in the product arose from Cl^-, which was present as a 6-7% impurity of the CuCN starting material. We estimated this percentage from the yield (ca. 20%) of **1**, and this figure was later corroborated by elemental analysis on the commercial CuCN used.[9] The colorless crystals obtained in ca. 25% yield from the same solutions had cell constants identical with the crystals obtained from the reaction of CuBr with 2 equiv of LiPh. The structure of this compound has not been completely solved due to disorder problems but is probably a cubane structure of formula $[(LiCuPh_2 \cdot Et_2O)_4]$.[11]

The anion of **1** (Figure 1) contains a trigonal bipyramid with two lithium (apical) and three copper (equatorial) atoms. Each Li–Cu vector is bridged by a phenyl group. The framework is very close to that described for $[Cu_5Ph_6]^-$ but the Li···Li distance is 3.63 (3) Å, so that the TBP cluster is not as "squashed" as it is in the $[Cu_5Ph_6]^-$ ion.[5] The close structural relationship shows that replacement of two copper atoms by lithium allows retention of the basic architecture, which has also been seen in related systems.[10] The Cu–C distances (typical value 1.929 (6) Å) are very close to those found in $[Cu(Mes)_2]^-$,[4] $[Cu_5Ph_6]^-$,[5] and [Li-(12-crown-4)$_2$][$CuPh_2$].[11] The Li–C distances in **1** are somewhat long (typical value 2.240 (14) Å), but they are shorter than those found in $[(LiPh \cdot Et_2O)_4]$.[12] The Cu–Cu distances (ca. 3.3 Å) preclude significant metal–metal bonding at the equatorial edges. A curious feature of **1** arises from its stoichiometry. If the ethers are disregarded the formula may be written as $[(LiCuPh_2)_3(LiCl)]$. Together with the compound $[(LiCuPh_2)_4]$ this bears a stoichiometric resemblance (again ignoring the ethers) to the halide-free and halide-rich phenyllithium species $[(LiPh)_4]$ and $[(LiPh)_3LiBr]$. Although there is no structural correspondence between the two copper compounds, it may be that the presence of a different species such as **1** in solution may account, in part, for the difference in reactivity between cuprates derived from CuBr and from CuCN contaminated by Cl^-.

The structure of the cation (Figure 2) is also of interest as it is the first structure of a lithium halide aggregate (outside of the lithium halides themselves). Various studies (including EXAFS)[13] have shown that lithium halides exist as tetramers in ether and as dimers in ethylene carbonate. The structure of the cation indicates that it may be possible to crystallize these and other complexes. The cation structure consists of a planar core of two Li and two Cl atoms; each Cl atom is also coordinated to a terminal Li. All the Li atoms are four-coordinate due to further coordination to either two or three ether molecules. The Li–O distances, ca. 1.96 Å, are close to those found in other etherates.[12,14] The terminal Li–Cl distance, 2.697 (12) Å, is longer than either of the bridging distances, 2.537 (12) and 2.505 (12) Å. This is probably due to the terminal Li atoms being more electron rich by coordination to one more ether instead of a Cl^- ion, which is a poorer electron donor.

Studies to isolate and structurally characterize other lithium organocuprates are in progress.

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Supplementary Material Available: Full tables of atom coordinates and bond distances and angles of **1** (4 pages). Ordering information is given on any current masthead page.

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Sensitivity-Enhanced NMR Detection of Nonprotonated ^{15}N Nuclei

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We wish to demonstrate that a simple modification of the INEPT experiment[1-3] allows polarization of nonprotonated ^{15}N nuclei in peptides. This selective polarization method yields a large enhancement in sensitivity and also correlates the ^1H and ^{15}N shift, providing assignment information. It has been demonstrated in the past, that selective pulse polarization transfer (SPT) can give large sensitivity enhancement for both protonated and nonprotonated ^{13}C and ^{15}N resonances.[4-7] However, the SPT method is very difficult to use in the case of complex coupling networks and if couplings are not resolved and is therefore generally not easily applicable to the study of resonances of nonprotonated ^{15}N nuclei.

Several new methods have been introduced in recent years that allow polarization transfer from protons to the heteronucleus, for example, ^{15}N, using only nonselective pulses.[1-3,7,8] The INEPT experiment, first introduced by Morris and Freeman,[1] is the oldest of these methods. The refocused INEPT sequence[3] is set out in Figure 1. This sequence works very well for protonated ^{15}N nuclei, and transverse magnetization can be enhanced by a factor of nearly $\gamma_{^1H}/\gamma_{^{15}N} = 10$, compared with that created by a single 90° (^{15}N) pulse without NOE. The INEPT sequence usually fails if one wants to enhance magnetization of nonprotonated ^{15}N nuclei, by optimizing the duration of the delays, Δ, for a certain long-range coupling, $^{lr}J_{NH}$. To clarify the advantages of our modification, we wish to comment first on why the regular INEPT experiment fails. First, if homonuclear proton coupling is present, significant dephasing of the protons occurs during the interval Δ_1 ($\approx 1/(2^{lr}J_{NH})$), and the $90°_{\pm y}$ (^1H) pulse will create a large amount of homonuclear multiple quantum coherence.[8-10] This multiple quantum coherence cannot directly be transferred into ^{15}N transverse magnetization. Second, the multiplet components of the ^{15}N magnetization that has been transferred are in antiphase just after the 90° ^{15}N pulse. One therefore has to wait for a time Δ_2, of the order of $1/(2^{lr}J_{NH})$, before proton decoupling can be started. If the ^{15}N nucleus is coupled to a number of protons, the ^{15}N signal will decay rapidly during this time, Δ_2, and little magnetization will be left when broad-band proton decoupling is started.

We propose the use of soft proton pulses (typical 90° flip angle $\approx$5 ms) in order to avoid the two problems mentioned above. If the proton pulses only affect one preselected proton, the dephasing due to homonuclear coupling will be refocused just before the second 90° proton pulse by the selective 180° pulse, applied at the midpoint of the interval, Δ_1. Therefore, no homonuclear multiple quantum coherence will be created by the second 90° (^1H) pulse, and all ^1H magnetization will be transfered to the ^{15}N nucleus, analogously to the case of a directly bonded ^{15}N–^1H pair, where a short value for Δ_1 can be used. The total precession of

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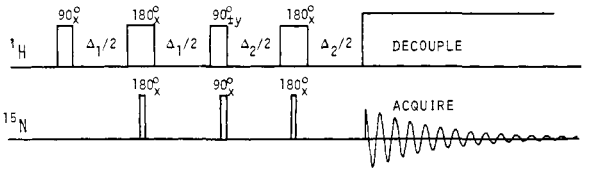

Figure 1. Pulse scheme of the INEPT experiment. The phase of the second 90° ^{1}H pulse is alternated along the $\pm y$ axis in successive experiments, and data are accordingly added and subtracted.[1,2] In the selective INEPT experiment the proton pulses are soft pulses ($\gamma H_2/2\pi \approx 50$ Hz), applied to a preselected proton. In both versions of the experiment, broad-band proton decoupling is used during acquisition. The delays $\Delta_1/2$ and $\Delta_2/2$ are, for a NH pair, of the order of $1/(4J)$, where J is the magnitude of the scalar coupling used in the transfer process.

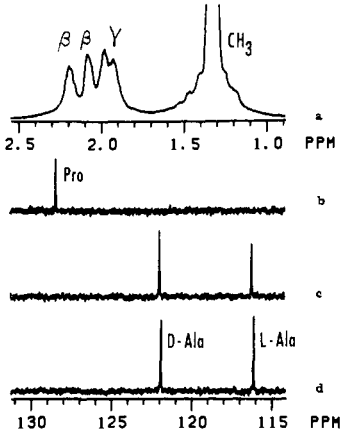

Figure 2. (a) Proton spectrum of *cyclo*-(D-Ala-L-Pro-L-Ala)$_2$ in $CDCl_3$, recorded at 500 MHz, using the decoupler coil of the 10-mm ^{15}N probe. (b) Selective INEPT spectrum of the proline ^{15}N resonance, obtained in 18 min. (c) Regular INEPT spectrum, showing only the alanine ^{15}N resonances, obtained in 2 min. (d) Conventional "one-pulse, FT" spectrum, obtained in 1 h, using continuous broad-band proton decoupling. ^{15}N spectra are referenced indirectly to NH_3, using Me_4Si as an intermediate.[16]

^{15}N magnetization vectors during the delay time Δ_2 is not affected by coupling to protons other than the one to which a selective 180° pulse is applied,[11,12] and therefore, after this time, Δ_2 ($\approx 1/(2^{lr}J_{NH})$), the ^{15}N doublet components will be parallel and broad-band proton decoupling can be started. In principle, this selective INEPT experiment can give the full factor of 10 in signal enhancement. Because the longitudinal relaxation time will generally be much shorter for the proton than for the nonprotonated ^{15}N nucleus, the experiment can be repeated much faster than a conventional "one pulse, FT" experiment, and the gain in sensitivity will even be larger.

The experiment is demonstrated for the detection of the proline ^{15}N resonance in a 0.3 M solution of the cyclic hexapeptide (D-Ala-L-Pro-L-Ala)$_2$[13] in $CDCl_3$, in a 10-mm sample tube. Experiments were performed on a NT-500 spectrometer. Figure 2a shows the proton spectrum obtained by using the decoupler coil of the ^{15}N probe, showing the rather poor ^{1}H resolution. The proline β proton at 2.08 ppm was used for the selective polarization transfer. The proton rf field strength was calibrated[14,15] to give a 90° pulse duration of 5 ms, using a sample of formamide and pulsing the α proton resonance. Figure 2b shows the proline ^{15}N resonance, obtained after 500 accumulations (18 min) with the selective INEPT experiment. Three-bond ^{1}H–^{15}N couplings are often of the order of 2–3 Hz, and on this basis, the delays $\Delta_1/2$ and $\Delta_2/2$ would have to be set to 50 ms. To minimize effects of relaxation during those delays, both delays were set to a compromise value of 30 ms. As a reference, Figure 1c shows the two ^{15}N resonances of D-Ala and L-Ala in the peptide, obtained with the regular INEPT experiment in 50 accumulations (2 min). Figure 1d shows the normal FID spectrum obtained from 1000 accumulations with broad-band decoupling throughout and a ^{15}N flip angle of 60° (1 h). Probably due to the small NOE and the long T_1, the ^{15}N proline is not observed.

From comparing Figure 2 parts b and c, it can be seen that the selective INEPT sequence is a factor of 4 less effective in enhancing the proline ^{15}N resonance than the conventional INEPT sequence is for the alanine resonances. Hence, the effective enhancement of the proline resonance is probably only a factor of 2, instead of the obtainable 10. Main reasons for this lower enhancement are the relaxation during the delays Δ_1 and Δ_2 and the fact that the selective pulses are not selective enough and also affect the nearby resonances of the γ protons and the other β proton. This also means that, in this case, a high magnetic field strength is needed in order to separate those resonances sufficiently. In principle other polarization sequences[7,8] could also be used for polarization transfer via long-range couplings, but because the total duration of those sequences is longer, relaxation effects will be stronger, and efficiency is expected to be worse.

To summarize, we have demonstrated that signal enhancement of nonprotonated ^{15}N nuclei in peptides is feasible by means of selective INEPT. The experiment is easy to set up and gives a large signal enhancement compared with conventional observation. It allows the natural abundance ^{15}N study of the structure-sensitive proline ^{15}N resonances in polypeptides.

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Molecular Structure and Dynamic Solution Behavior of the Bridging 1,3-Dimetallaallyl Ligand in $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)(\mu\text{-}C_3R_2SiMe_3)$ Compounds (R = H, Me, Ph) Formed by Insertion of Alkynes into a Bridging Alkylidyne Ligand

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The considerable current interest in the reactivity of $M_2(\mu\text{-}X)$ species, particularly with respect to C–C bond-forming reactions,[1] prompts us to report some preliminary findings concerning the reactivity of the $(Me_3SiCH_2)_4W_2(\mu\text{-}CSiMe_3)_2(M\text{-}M)$ molecule[2] toward alkynes, RC≡CR, where R = H, Me, and Ph, which proceed in hydrocarbon solvents according to eq 1.

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