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

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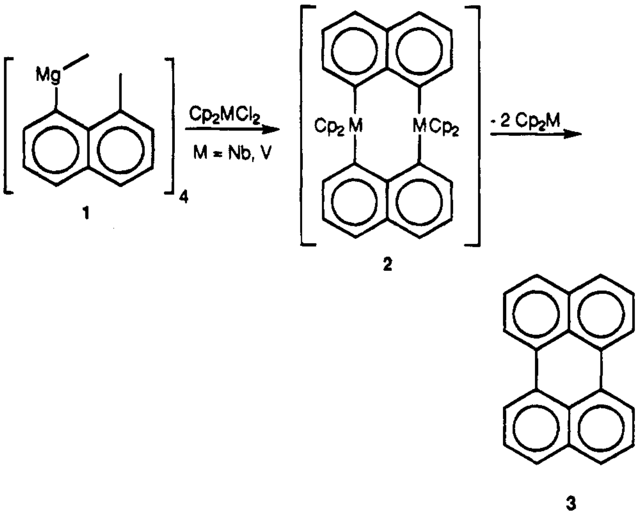
*Summary: The reaction between (1,8-naphthalenediyl)-magnesium (**1**) and Cp$_2$MCl$_2$ (M = V, Nb) gave perylene (**3**) in quantitative yield. However, reaction between **1** and Cp$_2$MoCl$_2$ in the presence of PMe$_3$ yielded the remarkable complex (η^5-Cp)Mo(PMe$_3$)$_2$(η^3-6b-H-7,9a-cyclopent[a]acenaphthylen-7-yl) (**4**). Its X-ray crystal structure revealed that one of the original cyclopentadienyl rings is η^3-bonded to the metal center and twice σ-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 ($I > 2.5\sigma(I)$).*

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]

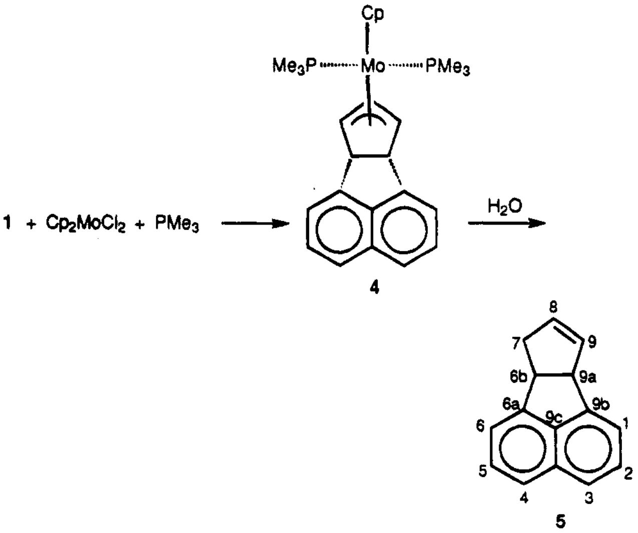
To investigate the applicability of **1** for the synthesis of four-membered metallacycles of group 5, we tried to prepare the analogous niobium and vanadium complexes. However, perylene (**3**) was formed in quantitative yield, presumably by reductive elimination from intermediates such as **2** (Scheme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

The reaction of **1** and Cp$_2$MoCl$_2$ in THF at −20 °C resulted in unidentifiable products. However, when a σ-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*]acenaphthylene (**5**).[4]

Scheme 1



Scheme 2



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

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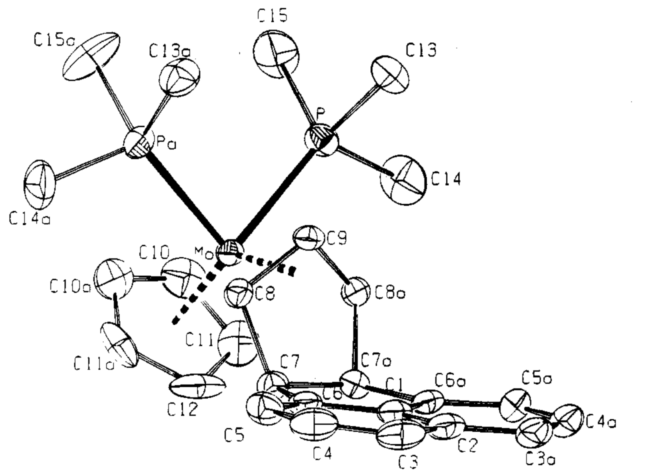
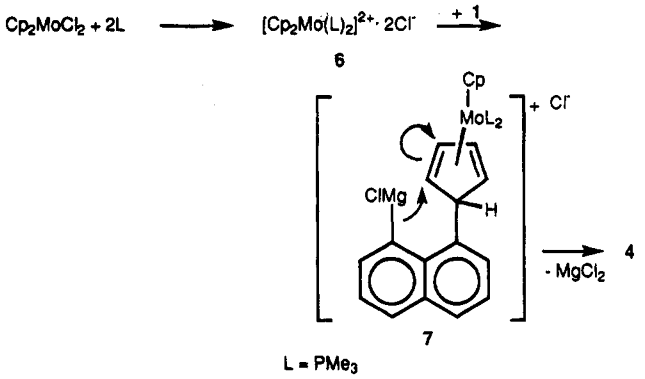


Figure 1. ORTEP drawing of **4**. Selected bond distances (Å) and angles (deg): Mo—C(8), 2.225(6); Mo—C(9), 2.157(8); Mo—C(10), 2.363(7); Mo—P, 2.442(3); P—C(13), 1.819(8); C(6)—C(7), 1.515(9); C(7)—C(8), 1.523(9); C(8)—C(9), 1.429(8); C(3)—C(2)—C(3a), 128.2(8); C(6a)—C(1)—C(6a), 112.4(7); C(13)—P—C(14), 99.3(4); C(7a)—C(7)—C(8)—C(9), −24.1(6).

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 naphthalene moiety and is η^3-bonded to the molybdenum. The dihedral angle between the planes through C(7)—C(8)—C(9) and through C(6b)—C(7)—C(9)—C(9a) is 142.2(7)°; the latter plane and that of the naphthalene ring form an angle of 117.1(3)°. The molecule has a C_s 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 acenaphthalene: 111.4(3)°.[5]

Scheme 3



The formation of **4** poses a number of interesting mechanistic problems. Formally, it involves a double addition of the 1,8-naphthalenediyl 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,[6] 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,[7] an electron-withdrawing ligand at the metal,[8] or the prior conversion of the metal complex to a cationic species, as illustrated by the reaction between sodium borohydride and molybdocene derivatives.[9] 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 **1** 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 η^4-bonded diene unit of **7** to the η^3-bonded allyl anion in the neutral final product **4**.

This type of complex, containing both η^3- and η^5-cyclopentadienyl ligands attached to the metal center, is not very common.[9–11] The closest structural analogy to **4** is that of $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}C_5H_5Cp_2)$,[11] which

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(3) Synthesis of and analytical data for **4**: The reaction was carried out in fully sealed and evacuated glassware.[12] To Cp_2MoCl_2 (0.0892 g, 0.30 mmol) was added PMe_3 (1 mL, 10 mmol) at −20 °C. After the mixture was stirred for 30 min, a solution of **1** (0.30 mmol) in THF (10 mL) was added. The resulting brownish green suspension was warmed to 4 °C over 30 min and stirred overnight at room temperature. The resulting mixture was filtered and the brownish yellow filtrate evaporated. The residue was extracted with toluene; according to the ^1H NMR spectrum, the compound was pure, and the yield was determined to be 71% with hexamethylbenzene as internal standard. Orange crystals were obtained from a saturated toluene solution at −20 °C. In a second, identical experiment, the reaction mixture was hydrolyzed and worked up as usual; 6b-*H*-7,9a-dihydro-7-cyclopent[*a*]acenaphthylene (**5**)[4] was obtained as white crystals (44 mg, 76%); the ^1H NMR ($CDCl_3$) spectrum was in accordance with the literature.[4] GC/MS (HP 5890/5970 MS, Chrompack BP1 (QSGE)): *m/z* (relative intensity) 192 (M^+, $C_{15}H_{12}$, 83), 191 ($M^+ - H$, 100), 165 (67), 152 (5), 94 (17). **4**: ^1H NMR (C_6D_6, 200 mHz, reference C_6D_5H at 7.30 ppm) δ 0.79 (d, $^2J(P-H) = 3.2$ Hz, PMe_3), 2.33 (m, 2 H, H(7,9)), 2.38 (m, 1H, H(8)), 3.75 (s, 2H, H(6b,9a)), 4.27 (t, $^3J(P-H) = 1.3$ Hz, 5H, Cp), 7.67–7.62 (m, 4H, H(1,3,4,6)), 7.52 (dd, $^3J(H-H) = 6.7$ Hz, $^3J(H-H) = 7.2$ Hz, 2 H, H(2,5)); ^{13}C NMR (C_6D_6, 62.9 MHz, reference C_6D_5H at 7.30 ppm; COSY) δ 133.1 (C(10)), 128.3 (C(6a,9b)), 128.0 (C(2,5)), 126.0 (C(11)), 122.2 (C(1,6)), 118.1 (C(3,4)), 85.8 (Cp), 61.5 (C(8)), 60.1 (C(7,9)), 49.4 (C(6b,9a)), 21.3 (PCH_3); ^{31}P NMR (C_6D_6, 162 MHz, reference 85% H_3PO_4 at 0 ppm): δ 19.1 (s, PMe_3); HRMS (Finnigan MAT 90) calcd for $C_{26}H_{34}P_2{}^{92}Mo$ 500.1199, found 500.1200. Crystallographic data for $C_{26}H_{34}MoP_2$ (**4**) were collected on an Enraf-Nonius CAD4 diffractometer for an orange crystal (0.25 × 0.25 × 0.50 mm) that crystallizes in the orthorhombic space group *Pnma* (No. 62): $a = 15.274(11)$ Å, $b = 14.953(3)$ Å, $c = 10.3620(14)$ Å, $V = 2366.6(18)$ Å^3, $Z = 4$; 11 939 reflections measured, 2836 unique; 295 K; Mo Kα (Zr-filtered) radiation; $1.33° < \theta < 27.50°$. The structure was solved by automated Patterson methods (DIRDIF92).[13] Refinement on *F* was carried out by full-matrix least-squares techniques (SHELX76).[14] H atoms were located on calculated positions. $R = 0.064$ and $R_w = 0.069$ for 144 parameters and 1814 reflections with $I < 2.5\sigma(I)$.

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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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