Schlenk's Early "Free" Carbanions

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Abstract: Nearly a century ago, Schlenk published the syntheses and isolation of two most remarkable and unstable complexes: crystalline $[Ph_3C^-][Me_4N^+]$ and $[PhCH_2^-][Me_4N^+]$. The crystal structure of the first complex contains a "free" Ph_3C^- ion, which displays the expected planar trigonal geometry at its central carbon atom. The phenyl groups are not orientated in the typical propeller arrangement, but instead display various orientations with respect to the molecular plane. These orientations can be directly related to the extent of charge delocalization and correlate well with other structural characteristics related to charge delocalization. The crystal structure also shows a network of $C{-}H^{\delta+}\cdots C^{\delta-}$ and $C{-}H\cdots\pi$ interactions. Only $C{-}H\cdots\pi$ interactions to the most negative charged phenyl rings are observed. The absolute Brønsted acidity of Me_4N^+ is calculated by the G2(MP2) method (287.7 kcal mol^{-1}) and is compared to the calculated acidity of Me_4P^+ (268.4 kcal mol^{-1}). On this basis, the pK_a value for Me_4N^+ is estimated at 29.6. This makes the existence, and especially Schlenk's early isolation, of the "free" carbanions $[Ph_3C^-][Me_4N^+]$ and $[PhCH_2^-][Me_4N^+]$ quite noteworthy.

Keywords: acidity · basicity · carbanions · crystal engineering · hydrogen bonds

Introduction

The life and work of one of the most remarkable German chemists, Wilhelm Schlenk, has recently been discussed in an excellent and detailed essay.[1] One of Schlenk's earlier and major accomplishments was the isolation and experimental proof of the first organic radical: $(4\text{-}PhC_6H_4)_3C^{\bullet}$.[2] An important era of his later research, unfortunately not described in the review article,[1] are his attempts to synthesize organic compounds with a pentavalent nitrogen (**1**, depicted in the original notation system of that time).

$R_5{\equiv}N$ (original notation)

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An early claim of the first hypervalent organic member in Group 15 (Me_5As)[3] spurred Schlenk, together with other chemists, to a search of pentaorganonitrogen compounds.[4–8] His success in the preparation of Ph_3CNa led to the experiment outlined in Equation (1).[5]

$$Me_4{\equiv}N^+\,Cl^- + Ph_3{\equiv}CNa \longrightarrow Me_4{\equiv}N{-}C{\equiv}Ph_3 + Na^+Cl^- \qquad (1)$$

(original notation)

Reaction of dried Me_4N^+Cl with a red solution of Ph_3CNa in diethyl ether resulted in a fast discoloration of the solution and the formation of a bright red precipitate, which was isolated. To separate the product from NaCl, pyridine was added and the resulting intensive blood red solution was filtered under nitrogen. The addition of diethyl ether to the mother liquor initiated a fast crystallization of the product and a crop of "beautiful glimmering red crystals with a bluish metal shine"[5] was isolated.

The reactivity of the product showed great similarity to that of Ph_3CNa itself. This, together with the observation that a solution in pyridine conducts electrical currents, led to the assumption that the fifth valence in the product shows a reactivity different than that of the four Me groups. Schlenk proposed an ionic bond between the Ph_3C group and the N atom, but it was still not clear how the bonding in the RNR'_4 molecule should be interpreted.[7] Later research on pentavalent Group 15 species with equal R groups, finally led to Wittig's major discovery of trimethylammonium methylide[8] followed by the discoveries of the academically and industrially important Wittig reagent[9] and the first pentaorganophosphoranes.[10] Syntheses of the phosphoranes could only be achieved by the use of organic groups lacking acidic α protons (Scheme 1).

In the light of today's knowledge, Schlenk's crystalline "$Ph_3C{-}NMe_4$" cannot be classified as the first pentaorganonitrogen compound;[11] however, it represents the first ion pair including a carbanion: $[Ph_3C^-][Me_4N^+]$. The combination of a quite reactive "free" carbanion and a relatively acidic Me_4N^+ ion, makes the existence of Schlenk's compound quite remarkable. Later work elucidated the structures of "free"

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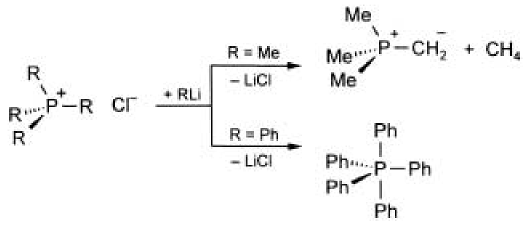

Scheme 1.

Ph_3C^- carbanions in the presence of several solvated metal cations,[12–14] however, Schlenk's first preparation of crystalline $[Ph_3C^-][Me_4N^+]$ was never cited. This is presumably due to the antiquity of Schlenk's early publication, but also to the fact that Schlenk did not recognize the existence of the "free" carbanion himself. In the course of our research on ammonium and phosphonium salts of cyclopendienyl (Cp) anions[15] we investigated the compound originally made by Schlenk: $[Ph_3C^-][Me_4N^+]$.

Results and Discussion

Crystals made according to Schlenk's original procedure were not suitable for X-ray diffraction. Initial attempts to slowly grow well-defined single crystals failed due to decomposition of the grown crystals overnight. Numerous attempts of analyzing crushed crystals with high-resolution powder diffraction using synchrotron radiation were unsuccessful due to the instability of the product.[16] The successful structure determination involved fast crystallization of the compound from a THF/Et_2O mixture followed by immediate mounting on the diffractometer precooled at $-90\,^\circ C$.

The structure of $[Ph_3C^-][Me_4N^+]$ is illustrated in Figure 1. The Ph_3C^- carbanion displays a perfect planar trigonal geometry at the central carbon atom (C_α) in Ph_3C^- (the sum of valence angles at C_α is 359.83(13)°). This feature, due to delocalization of negative charge in the phenyl rings, is observed in all other structural known "free" Ph_3C^- carbanions[12–14] and is also typical for Ph_3C^+ ions. Schlenk's Ph_3C^- carbanion, however, differs in one aspect from other "free" Ph_3C^- and Ph_3C^+ species. The phenyl rings in Ph_3C^- and Ph_3C^+ species are usually oriented such that a propeller exists. Analysis of 21 crystal structures[17] show that the angles between the phenyl rings and the central plane are in the range of about 21° to 41° (average 31.1 °). Schlenk's Ph_3C^- carbanion (Figure 1) shows a much larger variation: one phenyl ring is nearly coplanar with the central plane (11.5°), one is in the range expected (26.1°), and the third phenyl ring shows a more perpendicular orientation (61.1°). The average value of 32.9° is in the normal range again. This variance in orientation greatly influences the extent of charge delocalization in the different phenyl rings. The planar ring (Ph1) displays a large extent of charge delocalization, whereas charge delocalization is nearly shut off for the perpendicular phenyl ring (Ph3). Two structural parameters are very sensitive to charge delocalization: 1) the C_α–C_{ipso} bond length that shortens with increased charge delocalization and 2) the C-C-C angle within the phenyl ring at C_{ipso} that decreases with increased charge delocalization.[18] Both values show an excellent correlation with the angle between the correspondent phenyl ring and the central molecular plane (see Figure 1).[19]

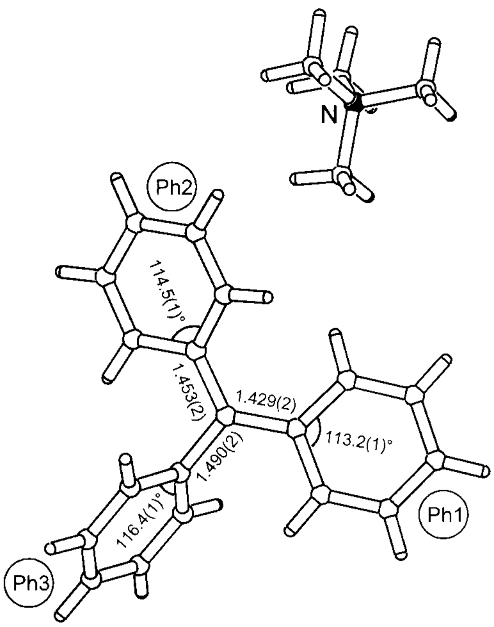

Figure 1. Crystal structure of $[Ph_3C^-][Me_4N^+]$ (projection on the central molecular plane of Ph_3C^-). The angles between the phenyl rings and the plane of projection are Ph1: 11.5°, Ph2: 26.1° and Ph3: 61.1°.

It has been stated that free unassociated anions are of significant structural and theoretical interest because distorting effects due to carbanion–metal interactions are completely absent.[12b)] The current structure, however, is different to other structurally known "free" Ph_3C^- carbanions. The origin of this difference is that the Ph_3C^- species in the crystals are not really free. Their structures are also influenced by crystal packing and by nonclassical hydrogen bonds (i.e. $C{-}H^{\delta+}\cdots C^{\delta-}$ contacts). Especially the latter are particularly strong in the current structure. Calculation of the charge distribution in Me_4N^+ shows that the positive charge is not located on the nitrogen atom but divided over the hydrogen atoms,[20] making the alkylammonium cations excellent donors in nonclassical hydrogen bonds.[15, 21] The hydrogen bond network in $[Ph_3C^-][Me_4N^+]$ (Figure 2) can be described as a quasi-linear arrangement of alternating Ph_3C^- carbanions and Me_4N^+ ions directed along one of the crystallographic 2_1 axes (neighboring chains run parallel). Some hydrogen atoms of the cation form $C{-}H^{\delta+}\cdots C^{\delta-}$ interactions to the negatively charged C_α (H1 and H4) and others form $C{-}H\cdots\pi$ interactions with the phenyl rings (H2 and H3). Note that $C{-}H\cdots\pi$ interactions are only formed to the two most electron-rich phenyl rings (Ph1 and Ph2 in Figure 1) and not to the perpendicularly oriented phenyl group for which charge delocalization has been largely shut off. The perpendicular phenyl group (Ph3) is not a good hydrogen bond acceptor, but acts as hydrogen donor in a $C{-}H\cdots\pi$ interaction to a Ph_3C^- unit of a neighboring chain (H5″). Likewise, a $C{-}H\cdots\pi$ interaction is accepted from the neighboring chain (H5). Other structures of "free" Ph_3C^- complexes[12–14] show similar $C{-}H^{\delta+}\cdots C^{\delta-}$ or $C{-}H\cdots\pi$ interactions.

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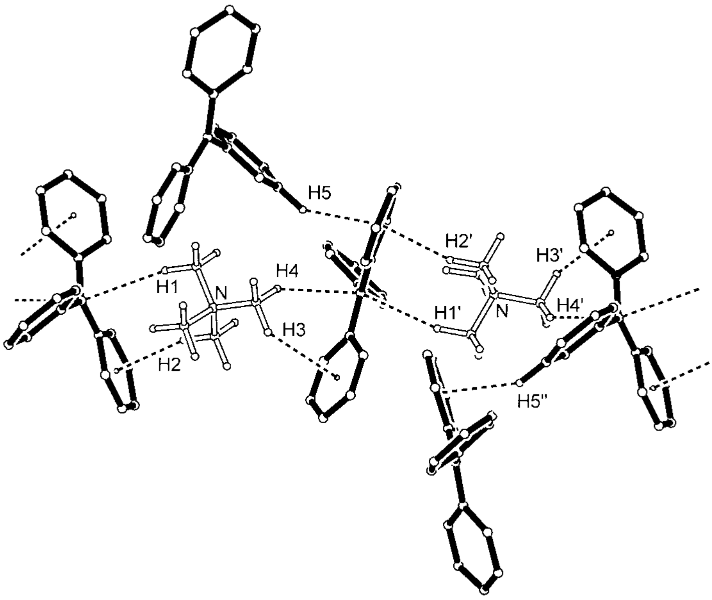

Figure 2. The quasi-linear arrangements of Ph_3C^- ions and Me_4N^+ ions directed along the 2_1 axis. Two Ph_3C^- ions of neighboring chains are depicted as well. The C–H···C and C–H···π interactions are shown by dashed lines; C–H···C (or C–H···ring$_{center}$) distances and angles (in parentheses): H2 2.472 (163.2°), H3 2.845 (128.0°), H5 2.589 (146.3°), H1 2.844 (156.7°), H4 2.790 (139.7°).

The shortest C–H···C distance in $[Ph_3C^-][Me_4N^+]$ (2.790 Å; H4) is considerably longer than that in $[Cp^-][Et_4N^+]$ (2.520 Å).[15] This is in contrast with expectation: the stronger base Ph_3C^- is a more potent acceptor in hydrogen bonds than the Cp^- ion. This oddity might be explained by steric hindrance of the central carbon atom in Ph_3C^-. Also, the additional formation of several C–H···π interactions to the phenyl rings might easily distort this nonclassical hydrogen bond (a network of intermolecular interactions is always a compromise). The C–H···C contact can be considered a transient point on the reaction path for proton transfer between Me_4N^+ and Ph_3C^-. Its excessive length might be the reason for the moderate stability of $[Ph_3C^-][Me_4N^+]$ and its major decomposition into Ph_3CMe instead of Ph_3CH.[17]

Schlenk was not only the first to crystallize the "free" Ph_3C^- carbanion but even succeeded in the preparation and isolation of $[PhCH_2^-][Me_4N^+]$. The compound precipitated as a red powder that, when dissolved in polar solvents, decomposed very fast.[22] The isolation of this compound is even more remarkable and evokes the question: what is the pK_a value of a Me_4N^+ ion? On basis of a large inductive effect, the pK_a value of the Me_4N^+ ion is assumed to be considerably lower than that of Me_3N. Deprotonation reactions and experimentally determined D/H exchange rate constants collectively suggest that Me_4N^+ has a pK_a value comparable with that of Ph_3CH.[23] The instability of the ylide $Me_3N^+{-}CH_2^-$ prevents any experimental equilibrium measurements and therefore an exact determination of a pK_a value for the Me_4N^+ ion. Only calculational methods can give information on the acidity of the Me_4N^+ ion.

The gas-phase acidity of Me_4N^+, and for comparison also that of Me_4P^+, were calculated by using the G2(MP2) method. These values are compared with the recently experimentally determined and calculated gas-phase acidities of Me_3N, Me_3P, and their borane adducts (Figure 3).[24] The excellent agreement between calculated and experimental values underscores the usefulness of advanced theoretical methods in the discussion of acidity. Complexation of the amine or phosphane with BH_3 greatly enhances its acidity by roughly 16–17 kcal mol^{-1} (ca. 12–13 pK_a units). This complexation technique was shown to be very useful in the α deprotonotion of amines and their subsequent functionalizations.[25] Complexation of Me_3N or Me_3P with the much stronger Lewis acid Me^+, results in an even larger acidification (experimental gas-phase acidities have not been reported). It should be noted that the relative gas-phase acidities for Me_3N and Me_4N^+ cannot be compared with solution acidities. Solvation will largely affect the stabilities of charged species and therefore also the relative acidities of Me_3N and Me_4N^+ (deprotonation of a neutral amine results in a charged species, whereas deprotonation of the charged Me_4N^+ results in a neutral species). However, a comparison of the calculated acidities of Me_4N^+ and Me_4P^+ is allowed (it is presumed that solvation energies of Me_4N^+ and Me_4P^+ are of the same order of magnitude). The alkylammonium cation is about 14.2 pK_a units less acidic than the alkylphosphonium cation for which in solution a value of 15.4 has been determined.[26] The estimated pK_a value for Me_4N^+ is therefore about 29.6. This classifies the Me_4N^+ ion as slightly more acidic than Ph_3CH for which a pK_a value of 30.6 has been determined.[27] For these reasons, Schlenk's early preparation of $[Ph_3C^-][Me_4N^+]$

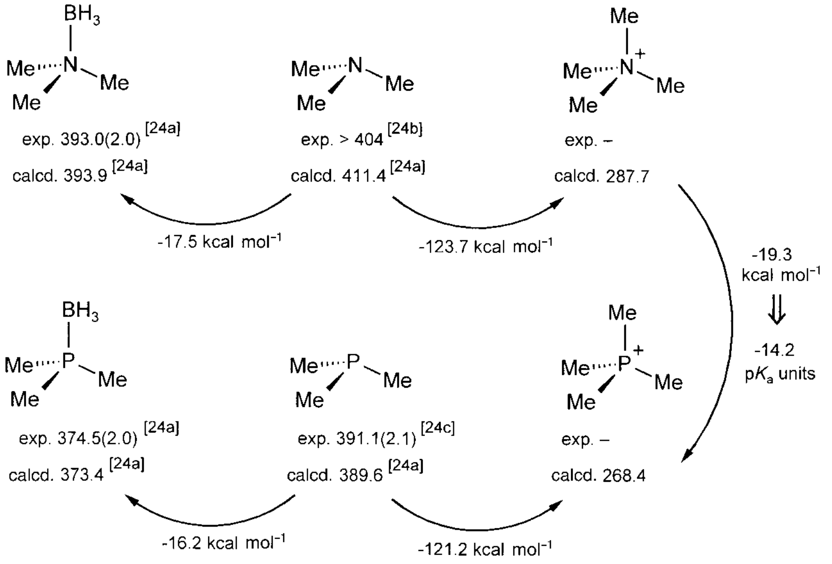

Figure 3. Experimental and calculated gas phase acidities (or Brønsted acidities) in kcal mol^{-1}.

and especially that of [$PhCH_2^-$][Me_4N^+] (toluene's pK_a value is estimated >40)[27, 28] have to be classified as highly remarkable results which deserve belated recognition.

Experimental Section

All experiments were carried out under argon using predried solvents and Schlenk techniques. The compound [Ph_3C^-][Me_4N^+] was prepared according to Schlenk's original procedure.[5]

Ab initio calculations were performed by using the G2(MP2) method incorporated in the GAUSSIAN-94 program system.[29]

Crystal structure determination: Crystals suitable for single-crystal X-ray diffraction were obtained by dissolution of the product in cold THF (0 °C) and layering the red mother liquor with Et_2O. The crystals start to grow immediately and display a respectable size after one hour. The dark red blocks were isolated, washed with a THF/Et_2O mixture and then with pure Et_2O. A bright red crystalline block was immediately mounted on the Enraf Nonius CAD4 diffractometer precooled at $-90\,^\circ C$. $Mo_{K\alpha}$, $2\theta_{max} = 52.0^\circ$, 4115 independent reflections ($R_{int} = 0.012$), 3586 reflections observed with $I > 2\sigma(I)$. Crystal data: orthorhombic, space group $P2_12_12_1$, $a = 9.9357(12)$, $b = 10.6379(12)$, $c = 17.4678(18)$ Å, $V = 1846.3(4)$ Å^3, formula [$C_{19}H_{15}$][$C_4H_{12}N$], $Z = 4$. The structure was solved by direct methods (SHELX-S)[30] and refined with SHELXL-97[31] against F^2 for all reflections: $R = 0.0320$, $wR2 = 0.0787$, GOF = 1.06, $\rho_{max} = 0.13$ e Å^{-3}, $\rho_{min} = -0.14$ e Å^{-3}. Friedels have been measured and the absolute structure was confirmed by refinement of the Flack parameter. The ammonium cation shows some disorder along one of its intrinsic threefold axes: three of the four methyl groups are disordered over two positions in a ratio of 87/13. Only the higher occupation is shown in Figure 1. Most of the hydrogen atoms have been found and were isotropically refined with free displacement factors. Only the hydrogen atoms belonging to the disordered minority part (13%) have been calculated and were refined in a riding model. For analysis of the hydrogen network, all hydrogen atoms have been calculated at distances of 1.08 Å.[15] Molecular illustrations and geometry calculations were performed with the PLATON package.[32] CCDC-172128 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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