}}$ was reduced stereoselectively by MoH_2Cp_2 to the monobromo stage. The reaction mechanism was studied with optically active $PhCH(Cl)CO_2Et$ and also with addition of some radical reagents to reveal a radical-chain mechanism. Selective reduction of α-dicarbonyl compounds to the α-ketol was effected by MoH_2Cp_2. A similar radical mechanism is proposed for this novel reaction.

Reductive dehalogenation of organic halides by metal hydrides, e.g., $LiAlH_4$, $NaBH_4$, $NaBH_3(CN)$, or LiCu(R)H, has been studied extensively in efforts to achieve regio- and stereo-selectivity [1]. Recently, some new metal hydrides, $LiBH(Et)_3$, or 9-borabicyclo[3,3,1]nonanatelithium, have achieved some of the desired selectivity [2]. The dehalogenation reactions of transition metal hydrides and their mechanisms, however, have been neither fully elucidated nor extensively explored. Recent advances in the chemistry of thermally stable transition metal polyhydrides led us to examine their application in the dehalogenation of organic halides. We have studied the reactions of $MH_2(\eta\text{-}C_5H_5)_2$ (M = Mo, W, $\eta^5\text{-}C_5H_5$ = Cp), $FeH_2(dppe)_2$ or $MH_4(dppe)_2$ (M = Mo, W; dppe = 1,2-bis(diphenylphosphino)ethane) with various organic halides. Since reactions of WH_2Cp_2 with some organic polyhalides have already been reported by Green and Knowles [3], we directed our attention particularly to the scope, selectivity and mechanisms.

From the mechanistic point of view, the reaction of organic halides with labile, low-valent transition metal complexes, e.g., $Pt(PPh_3)_4$, often is complicated by the presence of highly reactive species formed by dissociation of the ligands. A conspicuous feature of the coordinatively saturated hydrides used in the present study is the fact that they do not dissociate during the reaction. Therefore, the mechanism should be simplified for analysis of the reaction path. In the course of the present study, selective reduction of one of the carbonyl groups of α-diketones was found to be effected by MoH_2Cp_2. The mechanism and stereochemistry of these reductions of alkyl halides or α-diketones with transition metal polyhydrides were studied to examine the possible radical character of the reactive intermediates involved.

Results and discussion

Trends in the reactivity of alkyl halides toward MoH_2Cp_2

Generally, the reactivity of alkyl halides toward MoH_2Cp_2 is in a relative order similar to that observed toward $SnHR_3$. Thus, MeI or EtI reacted even at room temperature, but even reactive alkyl chlorides (allyl, benzyl) were inert. The relative reactivity order for the variation of halogen in RX is I > Br > Cl > F, and of the alkyl group is $CH_2Ar > CH_2\text{-}CH{=}CH_2 > CH_2\text{-}CO_2R > CH_3$ (Table 1). Alkenyl or aryl halides are much less reactive. Thus, ClCH=CHCl or PhCH=CHBr reacted only slowly at 60° C. Iodobenzene did not react even at 100° C. Polyhalogenated compounds are reduced in a stepwise fashion.

$$PhCHCl_2 \xrightarrow{\text{room temp.}} PhCH_2Cl \xrightarrow{80^\circ C} PhCH_3$$

$$CCl_4 \xrightarrow{-10^\circ C} CHCl_3 \xrightarrow{30^\circ C} CH_2Cl_2$$

The corresponding reactions of WH_2Cp_2, in general, were slower than those of MoH_2Cp_2. A competition reaction of CH_3I for an equimolar mixture of MoH_2Cp_2 and WH_2Cp_2 gave only MoI_2Cp_2. Coordinately saturated polyhydrides, $MoH_4(dppe)_2$, $WH_4(dppe)_2$ and $FeH_2(dppe)_2$, are generally unreactive to the usual alkyl halides when the reactions are attempted in the dark.

Perfluoro compounds, e.g., perfluoroheptane-1 or perfluorobutene-2, react

TABLE 1

REACTIVITY OF ORGANIC HALIDES OF DIFFERING STRUCTURES TOWARD MoH_2Cp_2

Reaction at room temperature [a]		No reaction (or only slight reaction)
in 1 h	in 1 day	in 1 day
CF_3I	C_2H_5I	PhI
CH_3I	$n\text{-}C_3H_7I$	EtBr
CH_2I_2	$i\text{-}C_3H_7I$	n-BuBr
CH_2Br_2	$CH_2{=}CH{-}CH_2Br$	$ClCH_2CH_2Cl$
MeO_2CCH_2I	$BrCH_2CH_2Br$	n-BuCl
$NCCH_2Br$	$PhCH_2Br$	$CHCl{=}CCl_2$
$BrCF_2CF_2Br$	CH_2Cl_2	$PhCH_2Cl$
MeO_2CCH_2Br	$CH_3O_2CCH_2Cl$	$Ph_2C{-}CH_2{-}C(Br)CO_2Et$
$CHCl_3$	$NCCH_2Cl$	
$(CHBrCO_2Me)_2$	$PhCHCl_2$	
	Ph_3CCl	

[a] Reactions run at room temperature (~20° C) in benzene or as the neat liquid with saturated solutions of MoH_2Cp_2. The halogen is replaced with H in the reactions with monohalo compounds. Vicinal dibromides are debrominated to the corresponding olefins. Geminal polyhalides are reduced stepwise (see text).

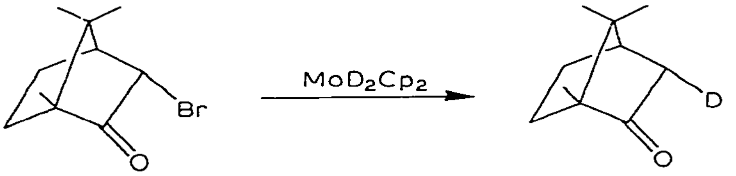
very slowly with MoH_2Cp_2 upon heating to 60—80°C. The deep brown product which was formed was not fully characterized, but preliminary data (IR and ^1H and ^{19}F NMR) indicate it to be MoF_2Cp_2.

The course of the reaction of MoH_2Cp_2 with an excess of allyl bromide was followed by ^1H NMR at 36°C in $(CD_3)_2CO$. The rate, as determined by the decrease of the concentrations of the reactants, was first-order in each reactant. During the kinetic runs, two sharp singlets at δ 5.03 and 5.60 ppm appeared and increased until ca. 50% reaction and then decreased. The peak at δ 5.60 ppm was found to be due to the dissolved $MoBr_2Cp_2$. The observed decrease of the peak is due to the precipitation of this final product. The peak at δ 5.03 ppm decreased at a faster rate prior to the decrease of the peak at δ 5.60 ppm and probably was due to the intermediate species, $MoHBrCp_2$. In support of this, a new hydrido proton signal appeared at δ —9.3 ppm (at lower field from the hydrido NMR peak of MoH_2Cp_2) and decreased synchronously with the peak at δ 5.03 ppm.

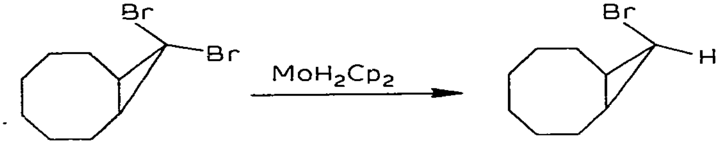
The reaction of MoH_2Cp_2 with benzyl bromide also was examined by ^1H NMR and the appearance of the same two peaks, δ 5.03 and 5.60 ppm, was observed. Continuous NMR observation of these reactions did not give any evidence for a CIDNP effect.

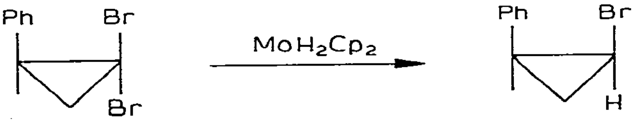
Stereochemistry

Among organic halides with activating α-substituents, an optically active secondary alkyl chloride $PhCH(Cl)CO_2Me$($[\alpha]_D$ (neat) + 58.4°), was examined in its reaction with MoD_2Cp_2 at room temperature. The organic product, $PhCHDCO_2Et$, which was isolated and examined (IR and NMR), was not optically active. For further confirmation, it was converted to the corresponding alcohol by reaction with $LiAlH_4$ in ether and the alcohol also was examined for optical activity: $[\alpha]_D^{20} \sim 0°$. (Optically pure $PhCHDCH_2OH$ has $[\alpha]_D^{25} \pm 1.51°$ (neat) [4]). α-Bromo-*d*-camphor reacted with MoH_2Cp_2 in perdeuteriotoluene for 18 h at 20°C to give camphor and $MoBr_2Cp_2$ in good yields. No deuterium was incorporated from the solvent into the camphor. The reactivity toward MoH_2Cp_2 was as expected for an α-bromoketone (see Table 1). Since the bromine substituent is situated on the chiral carbon atom in α-bromocamphor, the stereochemistry of the debromination was examined with MoD_2Cp_2. The deuterated camphor obtained in the reaction was investigated by ^1H NMR to reveal mostly retention of the stereochemistry at the α-carbon. The extent of deuteriation was found to be about 70% by NMR and by the mass spectrum. The hydrogen incorporated into the camphor seems to be derived from the hydrogen on the Cp ring of MoD_2Cp_2.



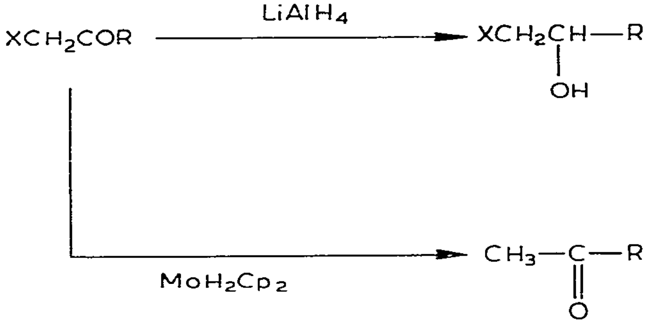
Since MoH_2Cp_2 reduces *gem*-dibromo compounds to the corresponding monobromo stage, the stereochemistry of this reaction was investigated with two cyclopropyl compounds. Thus, 9,9-dibromo-bicyclo[6.1.0]nonane was reduced selectively to the *cis*-monobromo compound and 1,1-dibromo-2-phenylcyclopropane to *cis*-1-bromo-2-phenylcyclopropane. The same type of debromination is known to occur with tin hydrides [5a]. In their reactions the stereoselectivity depended on the steric crowding at the metal. The observed high selectivity in the present reactions indicates severe steric crowding at the molybdenum site.





MoD_2Cp_2 as a reagent for deuteration

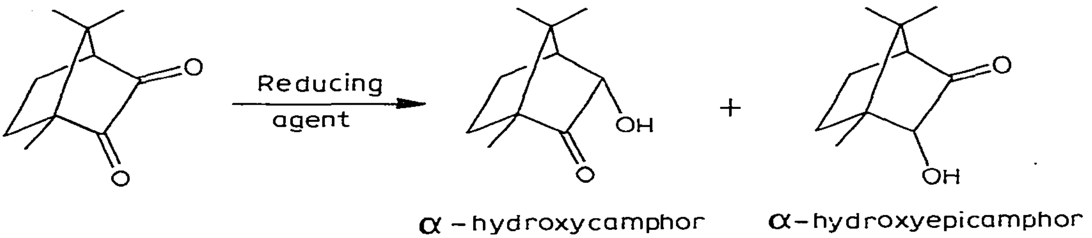
The behavior of MoH_2Cp_2 is different from that of typical hydride reagents, e.g. $LiAlH_4$, in its reaction with α-haloketones. $LiAlH_4$ reduces the carbonyl group of the haloketone but MoH_2Cp_2 replaces halide with hydrogen. This reaction can be utilized to introduce one D atom into the α-methyl or α-methylene group of ketones. One interesting use of MoD_2Cp_2 thus is as a reagent for the introduction of a deuterium atom into a specific position of an organic molecule. Reaction of MoD_2Cp_2 with α-bromocamphor gave α-*endo*-d_1-camphor. α,α-Dichlorotoluene gave α-chloro-α-*d*-toluene. The deuteriation reagent, MoD_2Cp_2, can be prepared simply by dissolution of MoH_2Cp_2 in a mixture of D_2O/CH_3CN at room temperature, followed by evaporation of the solution. The deuterium content can be improved by repetition of this procedure. WD_2Cp_2 can be obtained similarly from WH_2Cp_2.



$$MoH_2Cp_2 \xrightarrow{D_2O \text{ in } CH_3CN} MoD_2Cp_2$$

Selective reduction of α-dicarbonyl compounds

Benzil and phenylglyoxylate were slowly reduced by MoH_2Cp_2 in toluene to give benzoin(α-ketoalcohol) and ethyl mandelate, respectively. The reaction of benzil gave a deep brown complex, $MoCp_2(PhCO\cdot\dot{C}OPh)$, in which the diketone coordinates as a diphenylethylenediolato ligand, $Ph{-}C(O^-){=}C(O^-)Ph$. The stereochemistry and regioselectivity of this reduction was investigated in the reduction of camphorquinone. The reaction occurred at 80°C in 2 h to give α-hydroxycamphor in which one isomer predominated (see below). By contrast, similar reduction of camphorquinone with Zn/AcOH gave almost equal amounts of the isomeric α-hydroxycamphors [6]. The reaction of these α-dicarbonyl compounds with WH_2Cp_2 did not proceed even when they were heated at 80°C.



MoH_2Cp_2	9/1
Zn/AcOH	1/1

Reaction of MoH_2Cp_2 with alkyl halides in the presence of free radical or radical-trapping reagents

The mechanism of oxidative addition of alkyl halides to low-valent transition metal complexes has been investigated by several groups and a radical chain or non-chain mechanism have been proposed [7]. The present reaction is considered to be similar to the oxidative addition in that the initial interaction involves interaction of a low-valent metal complex with a reactive alkyl halide.

Small amounts of various free radical reagents, e.g., galvinoxyl, 1,3,5-triphenylverdazyl, *N,N*-diphenylpicrylhydrazyl and radical trapping reagents, e.g., duroquinone, were found to inhibit the reaction of MoH_2Cp_2 with α-bromocamphor at 20°C for several hours. On heating at 80°C, the reaction proceeded slowly. The reaction of 9,9-dibromobicylo[6,1,0]nonane with MoH_2Cp_2 was also strongly hindered by duroquinone for nearly one day. The inhibition strongly suggests that these reactions follow a radical chain pathway. No radical polymerization of methyl acrylate was observed with the system WH_2Cp_2/CCl_4 at 20°C. Thermally induced radical polymerization (at 120°C) of methyl acrylate is inhibited with MoH_2Cp_2 [8].

The stoichiometric reaction of MoH_2Cp_2 with di-t-butylnitroxide in toluene gave a deep green, air-sensitive solution. Addition of $PhCH(Cl)CO_2Et$ to the green solution yielded a brown precipitate of $MoCl_2Cp_2$. The solution species which resulted in the stoichiometric reaction of MoH_2Cp_2 with $t\text{-}Bu_2NO^\bullet$ showed no definite ESR signals. The accelerating effect of a small amount of $t\text{-}Bu_2NO^\bullet$ in the reduction of $PhCH(Cl)CO_2Et$ by MoH_2Cp_2 was demonstrated in a separate experiment in toluene. The dark brown precipitate of $MoCl_2Cp_2$ was formed in 10 min in the accelerated reaction. Without $t\text{-}Bu_2NO^\bullet$, the same reaction gave the precipitate in 1 h and was complete only after standing overnight.

Reaction mechanism

(a) Reaction of alkyl halides with MH_2Cp_2. The results described above are now combined for consideration of the reaction mechanism. A radical chain mechanism (eq. 1—4) is implied by (a) the presence of an induction period for relatively unreactive alkyl halides, (b) the stereochemical result (racemization at the chiral α-carbon), and (c) the inhibition of the reaction by suitable radical-trapping reagents. The relative reactivity trend with variation of the structure of alkyl halides also can be interpreted in terms of the ease in halogen atom abstraction to give the corresponding alkyl radicals.

$$R^{\cdot} + MH_2Cp_2 \rightarrow R{-}H + {}^{\cdot}MHCp_2 \qquad (1)$$

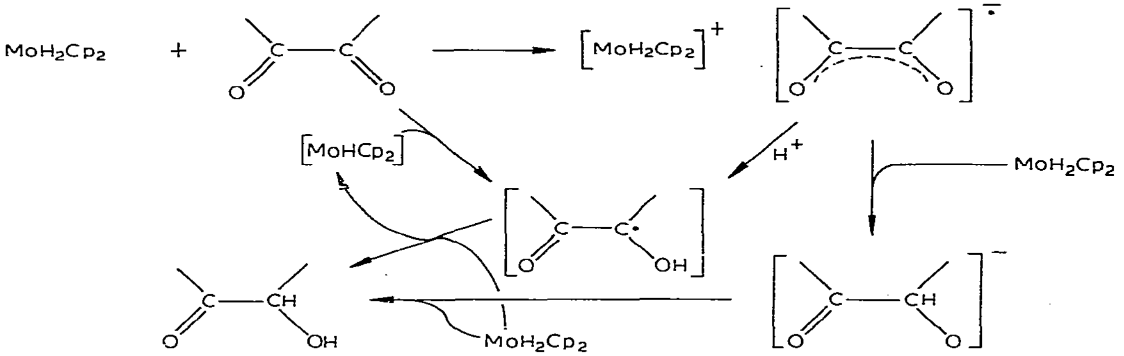
$$R^{\cdot} + MHXCp_2 \rightarrow R{-}H + {}^{\cdot}MXCp_2 \qquad (2)$$

$${}^{\cdot}MHCp_2 + R{-}X \rightarrow MHXCp_2 + R^{\cdot} \qquad (3)$$

$${}^{\cdot}MXCp_2 + R{-}X \rightarrow MX_2Cp_2 + R^{\cdot} \qquad (4)$$

A similar mechanism has been proposed for reaction of tin or germanium hydrides [11]. The abstraction of halogen probably is a relatively slow process. The rate law observed in reaction of allyl bromide with MoH_2Cp_2 lends support to this inference.

(b) Reaction of α-dicarbonyl compounds with MoH_2Cp_2. The radical character of this reaction is shown by the strong inhibition observed on addition of duroquinone. The radical species probably is generated by charge transfer from MoH_2Cp_2 to the dicarbonyl compounds. One electron reduction of α-dicarbonyl compounds to radical anions is well known [13]. By contrast, one electron oxidation of MoH_2Cp_2 destroys its stable electronic configuration and would result in hitherto uncharacterized unstable cationic species $[MoH_2Cp_2]^+$. This reactive hydride would then react with the dicarbonyl radical anion as shown below to form the hydrogenated product.



The regioselectivity observed in reduction of camphorquinone indicates preferential attack at the less-hindered side of the quinone by the hydridomolybdenum species. This type of selection could never be achieved with conventional reducing agents such as Zn/AcOH.

The lability at the metal—hydrogen bonds seems to be an important factor in this reaction since the isostructural tungsten hydride, WH_2Cp_2, did not reduce α-dicarbonyl compounds, even at higher temperature.

(c) Reaction of $MoH_4(dppe)_2$ with alkyl halides. The polyhydrides of general formula, $MH_n(dppe)_2$ (M = Fe, n = 2; M = Mo or W, n = 4) react only slowly with CCl_4 in the dark. On exposure to sunlight, the reaction readily proceeded to give the corresponding dichloro complexes, $MCl_2(dppe)_2$ (M = Fe, Mo, W). These coordinatively saturated polyhydrides are generally less reactive to alkyl halides as compared with MH_2Cp_2 type hydrides. They also are inert to α-dicarbonyl compounds such as benzil at ambient temperature. The inertness can be correlated with the inability of these polyhydrides to form charge transfer complexes with weak electron acceptors such as fumaronitrile or maleic anhydride [12].

Experimental

Materials and apparatus. MH_2Cp_2 (M = Mo, W) [14], $FeH_2(dppe)_2$ [15], $MH_4(dppe)_2$ (M = Mo, W) [16], (+)-$PhCHClCO_2Et$ [17], and $(t\text{-}Bu)_2NO$ [18] were prepared by methods in the literature. The other organic halides were commercial products. All the reactions of the air-sensitive metal hydrides were carried out under nitrogen.

Reaction of transition metal polyhydrides with organic halides

The reactions of MoH_2Cp_2 or WH_2Cp_2 were examined using their saturated toluene solutions (usually 50 mg in 2 ml). The organic halides were added in large excess to the solution at room temperature and the resulting color change was monitored. Occurrence of the reaction was evidenced by a change of the yellow color to brown. When the formation of MX_2Cp_2 exceeds ca. 3 mg, a brown precipitate of MX_2Cp_2 is formed. Since the halides, MX_2Cp_2, are almost insoluble in usual organic solvents, the amount of the precipitate readily indicates extent of the reaction.

The solution was examined by ^1H NMR spectroscopy to determine the structure and the yields of the dehalogenated organic products. In the case of mono- or *gem*-halo compounds, the halogen atom is replaced with hydrogen in almost quantitative yield. A *vic*-dibromo compound, $(CHBrCO_2CH_3)_2$, gave dimethyl fumarate. Since the hydride was not available in large quantities, the isolation of the dehalogenated organic products by distillation was not practical.

Stereochemistry of dehalogenation of optically active $PhCHClCO_2Et$ by MoD_2Cp_2

MoD_2Cp_2 (100 mg, isotopic purity 95%, 4 mmol) and optically active $Ph\overset{*}{C}H(Cl)CO_2Et$ (180 mg, 0.9 mmol, α_D + 58.4°) were dissolved in 3 ml of deaerated benzene. No apparent change occurred. On standing, the mixture became deep brown in 1 h and after 1 night, a deep brown precipitate and a brownish, clear solution resulted. For completion of the reaction the mixture was allowed to stand for a further night and finally warmed to 70°C for 1 h. A pale brown, clear solution with a deep brown, crystalline precipitate resulted. The clear supernatant liquid, after exposure to air, was separated and its rotation was measured to find, $[\alpha]_D^{20}$ 0° ~ +0.2° ([C_6H_6] 5). When consideration of a small amount of the unreacted optically active chloride was made, the rotation of $PhCHDCO_2Et$ is practically nil. For confirmation of the stereochemical result, the crude ester was reduced by excess $LiAlH_4$ in ether to the corresponding alcohol. The product isolated by distillation in a small tube was examined by ^{1}H NMR and by polarimetry to find presence of racemic $PhCHDCH_2OH$.

Reaction of 9,9-dibromo-bicyclo[6,1,0]nonane with MoH_2Cp_2

MoH_2Cp_2 (50 mg) and 0.1 ml of the dibromide were mixed in benzene. The color slowly turned red brown in 1 h at room temperature. After 3 h at room temperature, the mixture was heated to 80°C and kept for 1 h. A brown precipitate formed. Then the solvent was evaporated to give an almost colorless solid on the upper surface of the flask. The solid turned red and then bluish brown on contact with air after evaporation of the solvent in vacuo. The mixture was dissolved in $CDCl_3$ and examined by ^{1}H NMR in air. The presence of only the *cis*-isomer of 9-bromobicyclo[6.1.0]nonane was indicated. The same product had been found in the $HSnBu_3$ reaction with the dibromide [5].

Reaction of MoH_2Cp_2 *with 1,1-dibromo-2-phenylcyclopropane*

1,1-Dibromo-2-phenylcyclopropane (0.1 ml) and MoH_2Cp_2 (50 mg, 2 mmol) were mixed in nitrogen-saturated benzene. The solution became pale brown immediately and the color darkened to brown in 10 min. After 2 days at room temperature, the deep brown precipitate ($MoBr_2Cp_2$, 60 mg) was removed and the pale brown solution was distilled in vacuo. The colorless product was examined by ^{1}H NMR ($CDCl_3$). Only the *cis*-isomer of 1-bromo-2-phenylcyclopropane was present.

Reaction of α-bromocamphor with MoH_2Cp_2 *or* MoD_2Cp_2 *in toluene-*d_8 *or in undeuterated toluene.*

MoH_2Cp_2 (30 mg, 0.13 mmol) was allowed to react with α-bromocamphor (43 mg, 0.2 mmol) in toluene-d_8 (0.7 ml) for 1 day at room temperature and the resulting red brown solution/suspension was heated at 100°C for completion of the reaction. After removal of the solvent, the product was isolated by sublimation to give colorless crystals which were examined by GLC and ^{1}H NMR. Formation of an almost quantitative amount of undeuterated camphor was indicated. Similar reaction of α-bromocamphor with excess MoD_2Cp_2 in undeuterated toluene gave α-deuteriocamphor with ca. 70% deuteration at the *endo*-position as revealed by the ^{1}H NMR spectrum and the mass spectrum.

Reaction of MoH_2Cp_2 *with benzil*

MoH_2Cp_2 (32 mg, 0.14 mmol) and benzil (58 mg, 0.28 mmol) were allowed to react in benzene at room temperature for 20 h to give an almost black solution which was evaporated and sublimed giving benzoin (ca. 10 mg). The sublimation residue was crystallized from ether to give a compound, $MoCp_2(PhCOCOPh)$, as brown crystals (Found: C, 65.77; H, 4.50. $MoC_{24}H_{20}O_2$ calcd.: C, 66.06; H, 4.62%. ^{1}H NMR ($CDCl_3$); δ 5.55 (Cp), 7.25—7.55 ppm (Ph)). The IR spectrum showed the absence of peaks due to uncoordinated carbonyl groups.

Reaction of MoH_2Cp_2 *with d-camphorquinone*

A mixture of *d*-camphorquinone (49 mg, 0.30 mmol) and MoH_2Cp_2 (40 mg, 0.18 mmol) in benzene (3 ml) was left to stand at room temperature overnight and the resulting deep brown solution was heated at 80°C for 2 h. After removal of the solvent, colorless crystals were sublimed at 80°C/6 mmHg. The ^{1}H NMR spectrum ($CDCl_3$) indicated the presence of α-hydroxycamphor by the doublet signal ($J = 5$ Hz) at δ 4.22 ppm together with α-hydroxyisocamphor in about 1/10 amount (identified by a singlet at δ 3.78 ppm, see text for structure). For the purposes of comparison, similar reduction of camphorquinone was performed with Zn/AcOH and the product was isolated by sublimation in vacuo. The ^{1}H NMR spectrum of the sublimate showed the presence of a 1/1 mixture of α-hydroxycamphor and α-hydroxyisocamphor.

The molybdenum-containing reaction product obtained as the sublimation residue was a deep brown, air-sensitive solid which was soluble in DMSO. It showed one sharp NMR signal for the Cp protons in DMSO-d_6 to indicate the absence of chiral camphorquinone molecule coordinated to the metal.

Effect of duroquinone in the reactions of MoH_2Cp_2

(a) With ethyl iodide. The reaction in the presence of duroquinone was examined in benzene at 20°C. No sign of reaction between ethyl iodide and MoH_2Cp_2 was detected even after 5 h. After overnight standing, the clear solution turned to pale green. Then it was heated at 80°C to force the reaction to occur, a brown solution with some brown precipitates resulted.

(b) With ethyl α-chlorophenylacetate. A yellow solution of duroquinone and MoH_2Cp_2 in benzene was mixed with ethyl α-chlorophenylacetate at 20°C. Instantly, the solution became green, colorless crystals formed from the green solution in 1 h. Even after 1 night, no brown precipitate of $MoCl_2Cp_2$ formed. The colorless precipitate was isolated by decantation and was found to be durohydroquinone by IR.

(c) With benzil. The reaction between benzil and MoH_2Cp_2 was examined in the presence of duroquinone. Even after 3 h at 20°C, no change in color from the initial yellow was observed. The solution became deep brown on overnight standing. For completion of the reaction, it was heated at reflux to give $MoCp_2$-(PhCOCOPh).

(d) With camphorquinone. A yellow reaction mixture containing camphorquinone, MoH_2Cp_2, and duroquinone in benzene changed to a brown solution containing some colorless crystals of durohydroquinone in 1 h at 20°C. The amount of the crystals slowly increased during 4 h. In the absence of camphorquinone, no such precipitation of crystalline durohydroquinone (reduction of duroquinone) occurred.

Kinetics of the reaction of MoH_2Cp_2 with allyl bromide

A saturated acetone-d_6 solution (7 ml) of MoH_2Cp_2 (20 mg) was placed in an NMR tube under nitrogen and mixed with an excess of allyl bromide (45—72 mg). The reaction was monitored by the rate of decrease of the ^{1}H NMR peaks due to MoH_2Cp_2 and allyl bromide and also by the increase of the peaks due to propene and $MoBr_2Cp_2$. The peaks ascribable to unisolable "$MoHBrCp_2$" were observed at 5.03 and -9.3 ppm (TMS) during the kinetic runs. The reaction took about 1 day for completion at 36°C. The reaction with benzyl bromide went about 5-times faster and was inconvenient for the measurement. No induction period was observed in these reactions. The observed second order rate constant, as measured by the decrease in the concentration of MoH_2Cp_2, was $\sim 8 \times 10^{-2}$ mol^{-1} l^{-1} min^{-1}.

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