Inorgano-Grignard Reagents. Reactions and Crystal Structure of Bis-μ-[bis-(η-cyclopentadienyl)hydridomolybdenum]-bis{di-μ-bromo-[cyclohexylmagnesium(diethyl ether)magnesium]}; a Cyclic Compound Containing Covalent $MoMg_2$ Systems

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Summary The properties and crystal structure of the compound $[(\eta\text{-}C_5H_5)_2\ MoHMg(C_6H_{11})(\mu\text{-}Br_2)Mg(Et_2O)]_2$ are described.

MOLYBDENUM and TUNGSTEN compounds containing covalent bonds M–M′, where M=Mo or W, M′ = Li[1] or Al,[2,3] are readily formed by alkane elimination (1) where [M]–H indicates a complexed transition metal, *e.g.* $[(\eta\text{-}C_5H_5)_2MoH_2]$. Treatment of the dihydride $[(\eta\text{-}C_5H_5)_2MoH_2]$ (I) in toluene with Grignard reagents RMgX in ether precipitates pale yellow compounds which are normally crystalline. Examples are known where R and X = MeBr, MeI, Pr^iBr, Bu^nBr, PhBr, and $PhCH_2Br$, and some analogous tungsten derivatives may be similarly prepared from $[(\eta\text{-}C_5H_5)_2WH_2]$. The crystal structure of the product (II), formed by reaction between cyclohexylmagnesium bromide and (I) has been determined.

$$[M]\text{–}H + R\text{–}[M'] \rightarrow [M\text{–}M'] + RH \qquad (1)$$

Crystal data: compound (II), $C_{40}H_{64}Br_4Mg_4Mo_2O_2$, monoclinic, $a = 15{\cdot}671$, $b = 11{\cdot}996$, $c = 15{\cdot}085$ Å, $\beta = 109{\cdot}55°$, $Z = 2$, space group $C2/m$; four-circle diffractometer data,

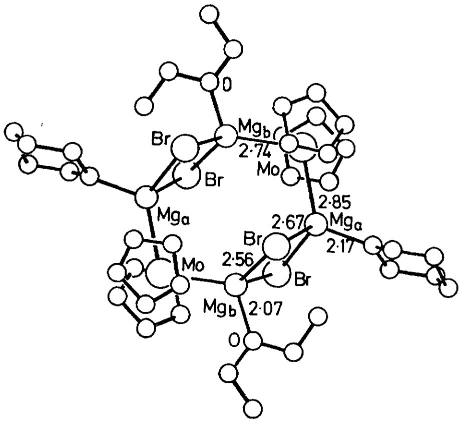


FIGURE. Crystal structure of (II).

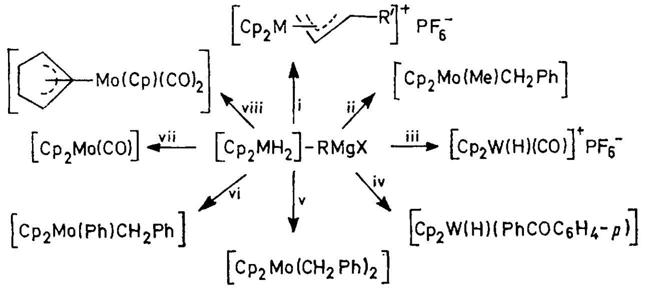
Mo-K_α radiation, 1530 independent reflections, conventional R 0·081. The unit cell contains two molecules of (II) with the structure shown in the Figure, together with two disordered molecules of ether of crystallization. In the molecule the diethyl ether ligand is disordered about the mirror plane and although F_{obs}. syntheses show the presence of a cyclohexyl group attached to Mg_a attempts at unconstrained refinement proved unsatisfactory. It is probable that the choice of the centrosymmetric space group dictated by the bulk of the scattering model does not fully represent the structure but also, perhaps, there is some degree of disordering of the ether and cyclohexyl ligands.

The Mo–Mg distances of 2·74 and 2·85 Å are entirely compatible with covalent bonding between these atoms. The difference, which is significant, may be presumed to reflect the different substituent effects of the C_6H_{11} group on Mg_a compared with that of the Et_2O group on Mg_b. The Mg_a–Mo–Mg_b angle is 108·8° and is larger than would be expected for a normal d^2 $[(\eta\text{-}C_5H_5)_2MoX_2]$ compound. It is similar to the Li–Mo–Li angle in $[(\eta\text{-}C_5H_5)_2MoHLi]_4$ where there is evidence of a hydrogen bonded to the molybdenum and located in the Li–Mo–Li angle.[2] The deuteriated $[^2H]$-(II) analogue of (II), derived from $[(\eta\text{-}C_5H_5)_2MoD_2]$, has been prepared. The i.r. spectrum of (II) shows bands at 1740 and 1720 cm^{-1} assignable to ν (Mo–H). These bands are absent in the spectrum of $[^2H]$-(II), whilst a new band appears at 1260 cm^{-1} which may be assigned to ν(Mo–D) : ν(Mo–H)/ν(Mo–D) = 1·39. This evidence, taken in conjunction with the requirements of the 18-electron rule, suggest that in (II) there is a hydrogen attached to the molybdenum and located in the plane within the Mg_a–Mo–Mg_b angle.

An X-ray examination of the product (III) from Pr^iMgBr and (I) shows it to have the same $[(\eta\text{-}C_5H_5)_2MoMgBr_2Mg]_2$ skeleton as (II), but apparent severe disordering of the other ligands, combined with limited data and high background scatter, prevented proper resolution of all its features.

Hydrolysis of (II) and (III) gives, apart from $[(\eta\text{-}C_5H_5)_2MoH_2]$ and Et_2O, the alkanes C_6H_{12} and C_3H_8 respectively; this supports the proposal that Et_2O and Pr^i groups are present in (III).

The Scheme shows some reactions of (II), (III), and of other Grignard-molybdenum or -tungsten adducts. The reactions are very similar suggesting all the adducts have closely related structures.



SCHEME. Some reactions of the adducts formed by treatment of $[(\eta\text{-}C_5H_5)_2Mo(\text{or } W)H_2]$ in toluene with excess of RMgX in Et_2O at room temperature.
i, R′ = H, allyl chloride, then NH_4PF_6 (aq.), (15%), for M = W, RMgX = Pr^iMgBr. R′ = Me, butadiene in THF (13%), for Mo, cyclohexylMgBr; ii, $PhCH_2Br$ (27%), for Mo, MeMgBr;[3] iii, CO (1 atm.), then NH_4PF_6 (aq.) (15%), for W, MeMgI; iv, Ph_2CO in THF at −70° (25%), for W, Pr^iMgBr; v, (II) or (III) in toluene suspension with $PhCH_2Br$ (30%); vi, $PhCH_2Br$ in THF (30%), for Mo, PhMgBr;[3] vii, (II) or (III) in THF, CO_2 (1 atm.) (85%); viii, (II) or (III) in THF, CO (1 atm.) then hydrolysis (40%).
THF = tetrahydrofuran. Cp = $\eta\text{-}C_5H_5$.

The compounds (II) and (III) and the recently described $[(\eta\text{-}C_5H_5)Fe(Ph_2PCH_2)_2MgBr]$[4] constitute the most definite examples of covalent transition metal–magnesium bonds. These compounds are highly reactive and normally behave as unusually strong nucleophiles. Finally, it seems that the reaction (1) will be a widely applicable route to covalent systems [M]–[M′], where M′ is Li, Mg, Al, or other highly electropositive metals and where [M] represents a transition metal complex which will not form a stable anion [M⁻].

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