Journal of Organometallic Chemistry, 290 (1985) C4—C6
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PREPARATION OF BIS(μ-CHALCOGENO) COMPLEXES $[(\eta^5\text{-RC}_5H_4)_2M(\mu\text{-E})]_2$ M = Zr, Hf; R = H, t-Bu; E = S OR Se FROM METALLOCENE DICHLORIDES, AND ISOLATION OF THE MIXED μ-COMPLEXES $[(\text{t-BuC}_5H_4)_2Zr_2](\mu\text{-O})(\mu\text{-E})$

GERARD TAINTURIER*, BERNARD GAUTHERON and MOHAMMED FAHIM

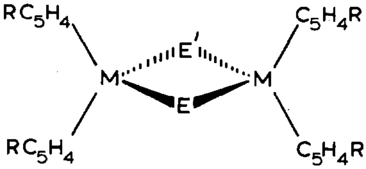
Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (UA 33), Faculté des Sciences, 6 bd Gabriel 21100 Dijon (France)

(Received April 16th, 1985)

Summary

Metallocene dichlorides $(\text{RCp})_2MCl_2$ (M = Zr, Hf; R = H, t-Bu) react with $E/2HLiBEt_3$ (E = S, Se) to give the symmetrical dinuclear compounds $[(\text{RCp})_2M(\mu\text{-E})]_2$. UV irradiation in toluene of $[(\text{t-BuCp})_2Zr(CH_3)]_2(\mu\text{-O})$ in the presence of powdered sulfur or gray selenium gives the new compounds $[(\text{t-BuCp})_2Zr_2](\mu\text{-O})(\mu\text{-E})$.

Many examples of bridging sulfur or selenium ligands are known [1—5] and some of them involve early transition metal atoms [6,7]. We recently reported the preparation of complexes 3b and 4b by UV irradiation of a mixture of the corresponding diphenyl-zirconocene (or -hafnocene) and powdered selenium [8]. These results were rationalized in terms of oxidation of the photochemically generated transient metallocenes. Unfortunately this method is confined to the special case of alkylcyclopentadienyl complexes 3b and 4b (Table 1).



We describe below a more general preparation of complexes containing μ-chalcogenides ligands starting from the appropriate dichloride. The starting compound is treated in THF at room temperature for a few days with the

0022-328X/85/$03.30

anhydrous reagent prepared from $LiHB(C_2H_5)_3$ and elemental chalcogen [9,10]. Compounds 1—4 are isolated as brightly colored, high melting crystals after evaporation of THF, extraction with CH_2Cl_2 (1, 2) or toluene (3, 4) by filtration of the solution, and cooling.

The compounds 3b and 4b were found to be identified with authentic samples [8].

TABLE 1

CHARACTERIZATION DATA OF ISOLATED (η^5-$RC_5H_4)_2M(\mu$-E)(μ-E') COMPOUNDS

	M	R	E	E'	^{1}H NMR ^{a} δ (ppm)	Ref.
1a	Zr	H	S	S	6.26s	[11]
1b	Zr	H	Se	Se	6.34s	
2a	Hf	H	S	S	6.22s	
2b	Hf	H	Se	Se	6.28s	
3a	Zr	t-Bu	S	S	6.42ps4H; 1.30s9H	
3b	Zr	t-Bu	Se	Se	6.52m4H; 1.28s9H	[8]
4a	Hf	t-Bu	S	S	6.37m4H; 1.32s9H	
4b	Hf	t-Bu	Se	Se	6.47m4H; 1.31s9H	[8]
5a	Zr	t-Bu	S	O	6.52pq1H; 6.30pq1H; 6.07pq1H; 5.87pq1H; 1.32s9H	
5b	Zr	t-Bu	Se	O	6.65pq1H; 6.32pq1H; 6.00pq1H; 5.81pq1H; 1.33s9H	

^{a} Solvent C_6D_6, internal ref. TMS. Multiplicity: s, singlet; m, multiplet; ps, pseudosinglet; pq, pseudoquadruplet.

Others were characterized by ^{1}H NMR spectroscopy (see Table 1), elemental analysis* and mass spectrometry.

A different synthesis of complex 1a (6.48 ppm; $CDCl_3$) was described recently [11].

The main feature of the NMR spectra is the substantial deshielding of cyclopentadienyl protons. For example, in 3b δ 6.52 ppm compared with δ 5.86 and 6.00 ppm in $(t\text{-BuCp})_2Zr(SePh)_2$ [12]. The low field shift in the resonance of cyclopentadienyl protons seems to be associated with the μ-character of the ligands.

The casual isochrony observed in C_6D_6 for the cyclopentadienyl protons in compound 3a disappears in $CDCl_3$ in which only the two pseudo-triplets characteristic of the expected AA'XX' pattern appear.

In the mass spectra the isotopic distribution in the molecular ion is in accordance with the dinuclear structure shown in Scheme 1. Successive losses of cyclopentadienyl ligands and chalcogen are generally observed.

For the syntheses compounds 1—4 were treated as moisture sensitive compounds. In fact the stability towards hydrolysis of alkylcyclopentadienyl compounds 3—4 is much greater than that of analogues 1 and 2; this observation is supported by the mass spectra of the latter compounds, which show additional signals which can be attributed to μ-oxo-μ-chalcogeno species. In order to confirm this suggestion, we prepared the μ-oxo derivatives 5. Treatment of a heptane solution of $(t\text{-BuC}_5H_4)_2Zr(CH_3)_2$ [13] with the stoechiometric

---

*Satisfactory C, H, M and E analyses were obtained in all cases.

amount of water (0.5 mol/mol) under ultrasonic activation leads to the μ-oxo complex* $[(t\text{-}BuC_5H_4)_2Zr(CH_3)]_2(\mu\text{-}O)$ (6). Yield 70%, m.p. 138°C. ^1H NMR (C_6D_6, TMS ref., δ (ppm): 6.10 (pq, 2H); 5.98 (pq, 2H); 5.87 (pq, 2H); 5.77 (pq, 2H); 1.26 (s, 18H); 0.49 (s, 3H). Mass spectrum: $(M-15)^+$; $(M-30)^+$. UV irradiation (Pyrex filter) of a toluene or heptane solution of 6 in the presence of a slight excess of sulfur or selenium powder affords the complexes 5a or 5b (Table 1), these compounds display the characteristic IR band associated with the Zr—O—Zr unit (ν 790 cm^{-1}, Nujol mulls) [15—17]. In the NMR spectra their cyclopentadienyl signals are split into four signals characteristic of alkylmetallocene bearing two different σ-ligands [18,19].

To the best of our knowledge, zirconium complexes of type 5 are unprecedented. In most of the known μ-oxo compounds the value of the Zr—O—Zr angle is not far from 180° [14,20—22], and this has been rationalized in terms of a *sp* hybridization of the bridging oxygen atom [22]. As such a value seems to be precluded in 5 a study of the structure of this compound would be of interest.

References

1 J.L. Vidal, R.A. Fiato, L.A. Cosby, and R.L. Pruett, Inorg. Chem., 17 (1978) 2574.
2 H. Puff, R. Gattermayer, R. Hundt and R. Zimmer, Angew. Chem. Int. Ed. Engl., 16 (1977) 547.
3 M. Wojnowska, N. Noltemeyer, H.J. Füllgrabe and A. Meller, J. Organomet. Chem., 228 (1982) 229.
4 H. Brunner, J. Wachter and H. Wintergerst, J. Organomet. Chem., 235 (1982) 77.
5 H. Brunner, W. Meier, J. Wachter, E. Guggolz, T. Zahn and M.L. Ziegler, Organometallics, 1 (1982) 1107.
6 W.A. Herrmann, H. Biersack, M.L. Ziegler and B. Balbach, J. Organomet. Chem., 206 (1981) C 33.
7 Yu.V. Skripkin, I.L. Eremenko, A.A. Pasynskii, Yu.I. Struchkov and V.E. Shklover, J. Organomet. Chem., 267 (1984) 285.
8 B. Gautheron, G. Tainturier and S. Pouly, J. Organomet. Chem., 268 (1984) C56.
9 J.A. Gladysz, J.L. Hornby and J.E. Garbe, J. Org. Chem., 43 (1978) 1204.
10 J.A. Gladysz, V.K. Wong and B.S. Jick, Tetrahedron, 35 (1979) 2329.
11 A. Shaver and J. McCall, Organometallics, 3 (1984) 1823.
12 B. Gautheron, G. Tainturier and P. Meunier, J. Organomet. Chem., 209 (1981) C49.
13 S. Couturier, G. Tainturier and B. Gautheron, J. Organomet. Chem., 195 (1980) 291.
14 W.E. Hunter, D.C. Hrncir, R.Y. Bynum, R.A. Pentilla and J.L. Atwood, Organometallics, 2 (1983) 750.
15 E.M. Brainina, R.K. Freidlina and A.N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 154 (1964) 1113.
16 A.F. Reid, J.S. Shannon, J.M. Swan and P.C. Wailes, Aust. J. Chem., 18 (1965) 173.
17 E. Samuel, Bull. Soc. Chim. Fr., (1966) 3548.
18 M.F. Lappert, C.J. Pickett, P.I. Riley and P.I.W. Yarrow, J. Chem. Soc. Dalton, (1981) 805.
19 P. Renaut, G. Tainturier and B. Gautheron, J. Organomet. Chem., 148 (1978) 43.
20 J.C. Clarke and M.G.B. Drew, Acta. Crystallogr. B30 (1974) 2267.
21 G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Am. Chem. Soc., 101 (1979) 1767.
22 J.L. Petersen, J. Organomet. Chem., 166 (1979) 179.

---

*For preparation of the parent $[Cp_2Zr(CH_3)]_2O$ see ref. 14.