Reaction of (1,8-naphtalenediy)magnesium with group 5 and 6 metallocene dichlorides. Formation and crystal structure of (ethasup5-Cp)Mo(PMEsub3)(ethasup3-6b-H-7,9a-dihydrocyclopent[a]acenaphtylen-7-yl)


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Reaction of (1,8-Naphthalenediyl)magnesium with Group 5 and 6 Metallocone Dichlorides. Formation and X-ray Crystal Structure of ($\eta^5$-Cp)Mo(PMe$_3$)$_2$($\eta^3$-6b-H-7,9a-dihydrocyclopent[a]acenaphthylene-7-yl)

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Summary: The reaction between (1,8-naphthalenediy1)-magnesium (1) and Cp$_2$MCl$_2$ (M = V, Nb) gave perylene (3) in quantitative yield. However, reaction between 1 and Cp$_2$MoCl$_2$ in the presence of PMe$_3$ yielded the remarkable complex (r$^3$-Cp)Mo(PMe$_3$)$_2$($\eta^3$-6b-H-7,9a-cyclopent[a]acenaphthylene-7-yl) (4). Its X-ray crystal structure revealed that one of the original cyclopentadienyl rings is $\eta^1$-bonded to the metal center and twice $\sigma$-bonded to C(1) and C(8) of the naphthalene moiety. Complex 4 crystallizes in the orthorhombic space group Pnma with $a = 15.274(11)$ Å, $b = 14.953(3)$ Å, $c = 10.3620(14)$ Å, V = 2366.6(18) Å$^3$, and Z = 4. Convergence was reached at R = 0.064 and R,$_w$ = 0.069 for 144 parameters and 1814 diffraction data ($I > 2.5dI$).

Bifunctional organomagnesium compounds such as (1,8-naphthalenediyl)magnesium$^{1a,b}$ (1; Scheme 1) have been used in the preparation of four-membered metallacycles. The reaction between 1 and titanocene dichloride in THF gave the (1,8-naphthalenediyl)titanocene complex,$^1a$ similarly, the analogous hafnium complex has been synthesized.$^2$

To investigate the applicability of 1 for the synthesis of four-membered metallacycles of group 5, we tried to prepare the analogous niobium and vanadium complexes. However, perylene (3) was formed in quantitative yield, presumably by reductive elimination from intermediates such as 2 (Scheme 1).

The reaction of 1 and Cp$_2$MoCl$_2$ in THF at -20 °C resulted in unidentifiable products. However, when a $\sigma$-donor such as PMe$_3$ was added to the metal dihalide before the addition of 1, the 18-electron complex 4 was formed in good yield (Scheme 2).$^3$ Compound 4 is stable to air and moisture at room temperature. Its NMR and mass spectral data are in agreement with the proposed structure, and upon hydrolysis, it was converted to 6b-H-7,9a-dihydro-7-cyclopent[a]acenaphthylen (5).$^4$

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Crystals of 4 were grown by gradually cooling a saturated solution in toluene to -20 °C. The X-ray crystal structure is shown in Figure 1; selected bond distances and bond angles are given in the legend of Figure 1 (note that the numbering of the crystal structure is that given in the figure; it differs, for
crystallographic reasons, from the IUPAC numbering used in the rest of the text).

The most conspicuous aspect of the structure of 4 is that one of the original cyclopentadienyl rings is bridging the 1- and 8-positions of the naphthylene moiety and is $\eta^7$-bonded to the molybdenum. The dihedral angle between the planes through C(7)-C(8)-C(9) and through C(6b)-C(7)-C(9a) is 142.2(7)°; the latter plane that of the naphthalene ring form an angle of 117.1-14.953(3)Å and angles (deg): Mo-C(8), 2.225(6); Mo-C(9), 2.157-24.1(6).

The molecule has a C plane through the molybdenum atom and the central bond of the naphthalene moiety. The bond angle C(6a)-C(9c)-C(9b) is 112.4(7)°, nearly equal to that in acenaphthalen: 111.4(3)°.

The formation of 4 poses a number of interesting mechanistic problems. Formally, it involves a double addition of the 1,8-naphtalenediyl dianion to one of the two cyclopentadienyl rings. A priori, this mode of reaction is unfavorable because it involves nucleophilic attack on (the equivalent of) a cyclopentadienyl anion. Indeed, few examples have been reported so far, and they usually require some form of electrophilic activation of the starting metal complex. Such activation may consist of Lewis acid catalysis by magnesium halides, an electron-withdrawing ligand at the metal, or the prior conversion of the metal complex to a catonic species, as illustrated by the reaction between sodium borohydride and molybdocene derivatives. We feel that the formation of 4 can be rationalized in analogy to this latter mechanism. First, the reaction of molybdocene dichloride with trimethylphospine may give rise to the formation of the cationic complex 6 (Scheme 3), which was not directly observed and must be postulated to occur in a low steady-state concentration. In 6, the molybdocene moiety is sufficiently electrophilic to undergo nucleophilic attack by one of the two organomagnesium functions of 4 at the cyclopentadienyl ring; the reaction is further facilitated by the reduction of Mo-(IV) to Mo(II), which serves as an electron sink. Although the resulting intermediate 7 is an 18-electron species, it is still positively charged and ready to undergo attack by the second organomagnesium function, which converts the $\eta^7$-bonded diene unit of 7 to the $\eta^7$-bonded allyl anion in the neutral final product 4.

This type of complex, containing both $\eta^7$- and $\eta^5$-cyclopentadienyl ligands attached to the metal center, is not very common. The closest structural analogy to 4 is that of ($\eta^5$-C$_5$H$_5$)MoCl$_2$. The formation of 4 with PMe$_3$ attached to the molybdenum causes the compound to be magnetic, which is not an unexpected consequence of the reaction.
reveals the same configuration of ligands around the metal.

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Supplementary Material Available: Figure giving the $^1$H NMR spectrum of 4 and tables giving full details of the structure determination of 4, including crystal data and structure determination details, atomic coordinates, bond lengths, bond angles, torsion angles, and anisotropic displacement parameters (8 pages). Ordering information is given on any current masthead page.

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