

Catalysts

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The assembling of a catalytic active copper site, in solution, followed by EXAFS

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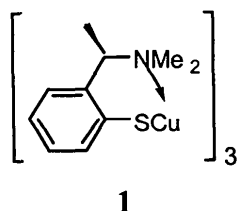
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Cuprates can be used as reagents for the formation of C-C bonds in organic reactions. The structure of these cuprates under working conditions is still unclear. In this study we will show that EXAFS is a powerful technique to obtain the structural information of these cuprates derived from $[\text{Cu}_3(\text{SAr})_3]$ catalysts. It will be shown that the reaction of a parent $[\text{Cu}_3(\text{SAr})_3]$ complex with a Grignard reagent (MeMgI) results in re-aggregation of the $[\text{Cu}_3(\text{SAr})_3]$ structure. In the case of a threefold excess of MeMgI a structure $[\text{R}_2\text{Cu}_4(\text{SAr})_2]$, including four Cu centres connected by two carbon and two sulfur bridges, for the newly formed aggregate is proposed. After adding a 6 fold excess of MeMgI to $[\text{Cu}_3(\text{SAr})_3]$, Cu-Mg, Cu-C and C-S contributions were found. For this complex a structure of the type $[\text{RCu}(\text{SAr})\text{Mg}(\text{I})]$ with bridging carbon or sulfur atoms is proposed.

Keywords: EXAFS; homogeneous catalysts; Copper; Cuprates; Grignard.

1. Introduction

Important reactions in the organic chemistry are the reactions involving the formation of C-C bonds. For these reactions the cuprates $[\text{LiCuR}_2]$ and $[\text{Li}_2\text{Cu}(\text{CN})\text{R}_2]$ are most widely applied. However the nature of these cuprates is still largely unknown. Earlier work revealed that the copper(I) complex **1** (abbreviated to $[\text{Cu}_3(\text{SAr})_3]$ with $\text{SAr}=\text{SC}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2$, see scheme 1) is active for the transfer of the R group from RMgX (Grignard) reagents to various organic substrates (Knotter 1992; van Klaveren 1994). Although the crystal structure of **1** is known (Knotter 1991), the fitting of the EXAFS data of this sample was



Scheme 1 Structure of $\text{Cu}_3(\text{SAr})_3$; the S atoms form bridges between two Cu centers

not trivial. To obtain structural data, which were chemically meaningful and agreed with other characterization techniques (like XRD, NMR and IR) it turned out to be necessary to include a Cu·C (the carbon atoms from the

methyl groups connected to the nitrogen atom) and Cu-N, Cu-S and Cu·Cu contributions to the fitting procedure (Janssen et al. 1998). When these carbon atoms were omitted no Cu·Cu contribution could be found due to the opposite phases of the Cu·C and Cu·Cu absorber-backscatterer pair, i.e., the summed Cu·Cu and Cu·C interactions could also be fitted (using k^3 -weighting) with only a Cu·Cu having a low coordination number. In the current contribution we will propose, based on EXAFS analysis, a structure for the pre-catalyst (i.e., without the substrate) formed from $[\text{Cu}_3(\text{SAr})_3]$ and MeMgI under reaction conditions.

2. Experimental

The EXAFS data on the Cu K-edge were measured at the SRS in Daresbury (beamline 8.1) using a Si (220) double crystal monochromator. The monochromator was detuned to 50% in order to remove the higher harmonics.

The data were analyzed using the XDAP program (Vaarkamp 1995). The spectra were fitted in R-space by minimizing the difference between the imaginary part and the magnitude of the Fourier Transform.

The preparation of the cuprates is described elsewhere (Knotter 1992; Janssen, 1995 and 1998). For the EXAFS measurements about 0.05 mmol $\text{Cu}_3(\text{SAr})_3$ was dissolved in 1.1 ml toluene. The spectra were recorded at room temperature.

3. Results and discussion

Figure 1 shows the k^3 -weighted Fourier Transforms of the $[\text{Cu}_3(\text{SAr})_3]$ complex mixed with different amounts of x MeMgI ($x=0,3,6$). Clearly the differences are significant between the different samples. The most significant change is seen in the signal at 1.9 Å. This signal decreases upon adding 3 equivalents of MeMgI. When more MeMgI is added (6 equivalents) a new

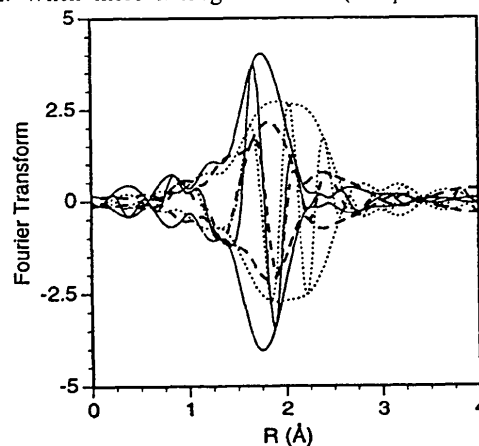


Figure 1 Fourier Transforms of $[\text{Cu}_3(\text{SAr})_3]$ (solid line), $[\text{Cu}_3(\text{SAr})_3] + 3\text{MeMgI}$ (--) and $[\text{Cu}_3(\text{SAr})_3] + 6\text{MeMgI}$ (· · ·); k^3 , $k=2.8\text{--}12\text{Å}^{-1}$

signal at longer distances is observed. The results of the fitting procedure of the different mixtures are given in Table 1.

Table 1 shows that after adding 3 equivalents of MeMgI to $[\text{Cu}_3(\text{SAr})_3]$ the Cu-N bond disappeared; moreover it was not necessary to include a long Cu·C interaction as was the case for $[\text{Cu}_3(\text{SAr})_3]$ (Janssen et al. 1998) to extract the Cu-Cu contribution. For the coordination parameters of $\text{Cu}_3(\text{SAr})_3 + x$ MeMgI we report a Cu·C (See table 1) contribution despite the fact that when a Cu·N was assumed an equally good fit was obtained. However, on the basis of earlier work on

$\text{Cu}_4(\text{SAr})_2(\text{Mes})_2$ (Lambert 1991; Knotter 1992) and the fact that MeMgI reacts with $\text{Cu}_3(\text{SAr})_3$ we speculate that a $\text{Cu}\cdots\text{C}$ rather than a $\text{Cu}\cdots\text{N}$ contribution is present. Moreover the proposed structure should be electrically neutral. Because Cu is positively charged (thus in total 4+) and both sulfur atoms are negatively charged it is more likely that two negatively charged carbon species (originating from the Grignard reagent) are involved rather than the neutral N species originating from the arenethiolate ligand. The large E_0 values reported in Table 1 might originate from the fact that theoretical references were used to fit the $\text{Cu}\cdots\text{C}$ data. The $\text{Cu}\cdots\text{C}$ bond length is typical for a methyl group bound to copper, note that it was not necessary to

Sample	Ab-Sc-pair	N	$\Delta\sigma^2$ (\AA^2)	R (\AA)	E_0 (eV)
$\text{Cu}_3(\text{SAr})_3$	Cu-N	0.8	0.011	2.08	0.13
	Cu-S	1.9	0.008	2.21	-0.91
	$\text{Cu}\cdots\text{Cu}$	1.7	0.023	2.86	-1.58
	$\text{Cu}\cdots\text{C}$	2.4	0.013	2.95	12.46
$\text{Cu}_3(\text{SAr})_3+3\text{MeMgI}$	Cu-C	1.2	0.018	1.93	7.10
	Cu-S	1.0	0.007	2.26	-6.67
	$\text{Cu}\cdots\text{Cu}$	2.2	0.023	2.78	6.11
$\text{Cu}_3(\text{SAr})_3+6\text{MeMgI}$	Cu-C	0.9	0.012	1.92	10.92
	Cu-S	1.0	0.004	2.22	-8.40
	$\text{Cu}\cdots\text{Mg}$	1.3	0.002	2.64	2.46

Table 1 Coordination parameters of $\text{Cu}_3(\text{SAr})_3+x\text{MeMgI}$; k^0 , R-space fit $R=0-3.5$, $k=2.9-12.5$. error margin in CN is about 10%

include multiple scattering paths in the fitting procedure. Based on these results we propose a preliminary structure for this aggregate as shown in Figure 2. This structure consists of four Cu nuclei which are connected by the two S atoms from the arenethiolate ligands and two carbon atoms form the methyl groups originating from the Grignard reagent. This structure is similar to the structure of $\text{Cu}_4(\text{SAr})_2(\text{Mes})_2$ which was published earlier (Lambert 1991; Knotter 1992). The problem with the proposed structure in Figure 2 is the long $\text{Cu}\cdots\text{Cu}$ bond for the copper atoms bridged by the methyl groups (2.78 \AA). It is known that this bond is typically 2.4 \AA (van Koten 1990). This was also

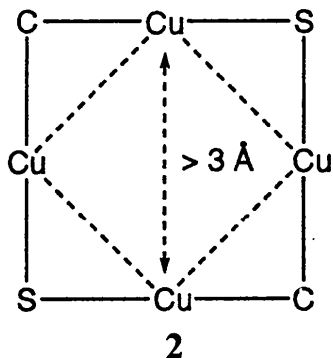


Figure 2 Proposed structure of the aggregate formed from $[\text{Cu}_3(\text{SAr})_3]^+ 3 \text{MeMgI}$ based on Cu-EXAFS

confirmed by an EXAFS study on the $[\text{Cu}_4(\text{SAr})_2(\text{Mes})_2]$ complex (not shown here). Therefore the proposed structure needs more refinement. Moreover the stoichiometry of the formation of the complex 2 is not satisfied, overall MgI_2 and $\text{MeMg}(\text{SAr})$ are left. It can be speculated that these species are coordinated to 2 via the nitrogen atom present in the arenethiolate ligands that form the bridges between the copper atom, which is not visible in the Cu-EXAFS (cf. the XRD structure of $[\text{Cu}_4(\text{Mes})_4(\text{Mg}(\text{SAr})_2)_2]$ Knotter 1992).

When 6 equivalents of MeMgI were added to $\text{Cu}_3(\text{SAr})_3$ it is clear from Table 1 that the structure of $[\text{Cu}_3(\text{SAr})_3]$ collapsed. No Cu-N and Cu-Cu contributions could be observed anymore, this was independent of the fact whether or not we included a Cu-C contribution at long distance (as for $[\text{Cu}_3(\text{SAr})_3]$). Therefore, we conclude that no Cu-Cu contributions are present. To obtain a good fit it was indispensable to include Cu-Mg, Cu-C and Cu-S contributions as shown in Table 1. Based on these data and our knowledge of the structure of similar complexes we proposed a structure for this complex which consists of a methyl(arenethiolato)copper magnesium unit in which either the carbon or the sulfur atom is proposed to be involved in bridging the copper and magnesium atoms. We believe this species is a hetero-cuprate complex $[\text{R}(\text{CuSAr})\text{Mg}(\text{I})]_n$. However, the value of n cannot be determined from EXAFS. We are currently studying whether the unit (n=1) is part of a larger aggregate comprising $\text{M}(\text{SAr})$ (M=Cu,Mg) units at long distances from Cu (cf. the XRD structure of $[\text{Cu}_8(\text{SAr}')_3\text{Br}_5]$ (Janssen 1996)

4. Conclusions

EXAFS gave information on the structure of cuprate species present in the working catalysts during Grignard reactions. When 3 equivalents of MeMgI were added to the $[\text{Cu}_3(\text{SAr})_3]$ the species formed is speculated to be an aggregate formed of 4 Cu nuclei with two sulfur atoms and 2 carbon atoms in bridging positions. When 6 equivalents of MeMgI were added the most likely structure is an aggregate with the structure $[\text{Cu}(\text{SAr})\text{RMg}(\text{I})]_n$ in which either the thiolate-S or the methyl-C atoms form a bridge between the Cu and Mg atoms.

References

- Janssen, M.D., Corsten, M.A., Spek, A.L., Grove, D.M., van Koten, G., *Organometallics*, (1996), 15, 2810-2820.
- Janssen, M.D., Mojet, B.L., Grove, D.M., van Koten, G., Koningsberger, D.C., *J.A.C.S.*, (1998), submitted.
- Janssen, M.D., PhD thesis, Utrecht University, 1995 chapter 6.
- van Klaveren, M., Lambert, F., Eijkelkamp, D.J.F.M., Grove, D.M. van Koten G., *Tetrahedron Letters*, (1994), 35, 6135-6138.
- Knotter, D.M., Grove, D.M., Smeets, W.J.J., Spek, A.L., van Koten, G., *J. Amer. Chem. Soc.*, (1992), 114, 3400-3410.
- Knotter, D.M., Van Maanen, H.L., Grove, D.M., Spek A.L., van Koten, G., *Inorg. Chem.*, (1991), 30, 3309-3317
- Van Koten, G., *J. Organometal. Chem.*, (1990), 400, 283-301.
- Lambert, F., Knotter, D.M., Janssen, M.D., van Klaveren, M., Boersma, J., van Koten, G., *Tetrahedron Asymm.*, (1991), 2, 1097-1100.
- Vaarkamp, M., Linders, J.C., Koningsberger, D.C., *Physica B* (1995), 208&209,159-160.
- van Zon, J.B., Koningsberger, D.C., van 't Blik, H.F.J., Sayers, D.E.J., *J. Chem. Phys.*, (1985), 82, 5742-5754.

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