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Preliminary communication

CLEAVAGE OF PHENYLDICHALCOGENIDES BY DIALKYL- AND DIARYL-ZIRCONOCENES. SYNTHESIS OF ZIRCONIUM COMPLEXES $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Zr(EPh)CH}_3$ AND $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Zr(EPh)}_2$ (R = H, t-Bu; E = Se, S)

S. POULY, G. TAINTURIER* and B. GAUTHERON

Laboratoire de Synthèse et d'Electrosynthèse Organométallique associé au CNRS (LA 33), Faculté des Sciences, 6 Boulevard Gabriel, 2100 Dijon (France)

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Summary

Reaction of PhEEPh (E = S, Se) with $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Zr(CH}_3)_2$ (R = H, t-Bu) affords the new complexes $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Zr(EPh)CH}_3$ and PhECH_3. Irradiation of these products by UV light finally gives the known complexes $(\eta^5\text{-RC}_5\text{H}_4)_2\text{-Zr(EPh)}_2$. The latter complexes can also be obtained from an irradiated mixture of $(\eta^5\text{-RC}_5\text{H}_4)_2\text{ZrPh}_2$ and PhEEPh. These reactions are thought to involve an $S_\text{H}2$ process at the metal center.

In recent communications [1,2] we described the synthesis of new organoselenides of dicyclopentadienyl-zirconium and -hafnium and reported the insertion of elemental selenium into the M—C bond. We now present a new route to the complexes $(\text{RCp})_2\text{Zr(EPh)}_2$ and the synthesis of the unknown $(\text{RCp})_2\text{Zr(EPh)CH}_3$ starting from phenyldiselenide.

A 1/1 solution of $\text{Cp}_2\text{Zr(CH}_3)_2$ and PhSePh protected from light gives the compounds shown in reactions 1a and 1b:

$$(\text{RCp})_2\text{Zr(CH}_3)_2 + \text{PhEEPh} \xrightarrow{\text{heptane}} \underset{\text{(I)}}{(\text{RCp})_2\text{Zr(EPh)CH}_3} + \underset{\text{(II)}}{\text{PhECH}_3} \qquad (1)$$

(a) R = H, E = Se;
(b) R = t-Bu, E = Se;
(c) R = H, E = S

Complexes I were characterised by ^{1}H NMR (Ia: δ 0.02 ppm (s, 3H); 5.60 ppm (s,10H); 7.03 ppm (m, 3H); 7.60 ppm (m, 2H). Ib: δ 0.23 ppm (s, 3H); 1.11 ppm (s, 18H); 5.86 ppm (m, 8H); 7.06 ppm (m, 3H); 7.67 ppm (m, 2H) C_6D_6, ref. TMS). Selenide II was identified to an authentic sample [3].

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Reaction 1b is much slower than 1a, presumably because of the bulk of the t-butyl group (Ia: quantitative yield, room temperature, overnight. Ib: quantitative yield, room temperature, a week). The same reactions occur with high rates upon mixing the solid substrates without solvent. This unusual procedure is an efficient method for preparing complexes Ia and Ib.

A subsequent substitution of the remaining methyl group of compound I by a phenylseleno group is possible when starting from a 1/2 solution of dimethylzirconocene and phenyldiselenide (reaction 2), but the formation of compounds III is much slower than that of compounds I.

$$(RCp)_2Zr(CH_3)_2 + 2\,PhSeSePh \xrightarrow{\text{heptane}} \underset{\text{(III)}}{(RCp)_2Zr(SePh)_2} + \underset{\text{(II)}}{2\,PhSeCH_3} \qquad (2)$$

(R = H, t-Bu)

Products III [1,4] were isolated as residues by washing the crude mixture with pentane. Compounds II and III were identified by their NMR spectra.

The products of reaction 1 do not react further in the dark but upon irradiation (UV light, pyrex filter, room temperature, heptane) of a 1/1 solution of complex I and selenide II disappearance of both starting compounds is observed and complex III (reaction 3) can be isolated.

$$\underset{\text{(I)}}{(RCp)_2Zr(EPh)CH_3} + \underset{\text{(II)}}{PhECH_3} \xrightarrow{\text{UV}} \underset{\text{(III)}}{(RCp)_2Zr(EPh)_2} + \text{unidentified products} \qquad (3)$$

The same products (III) can be prepared from diphenylzirconocenes instead of dimethylzirconocenes, but in this case we did not observe any reactions in the absence of UV light at room temperature. Irradiation (pyrex filter, room temperature, heptane) affords III and biphenyl (reaction 4).

$$(RCp)_2ZrPh_2 + PhSeSePh \xrightarrow{\text{UV}} \underset{\text{(III)}}{(RCp)_2Zr(SePh)_2} + PhPh \qquad (4)$$

The scope of reaction 1 can be extended to zirconium sulfur chemistry (reaction 1c) but the rate is much lower than that of reaction 1a (60% yield, room temperature, a week).

We can briefly comment upon the possible mechanism of the reactions described above. Dimethyl- and diaryl-zirconocenes are known to undergo homolytic cleavage of the σ-Zr—C bond [5—8]. Owing to the known tendency towards homolysis of the central bond of diselenides [9,10] and disulfides [11] we assume that the reactions described in this paper probably involve a homolytic substitution (S_H2) process [12]. This hypothesis is supported by the fact that the rates of reactions 1a and 1b are unaffected when the more polar solvent THF is used in place of heptane. Further studies are in progress to throw light on the mechanism.

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