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ORGANIC DERIVATIVES OF DIVALENT YTTERBIUM RYbX IN METALLATION REACTIONS

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Organic derivatives of divalent lanthanides, RLnX, are attracting ever increasing attention in light of their use in organic synthesis [1]. The usual method for their preparation is the oxidative addition of RX (R = Ar, Me, Bz, $CH_2{=}CH{-}CH_2$) to a zero-valent metal [2] or the reaction of organolithium compounds with LnX_2 salts.

The direct metallation of organic compounds using organic derivatives of divalent lanthanides has virtually not been studied. The only report available concerns the preparation of bis(phenylethynyl)ytterbium by the reaction of phenylacetylene with bis(pentafluorophenyl)- or bis(tert-butylethynyl)ytterbium [4]. The metallation of CH-acids by the action of RYbX has not been reported.

We have shown that PhYbX and CH_3YbI prepared in situ readily react with various CH-acids, RH, with pK_a from 18 to 26 [5] (R = phenyl-o-carboranyl, phenylethynyl, indenyl, pentafluorophenyl, 9-fluorenyl) in THF solution to form the corresponding ytterbium derivatives, RYbI. The compounds obtained were introduced without separation into reaction with D_2O, Me_3SiCl or Ph_3SnCl. In this case, RD, $RSiMe_3$ or $RSnPh_3$ were obtained in high yields. Distannane, $[Ph_3Sn]_2$ was obtained in 5-7% yield in the reaction with Ph_3SnCl. Tolan was obtained in 40% yield in the reaction of phenylethynylytterbium iodide with iodobenzene

$$Ph(Me)YbI + R'H \rightarrow [R'YbI] + PhH(MeH)$$

$$\begin{tikzcd} & & {[R'YbI]} \arrow[dll, "D_2O"'] \arrow[dl, "Me_3SiCl"] \arrow[d, "Ph_3SnCl"] \arrow[dr, "PhI"] & \\ R'D & R'SiMe_3 & R'SnPh_3 & R'Ph \end{tikzcd}$$

R' = phenyl-o-carboranyl, phenylethynyl, indenyl, pentafluorophenyl, and fluorenyl.

This synthesis requires the following reaction conditions: use of THF as the solvent, temperature range from —20° to +20°C, and the addition of the CH-acids to ArYbI or RYbI. As a consequence of the sensitivity of the organoytterbium compounds toward oxygen and atmospheric moisture, all the operations were carried out in an argon atmosphere.

The metallation in the reaction of PhYbI with phenyl-o-carborane and phenylacetylene should be carried out at the lowest possible temperature in order to avoid side reactions. In the case of the less reactive indene, the reaction is carried out at room temperature. The metallation of pentafluorobenzene is best carried out by the action of MeYbI. In the case of fluorene, the metallation is only 20% complete at 64°C over 3 h even using MeYbI and the reaction does not proceed at all with PhYbI. The metallation of triphenylmethane (pK_a = 33.5) cannot be achieved by the action of RYbI even under vigorous conditions (prolonged heating at reflux in THF).

The IR spectrum of R'D (R' = phenylethynyl) shows a band at 2600 cm^{-1} ($\nu C{\equiv}D$). The $\nu CH/\nu CD$ ratio = 1.28 is characteristic for the stretching vibrations of terminal C—H and

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C—D bonds in acetylene [6]. The relative extent of deuterium exchange calculated using these bands was 84%. In addition, the band at 2120 cm^{-1} (νC≡CH) disappears upon deuteration along with the strong doublet at 655 and 688 cm^{-1} (δ≡C—H).

The changes in the fluorene IR spectrum upon its deuteration are in accord with those reported in the literature [7]. The most significant changes are the diminution in the bands at 1400 and 692 cm^{-1} (δC—H in the CH_2 group) and the appearance of bands at 940 and 680 cm^{-1} related to the HC—C and H—CD bonds. In addition, bands arise at 1256 and 780 cm^{-1}

The IR spectrum of 1-deuteroindene which has, similar to 9-deuterofluorene, an active methylene group shows changes relative to indene analogous to those examined above upon the deuteration of fluorene: diminution of the band at 1400 cm^{-1} and the appearance of bands at 1200 and 680 cm^{-1}. The bands characteristic for the double bond at 3080 cm^{-1} (ν=C—H) and 1620 cm^{-1} (νC=C) are not altered upon deuteration.

It was also of interest to elucidate the feasibility of using other organic ytterbium halides such as RYbBr in the metallation reaction. According to Evans et al. [8], such bromides are not obtained in the oxidative addition of RBr to lanthanides. However, we have found that pentafluorophenylytterbium bromide is formed in the reaction of bromopentafluorobenzene with metallic ytterbium in THF at −35°C over 30 min. The action of C_6F_5YbBr on phenyl-o-carborane in THF gives the ytterbium derivative of this CH-acid in quantitative yield.

We note that the method of synthesizing of RYbX by the metallation of CH-acids (RH) is valuable when the corresponding RX are not obtained conveniently or do not undergo oxidative addition with lanthanides.

EXPERIMENTAL

The IR spectra of R'D were measured on a UR-20 spectrophotometer. A method involving dispersion in KBr was used for R' = fluorenyl, while solutions in CCl_4 were prepared for compounds with R' = phenylethynyl or indenyl.

Metallation of Phenyl-o-carborane by Phenylytterbium Iodide. A solution of 0.563 g phenyl-o-carborane in 10 ml THF was added at —20°C to a solution of phenylytterbium iodide (obtained from 0.813 g Yb and 0.862 g PhI in 10 ml THF). After 30 min, the reaction mixture was warmed to 15°C and a solution of 0.275 g Me_3SiCl in 10 ml THF was added at this temperature. The mixture was stirred for 1 h, decomposed with water, and extracted with ether. The ethereal extracts were dried over Na_2SO_4 and the ether was removed to yield 0.7 g (94.5%) phenyl-o-carboranyltrimethylsilane, mp 106°C.

Metallation of Phenylacetylene by Phenylytterbium Iodide. a) A solution of 0.375 g phenylacetylene in 10 ml THF to a solution of phenylytterbium iodide (from 0.756 g Yb and 0.714 g PhI in 20 ml THF) at 10°C. The reaction mixture was stirred for 1 h and cooled to 0°C. A sample of 1 ml D_2O was added at this temperature. THF was removed in vacuum. The residue was extracted by ether. The ethereal extracts were dried and the ether solvent was removed. IR spectroscopy indicated that the residue consisted of deuterated phenylacetylene.

b) A solution of 0.36 g phenylacetylene in 10 ml THF was added at 10°C to a solution of phenylytterbium iodide (from 0.77 g Yb and 0.73 g PhI in 20 ml THF). The reaction mixture was stirred for 1 h and then an additional 0.73 g PhI in 10 ml THF was added at ∿20°C. After about 16 h, the reaction mixture was decomposed as described above. The ethereal extracts were concentrated. Gas—liquid chromatography indicated the presence of 0.25 g (40%) tolan in the mixture.

Metallation of Indene by Phenylytterbium Iodide. A solution of 0.66 g indene in 10 ml THF was added to a solution of phenylytterbium iodide (from 1.098 g Yb and 1.16 g PhI in 20 ml THF). The mixture was stirred for 20 min at ∿20°C and decomposed by 0.2 ml D_2O. THF was removed in vacuum. The residue was extracted with ether and the ether was removed. The IR and PMR spectra indicated that the residue consisted of deuterated indene.

Metallation of Indene by Methylytterbium Iodide. A solution of 0.37 g indene in 10 ml THF was added dropwise at 15°C to a solution of methylytterbium iodide (from 1.002 g Yb and 0.74 g MeI in 20 ml THF). To complete the reaction, the mixture was stirred for 40 min at 20°C and then a solution of 1.225 g Ph_3SnCl in 20 ml THF was added. The temperature was raised from 20° to 28°C. The solution color changed from red-brown to gray-green. To complete the reaction, the mixture was stirred for 1 h. The mixture was decomposed as described above to yield 1.18 g (80%) indenyltriphenyltin, mp 128-129°C [10]. In addition, 0.09 g

(8%) hexaphenyldistannane with mp 237°C was also obtained. A mixed melting point with an authentic sample did not give a depressed mixed melting point.

Metallation of Pentafluorobenzene by Phenylytterbium Iodide. A solution of 0.433 g pentafluorobenzene in 20 ml THF was added to a solution of phenylytterbium iodide (from 0.822 g Yb and 0.877 g PhI in 20 ml THF) and stirred for 2 h at ∿20°C. Then, a solution of 1 g Ph_3SnCl in 30 ml THF was added and maintained for ∿16 h. The mixture was decomposed as described above to yield 0.56 g (42%) pentafluorotriphenyltin with mp 83-84°C [10].

Metallation of Pentafluorobenzene by Methylytterbium Iodide. A solution of 0.95 g pentafluorobenzene in 10 ml THF was added to a solution of methylytterbium iodide (from 1.09 g Yb and 0.952 g MeI in 20 ml THF) at 20°C. The green solution turned reddish. The mixture was stirred for 40 min and then, a solution of 1.75 g Ph_3SnCl in 30 ml THF was added. To complete the reaction, the mixture was stirred for 1 h and decomposed by the usual procedure to yield 1.61 g (80%) pentafluorophenyltriphenyltin, mp 85-86°C [10]. The yield of hexaphenyldistannane was 0.11 g (7%).

Preparation of Pentafluorophenylytterbium Bromide. A sample of 1.057 g ytterbium in 10 ml THF was activated by a drop of CH_2I_2 and a solution of 1.372 g bromopentafluorobenzene in 15 ml THF was added at from —30° to —35°C. The reaction began instantaneously. The color of the solution was bright orange. To complete the reaction, the mixture was stirred for 30 min at this temperature. In order to prove the formation of the required product, the mixture was warmed to 10-15°C and a solution of 1.282 g Ph_3SnCl in 20 ml THF was added; the solution became gray-green. The mixture was stirred for 1 h at ∿20°C and decomposed by the usual procedure to yield 1.55 g (90%) pentafluorophenyltriphenyltin with mp 85°C [10].

Metallation of Phenyl-o-carborane by Pentafluorophenylytterbium Bromide. A solution of 0.631 g phenyl-o-carborane in 20 ml THF was added to a solution of pentafluorophenylytterbium bromide (from 0.863 g Yb and 0.171 g bromopentafluorobenzene in 15 ml THF). The solution color gradually changed over 40 min from bright orange to dark brown. Then, a solution of 0.308 g Me_3SiCl in 20 ml THF was added. The reaction mixture was stirred for 1 h at ∿20°C and decomposed by the usual procedure to yield 0.8 g (96%) phenyl-o-carboranyltrimethylsilane, mp 106-107°C [9].

CONCLUSIONS

1. This is the first report of the direct metallation of CH-acids with pK_a from 18 to 26 by organic derivatives of divalent ytterbium, RYbX.

2. Fluoro-substituted aryl bromides were found to undergo oxidative addition reactions with ytterbium.

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