Reaction of (1,8-naphtalenediyilmagnesium 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 Metallocene Dichlorides. Formation and X-ray Crystal Structure of (η⁵-Cp)Mo(PMe₃)₂-
(η⁻³-6b-H-7,9a-dihydrocyclopent[a]acenaphthylene-7-yl)

M. Schreuder Goedheijt,‡ O. S. Akkerman,‡ F. Bickelhaupt,*† P. W. N. M. van Leeuwen,‡ N. Veldman,§ and A. L. SpeksJLI

Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands, Koninklijke/Shell Laboratorium Amsterdam, Badhuisweg 3, NL-1003 AA Amsterdam, The Netherlands, and Bijvoet Center for Biomolecular Research Vakgroep Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, NL-3584 CH Utrecht, The Netherlands

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Summary: The reaction between (1,8-naphthalenediyl)magnesium (1) and Cp₂MCl₂ (M = V, Nb) gave perylene (3) in quantitative yield. However, reaction between 1 and Cp₂MoCl₂ in the presence of PMe₃ yielded the remarkable complex (η⁵-Cp)Mo(PMe₃)₂(η⁻³-6b-H-7,9a-dihydrocyclopent[a]acenaphthylene-7-yl) (4). Its X-ray crystal structure revealed that one of the original cyclopentadienyl rings is η⁻⁵-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) Å³, and Z = 4. Convergence was reached at R = 0.064 and R = 0.069 for 144 parameters and 1814 diffraction data (I > 2.5σ(I)).

Bifunctional organomagnesium compounds such as (1,8-naphthalenediyl)magnesium (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; 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 Cp₂MoCl₂ in THF at -20 °C resulted in unidentifiable products. However, when a σ-donor such as PMe₃ was added to the metal dichloride 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

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
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 η²-bonded to the molybdenum. The dihedral angle between the planes through C(7)-C(8)-C(9)-C(9a) is 142.2(7)°; the latter plane that of the naphthalene ring form an angle of 117.1-3°. The molecule has a C, plane through the molybdenum atom and the central bond of the naphthalene.
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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