These cations should contain stronger Ti–O bonds than the electrically neutral Ti(dik)$_2$(OR)$_2$ complexes; yet the cations are nonrigid on the NMR time scale at −105°. The question of bond rupture vs. twisting is not settled by the NMR spectrum of the triacetylmethanate (triac) complex studied by Baggett et al.[6] since internal rotation in the partly dissociated triac ligand probably is slow at 35°; for Co(triac-d_3)$_3$, linkage isomerization is nine times slower than inversion at 105.2° and $\Delta H^\ddagger$ for linkage isomerization is higher by 8 kcal/mol.[10]

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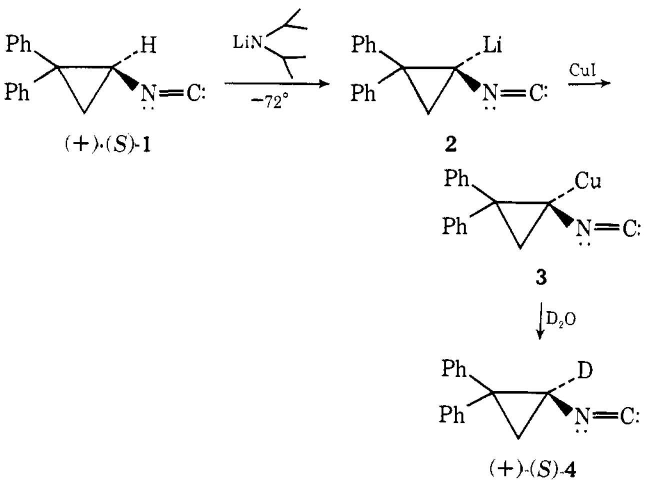
Cyclopropane. XXXVII. A Stable Chiral Copper Reagent[1]

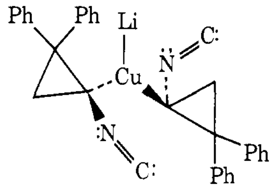
Sir:

In general, organocopper reagents are stereochemically unstable at ambient temperatures. This seems to be the case whether the copper is bound to an sp^3 or sp^2 carbon atom or whether or not the copper(I) is coordinated to stabilizing ligands.[2,3] We wish to report on the preparation of the first optically stable copper(I) reagent in which the copper(I) is directly attached to the chiral center.[4]

Recently[5] we reported that 1-lithio-1-isocyano-2,2-diphenylcyclopropane (**2**), generated from chiral (+)-(*S*)-1-isocyano-2,2-diphenylcyclopropane (**1**) by reaction with lithium diisopropylamide, is capable of maintaining its configuration at temperatures between −52 and −72° but racemizes at −5°. Treatment of **2**, formed at −72° in tetrahydrofuran, with cuprous iodide and allowing the temperature to slowly rise[6] to 10° over a period of 30 min produced **3**. The reaction mixture was hydrolyzed with water to regenerate (+)-(*S*)-**1** in 20% yield[7] and an optical purity of 95%. In another experiment the reaction mixture was quenched with deuterium oxide to yield (+)-(*S*)-**4** (16% yield)[7] with retention of configuration (98% optical purity) and 90 ± 1% deuterium incorporation. The configurational stability of **3** was unaffected by an increase in temperature and length of reaction time. For example, addition of cuprous iodide to **2** at −70° and allowing the reaction mixture to warm up to room temperature (23°) over a period of 30 min followed by deuterium oxide deuterolysis yielded (+)-(*S*)-**4** (70% yield)[6] with an optical purity of 91% and with 89% deuterium incorporation. Repeating this experiment but changing the reaction time from 30 min to 2 hr did not affect the stereochemistry nor the amount of deuterium incorporation. Based on these data it is concluded that **3** represents the first stable chiral organocopper(I) compound having an asymmetric carbon atom directly attached to copper(I).



We have observed that the addition of either 1 equiv of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), 2 equiv of triglyme, or 2 equiv of 15-crown-5 to a tetrahydrofuran solution of **2** at −72° did not affect the configurational stability.[8] Also, in the case of **3**, the addition of TMEDA at 23° for 30 min did not alter the stereochemical behavior but the addition of crown ether did have an effect. Thus, to a tetrahydrofuran solution of **3** at 23° 1 equiv of TMEDA was added, stirred for 30 min, and quenched with deuterium oxide to give **4** in 84% yield. The optical purity was found to be 94% and the deuterium incorporation was 95%. However, when the reaction was carried out using 1 equiv of 15-crown-5 a mixture of **1** and **4** was isolated (40% yield) with an optical purity of 88% and a deuterium content of 70%. Moreover, if the reaction time was increased to 12 hr at 23°, the optical purity of the product (20% yield) was reduced to 68% and the deuterium content was very low,[9] 19%.



5

The chiral cuprate (I) **5** has also been prepared by the addition of 0.5 equiv of cuprous iodide to 1 equiv of **2** at −72° and allowing the temperature to rise to −5° over a period of 30 min.[6] Quenching the reaction mixture with deuterium oxide yielded **4** which was 97% optically pure with 33% deuterium incorporated. However, if the reaction is run at 10° and then quenched with deuterium oxide the deuterium content of **4** remains the same but the optical purity is decreased to 70%.

A comparison of the optical stabilities of **2**, **3**, and **5** indicates that the order of stability is **3** > **5** > **2**. Further studies on the configurational stabilities of isocyano carbanions are in progress.

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(6) There was no apparent reaction with cuprous iodide at −72°. Reaction occurred, as evident by a color change starting at −50° from pale yellow to a dark green at −20°.
(7) The low yield is due to a copper–isocyanide complex being the major product. In later experiments, at 23°, the yields were improved by breaking up the complex with aqueous potassium cyanide.
(8) Unpublished results with M. P. Periasamy.
(9) A discussion of these results will be given in our full paper.

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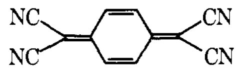
Oxidation of Organometallic Compounds with Tetracyanoquinodimethan

Sir:

Complexes of tetracyanoquinodimethan[1] (TCNQ), **1**, with organic donor molecules have attracted great interest because of their unusual structural and electrical properties.[2] This communication reports some results of a study of the reactions of TCNQ with organometallic compounds.



1

Shchegolev and coworkers have reported the preparation of both 1:1 and 1:2 complexes of bis(benzene)chromium with **1**[3] and the crystal structures of both materials have been determined.[4,5] We found that the analogous reaction between **1** and (toluene)chromium tricarbonyl, **2**, leads to quite different products which were unanticipated on the basis of the observation that (arene)$_2$Cr compounds are more easily oxidized than (arene)Cr(CO)$_3$. When 2 mmol each of **1** and **2** in acetonitrile were stirred for 3 days, toluene and 3 mmol of carbon monoxide were produced, along with a deep purple, noncrystalline solid, **3**. Evaporation of the solution from which **3** had separated allowed the recovery of 1 mmol of **2**. Elemental analysis indicated that **3** had the composition $\text{Cr(CH}_3\text{CN)}_2\text{(TCNQ)}_2$.[6] The conductivity of **3**, measured by the microwave technique on compressed pellets, was 2.2×10^{-4} $(\text{ohm cm})^{-1}$.[7] The infrared spectrum (Nujol mull) contained strong bands at 2100 and 2205 cm^{-1} but no absorptions due to toluene or carbonyl groups were found. Room temperature magnetic susceptibility measurements showed $\mu_{\text{eff}} = 4.08\ \mu_{\text{B}}$.[8]

A similar reaction with bicyclo[2.2.1]heptadiene molybdenum tetracarbonyl with **1** in acetonitrile afforded dark purple **4**, whose elemental analysis corresponded to $\text{Mo(CO)}_2\text{(CH}_3\text{CN)}_2\text{(TCNQ)}$, along with bicycloheptadiene and 2 equiv of carbon monoxide. Compound **4** was diamagnetic with $\mu_{\text{eff}} = 0.03\ \mu_{\text{B}}$ at 298 K. The infrared spectrum contained broad bands at 2090 and 2190 cm^{-1}; no discrete carbonyl bands were observed and they may overlap the C≡N stretching absorptions. No bands attributable to coordinated bicycloheptadiene were found. The conductivity was 2.3×10^{-4} $(\text{ohm cm})^{-1}$.

The magnetic susceptibility of **3** indicates that it contains high spin Cr^{3+}; a higher μ_{eff} than the spin-only value for this d^3 ion may be due to a contribution from $\text{TCNQ}\cdot^-$ [9,10] (vide infra). The presence of Cr^{3+} in **3** would require the presence of one $\text{TCNQ}\cdot^-$ and one TCNQ^{2-} in order to maintain electroneutrality.

The Mo 3d$_{3/2}$ and 3d$_{5/2}$ binding energies in **4** were 233.0 and 230.7 eV, respectively. Comparison of these ESCA data with those of Hughes and Baldwin[11] on a variety of molybdenum compounds suggests that **4** contains formal Mo(II). The presence of Mo(II) in this compound would again require that it be formulated as a derivative of TCNQ^{2-}.

The presence of C≡N stretching vibrations at 2100 cm^{-1} in **3** and **4** is also consistent with the presence of the TCNQ dianion since an absorption at lower frequencies than found in **1** (2210 cm^{-1}) or $\text{Li}^+\text{TCNQ}\cdot^-$ (2190 cm^{-1}) would result from addition of electron density to the C≡N π^* orbitals.

Although TCNQ can be reduced electrochemically to the dianion,[2d,12] the only example of a solid TCNQ^{2-} salt, prepared by Basolo and coworkers, is $[\text{Co}(N,N'\text{-ethylenebis(acetylacetonimine)}) (\text{C}_5\text{H}_5\text{N})_2]_2\text{TCNQ}$.[13] Like **3** and **4**, this material exhibits ν_{CN} at low frequencies (2102 and 2151 cm^{-1}). Formation of TCNQ^{2-} salts from **1** and organometallic compounds presumably occurs by electron transfer[14] followed by expulsion of the organic ligands. These results suggest that TCNQ^{2-} derivatives are readily obtainable and that **1** might be used to obtain materials having the metal in a less common oxidation state. Studies of the organometallic chemistry of TCNQ and of the magnetic and electrical properties of TCNQ^{2-} derivatives are continuing. It is of interest to note that the TCNQ dianion may be a low energy species in materials whose electrical conductivity involves fluctuations of doubly occupied ionic configurations.[2h]

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