Structure and reactivity of cyanocuprates containing the monoanionic C,N-chelating aminoaryl ligand $[C_6H_4CH_2NMe_2-2]^-$

Claudia M.P. Kronenburg, Johann T.B. H. Jastrzebski, Gerard van Koten *

Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Abstract

The 2:1 cyanocuprate $[Ar_2Cu(CN)Li_2(THF)_4]_\infty$ (**1**, $Ar = [C_6H_4CH_2NMe_2-2]^-$) is obtained as the only product in the reaction of two equivalents of ArLi with one equivalent of CuCN in tetrahydrofuran (THF) at $-78°C$. The X-ray crystal structure reveals an ionic polymeric chain consisting of consecutive $[Ar_2Cu]^-$ and $[(THF)_2LiCNLi(THF)_2]^+$ units. Its composition in THF solution has been investigated. ©2000 Elsevier Science Ltd All rights reserved.

The application of cyanocuprates of general formula $[R_nCu(CN)Li_n]$ ($n = 1$ or 2) to organic synthesis by Lipshutz et al. [1] in 1981 led to a lively discussion on their possible structure in the solid state and in solution in the following years. Depending on the stoichiometry of the reaction of alkyl- or aryllithiums (one or two molar equivalents) with copper(I) cyanide, two types of cyanocuprates can be formed: the so-called 1:1 cyanocuprates of type $[RCu(CN)Li]$, or the 2:1 cyanocuprates with formula $[R_2Cu(CN)Li_2]$. According to the initial proposal by Lipshutz, the high reactivity of the latter type of cyanocuprates is due to bond formation between the cyano anion and the copper(I) center, thereby forming a dianionic species of type $[R_2Cu(CN)]^{2-}$ (**A**) [2]. In addition to this proposal, three other structures were also postulated: a monoanionic copper species (**B**) [3,4], a neutral monomeric copper species (**C**) [5,6] and a 'cyano-Gilman' cuprate (**D**) [7].

A: $[R_2Cu(CN)]^{2-} 2[Li]^+$,   **B:** $[R_2Cu]^- [Li_2(CN)]^+$,

C: **D:** $R_2CuLi + LiCN$
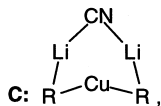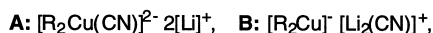
The discussion on the structural aspects of 2:1 cyanocuprates has mainly been focused on proposals **C** and **D**, although arguments were put forward to support each of the

four structures [8]. Moreover, recent spectroscopic studies (EXAFS [9–11] and NMR [12–14]) and molecular weight determinations [15] seemed also to support the structural proposals **C** and **D**.

Unambiguous proof of the structure of the thermodynamically most stable form of 2:1 cyanocuprates in the solid state has been obtained by crystal structure determinations. In 1998 both our group [15] and the group of Boche [16] reported the crystal structure of a 2:1 cyanocuprate. Remarkably, both structures, one alkyl- and one arylcyanocuprate, support proposal **B**. We reported on the synthesis, isolation and structural characterization of the bisarylcyanocuprate $[Ar_2CuLi_2(CN)(THF)_4]_\infty$ (**1**, $Ar = [C_6H_4CH_2NMe_2-2]^-$) (see Fig. 1). The solid state structure of this 2:1 cyanocuprate comprises a linear polymeric chain, consisting of alternating $[ArCu]^-$ anionic units and $[Li_2CN(THF)_4]^+$ cationic units. These are linked via intermolecular coordination by the nitrogen donor atom of the aryl ligand. The CN^- acts as a bridging C,N-coordinating ligand for two Li^+ to form a very stable $[Li_2CN]^+$ with a linear LiNCLi arrangement. Furthermore, the X-ray structure determinations of $[t-BuCu(CN)Li]$ [16] and $[Li(THF)_2\{Cu(CN)C_6H_3-2,6-Trip_2\}]_2$ ($Trip = C_6H_2-2,4,6-iPr_3$) have been reported [17].

To study the aggregation behaviour of cuprates in solution we measured the molecular weights by cryoscopy of various cuprates in tetrahydrofuran (THF) in collaboration with the group of Professor Krause (Table 1) [6]. Although for an anion/cation pair a calculated value of the aggregation state

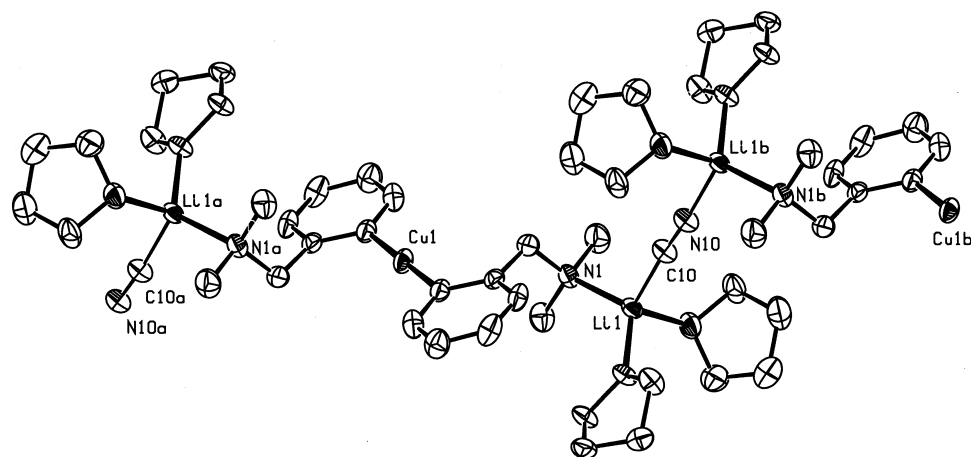* Corresponding author. Tel.: +31-30-2531813; fax: +31-30-2523615; e-mail: g.vankoten@chem.uu.nl

Fig. 1. ORTEP drawing (50% probability level) of $[Ar_2Cu(CN)Li_2(THF)_4]_\infty$ (**1**). C(1a)–Cu–C(1) 180°; Li(1)–C(10)–N(10) 175.6(3)°, C(10)–N(10) 1.156 Å. For X-ray structural data and tables of fractional coordinates, thermal parameters, bond distances and angles see [15].

Table 1
Cryoscopic data for cuprate compounds in THF

Entry	Cuprate	C_{nom} (mmolal)	$n = C_{nom}/C_{exp}$
1	$[Me_2CuLi_2(CN)]_n$	35.2–72.9	1.1–1.2
2	$[t\text{-}Bu_2CuLi_2(CN)]_n$	46.0–75.7	0.7–0.8
3	$[t\text{-}BuCu(CN)Li]_n$	70.4	1.1
4	$[Ph_2CuLi_2(CN)]_n$	25.5	1.2
5	$[PhCu(CN)Li]_n$	88.2	2.0
6	$[Ar_2CuLi_2(CN)]_n$	14.8–73.6	0.7–0.9
7	$[ArCu(CN)Li]_n$	79.9–147.2	0.9–1.4
8	$[Ar_2CuLi]_n$	24.8–84.2	2.0–1.7

Table 2
Results of the investigation of organocopper, -cuprates and -cyanocuprates with Ar as a ligand in the substitution reaction with a primary halide

Entry	$[Rcu]$ [a]	Substrate	Product	Yield (%)
1	$[(Ar)_2CuLi_2(CN)]$	Octyl-Br	Ar-octyl	53
2	$[Ph_2CuLi_2(CN)]$	Octyl-Br	Ph-octyl	40
3	$[ArCu(CN)Li]$	Octyl-Br	Ar-octyl	10
4	$[(Ar)_4Cu_2Li_2]$ [b]	Octyl-Br	Ar-octyl	10
5	$[ArCu]$ [c]	Octyl-Br	Ar-octyl	<1

[a] R:substrate = 1:1. Reaction conditions: THF, −78°C → RT, 1 h.
[b] van Koten and Noltes [20].
[c] van Koten et al. [21].

of 0.5 is expected, the measured values for the 2:1 cyanocuprates (entries 2 and 6) range from $n = 0.7$ to 0.9. This suggests the presence of a trinuclear $CuLi_2$ species, structure **C**, which can be regarded as a neutral cuprate complex comprising an anionic $[R_2Cu]^-$ and a cationic $[Li_2CN]^+$ unit. However, for the other cuprates described in Table 1, discrete monomeric or dimeric species are found.

It is noted that cryoscopic results may be deceptive, as association of anionic and cationic species to higher aggregates (ion-pair formation) [18] might occur. As a result of such association, a virtual aggregation state of almost 1 could be calculated.

The higher reactivity of the 2:1 cyanocuprates in most of the substitution reactions was ascribed to the fact that the CN^- was bound to copper. [The idea of using a CN group as a 'non-transferable' ligand was first introduced by Gorlier et al. [19].] In order to further test the hypothesis that the active species contains $[R_2Cu]^-$ in solution, we studied the influence of the nature of the various cuprate reagents on the outcome of a substitution reaction of a primary halide with such cuprate reagents (Table 2). These preliminary results (see Table 2) show that in the given reaction time (1 h) the 2:1 cyanocuprates (entries 1 and 2) transfer 50% of the R groups to the substrate, while the other Cu^I species tested are not reactive (entries 3–5).

The fact that only 50% of the R groups of the 2:1 cyanocuprate (see entries 1 and 2) is transferred suggests that the remaining cyanocuprate species, after transfer of the R group, assembles into a stable, and unreactive, 1:1 cyanocuprate (entry 3).

In conclusion, it can be stated that the solid-state structure of a 2:1 cyanocuprate of type $[Ar_2CuLi_2CN]_\infty$ has revealed the presence of ionic structural motifs. In addition, more insight into the apparent structure of some specific cyanocuprates in solution has been provided by cryoscopic measurements in THF.

Supplementary data

X-ray structural data for compound **1** are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request, quoting the deposition number SITYEZ.

Acknowledgements

References

[1] B.H. Lipshutz, R.S. Wilhelm, D.M. Floyd, J. Am. Chem. Soc. 103 (1981) 7672.

[2] B.H. Lipshutz, Synthesis (1987) 325.

[3] S.H. Bertz, J. Am. Chem. Soc. 112 (1990) 4031.

[4] T.A. Mobley, F. Müller, S. Berger, J. Am. Chem. Soc. 120 (1990) 1333.

[5] J.P. Snyder, D.P. Spangler, J.R. Behling, J. Org. Chem. 59 (1994) 2665.

[6] A. Gerold, J.T.B.H. Jastrzebski, C.M.P. Kronenburg, N. Krause, G. van Koten, Angew. Chem., Int. Ed. Engl. 36 (1997) 755.

[7] S.H. Bertz, G. Miao, M. Eriksson, Chem. Commun. (1996) 815.

[8] N. Krause, A. Gerold, Angew. Chem., Int. Ed. Engl. 36 (1997) 186 (review).

[9] T.L. Stemmler, T.M. Barnhart, J.E. Penner-Hahn, C.E. Tucker, P. Knochel, M. Böhme, G. Frenking, J. Am. Chem. Soc. 117 (1995) 12489.

[10] T.M. Barnhart, H. Huang, J.E. Penner-Hahn, J. Org. Chem. 60 (1995) 4310.

[11] T. Stemmler, J.E. Penner-Hahn, P. Knochel, J. Am. Chem. Soc. 115 (1993) 348.

[12] B.H. Lipshutz, S. Sharma, E.L. Elsworth, J. Am. Chem. Soc. 112 (1990) 4032.

[13] B.H. Lipshutz, B. James, J. Org. Chem. 59 (1994) 7585.

[14] S.H. Bertz, K. Nilsson, O. Davidsson, J.P. Snyder, Angew. Chem., Int. Ed. Engl. 37 (1998) 314.

[15] C.M.P. Kronenburg, J.T.B.H. Jastrzebski, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 120 (1998) 9688.

[16] G. Boche, F. Bosold, M. Marsch, K. Harms, Angew. Chem. 110 (1998) 1779.

[17] C.-S. Hwang, P.P. Power, J. Am. Chem. Soc. 120 (1998) 6409.

[18] M. Szwarc, Ions and Ion Pairs in Organic Reactions, Wiley-Interscience, New York, 1967 (chapter 1).

[19] J.-P. Gorlier, L. Hamon, J. Levisalles, J. Wagnon, J. Chem. Soc., Chem. Commun. (1973) 88.

[20] G. van Koten, J.G. Noltes, J. Chem. Soc., Chem. Commun. (1972) 940.

[21] G. van Koten, A.J. Leusink, J.G. Noltes, J. Chem. Soc., Chem. Commun. (1970) 1107.