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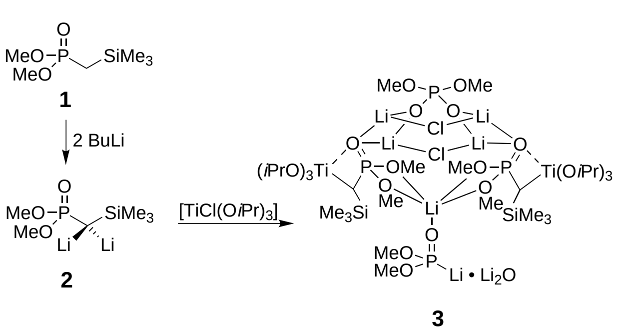
Carbanions Substituted by Transition Metals: Synthesis, Structure, and Configurational Restrictions of a Lithium Titanium Phosphonate

Jürgen F. K. Müller,* Klaus J. Kulicke,
Markus Neuburger, and Martin Spichty

Lithium “carbanions” that are stabilized by transition metals represent a new class of organodimetallic reagents in which an acceptor-substituted anionic C atom is directly connected to a transition metal.[1] Such compounds are expected to possess properties that differ from those of ordinary acceptor-stabilized lithium compounds. In principle, multiple C–C bond-forming reactions are possible by the subsequent addition of various electrophiles, while the reactivity of the anionic C atom and its configurational stability could be directed by the steric and electronic impact of the transition metal.[2] Our main goal is the design and development of chirally modified organodimetallic reagents that facilitate highly stereoselective asymmetric transformations. Recently, we reported on the structure determination of a lithiated titanium sulfone, an intermediate that occurs in the *E*-selective olefination of aldehydes.[1, 3] As part of our program for the exploration and structure determination of new chiral organodimetallic compounds, we have synthesized a lithiated titanium phosphonate, determined its solid-state structure by X-ray analysis, and compared the experimental data with the results of density functional theory (DFT) calculations on a model system.[4, 5]

Dilithiation of dimethyl (trimethylsilylmethyl)phosphonate **1** with 2.2 equivalents of *n*BuLi in diethyl ether in the presence of a trace of water, followed by addition of [TiCl(O*i*Pr)$_3$] and removal of LiCl by filtration gave the lithium titanium phosphonate **3** as green crystals in 48% yield.[6] Figure 1 depicts a C3D plot of the aggregate **3**.



Compound **3** contains two monolithiated titanium phosphonate units together with two LiCl, Li$_2$O, lithiated

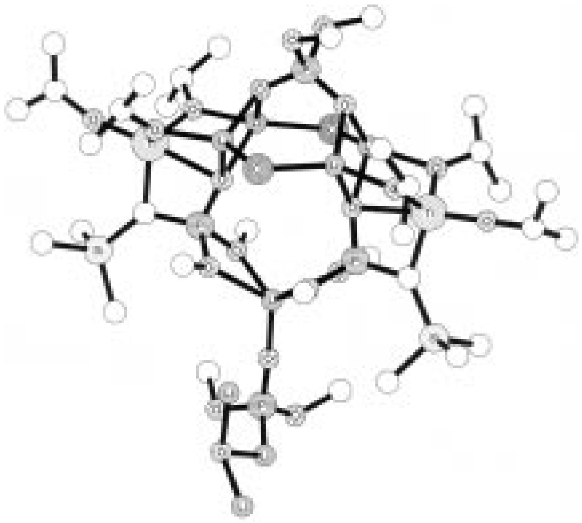


Figure 1. Molecular structure of **3**. Hydrogen atoms are omitted for clarity.

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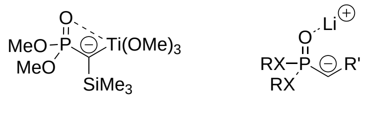
[*] Priv.-Doz. Dr. J. F. K. Müller, M. Neuburger
University of Basel
Institute of Inorganic Chemistry
Spitalstrasse 51, 4056 Basel (Switzerland)
Fax: (+41) 61-267-10-18
E-mail: juergen.mueller@unibas.ch

Dr. K. J. Kulicke, M. Spichty
University of Basel
Institute of Organic Chemistry
St.-Johanns-Ring 19, 4056 Basel (Switzerland)

dimethylphosphonate, and lithiated dimethylphosphate as additional bridging ligands. The center of the aggregate is an eight-membered (Li-O-Li-Cl)$_2$ ring that serves as an aggregation nucleus for crystallization.[1] Each terminal phosphonate oxygen atom bridges two lithium atoms of this ring. The two methoxyl oxygen atoms of the phosphonate ester units coordinate to an external Li cation, and together with an additional oxygen atom of a dimethylphosphonate ligand, they result in a distorted square-pyramidal coordination sphere. The phosphonate unit itself is characterized by a P–Li bond and the complexation of a Li_2O molecule. The presence of Li_2O is crucial for the crystallization of **3**. We were unable to grow suitable crystals of **3** in the absence of H_2O; however, the strong disorder of the Li_2O molecules caused a moderate quality of the crystal structure analysis.[4] The eight-membered (Li-O-Li-Cl)$_2$ ring is capped by a bridging dimethylphosphate ligand—a decomposition product of a dilithiation–titanation sequence—to give a cage-type structure.[7] The titanated phosphonate moieties form a characteristic four-membered Ti-C-P-O chelate ring, a structural feature very similar to that in a lithium titanium sulfone.[1] The titanated anionic C_α atom has an essentially planar coordination sphere (sum of angles at C_α: 359.9°) and is devoid of C–Li contacts, as is typical for monolithiated phosphonates.[7] Accordingly, the electron lone pairs occupy a p orbital perpendicular to the P-C-Ti plane, an ideal orientation for stabilizing hyperconjugative interaction of the lone-pair orbital with the σ* orbitals of the P–O(phosphate ester) bonds [n_C – σ*(PO)]. The Ti atoms are pentacoordinate with a distorted trigonal-bipyramidal geometry. The pseudoequatorial positions are occupied by two 2-propanolate O atoms and the C_α atom. The oxygen atom of the remaining 2-propanolate group and the phosphonate oxygen atom occupy the axial positions (O(*i*Pr)-Ti-O(phosphonate) 175.5(4)°). The Ti–C_α bond length in **3** of 2.01 Å is intermediate between normal Ti–C single bonds, as in a related titanated sulfone (2.174(4) Å), and those in titanium alkylidene complexes (2.008(4) Å).[8, 9] The P–C bond length of 1.64(1) Å is also significantly shortened after anionization and transmetalation relative to unmetalated phosphonates.[7] The additional complexation of the titanium atom by the terminal phosphonate oxygen atom results in a rather long Ti–O bond length of 2.302(8) Å, which compares to 1.883(8)–1.758(9) Å for the Ti–O bonds involving the alkoxyl O atoms and implies a relatively weakly bound Ti atom.

^{1}H, ^{13}C, ^{7}Li, and ^{31}P NMR spectra were recorded in [D$_8$]THF to gain some information on the solution structure of **3**. Whereas the ^{1}H NMR spectrum showed only very broad signals, the ^{13}C NMR spectrum revealed significant changes in chemical shift on metalation. The most dramatic effect was observed for the C_α signal, which shifted downfield to δ = 148.8 ($\Delta\delta$ = 135). For comparison, the ^{13}C chemical shift of the C_α carbon of a monotitanated sulfone is δ = 52.4, in contrast to a titanium carbene complex with δ = 191.[3b, 9] The increase of 23 Hz in the *J*(C,P) coupling constant is a strong indication for a C_α atom with sp^2 character. We therefore conclude that a carbene-like Ti–C_α double bond is not present in solution and that the sp^2 character of the C_α atom in the Ti–C_α bond is responsible for the large downfield shift. The ^{31}P NMR spectrum exhibits two sharp signals at δ = 52.6 and 38.6, as well as two broad signals at δ = 29.1 and 25.9 that suggest a dynamic exchange phenomenon. Therefore, we cannot draw conclusions about the state of aggregation in solution, but it is reasonable to assume that the LiCl formed in situ may act as a template for aggregation.

To obtain deeper insight into the structure of **3**, we carried out DFT calculations (B3LYP) on the titanated carbanionic model system **4**, devoid of Li cations.[5] The calculated structure agrees very well with the X-ray crystal structure of **3**: the typical planar four-membered Ti-C-P-O(phosphonate) ring represents a minimum on the potential energy surface. The dihedral Ti-C-P-O angle of 3.9° resembles that of about 1° in the crystal. The Ti–C (2.065 Å vs 2.00(1) Å and 2.01(1) Å) and P–C bond lengths (1.667 Å vs 1.65(1) Å and 1.64(1) Å) are marginally longer than in the solid state. Especially the short Ti–C bond suggests significant hyperconjugative stabilization of the anionic charge by the titanium atom. The angles around the titanium atom are also similar to those in the solid state. Our special focus lies on the configurational stability of these titanium-substituted "carbanions", which might be a serious concern for stereoselective transformations. In phosphoryl-stabilized anions of type **5**, the interaction of the C_α lone-pair orbital with the σ* orbitals of the P–X bonds is crucial for the configurational stability: it increases the energy barrier for rotation about the C_α–P bond.[7] However, the barrier is only 6–8 kcal mol^{-1}, which is insufficient to prevent rotation, even at low temperature. Hence, the question arises to what extent the additional chelation of the titanium atom by the phosphonate oxygen atom in **3** enhances the configurational stability. Therefore, we calculated the energy profile of the rotation around the C_α–P bond in **4** (Figure 2), starting at the calculated minimum-energy conformation described above (**4A**). Rotation around the C_α–P bond by 60° leads to the maximum **4B**, about 6.5 kcal mol^{-1} higher in energy than **4A**. Further rotation yields the two minima **4C** and **4D**, both about 4 kcal mol^{-1} less stable than **4A**. According to this profile, a substantial increase of the configurational stability of **3** relative to phosphoryl-stabilized lithium carbanions cannot be expected. A reason for this might be the competing interaction of the empty titanium valence shell orbitals with the C_α lone-pair orbital, which is also consistent with the short Ti–C bond.[10]



4

5, X = O, N

We have described a new general route to heterodimetallic compounds by means of a dilithiation–transmetalation sequence. The resulting intermediate **3** can be regarded as a titanium-stabilized lithium compound, with potential application as a chemo- and stereoselective bis-electrophile in C–C bond-forming reactions. We are investigating soft transition metals such as zinc or copper to induce higher configurational stability.

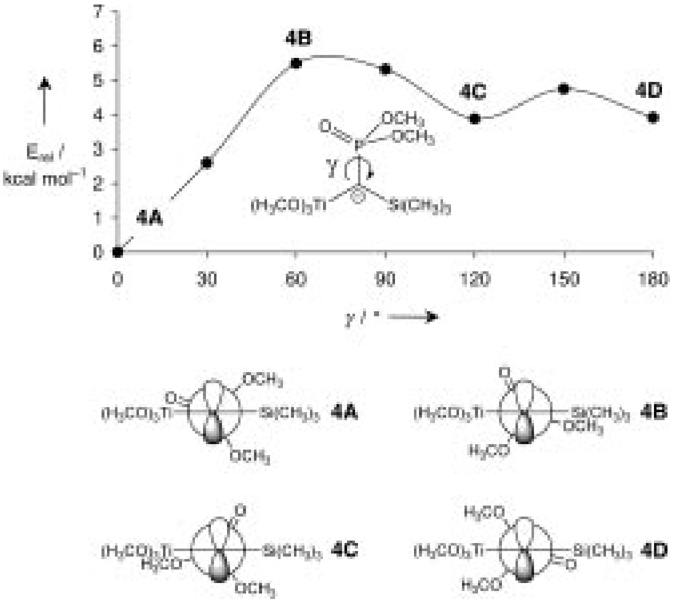


Figure 2. Energy profile for rotation about the C_α–P bond in **4**.

Experimental Section

3: A solution of **1** (100 mg, 0.51 mmol) in diethyl ether (2 mL) and H_2O in diethyl ether (0.45 mL, 0.11 M, 0.05 mmol) was treated with *n*BuLi in hexane (0.79 mL, 1.58 M, 1.25 mmol) at −78 °C. Stirring for 2 h at 0 °C was followed by addition of a solution of [TiCl(O*i*Pr)$_3$] (132 mg, 0.51 mmol) in diethyl ether (2 mL). After filtration of the turbid solution, the remaining liquid was concentrated in vacuo and stored for 24 h at −20 °C until green crystals of **3**, suitable for X-ray analysis, had formed (112 mg, 48 %).

^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): $\delta = -0.02-0.29$ (brs, 9H, SiMe$_3$), 0.74–1.62 (m, 18H, O*i*Pr), 3.45–3.56 (m, 2H, O*i*Pr), 3.65–3.81 (m, 1H, O*i*Pr), 4.60–4.78 (m, 3H); ^{13}C NMR (125 MHz, [D$_8$]THF, 25 °C): $\delta = -3.01, -2.65, -2.45, -2.13, -2.02$, 8.59, 11.45, 13.96, 14.08, 14.35, 24.28, 24.44, 24.59, 24.75, 26.54, 26.86, 32.16, 51.38, 51.71, 63.90, 69.69, 72.40, 72.84, 73.29, 73.64, 73.78, 74.11, 75.98, 77.43, 148.8 (d, J(C,P) = 154 Hz); ^{31}P NMR (202 MHz, [D$_8$]THF, 25 °C, (PhO)$_3$PO): $\delta = 52.64$, 37.12, 29.13, 25.96; ^{7}Li NMR (194 MHz, [D$_8$]THF, 25 °C, LiCl): $\delta = 1.65$.

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[4] X-ray crystal data for **3**: $C_{34}H_{84}Cl_2Li_{12}O_{22}P_4Si_2Ti_2$, $M_r = 1275.09$, triclinic, space group $P\bar{1}$, $a = 15.2286(9)$, $b = 16.6356(8)$, $c = 17.532(1)$ Å, $\alpha = 92.129(4)$, $\beta = 103.501(3)$, $\gamma = 115.368(3)°$, $V = 3854.39$ Å^3, $Z = 2$, $F(000) = 1332$, $\rho = 1.099$ Mg m^{-3}, $\mu = 0.44$ mm^{-1}, crystal dimensions $0.08 \times 0.10 \times 0.22$ mm, $T = 193$ K, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\omega/2\theta$ scans, $\theta_{max} = 23.26°$, 40810 measured reflections, 19311 independent reflections, 8312 reflections used in the refinement ($I > 3\sigma(I)$), 703 parameters, $R = 0.1136$, $R_w = 0.1294$, weighting scheme $\omega[1-(\delta F/6\sigma F)^2]^2$, $\Delta\rho = 1.60/-0.96$ e Å^{-3}, $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$, $R_w = [\Sigma(|F_o|-|F_c|)^2\omega)/\Sigma F_o^2\omega]^{1/2}$. Crystals of **3** were attached to a glass fiber with perfluoropolyether, mounted on the diffractometer, and cooled with an Oxford Cryostream to 193 K. Data were collected with a Nonius Kappa CCD area detector equipped with a graphite monochromator. The usual corrections were applied. The structure was solved by direct methods with the program SIR92.[11] Anisotropic least-squares full-matrix refinement was carried out on all non-hydrogen atoms by using the program CRYSTALS.[12] The positions of the hydrogen atoms were determined geometrically. The disordered Li_2O molecules in **3** were refined with appropriate restraints. Chebychev polynomial weights were used to complete the refinement.[13] Scattering factors were taken from the International Tables, Vol. IV, Table 2.2 B. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156555. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] All calculations were performed at the DFT level by using Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang, and Parr.[14, 15] The following basis set was used for titanium: Wachters–Hay all-electron basis set[16, 17] with the scaling factors of Raghavachari and Trucks for first-row transition metals[18] and with additional diffuse (s,p,d) and polarization (f) functions specified in Gaussian 98 with 6-311 + G* basis set. For all other atoms the standard basis set 6-31G(d) was used. Initial coordinates for the geometry optimization of **4** were obtained by extracting the coordinates of **3** (without Li$^+$ ions) from the crystal structure and replacing the isopropyl groups by methyl groups. The optimized geometry of **4** was then used as a starting point for the calculation of the rotation profile. The dihedral angle γ(Ti-C-P-O(phosphonate)) was increased in 30° steps from 0 to 180°. For each value of γ, the geometry was reoptimized while keeping γ constrained. The electronic energies of these optimized rotamers revealed the rotation profile. All calculations were carried out with the program package Gaussian 98.[19]

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Chemical Involvement of Solvent Water Molecules in Elementary Steps of the Fenton Oxidation Reaction**

Bernd Ensing, Francesco Buda, Peter Blöchl, and Evert J. Baerends*

The proposed reaction mechanisms for the oxidation of organic substrates with the Fenton reagents (a mixture of ferrous ions and hydrogen peroxide) can roughly be divided into two groups. The first group regards Fenton chemistry as the production of free hydroxyl radicals by the metal-catalyzed decomposition of the peroxide,[1] whereas the second group involves the formation of a highly reactive iron–oxo complex, such as the ferryl ion ($[Fe^{IV}O]^{2+}$), as the oxidative intermediate.[2] The issue is clearly of interest for both biooxidation research, in view of the prominent role of Fe ions, and for oxidation catalysis in general. However, despite the numerous studies over more than 60 years,[3–10] the controversy remains, since the extremely short lifetimes of the intermediates make definitive experiments very difficult. The major complication with quantum chemical calculations is that the water solvent has to be included in the study. Not only are the Fe^{2+} ions coordinated by six water molecules, but conceivable reaction products such as OH^-, H^+, and $OH^{\bullet}$ will also be solvated and/or propagate through the solution by chain reactions. It is therefore impossible to treat the solvent by just model potentials that describe interactions between intact H_2O molecules with other H_2O molecules and Fe^{2+} ions (let alone by a continuum model).

The explicit incorporation of the water solvent in the computational study is no longer an elusive goal. Indeed, the ab initio molecular dynamics (AIMD) method[11] allows for a parameter free, finite temperature simulation in which, at each time step, the forces are computed directly from the electronic structure determined by density functional theory (DFT). Therefore, within this approach there are no restrictions on reactive processes at the Fe center or in the solution.

Recently, we performed DFT calculations on the isolated (gas-phase) Fenton reactants,[12] and found that dissociation of the O–O bond of hydrogen peroxide molecule coordinated to pentaaqua Fe^{II} ions to form $[Fe(OH)(H_2O)_5]^{2+}$ and a $OH^{\bullet}$ cannot readily occur since this reaction is endothermic by 27 kcal mol^{-1}. This value is in fact already smaller than the approximate 60 kcal mol^{-1} required to break the O–O bond in isolated hydrogen peroxide. The reduction of the dissociation energy occurs because the $OH^{\bullet}$ that remains coordinated to the iron center leads to an Fe^{II}–$OH^{\bullet}$ bond (formally Fe^{III}–OH^-), which is stronger by about 30 kcal mol^{-1} than the original Fe^{II}–H_2O_2 bond. Nevertheless, there is still an endothermicity of 27 kcal mol^{-1}, and homolytic dissociation of the coordinated H_2O_2 molecule can only become exothermic through the energy gain associated with a second Fe–OH bond replacing a much weaker Fe–H_2O bond. This process occurs in the gas phase by the leaving $OH^{\bullet}$ abstracting a hydrogen atom from an adjacent coordinated H_2O molecule. A water molecule and a second strong Fe–OH bond is formed, and this process provides enough energy to make the reaction exothermic [Eq. (1)]. Hence, no $OH^{\bullet}$ results.

$$[Fe^{II}(H_2O)_5(H_2O_2)]^{2+} \rightarrow [Fe^{IV}(OH)_2(H_2O)_4]^{2+} + H_2O \qquad (1)$$

We now turn to the study of this reaction in solution. We had already observed in the gas phase that a single water molecule, when added in a "second solvation shell" position, reacts with the $[Fe(OH)_2(H_2O)_4]^{2+}$ complex to form the presumably reactive iron–oxo (ferryl) ion $[FeO(H_2O)_5]^{2+}$ and an H_2O molecule. The energy barrier for this transformation would be too high without the chemical involvement of the "solvent" water molecule. Hence, solvent simulation is necessary since solvent molecules may be chemically involved in the formation of the ferryl ion. Moreover, they may be involved in the alternative pathway of $OH^{\bullet}$ formation, since solvent molecules may react with the $OH^{\bullet}$ and propagate it through the solution by a chain reaction. We have, therefore, performed spin-polarized AIMD simulations of (high spin, $S=2$) Fe^{2+}/H_2O_2 in water using the CP-PAW code[13] with the BP[14, 15] exchange-correlation functional. We applied periodic boundary conditions, as usually done in MD simulations,[16] to a relatively small cubic unit cell containing an Fe^{2+} ion, a H_2O_2 molecule, and 31 water molecules to emulate the infinite bulk environment but keep the computation feasible. The formal concentration of the reactants is therefore high but not unrealistic (technical details of AIMD simulations of solvation and (radical) reactions in water may be found in ref. [17–21]). The same parameters for the basis set and dynamics were used as in our previous study of the S_N2 reaction in water,[17] namely, a constant temperature[22] of $T = 300$ K, a fictitious electron mass of $\mu_e = 1000$ a.u.; a MD time step of $\Delta t = 8$ a.u.; and a plane-wave cut-off of $k^2_{max} = 30$ Ry. The box size was $L =$

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[*] Prof. Dr. E. J. Baerends, Ir. B. Ensing, Dr. F. Buda
Theoretical Chemistry, Faculty of Exact Sciences
Vrije Universiteit Amsterdam
De Boelelaan 1083, 1081 HV Amsterdam (The Netherlands)
Fax: (+31) 20-44-47-629
E-mail: baerends@chem.vu.nl

Prof. Dr. P. Blöchl
Clausthal University of Technology
Clausthal-Zellerfeld (Germany)

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