Lithium 5-(2-diphenylphosphinoethyl)-1,2,3,4-tetramethylcyclopentadienide: regioselectivity of alkylation of the tetramethylcyclopentadienide anion

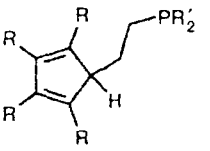
D. P. Krut'ko, M. V. Borzov, E. N. Veksler, E. M. Myshakin, and D. A. Lemenovskii*

Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 939 5546. E-mail: kdp@org.chem.msu.su

Treatment of a mixture of isomeric (2-chloroethyl)-1,2,3,4-tetramethylcyclopentadienes with lithium diphenylphosphide leads to novel 4,5,6,7-tetramethylspiro[2,4]hepta-4,6-diene among the reaction products. The reaction of spiroheptadiene obtained with excess $LiPPh_2$ at elevated temperature affords lithium 5-(2-diphenylphosphinoethyl)-1,2,3,4-tetramethylcyclopentadienide in almost quantitative yield. The regioselectivity of alkylation of the tetramethylcyclopentadienide anion is estimated from quantum-chemical calculations performed *ab initio* for $C_5Me_4H^-$. The full charges on the ring carbon atoms are determined within the framework of Bader's theory of atomic fragments in molecules.

Key words: tetramethylcyclopentadiene, alkylation, regioselectivity; cyclopentadienes with phosphorus-containing substituents; quantum-chemical calculations.

5-(2-Phosphinoethyl)-1,2,3,4-tetramethylcyclopentadienes are valuable promising ligands for fine organometallic synthesis. However, unlike their analogs that are not methylated at the cyclopentadienyl ring (A, R = H) (they are comparatively readily available and were used repeatedly and successfully for preparation of complexes of different transition metals[1–6]), the synthesis of ligands of the A type with R = Me (three compounds isomeric in positions of the double bonds) is not a trivial problem.



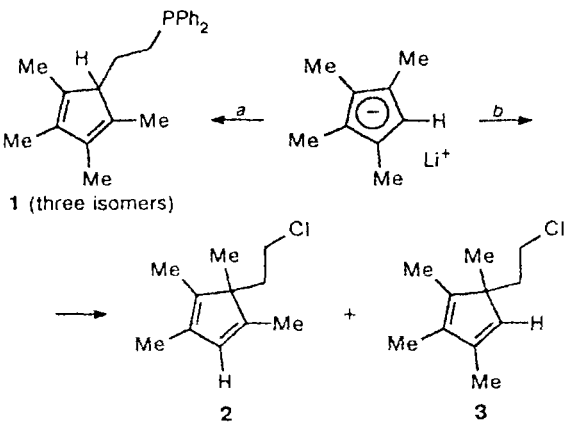
A

R = H, Me; R′ = Alk, Ar

There is a sole communication[7] reporting the synthesis of 5-(2-diphenylphosphinoethyl)-1,2,3,4-tetramethylcyclopentadiene (**1**), one of the cyclopentadienes of the A type (R = Me), which was obtained by direct 2-chloroethylation of lithium 1,2,3,4-tetramethylcyclopentadienide followed by substitution of the halogen atom in the side chain under the action of lithium diphenylphosphide (Scheme 1, pathway *a*). Later, the results of that work were disproved by another group of authors.[8] Thus, under similar conditions, only *gem*-dialkylsubstituted isomers **2** and **3** were found among products of the 2-chloroethylation of lithium tetramethylcyclopentadienide (Scheme 1, pathway *b*), from which it seems impossible to obtain target cyclopentadiene **1**.

Since available literature data are contradictory, we attempted to repeat the synthesis of compound **1** as well as to analyze the problem of the regioselectivity of alkylation of the tetramethylcyclopentadienide anion using calculation methods of quantum chemistry.

Scheme 1



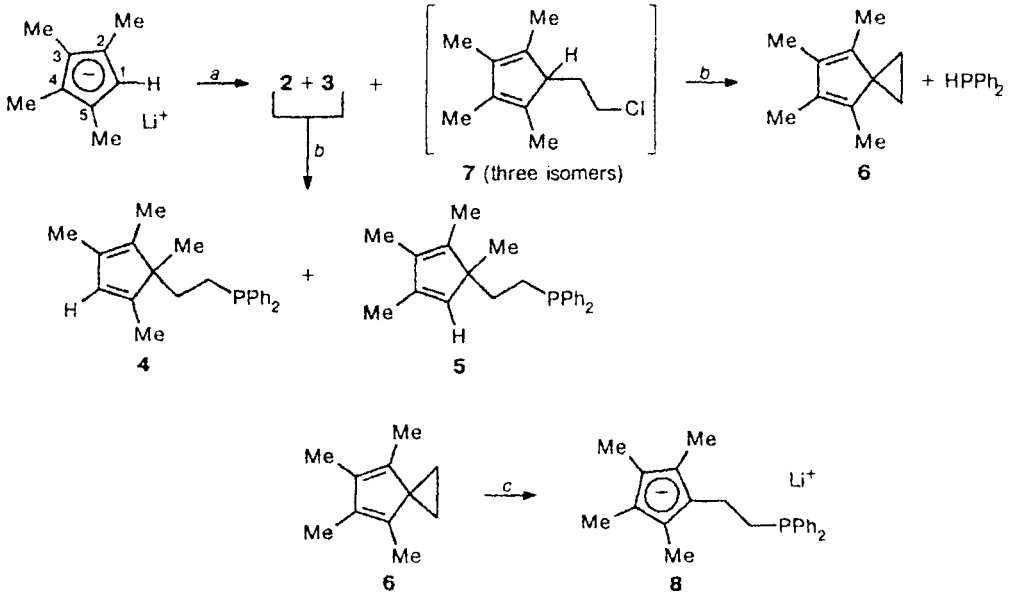
Reagents and conditions: *a*. (1) $TsOCH_2CH_2Cl$; (2) $LiPPh_2$, THF, −10 °C (see Ref. 7); *b*. $TsOCH_2CH_2Cl$, THF, −10 °C (see Ref. 8).

The reaction of lithium tetramethylcyclopentadienide with 2-chloroethyl *p*-toluenesulfonate in THF at −5 to +5 °C for 10 min produces a mixture of isomeric products, among which, in accordance with data obtained earlier,[8] only *gem*-dialkylsubstituted cyclopentadienes **2** and **3** were observed (from ^1H and $^{13}C\{^1H\}$ NMR spectra) (Scheme 2). Treatment of this mixture with $LiPPh_2$ (1 equiv.) in THF gave, along with expected products **4** and **5** (products of the substitution of the diphenylphosphino group for the chlorine atom), a small amount of 4,5,6,7-tetramethylspiro[2,4]-hepta-4,6-diene (**6**) and diphenylphosphine (molar ratio 1 : 1). Spiro compound

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 986–989, May, 1998.

1066-5285/98/4705-0956 $20.00

Scheme 2



Reagents and conditions: *a*. $TsOCH_2CH_2Cl$, THF, −5 to +5 °C; *b*. $LiPPh_2$, THF, −10 to +20 °C, *c*. $LiPPh_2$(excess), THF, 80 °C.

6 was isolated in the individual state (~10%) and characterized by ^1H and ^{13}C NMR spectroscopy (δ ^1H, δ ^{13}C, and $^1J_{CH}$ values are typical of cyclopropanes) and mass spectrometry (main peaks correspond to substituted tropylium cations $[C_7Me_nH_{7-n}]^+$, $n = 0$ to 4).

We believe that a direct precursor of compound **6** is 1,2,3,4-tetramethyl-5-(2-chloroethyl)cyclopentadiene (**7**), which is formed along with products **2** and **3** in the 2-chloroethylation of C_5Me_4HLi (see Scheme 2). Compound **7** is a mixture of three isomers by the relative position of the double bond system and the substituent $ClCH_2CH_2$, all protons and C atoms being chemically nonequivalent in two of them. This circumstance, along with the total low percentage of compound **7** in the mixture of products of the 2-chloroethylation of C_5Me_4HLi, makes its direct observation by NMR spectroscopy impossible against the background of products **2** and **3**.

To explain the regioselectivity of alkylation of the anion $C_5Me_4H^-$, we performed *ab initio* (RHF) calculations for the ground state of $C_5Me_4H^-$ in the valence-split 6-311+G(d,p) basis supplemented by polarization and diffusion functions (GAUSSIAN 94 program package[9]). Total charges on the atoms were determined within the framework of Bader's theory of atomic fragments in molecules[10] using the AIMPAC program package,[11] which was successfully applied to the analysis of electron density distribution in molecules.[12,13]

Assuming the orbital and charge controls of the alkylation of $C_5Me_4H^-$ to be the limiting cases, we found that under the orbital control conditions the expected ratio of products alkylated at C(1), C(2), and C(3) atoms is close to statistic (1 : 2 : 2, respectively), while in the case of charge control the same ratio changes in favor of C(1)-alkylation product (1 : 1 : 1) (Table 1, the atoms in the anion $C_5Me_4H^-$ are numbered in Scheme 2).

Table 1. Total charges (q) on atoms (according to Bader[10,11]) and the sum of the squares of HOMO orbital coefficients (the wave function RHF 6-311+G(d,p)) at competing positions of the $C_5Me_4H^-$ ring

Atom	q/e	Σ_{HOMO}[a]	Estimated ratio of alkylation products[b]	
			Charge control	Orbital control
C(1)	−0.0936	0.0819	1.00 (28.6%)	1.00 (18.5%)
C(2) + C(5)	−0.1140[c]	0.1794[d]	1.22 (34.8%)	2.19 (40.5%)
C(3) + C(4)	−0.1202[c]	0.1812[d]	1.28 (36.7%)	2.21 (40.9%)

[a] Σ_{HOMO} is the sum of the squares of HOMO orbital coefficients. Coefficients at the AO of two HOMO close in energy are taken into account (ΔE = 0.005 eV).

[b] The corresponding percentage is given in parentheses.

[c] Total charges are summarized for pairs of the equivalent atoms C(2), C(5) and C(3), C(4).

[d] The squares of orbital coefficients at AO are summarized for pairs of the equivalent atoms C(2), C(5) and C(3), C(4).

In all cases, quantum-chemical calculations predict the formation of comparable amounts of isomeric alkylation products of the **2**, **3**, and **7** types with the maximum of the expected content of type **7** product ~30% (in the case of full charge control). Taking into account that the mixtures of the isomers under discussion are generally difficult to separate, the possibility of using the direct alkylation of $C_5Me_4H^-$ in the preparative synthesis of cyclopentadienes of the **A** type (R = Me) seems to be doubtful.

We found that the interaction of tetramethylspiroheptadiene **6** with excess $LiPPh_2$ in THF under heating proceeds similarly to the known reaction of spiro[2,4]hepta-4,6-diene with lithium diorganophosphides[1] and almost quantitatively leads to lithium 5-(2-diphenylphosphinoethyl)-1,2,3,4-tetramethylcyclopentadienide (**8**), a disclosure product of the three-membered ring of the spiro[2,4]hepta-4,6-diene **6** system (see Scheme 2). Compound **8** was isolated in the individual state and characterized by ^1H, ^{13}C-{^1H}, and ^{31}P-{^1H} NMR spectroscopy methods.

There is no doubt that tetramethylspiroheptadiene **6** is a convenient precursor of almost every analog of cyclopentadiene **8** with other (aryl or alkyl) substituents at the P atom. Thus, the development of a suitable preparative procedure of the synthesis of spiroheptadiene **6** will make ligands of the **A** type with R = Me available and allow introducing them into organometallic synthesis.

Experimental

All synthetic operations, including preparation of samples for NMR spectroscopy, were carried out in sealed evacuated vessels of the Schlenk flask type. Solvents were dehydrated according to common procedures, degassed, and introduced into reaction vessels by recondensation on a vacuum line. 2-Chloroethyl *p*-toluenesulfonate,[14] tetramethylcyclopentadiene,[15] and diphenylphosphine[16] were prepared according to known procedures. Lithium tetramethylcyclopentadienide and lithium diphenylphosphide were obtained by the action of *n*-butyllithium on $C_5Me_4H_2$ and Ph_2PH in THF and pentane, respectively, and purified in the form of solid salts by repeated washings on a filter.

The ^1H, ^{13}C-{^1H}, and ^{31}P-{^1H} NMR spectra were recorded on a Varian VXR-400 instrument (400, 100, and 162 MHz, respectively) at 30 °C. The mass spectrum of compound **6** was obtained with a Varian MAT CH7a Fa spectrometer at 25 °C.

1,2,3,4-Tetramethyl(2-chloroethyl)cyclopentadiene (a mixture of isomers 2, 3, and 7). 2-Chloroethyl *p*-toluenesulfonate (4.10 g, 17.47 mmol) in 20 mL of anhydrous THF was added with vigorous stirring and cooling to −15 C to a suspension of lithium tetramethylcyclopentadienide (2.23 g, 17.4 mmol) in 20 mL of anhydrous THF. The lithium salt dissolved completely within the temperature range from −5 to +5 °C. The reaction mixture was allowed to warm up to room temperature and stirred for extra 30 min. The solvent was removed into a trap cooled with liquid nitrogen, and the residue was extracted with 30 mL of pentane. The extract was concentrated, and the residue was distilled in high vacuum. Colorless oil (1.69 g, 9.15 mmol, 52.6%) was obtained, b.p. 29—31 °C (10^{-2} Torr).

The reaction of 1,2,3,4-tetramethyl(2-chloroethyl)cyclopentadiene (2, 3, 7) with lithium diphenylphosphide. To a solution of the mixture (1.69 g, 9.15 mmol) of isomers **2**, **3**, and **7** in 20 mL of THF 0.4 *M* Ph_2PLi solution (23 mL, 9.20 mmol) in THF was added with cooling to −10 °C and stirring. The reaction mixture was allowed to warm up to room temperature and stirred for extra 1 h. The solution was concentrated to 10 mL, and 30 mL of pentane was added. Excess Ph_2PLi was removed by filtering it through a layer of degased silica gel (3 cm). After the solvents were removed, the viscous colorless oil was heated with stirring in high vacuum (70 °C, 10^{-3} Torr), collecting the highly volatile components in a trap cooled with liquid nitrogen. The main reaction products **4** and **5** (2.08 g, 6.22 mmol, 68.0%) were obtained as viscous colorless oil. ^{31}P-{^1H} NMR (C_6D_6), δ: −12.9 (s), −12.3 (s) (**4** and **5**).

The condensate collected in the trap is spiroheptadiene **6** admixed with Ph_2PH. Additional microdistillation in high vacuum (23 °C, 10^{-3} Torr) gave 0.14 g (0.94 mmol, 10.3%) of spiroheptadiene **6**.

^1H NMR (C_6D_6), δ: 0.98 (s, 4 H, CH_2); 1.48 (s, 6 H, CH_3); 1.85 (s, 6 H, CH_3). ^{13}C NMR (C_6D_6), δ: 8.91 (q, CH_3, $^1J_{CH}$ = 125 Hz); 10.83 (t, CH_2, $^1J_{CH}$ = 164 Hz); 11.70 (q, CH_3, $^1J_{CH}$ = 125 Hz); 37.66 (s, C(3)); 133.67, 133.96 (both s, C(4), C(7), and C(5), C(6)). MS (EI, 70 eV (fuming samples)), *m/z* (I_{rel} (%)): 148 $[M]^+$ (3), 147 $[C_7H_3Me_4]^+$ (100), 133 $[C_7H_4Me_3]^+$ (33), 119 $[C_7H_5Me_2]^+$ (11), 105 $[C_7H_6Me]^+$ (10), 91 $[C_7H_7]^+$ (16), 28 $[C_2H_4]^+$ (15).

Lithium 5-(2-diphenylphosphinoethyl)-1,2,3,4-tetramethylcyclopentadienide (8). To spiroheptadiene **6** (0.10 g, 0.67 mmol) 0.4 *M* solution of Ph_2PLi (5 mL, 2.0 mmol) in THF was added. The reaction mixture was heated to 80 °C and stirred for 4 h. The solution was concentrated to 1 mL and cooled to −20 °C. The precipitate that formed as white fine crystals was rapidly filtered off, washed on the filter with a minimum volume of cold THF (−30 °C), and dried in high vacuum. The yield of compound **8** was almost quantitative. ^1H NMR (THF-d_8), δ: 1.70, 1.75 (both s, each 6 H, 2-, 5-CH_3, 3-, 4-CH_3); 2.00, 2.40 (both br.m, each 2 H, H(6), H(7)); 7.24 (m, 6 H, H_m and H_p in PPh_2); 7.40 (m, 4 H, H_o in PPh_2). ^{13}C-{^1H} NMR (THF-d_8), δ: 11.2 (br.s, 2-, 3-, 4-, 5-CH_3); 23.4 (br.d, C(6), $^2J_{PC}$ = 15 Hz); 32.1 (br.s, C(7)); 105.9, 106.4 (both br.s, C(2), C(5) and C(3), C(4)); 112.4 (br.s, C(1)); 128.6 (s, C_p in PPh_2); 128.8 (d, C_m in PPh_2, $^3J_{PC}$ = 6 Hz); 133.6 (d, C_o in PPh_2, $^2J_{CP}$ = 18 Hz); 141.2 (br.s, C_{ipso} in PPh_2). ^{31}P-{^1H} NMR (THF-d_8), δ: −15.8 (br.s).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-34232a).

References

1. R. T. Kettenbach, W. Bonrath, and H. Butenschon, *Chem. Ber.*, 1993, **126**, 1657.
2. C. Charier and F. Mathey, *J. Organomet. Chem.*, 1979, **170**, C41.
3. A. M. Z. Slawin, D. J. Williams, J. Crosby, J. A. Ramsden, and C. White, *J. Chem. Soc., Dalton Trans.*, 1988, 2491.
4. T.-F. Wang, J.-P. Jung, and Y.-S. Wens, *J. Organomet. Chem.*, 1995, **503**, 117.
5. T. Cuenca, J. C. Flores, and P. Royo, *J. Organomet. Chem.*, 1993, **462**, 191.
6. J. C. Leblanc, C. Moise, A. Maisonnat, R. Poilblanc, C. Charier, and F. Mathey, *J. Organomet. Chem.*, 1982, **231**, C41.

7. J. Szmonyak, J. Besancon, A. Dormond, and C. Moise, *J. Org. Chem.*, 1990, **55**, 1429.
8. P. Jutzi and J. Dahlhaus, *Synthesis*, 1993, 684.
9. M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Roob, J. R. Cheeseman, T. Keith, G. A. Pedersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomprets, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Srewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *Gaussian 94, Revision D.1*, Gaussian, Inc., Pittsburgh (PA), 1995.
10. R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1994, 438 pp.
11. F. W. Biegler-König, R. F. W. Bader, and T.-H. Tang, *J. Comput. Chem.*, 1982, **3**, 317.
12. J. Cioslowski, *J. Am. Chem. Soc.*, 1989, **111**, 8333.
13. K. B. Wiberg and P. R. Rablen, *J. Comput. Chem.*, 1993, **14**, 1504.
14. R. S. Tipson and L. H. Cretcher, *J. Am. Chem. Soc.*, 1942, **64**, 1162.
15. C. M. Fendrick, L. D. Schertz, V. M. Day, and T. J. Marks, *Organometallics*, 1988, **7**, 1828.
16. D. Wittenberg and H. Gilman, *J. Org. Chem.*, 1958, **23**, 1063.

Received November 12, 1997