COPPER, SILVER AND GOLD

ANNUAL SURVEY COVERING THE YEAR 1974

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Contents

NOTE: This article on organometallic derivatives of Cu,Ag and Au and their reactions, is only comprehensive if read in conjunction with the survey for 1974 appearing in this journal entitled "Transition Metals in Organic Synthesis", by L.Hegedus. Duplications in these two surveys have been minimised.(J.Organometal.Chem.,105(1975)421-474.)

I. Organocopper compounds

A series of copper alkyls RCuL (R=Me,Et,Pr; L=Bipy, tricyclohexyl

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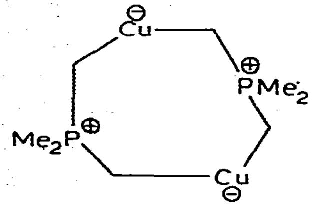
Copper, silver and gold, Annual Survey covering the year 1973 see J.Organometal.Chem., 95(1975)357-369.

phosphine) and MeCu have been prepared from $Cu(acac)_2$ and $R_2Al(OEt)$ in the presence or absence of L in ether at low temperatures. Only the $RCu\{P(C_6H_{11})_3\}$ complexes are thermally stable and further react with CO_2(R=Me) to give $MeCO_2Cu\{P(C_6H_{11})_3\}$ and $MeCO_2Cu(CO_2)\{P(C_6H_{11})_3\}$ [1]. Two new stable organocopper derivatives from aryl-Cu compounds and bis(diphenylphosphinosulphide)methane or malonitrile are reported [2]. Copper(I) t-butoxide with $NCCH_2CO_2H$ in THF gave $NCCH_2CO_2Cu$, which, when heated in DMF, decarboxylated to $NCCH_2Cu$. With $(NCCH_2CO_2)_2Cu$ the decarboxylation is accompanied by reduction to the same cyanomethylcopper(I) product [3]. A preliminary X-ray structural determination of $[Me_2P(CH_2)_2Cu]_x$ (I) has shown its dimeric nature (x=2). Cu-C bonds averaged 1.96 Å [4].



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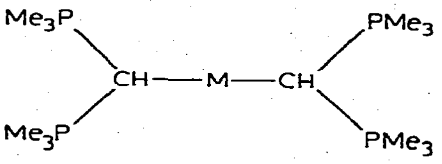


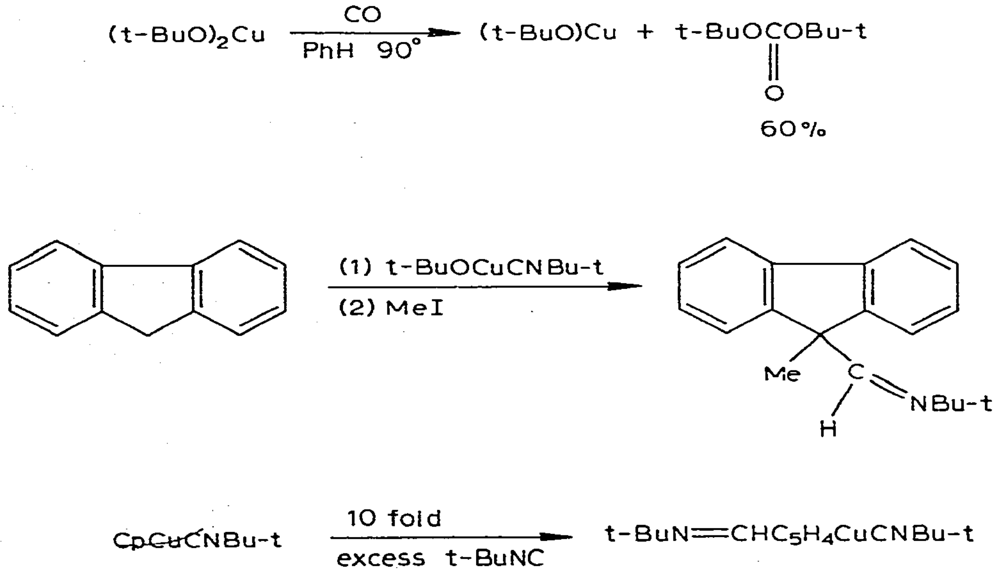
(M = Cu,Ag)

(2)

Other copper and silver ylides reported were $[(Me_3PCH_2)_2Cu]Cl$ and (2) from $CuCl(PPh_3)$ and MCl (M=Cu,Ag) with TMMP respectively. Similar mixed ylide systems were characterised with the ligands $PhMe_2PCH_2$ and $MePh_2PCH_2$, together with the product $Me_3SiCH_2CuCH_2PMe_2$[5]. An alternate synthetic route to vinylmetallic-copper(I) complexes $R_2Si(CH{=}CH_2)_2(CuCl)_2$ (R=Me,Bu,Ph) and $RSi(CH{=}CH_2)_3(CuCl)_2$(R=Me,Ph) from CuCl or CODCuCl has been found [6]

The IR spectrum of the interaction of CO with a series of matrix isolated fluorides including CuF_2 has been recorded. The CO high frequency band was correlated to the strength of the electric field of the metal ion at the

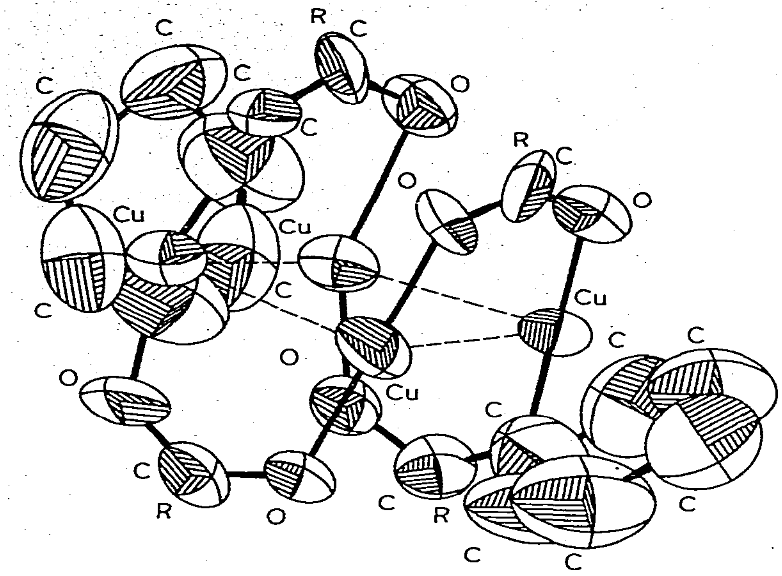
C nucleus [7]. The kinetics of carbonylation of [Cu(OMe)X] ($X=Cl,Br,MeCO_2$) to give dimethylcarbonate have been investigated. The autocatalytic nature of the reaction was ascribed to cuprous carbonyl formation. The rate determining step appears to be the rearrangement of a mixed valence dimer like [Cu(OMe)X.Cu(CO)X] to a labile carbomethoxycupric species [8]. The new heat-stable copper carbonyl and isocyanide complexes t-BuOCuL(L=CO, CNBu-t) have been prepared, with their thermal stability being attributed to the strong σ-characteristics of the t-BuO ligand. Insertion reactions were also studied (scheme 1) [9]. A review on the advances in the chemistry of isocyanide complexes has appeared [10]. ^{13}C chemical shifts, $^{1}J(^{14}N-^{13}C)$



(Scheme 1)

coupling constants and stretching frequencies of the isocyano group in the isocyanides $[(Me_3CNC)_4Cu]BF_4$ and $[(CH_2=C=CHNC)_4Cu]ClO_4$ have been determined. The results were discussed in terms of inductive and mesomeric substituent effects on the polarisation and charge density of the $-C-N\equiv C$ bonds[11].

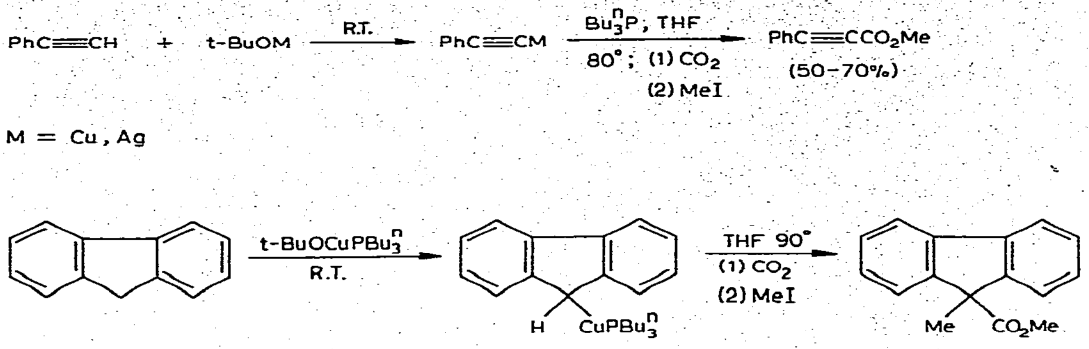
The ^{13}C NMR spectra of cyclo-olefincopper(I) complexes have been examined. The change in the chemical shift of the vinyl carbon upon co-ordination was compared to the change observed in the proton spectrum, and the Dewar-Chatt-Duncanson model for olefin-metal bonding was used to compare chemical shift changes observed in polyolefin and monoolefin complexes. The role played by π-back donation in the relatively large upfield shifts observed in monoolefin complexes was described. The use of copper(I) triflate as a ^{13}C NMR shift reagent for olefins was suggested [12]. It is of interest to note that in recent correspondence the validity of many papers rationalising ^{13}C chemical shifts for carbon atoms bound to transition metals has been convincingly questioned. Specifically, the proposal that very small upfield shifts for olefins bound to d^{10} Ag(I) supports the linear relationship observed between the shifts of π-bonded carbons and those of σ-bonded carbons in the same molecule is hardly convincing as ethylene bound to d^{10} Pt(0) exhibits a marked upfield shift on complexing as do olefins bound to Cu(I) [13]. Calculations on, [14] and the properties of [15], metal-olefin π-complexes of ethylene [14], allyl[14] and propylene [15] with Cu,Fe,Ni,Ag,Cu^+,Ni^+ and Pd^+ have appeared. The calculations on the propylene-π-complexes revealed that activation of the C–H bonds in the complexes depends greatly on the nature of the metal ions [15]. Copper(I) ions in Y-zeolite absorb ethylene in a 1:1 ratio. Characteristic IR specroscopy bands at 1428, 1533 and 1920 cm^{-1} are reported [16]. [CODCuCl.HgCl$_2$]$_n$ and [(CODCuBr)$_2$HgBr$_2$]$_n$ have been prepared from [CODCuX]$_2$ and HgX$_2$ (X=Cl,Br)[17]. A preliminary X-ray structural determination of the compound $Cu_4(CF_3CO_2)_4(C_6H_6)_2$ (3) has appeared. The basic framework consists of 4 Cu's in a plane with trifluoroacetate groups bridging two copper atoms. Each copper has a co-ordination of three by forming π-bonds to benzene in the *meta*-position. Other olefins readily replace the benzene group to give $[Cu(CF_3CO_2)(olefin)_y]_x$ (olefin = indene, y = 1, x = 4;olefin = cyclohexa-1,4-



(3)

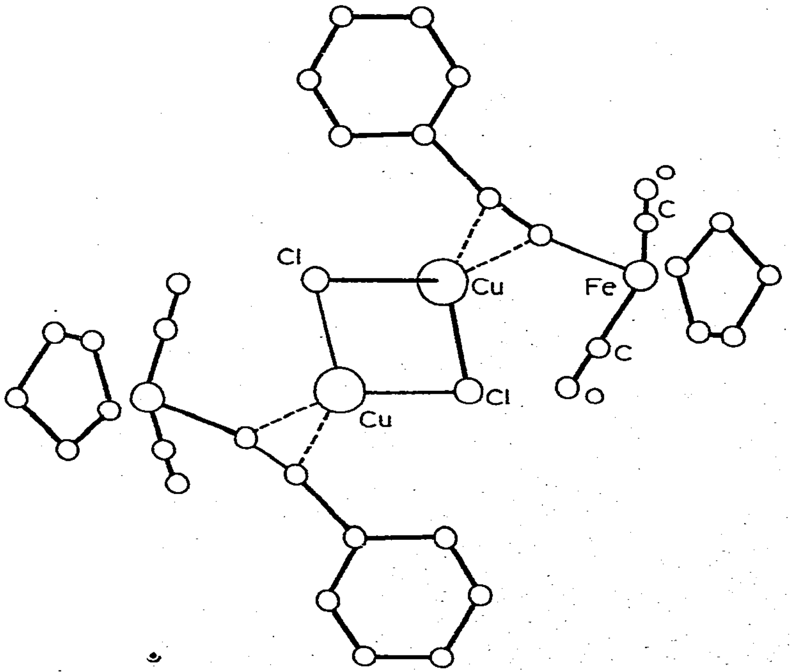
diene, cyclohexa-1,3-diene, y = ½, x=4), and it was postulated that $Cu_4(CF_3CO_2)_4$ is the basic unit for all copper fluoroacetic acid complexes including $Cu(CF_3CO_2)CO$ [18]. Eleven complexes of benzene and hexafluorobenzene with Ti, V, Cr, Mn, Fe, Co, Ni and Cu have been prepared and their thermal stabilities determined [19]. The spatial arrangement of the CuO_3SCF_3 matrix has dictated a unique stability ordering of alkylaromatics based more on their shape than on their π-basicity. This property was used as a basis of the separation of *p*-xylene from other C_8 arenes. The mechanism of the ligand exchange reaction was discussed and equilibrium constants were determined [20].

Increased carbanionic reactivity of the alkynyl group in copper or silver organo complexes by strong σ-donor ligands *e.g.* Bu^n_3P or *t*-BuNC, facilitates CO_2 insertion into the M-C bond (Scheme 2) [21]. Relevant parameters obtained from the crystal structure of $[\{CpFe(CO)_2(C{\equiv}CPh)\}CuCl]_2$ (4) are Cu-Cl 2.29Å, Cu--Cu 3.07Å and Cu-C (ethynyl) 2.01Å. The acetylene is



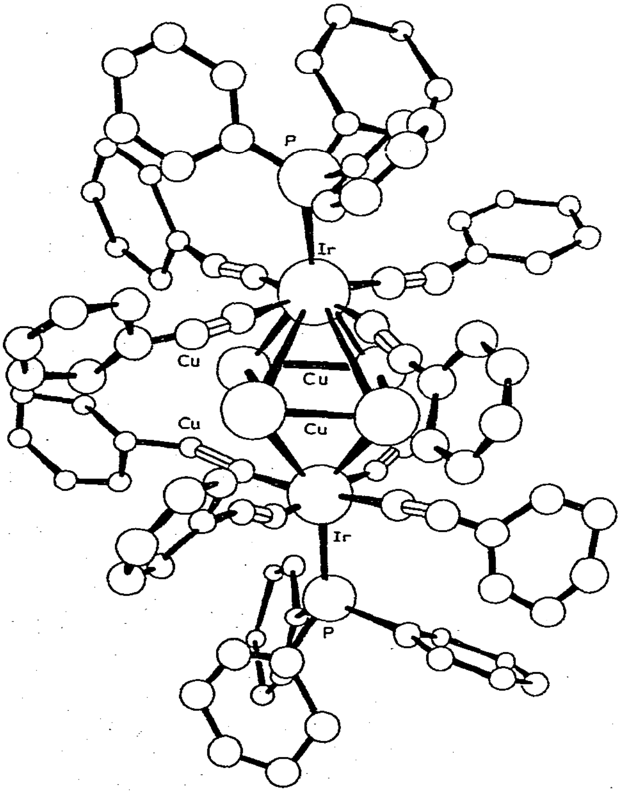
(Scheme 2)

π-bonded to the copper and the CuC_2 moiety is coplanar [22]. Full papers on the structure [23] and preparation [24] of $Cu_4Ir_2(PPh_3)_2(C{\equiv}CPh)_8$ (5) have appeared. Refined mean interatomic distances are Ir–Cu 2.87Å, Cu–Cu 2.74Å. Each Ir atom is bonded apically to a PPh_3 ligand, with Ir–P=2.26Å.



(4)

The 4 phenylethynyl ligands are σ-bonded to each Ir atom with Ir-C=2.04Å. Each acetylenic fragment simultaneously participates in an asymmetric π-interaction with Cu atoms in the octahedral meridian such that $Cu{-}{-}{-}C_{\alpha}$ is 1.99Å and $Cu{-}{-}{-}C_{\beta}$ is 2.185Å. Each Cu is thus bonded to 2 acetylene moieties [23]. Ligand substitution of $Ar_4Cu_6X_2$(X=Cl,I) with RLi produced $Ar_4R_2Cu_6$ which formed ArR exclusively on thermolysis. The ArR (Ar=o-$Me_2NC_6H_4$; R=PhC≡C, p-$MeC_6H_4C{\equiv}C$,2,4,6-$Me_3C_6H_2C{\equiv}C$) is presumably formed by an intramolecular process via a concerted homolytic Cu-C bond breaking and C-C bond formation. The specificity of the thermolysis was explained in terms of a template effect as seen in (6) [25]. Linear dicoordinate Cu(I)



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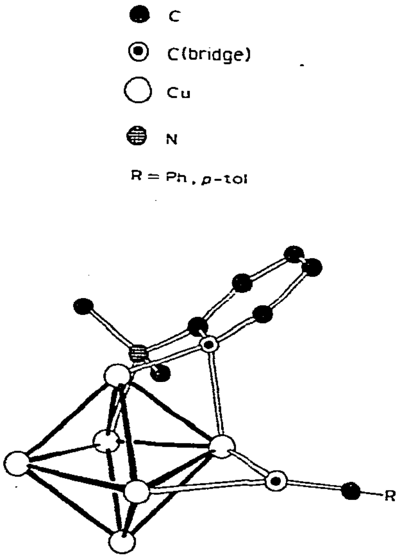


(6)

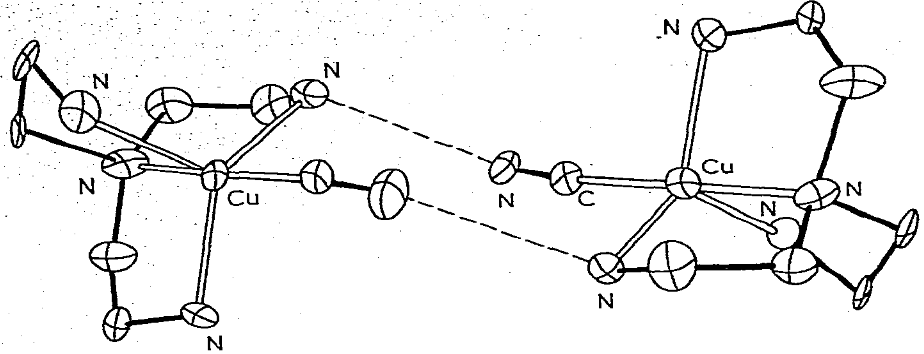
has been observed in the partially refined structure of $CpRu(PPh_3)_2(C{\equiv}CPh)CuCl$ [26]. Far IR and absorption spectra of a series of monomeric and polymeric copper organoacetylides have been measured. The absorption spectra of the polymers having the monomeric units $CuC{\equiv}CR$ ($R{=}Bu, CH_2{=}CH, Ph, PhC{\equiv}C$, p-$PhC{\equiv}CC_6H_4$) and $CuC{\equiv}CQC{\equiv}CCu$ ($Q{=}p$-phenylene, 4,4'-biphenylene and oxydi-p-phenylene) reflected charge transfer between Cu d'electrons and ligand π-electrons [27,28]

A review on cyanide complexes of the transition metals including those of Cu,Ag and Au has appeared [29]. The crystal structures of the two copper cyanide compounds, $[Cu_2(2,2',2''\text{-triaminotriethylamine})_2(CN)_2](BPh_4)_2$ (7) and μ-cyano-*bis*(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)dicopper(II) perchlorate (8) have been reported. (7) contains trigonal bipyramidal copper with the amine occupying 4 sites and an axially C-bonded cyanide ligand (Cu-C 1·97Å) in the fifth position. The cation is dimeric because of hydrogen bonding of the cyanide nitrogen to hydrogen on the amine [30]. In (8) the cyanide ligand bridges two copper atoms [31]. Stable mixed ligand copper cyanide complexes of formula $[Cu(Phen)_2CN]X.nH_2O$ ($X{=}Cl,Br,I,NO_3,ClO_4$), $Cu(Phen)_2(CN)_2$ and $Cu(Phen)(CN)_2$ have been isolated from aqueous solutions [32]. A study of the kinetic reaction of $Cu(CN)_4^{2-}$ in water and aqueous methanol by stopped flow-techniques has found the reaction to be second order in Cu(II) and inversely proportional to the uncomplexed CN^-. This was attributed to a reaction between $Cu(CN)_3^-$ and $Cu(CN)_4^{2-}$ occuring [33].

II. Reactions of organocuprates and related reagents

1. Organocuprates and lithium-copper compounds

ESR studies showed that $Cu(RNC)_n$ and $Cu_2O(RNC)_m$ complexes transfer electrons to various π-substrates such as nitrobenzenes, benzoquinone and



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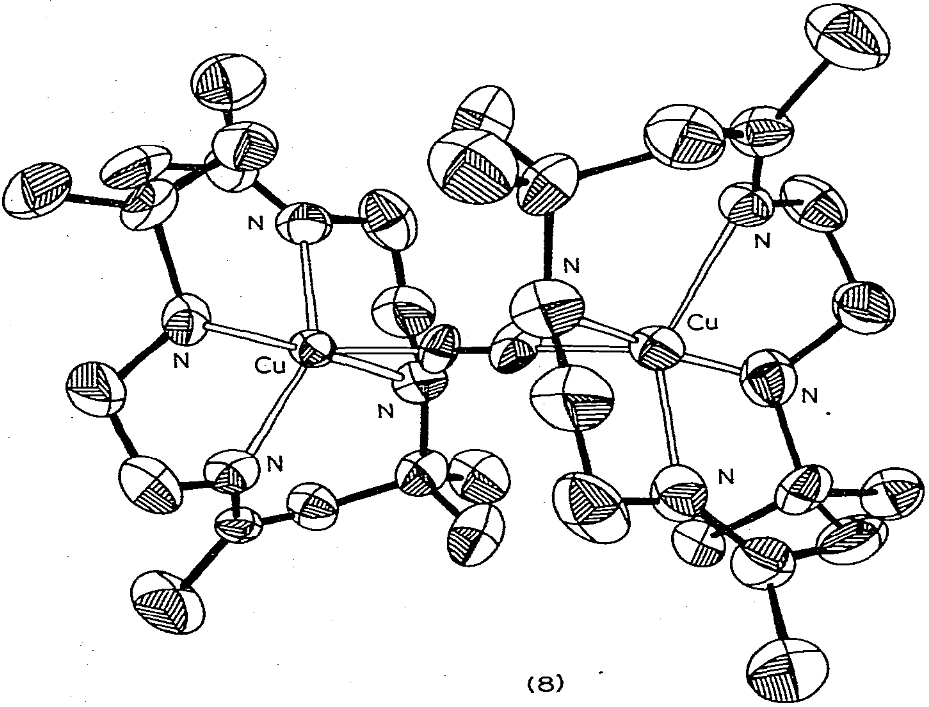
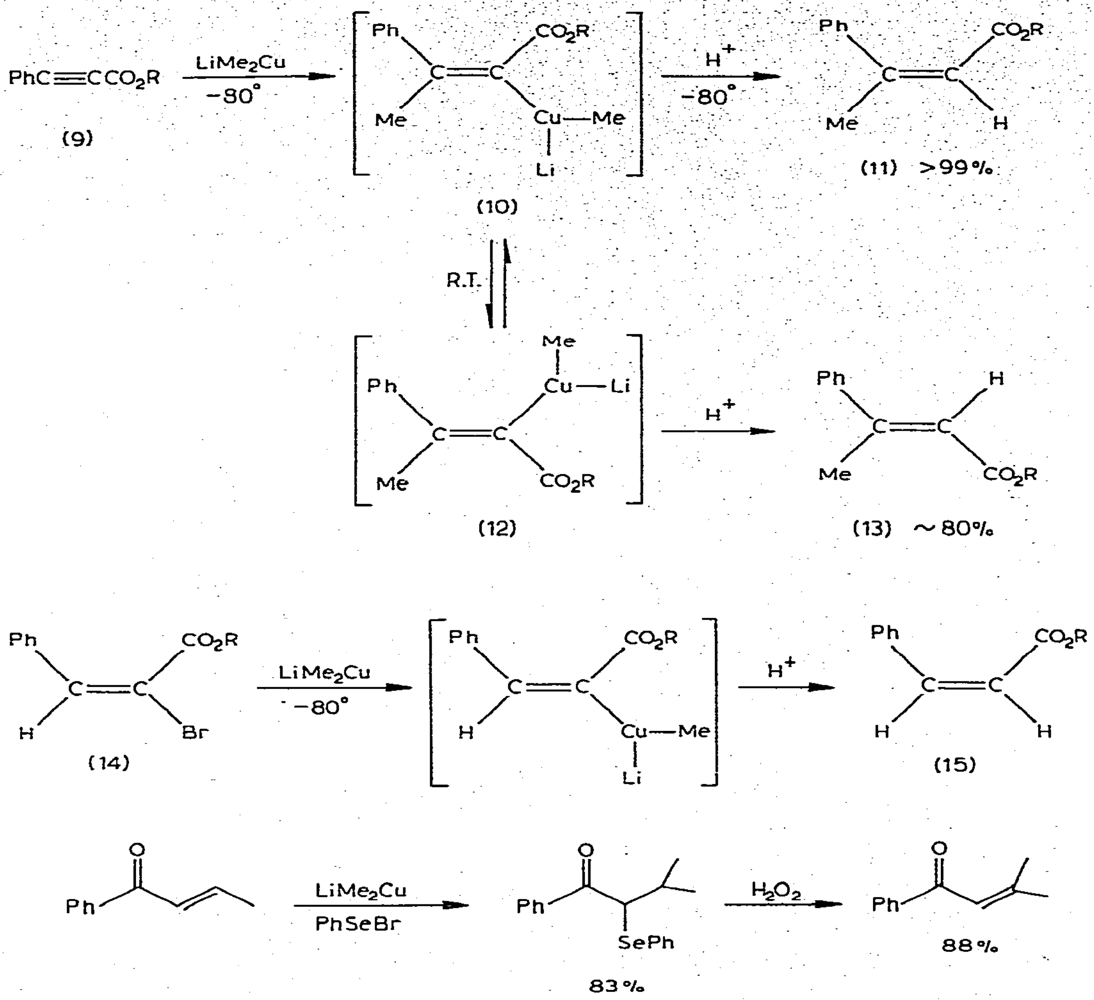


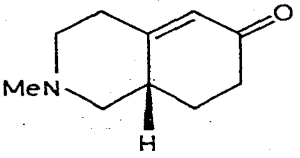
(8)

tetracyanoethylene, thus producing the anion radicals of these species [34]. The complex metal hydride $LiCuH_2$ was prepared by reaction of $LiMe_2Cu$ with $LiAlH_4$ in ether. The yellow precipitate was shown to be reasonably stable below 70° [35].



(Scheme 3)

The formation of a covalent Cu-C bond in the conjugate methylation of the phenyl acetylenic ester (9) is reported. If the reaction and subsequent protonation were performed at -80° only the *cis*-isomer (11) was formed, proving *cis*-addition of reagent across the triple bond. On warming the reaction mixture to RT before protonation the intermediates (10) and (12) reached equilibrium and 80% of the *trans*-isomer (13) resulted. Similarly retention of configuration was established for the reaction (14→15) [36]. Regeneration of the enone moiety after conjugate alkylation was achieved by trapping the enolate with PhSeX and oxidising with hydrogen peroxide (scheme 3) [37]. One of the steps used in the selective synthesis of 3-methyl-2-pentenylidene triphenylphosphorone uses $LiMe_2Cu$ *e.g.* $EtC{\equiv}CCO_2Me \xrightarrow{LiMe_2Cu} Et(Me)C{=}CHCO_2Me$ [38]. Stereospecific addition of $LiPh_2Cu$ to (16) gave the morphine phenylisoquinolinone fragment (17) [39]. Trapping of the intermediate enolate (18) as the silyl ether (19), partial purification, regeneration of the enolate with $LiNH_2$ and alkylation gave (20) in 47%



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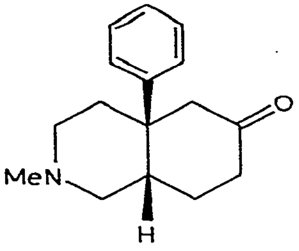

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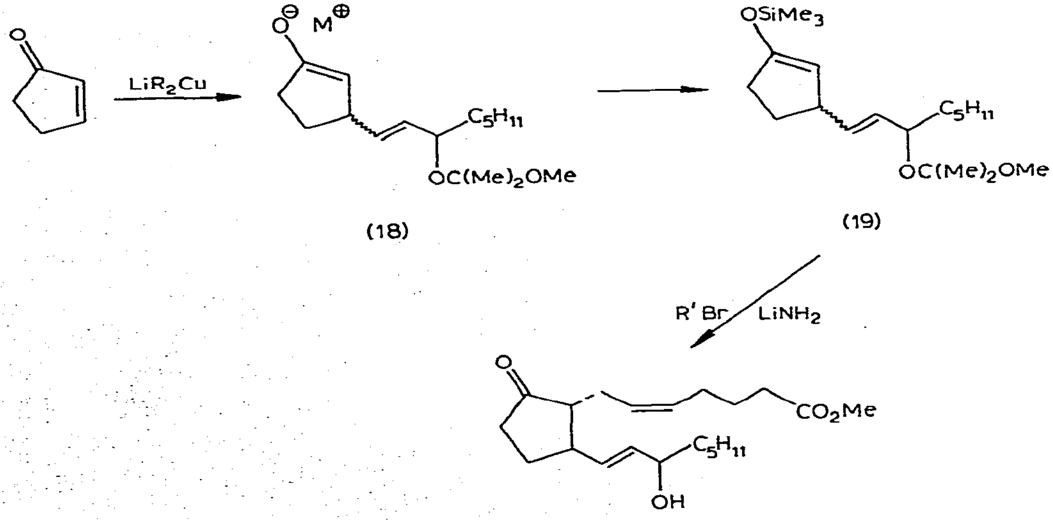
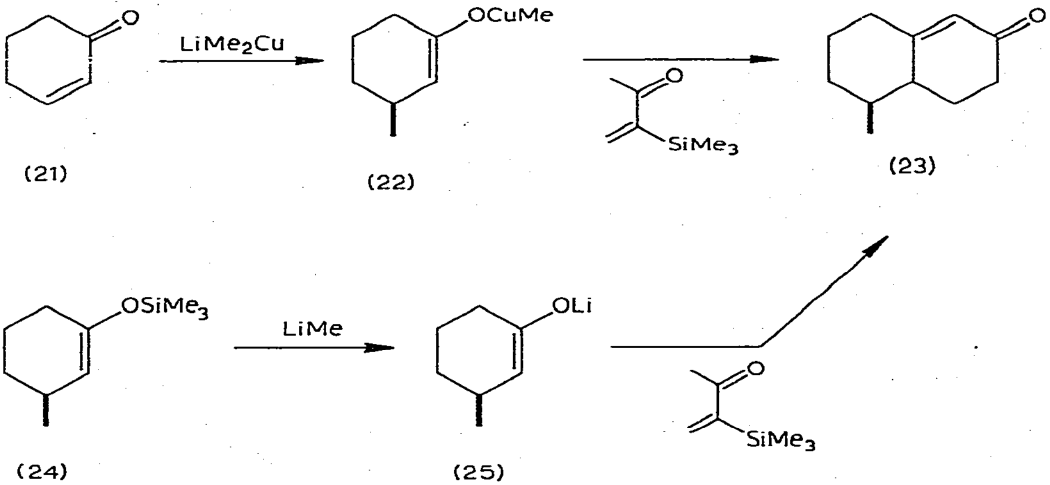


(18)

(19)

(20) racemic

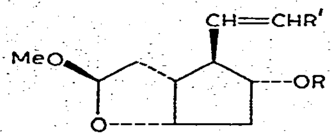
overall yield [40]. Organocopper enolates, generated by the action of lithium dialkyl cuprates on enones underwent regioselective annelation when treated with α-silylated vinyl ketones (22) → (23) [41]. The presence of copper ions was found not to be necessary for the regioselectivity of the subsequent alkylation steps. Even enolates could, under aprotic conditions, be alkylated regiospecifically, regardless of whether they were generated by $LiMe_2Cu$ action on enones (21)→(22)→(23), or by methyllithium reaction with the vinylsilyl ether (24)→(25)→(23) [42]. The enone



(21) (22) (23)

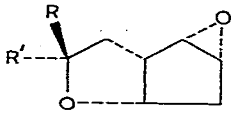
(24) (25)

(26) was prepared in 6 steps from the epoxy lactone (27) by a route involving ring opening of the epoxy lactol methyl ether (28) with the vinyl Gilman reagent, $Li(CH_2{=}CH)_2Cu$, to give (29) [43]. The epoxides (30) (R=R'=Me,Ph;R=Me,R'=Ph) were cleaved by $LiMe_2Cu$-LiI or MeCu-LiI to give a mixture of RR'C=CHCN, $RR'C(OH)CH_2CN$,RR'C(OH)CHMeCN and $[R'RC(OH)]_2CHCN$. The relative yields of RR'C(OH)CHMeCN and $[RR'C(OH)]_2CHCN$ were increased by using a 1:2 ratio of (30) and the copper-containing reagent [44]. The 2,6-dimethoxyphenyllithium cuprate reagent gave $2,6\text{-}(MeO)_2C_6H_3CH_2CH(OH)Me$



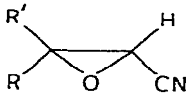
(26) R = p-PhC_6H_4NHCO ; R' = $CO(CH_2)_4Me$

(29) R = R' = H



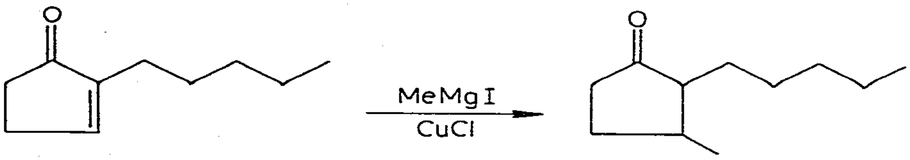
(27) R = R' = O

(28) R = OMe; R' = H



(30)

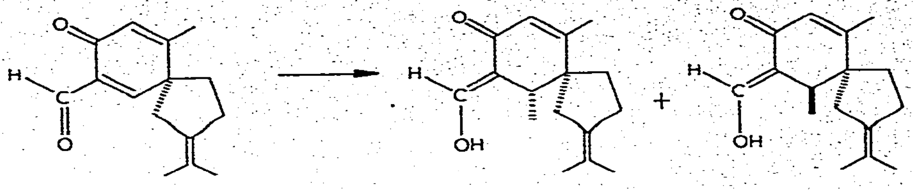
with propylene oxide, and no reaction with *trans*-2,3-epoxy-6-methyl heptane. The latter reaction, in fact, produced 2,6,2'6'-tetramethoxybiphenyl [45]. The final step in the synthesis of tetrahydrojasmone (31) was a conjugate



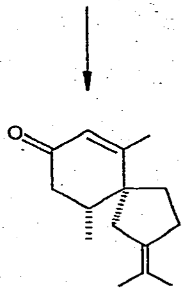
(31)

addition using a copper catalysed Grignard reagent [46]. Racemic β-vetivone (33), a fragrent component of vetiver oil, was synthesised by reaction of (32) with LiR_2Cu. The undesired epimer (34) was largely suppressed by using the heterocuprate $Li[MeCuBr].(Bu^i{}_2NH)_2$. The reaction is proposed to proceed via the intermediate (35) [47]. In a study of transition metal catalysed reactions of isophorones with $LiAlMe_4$, $Cu(acac)_2$ was found to be a very much less efficient catalyst than $Ni(acac)_2$. With $AlMe_3$, $Cu(acac)_2$ was more efficient than $Ni(acac)_2$, producing 85% of the 1,4-addition product (36) with isophorone and 2-cyclohexenone [48].

The reaction of dibromostilbene (37) with excess $LiMe_2Cu$ produced the mixture (38) + (39). Evidence supported the reaction mechanism outlined in scheme 4 for the formation of the dimer (39) [49]. Treatment of



(32) (ratio 5 : 1) (34)



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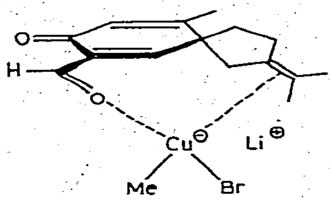

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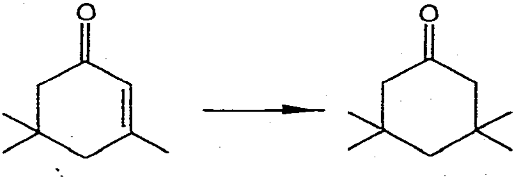
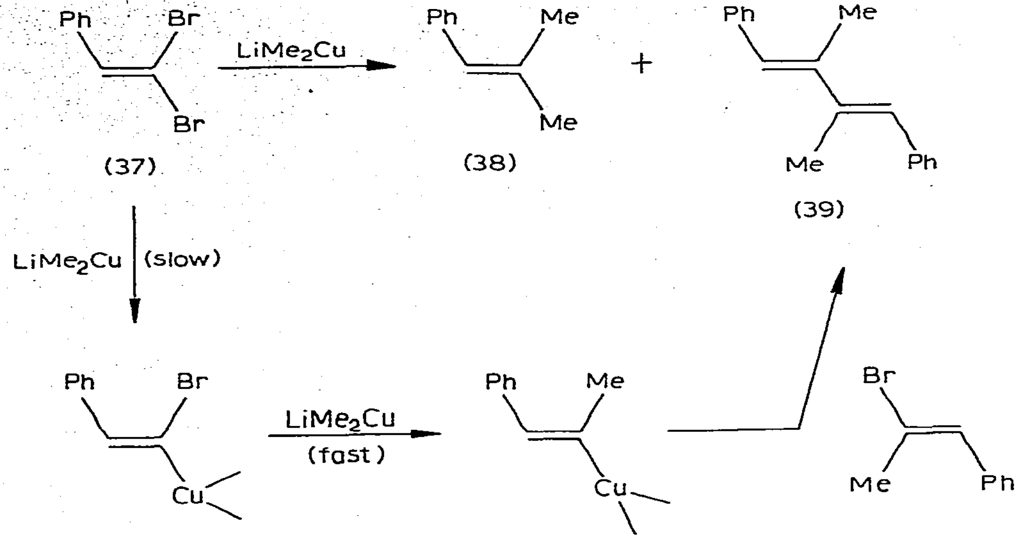
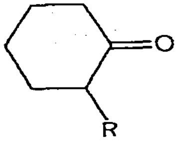


(36)

1-pyrrolidino-6-chlorocyclohexene with LiR_2Cu gave (40) [50]. (E)-MeCH=CHCl was reacted sequentially in ether with Li(containing 1% Na) at 13° and CuI at −78° to give $[(E)\text{-}MeCH=CH]_2CuLi$, which on addition of $Me(CH_2)_7I$ at −35° in the presence of $(Me_2N)_3PO$ formed $MeCH=CH(CH_2)_7Me$ in 90% yield (96% E- and 4% Z-isomer) [51]. The α-(41) and γ-(42)-allylated products were obtained from $CH_2=CHCH_2Br$ and the copper dienolate (43) in a 44:56 ratio. Corresponding reactions with (Z)-$CHD=CHCH_2Br$ establish that γ-attack is accompanied by complete allylic transposition of the allyl group [52]. Iodovinyls were alkylated by organomagnesium or lithium compounds in the presence of CuI with retention of configuration [53]. $CH_2=CRCH_2Cl$ (R=H,Me)



(Scheme 4)



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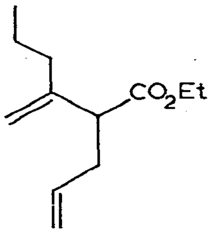

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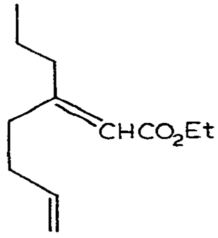

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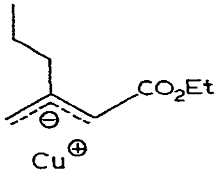
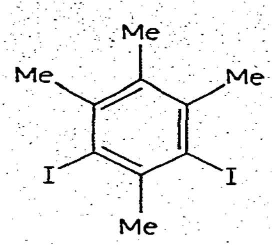


(43)

underwent halogen exchange with excess aq. HX(X=Br,I) at 44-80° in the presence of Cu_2Cl_2 to give the corresponding CH_2=$CRCH_2X$ in 72-90% yield [54]. A complete replacement of iodide groups by CN in (44) and (45) with CuCN has been effected in hexamethylphosphoric triamide [55]. Kinetic evidence indicated the intermediacy of an arylcopper in the substitution of iodide by chloride when an aryl iodide was treated with CuCl in refluxing DMF *e.g.* ArI + CuCl → [ArCuClI] → ArCl + CuI [56].



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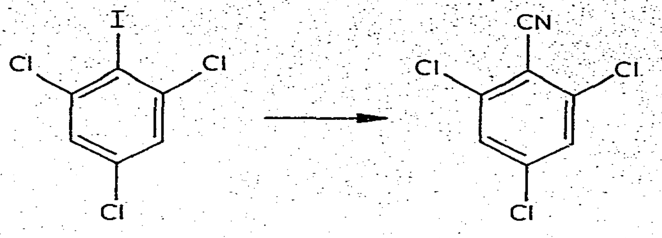
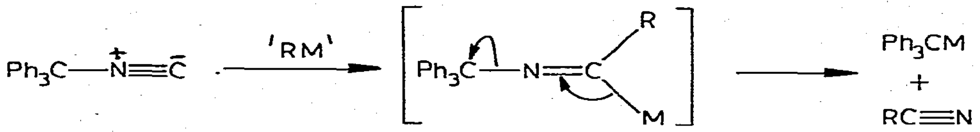
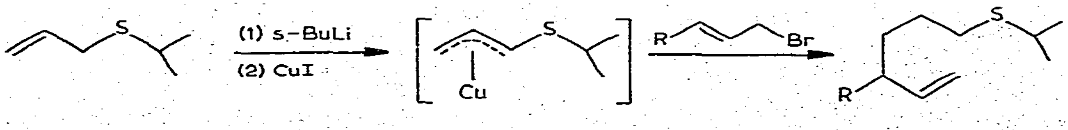


(45)

Heterogeneous reactions between alcohols or phenols and methylcopper have given copper(I) alkoxides, which are useful reagents for the formation of ethers by displacement of halide from organic halides. Thermal decomposition of primary alkoxycopper(I) generates intermediate alkoxy radicals, whereas with secondary alkoxycopper(I) reagents either a free radical process or a mechanism involving a copper hydride appears to operate [57]. Only moderate yields of cyanides were obtained from LiR_2Cu reactions with trityl isonitrile (scheme 5) [58]. Isopropyl thioallylcopper, generated by the successive actions of *sec*-butyllithium and cuprous iodide on allyl isopropyl sulphide, added allyl bromides exclusively at the carbon atom γ to sulphur, producing products of the type (46) (scheme 6) [59]. R-CH=CR'CH=CHX(R=H,



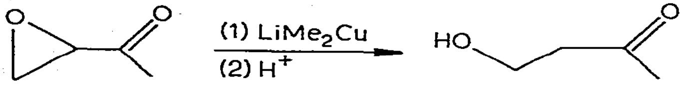
(Scheme 5)



(Scheme 6)

(46)

Me,Ph; R'=H,Me; X=PhS,Ph) were prepared in 23-80% yield (via a 1,2-elimination reaction of OAc and PhS groups) by treating RCH=CR'CH(OAc)CHXSPh with LiR^2_2Cu (R^2=Me,Bu) in ether at 0 to -35° for 1 - 1.5h. [60] Non-alkylative production of α,β-epoxy-ketones to the corresponding β-hydroxy-ketones (47) using two equivalents of $LiMe_2Cu$ was complete within 5 min at 0°.

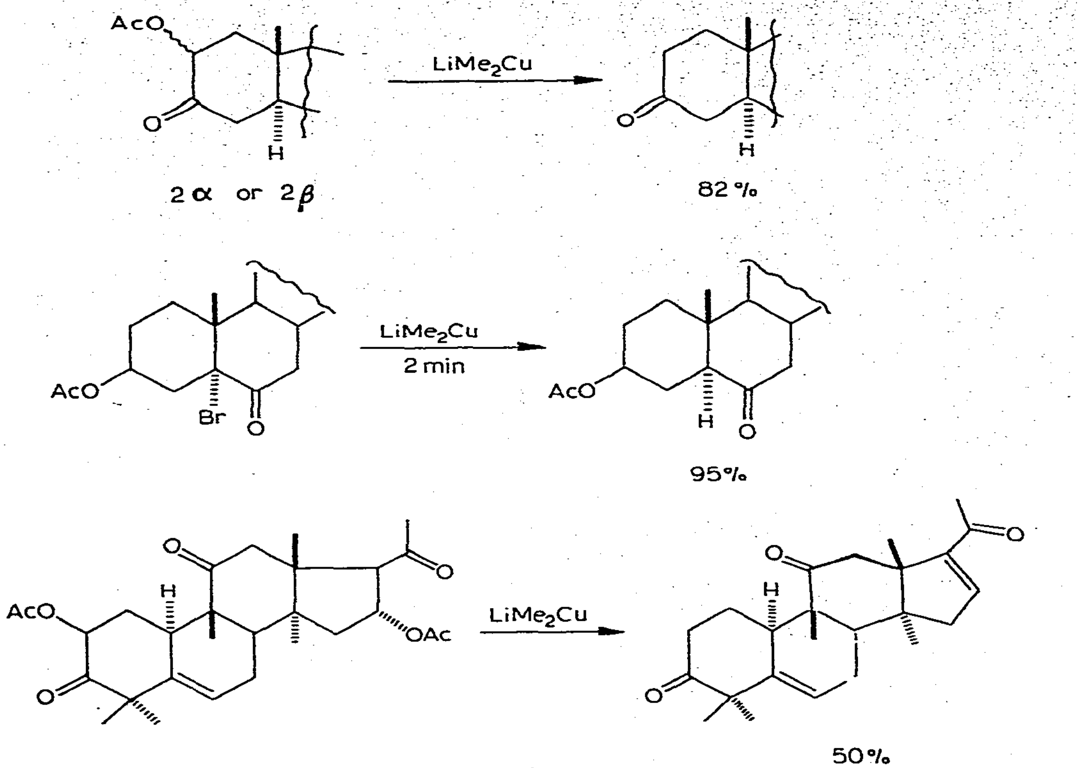


(47)

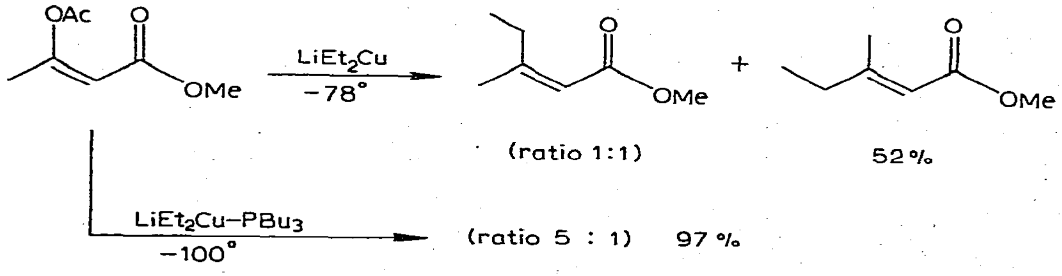
The cuprate is a better reagent than Li/NH_3 as the reaction can be carried out in the presence of unprotected carbonyl groups [61]. This reaction has been extended to include the reductive elimination of acetoxy - and halo-substituents adjacent to carbonyls, and proved to be viable for polyfunctional substrates (scheme 7) [62]. A dramatic increase in both the overall yield and the stereoselectivity of the reaction represented in scheme 8 was brought about by complexing the reagent with PBu_3 and dropping the temperature from -78° to -100° [63].

2. *General catalytic reactions*

A review on transition metal-carbon σ-bond fission contains references to Cu,Ag and Au complexes [64]. Ethyl geranate was synthesised in 99% yield by treating $Me_2C{=}CHCH_2CH_2C(SPh){=}CHCO_2Et$ with MeMgI and CuI [65]. $CuCl_2$ was used as a cocatalyst in the preparation of allylpalladium chloride dimers from *cis*- and *trans*-geranylacetone [66]. Group IB metal salts in alkylpolyamine solvents catalyse the homogeneous hydrogenation of nitroalkanes to oximes in good yield. An initial hydride, formed from the heterolytic splitting of H_2, is postulated as an intermediate [67].



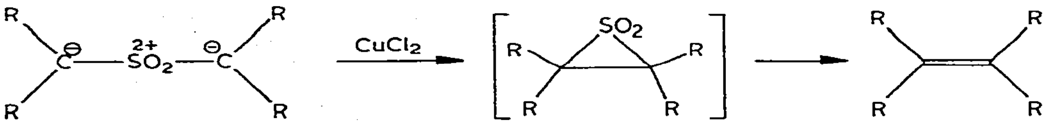
(Scheme 7)



(Scheme 8)

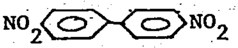
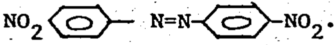
ClCHMeCH=CH$_2$ was isomerised to MeCH=CHCH$_2$Cl in dioxane at 25° with; (i) Cu(OAc)$_2$ within 150h or (ii) Cu(acac)$_2$ or CuCl$_2$ within 100h [68].

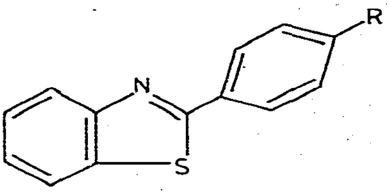
PdCl$_2$-CuCl$_2$ in acetic acid catalysed the rearrangement of the *endo*- and *exo*-isomers of 5,6-(*o*-phenylene)- and the unrearrangement of 5,6-(1,8-naphthylene)norborn-2-ene. For the latter, an alkene-Cu intermediate is proposed and the addition of copper salts to the reaction solution tended to depress carbonium ion formation [69]. Small amounts of Cu(II) halides, added to reaction mixtures of cyclohexanones and steroidal ketones in ethylene glycol, produced the corresponding acetals. With large amounts of $CuCl_2$, α-haloacetals were formed [70]. Compounds containing labile Hg-C bonds, *e.g.* $Hg(CH_2COR)_2$ (R=H,alkyl), react with LCuH[L=$(Me_2N)_3P$] to form Hg, AcR and $LCuCH_2COR$. The organocopper complex and CH_2=$CHCH_2Br$ gave Cu_2Br_2, Me_2CHBr, 88% CH_2=$CHCH_2CH_2CHO$ and CH_2=$CHCH_2PO(OCHMe_2)_2$ [71]. A study of the aldol condensation has concluded that a Claison-Schmidt type condensation is specifically catalysed by Cu^{2+} ions [72]. Sulphonyl-1,3-dianions were oxidised to olefins by the addition of 4-5 mol. equivalents of $CuCl_2$. The mechanism was not elucidated but presumed to proceed via a thiirane-S-S-dioxide intermediate (Scheme 9) [73]. The ratio of the products formed by oxidative decarboxylation of $AcO(CH_2)_nCHEtCO_2H$ (n=2,3), initiated by $Pb(OAc)_4$ and Cu (II) salts, was not affected by varying the copper ligands [74]. $RC{\equiv}CCO_2H$ ($R=H,CO_2H$) was decarboxylated in up to 80% yields by CuCl in nitrile solvents [75].



(Scheme 9)

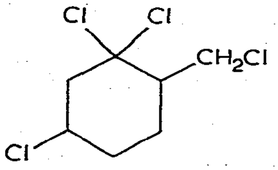
The Ullmann ether condensations have been reviewed [76]. The role of the complexes of diphenylmethanimine (=L) with copper chlorides, *i.e.*

CuLCl, CuL_2Cl,$CuCl_2L$ and $CuCl_2L_2$, in the oxidative coupling of L has been studied. The effective intermediate was found to be CuClL and the effect of oxygen on the reaction was noted [77]. When MeI was used as a radical trap in the reaction of p-$NO_2C_6H_4N_2^+BF_4^-$ with $[Cu(MeCN)_4]ClO_4$, p-$IC_6H_4NO_2$ was formed as well as  and . From a study of this reaction the mechanism was postulated to occur via aryl radical addition to Cu(I) followed by reaction of the resultant arylCu(II) intermediate with another aryl radical to produce diarylCu (III) species. This can now form biaryls in a reductive elimination step or be reduced by Cu(I) to diarylCu(II), which in turn, can be irreversibly reduced to organocopper(I) compounds capable of combining with diazonium ions to produce azoarene [78]. Benzothiazole was treated with p-$IC_6H_4NO_2$ in the presence of Cu_2O producing (48) in 72% yield. Also prepared were (48) (R=MeO) and 2,2'-dibenzothiazole [79]. The reaction of p-Tos-CR with R'MgBr in THF over Li_2CuCl_4 at -78° gave good yields of RR'(R=*e.g.* Et,Ph,octyl cyclohexyl; R'=Et,CMe_3,Ph,cyclohexyl) on slowly warming to RT [80]. A simple and convenient method for the preparation of vicinal alkoxythiocyano- and alkoxyiodoalkanes from the reactions of olefins with Cu(II) in alcohols has appeared [81]. The two new products E,Z-$PhCH=C(CO_2H)C(CO_2H)=CHPh$ and the Z,Z-compound were prepared in



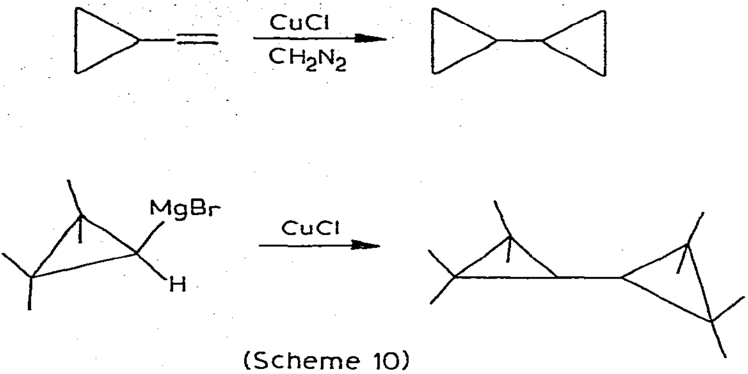
R = NO_2

(48)



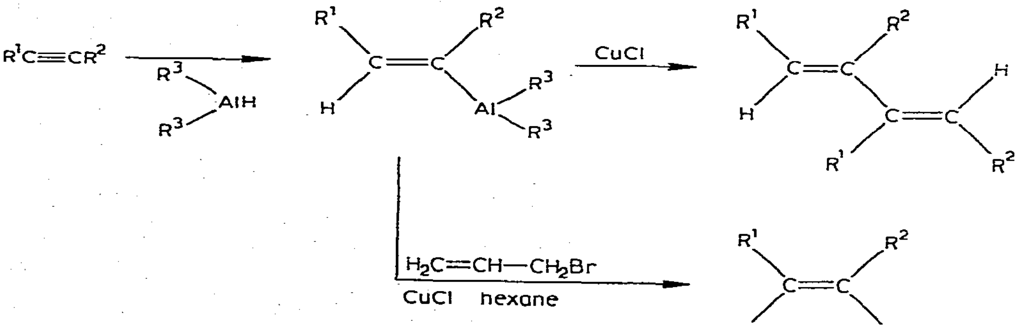
(49)

92% yield by the oxidative coupling of *trans*-PhCH=C(CO_2H)HgCl with Li_2PdCl_4-$CuCl_2$ [82]. Some of the bicyclopropanes used in the study on rotational isomerisation were obtained by scheme 10, as this method gave

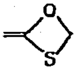


(Scheme 10)

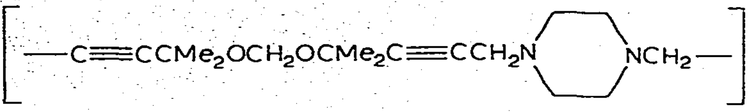
the highest yields [83]. The reaction of $CH_2=CH(CH_2)_2CHClCH_2CCl_3$ and $CuCl_2$ in MeCN containing Et_3N-HCl gave *cis*- and *trans*-(49) via radical intermediates. Other cyclisations were reported [84]. Isomerically pure *trans*-1,4-dienes were obtained by a reaction sequence given in scheme 11[85].



(Scheme 11)

The oligomerisations of acetylenes in the presence of transition metal compounds is reviewed [86]. Propargyl and allyl halides have been condensed with terminal alkynes in the presence of Cu(I) salts. The role of Cu^+ and the influence of the leaving group are discussed [87]. Unsymmetrically coupled products were obtained from reactions of RCu and $R'C{\equiv}CCu$. With conjugated acetylenic acids and MeCu, similar products are obtained from decarboxylation followed by coupling [88]. $Cu(py)_5^{2+}$ species have been shown, by EPR, to occur in the homogenous phase oxidative couplings of $PhC{\equiv}CH$ catalysed by $Cu(py)_4(NO_3)_2$ [89]. Oxidative dimerisation of *trans*-$HOCMe_2CH{=}CHC{\equiv}CH$ with Cu_2Cl_2 and oxygen in pyridine yielded 84% of *trans*-*trans*-$HOCMe_2CH{=}CHC{\equiv}CC{\equiv}CCH{=}CHCMe_2OH$. Corresponding condensations of the *trans*-acetylene in the presence of Cu_2Cl_2 gave (i) *trans*-$HOCMe_2CH{=}CHC{\equiv}CC{\equiv}CCMe_2OH$ in ethanol and (ii) *trans*-$HOCMe_2CH{=}CHC{\equiv}CCH_2NEt_2$ with HCHO and Et_2NH in benzene [90]. The linear acetylenic polyamines, *e.g.* (50), were prepared by a Mannich reaction of dimethylethynylcarbinolformal, piperazine and HCHO, using Cu_2Cl_2 as catalyst [91]. Treatment of *m*-$IC_6H_4C{\equiv}CH$ with CuCl in aq. NH_3 gave 39% of *m*-$IC_6H_4C{\equiv}CCu$, which on Stephens-Castro coupling gave 5% of (51) [92]. The diacetal (52) ($R'{=}(OMe)_2, R{=}(MeO)_2CH$) and the acetylene (53) were prepared from (52) (R'= ) and $(MeO)_2CHC{\equiv}CCu$, and from the copper salt of 2-ethynylthiophene with 5-iodo-2-thiophene carboxaldehyde respectively [93].

The products $X'CH{=}CX''R$ were obtained from halogenation of $HC{\equiv}CR$ with CuX_2 ($X{=}X'{=}X''{=}Cl,Br$; $R{=}CN, CH{=}NOH$) and $CuCl_2$-$CuBr_2$ mixtures ($X'{=}Cl$, $X''{=}Br$; $R{=}CN$) [94]. Radical addition of $XCCl_3$ ($X{=}Cl,Br$) to $CH_2{=}CHCN$ and CuX_2 gave high yields of Cl_3CCH_2CHXCN [95]. Mono- and dihalogenations of α-tetralone and indanone with CuX_2($X{=}Cl,Br,SCN$) took from between 30–50 min and up to several hours respectively [96]. Addition of HX($X{=}Br,I$) to RCH_2Cl ($R{=}CH_2{=}CH$, $CH_2{=}CMe$, $MeCCl{=}CH$) using Cu_2Cl_2 as catalyst gave



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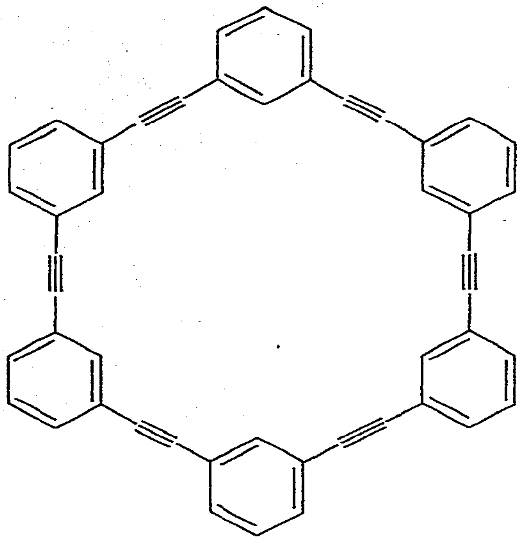

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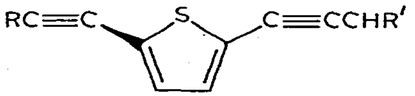

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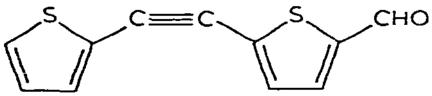
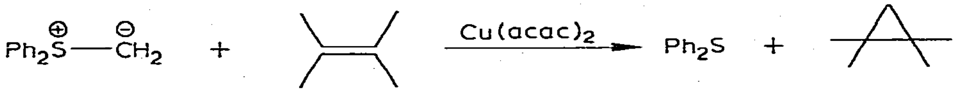


(53)

RCH$_2$X [97]. The kinetics of thermal reactions of CuCl$_2$ and styrene, cyclohexene and but-2-ene in the dark have been studied. The exclusive formation of dichlorides and the total nonstereospecificity indicated a chloroalkyl intermediate [98]. A series of papers on the oxidative halogenation [102] and the kinetics of oxidative chlorinations and hydrochlorinations of acetylenes in the presence of (i) copper salts and phosphines [103] (ii) copper and mercuric halides [104–105] has appeared. The intermediate ClCuCH=CHCl was postulated in one case [104]. $RCCl_2X$($R=Cl, X=Br$; $R=MeO_2C, EtO_2C, X=Cl$) underwent heterolytic addition to $R'CH=CR^2C\equiv CR^3$ ($R'=R^3=H, R^2=H, Me$; $R'=R^2=(CH_2)_4, R^3=H$; $R'=R^2=H, R^3=CMe_2OH, CMe_2OMe$, CMeEtOH, CMeBuOH, CMe_2Cl, CMe_2OAc) in ROH (R=Me,Et) containing Cu_2O [106].

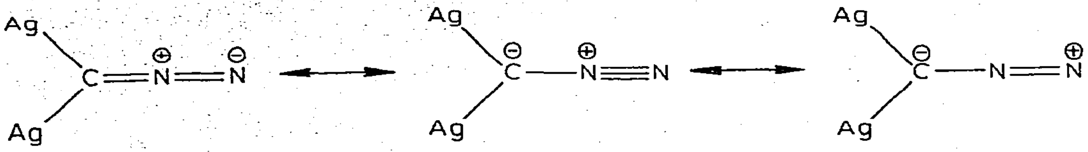
The new copper complex of the polyoxime $\{(CH_2)_{1\cdot6}[C(=NOH)C(=NOH)]_{0\cdot8}[C(=O)]_{0\cdot2}\}$ catalyses a Michael type addition of acrolein and an alcohol, to give exclusively β-alkoxypropionaldehyde. The copper complex, after treatment with hydrazine hydrate, absorbs O_2 and CO [99]. Copper salts catalyse the reaction of thiophene with diisopropyl peroxydicarbonate, forming thienyl isopropyl carbonates [100], and the cyclopropanation of olefins by sulphur ylides [101] (scheme 12). It was suggested that the latter may be a more readily accessible route to cyclopropanes than diazomethane reactions[101].



(Scheme 12)

III Silver–carbon bonds

The formation and thermal decomposition of several primary and secondary $alkylAgPBu_3$ complexes has been studied. For $BuAgPBu_3$ the evidence points to a process in which C-C bond formation is concerted with Ag-C bond breaking. For *sec*-$BuAgPBu_3$ the products point to a possible Ag-H intermediate [107]. Addition of AgOAc in pyridine to an excess of CH_2N_2 in ether at -5° rapidly gave a yellow orange precipitate of Ag_2CN_2py. Pyridine was readily lost *in vacuo* at 25° to produce a crimson complex of formulation (54) [108].

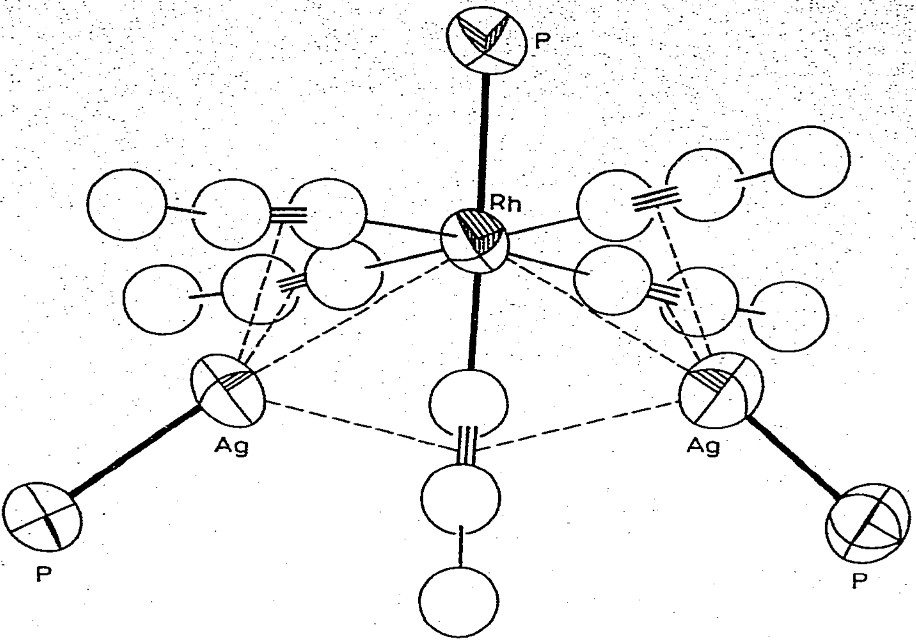


(54)

AgCN reacts with KSCN to form K[Ag(CN)(SCN)] and $K_2[Ag(CN)(SCN)_2]$, which were characterised by X-ray analysis [109]. Alkyl halides and $Me_4N[Ag(CN)_2]$ gave the corresponding alkyl isocyanides in quantitative yields [110].

Treatment of $RhCl(PPh_3)_3$ with $Ag(C{\equiv}CC_6F_5)$ afforded $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$, the structure of which has been resolved crystallographically (55). The rhodium atom is essentially octahedral and the Ag essentially tetrahedral. Each Ag atom is linked asymmetrically to three acetylene bonds. Main mean parameters observed were; Rh-P 2.34Å, Rh-C 2.25Å, C≡C 1.19-1.22Å. Ag-C bond distances to nearest carbon of the acetylene lie between 2·34 - 2·64Å and to farthest 2.60-3.13Å [111].

Thermodynamic data for the formation of complexes of Ag^+ and Cu^+ with a series of liquid monoolefins has been discussed with regard to the influence of structural parameters of the olefins on the data. This influence may often be marked when comparing log K values owing to marked changes in $\Delta S°$ values. Opposing trends observed in the thermodynamic data for desolvation may explain contradictions observed in the literature with increasing alkyl substitution [112]. Formation constants for Ag(I) complexes of several olefinic alcohols have been measured and values for some of the olefins support the chelate structure (56) in solution [113]. The silver salt of trifluoromethanesulphonic acid forms similar complexes with aromatics to those of copper [114]. The crystal structures of naphthalene-[115] (57) and anthracene-[116]-$(AgClO_4)_4$ have been completed. These structures are



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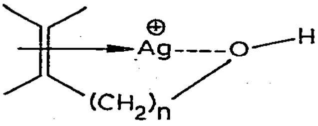
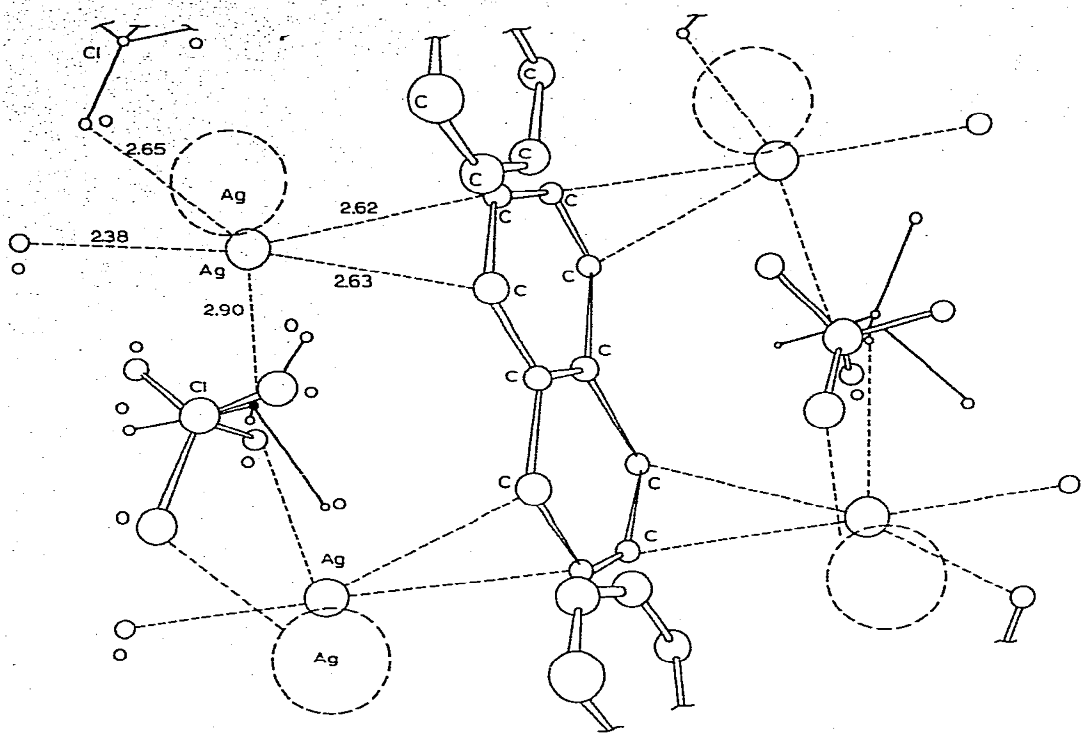


(56)

very similar and comprise of parallel sheets in the order -aromatic-$AgClO_4$-H_2O-H_2O-$AgClO_4$-aromatic-. The sheets are made up of two $AgClO_4$ chains held together by weak Ag-O interactions and Van Der Waal's forces. Each naphthalene is associated with four different hydrated Ag ions with equal Ag-C bonds of 2.61Å, and the compounds are best described as arene clathrates. For $(CF_3COOAg)_2C_6H_6$ the molecule comprises of parallel linear chains of metal atoms with alternating short and long distances of ~2.9 and 6·8Å respectively. Novel features of this structure are; planar 3-coordinate

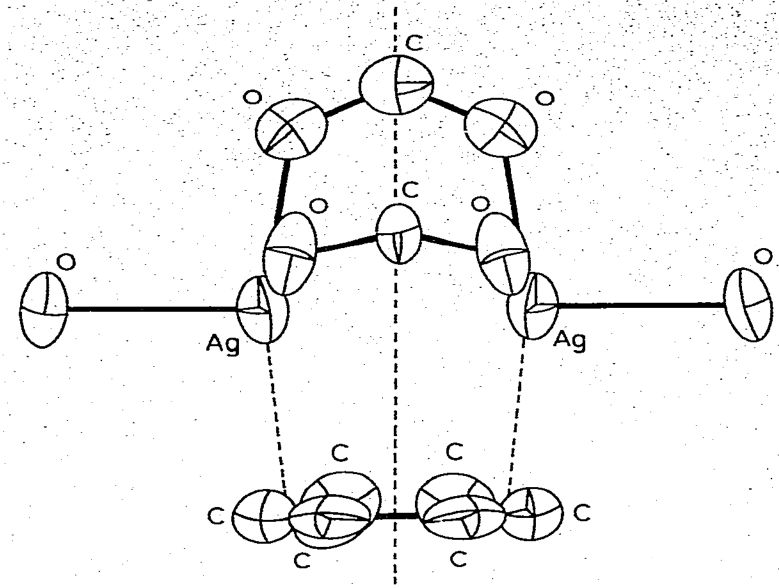


(57)

oxygen atoms and a silver atom; two different geometric configurations for the Ag ion in the same structure, and bridging benzene ligands. (58–59) [117].

IV Catalysis by silver salts

A series of papers has appeared on the Ag^+ catalysed rearrangement of strained carbon-carbon bonds. From studies [118-120] on effects of structural changes on the rearrangement mechanism in the $AgClO_4$ promoted isomerisation of tricyclo$[4.1.0.0^{2,7}]$heptanes it was shown that, with C_1 functionalised, the 1,2-hydride and alkyl shift to an argento carbonium ion centre, from suitable constructed side chains, competes favourably with migration of



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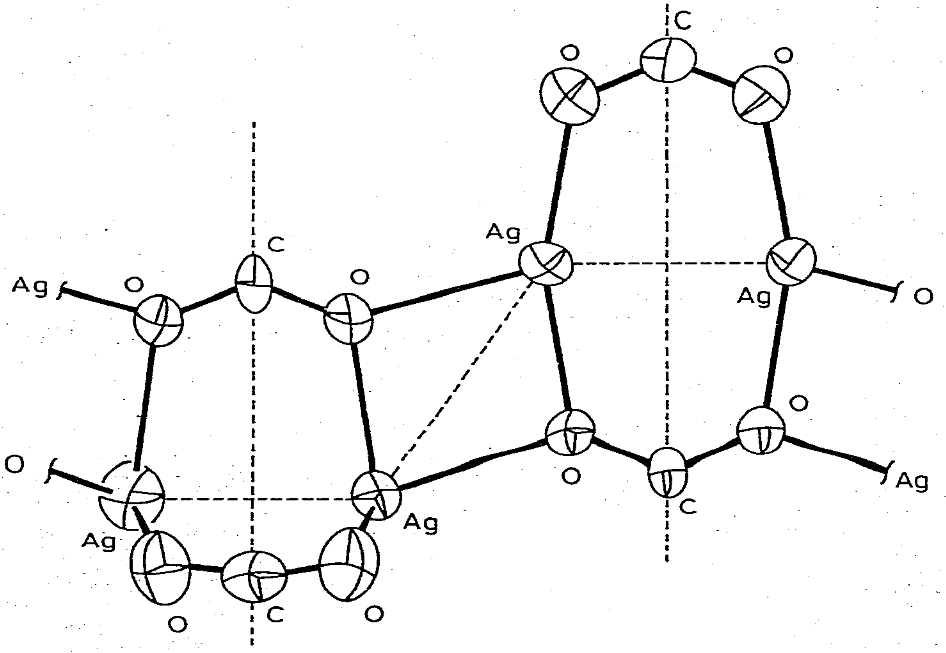
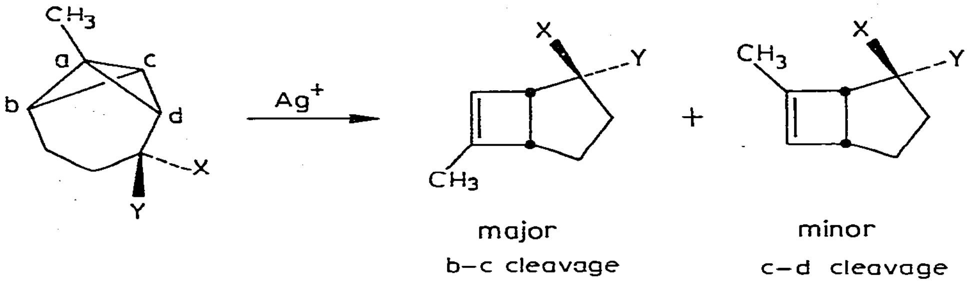
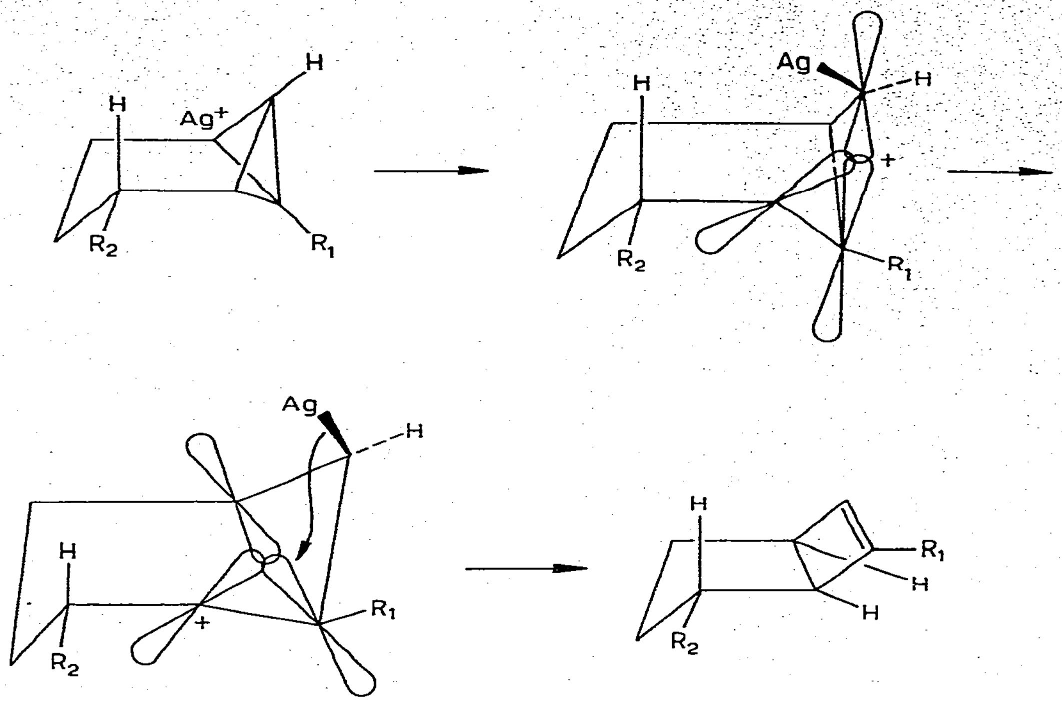


(59)

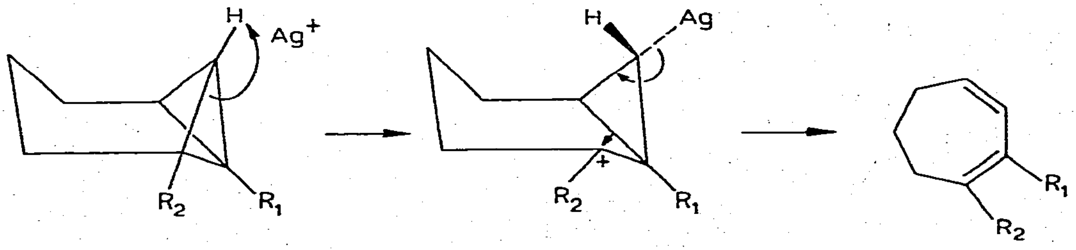
the allylic cyclohexene hydrogen [118]. The mechanistic diversion from the exclusive α-rearrangement to the β, γ or δ pathways is further partitioned as the bulk of the substituent at C_1 is increased, with the ensuing stereospecific formation of bicyclo[3.2.0]hept-6-enes (γ-pathway). The consistency of isomeric product distribution from isomeric tricycloheptanes indicated that a secondary influence via conformational effects, from substituent effects at the 3-position, was in operation, and served to demonstrate the the regioselectivity of the isomerisations (scheme 13) [119]. The mechanism of the γ-rearrangement is consistent with a bimolecular reaction between Ag^+ and the strained ring involving competitive edge attack at bonds b–c or c–d and ultimate 1,2-carbon shift (scheme 14) [120]. To account for the α-rearrangement, an attack by Ag^+ above the plane defined by the two edge-bonds flanking C_7 was postulated [120] (scheme 15). The rearrangement of the 9,10-diazobasketanes (60) by Ag^+ to 9,10-diazosnoutanes was sensitive to the nature of R and position of substitution, particularly for R=CN [121]. The reaction of Ag^+ with (61) gave 1,3-cyclohexadiene [122], and with bicyclic organoboranes to give a mixture of monocyclic ketone and *cis*-monocyclic olefin. In the latter case a diradical intermediate is proposed (scheme 16) [123]. An ionic mechanism appears to operate for the Ag^+ isomerisations



(Scheme 13)



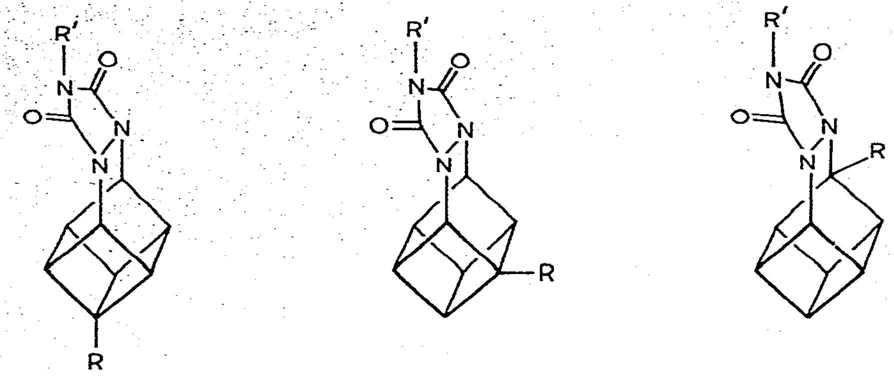
(Scheme 14)



R_2 = electron donating

(Scheme 15)

of quadricyclanes (scheme 17). The study, which compared the various effects of Rh(I), Pd(II) and Ag(I), showed that with Ag(I) in aprotic solvents in all cases the sole product is (62). In MeOH or protic solvents only Ag(I)



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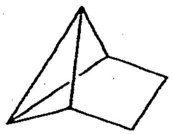

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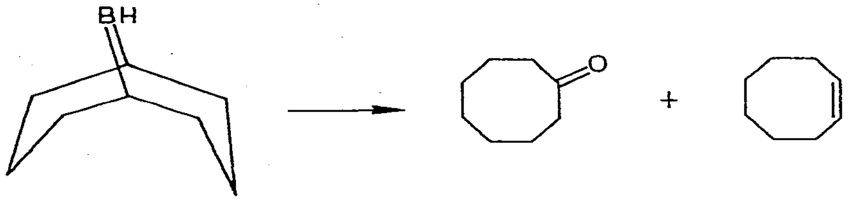
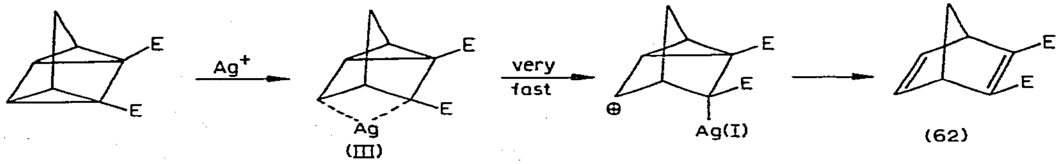
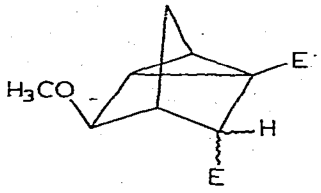


(Scheme 16)



(Scheme 17)

gave a mixture of isomeric products of (63) [124]. The Ag(I) promoted alkoxyl group ionisation process in neutral solvents of negligible nucleophilicity has been studied. Mechanistic aspects (scheme 18) and synthetic applications (scheme 19) were discussed. Ag^+ in dry benzene was found to



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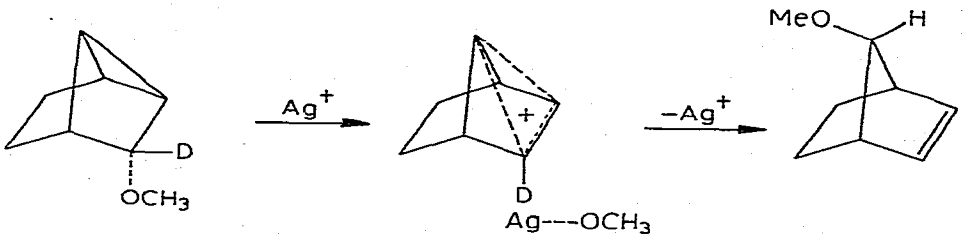
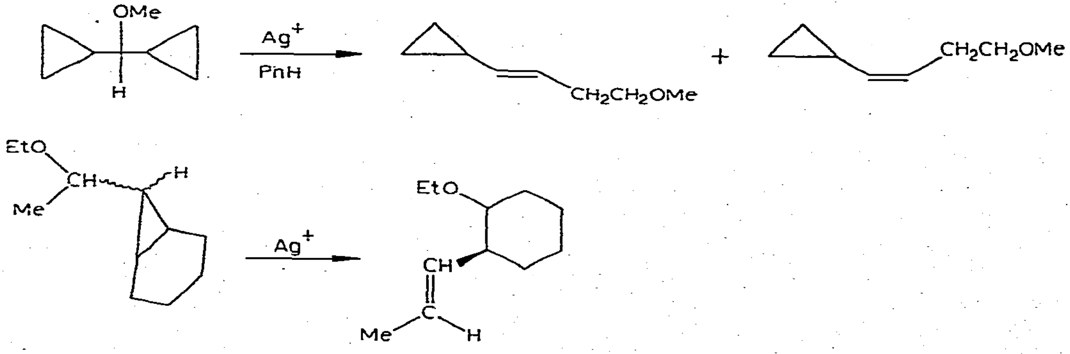
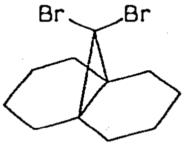


(Scheme 18)



(Scheme 19)

be an exceedingly mild method for removal of benzhydryl blocking groups in benzhydryl ethers [125]. From the majority of products obtained from the silver ion assisted solvolysis of the compounds (64–66), an intermediate cyclopropyl cation (67) or a partially opened species (68) were



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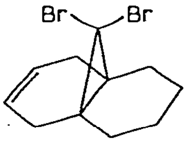

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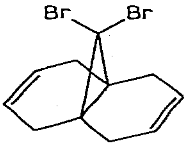

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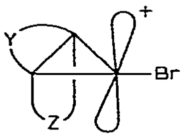
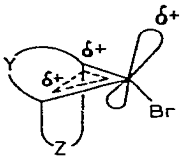


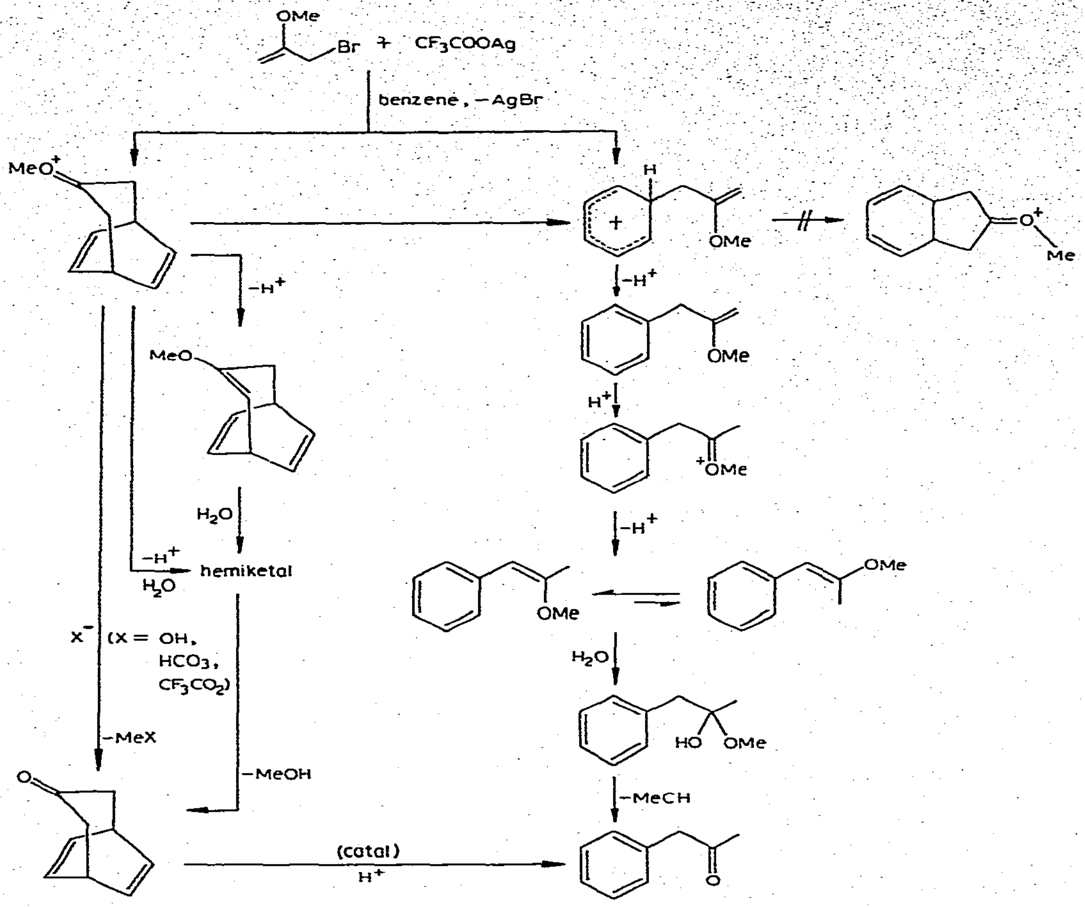
(67)



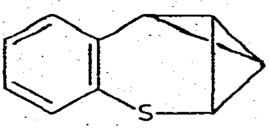
(68)

proposed [126]. The 2-methoxyallyl cation generated from the bromide by $[Ag(CF_3COO)]_x$ has been shown to react under remarkably mild conditions with benzene, toluene p-xylene and mesitylene to produce a range of new bicyclics (scheme 20) [127]. The heptene (69) gave (70) with Ag(I) salts [128].

The use of benzene as solvent for the substitution reactions of AgX ($X=ClO_4$, Triflate) with alkyl iodides inhibited isomerisation and was used as an effective selective synthetic procedure for forming simple primary perchlorates or triflates [129]. $AgBF_4$ facilitates the DMSO oxidations of alkyl halides by promoting the removal of the halide as insoluble AgX. The route was found to be a convenient technique for the conversion of a variety of organic halides to the corresponding carbonyl compounds under



(Scheme 20)



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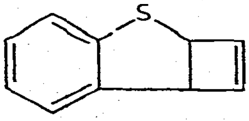
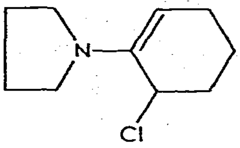


(70)

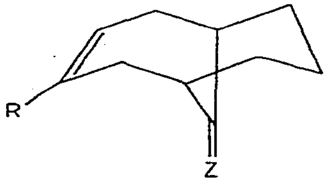
mild conditions [130]. AgO in acetone solutions is an excellent catalyst for highly selective Anti-Markownikov additions, giving straight chain methyl alkyl ketones in 73-83% yields via free radical pathways [131].

Direct evidence that complexation of a carbon bonded halogen with Ag^+ can be followed by a reaction in which the halogen migrates from carbon to carbon has been obtained. Thus 3-chlorobut-1-ene with $AgClO_4$ in MeCN gave, as well as the usual products, a mixture of *cis*- and *trans*-but-2-enyl chlorides [132]. (71) underwent cycloadditions in CH_2Cl_2 at -60° with various 1,3-dienes in the presence of $AgBF_4$ to produce (72-76) [133].

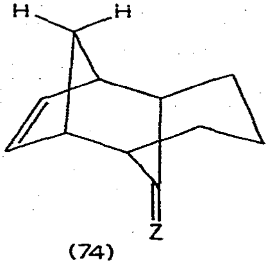


(71)

$Z = \overset{+}{N}(CH_2)_4 BF_4^-$



(72) R = H
(73) R = Me



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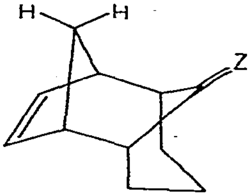

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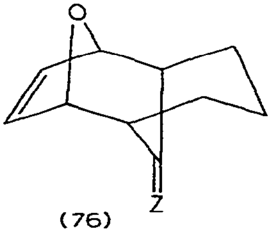
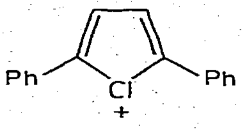


(76)

The Ag^+ assisted solvolysis of (E,Z) and (Z,Z)-PhCCl=CHCH=CBrPh in AcOH and the (E,Z) isomer in Ac_2O gave (E,Z) and (Z,Z)-PhCCl=CHCHCPhOAc and (Z)-PhCCl=CHC≡CPh respectively. The intermediate chloronium ion (77) is postulated [134]. Cyclohexene was treated with equimolar amounts of

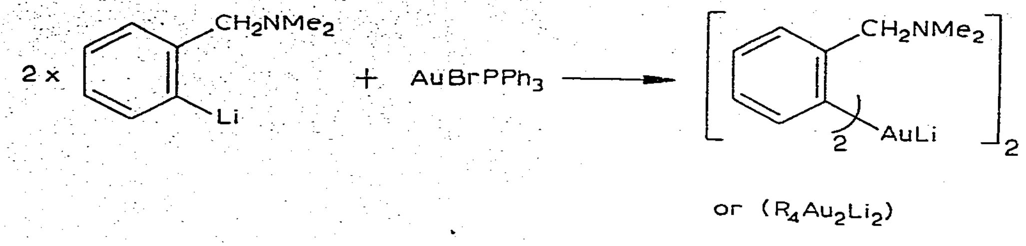


(77)

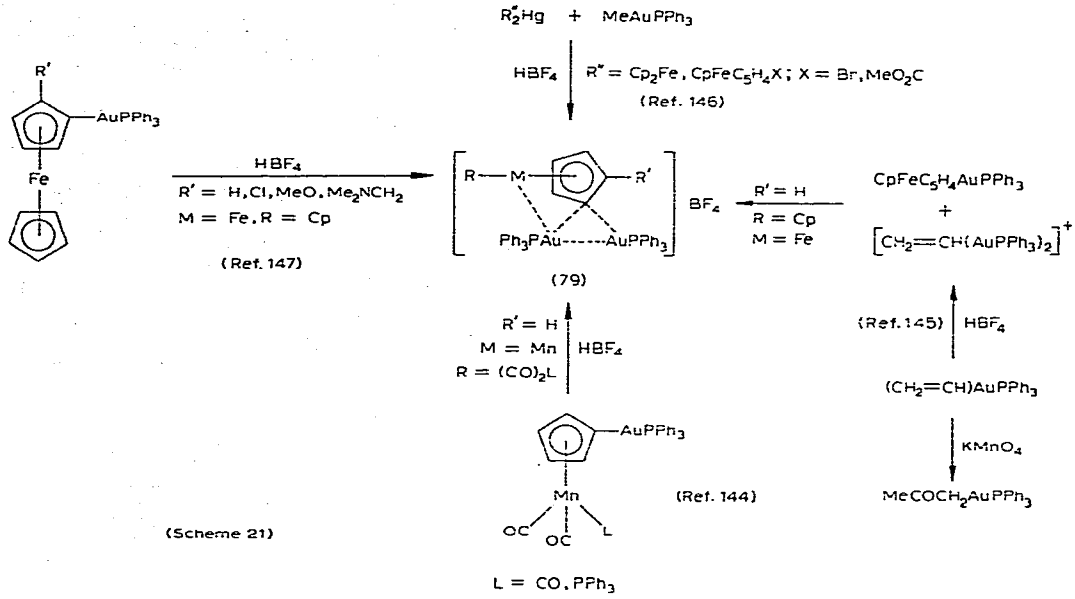
$C_6H_5CH_2OAgI$ and AcOAgX (X=Br,I) in anhydrous solvents to give *trans*-1,2-cyclohexylene esters, and in $AcOH-H_2O$ to give diols of predominately the *cis*-isomer [135]. The reaction of $ONCF_2CF_2COX$ (X=Cl) with NH_3,NaF,AgCN and NaN_3 gave the product with X=NH_2,F and CN (48-82%) and $ONCF_2CF_2NCO$ (32%) [136]. 1-(N-alkylformimidoyl)imidazoles and -triazoles were prepared by the AgCl-catalysed insertion of alkyl isonitriles into the N-H bond of the imidazole and triazole respectively [137].

V Gold-carbon bonds

A review with 48 refs. on the preparation and reactions of organogold complexes has appeared [138]. The reaction of $AuBrPPh_3$ with Me_2CO or $MeCOCH_2COMe$ in the presence of Ag_2O gave $MeCOCH_2AuPPh_3$ and $MeCOCH(AuPPh_3)COMe$ [139]. Choro(1,4-oxathian)gold(I) in a solution of MeCN, 2,6-dimethylpyridine and Et_3N under argon at -10°, reacted with ketene to form $Au_2C_2O.(2,6\text{-Mepy})$, which gave Au_2C_2O on heating to 25°. Au_2C_2O and PhC≡CH gave [AuC≡CPh] and acetanilide [140]. The arylgold species $R_4N[R'AuX_3]$ (R'=Ph,p-ClC_6H_4,p-BrC_6H_4,p-$NO_2C_6H_4$) were obtained from interactions of phenyl or substituted phenylhydrazine hydrochloride and $R_4N[AuX_4]$ (R=Et,*n*-Bu;X=Cl,Br). A nitrene intermediate, in which nucleophilic attack by the carbon atom bonded to the nitrogen on to the gold(III) species, is proposed [141]. Treatment of $Ph_2C{=}CHMgBr$ with $AuClPPh_3$ in THF gave $Ph_2C{=}CHAuPPh_3$, which on addition of HBF_4 in Et_2O, produced $[Ph_2C^+CH(AuPPh_3)_2]BF_4^-$ [142]. Gold cluster compounds were obtained by scheme 21. Further reaction of (78) with CuBr gave $R_4Au_2Cu_2$ [143]. A series of papers on the unusual products obtained from protonation reactions with organogold complexes have appeared [144-148] and the structure of one of the products (79) (R=Cp,R'=H,M=Fe) has been determined [147,148]. The two new gold olefin complexes COTAuCl and $COTAu_2Cl_4$ were obtained from COT and $AuCl_3$ [149]. Displacement of CO from AuCOCl with 2,4,6-triphenylphosp

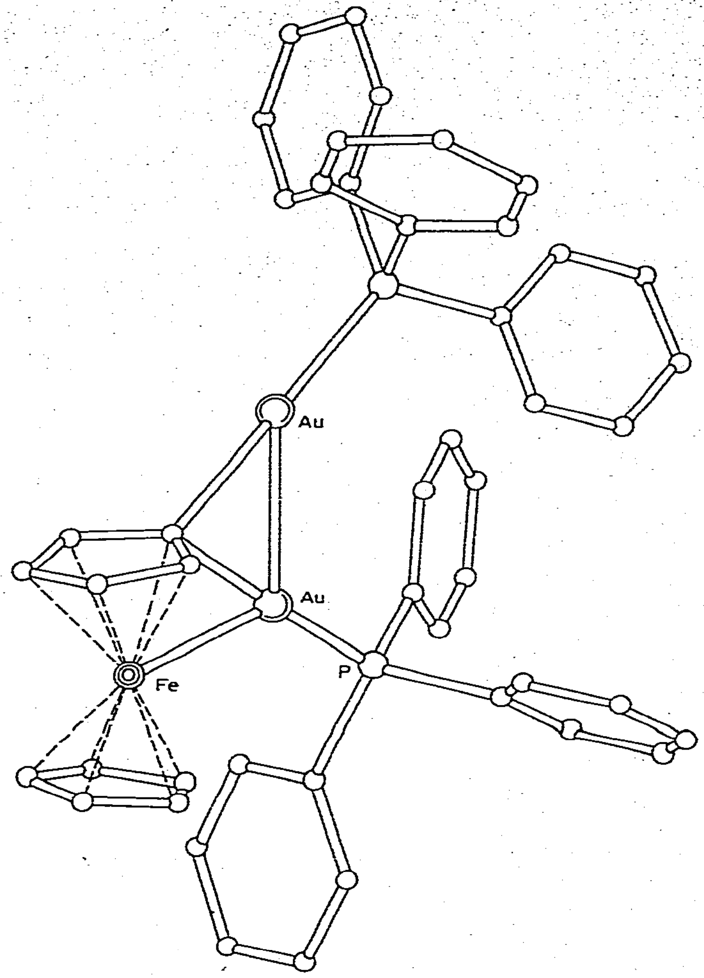


(78)

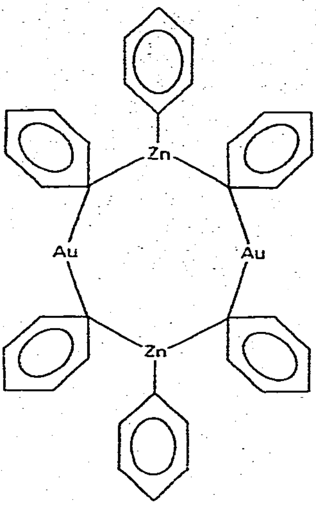


(Scheme 21)

habenzene or Ph_2Zn gave 1:1 complexes [150] and Ph_3AuZn (80) [151] respectively. Benzenethiol cleaved the metal-C bond in methylgold and methyl platinum by a free radical chain mechanism. A similar but slower reaction with methylgold(III) proceeds by a different mechanism presumably because Au(IV) would be involved in the radical process [152]. Alkyl isomerisation, *cis-trans*-rearrangement and reductive elimination reactions were observed with RMe_2AuPPh_3(R=Me,Et,Pr,Me_2CH,Me_3C,Me_2CHCH_2). Rates of alkyl isomerisation



(79)

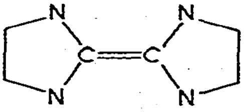


(80)

and reductive elimination of these complexes were retarded by PPh_3, indicating a dissociative mechanism. *cis-trans* Rearrangement was relatively unaffected by PPh_3 additions and a unimolecular process, possibly involving a tetrahedral gold(III) intermediate, was suggested [153]. Oxidative additions of $TlX'(C_6F_5)_2$ (X'=Br,I) to AuXL(X=Cl,Br,I; L=PPh_3,$AsPh_3$) gave $AuX(C_6F_5)_2L$. The products $AuX(C_6F_5)L$ (X=C_6F_5,Ph,NO_3,OAc,SCN,PPh_3) were also characterised [154]

Oxidative additions of MeI to MeAuL(L=PPh_3,PMe_3) follow a multistep mechanism for L=PPh_3 giving C_2H_6 and $IAuPPh_3$. The initial $Me_2AuIPPh_3$ formed exchanges further with MeI to give Me_3AuPPh_3, which undergoes reductive elimination to C_2H_6 and $MeAuPPh_3$. The more reactive gold complex (L=PMe_3) gives, however, a more stable Me_3AuPMe_3, which does not undergo reductive elimination. Instead a slow reaction with $AuIPMe_3$ and MeI occurs, producing $Me_2AuIPMe_3$ in high yields. Oxidative additions to other alkyl gold species were also studied [155].

Treatment of $AuClPPh_3$ with the electron rich olefin (81)(=L_2) gave the *bis*-carbene complex AuL_2PPh_3 [156]. The gold(III) anion $AuCl_4^-$ reacted with $HO(CH_2)_nNC$ (n=2,3) to give (82), which further reacted with the isocyanide to give the cation (83), isolated as the BPh_4 salt [157].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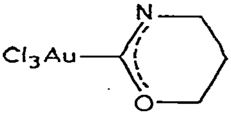
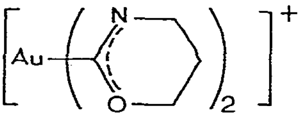
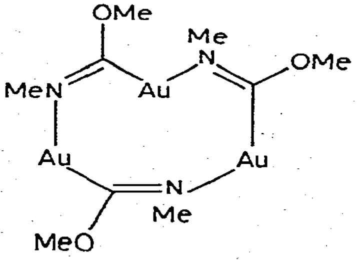
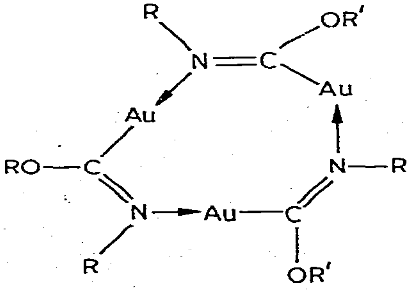

(82)


(83)

With isocyanides and amines, $AuCl_4^-$ produced the *bis*-carbene complex $Au[C(NRR')(NR'H)]_2^+$ (R=H,R'=Me; R=R'=Me). The cyclic product (84) is


(84)

formed from reactions of $AuClPPh_3$,MeNC and methanol, and undergoes cleavage by HCl to give [HNMe(MeO)C]AuCl. The carbenes $Au\{C(NHMe)_2\}_2^+$, $Au\{C(NHMe)NMe_2\}_2^+$ and {HNMe(MeO)C}AuCl yield HC(NMe)NHMe, $HC(NMe)N(Me)_2$ and HC(OMe)NMe respectively with CN^- in Me_2SO, whereas the diamidide MeN=CHNMeCH=NMe is the result of MeNC and $Au\{C(NHMe)_2\}_2^+$ reactions. These ligand displacement reactions establish carbene complexes as intermediates in the α-addition of protic nucleophiles with isocyanides [158]. The reaction of AuClL($L=Me_2S,PPh_3$) with an isocyanide and KOH in alcohol gave $[(RO)(R'N=)CAu]_3$, which was also obtained from the reversible deprotonation reactions of the carbene complexes [(RO)(R'NH)C]AuCl. The structure proposed for the trimer is (85) [159]. The organic product $(p\text{-}MeC_6H_4NH)_2CO$ is the result of stirring a 50% aq.Me_2CO solution of the carbene complex *trans*-$[\{(p\text{-}MeC_6H_4NH)_2C\}_2AuI_2]ClO_4$ in air [160].



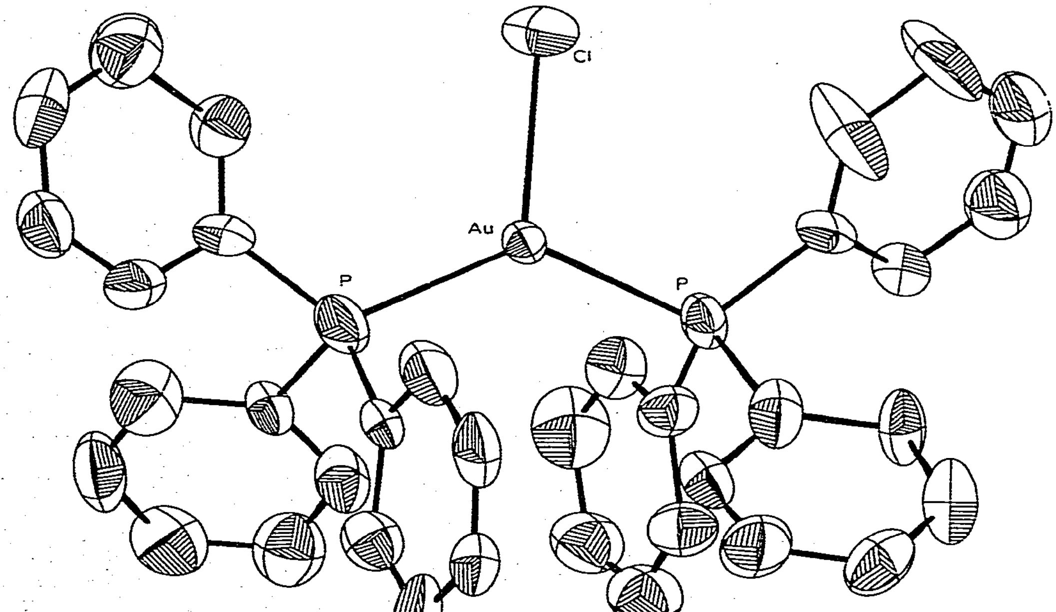
(85)

$R' = Me; R = Et, Me, CH_2Ph, C_6H_{11}, p\text{-}MeC_6H_4$

$R' = Me_2CH ; R = p\text{-}MeC_6H_4$

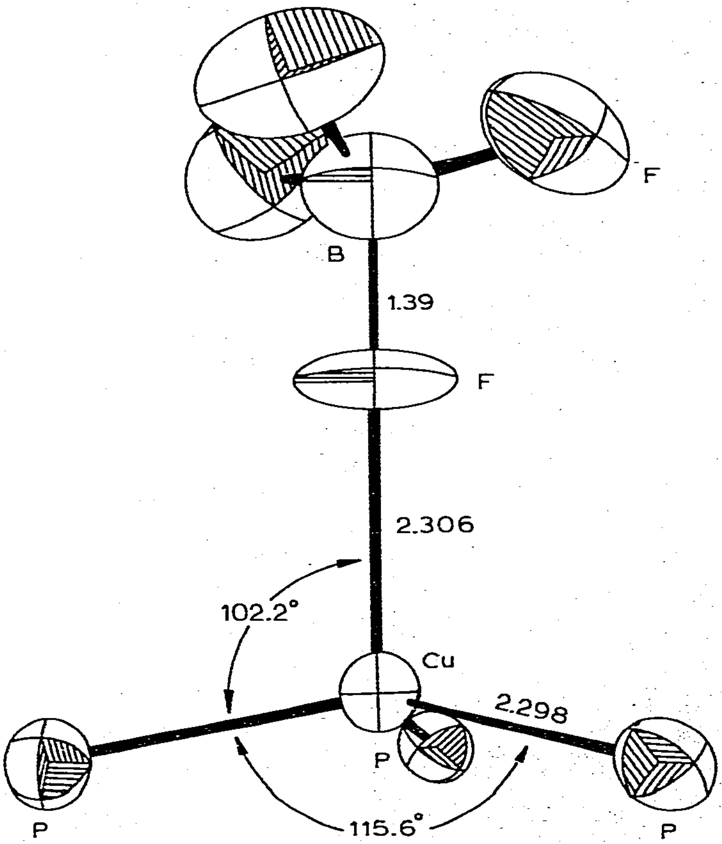
VI Complexes of general interest

A review, with 66 refs., of phosphine- and arsine-olefin complexes of Pd,Pt,Cu,Ag and Au has appeared [161]. The 1:1 adduct of $Cu(Hfacac)_2$ and PPh_3 undergoes structural isomerisation in which the PPh_3 ligand occupies an axial or basal coordination position [162]. The new phosphite-type complexes $\mathrm{AgCl\{P(OEt)Ph_2\}_2}$, AgClL [L=$\mathrm{P(OMe)Ph_2}$, $\mathrm{P(OR)Ph_2}$; R=Me,Et [163]], AuXL[X=Cl, L=$\mathrm{P(OEt)Ph_2}$ [163];X=Cl,Br,L=$\mathrm{P(OCH_2)_3CEt}$[164]], [AuLL'] $\mathrm{ClO_4}$[L=$\mathrm{P(OCH_2)_3CEt}$,L'=MeCN;L=L'=$\mathrm{P(OCH_2)_3CEt}$[164]], $\mathrm{[ML_4]ClO_4}$[M=Au,L=$\mathrm{P(OCH_2)_3CEt}$[164]; M=Cu,Ag,Au,L=$\mathrm{P(OR)_3}$[165]; $\mathrm{P(OR)_2Ph}$,$\mathrm{P(OR)Ph_2}$[166]; R=Me,Et] have been prepared by either ligand displacement reactions in polar solvents or by reaction with metal halide or olefin complex in a suitable solvent. The non-conducting compounds $\mathrm{[(AgNO_3)_2L]}$ (L=DPE,DPM,*cis*-1,2-bisdiphenylphosphinoethylene, *o*-phenylenebisdimethylarsine) have been synthesised [167]. The sign and magnitude of *trans*-$^2J_{P-P}$ in $\mathrm{[Au(PMe_3)_2]^+}$ have been recorded by the ^{1}H{^{31}P} INDOR technique [168]. IR, far IR and Raman spectra have been measured for the complexes $\mathrm{NiL(CO)_3}$, AuXL(X=Cl,Br,L=$\mathrm{PPh_3}$,$\mathrm{AsPh_3}$) [169], $\mathrm{R_4N[AuCl_4]}$[170] and $\mathrm{AuXP(4\text{-}FC_6H_4)_3}$ (X=Cl,Br)[171] and the various parameters tabulated. $\mathrm{AuCl_3L}$ (*e.g.* L=PhCN, *p*-$\mathrm{MeC_6H_4CN}$,$\mathrm{PhCH_2CN}$) products



(86)

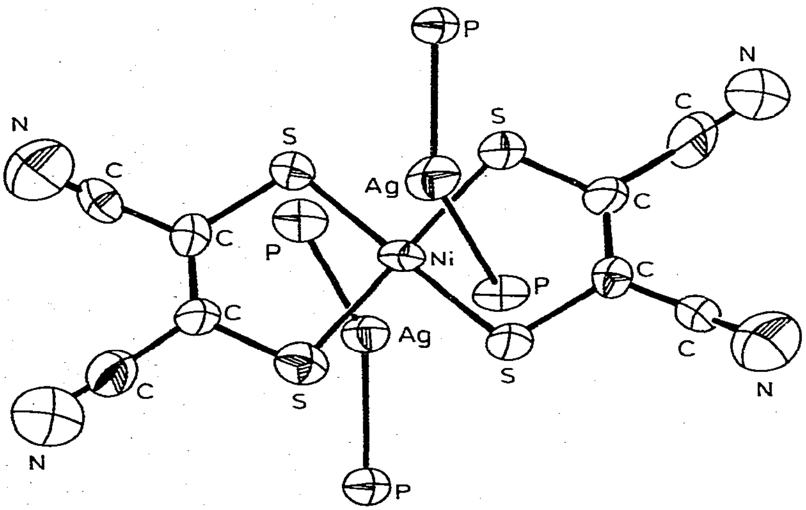
were found to form in anhydrous solvents, and not ring metallated species as previously reported [172]. A study of the kinetics of autoxidation of $[Cu(MeCN)_4]ClO_4$ has inferred the formation of at least 2 different unstable $Cu-O_2$ adducts [173]. The *tris*-(triphenylphosphinegold)oxonium salts $[(PPh_3Au)_3O]X(X=MnO_4,BF_4)$ were prepared from $AuClPPh_3$ and $Ag_2O-KMnO_4$ or $Ag_2O-NaBF_4$ [174,175]. A review of crystal structure determinations of Cu,Ag and Au complexes has appeared (132 Refs.) [176]. A series of X-ray structural determinations for a range of Cu,Ag and Au compounds has been reported.



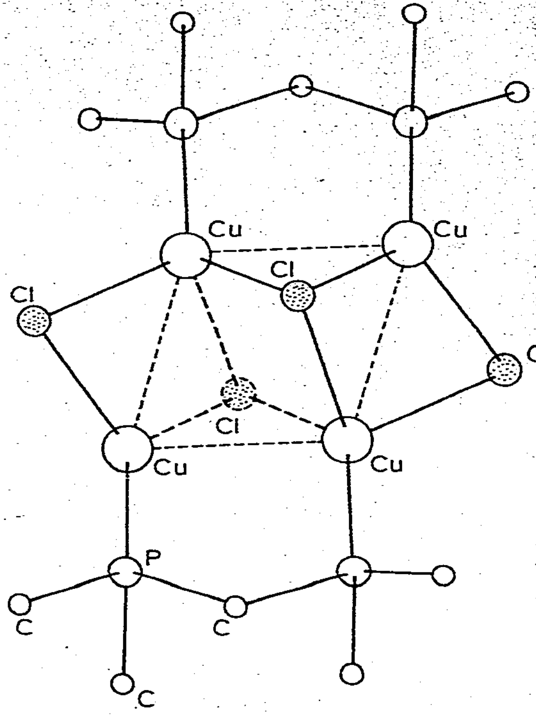
(87)

Mean relevant parameters observed are (i) $AuCl(PPh_3)_2.C_6H_6$(86); Au-Cl 2.5Å, Au-P 2.33Å, P-$\widehat{Au}$-P 132.1° [177], (ii) $CuBF_4(PPh_3)_3$ (87); Cu-P 2.30Å {longest Cu-P distances so far observed}, Cu-F 2.31Å [178] (iii) $[Ag(PPh_3)_2]_2[Ni(S_2C_2\{CN\}_2)_2]$ (88); Ag-P 2.48Å [179] (iv) $(CuCl)_4(DPM)_2$ (89); Cu-Cl 2.27, 2.74Å; Cu-P 2.195Å [180] (v) $Ph_4As[Cu_2Cl_6]$; Cu-Cl 2.32Å (bridging), 2.21Å (terminal); Cl-$\widehat{Cu}$-Cl 145° [181] (vi) $Ph_4P[Cu_2Cl_6]$ (90) Cu-Cl 2.19Å (terminal) 2.305Å (bridging) [182] (vii) $(CuClPPh_3)_4$ (91), Cu-Cl 2.4Å; Cu-P 2.19Å [183] (viii) $(CuBrPPh_3)_4.2CHCl_3$ (92); Cu-Br 2.38 – 2.66Å; Cu-P 2.20Å [184] (ix) $(CuIPEt_3)_4$ (93) (M=P); and $(CuIAsEt_3)_4$ (93) (M=As); Cu-I 2.68Å; Cu-P 2.25Å; Cu-As 2.36Å.[185]. For the tetrameric structure no predictions could be made as to why "cubane" or "chair structure" is preferred.

A review on metallation reactions of organoboranes focuses on their salts with Ag,Cu,Pb,Hg and Tl [186]. The reactions of MCl_2 (M=Co,Ni,Cu, Pd,Pt) with $NaBH_4$ and $NaBH_3CN$ has been studied and various products were



(88)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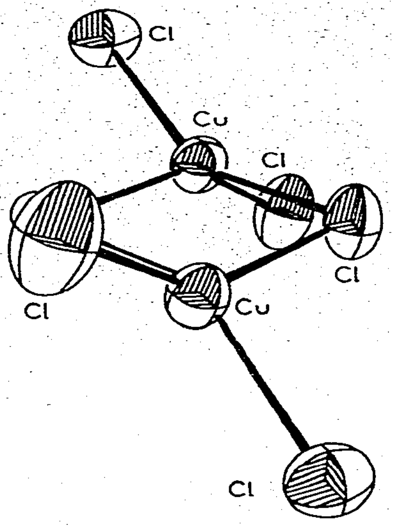
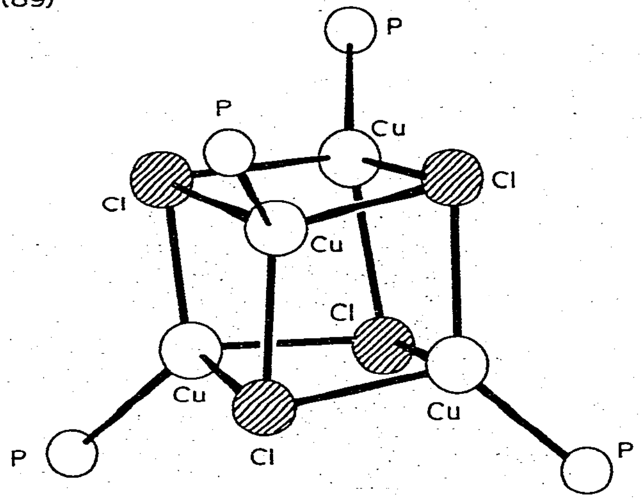
Cu
Cl
Cl
Cl
Cl
Cu
Cu
P
C
C
C

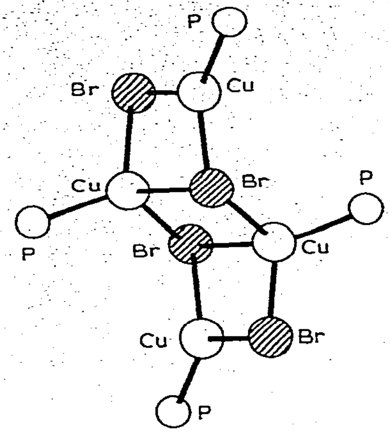
(89)


Cl
Cu
Cl
Cl
Cl
Cl
Cu
Cl

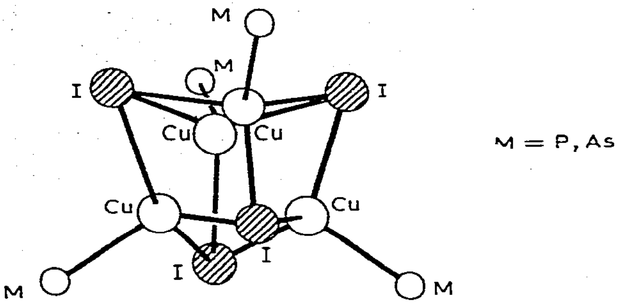
(90)


P
P
Cu
Cl
Cl
Cu
Cl
Cu
Cl
Cu
P
P

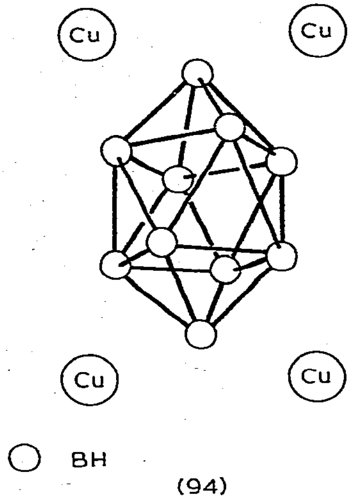
(91)


P
Br
Cu
Cu
Br
P
P
Br
Cu
Cu
Br
P

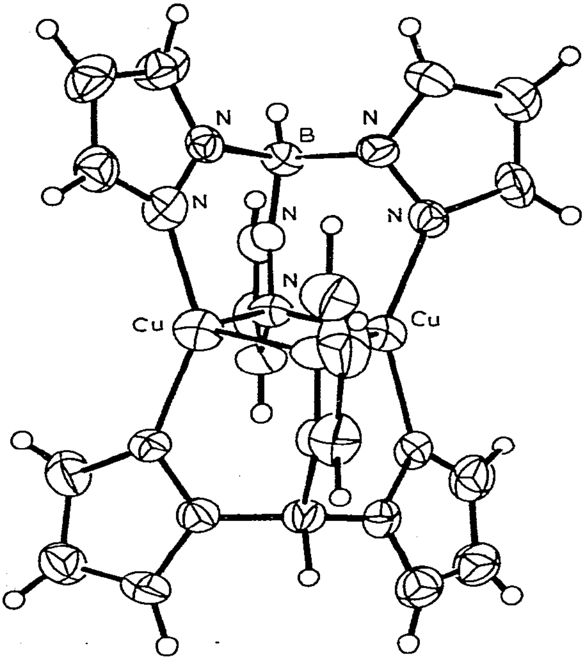
(92)


M
M
I
I
Cu
Cu
Cu
Cu
I
I
M
M
M = P, As

(93)


Cu
Cu
Cu
Cu
BH

(94)


N
B
N
N
N
N
N
Cu
Cu

(95)

characterised [187]. With *o*-ethylboranocarbonate (=L) as a ligand, the compounds CuL$(PPh_3)_2$ and AgL$(PPh_3)_3$ have been prepared. The data on these complexes points to a double H-bridge for Cu and a single H-bridge for Ag [188]. X-ray determinations on μ-bis(cyanotrihydroborato) tetrakis(triphenylphosphine)dicopper(I) [189], $Cu_2B_{10}H_{10}$ (94) [190] and $[Cu(HBpz_3)]_2$ (95) (HBpz=pyrazoylborate) [191] have been completed. For $Cu_2B_{10}H_{10}$ it has been proposed that covalent interaction of the Cu atoms with the borane aggregate occurs via 3-centre bonds of sp hybrid Cu(I) with B-B edges, or a tetrahedrally hybridised Cu(I) interaction with the four nearest boron atoms [190]. $[Cu(HBpz_3)]_2$ takes up one mole of dry O_2 irreversibly to give a green paramagnetic substance of formula $Cu_2(HBpz_3)_2O_2$ [191].

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