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^{1}H NMR SPECTRA OF ARYLCOPPER(I) COMPOUNDS

A. BAICI, A. CAMUS AND G. PELLIZER
Institute of Chemistry and CNR Center of Coordination and Organometallic Compounds, University of Trieste, 34127 Trieste (Italy)

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SUMMARY

The ^{1}H NMR spectra of the arylcopper(I) compounds *o*-, *m*-, *p*-tolyl-, *o*-anisyl-, (2,4-dimethylphenyl)copper are described. The resonance peaks of the aromatic protons and the protons of methyl groups *ortho* to the metal atom are shifted downfield with respect to those of the free arenes, while those from *meta* and *para* positions are slightly shifted upfield. The spectrum of *o*-anisyl copper, shows anomalous and much larger effects, and possible explanations of this are advanced. Magnetic anisotropy centered between carbon and copper is suggested to be the main factor influencing the proton shielding constants. The temperature dependence of some spectra, indicates that there is hindrance to rotation for methyls *ortho* to copper.

INTRODUCTION

While use of copper organometallic compounds in organic preparative chemistry is increasing rapidly*, there is little information available about their physicochemical characteristics, mainly because the stability and solubility of the compounds are generally low.

We recently prepared and isolated some copper aryls[2], and now describe the proton resonance spectra of the following compounds: *o*-, *m*-, *p*-tolyl-, *o*-anisyl-, 2,4-dimethylphenylcopper [mesityl- and (2,6-dimethoxyphenyl)copper compounds are not suitable for NMR study, because of insufficient solubility].

To our knowledge the only previous ^{1}H NMR study of copper organometallic compounds involved cyclopentadienyl(triethylphosphine)copper(I)[3]. However, several NMR studies of metal aryls have been described[4-7] and have given qualitative information about the important question of the ionic character of metal–carbon bonds in these compounds.

RESULTS AND DISCUSSION

The NMR spectra are presented in Fig. 1 and proton resonances, for which assignment could be clearly made by the first order approximation, are listed in Table

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* See for example ref. 1.

TABLE 1

τ VALUES OF ARYLCOPPER(I) COMPOUNDS

Compound	H_2	H_3	H_5	H_6	CH_3	
o-tolylcopper				2.1	7.2	
m-tolylcopper					7.75	
p-tolylcopper	2.1	3.0	3.0	2.1	7.75	
o-anisylcopper		3.85		1.4	7.75	
2,4-dimethylphenylcopper				2.15	7.3	($2-CH_3$)
					7.8	($4-CH_3$)

1. Integrations are not shown in Fig. 1, but are in agreement with our assignments. The proton peaks are broad, but that this was not due to bad instrumental resolution was shown by the sharpness of the internal standard TMS signal.

As the copper compounds react rapidly with the solvent ($CDCl_3$) at room temperature, the spectra were normally recorded at $-20°$, under which conditions no appreciable reaction occurs during several hours. However free arene peaks are always present, because of partial hydrolysis of the compounds, caused by solvent moisture. We did not try to obtain samples free from arenes but instead used their peaks as references. The presence of toluene in spectra (d) and (e) is due to the difficulty in completely removing the solvent of crystallization from the derivatives.

In all the spectra there are aromatic proton resonances which are strongly shifted to low fields with respect to those of the corresponding unsubstituted arenes. Integration shows that the number of proton resonating at low field corresponds to the number of hydrogens *ortho* to copper. On this basis and by analogy with the other aryl metal compounds[4-7], we assigned these resonances to proton(s) *ortho* to metal atom. The other aromatic protons are shifted upfield, but their resonances are much closer to those of the parent compounds. The methyl group resonance shows the same dependence on its position in the ring with respect to the copper (see Table 1).

Under our experimental conditions it is unlikely that solvent or concentration effects alter the main features of the spectra, and the most important factors should arise from intramolecular effects. If we assume the ring current variation to be negligible[4], it is unlikely that the electronic transmission from copper is the main factor responsible of the observed shifts. Moreover the electric field generated by the Cu–C dipole is unlikely to give such strong shifts[8] and should in any case shift the *ortho* and *meta* proton resonances in the same direction. Thus the only factor which can explain directly the observed results is magnetic anisotropy.

This effect can be attributed to the Van Vleck paramagnetic term arising from mixing of the bonding orbital σ(M–C) with the low lying excited orbital π^*, in the presence of magnetic field[9]. Fraenkel *et al.*[4,5] found that the anisotropy, as measured from *ortho* proton chemical shifts, increased with increasing the paramagnetic term, this being inversely proportional to the $\sigma(C-M)\rightarrow\pi^*$ transition energy determined from the UV spectra, and that it could be an indication of the ionic character of the metal–carbon bond (the more ionic the bond, the lower being the transition energy and the higher the paramagnetic term).

The electronic spectra of our compounds[10] have patterns very similar to those of lithium and magnesium aryls. The $\sigma(Cu-C)\rightarrow\pi^*$ transition is shifted even to lower

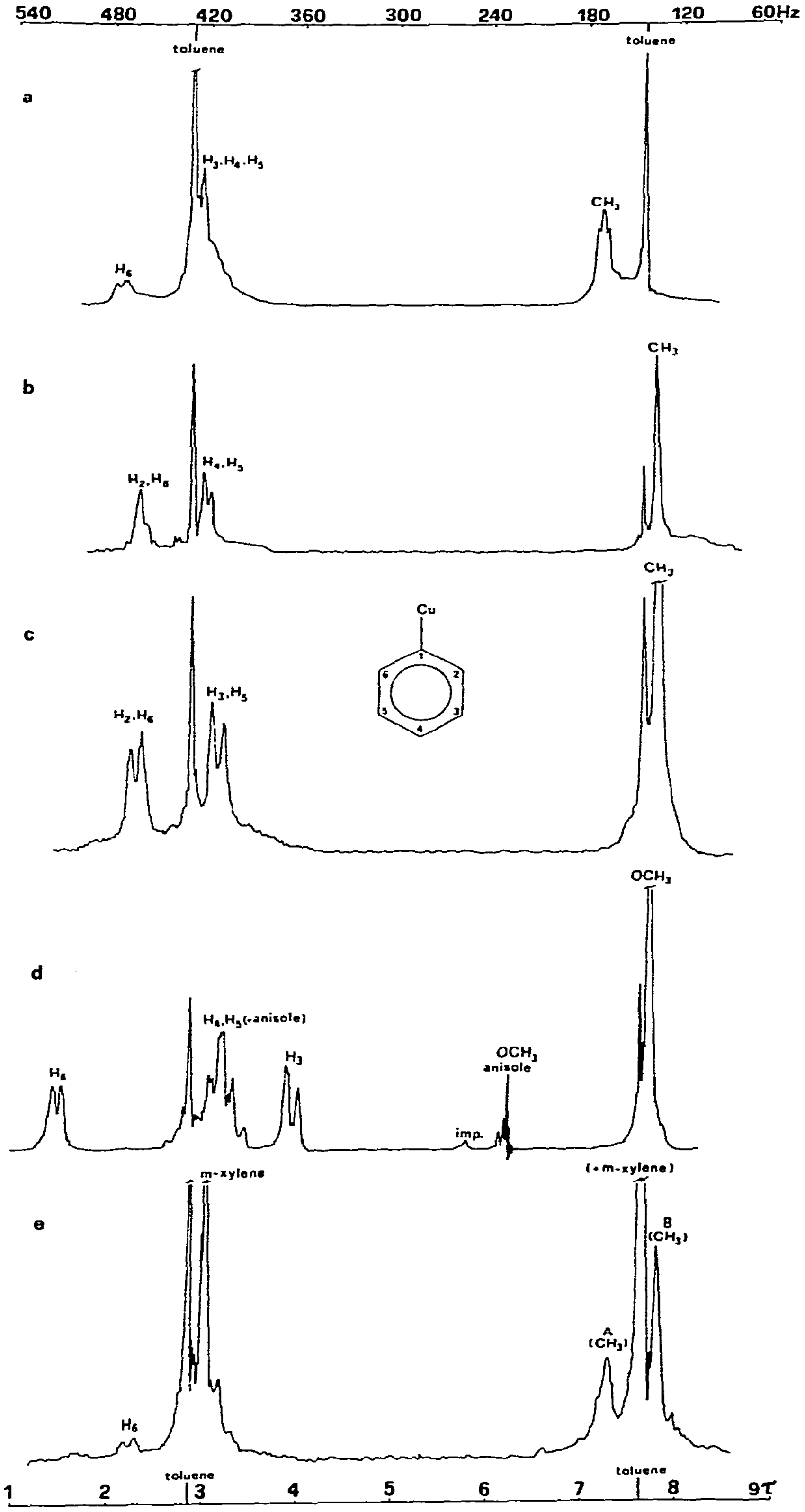

Fig. 1. ^{1}H NMR spectra of arylcopper(I) compounds in $CDCl_3$ at $-20°$; (a) *o*-tolylcopper; (b) *m*-tolylcopper; (c) *p*-tolylcopper; (d) *o*-anisylcopper; (e) (2,4-dimethylphenyl)copper, A = 2-methyl, B = 4-methyl.

frequencies, so that the paramagnetic term associated with the copper–carbon bond should be even larger. We have to take in account also, however, the possibility of bonding between the copper d electrons and the aromatic π system. Moreover the paramagnetic term associated with d electron cloud deviation from spherical symmetry under the electric field may be not negligible and the same may be true for the magnetic anisotropy of a purely covalent copper–carbon bond. Thus for our molecules we prefer a McConnell model[11], where the anisotropy center is at some point between carbon and copper.

Assuming that in *p*-tolylcopper the variation of the methyl proton chemical shift from toluene is due purely to the anisotropy effect, the anisotropy value was calculated as a function of the position of its center. With the assumption that even the proton *meta* to copper feels only the anisotropy effect, the position of the anisotropy center (*i.e.* the point for which the same value of anisotropy gives the experimentally observed shifts of methyl in *para* and of proton in *meta*) was located 0.8 Å from C_1 (see Fig. 2).

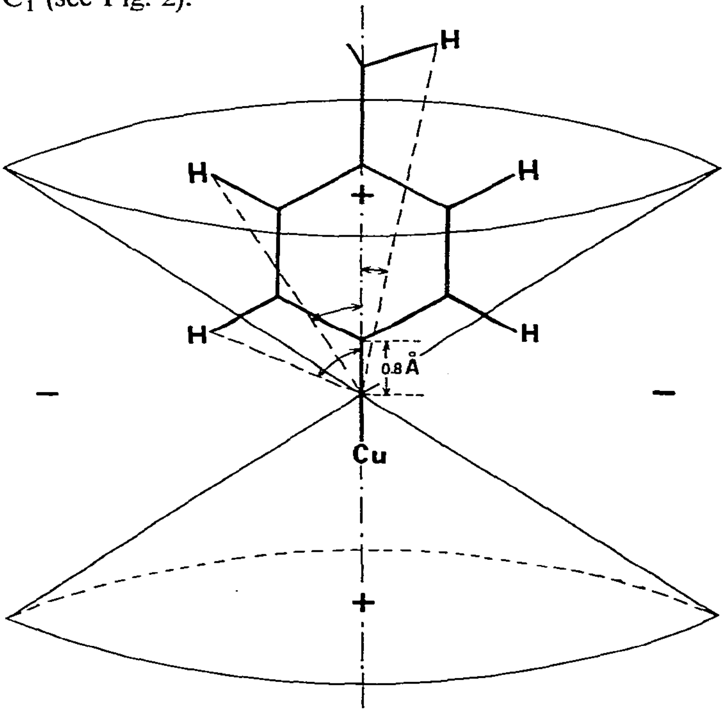

Fig. 2. Shielding cone produced by anisotropy for an axial tensor localized at 0.8 Å from carbon.

By these values the McConnell approximation gives a $\Delta\sigma$ for a proton *ortho* to copper of -0.60 ppm, which is in surprisingly good agreement with the experimental value (-0.65 ppm), when we consider that the point dipole treatment is inaccurate for position so near to copper–carbon bond and that our assumptions are just rough approximations. As a matter of fact, in the interpretation of the aryllithium and -magnesium spectra, the variation of the electron density on the *para* carbon was attributed only to inductive effects, and considered negligible, while in our compounds resonance effects can also be operating. Nevertheless it seems likely that even here the ring carbon electron density variation affects the *para* methyl proton resonances only to a minor extent.

We did not attempt anisotropy calculations for the other molecules, because it was not possible to get enough accurate values of chemical shifts for all the positions directly from spectra and also because the anisotropy effect may be significantly altered by different molecular symmetry. However the main features of the spectral patterns are in agreement with our interpretation.

We should point out that the *o*-anisylcopper spectrum differs markedly from those of the tolyl and xylyl compounds. The methoxyl proton resonance is strongly shifted to high field relatively to anisole (+1.55 ppm) *i.e.* by an amount which is an order of magnitude higher than is found in conventionally *ortho* substituted anisoles[12]. Moreover there is one aromatic proton resonance at low field (~1.3 ppm lower than in benzene), which must be due to the proton 3 or 6 and which was tentatively attributed to the proton *ortho* to copper by analogy with previous spectra, the τ 3.85 ppm peak being so assigned to proton 3.

Though it is known that NMR interpretation of *ortho* disubstituted benzenes is generally complex[13], in our spectrum the chemical shift variations are exceptionally strong. A reasonable interpretation of this spectrum can be obtained assuming a variation of the magnitude, axis, and position of the magnetic susceptibility tensor, localized in the copper–carbon region. This variation can be due to the closeness in space of the copper atom and the methoxyl group, so that copper feels a rather strong electric field from oxygen, which can further distort the *d* electron cloud and alter the paramagnetic term.

All NMR spectra were examined at variable temperature. A significant temperature dependence was found only for methyl protons *ortho* to copper, *i.e.* in *o*-tolyl and (2,4-dimethylphenyl)copper (Fig. 3). Decreasing temperature broadened

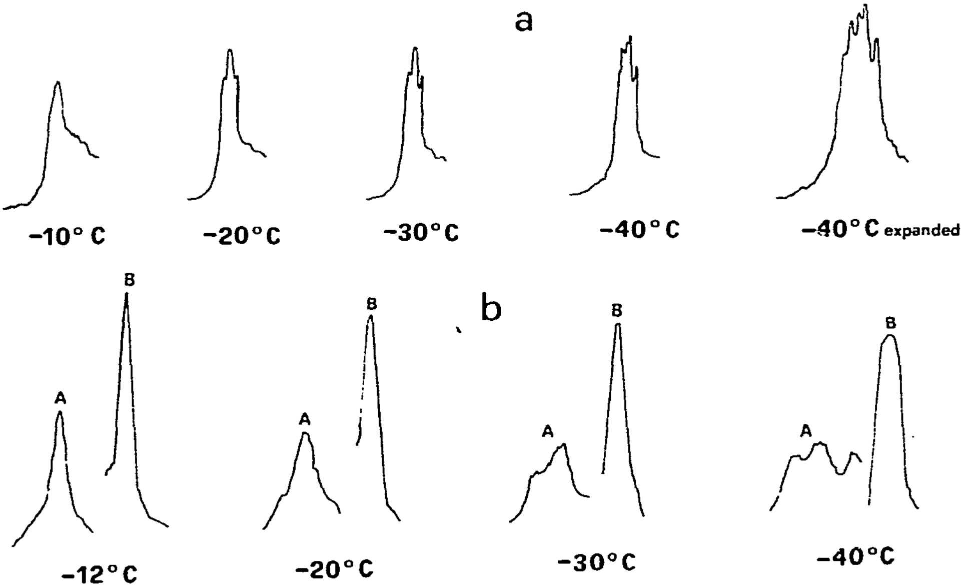

Fig. 3. Temperature dependence of ^{1}H NMR spectra of *o*-methyl substituted arylcopper(I) (a) *o*-tolylcopper; (b) (2,4-dimethylphenyl)copper, A = 2-methyl, B = 4-methyl.

the methyl peak and splitting became appreciable. The effect is especially significant with the second compound, where the difference between the methyls *ortho* and *para* to copper is evident. (The lower field peak is attributed to the methyl *ortho* to copper by analogy with *o*-tolylcopper). The temperature dependence can be explained in terms of hindrance to rotation of the methyl groups by the large copper atom.

CONCLUSIONS

The main factor in ^{1}H NMR spectra of our arylcopper compounds seems to be the magnetic anisotropy, which is due to a strong paramagnetic term and is localized in the carbon–copper region. Other effects, such as the electronic transmission and the parallel electric field effect due to the copper–carbon bond are probably present, but completely masked by the former.

Though the experimental conditions are different and do not permit a direct comparison of the results, UV spectra and chemical shifts of our compounds are very similar to those of lithium derivatives[5,7]. Thus a larger amount of ionic character must be associated with the copper–carbon bond, according to Fraenkel and Ladd, although their correlation between *ortho* proton chemical shift and ionicity of metal–carbon bond is not wholly applicable in our case. The assumptions under which this correlation is valid, *viz.* (*i*) *ortho* protons chemical shift depending mainly on the anisotropy magnitude, (*ii*) anisotropy localized on negatively charged carbon, (*iii*) anisotropy increasing with increasing the paramagnetic term, and (*iv*) $\sigma \rightarrow \pi^*$ energy difference determined only by the charge donated by the metal via σ, are suited for non transition metal aryls. In the case of copper the metal atom may be itself a center of anisotropy and the $\sigma \rightarrow \pi^*$ energy difference is influenced by π bonding between d orbitals and aryl π orbitals, which will affect also the center and the shape of the paramagnetic ellipsoid. So, while our results probably indicate a good amount of ionic character in the copper–carbon bond, we cannot use them as a measure of relative ionicity with respect to the other metal–carbon bonds.

In the interpretation of NMR spectra we have assumed that ring current variations are negligible. However if we take 0.3 ppm as a reasonable maximum variation in the aromatic protons chemical shift due to this effect, the conclusions are not considerably changed. A decrease in ring current means that all the aromatic protons are deshielded by the other effects with respect to the parent organic compounds, a result not easily interpretable; an increase in ring current is still in agreement with our simple explanation of the spectra, if it is assumed that electronic effects are important as well as magnetic anisotropy.

EXPERIMENTAL

NMR spectra (internal standard TMS) were recorded at 60 MHz, with a JEOL JNM-C-60 HL spectrometer. Chemical shift values were read directly from calibrated paper and the instrument reproducibility tested each time by recording the spectrum of ethylbenzene and measuring the aromatic proton peak distance from TMS. The accuracy of chemical shift measures is better than ±0.03 ppm. The temperature was accurate to ±2°C.

The organocopper compounds were prepared as previously described[2]. Except for *o*-anisylcopper, the compounds are highly air and temperature sensitive and sparingly soluble in organic solvents. In chlorinated hydrocarbons they show however a moderate solubility, but there is a rapid reaction with the solvent at temperatures of 0° or higher, so samples for the measurements were prepared, under nitrogen, at temperatures below −20°. $CDCl_3$ of 99.5% isotopic purity was used as solvent.

The properties of the compounds prevent the preparation of solutions of prefixed concentration. We usually used saturated filtered samples, the concentration of which were low enough for us to neglect interactions between solute molecules (the most soluble derivative, *o*-anisylcopper, gives about a 0.3 *M* solution at −20°).

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