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LETTERS
TO THE EDITOR

Reaction of Ytterbium(II) and Praseodymium(III) Phenylethynyl Cuprates with Trimethylsilyl Iodide

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We have developed preparative methods for phenylethynyl lanthanide cuprates [1] which make them available as an object of study. Like lithium organocuprates, which are highly selective alkylating and arylating agents, they can be used in organic and organometallic syntheses. It has been shown [2] that praseodymium and ytterbium phenylethynyl cuprates react peculiarly with acyl halides to give polyfunctional organic and organometallic compounds. Therefore it was interesting to study their reactivity toward trimethylsilyl halides.

Praseodymium(III) phenyethynyl cuprate $[(PhC{\equiv}C)_3Cu]_3Pr_2(THF)_6$ reacts with trimethylsilyl iodide in a 1:6 ratio in THF solution at room temperature. The reaction is accompanied by the formation of a yellow precipitate of phenylethynylcopper and phenylethynyltrimethylsilicon. Prolonged (up to 10 days) standing of the reaction mixture resulted mainly in phenylethynylpreseodymium diiodide coordinated with THF.

$$[(PhC{\equiv}C)_3Cu]_3Pr_2(THF)_6 + Me_3SiI$$
$$\rightarrow PhC{\equiv}CCu + Me_3SiC{\equiv}CPh + PhC{\equiv}CPrI_2(THF)_3.$$

The yields of the reaction products are close to quantitative. The reaction results in the elimination of phenylethynylcopper and two-stage dealkynylation of $(PhC{\equiv}C)_3Pr$ fragment. It little differs from the reaction of tri(phenylethynyl)praseodymium tristetrahydrofuranate with trimethylsilyl iodide [3], accompanied by the formation not only of the mixed phenylethynyl lanthanide derivative, but also of praseodymium(III) iodide.

Similarly, ytterbium(II) phenylethynyl cuprate reacts with trimethylsilyl iodide in 1:4 ratio at room temperature in THF to give phenylethynylcopper and trimethylsilyl phenylacetylenide in high yields and also phenylethynylytterbium(II) and ytterbium(II) iodides in yields of 65 and 23%, respectively.

$$\{[(PhC{\equiv}C)_3Cu]Yb(THF)_2\}_2 + Me_3SiI \rightarrow PhC{\equiv}CCu$$
$$+ Me_3SiC{\equiv}CPh + PhC{\equiv}CYbI(THF)_3 + YbI_2(THF)_3.$$

Like in the case of praseodymium(III) organocuprate, similar ytterbium(II) complex eliminates phenylethynylcopper and undergoes a stepwise dealkynylation to form the cross-coupling product (trimethylsilyl phenylacetylenide) and a mixture of the above ytterbium(II) iodides. The reaction mixture contains phenylacetylene (5–10%) due likely to the generation of phenylethynyl radicals as a result of a side process involving the act of one-electron transfer, noted earlier [3] in the reaction of lanthanide compounds with phenylethynyl halides R_3EX (E = Si , Ge, Sn; X = Cl, I; R = alkyl, phenyl).

The ytterbium(II) and praseodymium(III) phenylethynyl cuprate complexes are inferior to the corresponding homoleptic lanthanide compounds [4] in the reactivity with respect to trimethylsilyl iodide, but the reaction of al these compounds occurs under mild conditions in the absence of a catalyst.

The IR spectra were recorded on a FSM 1201 FT-IR spectrometer. The samples of these unstable in air compounds were prepared in a vacuum or in an argon atmosphere as suspensions in mineral oil. The NMR spectra were registered on a spectrometer Bruker DPX-200 (^1H at 200 MHz, ^{13}C at 50 MHz). The chemical shifts are given in parts per million (ppm) relative to tetramethylsilane as an internal reference. The chromatographic analysis of volatile compounds was carried out on a Tsvet-100 chromatograph equipped with katharometer [column 100×0.3 cm, 200×0.3 cm filled with PEG-1500 (20%) on Chesasorb AW-HMDS], carrier gas helium. The melting and decomposition points were determined in evacuated sealed capillaries. The melting and decomposition points were not corrected. The magnetochemical measurements were performed by the method of [5].

The preparation, purification and separation of the unstable in air compounds were carried out in evacuated sealed ampules using the Schlenk techniques. The organic solvents were purified by the known methods [6]. THF and hexane were distilled over sodium benzophenone, degassed, and placed in an evacuated ampule with a pre-prepared sodium mirror. The required amount of the solvent was collected by condensation in a vacuum.

The rare-earth metals of Russian production of 99.90–99.99% purity were used.

The reaction of $\{[(PhC\equiv C)_3Cu]Yb(THF)_2\}_2$ with trimethylsilyl iodide. To a solution of 1.98 g (1.44 mmol) of $\{[(PhC\equiv C)_3Cu]Yb(THF)_2\}_2$ in 20 ml of THF was added 1.15 g (5.76 mmol) of trimethylsilyl iodide. The reaction mixture was kept at room temperature for 10 days. A crystalline precipitate of ytterbium(II) iodide was formed. Its diamagnetic state was confirmed by the magnetochemical measurements. The precipitate was separated, washed with THF, and dried in a vacuum. Yield 23.6% (0.22 g, 0.34 mmol). Found, %: Yb 26.67; I 37.93. $C_{12}H_{24}I_2O_3Yb$. Calculated, %: Yb 26.90; I 39.50.

THF was distilled off from the filtrate into a trap cooled with liquid nitrogen. The trap contained 0.08 g (0.86 mmol, 10%) of phenylacetylene, identified by GLC.

To the residue in the ampule was added benzene to collect the phenylethynylcopper formed in 82.2% yield (0.39 g, 2.37 mmol). Yellow amorphous substance, decomp. 225°C. Found Cu, %: 38.60. C_8H_5Cu. Calculated Cu, %: 38.79.

Benzene was distilled off from the filtrate into a trap cooled with liquid nitrogen. To the residue was added hexane. The solid residue was washed with hexane (5×40 ml) and dried in a vacuum to a constant mass. Yield of $PhC\equiv CYbI(THF)_3$ 1.15 g (65%, 1.86 mmol), light brown amorphous substance, insoluble in hexane, decomp. 200°C. IR spectrum (mineral oil), ν, cm^{-1}: 2200 m ($PhC\equiv C$), 1880 w, 1790 w, 1461 s, 1379 s, 1300 s, 1071 m, 1026 s, 914 s, 757 m, 689; 1040 m, 840 m (coordinated THF). Found, %: Yb 30.50; I 21.39. $C_{20}H_{29}IO_3Yb$. Calculated, %: Yb 28.04; I 20.58.

The solvent was removed from the hexane extracts to give $Me_3SiC\equiv CPh$. Yield 62% (0.61 g, 3.55 mmol), pale yellow oil, readily soluble in THF, benzene, bp 153°C (6 mm Hg) [7]. IR spectrum (mineral oil), ν, cm^{-1}: 3080 m, 3060 m, 3027 m, 2956 s; 2160 s ($C\equiv C$), 1950 w, 1598 m, 1488 s, 1444 m, 1251 s, 1100 s, 1029 m, 866 s, 843 s, 757 s, 689 s, 645 m, 535 s. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.28–7.45 m (5H), 0.10 s [9H, $Si(CH_3)_3$]. Found, %: C 75.46; H 7.96. $C_{11}H_{14}Si$. Calculated, %: C 75.86; H 8.04.

The reaction of $[(PhC\equiv C)_3Cu]_3Pr_2(THF)_6$ with trimethylsilyl iodide. To a solution of 2.12 g (1.16 mmol) of $[(PhC\equiv C)_3Cu]_3Pr_2(THF)_6$ in 20 ml of THF was added 1.39 g (6.96 mmol) of trimethylsilyl iodide. The reaction mixture was kept at room temperature for 10 days. Phenylethynylcopper formed as a yellow precipitate. Yield 91% (0.52 g, 3.19 mmol). It is identical to the compound obtained in the previous experiment.

THF was distilled off from the filtrate into a trap cooled with liquid nitrogen. The trap contained phenylacetylene (yield 5%, by GLC). To the residue was added hexane. The solid residue was washed with hexane (5 × 40 ml) and dried in a vacuum to a constant mass. Yield of $PhC\equiv CPrI_2(THF)_3$ 1.53 g (92%, 2.14 mmol), brown amorphous substance, insoluble in hexane, decomp. 190°C. IR spectrum (mineral oil), ν, cm^{-1}: 2200 m ($PhC\equiv C$), 1880 w, 1790 w, 1458 s, 1379 s, 1251 s, 1074 m, 1029 s, 914 s, 757 m, 689 s; 1050 m, 843 m (coordinated THF). Found, %: Pr 18.98; I 35.35. $C_{20}H_{29}I_2O_3Pr$. Calculated, %: Pr 19.80; I 35.67.

The solvent was removed from the hexane extracts to give $Me_3SiC\equiv CPh$. Yield 66% (0.79 g, 4.59 mmol). This compound is identical to that obtained in the previous reaction.

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