

SUBSTITUTED PHENYLCOPPER(I) COMPOUNDS

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SUMMARY

The reaction of CuBr with methyl- and methoxyphenyllithium derivatives and the isolation of the *o*-tolyl-, *m*-tolyl-, *p*-tolyl- and *o*-anisylcopper are described. Thermal decomposition, hydrolysis and some other reactions are examined. IR and X-ray powder spectra (including phenylcopper) are reported.

INTRODUCTION

Well characterized organometallic compounds, with a direct copper-carbon σ -bond, are very few in number in comparison with those of transition and post transition organometallic compounds¹.

Substituted phenylcopper(I) derivatives have been mentioned as products from addition of copper(I) halides to arylmetallic compounds²⁻⁵ or from addition of iodine-containing polyaromatic compounds to lithium dimethylcopper^{4,5}. They have also been obtained by decomposition of diazonium borofluorides in the presence of metallic copper⁶, but no pure samples were isolated.

In extension of our researches in this field^{7a-c}, we report the preparation and characterization of some aromatic copper(I) derivatives, which appear to be promising for further physico-chemical investigations.

Evidence for the formation of complexes with the aryllithium reagent and chelating agents is also presented.

We were unable to obtain the previously reported copper(II) derivatives^{8,9}.

RESULTS

We have studied the reaction of CuBr with *o*-, *m*-, *p*-tolyl and *o*-, *p*-anisyllithium.

In anhydrous diethyl ether, with a ratio Li/Cu ≤ 1 , deep coloured solutions were formed, from which *o*-, *m*-, *p*-tolyl and *o*-anisylcopper slowly precipitated or were obtained as specified in the experimental part. (We did not succeed in isolating pure samples of *p*-anisylcopper.) The isolated compounds were microcrystalline diamagnetic powders: almost white (*o*-tolyl-, *m*-tolyl-), yellow (*p*-tolyl-) and orange (*o*-anisylcopper). The IR spectra in the region 2000-200 cm^{-1} are shown in Fig. 1; powder spectra, including data for phenylcopper, are reported in Table 1.

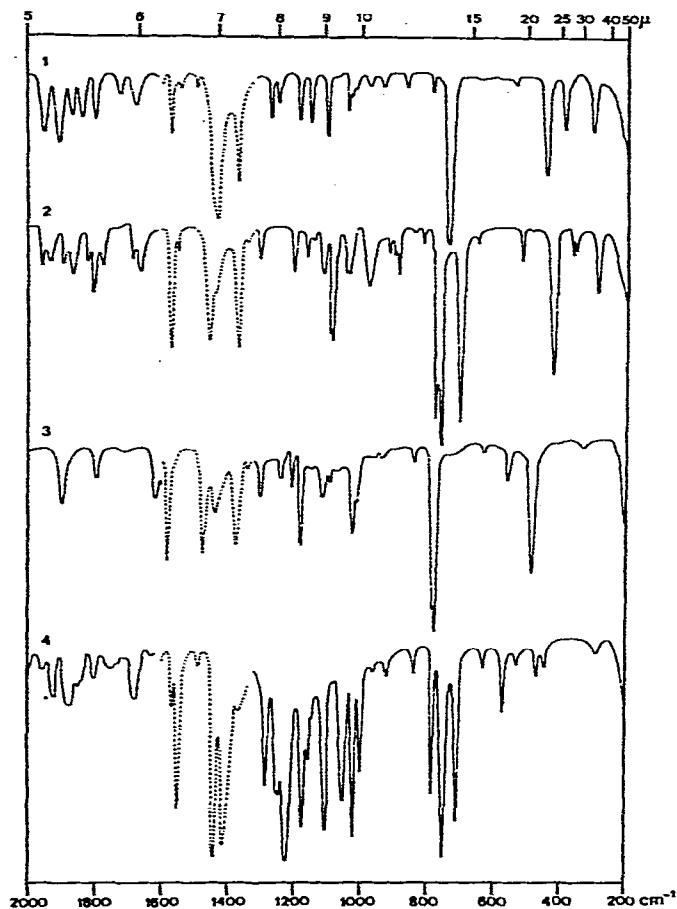


Fig. 1. IR spectra of phenylcopper derivatives; 2000–1600 cm^{-1} : nujol, higher concentration; 1600–1330 cm^{-1} : hostaffon; 1330–200 cm^{-1} : nujol. (1) *o*-Tolylcopper; (2) *m*-tolylcopper; (3) *p*-tolylcopper; (4) *o*-anisylcopper.

In most organic solvents deep yellow to red solutions were obtained, which apparently were stable only at low temperature. Molecular weights, in agreement with a low aggregation state (monomeric to dimeric species), were obtained at 25° in various solvents (toluene, THF, CCl_4) by extrapolating to zero time the values measured shortly after the preparation of the solutions. The mol. wts. appeared to increase with time, and a reaction with the solvent was indicated, *e.g.* in CCl_4 solutions by formation of Cl^- .

No measurements were possible for the very unstable *m*-tolylcopper solutions. *m*-Tolylcopper was also less stable to thermal decomposition than phenylcopper, but the *o*- and *p*-derivatives showed a stability similar to the latter. In the solid state, weak explosions, with almost quantitative yield of the corresponding diaryl derivative, were observed under vacuum with a heating rate of 5–10°/min at about 100° for *m*-tolyl- and between 110–120° for *o*- and *p*-tolylcopper. The explosion of *o*-anisylcopper was observed at about 150° and in addition to *o*, *o'*-bianisole some

TABLE I

POWDER SPECTRA, $\lambda = 1.5418 \text{ \AA}$ (Cu-K $_{\alpha}$)

Phenylcopper		<i>o</i> -tolylcopper		<i>m</i> -tolylcopper		<i>p</i> -tolylcopper		<i>o</i> -anisylcopper	
<i>d</i>	Int.	<i>d</i>	Int.	<i>d</i>	Int.	<i>d</i>	Int.	<i>d</i>	Int.
9.71	vs	9.83	s	10.16	vs	12.63	vs	10.91	vs
6.86	w	8.70	w	9.31	vw	10.40	s	10.02	vs
5.25	m	7.14	vs	8.08	vw	9.37	s	8.73	s
4.60	s	6.54	s	7.20	m	8.64	s	8.04	w
4.33	m	6.10	m	6.01	w	7.06	mw	7.26	w
4.15	w	5.20	w	5.79	s	6.56	w	6.51	ms
3.83	m	4.90	vw	5.19	m	6.22	w	5.67	w
3.55	w	4.60	w	5.01	vw	5.68	s	5.29	w
3.43	vw	4.31	vw	4.52	s	5.13	mw	4.92	m
3.15	vs	4.12	w	4.22	w	4.71	w	4.69	w
3.00	vw	3.89	w	3.83	vw	4.42	vw(b)	4.11	vw
2.64	w	3.62	m	3.53	w	4.04	vw	3.99	m
2.48	vw	3.29	m	3.43	m	3.95	mw	3.85	w
2.39	vw	3.22	vw(b)	3.33	w	3.83	w	3.73	w
2.34	vw	3.04	vw(b)	2.98	w	3.73	w	3.61	w
2.21	m	2.78	w	2.84	w	3.63	vw	3.46	w
2.16	vw	2.65	vw	2.76	w	3.33	vw	3.27	m
2.10	w	2.53	vw(b)	2.66	w	3.28	w	3.07	w
1.95	vw	2.34	w	2.57	vw	3.12	w	2.95	w
1.93	m	2.27	w	2.49	vw	2.93	w(b)	2.91	w
1.90	vw	2.19	vw	2.41	vw	2.58	vw(b)	2.83	m
1.86	w	2.10	vw	2.29	vw	2.42	vw(b)	2.73	m
1.80	w	2.04	vw	2.20	w(b)	2.25	vw(b)	2.57	w
1.62	vw	1.97	w	2.08	vw	2.19	vw	2.45	w
1.58	vw	1.91	w	1.99	w	2.14	w	2.36	w
1.54	w	1.84	w	1.89	vw	2.06	vw	2.30	w
1.49	vw			1.79	vw	2.03	vw	2.24	w
1.44	vw					2.00	vw	2.14	m
1.37	vw					1.91	vw(b)	2.06	w
						1.83	vw(b)	2.01	vw
								1.94	w
								1.86	vw
								1.80	vw
								1.76	vw

anisole was formed; the latter was probably formed by interaction with the small amount of solvent usually present.

On hydrolysis in most organic solvents all the above compounds yielded quantitatively the corresponding arenes. (*o*-Anisylcopper was more resistant to the hydrolysis than the tolyl derivatives.) The compounds are sensitive to oxygen: suspensions in ether or pentane gave the corresponding diaryls, phenols and small quantities of arenes, diaryl ethers and phenol derivatives when exposed to oxygen. Detonations sometimes occurred, mainly with *p*-tolylcopper, when solid samples of about 0.5 g were exposed to oxygen even at 0°. The autoxidations are being further studied.

Formation of complexes between aryllithium and arylcopper is indicated by the stoichiometry of the reaction of CuBr with aryllithium. Free aryllithium (Michler

colour test) could be detected in the reaction solutions, starting from a reactants ratio $\text{Li}/\text{Cu} > 2$.

A complex with a Li/Cu ratio = 1 precipitated with *m*-tolylcopper. It was a yellow powder, stable at room temperature but extremely reactive towards moisture and inflammable in air.

The other organocopper derivatives gave solutions from which only products with non-reproducible composition could be isolated by long standing, solvent removal or by dioxane addition.

Evidence has been obtained for complex formation on addition of bidentate or trisubstituted phosphines. These latter pale yellow complexes were stable at room temperature and similar to those obtained from phenylcopper^{7c}. With 2,2'-dipyridine and 1,10-phenanthroline deep red complexes were formed, which were less stable than the parent organocopper compounds. Two or more moles of organocopper were present per mole of ligand.

The organocopper compounds reacted with imidazole, forming the corresponding arene and Cu^{I} imidazolate. Analogous reactions were observed with benzimidazole or 1,2,4-triazole.

EXPERIMENTAL

General procedures, apparatus and reagent preparations have been previously described^{7d}.

IR spectra were recorded as nujol and hostafion mulls with a Perkin-Elmer 225 Spectrophotometer.

o-Tolylcopper

Cuprous bromide (1 g, 6.98 mmoles) was suspended in ethyl ether (30 ml) and allowed to react dropwise at 0° with 6.6 ml of a clear solution of *o*-tolyllithium (1 *M*). The colour changed to yellow and then to a deep orange brown, while the solid dissolved. A white microcrystalline powder was formed after a few min. The precipitate, washed several times with ether, was dried for 8 h in high vacuum and yielded about 50% of a pale beige powder. (Found: C, 54.07; H, 4.63; Cu, 41.00; [toluene]/[Cu], 0.99. $\text{C}_7\text{H}_7\text{Cu}$ calcd.: C, 54.35; H, 4.56; Cu, 41.08%; [toluene]/[Cu], 1.00.)

Reaction with HgBr₂. To a stirred suspension of *o*-tolylcopper (0.59 g, 3.82 mmoles) in THF (30 ml) a solution of HgBr_2 (1.60 g, 4.44 mmoles) in THF was added at 0°. The colour changed from yellow-orange to greenish. From the filtrate, by addition of water, *o*-tolylmercuric bromide was obtained as a white precipitate, m.p. 167–169° (1.252 g, 88.3%); recrystallized from acetone m.p. 170–172° (lit.¹⁰: 168°). (Found: C, 22.76; H, 1.85. $\text{C}_7\text{H}_7\text{HgBr}$ calcd.: C, 22.62; H, 1.90%.)

p-Tolylcopper

The preparation was the same as for *o*-tolylcopper. From brown black solutions a yellow microcrystalline powder with traces of solvent was isolated. The yield, based on *p*-tolyllithium, was more than 90%. (Found: C, 54.92; H, 4.87; Cu, 40.47; [toluene]/[Cu], 1.02. $\text{C}_7\text{H}_7\text{Cu}$ calcd.: C, 54.35; H, 4.56; Cu, 41.08%; [toluene]/[Cu], 1.00.)

Reaction with imidazole. To a stirred suspension of *p*-tolylcopper (0.55 g, 3.56

mmoles) in diglyme (15 ml) a solution of imidazole (0.3 g, 4.41 mmoles) in diglyme was added at 0°. Immediately a white powder was formed which after a few hours was filtered, washed several times with diglyme and ethyl ether and dried *in vacuo*. The white grayish solid was insoluble in most organic solvents. (Found: Cu, 28.19; H, 2.27; Cu, 47.78; N, 21.49. $\text{CuC}_3\text{H}_3\text{N}_2$ calcd.: C, 27.58; H, 2.31; Cu, 48.65; N, 21.47%.)

m-Tolylcopper

The preparation was the same as for *o*-tolylcopper, but stoichiometric amounts of CuBr and *m*-tolyllithium were allowed to react. After $\frac{1}{2}$ h from the deep red-brown solutions a white powder usually precipitated, while the colour changed to a deep green. Sometimes the change of colour was noticed but it was impossible to bring about the precipitation of the compound.

The isolated *m*-tolylcopper was a pale beige, microcrystalline powder with traces of solvent. Yield about 60–70%. (Found: C, 54.32; H, 4.69; Cu, 40.41; [toluene]/[Cu], 1.02. $\text{C}_7\text{H}_7\text{Cu}$ calcd.: C, 54.35; H, 4.56; Cu, 41.08%; [toluene]/[Cu], 1.00.)

Complex m-tolylcopper-m-tolyllithium. Cuprous bromide (1 g, 6.98 mmoles) was suspended in ethyl ether (30 ml) and treated dropwise at 0° with 14 ml of a clear solution of *m*-tolyllithium (1 M) under stirring. Michler test negative. From the deep green solution a white yellow crystalline precipitate was formed after a few min. It was washed several times with ether and dried *in vacuo* at room temperature. (Found: Cu, 25.30; [Li]/[Cu], 0.95; [toluene]/[Cu], 1.97. $\text{C}_{14}\text{H}_{14}\text{CuLi}$ calcd.: Cu, 25.14%; [Li]/[Cu], 1.00; [toluene]/[Cu], 2.00.)

Owing to the instantaneous decomposition in air it was impossible to obtain satisfactory analysis for C and H.

o-Anisylcopper

The reaction was the same as for *o*-tolylcopper. The brown solution was evaporated to dryness, the residue was extracted with toluene and filtered through a bed of dry Al_2O_3 . The orange solution, reduced to a small volume by evaporation, separated small orange crystals after cooling. They were filtered and washed three times in the cold with a few ml of toluene. Under high vacuum the crystals changed in a microcrystalline powder, but retained in part the solvent. Yield about 20%, but very dependent on the experimental conditions. (Found: C, 51.76; H, 4.33; Cu, 36.19. $\text{C}_7\text{H}_7\text{CuO} + 4\%$ toluene, calcd.: C, 51.65; H, 4.32; Cu, 35.74%.)

On the same sample by GLC, after hydrolysis, a ratio [anisole]/[Cu] = 1.03 and 5% of toluene were found.

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