Journal of Organometallic Chemistry, 301 (1986) C45—C48
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REACTIVITY OF ZIRCONOCENE AND HAFNOCENE DIHYDRIDES TOWARDS ELEMENTAL SELENIUM AND SULFUR. STRONG EVIDENCE FOR INSERTION OF A CHALCOGEN UNIT INTO THE METAL—HYDROGEN BOND

MOHAMMED FAHIM and GÉRARD TAINTURIER*
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (U.A. 33), Université de Dijon, 6 bd Gabriel 21100 Dijon (France)

(Received November 12th 1985)

Summary

Dimeric metallocene dihydrides $[(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{MH}(\mu\text{-H})]_2$ (1; M = Zr, Hf) react with elemental chalcogens to give the four-membered metallacycles $[(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{M}(\mu\text{-E})]_2$ (2, E = Se; 3, E = S). In the case of sulfur, the reaction also gives $(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{MS}_5$ (4). Both 3 and 4 are shown to come from subsequent reactions of the primary insertion product $(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{M(SH)}_2$.

Zirconocene hydrides have been much studied since 1970 [1]. Their reactivity has been shown to stem both from the unsaturated character of the metallic center [2, 3] and from the highly hydridic nature of the metal-bonded hydrogens [4, 5]. Many insertion reactions into the Zr—H bond have been described [2, 3, 6—10], but to our knowledge none of them have involved Group 16 elements.

Some years ago we observed insertion of elemental selenium into the zirconium—methyl bond of dimethylzirconocene [11]. We now outline the results of some experiments on the reaction of selenium and sulfur with $[(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{MH}(\mu\text{-H})]_2$ (1a, M = Zr; 1b, M = Hf).

When a solution of 1 [12, 13] was added at room temperature to a well stirred mixture of grey selenium powder and toluene the colorless supernatent liquid slowly turned green. After one day removal of the excess of selenium and evaporation of the solvent gave the known [14, 15] four-membered metallacyclic compounds 2. The overall reaction is represented by eq. 1.

$$\underset{(1)}{[(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{MH}(\mu\text{-H})]_2} + 2\text{Se} \rightarrow \underset{\substack{\text{2a, M = Zr;}\\ \text{2b, M = Hf)}}}{[(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{M}(\mu\text{-Se})]_2} + 2\text{H}_2 \tag{1}$$

Monitoring of the reaction by ^{1}H NMR spectroscopy in C_6D_6 revealed the evolution of dihydrogen, but no intermediate could be detected.

A similar experiment starting from sulfur instead of selenium gave a somewhat more complex result. The main product was again the four-membered dimetallacyclosulfanes $[(\eta^5\text{-t-BuC}_5H_4)_2M(\mu\text{-S})]_2$ (**3a**, M = Zr; **3b**, M = Hf) [15], but this was accompanied by derivatives of the well-known [16] metallacyclohexasulfanes $(\eta^5\text{-t-BuC}_5H_4)_2MS_5$ (**4a**, M = Zr, NMR (C_6D_6, 25°C, TMS ref., δ (ppm)) 5.85 (t, 4H, C_5H_4) 5.68 (t, 4H, C_5H_4) 1.10 (s, 18H, t-Bu) [17] **4b**, M = Hf, NMR 5.81 (4H, C_5H_4) 5.65 (4H, C_5H_4) 1.11 (s, 18H, t-Bu)). Compounds **4** could not be separated from **3**, but were identified in the mixture by comparison with authentic samples, prepared from the corresponding metallocene dichlorides by a published procedure [16]. The relative yields of compounds **3** and **4** depended on the exact experimental conditions but **3** was always formed. The ^{1}H NMR spectra of the mixture recorded during the reaction showed, in addition to dihydrogen, two other products which were identified as H_2S and $(\eta^5\text{-t-BuC}_5H_4)_2M(SH)_2$ (**5a**, M = Zr, NMR (C_6D_6, TMS ref., δ (ppm)) 5.88 (t, 4H, C_5H_4) 5.71 (t, 4H, C_5H_4) 2.21 (s, 2H, SH) 1.22 (s, 18H, t-Bu); **5b**, M = Hf, NMR 5.78 (t, 4H, C_5H_4) 5.62 (t, 4H, C_5H_4) 1.75 (s, 2H, SH) 1.23 (s, 18H, t-Bu)); **5** was the major product at the beginning of the reaction but it slowly disappeared to give both **3** and **4**.

The behaviour of compounds **5** was studied starting from authentic samples made by a procedure used for similar compounds [16, 18], the samples being treated separately with each component of the mixture. With the starting dihydrides **1** they gave the metallacycles **3** in good yield (**3a**, recryst, 54%; **3b**, 76%) (eq. 2).

$$\underset{(5)}{2(\eta^5\text{-t-BuC}_5H_4)_2M(SH)_2} + \underset{(1)}{[(\eta^5\text{-t-BuC}_5H_4)_2MH(\mu\text{-H})]_2} \longrightarrow \underset{(3)}{2[(\eta^5\text{-t-BuC}_5H_4)_2M(\mu\text{-S})]_2} + 2H_2 \qquad (2)$$

The high rate of this reaction accounts for the fact that the complexes **3** were always identified as products of the reaction of **1** with sulfur whatever the experimental conditions. With elemental sulfur, compounds **5** gave the metallacyclohexasulfanes (**4a**, 53% yield; **4b**, 57% yield) (eq. 3). Such a reaction was reported a long time ago for $(\eta^5\text{-C}_5H_5)_2Ti(SH_2)_2$ [19] and more recently for the isoleptic zirconium compound [16].

$$\underset{(5)}{2(\eta^5\text{-t-BuC}_5H_4)_2M(SH)_2} + S_8 \rightarrow \underset{(4)}{2(\eta^5\text{-t-BuC}_5H_4)_2MS_5} + 2H_2S \qquad (3)$$

Thermally-induced dimerisation of the parent of **5** containing the C_5H_5 ligand was recently shown to occur fairly readily [16]. However dimerisation of **5** itself (eq. 4) needed more drastic conditions (boiling toluene, 30 h; isolated yields: **3a**, 65%; **3b**, 55%) presumably because of steric hindrance by the t-butyl groups. In view of the mild conditions used for the reaction of **1** with sulfur it seems unlikely that the reaction shown in eq. 4 is involved in the production of metallacycles **3**.

$$2(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{M(SH)}_2 \xrightarrow{110^\circ\text{C}} [(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{M}(\mu\text{-S})]_2 + 2\text{H}_2\text{S} \qquad (4)$$

(5) **(3)**

Compounds **4** acted as sulfur reservoirs and reacted with dihydride **1** to give a mixture of **3** and **5**. These species could not be separated, but were identified by ^{1}H NMR spectroscopy in the product mixture. When **1** and **4** were allowed to react in 2/1 molar ratio, complexes **3** were isolated (**3a**, 63% yield; **3b**, 36% yield) (eq. 5).

$$4[(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{MH}(\mu\text{-H})]_2 + 2(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{MS}_5 \longrightarrow$$

(1) **(4)**

$$5[(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{M}(\mu\text{-S})]_2 + 8\text{H}_2 \qquad (5)$$

(3)

Finally, at room temperature we observed the fast reaction of the acidic hydrogen sulfide with the hydridic hydrogen atoms of the starting dihydride **1** (eq. 6) to give the compounds **5** (**5a**, 56% yield; **5b**, 83% yield).

$$[(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{MH}(\mu\text{-H})]_2 + 4\text{H}_2\text{S} \rightarrow 2(\eta^5\text{-t-BuC}_5\text{H}_4)_2\text{M(SH)}_2 + 4\text{H}_2 \qquad (6)$$

(1) **(5)**

The above results clearly show that compounds **5** are the initial products of the reaction of sulfur with dimeric dihydrides **1**, and they are assumed to be formed by direct insertion of a sulfur unit into the metal hydrogen bond. But since in the dimeric complexes **1**, the valence orbitals of the metal are all involved in the bonding [20] the reaction must start from the monomeric hydride, which is probably in equilibrium with the predominant dimeric species [21]. However we should note that compounds **2**, **3** and **4** were previously prepared from photochemically [14, 22] or thermally [17] generated metallocenic species, and since the reactivity of zirconocene dihydrides may arise from participation of reduced metallocenic species [23] a mechanism involving such species cannot be excluded in accounting for the production of metallacycles **2**, **3** and **4**.

Acknowledgment. We thank Mrs Geneviève Delmas for technical assistance in some preliminary experiments.

References

1 P.C. Wailes and H. Weigold, J. Organomet. Chem., 24 (1970) 405.
2 J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, J. Amer. Chem. Soc., 98 (1976) 6733.

3 J.E. Bercaw, Adv. Chem. Ser., 167 (1978) 136 and references therein.
4 P.C. Wailes and H. Weigold, J. Organomet. Chem., 24 (1970) 413.
5 J.A. Labinger and K.H. Komadina, J. Organomet. Chem., 155 (1978) C 25.
6 J. Schwartz and J.A. Labinger, Angew. Chem. Int. Ed. Engl., 15 (1976) 333.
7 G. Fachinetti, C. Floriani, A. Roselli and S. Pucci, J. Chem. Soc., Chem. Commun., (1978) 269.
8 J.M. Manriquez, D.R. McAlister, R.D. Sanner and J.E. Bercaw, J. Amer. Chem. Soc., 100 (1978) 2716.
9 P.T. Wolczanski and J.E. Bercaw, J. Amer. Chem. Soc., 101 (1979) 6450.
10 S. Gambarotta, M. Basso-Bert, C. Floriani and G. Guastini, J. Chem. Soc., Chem. Commun., (1982) 374.
11 B. Gautheron, G. Tainturier and Ph. Meunier, J. Organomet. Chem., 209 (1981) C49.
12 S. Couturier, G. Tainturier and B. Gautheron, J. Organomet. Chem., 195 (1980) 291.
13 A. Laarif, F. Theobald, B. Gautheron and G. Tainturier, J. Appl. Cryst., 16 (1983) 277.
14 B. Gautheron, G. Tainturier and S. Pouly, J. Organomet. Chem., 268 (1984) C56.
15 G. Tainturier, B. Gautheron and M. Fahim, J. Organomet. Chem., 290 (1985) C4.
16 A. Shaver and J.M. McCall, Organometallics, 3 (1984) 1823.
17 G. Erker, T. Mühlenbernd, G. Tainturier and B. Gautheron, Organometallics, in press.
18 H. Köpf and M. Schmidt, Angew. Chem. Int. Ed. Engl., 4 (1965) 953.
19 H. Köpf, B. Block and M. Schmidt, Chem. Ber., 101 (1968) 272.
20 S.B. Jones and J.L. Petersen, Inorg. Chem., 20 (1981) 2889.
21 D.C. Bickley, Nguyen Hao, P. Bougeard, B.G. Sayer, R.C. Burns and M.J. McGlinchey, J. Organomet. Chem., 246 (1983) 257.
22 G. Tainturier and M. Fahim, unpublished results.
23 S.B. Jones and J.L. Petersen, J. Amer. Chem. Soc., 105 (1983) 5502.