The complex ion $[Fe(CN)_5NH_3]^{2-}$ lies in the mirror plane and has approximately C_{4v} symmetry if the three hydrogen atoms are not taken into consideration. The $Fe-C-N$ bonds are approximately linear, and the cyanide group *trans* to the ammonia molecule appears to be more firmly bonded than the rest of the ligands. There is no significant hydrogen bonding to the water molecules.

A projection of the unit cell of $Na_2[Fe(CN)_5NH_3].2H_2O$ along the a-axis is shown in Fig. 1 and the most important distances are listed in Table 2.
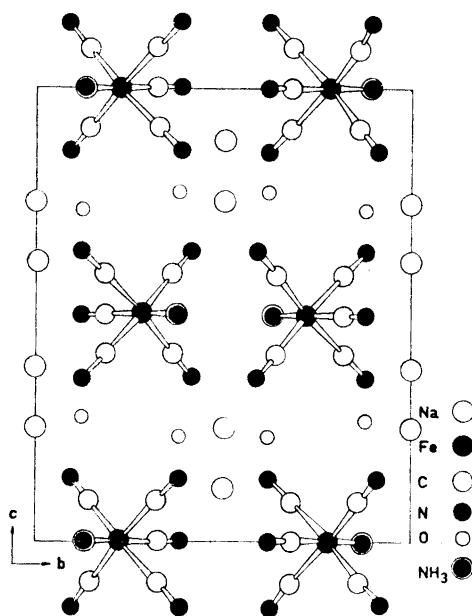
Fig. 1. Projection of the structure of $Na_2[Fe(CN)_5NH_3].2H_2O$ along the a-axis.

Table 2. Interatomic distances and angles within the complex ion $[Fe(CN)_5NH_3]^{2-}$.

Bond	$d(Å)$	Angle	Value($°$)
$Fe-C_1$	1.89	$Fe-C_1-N_1$	179.8
C_1-N_1	1.17	$Fe-C_2-N_2$	176.2
$Fe-C_2$	1.94	$Fe-C_3-N_3$	176.0
C_2-N_2	1.14		
$Fe-C_3$	1.94		
C_3-N_3	1.15		
$Fe-N_4$	2.00		

A complete report of the investigation will be published in due course.

1. Brauer, G. *Handbuch der präparativen anorganischen Chemie* 2 (1962) 1318.
2. Manoharan, P. T. and Hamilton, W. C. *Inorg. Chem.* 2 (1963) 1043.
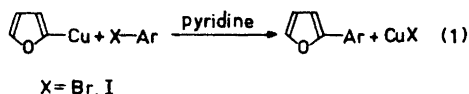
2-Arylfurans from 2-Furylcopper and Halogenoarenes

CHRISTINA ULLENIUS

*Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden**

2-Arylfurans can be prepared by the decarboxylative coupling between 2-furoic acid and iodoarenes in quinoline in the presence of copper(I) oxide, but the yields (so far) are low.[1] 2-Iodofuran itself is rather unstable [2] and has apparently not been used in Ullmann reactions.[3] The use of organocopper compounds often provides a useful method for the formation of carbon-carbon bonds. Recently the preparation of 2-arylthiophenes from 2-thienylcopper and halogenoarenes was described together with a preliminary result for 2-furylcopper.[4]

* Present address: Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-402 20 Göteborg, Sweden.

$$X = Br, I$$

2-Furylcopper has now been obtained from 2-furyllithium and copper(I) bromide. Its reactions with some halogenoarenes at moderate temperatures have been studied (reaction 1).

2-Arylfurans are formed in fairly good yields. Like 2-thienylcopper [4] and phenylcopper [5] 2-furylcopper is soluble only in solvents like pyridine or quinoline. Pyridine was used as a solvent for the reactions of 2-furylcopper with 4-iodoanisole, methyl 2-iodobenzoate, methyl 2-bromobenzoate, and 2-iodothiophene, respectively. The reactions were followed by gas chromatography. The experimental data are summarized in Table 1. The yields are based on the butyl-lithium used for the preparation of 2-furylcopper, and are largely determined by the yield of 2-furylcopper. In preparative work an excess of 2-furylcopper should be used to improve the yields of 2-arylfurans. The 2-furylcopper preparations contain some unreacted copper(I) bromide, lithium bromide and retai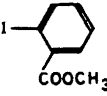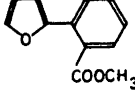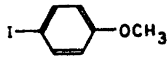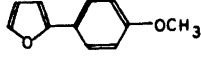n ether. For comparison of reaction rates the time for formation of 50 % of the final yield of the coupling product is given. For comparison the corresponding times for the reactions between 2-thienylcopper and halogenoarenes [4] are included.
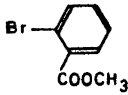
Some organocopper compounds have been found to undergo metal-halogen exchange (reaction 2), giving a new organocopper compound which can react further in coupling reactions.

$$Ar - Cu + I - Ar' \rightleftharpoons \overset{\text{pyridine}}{} Ar' - Cu + Ar - I \qquad (2)$$
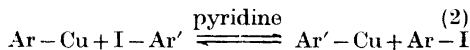
Phenylcopper gives three different biphenyls on reaction with iodoarenes.[6] 1-Methyl-2-pyrrolylcopper reacts with 2-iodothiophene to give 2-iodo-1-methylpyrrole and 2,2'-bithienyl.[7] However, 2-thienylcopper [4] and 3,4,5-trichloro-2-thienylcopper [8] do not undergo metal-halogen exchange (reaction 2) with iodobenzenes. In the reaction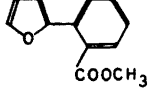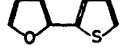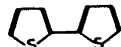s between 2-furylcopper and halogenobenzenes we found no evidence for metal-halogen exchange. However, 2-furylcopper and 2-iodothiophene give 2-iodofuran, 2-(2-furyl)-thiophene and 2,2'-bithienyl. No 2,2'-bifuryl was observed. The reaction was followed by gas chromatography-mass spectrometry.

Table 1. Reactions of 2-furylcopper with halogenoarenes in pyridine (0.4 M solutions). Yields are based on the butyl-lithium used to prepare the 2-furylcopper and were determined by weighing the isolated products.

Halogenoarene	Coupling product	Yield %	Reaction temperature °C	Time for 50 % reaction, min	Time for corresponding reaction with 2-thienyl-copper,[5] min
		39	52	6 − 8	11 − 12
		31	115	25 − 28	30 − 35
		21	70	35	5 − 10(110°)
		15	75	9	
		10		15	35 − 40

2-Thienylcopper thus seems to be more stable than phenylcopper, 1-methyl-2-pyrrolylcopper, and 2-furylcopper with respect to metal-halogen exchange (reaction 2), and is a convenient reagent for preparation of 2-arylthiophenes. Likewise, 2-furylcopper is more stable than phenylcopper or substituted phenylcopper and reacts selectively according to reaction 1 with substituted halogenobenzenes.

The influence of substituents in the iodoarenes on the rate of the coupling reaction is found to be the same for 2-furylcopper as has earlier been found for copper(I) acetylides,[9] phenylcopper,[6] and 2-thienylcopper.[4] Electron-attracting substituents increase the reaction rate compared to electron-donating substituents. Nucleophilic aromatic substitution has been used as a model for the attack of arylcopper compounds on iodoarenes.[10] The analogy is supported by the observation that 2-furylcopper and 2-thienylcopper form Meisenheimer complexes, σ-complexes, with 1,3,5-trinitrobenzene.[10]

Finally it can be concluded that 2-furylcopper and 2-thienylcopper have very similar properties. Their rates of reaction with halogenobenzenes are of the same magnitude. They are easily decomposed in air and have to be handled and stored under nitrogen.

Experimental. The experiments were performed analogous to those with 2-thienylcopper in Ref. 4 unless otherwise stated. The structures of known compounds were checked by NMR, IR or UV spectroscopy.

2-Furylcopper and 4-iodoanisole. 2-Furyl-lithium in 100 ml ether prepared from furan and butyl-lithium (25 mmol) at $-20°$ was slowly added to copper(I) bromide (25 mmol) in 50 ml ether at $0°$. The colour of the suspension changed from yellowish white to orange to brown. After stirring for 2 h a greenish yellow solid was filtered off under nitrogen and dried. The 2-furylcopper (2.89 g) was dissolved in pyridine (50 ml) giving a green solution. Naphthalene, as internal standard, and 4-iodoanisole (21 mmol) were added. The reaction flask was kept at $115°$ for 125 min. Samples were withdrawn and analysed by gas chromatography. The mixture was diluted with ether, copper(I) iodide-pyridine complex filtered off, and pyridine removed by extraction. The crude reaction product was chromatographed on silica gel giving naphthalene, 4-iodoanisole (10 mmol) and 2(4-methoxyphenyl)furan[1] (7.8 mmol), m.p. $53-54$ (methanol).

2-Furylcopper and 2-iodothiophene. 2-Furylcopper (2.61 g) was reacted in pyridine (50 ml) with 2-iodothiophene (20 mmol) at $75°$ for 90 min. The crude reaction products were chromatographed twice on silica gel giving 2-iodothiophene (3.2 mmol), 2,2'-bithienyl (2.0 mmol) m.p. $29-31°$, lit.[11] m.p. $32-33.5°$, a mixture (46:54) of 2,2'-bithienyl and 2(2-thienyl)furan (0.23 g), and 2(2-thienyl)furan (3.7 mmol) distilled at $118-122°/10$ mmHg. The UV spectrum agrees with literature data.[12] Mass spectrum of the 2(2-thienyl)furan was obtained after injection *via* the gas chromatograph; molecular ion $m/e = 150$ (100), fragments at $m/e = 122$ (29) and at $m/e = 121$ (70), corresponding to losses of CO and HCO, respectively.

A second experiment was run with 4-chloroanisole as internal standard at $75°$. The reaction was followed by gas chromatography-mass spectrometry. 2-Iodofuran was formed together with 2,2'-bithienyl and 2(2-thienyl)furan. The concentration of 2-iodofuran decreased after *ca.* 10 min. The yields of 2,2'-bithienyl and 2(2-thienyl)furan were 27 % and 16 %, respectively, based on 2-iodothiophene. 2-Iodofuran was too unstable to be isolated in the previous experiment.

2-Furylcopper and methyl 2-iodobenzoate. 2-Furylcopper (from 10 mmol butyl-lithium) was reacted at $52°$ for 75 min with methyl 2-iodobenzoate (10 mmol) in pyridine (25 ml). Isolated: methyl 2-iodobenzoate (5.7 mmol) and methyl 2-furylbenzoate (3.9 mmol), distilled to give 2.8 mmol, b.p. $129-133°/ca.$ 2 mmHg. The NMR spectrum showed absorptions for the furyl protons at $\tau_{H_3} = 3.26$, $\tau_{H_4} = 3.49$, $\tau_{H_5} = 2.40$, with the following coupling constants $J_{H_3-H_4} = 3.5$, $J_{H_4-H_5} = 1.8$, and $J_{H_3-H_5} = 0.8$ Hz.

2-Furylcopper and methyl 2-bromobenzoate. Butyl-lithium (20 mmol) was added to furan (40 mmol) in ether at $0°$. The ether solution (50 ml) of 2-furyl-lithium was refluxed for 20 min, and then slowly added to copper(I) bromide (20 mmol) in ether (50 ml) at $0°$. The colour of the suspension changed from yellowish white to orange. After stirring for 2 h at room temp. the light brown solid was allowed to settle and most of the ether decanted. Pyridine (40 ml) was added, the temperature raised to $70°$ and remaining ether distilled off. 2-Methoxynaphthalene, as internal standard, and methyl 2-bromobenzoate (20 mmol) in pyridine (10 ml) were added. The reaction was followed by gas chromatography during 172 min. Isolated methyl 2-furylbenzoate gave a mass spectrum with molecular ion at $m/e = 202$ (100), fragments at $m/e = 171$ (38), 159 (43), 143 (28), 131 (21), 115 (57), 103 (18), and

metastable peaks corresponding to the fragmentations $202 \rightarrow 174$, $187 \rightarrow 159$, $143 \rightarrow 131$, $115 \rightarrow 103$, and $131 \rightarrow 103$ due to successive losses of CO and C. The fragment at $m/e = 115$ seems to be typical for phenylthiophenes [7,13] and phenylfurans. Methyl 2-furylbenzoate was hydrolysed, giving 2-furylbenzoic acid in 87 % yield, m.p. ca. 90°, decomp. (Found: C 69.4; H 4.4. Calc. for $C_{11}H_8O_3$: C 70.2; H 4.3.) The mass spectrum of 2-furylbenzoic acid showed molecular ion at $m/e = 188$ (100) and fragments at $m/e = 160$ (52), 159 (46), 131 (64), 115 (60), 103 (33), 77 (41), metastable peaks corresponding to the fragmentations $188 \rightarrow 160$, $159 \rightarrow 131$ due to losses of CO.

Most of the arylfurans decompose slowly at room temperature.

1. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **22** (1968) 1998.
2. Nazarova, Z. N., Babaev, Yu. A. and Natal'ina, T. N. *Zh. Obshch. Khim.* **33** (1963) 1431.
3. Fanta, P. *Chem. Rev.* **64** (1964) 613.
4. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **24** (1970) 2379.
5. Costa, G., Camus, A., Marsich, N. and Gatti, L. *J. Organometal. Chem.* **8** (1967) 339.
6. Nilsson, M. and Wennerström, O. *Acta Chem. Scand.* **24** (1970) 482.
7. Gjøs, N. and Gronowitz, S. *Acta Chem. Scand.* **25** (1971) 2596.
8. Nilsson, M. and Ullenius, C. *Acta Chem. Scand.* **25** (1971) 2428.
9. Stephens, R. D. and Castro, C. E. *J. Org. Chem.* **28** (1963) 3313.
10. Nilsson, M., Ullenius, C. and Wennerström, O. *Tetrahedron Letters* **1971** 2713.
11. Sease, J. W. and Zechmeister, L. *J. Am. Chem. Soc.* **69** (1947) 270.
12. Wynberg, H., Sinnige, H. J. M. and Creemers, H. M. J. C. *J. Org. Chem.* **36** (1971) 1011.
13. Bowie, J. H., Cooks, R. G., Lawesson, S.-O. and Nolde, C. *J. Chem. Soc.* **B 1967** 616.

ESCA and Mössbauer Investigations of Some Porous Teflon-Active Carbon-Phthalocyanine Electrodes

RAGNAR LARSSON,[a] JIRI MRHA[b] and JAN BLOMQVIST[c]

[a] *Inorganic Chemistry I, Chemical Center, Lund, Sweden.* [b] *Heyrovsky Institute of Polarography, Prague, Czechoslovakia.* [c] *Institute of Physics, University of Stockholm, Stockholm, Sweden*

In a study [1] on the electrocatalytic effect of iron-phthalocyanine polymers in porous active carbon-teflon electrodes in acid medium for use in, e.g., metal-air batteries it was observed that the catalytic effect decreased with time.

As it is of great importance to understand the mechanism behind this decrease we have made some spectroscopic investigations including Mössbauer and ESCA [2] measurements. Four different samples were compared, composed and treated as follows.
A: NORIT FNX + 10 % Pc-Fe(II) 280°(A) (3 parts) and Teflon (1 part).
B: As in A, but kept in 2.25 M H_2SO_4 for a week.
C: As A but kept in 2.25 M H_2SO_4 in the presence of oxygen for one week.
D: As A but treated as C and also used as cathode with a 20 mA/cm² current density.

Table 1. Mössbauer data (in mm/s) for samples A—D.

| | I[a] | | II[a] | | I/II[b] |
	IS(SS)	ΔE_Q	IS(SS)	ΔE_Q	
A	1.25	3.01	0.21	0.62	0.27
B	1.24	2.98	0.18	0.60	0.28
C	1.24	2.91	0.14	0.64	0.33
D	1.24	2.99	0.16	0.60	0.30

IS(SS) = Isomer shift relative to stainless steel.
ΔE_Q = Quadrupole splitting.
[a] The Mössbauer spectra show two well-resolved doublets, I and II. I can be attributed to a high spin form, and II is most probably due to a low spin form.
[b] I/II = Ratio between the surfaces of the bands of I and II, respectively.