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Interaction of *t*-butyllithium and triphenylmethylenephosphoranes

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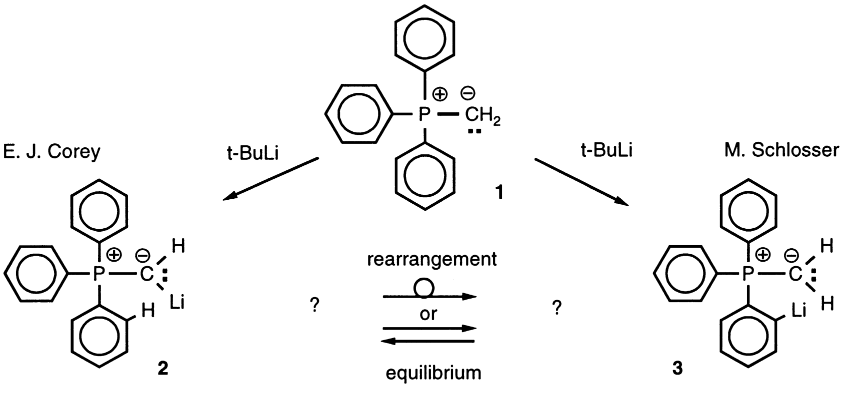
Abstract

NMR experiments show that a directed *ortho*-metalation occurs at one of the aromatic rings of triphenylmethylenephosphoranes (Ph_3P-CHR, R = H, Me) when the phosphorus ylide is treated with 1 equiv. *t*-BuLi. If pre-coordination of *t*-BuLi is inhibited by a sterically demanding and electron-withdrawing substituent (R = $SiMe_3$) no metalation is observed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: lithiation; phosphoranes; ylides; NMR data.

The lithiation of the simplest Wittig reagent, triphenylmethylenephosphorane **1**, has been the origin of a debate between Corey and Schlosser for some years.[1–6] The controversy has been whether **1** reacts with *t*-BuLi yielding α-lithiated ylide **2** or ortho-lithiated species **3** (Scheme 1).



Scheme 1.

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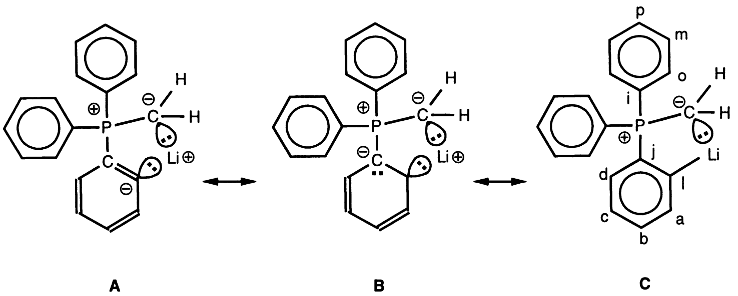
Trapping reactions of the formed metalated species were difficult to interpret and not definite.[2,4,7] Recently, Grützmacher et al. were able to show that related α-zincated triphenylmethylenephosphorane is able to undergo a base-induced rearrangement to yield the corresponding *ortho*-metalated chelate species.[8] On the other hand, Bertrand found some spectroscopic evidence for an equilibrium at the α-lithiated ylide $(^i\mathrm{Pr_2N})_2^n\mathrm{BuP\text{-}C(SiMe_3)Li}$ but this one has been attributed to a mixture of rotamers.[9] As there is no statement in literature as to whether **2** or **3** are able to convert into each other irreversibly or whether there is an equilibrium between these two species we were interested to investigate this problem by multinuclear NMR experiments.

The α-lithiated compound **2** is selectively formed by an iodine–lithium exchange reaction when $\mathrm{Ph_3P\text{-}CHI}$ (**4**) is treated with PhLi in THF-d_8. We were able to confirm the spectroscopic results published previously within that debate.[4] The corresponding isomer **3** is prepared by the reaction of **1** with 1 equiv. of *t*-BuLi in THF-d_8/hexane (–78°C) and we were able to obtain the complete set of NMR spectroscopic data of **3**. An interesting aspect can be concluded from the resonance of the lithiated aromatic carbon atom *l* of **3** which is shifted to an unusual spectroscopic range at 211.3 ppm.[†] This shift is in excellent agreement to ^{13}C NMR values of imidazol-2-ylidenes published by Arduengo et al.[10] Based on our NMR spectroscopic data we propose therefore an electronic structure of **3** that can be formally depicted by the mesomeric forms A–C (Scheme 2).



Characteristic ^{13}C NMR values of 3

C_l : 211.3 ppm, dq, J(CP) = 60 Hz, J(C^7Li) = 26 Hz

C_j : 140.8 ppm, d, J(C_j P) = 117 Hz

C_i : 138.5 ppm, d, J(C_i P) = 68 Hz

CH_2: -4.5 ppm, d, J(CP) = 49 Hz

Scheme 2.

The mesomeric form B represents a singlet carbene stabilised by adjacent filled π-orbitals coordinating at Li^+. Since a clear $^{13}C\text{-}^7Li$ coupling pattern (dq) is only observed on atom *l*, Li^+ seems to be bound more tightly to the *ortho* C_{aryl} and coordinated by the ylidic carbon atom. At the same time the $^{13}C\text{–}^7Li$ coupling pattern (dq) makes sure that the atom *l* is connected with only one Li^+. In accord with known structures of *ortho*-metalated iminophosporanes or phosphorus

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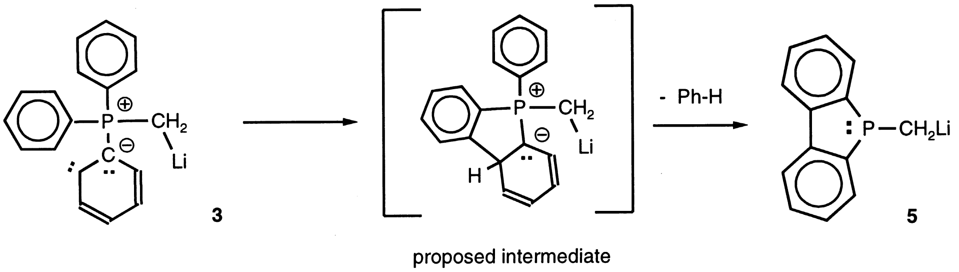
[†] Preparation of **3**: A solution of 100 mg (0.35 mmol) $\mathrm{Ph_3P\text{-}CH_2}$ in 2 ml of THF-d_8 was cooled to –78°C and 0.22 ml of *t*-butyllithium (0.35 mmol, 1.6 M in hexane) were added with a syringe. The solution changed its colour from yellow to red and was stirred for 15 min at –78°C. The solution was concentrated at –78°C in vacuum (10^{-3} mbar) to 1 ml and transferred into a precooled, argon-charged NMR tube. The NMR experiments were done at –100°C. ^{1}H NMR (400.13 MHz, THF-d_8): δ 8.20 (d, J(HX) = 6.2 Hz, 1H), 7.52 (q, J(HX) = 10.6 Hz, J(HX) = 8.05 Hz, 4H), 7.45 (q, J(HX) = 5.85 Hz, J(HX′) = 7.68 Hz, 4H), 7.28–7.38 (m, 2H), 6.96 (t, J(HX) = 6.95 Hz, 1H), 6.86 (t, J(HX) = 8.42 Hz, 1H), 6.73–6.80 (m, 1H), 0.04 (d, ^{2}J(HP) = 5.5 Hz, 2H). Comment: X and X′ are either coupled protons or phosphorus nuclei. ^{13}C NMR (100.32 MHz, THF-d_8): δ 211.3 (dq, ^{2}J(CP) = 60 Hz, ^{1}J(C^7Li) = 26 Hz, C_l), 142.25 (d, ^{3}J(CP) = 31 Hz, C_a), 140.8 (d, ^{1}J(CP) = 117 Hz, C_j), 138.5 (d, ^{1}J(CP) = 68 Hz, C_i), 132.7 (d, ^{2}J(CP) = 9 Hz, C_o), 131.7 (d, ^{3}J(CP) = 26 Hz, C_c), 130.2 (d, ^{4}J(CP) = 2 Hz, C_P), 128.5 (d, ^{3}J(CP) = 10 Hz, C_m), 126 (d, ^{4}J(CP) = 4 Hz, C_b), 121.9 (d, ^{2}J(CP) = 14 Hz, C_d), –4.5 (m at –100°C; d at –60°C ^{1}J(CP) = 49 Hz, ^{1}J(CH) = 135 Hz, CH_2). ^{31}P NMR (161.97 MHz, THF-d_8): δ 31.8 (s). ^{7}Li NMR (155.04 MHz, THF-d_8): δ 4.1 (s).

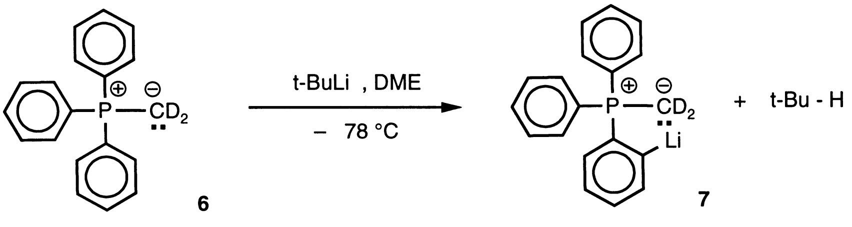
ylides a monomeric chelate structure (Li is most probably coordinated with additional THF) seems to be more likely than a dimeric or chain type structure.[8,13,15] The very low field shift of the ^{7}Li NMR signal of **3** (4.1 ppm) seems to indicate that Li^+ is within the influence of aromatic ring current effects.

Schlosser proposed that degradation of **3** to **5** is initiated by a nucleophilic attack of the *ortho*-lithiated carbanion at the neighbouring phenyl ring.[4] His NMR data of the presumable intermediate do not exclude the interpretation that degradation may be initiated by an insertion of a nucleophilic carbene (mesomeric form B) into the C–H bond of an adjacent aromatic ring (Scheme 3).



Scheme 3.

In a NMR sample of **3** prepared at –78°C no conversion or equilibrium between the two discrete and stable isomers **2** and **3** has been detected in the temperature range of –100 to –20°C. In order to prove that **3** is not formed via the α-lithiated ylide **2**, that could have been the intermediate of a kinetically controlled deprotonation, we reacted deuterated $Ph_3P\text{-}CD_2$ (**6**) with *t*-BuLi in DME (Scheme 4).[‡] The reaction has been monitored with ^{2}H NMR and only one signal is observed due to **7**.[§,¶] No deuterated products in a 1:1 molar ratio ($Ph_3P\text{-}CDLi$ and *t*-Bu-D) were observed. As expected, the ^{2}H NMR shift of **7** is within the spectroscopic range of the CH_2 group of **3**. We conclude that formation of **7** does not include a α-metalated species as intermediate.



Scheme 4.

[‡] $Ph_3P\text{-}CD_2$ was synthesised using CD_3I, Ph_3P and $NaN(SiMe_3)_2$ following a procedure by Bestmann.[14]

[§] ^{2}H NMR (61.4 MHz, dme): δ –0.2 (CD_2).

[¶] As only traces of *t*-Bu-D (^{2}H NMR; 61.4 MHz, DME; δ 1.51 ppm) were detected we assume that it was formed from $D\text{–}N(SiMe_3)_2$ remaining from the synthesis of the deuterated ylide. The amine could not be removed completely.

The general aspects of *ortho*-metalation reactions have been reviewed elsewhere.[11] To gain more information about this special directed *ortho*-metalation Ph_3P-CHMe (**8**) and Ph_3P-$CHSiMe_3$ (**9**) were reacted with *t*-BuLi/hexane in THF at –78°C. It was found that the sterically hindered and less acidic ylide **8** reacts readily with *t*-BuLi, but at higher temperatures (–40°C) than **1** to give an ortho-metalated species.[‖] The electronically stabilised and probably more acidic ylide Ph_3P-$CHSiMe_3$ (**9**) does not react with *t*-BuLi even at room temperature. This is in accord with the point of view that the ortho-metalation is strongly dependent on pre-coordination of the ylide function to Li^+. If the coordination is hindered *t*-BuLi is not directed to the kinetically favoured ortho position of the aromatic ring system. Similar observations have been made in ortho-metalation reactions of phosphine oxides and phosphine imides which are isolelectronic to phosphorus ylides.[12,13]

Acknowledgements

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[‖] Preparation of **8**: Same procedure as in †; 100 mg (0.34 mmol) Ph_3P-CHMe; 0.22 ml (0.35 mmol, 1.6 M) *t*-BuLi in hexane. The reaction was monitored spectroscopically while warming the NMR tube several times for 30 s to room temperature until ^{31}P spectra indicated complete deprotonation. Slow warming of another sample in the NMR probe head indicated that the deprotonation reaction starts at –40°C. ^1H NMR (400.13 MHz, THF-d_8, –100°C): δ 8.10 (broad signal, 1H), 7.5–7.1 (broad signal, m, 10 H), 6.8 (broad signal, 1H), 6.65 (broad signal, 1H), 6.55 (broad signal, 1H), 1.45 (d, J(HX) = 20.2 Hz, 3H), 0.2 (s, 1H). Comment: Neither at –40°C nor at –100°C was high resolution of all signals achieved. ^{13}C NMR (100.32 MHz, THF-d_8, –100°C): δ 211.4 (dq, $^2J(CP) = 50$ Hz, $^1J(C^7Li) = 29$ Hz, C_l), 142.1 (d, $^3J(CP) = 29$ Hz, C_a), 139.9 (d, $^1J(CP) = 117$ Hz, C_j), 135.3 (d, $^1J(CP) = 65$ Hz, C_i), 133.5 (d, $^2J(CP) = 8$ Hz, C_o), 131.2 (d, $^3J(CP) = 25$ Hz, C_c), 130.2 (d, $^4J(CP) = < 2$ Hz, C_P), 128.5 (d, $^3J(CP) = 9$ Hz, C_m), 126.0 (d, $^4J(CP) = 4$ Hz, C_b), 122.2 (d, $^2J(CP) = 13$ Hz, C_d), 35.9 (d, $^2J(CP) = 19$ Hz, P-CH*Me*), 4.1 (m at –100°C, d at –60°C, $^1J(CP) = 62$ Hz, $^1J(CH) = 137$ Hz, P-*C*HMe). ^{31}P NMR (161.97 MHz, THF-d_8, –100°C): δ 24 (s). ^7Li NMR (155.04 MHz, THF-d_8, –100°C): δ 3.8 (s).