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Preliminary communication

First amido-functionalized *ansa*-molybdenocene-type complexes ☆

Wolfgang A. Herrmann *, Walter Baratta [1], Marcus J.A. Morawietz [2]

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

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Abstract

First examples of tetravalent molybdenocene-type compounds containing *N*-functionalized π-aromatic ligands are described. Thus, the "metal amide route" starting from $Mo[N(CH_3)_2]_4$ was used to synthesize $[Si(CH_3)_2(C_5H_4)(NC_6H_5)]Mo[N(CH_3)_2]_2$ from the ligand $Si(CH_3)_2(C_5H_5)(NHC_6H_5)$ in 60% yield. Related Mo(IV) complexes are reported. It appears that the Mo(IV) amides are least susceptible to redox side reactions.

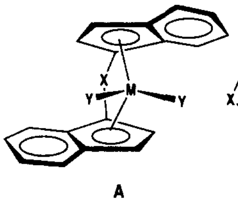
Keywords: Molybdenum; Amino-functionalized cyclopentadienyl; Amide

1. Introduction

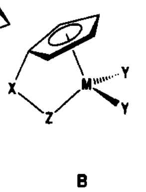
Beyond the vast number of publications on titanium, zirconium, and hafnium complexes of type **A** in the context of olefin polymerization [1], a rapidly growing interest concentrates on bridged half-sandwich derivatives [2]. Although an efficient synthesis of type **B** complexes ($X = (CR_2)_n$, SiR_2; $Y = Hal$, NR_2; $Z = N$–R, O) of Group IV metals is known [2c–e], there is a striking paucity of these constitutional types for other transition metals. This is due to the fact that *ansa*-zirconocenes **A** have dominated the industrial and academic scene since the C_2-symmetry metallocene catalysts were recognized in 1984 to isotactically polymerize propylene [3]. A number of new constitutional catalyst concepts have recently appeared in the literature [2a–d,4]. However, cyclopentadienyl compounds of quadrivalent molybdenum have received little attention. Although $(C_5H_5)_2MoCl_2$ has long been known [5], *ansa*-derivatives have not been considered up to a very recent communication by Green *et al.* [6].

In the present communication, we report a molybdenum(IV) complex **C** that opens up a new class of molybdenocenes. At this occasion, we show that the "metal amide route" [2c–e] provides us with an opportunity of handling even redox-sensitive systems of this kind.

If a solution of tetrakis(dimethylamido)molybdenum(IV) **1** in ether is treated with an equimolar amount of the aminosilyl derivative **2** of cyclopentadiene at 25°C, double deprotonation of the latter occurs with concomitant formation of (volatile) dimethylamine. The new molybdenum(IV) complex **3** forms nearly quantitatively, as monitored by ^1H NMR spectroscopy. After appropriate work-up a 60% (isolated) yield is obtained (Scheme 1).



A



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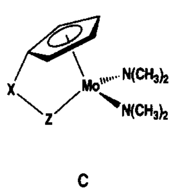
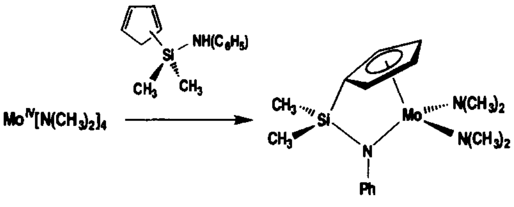


C



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Scheme 1. Conditions: Et_2O, 12 h, 25°C, $-2\ HN(CH_3)_2$.

☆ Dedicated to Professor Hans-H. Brintzinger on the occasion of his 60th birthday.

* Corresponding author.

[1] Research fellow of the Alexander von Humboldt-Foundation (1994–1995).

[2] Present address: Degussa AG, GB Industrie- und Feinchemikalien, D-63403 Hanau (Germany).

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The dark-brown compound is highly soluble in toluene (> 100 mg : 1 ml) and decomposes when heated above 100°C. The compound **3** represents a very reactive [7] and water-sensitive, crystalline material, that can only be handled under scrupulous exclusion of moisture. The synthesis is straightforward, avoiding any redox process so typical of precursor compounds such as molybdenum(IV) halides. A special advantage is the use of the *parent* CH–/NH acidic ligand precursor of type **2**. Tetrakis(dimethylamido)molybdenum(IV) **1** also reacts in ether with equimolar amounts of $Si(CH_3)_2(C_9H_7)(NHtBu)$ and $C(CH_3)_2(C_5H_5)(C_{13}H_9)$. The monocyclopentadienyl amide $(C_5H_5)Mo[N(CH_3)_2]_3$ **4** forms in ether from **1** with an excess of cyclopentadiene. **4** disproportionates in solution within several hours to yield $Mo[N(CH_3)_2]_6$ [8]. The ^1H and ^{13}C spectra in C_6D_6 show one resonance each at $\delta = 3.21$ and 51.77 ppm respectively [9], the CI mass spectrum exhibits a signal at 362.2 [M^-]. In addition, insoluble products of as yet unknown composition are formed. It is interesting to note that the chromium(IV) amide $Cr[N(CH_2CH_3)_2]_4$ reacts with cyclopentadiene to chromocene [10].

We conclude that *ansa*-bridged cyclopentadienyl ligands stabilize metal complexes in medium oxidation states as compared with the unbridged derivatives. Disproportionation thus does not come to the fore in the present case. This simple and efficient "metal amide route" makes the described new class of compounds easily accessible.

2. Experimental details

All operations were carried out with absolutely dry solvents and in a dry atmosphere (Schlenk tube and Glove-box techniques). The molybdenum(IV) amide was prepared as reported in the literature [11] and used as a sublimed material (subl. 80°C/10^{-1} Torr). The ligand **2** was synthesized [2d] from two equivalents of aniline and $(C_5H_5)Si(CH_3)_2Cl$; the latter compound was obtained from dichlorodimethylsilane and lithium cyclopentadienyl.

2.1. *Bis(dimethylamido)[η^1 : η^5-{(N-phenylamido)dimethylsilyl}cyclopentadienyl]molybdenum(IV) 3*

$Mo[N(CH_3)_2]_4$ (200 mg, 0.735 mmol) was dissolved in 10 ml of Et_2O. The purple solution was cooled at −78°C. The ligand $Si(CH_3)_2(C_5H_5)(NHC_6H_5)$ (158 mg, 0.734 mmol), dissolved in 15 ml of Et_2O, as added slowly. The mixture was allowed to attain room temperature, and the solution was stirred overnight (1 atm). The dark-red solution was then refluxed for 2 h. After filtration, the solution was evaporated in vacuo to obtain a brown oil. *n*-Pentane (1 ml) was added, with a solid gradually separating on standing at −78°C overnight. The product was filtered and dried under reduced pressure (175 mg, 60% yield). Anal. Found (Calc.) for $C_{17}H_{27}N_3MoSi$: C 51.33 (51.40); H 6.83 (6.80); N 10.01 (10.57). Spectroscopic data: ^1H NMR (400 MHz, C_6D_6, 25°C, TMS): $\delta = 0.25$ (s, 6 H; $Si(CH_3)_2$), 3.20 (s, 12 H; $N(CH_3)_2$), 4.88 (t, 2 H, $^3J(H, H) = 2.1$ Hz, C_5H_4), 6.04 (t, 2 H, $^3J(H, H) = 2.1$ Hz, C_5H_4), 6.84 (t, 1 H, $^3J(H, H) = 7.1$ Hz, *para*-C_6H_5), 7.07 (d, 2 H, $^3J(H, H) = 8.6$ Hz, *ortho*-C_6H_5), 7.23 (t, 2 H, $^3J(H, H) = 8.0$ Hz, *meta*-C_6H_5). $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 25°C, TMS): $\delta = -0.2$ (s; $Si(CH_3)_2$), 65.3 (s; $N(CH_3)_2$), 95.5 (s; C_5H_4), 96.0 (s; C_5H_4), 107.5 (s; C_5H_4), 119.6 (s, *para*-C_6H_5), 121.7 (s; *ortho*-C_6H_5), 128.6 (s, *meta*-C_6H_5), 155.8 (s, C_6H_5). ^{29}Si NMR (DEPT, 79.5 MHz, C_6D_6, 25°C, TMS): $\delta = -20.6$ (s; $Si(CH_3)_2$). MS (CI): m/z (%) = 399.1 (100) [M^+], 354.1 (11) [$M^+ - HNMe_2$].

2.2. *Tris(dimethylamido)cyclopentadienylmolybdenum(IV) 4*

^1H NMR (400 MHz, C_6D_6, 25°C, TMS): $\delta = 2.93$ (s, 18 H; $N(CH_3)_2$), 5.13 (5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (100.4 MHz, C_6D_6, 25°C, TMS): $\delta = 57.5$ (s; $N(CH_3)_2$), 97.3 (s; C_5H_4). MS (CI): m/z (%) = 295.2 (100) [M^+].

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