A NEW ROUTE TO OLEFIN COMPLEXES OF COPPER(I) COMPOUNDS

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SUMMARY

The preparation of olefin complexes of Cu^I compounds by the following reaction is described:

$$CuX_2 + \text{olefin} + (RO)_3P \rightarrow [\text{olefin}_x(CuX)_y]_n + (R'O)_3P=O$$

where $X = Cl, Br, ClO_4$ or BF_4, $R = $ alkyl or phenyl, $R' = H$, alkyl or aryl not necessarily the same as R, x, $y = 1$ or 2, $n = $ unknown.

The IR spectra of these complexes have been studied, and are discussed in relation to the structure of the compounds.

INTRODUCTION

The reactions of copper(I) halides with olefinic and acetylenic hydrocarbons have previously received considerable attention[1-8] and preparative routes based on the reduction of a cupric salt in the presence of an olefin either chemically[5-7] or electrochemically[9,10] have been described.

We now describe a novel preparation of olefin complexes of copper(I) compounds which consists of reducing a cupric salt with an alkyl or aryl phosphite in the presence of the desired olefin.

The use of organic phosphites as reducing agents in organic chemistry has been known for some time[11]. The only well-defined examples of their reducing power in inorganic chemistry has been in the preparation of complexes such as $M^0[(RO)_3P]_4$ $(M = Ni$ or $Co)^{12,13}$, $[(RO)_3P]_{3/4}CoCl^{14}$ and more recently $[(RO)_3P]_5CoH$ and $[(RO)_3P]_4FeH_2^{15}$.

Usually, evidence for co-ordination of an olefin to a metal is based on the shift to lower frequencies of the C=C stretching band of the olefin. This group frequency, although it is the most characteristic in the IR spectrum, of an olefin is nevertheless of very low intensity and consequently difficult to observe with certainty. In the work presented here we have attempted to use data from other more intense bands of the spectrum, in particular, the transverse C–H deformation of *ca.* 1000–700 cm^{-1}. This is usually the strongest band associated with vibrations of an olefin group and the most likely to show a large shift in position when the environment of the olefin is changed. We have also investigated the far IR spectra of these complexes in an

attempt to correlate the observed Cu–X stretching frequencies with known crystal structures.

RESULTS AND DISCUSSION

1. *Preparation*

The reduction of an alcoholic solution of a cupric salt (Cl^-, Br^-, ClO_4^- or BF_4^-) in the presence of an olefin, with a trialkyl or triphenyl phosphite precipitated the olefin–cuprous compound as analytically pure crystals. Concomitantly the trialkyl phosphite was oxidised to the corresponding phosphate. Triphenylphosphite, on the other hand underwent a more complicated redox reaction, which involved the solvent, and in ethanol and higher aliphatic alcohols we were unable by chemical means to completely resolve the composition of the reaction mixtures. NMR and IR studies have indicated that apart from phenol, dialkyl and alkyl aryl phosphites are also present in these solutions. The alkyl residues originate from the solvent, while the organic phosphites may arise from a reaction such as

$$(RO)_3P + HCl \rightarrow (RO)_2HP=O + RCl$$
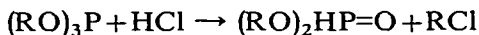
The evolution of hydrogen chloride during the reduction was observed and confirmed by the usual tests.

The facile nature of the trans-esterification process, evidenced by the isolation of $(MeO)_3P \cdot CuCl$ when triphenyl phosphite is used as the reductant in methanol, is unusual. Normally this reaction occurs under more stringent reaction conditions[16].

Formally, the redox step may be written as

$$2\ CuCl_2 + (RO)_3P + H_2O \rightarrow 2\ CuCl + (RO)_3P=O + 2\ HCl$$
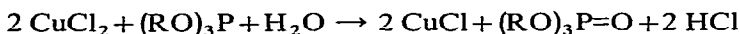
However, the stoichiometric amount of phosphite resulted in a poor yield of olefin complex and in practice a 1/1 ratio versus cupric halide was used. Increasing the proportion of phosphite added from a 1/1 ratio to two equivalents of phosphite per equivalent of cupric halide had little further effect on the yield of complex. It is possible that the additional mole of phosphite is required to react with the products of the initial reduction step such as hydrogen chloride. The compositions of the olefin copper complexes were unaffected by the use of different organo-phosphites.

The complexes formed between cyclic polyenes and cuprous halides have compositions similar to those previously described[6,7] namely 1/1 or 1/2, olefin/CuX.

1,5-Cyclooctadiene complexes of cuprous tetrafluoroborate and perchlorate have also been prepared. The isolated complexes had the same composition (olefin)$_2$-CuX (X=BF_4^- or ClO_4^-), and IR spectra as those prepared previously by electrolytic methods[9,10].

A butadiene complex, $C_4H_6(CuCl)_2$ was also isolated. This compound had previously been prepared by direct reaction of butadiene with cuprous chloride[17–19]

The complexes prepared by the present method, together with analytical data are summarised in Table 1.

2. *Infrared spectroscopy*

Table 2 summarises the near IR data for the olefin complexes. The norbornadiene–silver nitrate complexes were synthesised by established routes[5,20–23] in

TABLE 1

COPPER(I)–OLEFIN COMPOUNDS

The following results were obtained from reactions involving other olefins carried out in the manner described for the preparation of 1,5-cyclooctadiene·cuprous chloride. For convenience the yields are given in grams based on a weight of 1 g $CuCl_2 \cdot 2 H_2O$ employed.

Coordinated olefin	Complex formula	Yield (g/1 g $CuCl_2$)	Analysis found (calcd.) (%)			Colour
			C	H	X	
Cyclopentadiene dimer	$C_{10}H_{12}CuCl$	0.5	52.0 (51.9)	5.3 (5.2)	15.3 (15.3)	White
Norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)	$C_7H_8(CuCl)_2$		30.2 (29.0)	3.2 (2.8)	24.3 (24.4)	Pale-yellow
Norbornadiene dimer	$C_{14}H_{16}(CuCl)_2{}^a$	0.8	45.6 (44.0)	4.6 (4.2)	17.4 (18.5)	White
1,5-Cyclooctadiene	$C_8H_{12}(CuBr)$	0.5^b	37.7 (38.2)	4.9 (4.8)	30.4 (31.8)	White
Cyclooctatetraene	$C_8H_8(CuCl)_2$	0.7	31.7 (31.8)	2.9 (2.7)	23.2 (23.5)	Yellow-orange
cis,trans,trans-Cyclododecatriene	$C_{12}H_{18}(CuCl)_2$	0.5	41.0 (40.0)	5.4 (5.0)	19.8 (19.7)	White
trans,trans,trans-Cyclododecatriene	$C_{12}H_{18}(CuCl)_2$	0.3	40.2 (40.0)	5.1 (5.0)	19.3 (19.7)	White

^{a} Possibly contaminated with unreacted olefin. ^{b} Based on 1 g $CuBr_2$.

order to test our spectral assignments.

The metal–halide absorption frequencies in the olefin–copper compounds are recorded in Table 4 and they are discussed in relation to structures established by X-ray diffraction studies.

(a). *Near infrared frequencies cyclopentadiene dimer complex.* Table 3 shows that the frequency of the C=C band is dependent on the strain in the ring containing the double bond. Thus, in cyclopentadiene dimer the ν(C=C) frequencies at 1613 cm^{-1} and 1570 cm^{-1} can be assigned to the double bonds in the cyclopentene and norbornene rings respectively. In the complex (Table 2) the absorption bands occur at 1615 cm^{-1} and 1470 cm^{-1}. This would indicate that while the double bond in the C_5 ring is relatively unperturbed, the absorption band associated with the double bond in the norbornene ring has been lowered to 1470 cm^{-1} by π-complexing. This differs from the previously proposed structure[6] where bonding to the C_5 ring was assumed. We are, however, in agreement with the four-centre bridging structure for the copper–halogen links (see later).

(b). *Norbornadiene complexes.* Norbornadiene forms 1/1 and 1/2 adducts with copper(I) halides[5–7]. Prior to the present work only the 1/1 complex with CuCl was known, although the 1/1 and 1/2 complexes with CuBr have been described[5,7]. The 1/1 complex with cuprous chloride is reported to contain a C=C stretching frequency at 1563 cm^{-1}, close to the position in free norbornadiene, indicating that only one double bond of the diolefin is co-ordinated[6,7]. The same vibration in the co-ordinated

TABLE 2

NEAR IR FREQUENCIES OF OLEFIN–COPPER(I) COMPLEXES (IN CM^{-1})

Olefin	Formula	ν(C=C)		γ(C=C–H)			
Cyclopentadiene dimer	$C_{10}H_{12}$	1613	1570	752	723		
	$C_{10}H_{12}CuCl$	1615	1470		745		
Norbornadiene	C_7H_8	1645	1545	730		660	
	$C_7H_8(CuCl)_2$		1470				
	$C_7H_8(CuBr)_2$	1555	1470			690	
Norbornadiene dimer	$C_{14}H_{16}$	1562			720		
	$C_{14}H_{16}(CuCl)_2$	1470					
Butadiene	C_4H_6	1600 doublet		1010		910	
	$C_4H_6(CuCl)_2$	1565	1500	950	765		
1,5-Cyclooctadiene	C_8H_{12}	1655		722	710		
	$C_8H_{12}CuCl$	1620	1550	750	720		
	$C_8H_{12}CuBr$	1587					
	$(C_8H_{12})_2CuBF_4$	1588		770	740		
	$(C_8H_{12})_2CuClO_4$	1590		770	740		
Cyclooctatetraene	C_8H_8	1635		800	675		625
	$C_8H_8(CuCl)_2$	1540	1515		730		
cis,trans,trans-1,5,9-Cyclododecatriene	$C_{12}H_{18}$	1675	1633	978 (trans)			715 (cis)
	$C_{12}H_{18}(CuCl)_2$	1560		970	960		
trans,trans,trans-1,5,9-Cyclododecatriene	$C_{12}H_{18}$	1672		978	952		
	$C_{12}H_{18}(CuCl)_2$	1560		970	960 m		

TABLE 3

FREQUENCIES OF CYCLIC OLEFIN BANDS (IN CM^{-1})

Olefin	ν(C=C)	ν(C=C–H)
Cyclohexene	1646	718
Cyclopentene	1611	685
Norbornene	1568	725
Cyclopentadiene dimer	1613	752
	1570	723

ligand is stated[6] to occur at 1470 cm^{-1}. This structure has been confirmed by X-ray studies[24]. The spectrum of norbornadiene (Fig. 1) exhibits two high frequency bands at 1645 and 1545 cm^{-1}. It is easy to predict that two such modes would occur in the vibrations of cyclopentadiene dimer, because the molecule is unsymmetrical and the double bonds occur in different sized rings (see Table 3). In norbornadiene the molecule is symmetrical and the double bonds are identical but the stretching vibrations of each can interact across the ring and two bands are to be expected from in-phase and out-of-phase reactions of the two double bond oscillations. In this way the two bands at 1645 cm^{-1} and 1545 cm^{-1} may be explained and if such duality is found for the ν(C=C) it should also be observed for the transverse ν(C=C–H) vibrations which can couple in the same way. In the norbornadiene spectrum there are two strong bands at 730 and 660 cm^{-1}, which may be assigned to the dual C=C–H deformation modes.
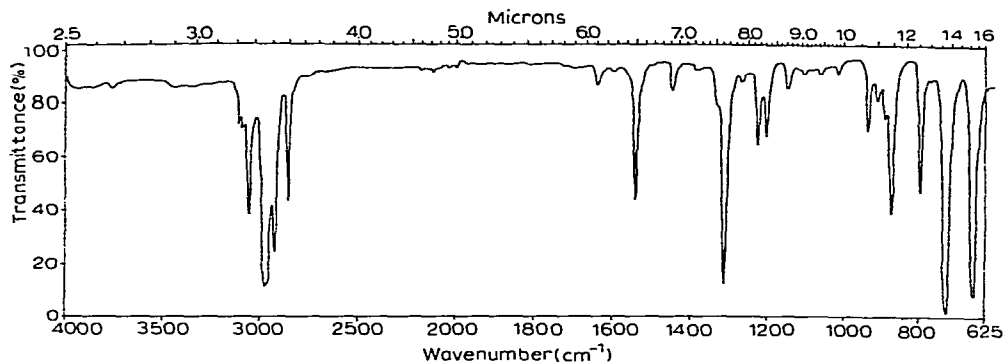
Fig. 1. Infrared spectrum of norbornadiene, liquid 25 μ cell.

Abel, Bennett and Wilkinson[5] only assigned the 1645 cm^{-1} band to ν(C=C), we assume that the 1545 cm^{-1} band lies underneath a strong absorption from the CS$_2$ they used as a diluent. Alexander et al.[25] agree that the 1545 cm^{-1} is present as a strong band in the norbornadiene spectrum but do not assign it. None of the above authors investigated the behaviour of bands in the 700 cm^{-1} region.

The orbital overlap that occurs on co-ordination of a metal atom with a double bond is known to produce a lowering of the frequency of the absorption bands associated with double bond vibrations. If both double bonds in norbornadiene are co-ordinated to a metal, large changes would be expected in the spectrum in both the 1600 cm^{-1} region and the 700 cm^{-1} region which might be observed as a disappearance of all bands from these regions. If one double bond only is co-ordinated one band of each original pair should still be observed in each region, probably at an intermediate frequency (not necessarily mid-way). In the norbornene spectrum in which one side only of the molecule is saturated bands at 1568 and 725 cm^{-1} are observed For the co-ordinated double bonds absorption bands below 1500 cm^{-1} might be expected to be observed. (However these are notoriously difficult to observe in olefin complexes; therefore their detection may be used as good evidence of co-ordination but the contrary is not necessarily true).

Schrauzer and Eichler[6] use arguments concerning the C=C stretching frequencies similar to those presented above.

A re-examination of norbornadiene–silver nitrate adducts demonstrated that the 700 cm^{-1} region is useful in revealing the number of norbornadiene double bonds co-ordinated, particularly since the strong nitrate bands mask the C=C bands present in the 1500 cm^{-1} region.

The adduct C$_7$H$_8$(CuCl)$_2$ was the only one obtained by our method and analyses consistently agreed with the calculated figures. Despite numerous attempts to repeat previous work[6,7] we were unable to obtain a complex which had analysis figures consistent with a 1/1 complex. The analytical figures were closer to a 2/3 stoichiometry and the IR spectra showed an uncoordinated double-bond frequency at 1555 cm^{-1}. Using the method of Haight et al.[7] we obtained a 1/2 complex which had an IR spectrum identical to that 1/2 complex prepared by the present method (Table 2).

The 1/2 cuprous bromide adduct was prepared exactly as described by Abel and co-workers[5]. The addition of organic phosphite to this reaction apparently made

little difference to the structure of the complex and the IR results were practically identical.

The 1/2 norbornadiene–cuprous chloride complex shows only fully co-ordinated C=C groups, with an absorption at 1470 cm^{-1}. In support of this both the bands 730 cm^{-1} and 660 cm^{-1} present in uncomplexed norbornadiene are absent. The strong band at 790 cm^{-1} always occurs in coordinated norbornadiene spectra and is the band due to the rocking of the *endo*-methylene group. Thus, this compound contains norbornadiene coordinated by both double bonds to a copper atom which correlates well with the analytical composition.

The spectrum of the 1/2 cuprous bromide complex, on the other hand, indicates that one double bond is not coordinated because strong absorptions occur at 1555 cm^{-1} and 690 cm^{-1}. The absence of a band at 730 cm^{-1} and the presence of a band at 1470 cm^{-1} is evidence that coordination to the metal has occurred through only one double bond. These conclusions differ from those published previously[5] and the structure of the complex is presumably different from the cuprous chloride adduct.

(c). *Butadiene complex*. The structure of the butadiene complex with cuprous chloride, $C_4H_6(CuCl)_2$ is unknown, but the possibility of butadiene functioning as a chelate or a bridging ligand has been discussed[19]. Our compound, showed the appearance of new bands at 950 cm^{-1} and 765 cm^{-1} in the butadiene spectrum[26]. The frequencies of these absorptions suggest that they might arise from *cis* and *trans* vibrations of the C–H bonds on carbon atoms 2 and 3 of the butadiene molecule. It is reasonable to postulate that if one butadiene molecule π-coordinates to copper atoms above and below the plane of the molecule the normal wagging and twisting modes of the terminal =CH$_2$ groups will be restricted. If delocalisation of the double bonds occurs the molecule may vibrate as *cis* or *trans* X–CH–CH–X, where X can be regarded as a large substituent simulating the presence of copper atoms coordinated to the terminal double bonds of butadiene.

The v(C=C) region provides further confirmation of π-coordination of both double bonds because the doublet of butadiene 1600 cm^{-1} is present in the complex spectrum at 1565 and 1500 cm^{-1}.

(d). *1,5-Cyclooctadiene complex*. Two determinations have been reported on the structure and IR spectrum of 1,5-cyclooctadiene cuprous chloride[27,28]. Our compound showed a comparable IR spectrum, and the minor details of the CH$_2$ bands of the spectrum recorded by us agree with that of the polymeric structure[27], although this is not consistent with the analysis figures, it is possible that such spectral details are merely indicative of the "boat" rather than the "chair" configuration of the ring.

Manahan[9,10] has previously described the preparation of $(C_8H_{12})_2CuClO_4$ and $(C_8H_{12})_2CuBF_4$. Our method of preparation led to the same complexes. These two compounds differ from the cuprous halide compounds, in containing two cyclooctadiene molecules per copper atom. The copper(I) perchlorate complex was quoted[9] as having two bands in the IR spectrum at 1638 and 1595 cm^{-1} replacing the 1660 cm^{-1} C=C bond of the uncomplexed diene. We do not observe a band around 1600 cm^{-1}, but both complexes show a C=C absorption at 1590 cm^{-1}, similar to the halide complexes. Unfortunately the strong absorption of the BF$_4^-$ and ClO$_4^-$ ions complicate the spectra of the 1100 and 700 cm^{-1} regions.

(e). *Cyclooctatetraene complex*. The X-ray structure of the 1/1 cyclooctate-

traene complex has been determined[29] and found[30] to be similar to cyclooctatetraene $AgNO_3$. Unfortunately, no correlating IR data are given in the literature for these complexes. Schrauzer and Eichler[6] quote for their 1/2 complex two weak bands at 1613 and 1525 cm^{-1} indicative of free and bonded C=C bonds. With cuprous bromide they[6] obtained a 1/1 complex, here again bands at 1625 and 1525 cm^{-1} were observed. Our 1/2 chloro-complex shows only bands at 1540 and 1515 cm^{-1}, which would suggest that in some way all the four double bonds in cyclooctatetraene are used equivalently in complex formation.

(*f*). *Cyclododecatriene complexes*. It is interesting to note that when *cis* and *trans* double bonds are present in the same molecule it is the *cis* which appears to coordinate preferentially to the metal. This observation parallels previous equilibrium constant work on silver–olefin complexes[31].

The preference for *cis* double bonds can be clearly seen in the *cis,trans,-trans*- and *trans,trans,trans*-cyclodecatriene complexes. In the *cis* compound the absorption band between 700–750 cm^{-1} decreases markedly in intensity on complex formation, whereas the *trans* bands at 950–970 cm^{-1} are still observed as very intense absorptions.

Copper–halogen frequencies

Further evidence concerning the structure of these complexes can be obtained from the absorption bands of the copper–halogen bonds (Table 4).

TABLE 4

COPPER–HALOGEN IR FREQUENCIES IN OLEFIN–COPPER(I) COMPLEXES (IN CM^{-1})

Olefin	Formula	v(Cu–X)
Cyclopentadiene dimer	$C_{10}H_{12}CuCl$	227[a]
Norbornadiene	$C_7H_8(CuCl)_2$	255, 230, 180[a], 165
Norbornadiene	$C_7H_8(CuBr)_2$	200, 165, 130[a], 105
Norbornadiene dimer	$C_{14}H_{16}(CuCl)_2$	238[a]
Butadiene	$C_4H_6(CuCl)_2$	263, 180[a]
1,5-Cyclooctadiene	$C_8H_{12}CuCl$	227[a]
Cyclooctatetraene	$C_8H_8(CuCl)_2$	254[a], 222
cis,trans,trans-1,5,9-Cyclododecatriene	$C_{12}H_{18}(CuCl)_2$	240, 200[a]
trans,trans,trans-1,5,9-Cyclododecatriene	$C_{12}H_{18}(CuCl)_2$	248[a], 223

[a] Strongest band.

Copper–chlorine stretching frequencies extend over a very wide range. Adams and Lock[32] have shown that the overall range for v(Cu^{II}–Cl) is 330–220 cm^{-1} and that bridging

$$Cu\underset{Cl}{\overset{Cl}{<>}}Cu$$
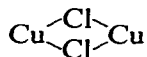
frequencies occur at the lower end of that range at *ca.* 230 cm^{-1}. They do not comment upon any frequencies in Cu^I compounds or Cu^{II} compounds in polymeric chains. These authors[32] quote the range of frequencies for v(Cu^{II}–Br) as 278–168 cm^{-1}.

The simplest Cu^I compound is cuprous chloride $(CuCl)_n$ which is believed to exist in sequences of –Cu–Cl–Cu–Cl atoms[33] probably formed into a planar six-membered ring of bond length 2.16 Å. The IR spectrum of $(CuCl)_n$ shows only one

broad band with its maximum at 170 cm^{-1}, a very low frequency for a metal halogen stretching vibration. The force constant must be extremely low in this compound to account for such a low frequency because bonds of comparable length 2.28 Å in $CuCl_2$ give[32] an absorption frequency of 290 cm^{-1}.

The metal–halide absorption frequencies in the olefin–copper compounds are shown in Table 4. The various X-ray structures which have been determined[24,28,29] are useful in characterising the strong Cu–Cl bands at *ca.* 230–240 cm^{-1} as those of a four-membered bridge system

$$Cu\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{<\quad>}}Cu.$$
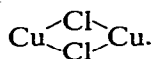
The absorptions occurring in the range 220–160 cm^{-1} would appear to be associated with a polymeric sequence of copper–halogen atoms which may have a cyclic form as in norbornadiene · cuprous chloride[24], although linear and cyclic polymers of different ring size probably absorb within the same range.

The lower frequencies (200–100 cm^{-1}) for the Cu–Br absorption are consistent with the greater mass of bromine compared with that of chlorine.

EXPERIMENTAL

The hydrated cupric salts, organic phosphites and olefins were commercially available compounds and used without further purification. Cupric tetrafluoroborate hexahydrate was prepared by the method of Funk and Binder[34].

The near IR spectra were recorded on KBr discs or as solid dispersions in suitable oils at room temperature on the Perkin–Elmer 257. The copper–halogen frequencies were determined as solid dispersions in paraffin oil on Grubb–Parsons D.M.4 and Beckman IR II Instruments.

Other olefin–copper complexes used for IR comparison were prepared by the existing methods[5–7,9,10].

The general procedure is illustrated by the preparation of 1,5-cyclooctadiene · cuprous chloride.

1,5-Cyclooctadiene · cuprous chloride

8.5 g (0.05 mole) $CuCl_2 \cdot 2H_2O$ were dissolved in methanol (100 ml) at room temperature. 15.5 g (0.05 mole) triphenyl phosphite were added, followed immediately by the addition of excess 1,5-cyclooctadiene (10 ml). The solution was shaken to mix the components and then left to stand for 1 h. During this time the solution changed in colour from dark-brown to pale-yellow with the deposition of large colourless rods. The complex (6.3 g, 61 %) was filtered and washed with 10 ml ice-cold methanol containing *ca.* 1 ml of 1,5-cyclooctadiene and dried by suction at the water pump for 15 min. (Found: C, 46.9; H, 6.1; Cl, 17.4. $C_8H_{12}ClCu$ calcd.: C, 46.4; H, 5.8; Cl, 17.1 %.) This procedure was repeated under substantially identical conditions using other polyenes. The results are tabulated in Table 1.

The preparation of 1,5-cyclooctadiene · cuprous chloride was repeated using $(MeO)_3P$, $(EtO)_3P$ and $(iso-PrO)_3P$ as reducing agents, respectively. No change in the composition of the product occurred.

The experiments could also be carried out in ethanol as solvent.

Butadiene · bis(cuprous chloride)

A solution of $CuCl_2 \cdot 2H_2O$ (2 g) dissolved in methanol (20 ml) was reacted with triphenyl phosphite (2 ml) and butadiene was then immediately bubbled through the solution at room temperature for 20 min. A bright yellow crystalline precipitate formed. This compound was filtered and washed with 2 ml of cold methanol, previously saturated with butadiene. Yield 0.4 g (Found: C, 18.9; H, 2.4; Cl, 28.0. $C_4H_6Cl_2Cu_2$ calcd.: C, 19.1; H, 2.4; Cl, 28.1%.)

Bis(1,5-cyclooctadiene) · cuprous tetrafluoroborate

$Cu(BF_4)_2 \cdot 6H_2O^{34}$ (3.5 g) dissolved in methanol (15 ml) was treated with 1,5-cyclooctadiene (3 ml) and then with triphenyl phosphite (5 ml). The solution changed in colour from blue to green and on standing 1 day deposited, in small yield, colourless, rhombic crystals. More product (1.5 g) was obtained by leaving the filtrate to stand further. (Found: C, 52.9; H, 6.9; Cu, 17.4. $C_{16}H_{24}BCuF_4$ calcd.: C, 52.4; H, 6.6; Cu, 17.3%.)

The bis(1,5-cyclooctadiene) · cuprous perchlorate complex was prepared similarly. These two complexes appear from IR and general physical properties to be the same as obtained previously by Manahan[9,10].

Reactions of organic phosphites with cupric chloride

The following experiments illustrate the fate of the organic phosphite when reacted with cupric chloride dihydrate in the absence of olefin in various alcoholic media.

Reaction of trimethyl phosphite with a methanolic solution of cupric chloride. Trimethyl phosphite (25 ml) was added dropwise over 10 min to a stirred solution of $CuCl_2 \cdot 2H_2O$ (35 g) dissolved in methanol (200 ml).

The mixture exothermically warmed to 55° and the colour of the solution changed from green to dark-brown and then to a pale yellow with the precipitation of a white crystalline solid. The reaction mixture was stood for 1 h and the solid (cuprous chloride, 7.5 g) was removed by filtration. The pale-yellow filtrate was distilled, first at atmospheric pressure to remove methanol and then at reduced pressure. A further 9.7 g of cuprous chloride deposited during these distillations and was removed. 10 ml of a colourless oil boiling at 86–90°/20 mm were obtained. Approximately 5 ml of a viscous oil remained in the still. The distillate (n_D^{25} 1.3957) was trimethyl phosphate (n_D^{25} 1.3950) confirmed by IR NMR and mass spectrometry. (Found: C, 25.8; H, 6.7. $C_3H_9O_4P$ calcd.: C, 25.7; H, 6.5%.)

Reaction of triphenyl phosphite with a methanolic solution of cupric chloride. A solution of $CuCl_2 \cdot 2H_2O$ (17 g, 0.1 mole) in methanol (100 ml) was stirred and triphenyl phosphite (50 ml, approximately 0.2 mole) was added dropwise over 30 min. The colour of the solution changed through green to brown and then to pale-yellow with the precipitation of a white crystalline solid (9.6 g). This substance had m.p. 210–212° (corrected). Reported[35] for $(MeO)_3P \cdot CuCl$: 216–217°. (Found: C, 16.7; H, 4.2; P, 13.9; $C_3H_9O_3PClCu$ calcd.: C, 16.2; H, 4.1; P, 13.9%.)

The filtrate was concentrated at 60°/20 mm. Hydrogen chloride was evolved and confirmed by the usual tests. The liquid residue after removal of methanol and filtration from a further quantity of white solid (cuprous chloride) was fractionally distilled. A number of fractions boiling between 80–108°/22 mm were obtained. The

lower boiling fraction solidified on cooling and redistillation of this yielded pure phenol (30 g). The remaining fraction (30 g) consisted of trimethyl phosphate contaminated with phenol as ascertained from IR, ^{31}P and mass spectroscopic measurements.

Repeating the above experiment using solvents other than methanol led to complex mixtures which were impossible to separate. NMR analysis results suggested that the principle components, apart from phenol, were the dialkyl (or mixed alkyl, aryl) phosphites.

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