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Preliminary communication

REACTION OF PHOTOGENERATED TRANSIENT ZIRCONOCENE AND HAFNOCENE WITH ELEMENTAL SELENIUM. SYNTHESIS AND CHARACTERIZATION OF $[(\eta^5\text{-t-BuC}_5H_4)_2M(\mu\text{-Se})]_2$ M = Zr, Hf

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Summary

UV photolysis of mixtures of dialkyl or diaryl complexes of Group IVA metals $(\eta^5\text{-t-BuC}_5H_4)_2M(CH_3)_2$ (M = Zr, Hf) containing grey selenium gives the new complexes $[(\eta^5\text{-t-BuC}_5H_4)_2M(\mu\text{-Se})]_2$ (II). These complexes are also formed by UV irradiation of a solution of equimolar amounts of I and $(\eta^5\text{-t-BuC}_5H_4)_2M(SePh)_2$.

UV photolysis of mixtures of dialkyl or diaryl complexes of Group IVA metals with potential ligands in one-pot reactions is well documented [1—5]. Obviously the structure of the final compounds depends mainly on the nature of the added ligand. For example, irradiation of diarylzirconocene gives biaryls via intramolecular coupling [3], and the dicyclopentadienylzirconium(II) moiety can be trapped by 1,4-diene to give η^4-dienezirconocene complexes [5]. We now report the results of irradiations of diaryl- or dimethyl-zirconocene and -hafnocene solutions containing elemental selenium.

Overnight irradiation (UV light, Pyrex filter, room temperature) of a well-stirred heptane solution of $(\eta^5\text{-t-BuC}_5H_4)_2MPh_2$ (I) [6a] containing grey selenium powder gave biphenyl (1 mol per mol of I) and bright green crystals of II, which were isolated by filtration, washing with pentane, and recrystallization (heptane solvent).

The diamagnetic compounds II were characterized by elemental analyses and NMR spectrometry: IIa, M = Zr, Yield: 70%, m.p. ≃ 290°C, Found: C, 52.57; H, 6.31. $C_{36}H_{52}Se_2Zr_2$ calcd.: C, 52.47; H, 6.20%. NMR (C_6D_6, TMS ref., δ (ppm)). ^{1}H: 6.52 (AA'BB' pattern, 4 H, C_5H_4); 1.28 (s, 9 H, t-Bu). ^{13}C: 31.7 (CH_3); 32.5 (t-Bu); 110.9 and 109.0 (C_5H_4). ^{77}Se: 802.6 [6b].

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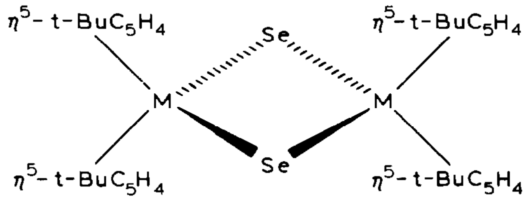

(IIa : M = Zr ; IIb : M = Hf)

IIb, M = Hf, Yield: 60%, m.p. > 300°C, Found C, 42.17; H, 5.10. $C_{36}H_{52}Se_2Hf_2$ calcd.: C, 43.25; H, 5.20%. NMR (C_6D_6, TMS ref., δ (ppm)). ^1H: 6.47 (4 H, C_5H_4); 1.31 (9 H, t-Bu).

These results, and particularly the ^1H NMR patterns which are practically unchanged on cooling, are consistent with complexes containing monosubstituted cyclopentadienyl ligands in a symmetrical environment [7—9].

The mass spectra of both compounds exhibit isotopic distribution patterns typical of ions containing two zirconium or hafnium atoms, clearly indicating the dinuclear character of complexes II.

The μ-bonded character assigned to selenium atoms is well known for analogous organometallic complexes bearing bridging sulfur atoms [10], and is not unprecedented in selenium chemistry [11]. A preliminary X-ray study of IIa [12] shows the almost square plane character of the central Zr_2Se_2 entity.

The compounds II were also isolated from the mixture obtained after UV irradiation (Pyrex filter, room temperature, heptane) of $(t\text{-}BuC_5H_4)_2M(CH_3)_2$ in the presence of selenium powder. But in this case the by-products were not characterized and the overall yield was somewhat lower.

The same complexes II were also generated by a quite different route, starting from $(t\text{-}BuC_5H_4)_2M(SePh)_2$ [13,14] and an equimolecular amount of the corresponding complex I. Overnight irradiation (usual conditions) gave a mixture of II and biphenyl. The fate of the phenyl group of the phenylselenide ligand in this reaction is still unknown.

Further synthetic and structural studies of analogous complexes are in progress.

References

1 H. Alt and M.D. Rausch, J. Am. Chem. Soc., 96 (1974) 5936.
2 E. Samuel and C. Giannotti, J. Organomet. Chem., 113 (1976) C17.
3 G. Erker, J. Organomet. Chem., 134 (1977) 189.
4 M.D. Rausch, W.H. Boon and E.A. Mintz, J. Organometal. Chem., 160 (1978) 81.
5 G. Erker, J. Wicher, K. Engel, F. Rosenfeldt, W. Dietrich and K. Krüger, J. Am. Chem. Soc., 102 (1980) 6346.
6 (a) B. Gautheron, G. Tainturier, S. Pouly, F. Théobald, H. Vivier and A. Laarif, Organometallics, submitted for publication; (b) P. Granger, B. Gautheron, G. Tainturier, S. Pouly, Org. Magn. Res., in press.
7 M.F. Sullivan and W.F. Little, J. Organomet. Chem., 8 (1967) 277.
8 P. Renaut, G. Tainturier and B. Gautheron, J. Organomet. Chem., 148 (1978) 43.
9 M.F. Lappert, C.J. Pickett, P.I. Riley and P.I.W. Yarrow, J. Chem. Soc. Dalton, (1981) 814.
10 J.L. Vidal, R.A. Fiato, L.A. Cosby and R.L. Pruett, Inorg. Chem., 17 (1978) 2574.
11 M. Wojnowska, N. Noltemeyer, H.J. Füllgrabe and A. Meller, J. Organomet. Chem., 228 (1982) 229.
12 A. Laarif, F. Théobald and H. Vivier, in preparation.
13 B. Gautheron, G. Tainturier and Ph. Meunier, J. Organomet. Chem., 209 (1981) C49.
14 S. Pouly, G. Tainturier and B. Gautheron, J. Organomet. Chem., 232 (1982) C65.