

Preliminary communication

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

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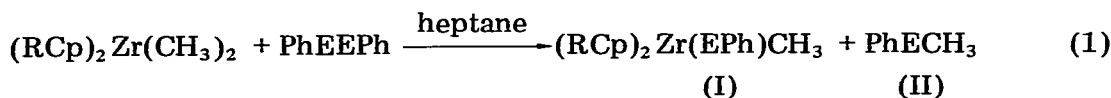
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Summary

Reaction of PhEPh (E = S, Se) with $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Zr}(\text{CH}_3)_2$ (R = H, t-Bu) affords the new complexes $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Zr}(\text{EPh})\text{CH}_3$ and PhECH₃. Irradiation of these products by UV light finally gives the known complexes $(\eta^5\text{-RC}_5\text{H}_4)_2\text{Zr}(\text{EPh})_2$. 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 PhEPh. These reactions are thought to involve an $\text{S}_{\text{H}}2$ 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 $(\text{RCp})_2\text{Zr}(\text{EPh})_2$ and the synthesis of the unknown $(\text{RCp})_2\text{Zr}(\text{EPh})\text{CH}_3$ starting from phenyldiselenide.

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



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

Complexes I were characterised by ¹H 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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