

Benefits of the Chelate Effect: Preparation of an Unsymmetrical *ansa*-Bis(imido)molybdenum Complex Containing a Seven-Membered Chelate Ring[†]

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Introduction

We recently described the syntheses and crystal structures of the bis(organoimido)molybdenum complexes $[(\text{CH}_2)_n(2\text{-C}_6\text{H}_4\text{N})_2]\text{MoCl}_2\cdot\text{DME}$ ($n = 1, 2$) together with a number of derivatives of the general type $[(\text{CH}_2)_n(2\text{-C}_6\text{H}_4\text{N})_2]\text{Mo}(\text{X})(\text{Y})$ ($\text{X}, \text{Y} = \text{monoanionic ligands}$).² These compounds, which represent the first examples of *ansa*-bis(imido) complexes, are isolobal analogues of the technologically relevant *ansa*-zirconocene derivatives.³ They contain an eight- ($n = 1$) or nine-membered ($n = 2$) chelate ring. Whereas the nine-membered ring is quite flexible, the eight-membered molybdacycle is perfectly rigid on the NMR time scale even at 110 °C. This is due to a considerable amount of ring strain, as is evidenced by relevant bond parameters of $[\text{CH}_2(2\text{-C}_6\text{H}_4\text{N})_2]\text{MoCl}_2\cdot\text{DME}$. This finding gave rise to the question whether eight already represents the lower limit for the chelate ring size in such compounds. Here we report on an *ansa*-bis(imido) complex which contains a seven-membered molybdacycle.

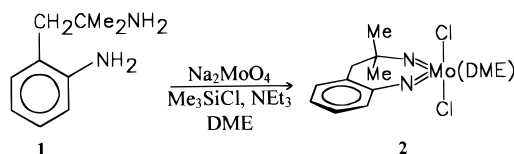
Results and Discussion

In an attempt to synthesize an *ansa*-bis(imido)molybdenum complex with a seven-membered chelate ring containing four sp^2C atoms, enantiomerically pure 2,2'-diamino-1,1'-binaphthyl was reacted under standard "one-pot" conditions with sodium molybdate in DME in the presence of triethylamine and chlorotrimethylsilane. However, only intractable material was obtained. Extensive variations of the reaction conditions did not prove successful.

Surprisingly, in a similar experiment the diamine $\text{H}_2\text{NCMe}_2\text{-CH}_2\text{-}2\text{-C}_6\text{H}_4\text{NH}_2$ (**1**) was cleanly converted to $(\text{NCMe}_2\text{CH}_2\text{-}2\text{-C}_6\text{H}_4\text{N})\text{MoCl}_2\cdot\text{DME}$ (**2**), which was isolated in 77% yield as an orange, microcrystalline solid (Scheme 1).

The product is very soluble in all common organic solvents except aliphatic hydrocarbons. Unfortunately, single crystals

Scheme 1. One-Pot Synthesis of Complex 2



suitable for an X-ray diffraction study could not be obtained so far. Its monomeric nature was proved by cryoscopy in benzene.

Compound **2** is unusual in two ways. First, it contains a seven-membered chelate ring, which undoubtedly is very strained. Second, it is an unsymmetrical bis(imido) complex, containing a mixed set of imido ligands. Mixed molybdenum imido complexes have recently attracted considerable attention.⁴ However, no general method for the selective synthesis of such species has been reported to date. The chelate effect is responsible for the high-yield formation of **2**, even though a strained chelate ring is formed. **2** is perfectly stable in benzene solution at 110 °C (sealed NMR tube), and even after 30 days at this temperature no imido exchange products are detectable in its ¹H NMR spectrum. This finding strongly suggests that the clean formation of **2** is due to thermodynamic reasons.

In the case of $[(\text{CH}_2)_n(2\text{-C}_6\text{H}_4\text{N})_2]\text{MoCl}_2\cdot\text{DME}$ the bis(imido) "bite angle" has a value of 107.13(7) ($n = 2$, nine-membered chelate ring) and 100.8(5)° ($n = 1$, eight-membered chelate ring), respectively.² Therefore, the NMoN bite angle is assumed to be well below 100° in the case of **2**.

It is well established in the chemistry of *ansa*-zirconocene dichlorides and related species which are used as precatalysts in the Ziegler–Natta polymerization of α -olefins that the cyclopentadienyl bite angle, which can be controlled by the *ansa*-bridge length, has a marked influence on their reactivity.³ It has been noted that the reactivity differences are due to both steric and electronic effects, and detailed discussions of the dependence of the frontier orbital situation of bent metallocenes on the bite angle are available.⁵

We have investigated whether an analogous dependence is found for the bis(imido)molybdenum system $(\text{HN})_2\text{MoCl}_2$, which is (i) a straightforward isolobal analogue of the prototypical Ziegler–Natta precatalyst Cp_2ZrCl_2 and (ii) bears direct relevance to the chemistry of the six-coordinate species $(\text{RN})_2\text{-MoCl}_2\cdot\text{DME}$, since the DME ligand in such compounds is usually coordinated fairly loosely, so that in solution four-coordinate complexes of the type $(\text{RN})_2\text{MoCl}_2$ are often formed in equilibrium with $(\text{RN})_2\text{MoCl}_2\cdot\text{DME}$.⁶ The results of our investigation are presented in a Walsh diagram (Figure 1).

Similar to Cp_2ZrCl_2 ,^{5a} the LUMO is mainly constituted from a d_z^2 orbital at the central transition metal, whereas the HOMO has no significant metal d orbital contribution. The frontier orbital energies depend markedly on the NMoN bite angle. By far the largest effect is observed close to a value of 100°, where

[†] This paper is dedicated to Prof. Peter Jutzi on the occasion of his 60th birthday.

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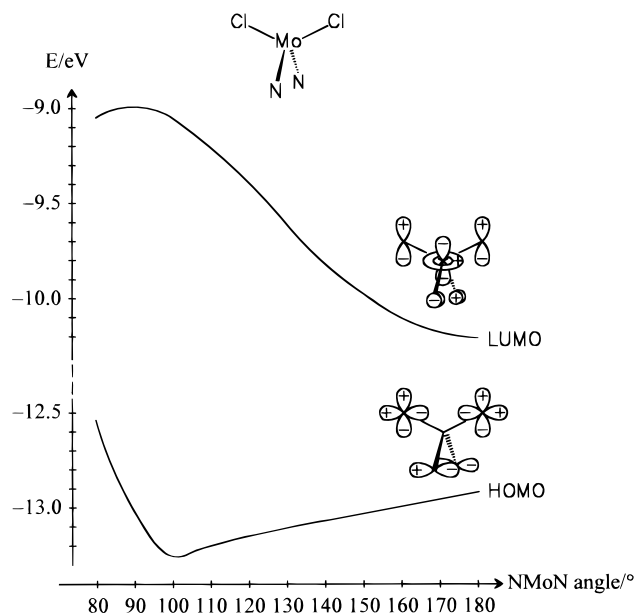


Figure 1. Walsh diagram of the frontier orbitals of geometry-optimized $(\text{HN})_2\text{MoCl}_2$.

the HOMO–LUMO energy gap is widest and where a decrease of the bite angle from 100 to 80° leads to a pronounced increase of the HOMO energy of ca. 0.7 eV.

The metal center in bis(imido)molybdenum complexes is sterically less shielded than in analogous metallocene derivatives, since the organic ligand framework is comparatively more remote. Hence, a variation in the bite angle should have influences reflecting electronic effects much more in the case of bis(imido) species than in the case of the corresponding metallocene derivatives, where experimental studies cannot separate electronic from steric bite angle effects. Similar to Cp_2ZrCl_2 , where theoretical predictions concerning the electronic bite angle effect are not unambiguous,^{5a} our calculational results are of limited prognostic value, their only clear-cut consequence being that the largest effects are to be expected at bite angles below 100°. Further research will therefore be needed to investigate whether electronic influences on the chemical behavior of relevant bis(imido) complexes are of appreciable magnitude.

Experimental Section

All manipulations were performed in an inert atmosphere (purified argon or dinitrogen) by using standard Schlenk and cannula techniques or a conventional glovebox. Solvents and reagents were appropriately dried and purified by using standard procedures. NMR spectra were

recorded at 300 K with a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^1H ; TMS was used as external reference. Melting points were obtained in sealed capillaries with a Büchi 510 melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld. 2-(2-Amino-2-methylpropyl)aniline (**1**) was prepared in a two-step reaction starting from commercially available 2-nitrobenzyl chloride and 2-nitropropane by a slight modification of a published procedure.⁷

Synthesis of Complex $[\text{NCMe}_2\text{CH}_2\text{-2-C}_6\text{H}_4\text{N}]\text{MoCl}_2\cdot\text{DME}$ (2**).** Triethylamine (9.51 g, 94.0 mmol), chlorotrimethylsilane (20.4 g, 188 mmol), and a solution of **1** (3.85 g, 23.5 mmol) in DME (20 mL) were added sequentially to a suspension of sodium molybdate (4.84 g, 23.5 mmol) in DME (200 mL) placed in a thick-walled Rotaflo ampule. The mixture was stirred at 70 °C for 20 h. Insoluble material was filtered off and washed with DME (2 × 50 mL). The red solution was reduced to dryness in vacuo. The remaining solid was washed with *n*-hexane (3 × 40 mL). One recrystallization from boiling DME afforded **2** (7.51 g, 77%) as a dark orange, microcrystalline solid in two crops. Mp: 108 °C. ^1H NMR (C_6D_6): δ 1.18 (s, 6 H, CCH_3), 3.20 (s, 4 H, OCH_2), 3.43 (s, 8 H, ArCH_2 and OCH_3), 6.55 (m, 1 H, ArH), 6.68 (m, 1 H, ArH), 6.75 (m, 1 H, ArH), 6.93 (m, 1 H, ArH). ^1H NMR (CDCl_3): δ 1.27 (s, 6 H, CCH_3), 3.78 (s, 6 H, ArCH_2 and OCH_2), 3.82 (s, 6 H, OCH_3), 6.52 (m, 1 H, ArH), 7.01 (m, 2 H, ArH), 7.17 (m, 1 H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 26.0 (CMe_2), 48.8 (ArCH_2), 62.2 (OMe), 70.8 (OCH_2), 71.0 (CMe_2), 118.0 (CH), 127.0 (CH), 128.3 (CH), 133.5 (CH), 141.7 (arom. CCH_2), 152.0 (arom. CN). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{N}_2\text{Cl}_2\text{MoO}_2$ (417.2): C, 40.30; H, 5.31; N, 6.71. Found: C, 40.22; H, 5.29; N, 6.66. $M_w = 405$ (cryoscopy in benzene, average of three independent determinations).

Computational Methods. The quantum-chemical calculations for the construction of the Walsh diagram of $(\text{HN})_2\text{MoCl}_2$ were performed with the extended Hückel (EH) method,^{8a} utilizing the modified Wolfsberg–Helmholtz formula.^{8b} The following ionization potentials (in eV) [Slater exponents] were used: Mo 5s [1.96] –8.34, 5p [1.90] –5.24, 4d [4.54, 1.90] –10.5; N 2s [1.95] –26.0, 2p [1.95] –13.4; Cl 3s [2.183] –26.3, 3p [1.733] –14.2; H 1s [1.3] –13.6. The following bonding parameters (bond lengths in Å, bond angles in degrees) were assumed on the basis of density functional calculations (B3LYP/LANDZ): Mo–N 1.75, N–H 1.00, Mo–Cl 2.39; H–N–Mo 154.0, Cl–Mo–Cl 160.4.

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