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Reactions of Bis(phenylethynyl)ytterbium with Trimethylsilicon, Triphenylgermanium, and Triphenyltin Chlorides

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Abstract—The ytterbium phenylethynyl compound $(PhC{\equiv}C)_2Yb(THF)_4$ reacts with trimethylsilicon, triphenylgermanium, and triphenyltin chloride in tetrahydrofuran (THF) at room temperature to give the corresponding cross-coupling products: phenylethynylytterbium chloride $PhC{\equiv}CYbCl(THF)_2$ and ytterbium chloride $YbCl_2(THF)_2$.

We have reported previously [1] that the most convenient synthetic route to homoleptic phenylethynyl derivatives of lanthanides is reaction of phenylethynylsodium with rare-earth metal iodides. The resulting compounds were isolated pure. They are highly reactive [2, 3]. In particular, it is known [4–6] that organolanthanide analogs of Grignard reagents, RLnX (R = alkyl, aryl; Ln = Yb, Eu, Sm, Ce; X = I, Br, Cl), prepared in situ, react with trimethylsilicon and triphenyltin chlorides, as well as with alkyl and aryl halides, in the presence of palladium and nickel complexes to give the cross-coupling products in high yields:

$$PhLnX + R{-}I \xrightarrow[\text{THF, 25°C}]{Pd(PPh_3)_4} Ph{-}R + LnXI.$$

In this study, we examined the reactivity of lanthanide phenylethynyl derivatives. As an example, we chose the reactions of bis(phenylethynyl)ytterbium with mixed organometallic compounds R_3ECl (R = CH_3, Ph; E = Si, Ge, Sn).

We found that bis(phenylethynyl)ytterbium reacts with trimethylsilicon, triphenylgermanium, and triphenyltin chlorides in THF at room temperature even in the course of mixing the reactants. The mixture, however, was allowed to stand for 24 h to bring the reaction to completion. As seen from the table, the major reaction products are the corresponding unsymmetrical organic derivatives of silicon, germanium, and tin (cross-coupling products), phenylethynylytterbium chloride $PhC{\equiv}CYbCl(THF)_2$, and ytterbium chloride $YbCl_2(THF)_2$.

The mechanism of formation of the reaction products apparently involves stepwise dealkynylation of the organolanthanide compound.

$$(PhC{\equiv}C)_2Yb(THF)_4 + R_3ECl \xrightarrow{THF} R_3EC{\equiv}CPh + (PhC{\equiv}C)YbCl(THF)_2,$$

$$(PhC{\equiv}C)YbCl(THF)_2 + R_3ECl \xrightarrow{THF} R_3EC{\equiv}CPh + YbCl_2(THF)_2.$$

As seen from the table, bis(phenylethynyl)ytterbium is dealkynylated most readily under the action of trimethylsilicon chloride. Replacement of the methyl group by phenyl (Ph_3GeCl, Ph_3SnCl) results in decreased yield of ytterbium chloride. The yield of the cross-coupling product decreases also.

Thus, bis(phenylethynyl)ytterbium reacts with trimethylsilicon, triphenylgermanium, and triphenyltin chlorides under mild conditions without a catalyst, giving cross-coupling products in high yields.

EXPERIMENTAL

All manipulations with air- and moisture-sensitive compounds were performed in evacuated sealed am-

Reactions of bis(phenylethynyl)ytterbium with R_3ECl (E = Si, Ge, Sn; R = CH_3, C_6H_5; molar ratio 1 : 2) in THF at room temperature for 24 h

R_3ECl	Reaction products, moles per mole of starting $(PhC{\equiv}C)_2Yb(THF)_4$		
	$PhC{\equiv}CER_3$	$PhC{\equiv}CYbCl(THF)_2$	$YbCl_2(THF)_2$
Me_3SiCl	1.90	0.15	0.85
Ph_3GeCl	1.35	0.64	0.33
Ph_3SnCl	1.36	0.40	0.39

pules using thoroughly dried and degassed solvents. The IR spectra were recorded on an IKS-25 spectrometer; samples were prepared as mulls in mineral oil under argon. The ytterbium phenylethynyl derivative was prepared by the reaction of ytterbium diiodide with phenylethynylsodium in THF. The melting (or decomposition) points of the starting compounds and reaction products were determined in sealed capillaries (the uncorrected values are given).

Reaction of $(PhC{\equiv}C)_2Yb(THF)_4$ with Me_3SiCl. An 0.40-g portion of Me_3SiCl was added to a solution of 0.81 g of $(PhC{\equiv}C)_2Yb(THF)_4$ in 30 ml of THF. The solution changed color, and a precipitate formed. The mixture was allowed to stand for a day at room temperature. The solvent was vacuum-evaporated, and the residue was treated with hexane. The precipitate formed in THF contained 0.54 g of $YbCl_2(THF)_2$, a light yellow substance unstable in air and insoluble in THF and hexane; mp >350°C. Found, %: Cl 15.46; Yb 41.68. $C_8H_{16}Cl_2O_2Yb$. Calculated, %: Cl 18.29; Yb 44.58.

The yellow solid insoluble in hexane was vacuum-dried for 1 h at room temperature; 0.10 g of $PhC{\equiv}C \cdot YbCl(THF)_2$ was obtained as a yellow amorphous substance, mp 285–290°C, sensitive to atmospheric oxygen and moisture, soluble in THF and benzene, and insoluble in hexane. IR spectrum, ν, cm^{-1}: 2200 m (PhC≡C), 2050 m (C≡C), 1880 w, 1790 w, 1445 s, 1380 s, 1300 s, 1070 m, 1025 s, 995 s, 730 m, 670 s, 490 m; 1040 m, 840 m (coordinated THF). Found, %: Cl 6.48; Yb 37.23; $C_{16}H_{21}ClO_2Yb$. Calculated, %: Cl 7.82; Yb 38.14.

From the combined hexane extracts, the solvent was slowly removed, and 0.46 g of $Me_3SiC{\equiv}CPh$ was obtained as an air-stable yellow oily substance, bp 82°C (6 mm) [5], readily soluble in THF, benzene, and hexane. Found, %: C 75.36; H 7.90. $C_{11}H_{14}Si$. Calculated, %: C 75.86; H 8.04.

Reaction of $(PhC{\equiv}C)_2Yb(THF)_4$ with Ph_3GeCl. An 0.34-g portion of Ph_3GeCl was added to a solution of 0.32 g of $(PhC{\equiv}C)_2Yb(THF)_4$ in 30 ml of THF. The mixture was allowed to stand for a day at room temperature, the solvent was vacuum-evaporated, and the residue was treated with hexane. The precipitate formed in THF contained 0.063 g of $YbCl_2(THF)_2$. Found, %: Cl 23.09; Yb 40.68. $C_8H_{16}Cl_2O_2Yb$. Calculated, %: Cl 18.29; Yb 44.58.

The yellow solid insoluble in hexane was vacuum-dried for 1 h at room temperature; 0.12 g of $PhC{\equiv}C \cdot YbCl(THF)_2$ was obtained. Its IR spectrum coincided with that of the similar product obtained in the reaction with Me_3SiCl. Found, %: C 42.44; H 4.47; Cl 9.48; Yb 41.93. $C_{16}H_{21}O_2YbCl$. Calculated, %: C 42.33; H 4.63; Cl 9.30; Yb 45.34.

From the combined hexane extracts, the solvent was evaporated, and 0.26 g of $Ph_3GeC{\equiv}CPh$ was obtained as a white air-stable crystalline substance, mp 84°C, readily soluble in THF, benzene, and hexane. IR spectrum, ν, cm^{-1}: 3040 s, 2165 s (C≡C), 1480 s, 1425 m, 1085 s, 1065 w, 1020 w, 995 m, 730 s, 690 s, 460 s. Found, %: C 74.10; H 6.04. $C_{26}H_{20}Ge$. Calculated, %: C 74.45; H 6.56.

Reaction of $(PhC{\equiv}C)_2Yb(THF)_4$ with Ph_3SnCl. A 0.50-g portion of Ph_3SnCl was added to a solution of 0.43 g of $(PhC{\equiv}C)_2Yb(THF)_4$ in 30 ml of THF. The mixture was allowed to stand for a day at room temperature, the solvent was vacuum-evaporated, and the residue was treated with hexane. The precipitate formed in THF contained 0.10 g of $YbCl_2(THF)_2$. Found, %: Cl 20.02; Yb 42.98, $C_8H_{16}O_2YbCl_2$. Calculated, %: Cl 18.29; Yb 44.58.

The yellow solid insoluble in hexane was vacuum-dried for 1 h at room temperature; 0.12 g of $PhC{\equiv}C \cdot YbCl(THF)_2$. was obtained. Its IR spectrum coincided with that of the similar product obtained in the reaction with Me_3SiCl. Found, %: Cl 5.48; Yb 36.33. $C_{16}H_{21}O_2YbCl$. Calculated, %: Cl 7.82; Yb 38.14.

From the combined hexane extracts, the solvent was slowly evaporated, and 0.39 g of $Ph_3SnC{\equiv}CPh$ was obtained as a colorless air-stable crystalline substance, mp 62°C (in agreement with published data [7]), readily soluble in THF, benzene, and hexane. Found, %: C 69.53; H 4.39. $C_{26}H_{20}Sn$. Calculated, %: C 69.33; H 4.44.

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