Direct Synthesis of Organometallics, II[1]

Selective Activation of Aromatic C–H Bonds with Lithium Atoms at 77 K

Matthias Tacke

Institut für Anorganische Chemie der Universität (TH) Karlsruhe,
Engesserstr. Geb. 30.45, D-76128 Karlsruhe, Germany

Received September 7, 1994

Key Words: C–H bond activation / Lithum atoms / Cocondensation / Aryllithium

In the presence of donor bases like THF lithium atoms are able to activate benzene derivatives under cryogenic reaction conditions. Only ring-metalated products and solid lithium hydride are formed selectively. The thermodynamically favored product benzyllithium or biphenyl generated by dimerization of free phenyl radicals are not found. This is one of the very few examples of metal atoms undergoing a C–H activation without further photoexcitation.

Activation of aliphatic and aromatic hydrocarbons[2] by σ-bond metathesis using extremely electrophilic metal centers ($Cp^{*}_{2}LuCH_3$ + $^{13}CH_4$[3]) or oxidative addition in the presence of highly subcoordinated metal complex fragments (CpRhCO + c-C_6H_{12}[4]; Cp_2W + C_6H_6[5]) is a field of interest since the early 1980s. In addition, there are some reactions of photochemically activated metal atoms ($Al^* + CH_4 + h\nu \rightarrow HAlCH_3$) especially with methane under matrix conditions[6]. In this paper it is shown that lithium atoms are a powerful reagent for ring metalation of toluene and benzene under cocondensation conditions[7] at 77 K.

Synthesis of the aryllithium compounds is carried out by cocondensation of lithium atoms with benzene or toluene and THF at the temperature of liquid N_2 in a high-vacuum system [Eq. (1)].

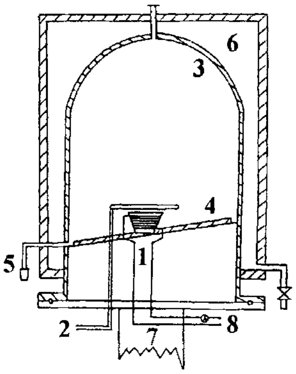
$$8\,Li(g) + 4\,PhR(g) + 4\,THF(g) \xrightarrow[77K]{\text{cocond.}} [p\text{-}R\text{-}C_6H_4\text{-}Li(THF)]_4 + 4\,LiH(s) \quad (1)$$
$$(R = H \text{ or } Me)$$

For the reaction a stainless-steel metal-vapor apparatus has been used. This equipment excludes reactions in the gas phase. Because of the low pressure inside the system the gaseous species cannot react before they reach the cold condensation vessel. The metal vapor synthesis (MVS) machine is distinctly different from standard arrangements[8]. It is equipped with a cooled internal drain in the cocondensation vessel, which allows the isolation of products under Schlenk-type conditions at low temperature. Details of the construction similar to an earlier report[9] are shown in Figure 1.

Warming up of the frozen matrix leads to aryllithium compounds which are trapped in solution or isolated by evaporation of the solvent under reduced pressure followed by direct characterization.

Selective aromatic C–H activation of hydrocarbons by lithium atoms forming ring-metalated products only is an unexpected thermal reaction. The thermodynamically favored product benzyllithium is not found. This can be understood by a reaction mechanism involving a single-electron transfer (SET) to the LUMO of the aromatic compound. These mechanistic investigations as well as new examples of this type of reaction will be published later[10]. The formation of the strong Li–C bond and the high lattice energy of solid LiH are the driving force of the observed reaction. Even under standard reaction conditions the reaction is exothermic but hindered by a strong and nonpolar C–H bond. Under cocondensation conditions the activation energy which lies in the magnitude of the C–H bond energy of benzene is available and leads to the observed process [Eq. (2) and (3)].

Figure 1. Cocondensation apparatus: (1) crucible, (2) inlet system, (3) cocondensation vessel, (4) internal drain, (5) outlet system, (6) liquid N_2, (7) high-vacuum pump, (8) power supply



$$2\,Li(s) + C_6H_6(l) \rightarrow LiH(s) + PhLi(s)^{[11]} + 21.1\ \text{kcal/mol} \quad (2)$$

$$2\,Li(g) + C_6H_6(g) \rightarrow LiH(s) + PhLi(s) + 105.4\ \text{kcal/mol} \quad (3)$$

The isolated aryllithium compound (PhLi or p-TolLi) is tetrameric[12] and solvated by THF which increases the reaction enthalpy even more.

Further characterization of the cocondensation products is carried out by addition of an excess of acetophenone. After hydrolysis [Eq. (4) and (5)], 1,1-diarylethanol and α-methylbenzyl alcohol are observed by GC MS and GC IR.

$$ArLi + PhC(O)Me \xrightarrow{H^+} Ph(Ar)C(OH)Me \quad (4)$$
$$(Ar = Ph \text{ or } p\text{-Tol})$$

$$LiH(s) + PhC(O)Me \xrightarrow{H^+} PhCH(OH)Me \quad (5)$$

In addition, aldol products initiated by deprotonation of acetophenone were found, but no biphenyl derivatives which would indicate a radical mechanism for the formation of aryllithium compounds [Eq. (6)].

0009–2940/95/0101–0091 $ 10.00+.25/0

$$2\,PhC(O)Me \xrightarrow{\text{base}} PhC(O)CH_2C(OH)(Ph)Me \xrightarrow[-H_2O]{} PhC(O)CH{=}C(Ph)Me \quad (6)$$

The observed relative molar product distribution according to Eq. (4):(5):(6) = 1:0.17:0.21 for Ar = Ph and 1:0.23:0.19 for Ar = *p*-Tol. The low product yield [Eq. (5)] is probably caused by less effective wash-out of LiH(s) in contrast to the better soluble aryllithium compound and the deprotonation of acetophenone instead of reduction of the carbonyl function.

The author thanks the *DFG*, the *Fonds der Chemischen Industrie* and the *GSF* (München) for generous support. Special thanks are due to *Gabriele Schrovenwever* and Dr. *Harald Ziemer* for GC-MS and GC-IR investigations.

Experimental

All experimental procedures were performed under dry Ar by using standard Schlenk techniques. Solvents were dried by refluxing with the appropriate drying agent and were distilled before use. The lithium metal (purity 99.9%) was purchased from Chemetall GmbH. – NMR (recorded at ambient temperatures): Jeol FX 90 (^1H), EX 400 (^{13}C), Bruker ACP 200 (^7Li; LiBr in D_2O as standard). – IR: Bruker IFS 66V. – GC IR: IFS-48 (Bruker) GC-8A (Shimadzu). – GC MS: CH7A + Spectrosystem 200 (Finnigan MAT)/GC-1400 (Varian).

Preparation of (p-TolLi · THF)₄ and (PhLi · THF)₄: In a typical experiment 1.6 g (0.23 mol) of lithium metal was vaporized from a stainless-steel crucible at 800°C during 80 min and cocondensed with a mixture of 40 ml (0.43 mol) of toluene and 40 ml (0.56 mol) of THF. The pressure which was measured at the bottom of the cocondensation vessel was kept below $5 \cdot 10^{-5}$ mbar to avoid gas-phase reactions of metal atoms and reactants. At the end of the experiment the frozen matrix was allowed to warm up under Ar. The molten reaction mixture flowed through an internal drain into a Schlenk-type tube which was kept at −78°C. For a final isolation the solvent was evaporated under reduced pressure at −20°C to avoid cleavage of the ether by lithium, which was observed at ambient temperatures. The residue was dissolved in toluene and the solution filtered from the solid lithium hydride and unreacted lithium metal. After removal of the solvent in vacuo, the corresponding aryllithium compound was isolated in 23% (p-TolLi · THF)$_4$ or 12% (PhLi · THF)$_4$ yield as red oils, respectively. These substances transformed into red-brown solids after a longer period in the refrigerator. – *(p-TolLi · THF)₄:* ^1H NMR (C_6D_6, 90 MHz): δ = 1.01 (m, 4H, CH_2), 2.35 (s, 3H, CH_3), 2.98 (m, 4H, CH_2), 6.98–7.35 (m, 2H, CH), 8.08 (m, 2H, CH). – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 22.1 (CH_3), 25.1 (CH_2), 67.9 (CH_2), 126.9 (CH), 135.0 (*p*-C), 141.9 (CH), 173.3 (*i*-C). – ^7Li NMR (C_6D_6, 104.9 MHz): δ = 2.36 (s). – For the synthesis of (PhLi · THF)$_4$ a mixture of 60 ml (0.83 mol) of THF and only 20 ml (0.26 mol) of benzene was used to obtain a low-melting matrix which was able to wash out the products more efficiently. The yield of the aryllithium compound was significantly lowered compared to the toluene experiment. – *(PhLi · THF)₄:* ^1H NMR (C_6D_6, 90 MHz): δ = 1.11 (m, 4H, CH_2), 3.13 (m, 4H, CH_2), 7.31 (t, 1H, *p*-CH), 7.40 (t, 2H, *m*-CH), 8.33 (d, 2H, *o*-CH). – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 25.6 (CH_2), 67.8 (CH_2), 125.9 (*p*-C), 126.9 (*m*-C), 141.1 (*o*-C), 174.0 (*i*-C). – ^7Li NMR (C_6D_6, 104.9 MHz): δ = 2.51 (s).

GC-MS and GC-IR Measurements: A typical experiment was conducted and the nonfiltered reaction mixture was combined with an excess of acetophenone (10 ml, 0.10 mol) at −78°C. After stirring for 12 h at −78°C and for 12 h at −20°C, solvents and excess reagent were removed in vacuo. 50 ml of Et_2O was added and the suspension was hydrolyzed under Ar at 0°C carefully. The ether phase was isolated, neutralized with 2 N HCl, dried with $MgSO_4$ and directly injected into the GC part of the analytical instrument.

---

[1] M. Tacke, *Organometallics*, **1994**, *13*, 4124.

[2] For a recent review see: J. A. Davies, P. L. Watson, J. F. Liebmann, A. Greenberg (Eds.), *Selective Hydrocarbon Activation*, VCH Verlagsgesellschaft, Weinheim, **1990**.

[3] M. Frederick, T. J. Marks, *J. Am. Chem. Soc.* **1984**, *106*, 2214.

[4] E. P. Wasserman, C. B. Moore, R. G. Bergman, *Science* **1992**, *255*, 315.

[5] C. Giannotti, M. L. H. Green, *J. Chem. Soc., Chem. Commun.* **1972**, 1114.

[6] J. M. Parnis, G. A. Ozin, *J. Phys. Chem.* **1989**, *93*, 1204.

[7] Lagow and co-workers report the C–H activation with lithium, but it is unclear whether a gas-phase reaction is observed or not: L. A. Shimp, C. Chung, R. J. Lagow, *Inorg. Chim. Acta* **1978**, *29*, 77.

[8] P. L. Timms, *Adv. Inorg. Chem. Radiochem.* **1972**, *14*, 121.

[9] M. L. H. Green, F. G. N. Cloke, *J. Chem. Soc., Dalton Trans.* **1981**, 1938.

[10] M. Tacke, unpublished results.

[11] T. Holm, *J. Organomet. Chem.* **1974**, *77*, 27.

[12] E. Wehmann, J. Jastrzebski, J.-M. Ernsting, D. M. Grove, G. van Koten, *J. Organomet. Chem.* **1988**, *353*, 133; L. M. Jackman, L. M. Scarmoutzos, *J. Am. Chem. Soc.* **1984**, *106*, 4627.

[357/94]