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ARYLCOPPER–MAGNESIUM COMPOUNDS

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SUMMARY

The compounds $Cu_4Mg(phenyl)_6 \cdot Et_2O$, $Cu_4Mg(p\text{-tolyl})_6 \cdot Et_2O$, and $Cu_4Mg(p\text{-tolyl})_6 \cdot x$ THF (x possibly 5) have been prepared by reaction of copper(I) bromide or copper(II) bromide with the bis(aryl)magnesium in ether or THF. These compounds are quite sensitive to air, especially oxygen, but when such contamination is avoided they are remarkably stable. Molecular weight measurements and solubility properties are consistent with a discrete metal cluster unit with pendant aryl groups. Proton magnetic resonance spectra suggest the presence of at least two, and probably more, aryl group environments on the metal cluster unit. Phenyl group exchange between $Cu_4Mg(phenyl)_6 \cdot Et_2O$ and diphenylmagnesium in ether is also observed.

INTRODUCTION

Phenylcopper is insoluble in all solvents with which it does not react and is often regarded as a coordination polymer[1]. Since it is also only moderately stable and rather difficult to manipulate[2], there is essentially no information available concerning its structure. Phenylcopper can be solubilized in tetrahydrofuran (THF), toluene, benzene, or diethyl ether to give yellow products by complex formation with triphenylphosphine[1]. The solubilization is presumably due to triphenylphosphine reducing the polymer to lower aggregates by competition with phenyl groups as ligands[1].

Substituted phenylcopper(I) compounds, *i.e.* *o*-, *m*- *p*-tolyl and *o*-anisyl, have recently been prepared from the corresponding organolithium compounds and CuBr[3]. The compounds were reported as being soluble in organic solvents giving deep yellow to red solutions which were stable only at low temperature. Molecular weight measurements in toluene, THF and CCl_4 at 25° were in agreement with a low aggregation state of monomer to dimer, although the molecular weights appeared to increase with time.

In contrast to the hydrocarbon derivatives, Cairncross *et al.* have found fluorinated arylcoppers to exist as discrete stable tetramers and octamers having fairly good solubility properties[4].

Costa *et al.* found that pure phenylcopper could be obtained by treating phenyllithium with a slight excess of cuprous bromide suspended in ethyl ether, but when even a slight excess of phenyllithium was used the complex $(C_6H_5Cu)_4 \cdot C_6H_5Li \cdot 3.5\ Et_2O$ was obtained[1]. They also observed that a compound free from Grignard reagent could not be obtained from the reaction of phenylmagnesium bromide with cuprous bromide, and when the solvent used was THF, the complexes $(CuBr)_{2.5}(C_6H_5)_2Mg \cdot n$ THF and $(C_6H_5Cu)_2 \cdot (C_6H_5)_2Mg \cdot n$ THF were isolated using equimolar amounts or an excess of Grignard reagent respectively.

Parker *et al.* found that the reaction of cuprous bromide with ethyl- and propylmagnesium bromides in n-butyl ether leads to stable, deep red solutions only when an excess of Grignard reagent is present[5]. Dilution with n-butyl ether resulted in precipitation of all the colored material as an unstable solid, presumably an organocopper compound. Thus a fairly high concentration of Grignard reagent is necessary to stabilize the red solution, indicating complexing between the Grignard reagent and the copper compound.

In this paper we report the preparation and characterization of aryl coppermagnesium compounds of the type Cu_4MgAr_6, where Ar is phenyl or *p*-tolyl. We have found these compounds exhibit remarkable thermal and photolytic stability and reasonable solubility in aromatic solvents. These properties allow the recording of NMR spectra and molecular weight measurements, with the latter indicating that the formula given represents a discrete metal cluster unit. We believe the properties of these compounds, plus the fact that crystals can be obtained, makes them prime candidates for X-ray diffraction studies.

RESULTS AND DISCUSSION

Phenyl compounds

Anhydrous $CuBr_2$ and CuBr (and the corresponding chlorides) will completely dissolve in diethyl ether solutions of diphenylmagnesium when $Mg/Cu \geqslant 1$ to give green and yellow-green solutions, respectively. When $Mg/Cu < 3$, preferably about 2, a pale yellow solid (I) crystallizes from solution. Chemical analyses, NMR and UV-visible spectra leave no doubt that the same compound crystallizes from solution when either $CuBr_2$ or CuBr is used. Copper, magnesium, phenyl group and ether analyses (see experimental section) of (I) are in reasonable agreement with $Cu_4Mg(C_6H_5)_6 \cdot OEt_2$. (Found: C_6H_5/Cu, 1.31 ± 0.06; Cu/Mg, 3.93 ± 0.08; C_6H_5/Et_2O, 7.0 ± 0.5; Cu, 32.8 ± 0.9. $Cu_4Mg(C_6H_5)_6 \cdot OEt_2$ calcd.: C_6H_5/Cu, 1.50; Cu/Mg, 4.0; C_6H_5/Et_2O, 6.0; Cu, 31.2%. All tests for bromide were negative.) The experimental phenyl/copper ratio is slightly lower than expected for the formula given, although we believe this is due to some reaction with oxygen producing biphenyl during the analysis procedure. UV spectra and GLC analysis of the n-heptane distillate containing benzene show the presence of a small amount of biphenyl but it is not feasible to determine it quantitatively. We used the same analysis procedure on phenylcopper prepared by Costa's method and found the phenyl/copper ratio to be very close to 1.0. However, there is considerably less biphenyl produced in the analysis of phenylcopper than in the analysis of (I), apparently due to (I) being more sensitive to oxygen than phenylcopper.

There is another reason for believing the formula is as given above instead of $Cu_4Mg(C_6H_5)_5 \cdot Et_2O$ which is also fairly consistent with the analysis data. If the formula were the latter, a reduction would be required in the reaction of CuBr with diphenylmagnesium, and we certainly find no evidence for this. Phenyl group would appear to be the most likely reducing agent, in which case one would expect such

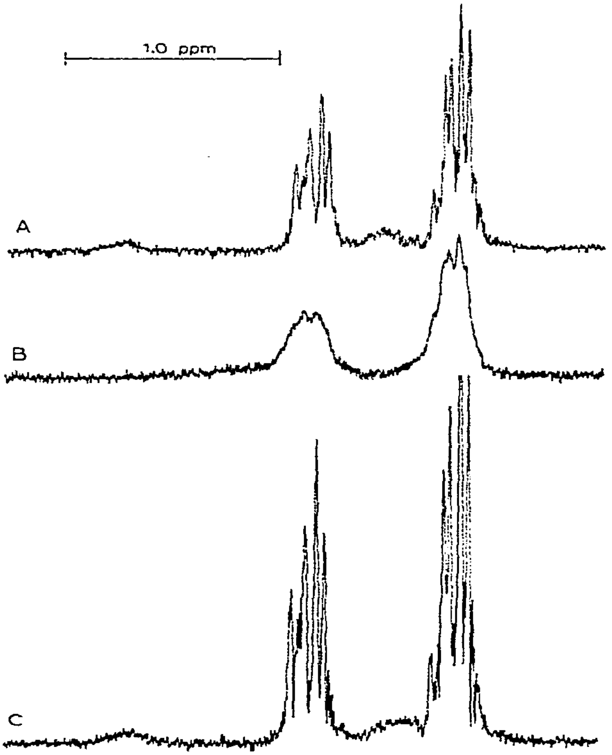

Fig. 1. 60 MHz proton spectra: (A) diphenylmagnesium–CuBr, Mg/Cu≈3, in diethyl ether at −10°; (B) same as (A) except at +32°; (C) Solid (I) dissolved in etheral diphenylmagnesium solution. See text for assignments of resonances.

products as biphenyl, benzene or perhaps even bromobenzene. However, it is clear from the NMR spectra shown in Fig. 1 that such products are not present. Therefore, we believe all of the copper atoms in the compound are in the +1 oxidation state.

The possibility of a Cu–H or Mg–H bond in the molecule was considered. This can be ruled out since vacuum line experiments designed to measure released hydrogen upon hydrolysis of (I) with 1 *M* hydrochloric acid showed that no hydrogen was evolved. Furthermore, a good source of hydride does not appear to be available in the reaction system.

Cryoscopy in benzene gives a molecular weight of 767 ± about 50, which is in reasonably good agreement with 814 expected for $Cu_4Mg(C_6H_5)_6 \cdot OEt_2$. Solubility limited us to working with molalities on the order of 0.008 to 0.02.

Compound (I) is only slightly soluble in ether at room temperature; it is somewhat more soluble in benzene, particularly when the solid is finely divided. Freshly prepared solutions of (I) in either benzene or ether are pale yellow, but after standing at room temperature for several minutes they become green in appearance for reasons which are not understood at this time. The UV-visible spectra of (I) in benzene which have stood for several hours at room temperature show bands at 365 nm (strong) and about 610 nm (weak), while ether solutions treated similarly have absorption maxima at 365 nm (strong) and approximately 570 nm (weak). It is noteworthy that the 365 nm band, which appears to be particularly characteristic of (I), is insensitive to solvent.

Compound (I) exhibits much greater thermal and photolytic stability than phenylcopper. Solutions of (I) in either ether or benzene, or the solid itself, can stand at room temperature in indirect light for several days (in the absence of oxygen and water of course) with very little evidence of decomposition. In contrast, the decomposition of phenylcopper in similar conditions would be considerable, and likely complete, in the same periods of time. When heated, compound (I) decomposes without melting. The compound was placed in a sublimator and heated from room temperature to 130° over a period of about one hour. The solid turned bright green and only a few small crystals, which were identified by UV as being biphenyl, collected on the cold tip of the sublimator. The reason for the change in color is not clear; PMR spectra of the green solid and the original yellow solid appear identical.

Proton NMR spectra of the solutions which result when copper(I) bromide and copper(II) bromide are dissolved in etheral diphenylmagnesium are shown in Figs. 1 and 2, respectively. The spectra recorded at −10° show a broad resonance at low field and another broad resonance between the well-resolved phenylmagnesium

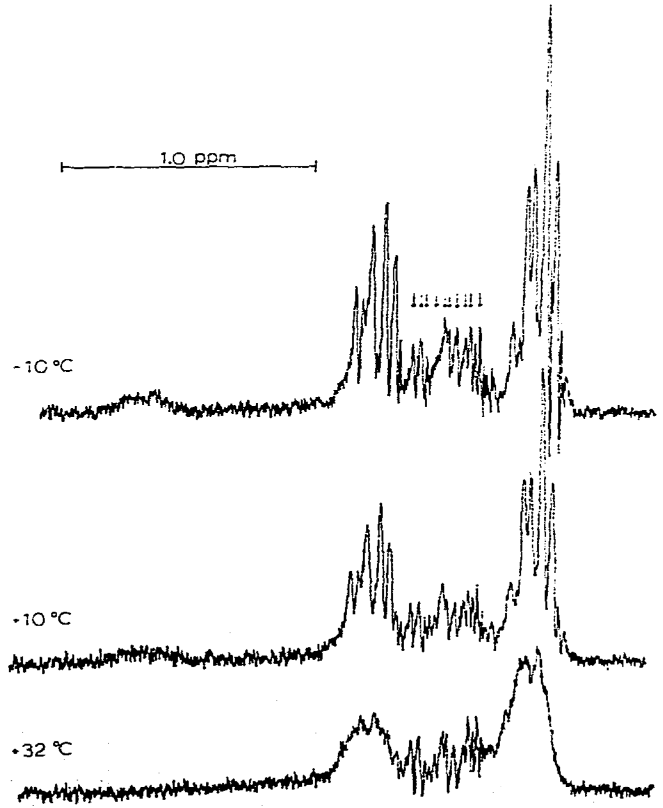

Fig. 2. 60 MHz spectra of diphenylmagnesium–copper(II) bromide in diethylether, Mg/Cu 3. The resonances at the positions indicated by the small arrows are due to biphenyl. See text for assignments of the other resonances.

multiplets. That these broad resonances are due to compound (I) is indicated by the fact that a spectrum of a solution obtained by dissolving solid (I) in etheral diphenylmagnesium (spectrum C of Fig. 1) is very similar to a spectrum of a CuBr–$(C_6H_5)_2Mg$ solution (spectrum A of Fig. 1). The separation between the well-resolved phenylmagnesium multiplets in Figs. 1 and 2 is intermediate between what is expected for pure diphenylmagnesium or for pure phenylmagnesium bromide, indicating the presence of both and consequent rapid phenyl group exchange between them. It is also apparent from the temperature dependence of the spectra in Figs. 1 and 2 that there is a relatively slow exchange of phenyl groups between compound (I) and diphenylmagnesium and/or phenylmagnesium bromide.

In Fig. 2, the sharp signals at the positions indicated by the small arrows are are due to biphenyl. Thus in the reaction of $CuBr_2$ with diphenylmagnesium, Cu^{II} is reduced to Cu^{I} by oxidation of phenyl groups. It is noteworthy, however, that no benzene is produced, a result which would appear to indicate that the mechanism of the biphenyl formation *does not* involve "free" phenyl radicals. One could speculate that this process occurs thru an intermediate associated phenylcopper bromide species in which there is pairwise loss of phenyl groups.

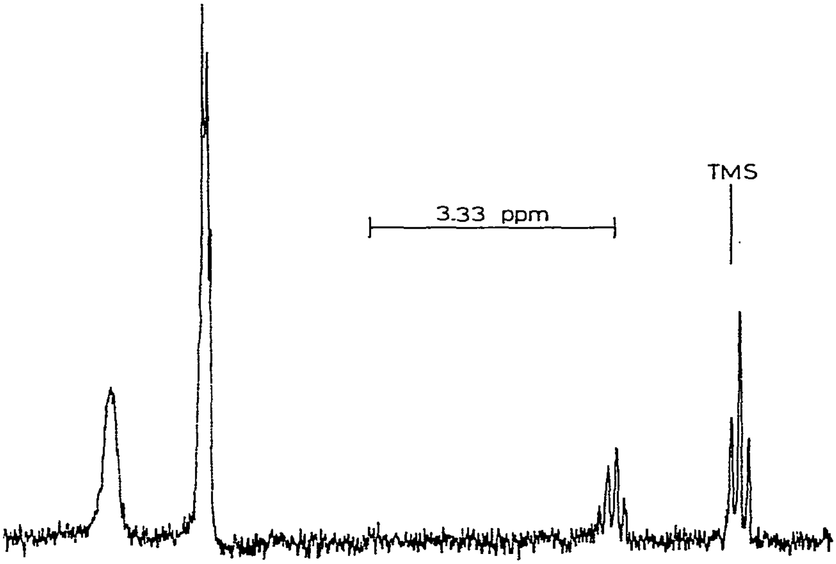

Fig. 3. 60 MHz NMR spectrum of $Cu_4Mg(C_6H_5)_6 \cdot OEt_2$ dissolved in C_6D_6.

A typical proton spectrum of compound (I) in C_6D_6 is shown in Fig. 3. The chemical shift separation between the relatively broad phenyl group resonances at low field is the same as the broad resonances in Fig. 1 and 2, providing further support for the assignment of the broad resonances in those spectra to compound (I). The fact that the phenyl group resonances are broadened, and the more environment sensitive *ortho* set (the lowest field peak*) more so than the *meta/para* set, indicates that the phenyl groups are in several different environments on the molecule. The

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* For discussions of the NMR spectra of phenyl–metal compounds, see ref. 6.

triplet and the quartet of the coordinated ether are shifted upfield considerably and the separation between them decreased, with respect to free ether. We believe this is due to an anisotropy effect from ring currents in the phenyl rings; on the average the ethyl groups being located near and above the planes of adjacent phenyl groups. When free ether is present in the C_6D_6, there is evidence of exchange between free and coordinated ether. In the absence of free ether comparison of triplet and quartet areas with phenyl group areas are in good agreement with a 6/1 phenyl/ether ratio as expected for one coordinated ether per molecule.

An indication of the rather good thermal stability of compound (I) in benzene is given by the fact that the spectrum shown in Fig. 3 did not change after the sample had been heated at 70° for about two and one-half hours. There was no evidence of biphenyl, an expected decomposition product.

To obtain NMR spectra of (I) in benzene it was necessary to make nearly saturated solutions at room temperature from finely divided solid and obtain the spectra as soon as possible after the samples were prepared. This was necessary because yellow crystals would form in the NMR tube after a period of time which varied from sample to sample but on the order of one-half to one hour. Analysis of these yellow crystals is consistent with the formula $Cu_4Mg(C_6H_5)_6 \cdot OEt_2 \cdot 2\,C_6H_6$. (Found: Cu, 25.7; Mg, 2.5; phenyl, 59.2; Et_2O, 7.2. $Cu_4Mg(C_6H_5)_6 \cdot OEt_2 \cdot 2\,C_6H_6$ calcd.: Cu, 26.2; Mg, 2.5; phenyl, 63.0; Et_2O, 7.6%.) To gain further proof of this formula, yellow crystals obtained from a solution of (I) in C_6D_6 were hydrolyzed and the resulting benzene removed from the reaction mixture by distillation. Mass spectral analysis of the distillate is in good agreement with a C_6H_6/C_6D_6 ratio of 3. Since the 365 nm band in the UV mentioned above remains unchanged as the solvent is changed from ether to benzene, we believe the rather insoluble yellow crystals represent clathrate formation rather than an acid-base adduct. The corresponding *p*-tolyl compounds discussed below do not exhibit this crystallization property.

p-Tolyl compounds

A *p*-tolyl derivative [compound (II)] can be prepared in a manner analogous to the phenyl compound (I) by simply substituting bis(*p*-tolyl)magnesium for diphenylmagnesium. Compound (II) is a yellow crystalline solid which is less soluble in ether, more soluble in benzene and appears to have greater thermal and photolytic stability than the phenyl derivative. A complete analysis of (II) was not performed; however, a molecular weight measurement by cryoscopy in benzene (0.040 molal) yielded a value of 940 which is in good agreement with 898 expected for $Cu_4Mg(p\text{-tolyl})_6 \cdot OEt_2$. The NMR spectra (Fig. 4) are also consistent with a *p*-tolyl/ether ratio of 6. The band at 365 nm in the UV spectrum of (I) is at 360 nm in (II).

Solutions of (II) in ether or benzene are pale yellow when first prepared and then turn green or yellow-green upon standing, although the color change occurs much more slowly with (II) than (I). Solid (II) also turns bright green when heated to 80° or more, but again NMR spectra of the original yellow solid and the green solid appear the same. A proton spectrum of (II) which had been heated from room temperature to a maximum of 115° over a period of about an hour is shown in Fig. 4A. The amount of decomposition was small as indicated by the small amount of *p,p'*-bitolyl present. A spectrum of the same sample after being heated at 70° for 25 min (glass sealed NMR tube) followed by exposure to an ultraviolet sun lamp for 2 hours

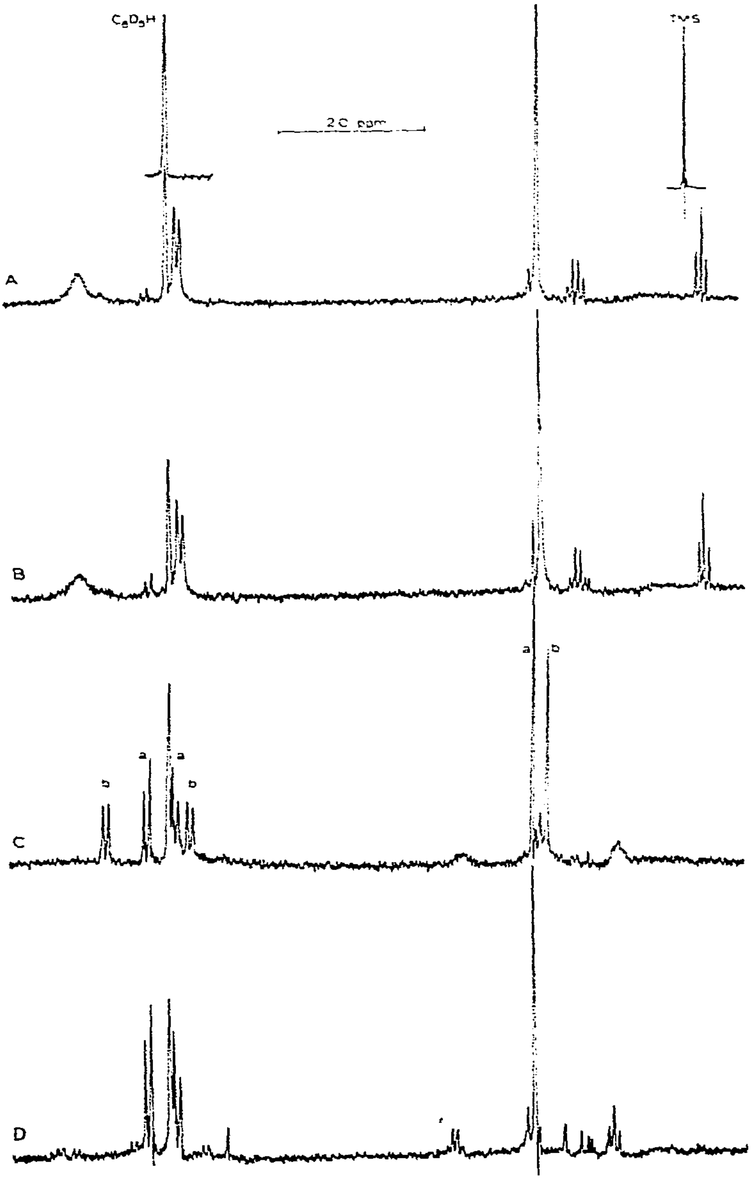

Fig. 4. 100 MHz PMR spectra of $Cu_4Mg(p\text{-tolyl})_6 \cdot OEt_2$ in C_6D_6. See text for detailed discussion of the spectra. The positions of C_6D_5H and TMS in deuterobenzene are given at the top of the figure.

(lamp about 2 feet from sample) is shown in Fig. 4B. Another indication of the stability of (II) is given by the fact solid (II) kept under an etheral bis(*p*-tolyl)magnesium solution remained unchanged for a period of one month.

Contamination from exposure to air is indicated by the yellow solid turning brown and a characteristic change in the NMR spectrum as shown in Fig. 4B, C, and D. Spectra A and B are typical spectra of uncontaminated samples of the *p*-tolyl compound. Spectrum C represents a sample which was purposely exposed to air for a very brief period by removing a polyethylene NMR tube cap. The pair of doublets and the singlet marked (a) in spectrum C are due to *p,p'*-bitolyl, whereas the pair of doublets and singlet marked by (b) are due to some intermediate "oxidized" organocopper–magnesium compound of unknown nature. Further exposure to air results in spectrum D, which is principally *p,p'*-bitolyl. As the decomposition proceeds, coordinated ether becomes free, and an exchange of free and coordinated ether result (see spectrum C).

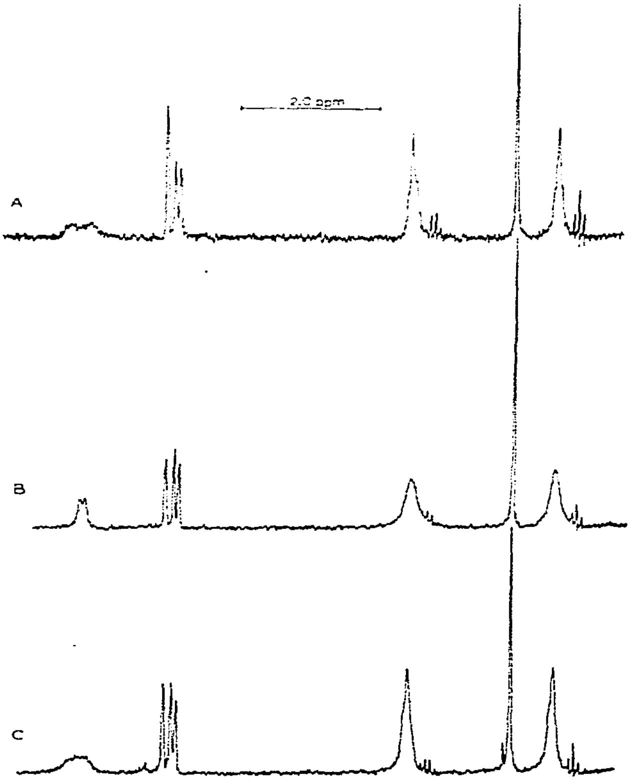

Fig. 5. 100 MHz PMR spectra of $Cu_4Mg(p\text{-tolyl})_6 \cdot x$ THF in C_6D_6. (A) recorded at +34° just after preparation; (B) recorded at +58° just after preparation; (C) recorded at +34° after sample had been heated to 80° for 18 h followed by exposure to an ultraviolet sunlamp for 72 h. See text. See experimental section for an explanation of the small amount of ether present.

A *p*-tolyl compound with coordinated THF [compound (III)] can be prepared by simply employing bis(*p*-tolyl)magnesium in THF instead of ether. Compound (III) is also soluble in aromatic solvents, although slightly less so than (II), and NMR spectra of (III) are shown in Fig. 5. It is evident that there are a greater number of coordinated solvent molecules per Cu_4Mg unit in (III) than in (II) or (I), *i.e.* about 5 compared to one, and the THF resonances are not shifted upfield as the ether resonances in (II) or (I). The broadness of the *ortho*-proton resonances at +34° (spectra A and C, Fig. 5) is apparently due to there being several *p*-tolyl environments on the molecule. As the temperature is raised to 58°, the rate of exchange among these enviroments increases and the resonances sharpen accordingly (spectrum B). While the *p*-tolyl group resonances sharpen as the temperature is increased, the THF resonances broaden and move upfield. (The movement upfield is not very evident in Fig. 5, but is obvious in spectra recorded with toluene solutions at 70° which are not shown.) Apparently there is an exchange between two THF environments at the higher temperatures, with the upfield environment population being rather small. It may be that the upfield THF environment is similar to the environment of the coordinated ether in (II) or (I).

We have found the thermal and photolytic stability of (III) to be extraordinary for a nonfluorinated organocopper compound. This is shown by comparing spectra A and B of Fig. 5. Spectrum A was recorded just after preparation of the sample (glass sealed tube), whereas spectrum C was recorded after the sample had been heated at 80° for 18 h and then exposed to an ultraviolet sun lamp for 72 h (21 and 51 h with the sample at a distance of about 18″ and 10″, respectively). It is obvious that very little decomposition occurred.

It must be emphasized that in order to observe the good stability mentioned above, it is very important that the sample be completely free of oxygen contamination, *i.e.* the solution should appear light yellow or yellow-green (contaminated solutions are deep brown or reddish-brown) and should not have NMR signals at positions (b) in spectrum C of Fig. 4. For example, if two glass sealed NMR samples, one containing slightly contaminated solution and the other pure solution, are allowed to stand at room temperature for a three-week period, it is likely the contaminated sample will be completely decomposed whereas there will be very little decomposition of the pure sample.

CONCLUSIONS

The molecular weight data and solubility properties of (I) and (II) are consistent with a discrete Cu_4Mg metal cluster with pendant aryl groups and one tightly held ether molecule [or possibly 5 THF molecules in the case of (III)]. The arrangement of the atoms in the cluster cannot be deduced from the information given herein, but it is clear from the NMR spectra that there are at least two, and probably more, aryl group environments around the Cu_4Mg cluster. The chemical shift separation between the *ortho* and the *meta* protons of the aryl group on the Cu_4Mg cluster are even greater than for phenyllithium[6], *p*-tolyllithium[6] or *p*-tolylcopper[7]. In nontransition metal derivatives, this separation has been found to increase as the ionicity of the metal–aryl bond increases. Although possible anisotropy contributions from the Cu atoms or the Cu_4Mg cluster make it impossible to use the *ortho*/*meta* separation as a measure of relative ionicity with respect to lithium derivatives[7], it still appears likely that the metal–aryl bonds in the Cu_4Mg cluster have considerable ionic character.

EXPERIMENTAL

Preparations of the solids and solutions of the compounds were carried out in an inert atmosphere glove box containing argon. Traces of oxygen and water were removed by continuous circulation of the atmosphere through molecular sieve and manganese(II) oxide columns as described previously[8].

Ether and THF were distilled from lithium aluminum hydride and stored in the glove box over sodium. These solvents were used as soon as possible after being distilled.

Diphenyl- and bis(*p*-tolyl)magnesium were prepared by reaction of magnesium with the corresponding organomercury compounds (Eastman Organic Chemicals) in either ether or THF. A touch of mercuric chloride was usually necessary to get the *p*-tolyl reaction started. Sometimes THF solutions of bis(*p*-tolyl)magnesium were prepared by evaporating ether solutions to dryness and redissolving in THF. These solutions, however, always contained some ether and this is how the small amount of ether got into the solutions whose spectra are shown in Fig. 5.

Anhydrous CuBr and $CuBr_2$ were obtained from Fisher Scientific Company (Certified Reagent). Some of the cuprous bromide was purified by dissolving the commercial material in hydrobromic acid in the presence of copper metal, precipitating by dilution with water, filtering under a nitrogen atmosphere and finally drying in a vacuum at elevated temperatures. However, it did not appear to matter which CuBr was used, purified or commercial grade.

Copper and magnesium analyses were obtained by standard EDTA titrations[9]. Phenyl group analyses were accomplished by hydrolysis of a suspension of (I) in n-heptane (spectroanalysis grade), followed by distillation and gas chromatographic analysis of the benzene (also ether) in the distillate. An SE-30 column in a Hewlett–Packard F & M 700 chromatograph equipped with a thermal conductivity detector was employed. Concentrations of benzene and ether were determined using the internal standard technique with chloroform as the standard. The standardization was checked each time an unknown sample was run.

A typical preparation of (I) is as follows. Ten ml of 0.5 *M* diphenylmagnesium in ether is measured into a 25 ml glass stoppered Erlenmeyer flask containing a magnetic stirring bar. Solid $CuBr_2$ (0.58 g) or CuBr (0.36 g) is slowly added while the solution is being stirred vigorously. After CuBr or $CuBr_2$ is added, stirring is continued until 15 or 20 min after (I) begins crystallizing from solution. Compound (I) is then filtered from the solution, washed about 5 times with small portions of ether, and dried for 15 to 30 min under vacuum at room temperature. The preparations of the *p*-tolyl ether(II) and *p*-tolyl THF(III) compounds were performed similarly.

The 60 MHz NMR spectra were recorded with a Varian A-60 spectrometer and the 100 MHz spectra with a Varian XL-100 spectrometer using internal deuterium lock (C_6D_6 or $C_6D_5CD_3$). UV-visible spectra were obtained with a Cary model 11 spectrophotometer and an AEI MS 9 spectrometer was employed for the mass spectral analyses.

The sunlamp was a General Electric 275 watt ultraviolet lamp.

The molecular weight data was obtained from a freezing point lowering apparatus consisting of a thermistor sensor in a Wheatstone bridge. The apparatus, with the cold well located inside the glove box, is very similar to that described by Brown *et al.*[10]. Molalities were determined graphically from a calibration graph of freezing point depression *vs.* molality for standard solutions of biphenyl or fluorene.

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