COPPER, SILVER, AND GOLD

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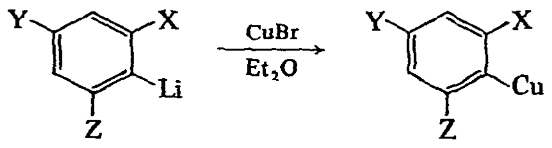
CONTENTS

A review on metal fulminate complexes which includes copper, silver and gold complexes has appeared[1].

COPPER

The novel tetramers, pentafluorophenyl copper and *o*-(trifluoromethyl)phenylcopper, have been prepared from the aryl Grignard reagent by metathesis with CuBr[2].

The synthesis of the substituted aryl copper compounds (1) has been reported[3]; in all cases, the substitution results in greater thermal stability. The expected coupling products result from reaction of (1) with acyl and allyl halides.



(1)

$X = Z = OCH_3, Y = H$
$X = Y = Z = OCH_3$
$X = Z = H, Y = N(CH_3)_2$
$X = N(CH_3)_2, Y = Z = H$
$X = Z = H, Y = PPh_2$
$X = SO_2N(CH_3)_2, Y = Z = H$

Octameric *m*-(trifluoromethyl)phenylcopper (2) has been prepared[4] from the Grignard and cuprous bromide. On the basis of kinetic data, the authors suggest that the decomposition of (2) proceeds via pairwise loss of alkyl groups and formation of a Cu^0-Cu^1 cluster compound (3).

$$\underset{(2)}{R_8Cu_8} \rightarrow R_2 + \underset{(3)}{R_6Cu_8} \rightarrow R_2 + R_4Cu_8$$

Baica, Camus and Pellizer[5] measured the ^1H NMR spectra of *o*-, *m*-, *p*-tolyl-, *o*-anisyl-, and 2,4-dimethylphenylcopper. The resonance peaks of the aromatic protons and of the methyl protons *ortho* to the metal are shifted downfield, those in *meta* and *para* positions are shifted upfield. The authors suggested that magnetic anisotropy centred between carbon and copper is the main influence on the proton shielding constants. The temperature dependence of the spectra indicated hindrance to rotation for the methyl groups *ortho* to the copper.

Adsorption properties of methyl-substituted and unsubstituted benzene on Cu^{II} montmorillonite surfaces have been investigated[6,7] by spectroscopic methods. Benzene formed two types of complex: the first, green, with a higher degree of hydration involves a planar aromatic ring; the second, red, has a greatly distorted ring with the π electrons probably localized and has not been observed in homogeneous solution. The methyl-substituted benzenes form exclusively complexes of the first type.

In the IR spectra[8] of the π-complexes formed from copper(I) chloride and the cyclic allenes, 1,2,6-cyclononatriene, 1,2,6-cyclodecatriene and 1,2,6,7-cyclodecatetraene, two new bands between 1650 and 1900 cm^{-1} appear replacing the single band around 1950 cm^{-1} in the uncoordinated allenes. Both monomeric and polymeric structures are possible.

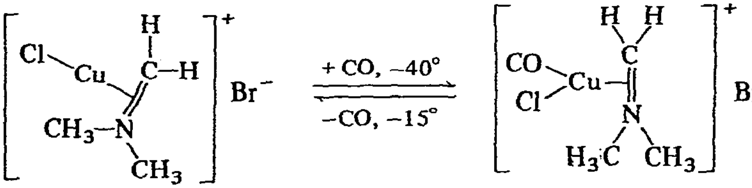
The temperature dependence of the equilibrium constant and the thermodynamic parameters at 25° of equilibrium were determined of the equilibrium[9]:

$$R(aq) + Cu^+(aq) \rightleftharpoons R\,Cu^+(aq)$$

$$R = C_3H_6, C_4H_8$$

Also determined[10] was the equilibrium constant for the formation of the 1/1 copper-2-methyl-1,3-butadiene π-complex.

Complexes of copper(I) with dimethylmethyleneammonium (4) have been found[11] to reversibly coordinate CO over the temperature range −40° to −15°. Similar behaviour is reported for NO.



(4)

Treatment of neat vinylmetallics with copper(I) chloride produced[12] the alkylvinylsilane and alkylvinyltin complexes of copper(I) chloride. *d–d* bonding from Cu^I to the Group IV metal is invoked to explain the unusual stability of these complexes. Also, reaction of 1,4-cyclooctadiene (COD) with Cu^I chloride gave[13] $[Cu(1,4\text{-}COD)Cl]_2$, intermediate in stability between the analogous 1,3-COD and 1,5-COD complexes.

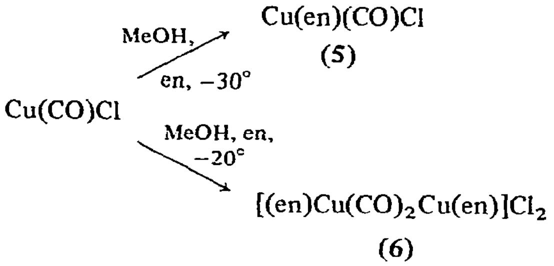
The thermal decomposition of the vinylic copper(I) complexes, *cis*- and *trans*-1-propenyl copper(I), *cis*- and *trans*-1-propenyl(tri-n-butylphosphine)copper(I) gave the products Cu^0 and 2,4-hexadienes with retention of stereochemistry[14]. The authors postulate that decomposition does not proceed by a free radical mechanism and extend this conclusion to analogous reactions with other transition elements.

Zelonka and Baird[15] have observed, but not isolated 1/1 five-coordinate adducts of anhydrous bis(hexafluoro-acetylacetonate)copper with phenylacetylene or several olefins.

Copper complexes, $RC{\equiv}CCuMCl_3$ (M = P, As; R = Ph, Bu) were synthesized[16] from copper(I) acetylides and MCl_3. The IR stretching frequency of the acetylenic moiety increases by about 40 cm^{-1} with increased intensity. The UV spectra (300–700 nm) of acetylenic copper complexes indicate[17] that substituents on acetylene have little effect on the absorption between 370–420 nm. Absorption and photoconductivity spectra of the complexes, $CuC{\equiv}CMR_2$ (R = Ph, Bu; M = P, As), have been reported[18].

Cocondensation of copper with excess carbon monoxide has produced[19] copper carbonyls ($\nu(C{\equiv}O)$ at 1989 and 1975 cm^{-1} assigned to terminal carbonyl groups).

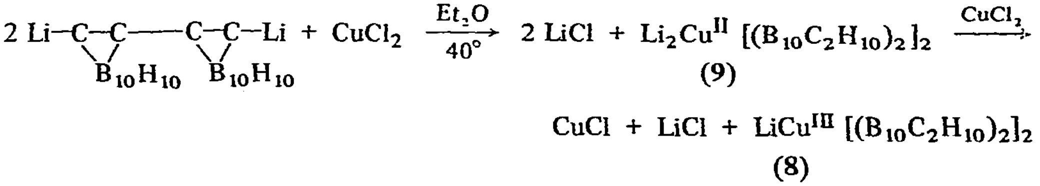
Both mononuclear (5) and binuclear (6) ethylenediaminecopper(I) carbonyl complexes have been prepared[20]. The IR spectra showed terminal and bridging carbonyl bands for (5) and (6) respectively. In methanol, the equilibrium between (5) and (6) favours (5) at temperatures above –30°.

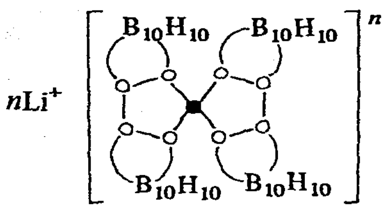


The hydration of 2-cyanopyridine to 2-pyridine carboxamide is catalyzed[21] by bis(ethylenediamine)copper(II) chloride dihydrate.

Stanko, Klimova and Brattsiv[22] have prepared bis(tetraethylammonium)bis(dicarbaundecahydroundecaborato)cuprate(II).

Owen and Hawthorne reported[23] the preparation and characterization by IR, UV and ^1H NMR spectra of the air stable bis[σ,σ-2,2′-dicarboranylcopper(IV-m)]$^{m-}$ (m = I (8), m = II (9)) complexes. The authors have proposed that (8) and (9) have the central metal atom bonded to the four carbon atoms of the polyhedra. The air stability of the complexes is attributed to the steric hindrance of the polyhedra and favourable coulombic interactions.





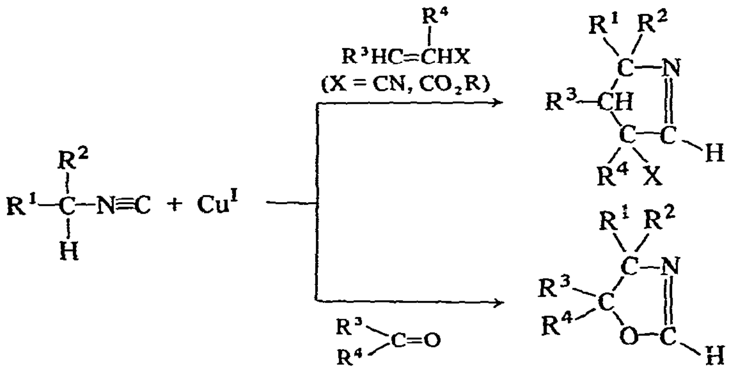
○ = C
● = Cu
(8) $n = 1$
(9) $n = 2$

Cyclopentadienyl(t-butylisocyano)copper(I) (**10**) and indenyltris(t-butylisocyano)-copper(I) catalyze[24] the reaction of cyclopentadiene homologs with carbonyl compounds producing the corresponding fulvene derivatives; (**10**) also catalyzes Michael-type reactions with active hydrogen compounds.

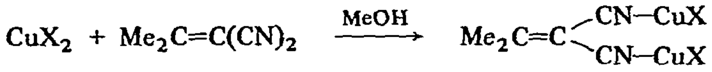
$$Cu_2O\text{-t-Bu—NC} + C_5H_6 \rightarrow (C_5H_5)(\text{t-Bu—NC})Cu^I$$

(**10**)

Other Cu^I systems[25] catalyzed the codimerization of α,β-unsaturated carbonyl and nitrile compounds as well as Michael-addition reactions.



Treatment of cupric chloride or bromide with dicyano geminally substituted ethylene gave[26] a product with each CN group coordinated to one CuX unit.



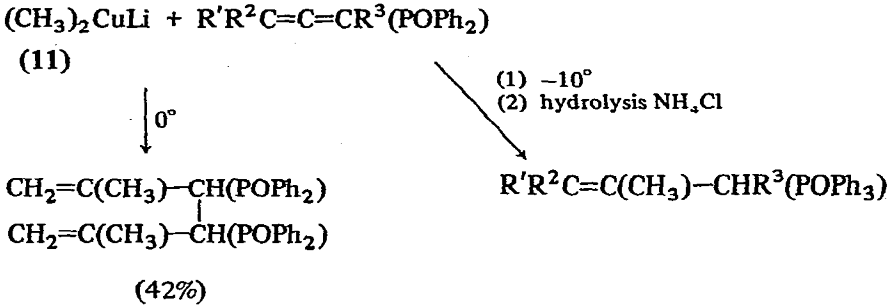
$$CuX_2 + Me_2C{=}C(CN)_2 \xrightarrow{MeOH} Me_2C{=}C\begin{matrix} CN{-}CuX \\ CN{-}CuX \end{matrix}$$

Braterman and Wilson[27] have reported the preparation of the insoluble complexes, $[(\pi\text{-}C_5H_5)_2Ti(SR)_2CuX]_n$ and the chelating disulphide copper halides, $(RSCH_2CH_2SRCuX)_n$ (n unknown) (R = Me, Ph; X = Cl, Br). The electronic spectra suggest that a Cu-Ti bond exists.

Reactions of lithium copper compounds

(a) With unconjugated alkenes and alkynes

Methylation of allenic diphenylphosphine oxide using $LiCuMe_2$ (**11**) has been reported[28]. With higher reaction temperatures, more of the coupled product was obtained.

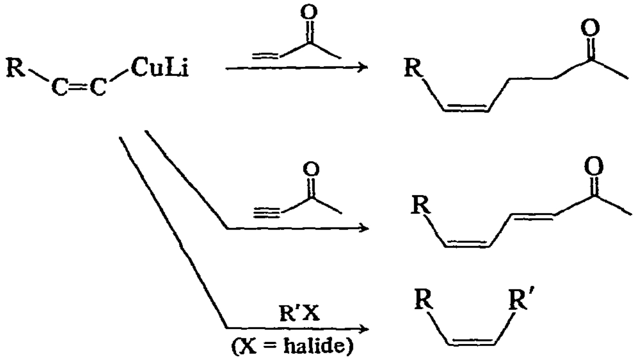


Coupled products were also obtained[29] from the reaction of lithium phenylacetylene copper with alkyl halides.

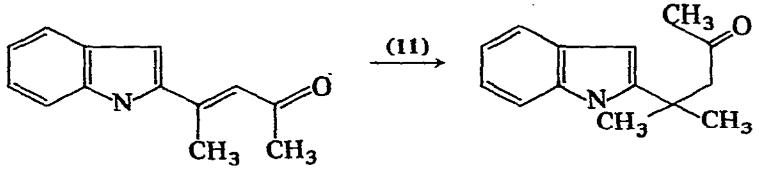
$$\mathrm{BuLi + PhC{\equiv}CCu \xrightarrow[ether]{THF} (PhC{\equiv}CCu)Li \xrightarrow[PhCH{=}CHBr]{\Delta} PhCH{=}CH{-}CH{=}CH{-}Ph}$$

(*b*) *With unsaturated ketones*

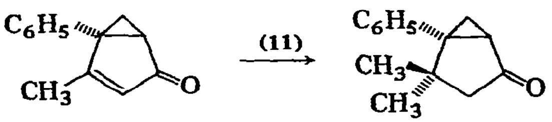
Näf and Degen[30], investigating the conjugate addition of (*cis*- or *trans*-1-alkenyl)-CuLi · X_n to α,β-unsaturated carbonyl compounds and to *cis*- or *trans*-ethylenic carbonyl compounds, have found stereospecific retention of the double bond geometry in the products.



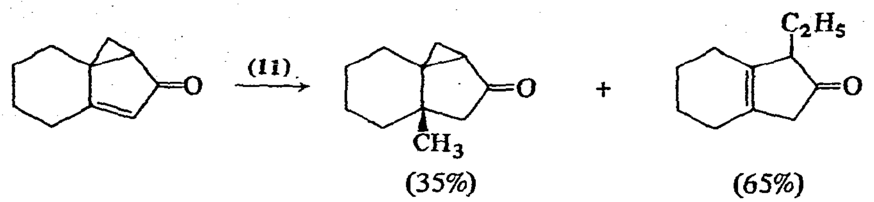
Because of the excellent stereospecific methylation, (11) has been used extensively in organic syntheses[31-37].

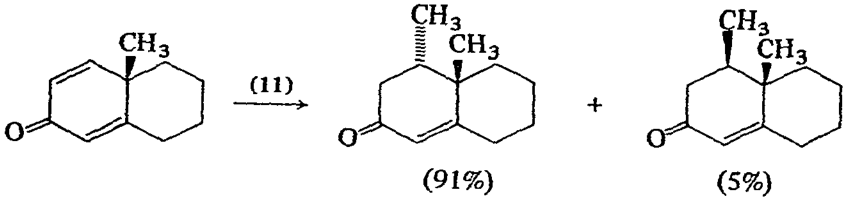


(ref. 31)



(ref. 32)





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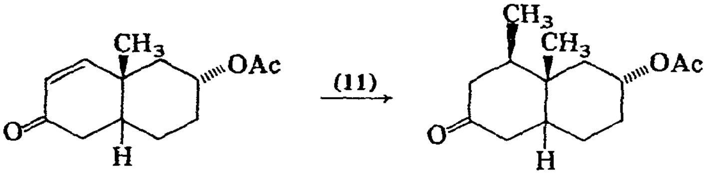

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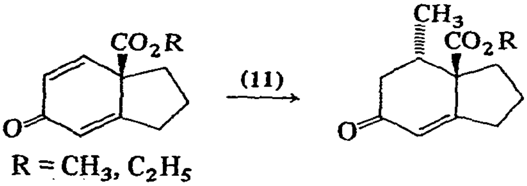

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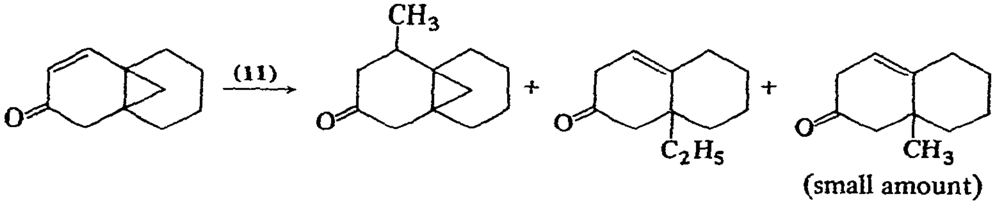

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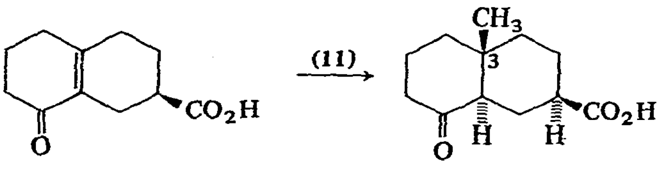
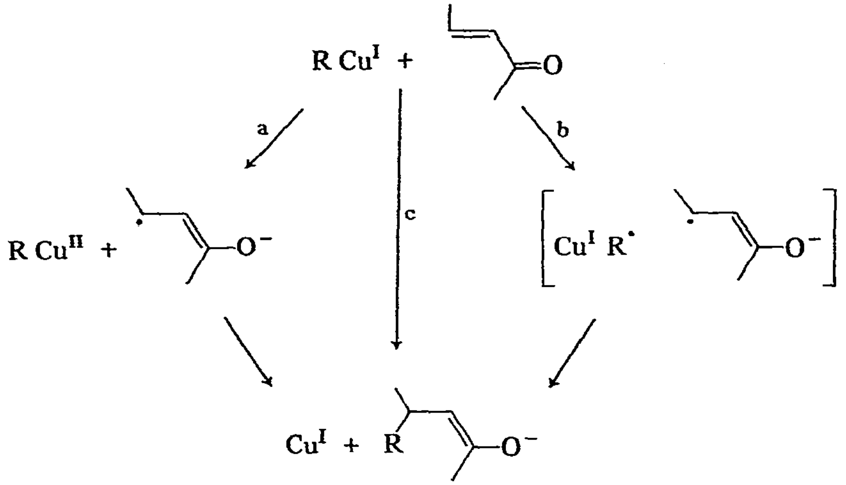


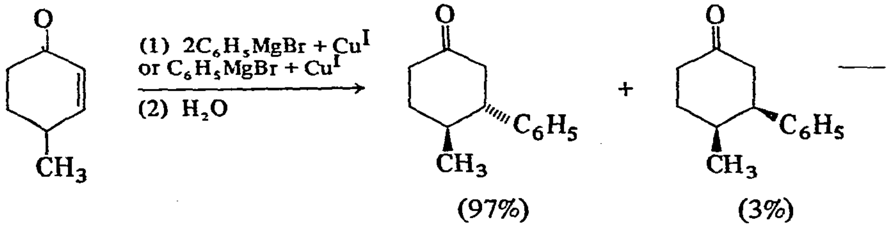
(100% yield of methyl in
3 position but 3 isomers ≈ 1/1/1)

(ref. 37)

Casey and Boggs[38] suggested that the addition of isomeric lithium divinylcuprates to α,β-unsaturated ketones proceeds without free radical intermediates though the product formation is compatible with a free radical (pathway a) or a caged free radical mechanism (pathway b).



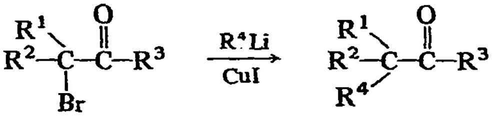
Stereospecificity was also evident in the copper(I) catalyzed additions to 4-methyl-2-hexenone[39].



An investigation[40] into the regioselectivity of the conjugate addition of (11) to cyclohexadienones suggested that conjugation in the transition state does not cause a strong directive effect while steric control does account for the relative amounts of 1,4 and 1,6 addition products.

(c) With unconjugated carbonyl compounds

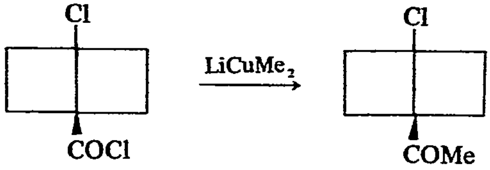
The synthesis of sterically hindered ketones from Grignard reagents has been catalyzed[41] by cuprous halides.



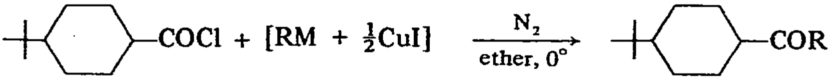
$$R^1R^2C(Br)-C(=O)-R^3 \xrightarrow[CuI]{R^4Li} R^1R^2C(R^4)-C(=O)-R^3$$

(*d*) *With acyl chlorides*

Cain[42] used (**11**) for bridgehead substitution on a substituted [2.2.0]bicyclohexane.



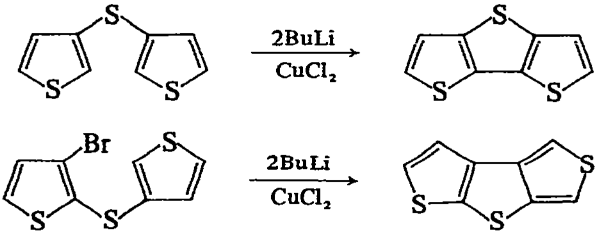
With both alkyllithium and -magnesium compounds and Cu^I, Loung-Thi *et al.*[43] prepared substituted ketones.



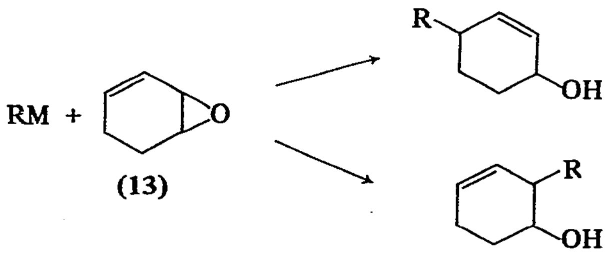
(*e*) *Miscellaneous*

Dubois *et al.*[44] have investigated the optimum conditions for the cuprous halide catalyzed synthesis of hindered aliphatic ketones by condensation of either alkyllithium or alkylmagnesium bromide with acyl chlorides. Four factors were considered: the influence and nature of the CuX; influence of the metal (*i.e.*, Li or Mg); mode of addition of reagents; reaction temperature.

Using the butyllithium–cupric chloride system, ring closure to form thienothiophenes (**12**) has been studied[45].

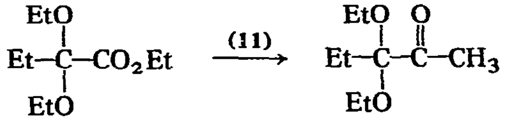


Wieland and Johnson[46] have investigated the addition reactions of 3,4-epoxycyclohexene (**13**) with organolithium and lithium organocopper compounds. With $LiCuR_2$ (R = Me, Ph), high *trans* selectivity was observed for both 1,2 and 1,4 additions. With



R = t-butyl, the mechanism proposed for the conjugate addition involves an intermediate radical anion.

3,3'-Diethoxy-2-pentanone (**14**) and acetophone were prepared[47] using (**11**).



$$\mathrm{Et{-}C(OEt)_2{-}CO_2Et} \xrightarrow{(11)} \mathrm{Et{-}C(OEt)_2{-}C(=O){-}CH_3}$$

(**14**)

Substitution of acyl chlorides has been achieved[39] using phenylmagnesium bromide-copper iodide systems.

$$\mathrm{RCOCl} \xrightarrow[+\ \mathrm{CuI}]{n\mathrm{C_6H_5MgBr}} \mathrm{RCOC_6H_5}$$

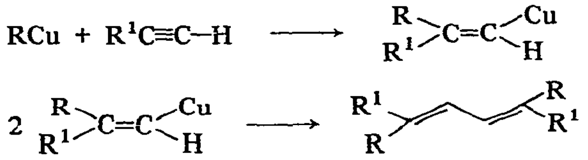
$R = C_6H_5, C_6H_{11}; n = 1,2$

Coupling reactions

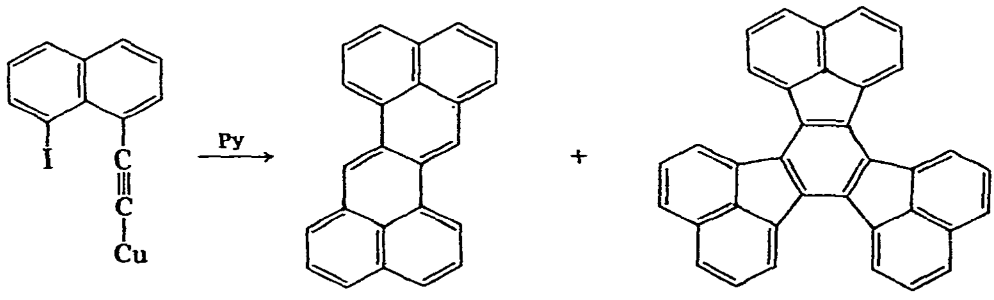
Compounds of copper(I) catalyzed[48–50] coupling reactions involving alkyl Grignard reagents and alkyl halides.

$$\mathrm{BuMgBr} + 1\text{-}\mathrm{C_6H_{11}Br} \xrightarrow{\mathrm{Cu^I}} \mathrm{C_{10}H_{22}}$$

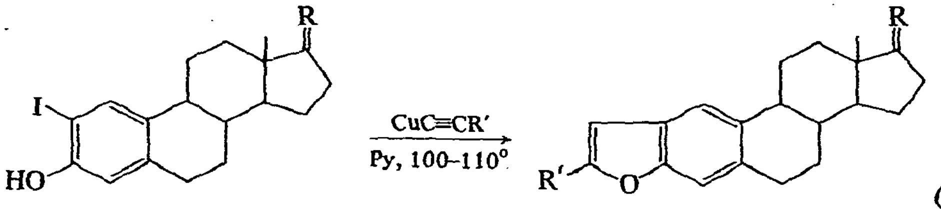
Normant and Bourgain[51] showed that the reaction of organocopper compounds with substituted acetylene resulted in a dimerization, the product of two stereospecific reactions.



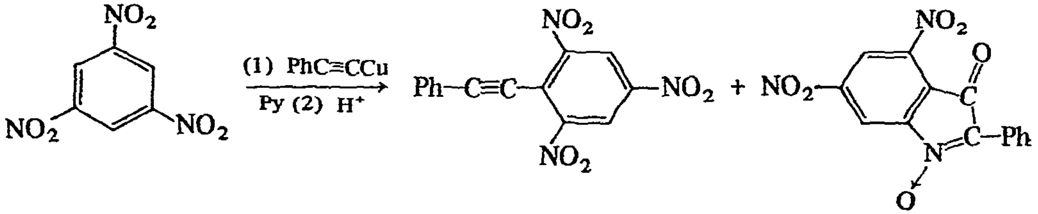
Several syntheses have been reported[52–55] using substituted acetylenic copper as a coupling reagent.



(ref. 53)



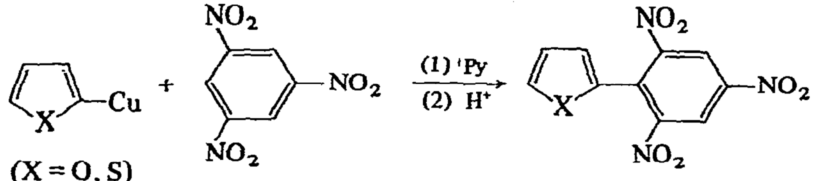
(R = O, CHCOH); R' = alkyl, Ph, CH_2CH_2OH) (ref. 54)



(ref. 55)

$RC{\equiv}CCu + BrC{\equiv}CCH_2OH \rightarrow RC{\equiv}C{-}C{\equiv}C{-}CH_2{-}OH$ (ref. 57)

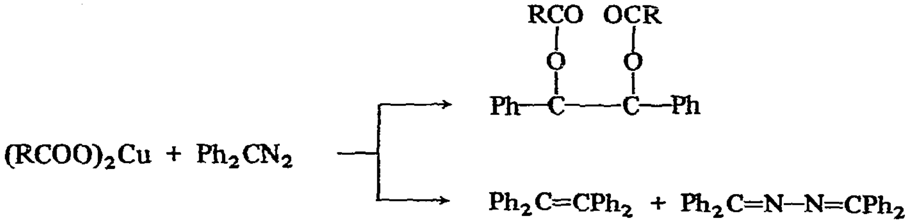
With heterocyclic copper and 1,3,5-trinitrobenzene, only the simple coupled product (15) was obtained[56].



(X = O, S)

(15)

In the coupling reaction of copper(II) carboxylates with Ph_2CN_2 the nature of the product was dependent[57] on the carboxylate substituent.



Rathke and Lindert[58] have reported a convenient synthesis of dialkylsuccinate esters via copper promoted coupling of ester enolates.

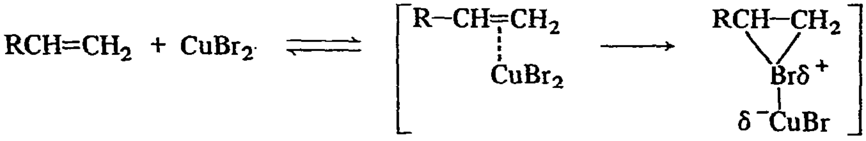
The copper(II) chloride-lithium aluminum hydride system has been used[59] to hydrogenate carbon-sulphur bonds.

$$p\text{-MeOC}_6H_4CH(SEt)Ph \xrightarrow[2\,LiAlH_4]{CuCl_2} p\text{-MeOC}_6H_4CH_2Ph$$

Addition to olefins

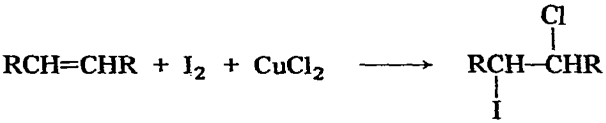
(*a*) *Halogenation*

Koyano and Watanabe have studied the kinetics and mechanism of chlorination[60] and bromination[61] of olefins by cupric halide. Chlorination of 1-octene in methanol yielded dichloro as well as monochloro methoxy products. The authors proposed that the chlorination involves an initial formation of a copper chloride olefin complex followed by competitive attack of chloride and methoxy ions. The bromination was suggested to proceed via a bridged brominium ion type species.



In methanol, methoxy-substituted products are found.

Chloroiodo products were formed[62] in the reaction of iodine and cupric chloride with olefins.



$$RCH{=}CHR + I_2 + CuCl_2 \longrightarrow RCH(I){-}CH(Cl)R$$

With conjugated diolefins, the major product is the dichloride formed by halogen exchange after the production of the chloroiodo addition compound.

Baird and Surridge[63] reported two preparations of dehydroadiponitrile (16) using cupric salts.

$$CH_2{=}CH{-}CH{=}CH_2 + I_2 + 2CuCN \longrightarrow \underset{(17)}{ICu \cdot NCCH_2CH{=}CHCH_2CN \cdot CuI}$$

$$CH_2{=}CH{-}CH{=}CH_2 + 2CuBr_2 + 2CuCN \longrightarrow \underset{(18)}{BrCu \cdot NCCH_2CH{=}CHCH_2CN \cdot CuBr} + 2CuBr$$

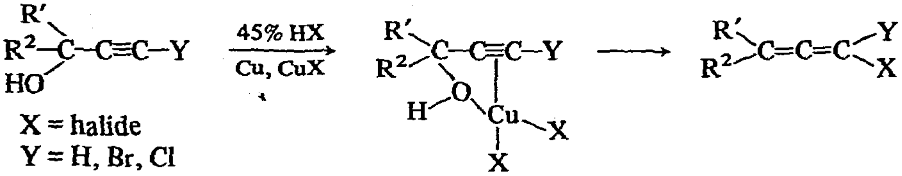
$$(17)\text{ or }(18) + 2HCN \xrightarrow{H_2O} 2CuCN + X_2 + H_2 + \underset{(16)}{NCCH_2CH{=}CHCH_2CN}$$

Vicinal halogenation of the cyclic nonconjugated alkenes, hexene[64] and 1,3- and 1,5-cyclooctadiene[65] was achieved by reaction with cupric halides.

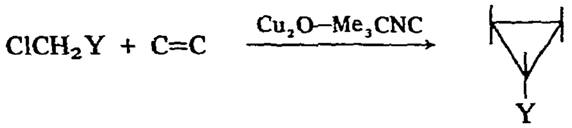
(*b*) *Miscellaneous*

Cuprous chloride catalyzes the stereospecific hydrosilation of styrene[66], and the ring closing reactions of CH_2N_2 with pyrrole[67]; cupric chloride-ethanolamine catalyzed the addition of polyhaloalkanes to substituted olefins[68]; $PdCl_2$-$CuCl_2$ in acetate buffer catalyzed the chlorination of bicyclic olefins[69].

Acetylenic alcohol has been converted into substituted allene[70].



Various substituted cyclopropane compounds have been prepared[71] from olefins and α-chloro compounds using the copper(I) oxide-isonitrile system as a catalyst.



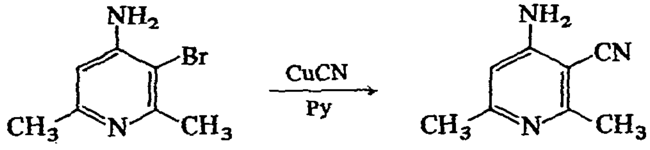
The copper(II) chloride catalyzed addition of substituted sulphonyl chlorides to alkenes[72] and alkynes[73,74] improved the syntheses of *trans*-1-aryl-2-(arenesulphonyl) ethanes and β-chlorovinylsulphone.

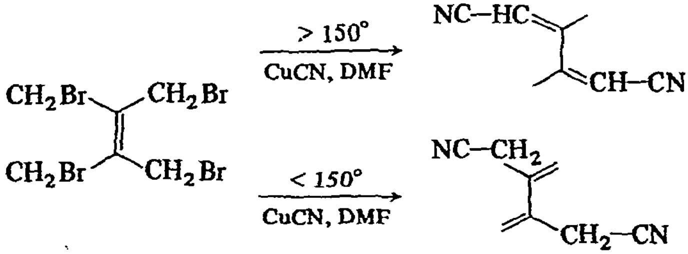
$$RSO_2Cl + R'C{\equiv}CR'' \xrightarrow{CuCl_2} RSO_2CR'{=}CClR''$$

Amiel[75] has proposed that the additions proceed through a sulphonyl radical attack on the multiple bond followed by addition of the halide from the copper halide complex.

Other reactions

Bromide has been replaced by cyanide using copper(I) cyanide in heterocyclic[76], polycyclic[77] and alkenic[78] systems.





Lizzani *et al.*[79] demonstrated from IR and ^1H NMR spectra that the addition of copper to ethanolic solutions of allylic halides yielded ethylenic ethers, not biallylic products.

When various phenylthallium(III) compounds reacted[80] with copper(II) chloride or copper(I) chloride, the main product was chlorobenzene. Solvent effects were large and a four center reaction was proposed. A similar ligand transfer of halides and pseudohalides of copper(II) to alkyl radicals has been reported[81]. With trialkylboron compounds, ligand transfer from Cu^{II} chloride and bromide has been achieved[82] requiring two copper moieties per alkyl group.

$$B(alkyl)_3 + CuX_2 \xrightarrow{H_2O} alkyl\text{-}X$$

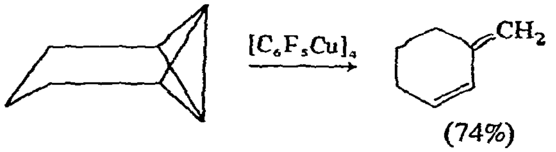
Cummings and Milner[83] suggested the ligand transfer reaction of copper(II) halides with substituted aromatic hydrocarbons proceeds via the formation of a radical cation followed by substitution.

$$HArMe \xrightarrow{CuCl_2} HArMe^{+} \xrightarrow{CuCl_2} ClArMe$$

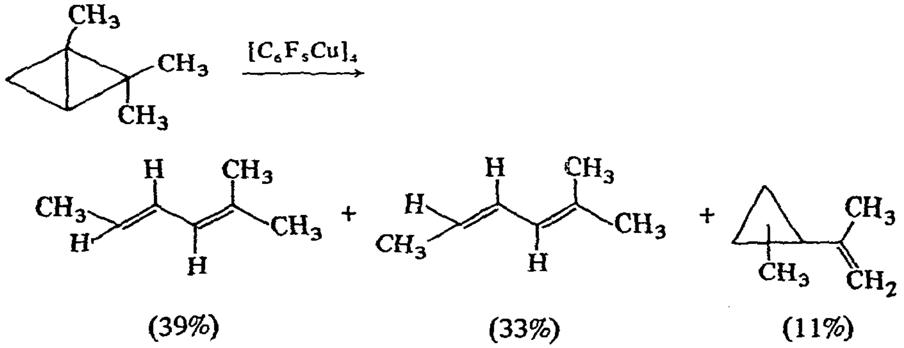
Studies on the polymerization of methyl methacrylate have indicated[84] that the catalytic system $Et_3N\text{-}Cu^{I}Cl$ may operate via a radical initiation; with β-diketonato complexes of Cu^{II}, the polymerization is accelerated[85] by the addition of 1,10-phenanthroline to the system.

Rearrangements

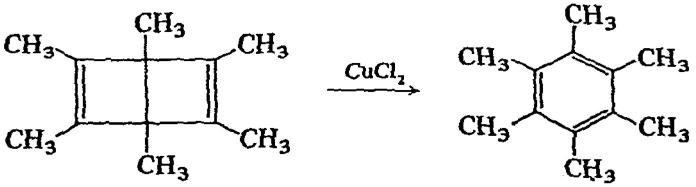
Several copper-catalyzed rearrangements of hydrocarbon compounds were reported[86–89].



(ref. 86)



(ref. 87)



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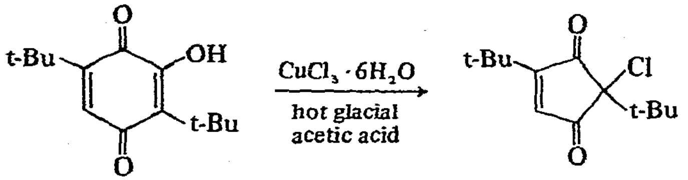
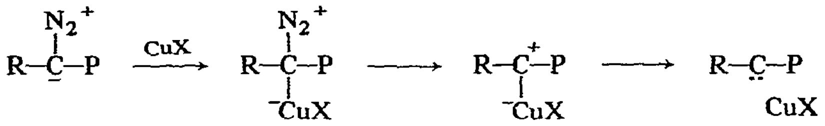


(ref. 89)

An example of the well known copper-catalyzed azide elimination was[90] the decomposition of dimethylphosphono-substituted diazoalkanes.

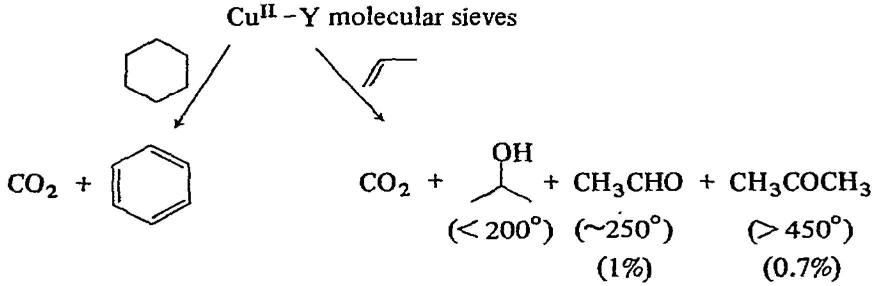
$$XCH_2C(N_2)P(O)(OMe)_2 \xrightarrow{CuX} XCH_2\ddot{C}P(O)(OMe)_2$$

The authors proposed that the elimination proceeds through initial coordination of the azide-bearing carbon center to the copper complex, followed by the elimination of the azide with the subsequent cleavage of the copper-carbon bond.



Organocopper intermediates have been postulated in the oxidation of t-butyl alcohol by copper(II)[91].

Mochida *et al.*[92,93] report the oxidative behaviour of Cu^{II}-Y molecular sieves with cyclohexane and propylene yielding predominantly carbon dioxide and small amounts of partially oxidized hydrocarbon.



Reich and Jadrnicek[94] have determined that the copper(II) acetylacetonate complex is the least effective catalyst in a series of analogous transition metal complexes for the autooxidation of atactic propylene film (measured by carbonyl formation).

The use of a Cu^{II} cocatalyst in a 5–500 molar excess in the Pd^{II} catalyzed preparation of α,β-unsaturated carbonyl compounds enhanced[95] the stereoselectivity.

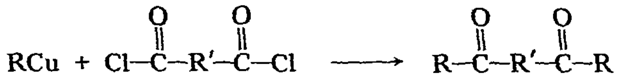
A study[96] on the comparative activity of metal sulphates in the dehydrogenation of haloethanes on silica gel at 300°C, gave a correlation of the ratio of log ([*trans*-1,2-product]/[*cis*-1,2-product]) to log ([1,1-product]/[1,2-product]). The log ([*trans*-1,2-product]/[*cis*-1,2-product]) decreased as the electronegativity of M^{n+} increased.

Wulfman *et al.*[97] suggested that the homogeneous copper(I) catalysis of the decomposition of dimethylmalonate proceeded by an attack of the diazo compound upon the complex, displacement of the associated anion, loss of nitrogen from the resulting diazonium ion, displacement of the carbene by the anion and subsequent addition to an olefin. The leaving group ability of the anion influences the effective spin multiplicity distribution of the carbenoid species. Product distributions[98] of the copper(I) catalysed decomposition of diazomalonic esters with cyclohexene using phosphite copper iodide catalysts with varied amounts of cuprous and cupric chloride added have been reported.

Jenkins and Kochi[99] have demonstrated that the rates of ligand transfer oxidation of alkyl radicals, such as cyclopropenylmethyl, allylcarbinyl, cyclobutyl, by copper(II)–X_2, (X = SCN, Cl, Br) approach the diffusion controlled limit with second order rate constants in the order 10^8–10^9.

The oxidation of ethanol by peroxydisulphate[100] modified by copper(II) has been found to obey the rate law, rate $= K_{3/2}\ [S_2O_8^{2-}][Cu^{II}]^{1/2}$. $Cu^{II}Cl_2$ also enhanced[101] the nickel-catalyzed reactions of benzyl alcohol.

Disubstitution of diacid chlorides has been achieved[102] using perhaloarylcopper compounds.



$$\mathrm{RCu} + \mathrm{Cl{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Cl} \longrightarrow \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R}$$

R = C_6H_5, C_6Cl_5, 2,3,5,6-tetrachloro-4-pyridyl

Phosphine complexes

Conductivity and molecular weight studies[103] on the bis(triphenylphosphine)metal-diethyldithiocarbamate (metal = Au^I, Ag^I, Cu^I) indicate that they are non-electrolytes and that dissociation occurs, increasing in the order Cu < Ag < Au.

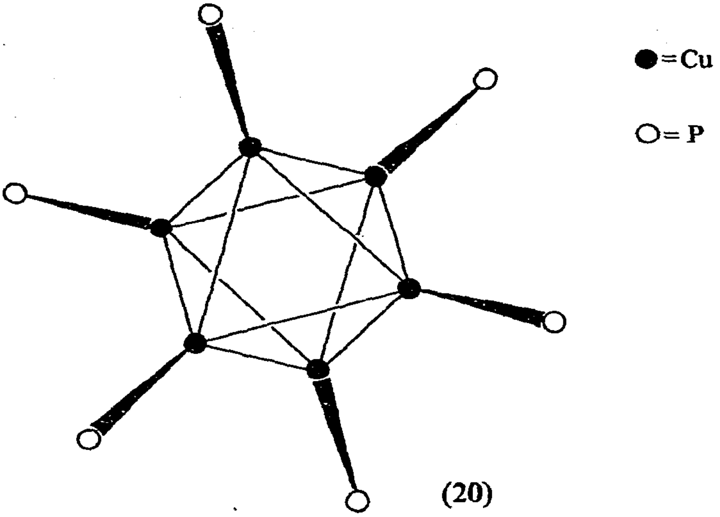
$$(Ph_3P)_2M(R_2dtc) \rightleftharpoons (Ph_3P)M(R_2dtc) + Ph_3P$$

From X-ray diffraction data[104], the crystal structure of diazido-μ-1,2-bis(diphenylphosphino)ethanebis(1,2-bis(diphenylphosphino)ethane)dicopper(I) (**19**) has been determined. The three copper–phosphorus bond lengths are the longest observed in copper(I) phosphine complexes. With single crystal X-ray data, the crystal structure of μ-diazidotetrakis(triphenylphosphine)dicopper(I) was shown[105] to involve two azido bridges.

A new synthetic method[106] for copper hydrides has been developed.

$$(i\text{-}C_3H_7O)_3PCuCl + (C_2H_5)_3SnH \rightarrow (i\text{-}C_3H_7O)_3PCuH + (C_2H_5)_3SnCl$$

The molecular structure of hexameric triphenylphosphine copper hydride complex (**20**) prepared from a DMF solution of $[Ph_3PCuCl]_4$ and sodium trimethoxyborohydride was reported[107].



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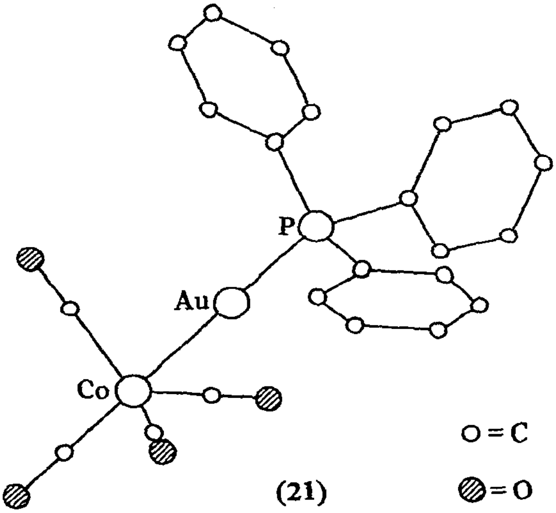

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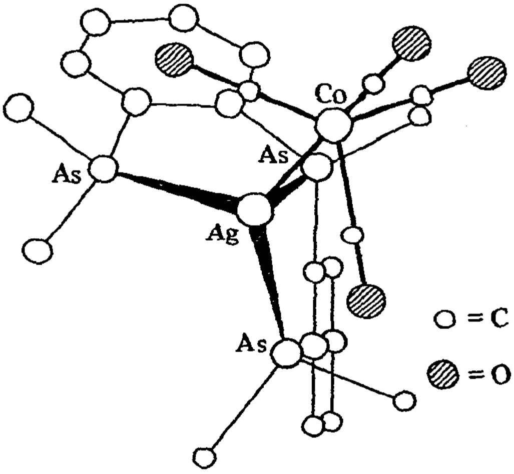


(22)

From the known structures of $(Ph_3P)_2CuX$ (X = bidentate monoanion), several factors influencing the stereochemistry have been deduced[108].

Comparison of the variable temperature ^1H NMR spectra of $L_2CuB_3H_8$ (L = PPh_3, $(PhO)_3P$) confirm[109] that the intramolecular exchange mechanism involves Cu–B_3H_8 bond breakage as the rate-determining step.

Efficient boron hydrogen spin decoupling due to quadrupole-induced ^{10}B and ^{11}B spin relaxation has been observed[110] in $(Ph_3P)_2CuL$ (L = BH_4, B_3H_8). Intramolecular exchange is retarded presumably because of the strength of the Cu–H bond.

The complexes LAuX and diphosAu_2X_2 (L = PPh_3, $AsPh_3$; X = NCO^-, SCN^-, $SeCN^-$) have been prepared[111] and the pseudohalide bonding modes determined from IR spectra. Bromine can be oxidatively added to these complexes.

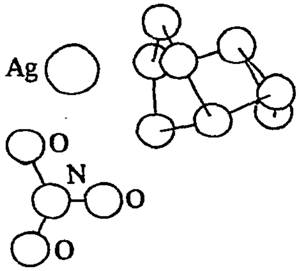
Blundell and Powell[112] have determined the molecular structures of $Ph_3PAu[Co(CO)_4]$ (21) and $[Co(CO)_4]Ag[(Me_2AsPh)_2AsMe]$ (22).

The new complexes $LAuFe(CO)_3NO$ and $Ph_3PAuFe(CO)_2(NO)L$ (L = phosphine, phosphite) have been reported[113]. In donor solvents, the complexes dissociate. The cluster compounds $Au_{11}L_7X_3$[114] (L = tris(*p*-chlorophenyl)phosphine, X = I, SCN, CN; L = tris(*p*-methylphenyl)phosphine, X = SCN; L = tris(*p*-fluorophenyl)phosphine, X = SCN, I) and $[Au_9L_8]X_3$[115] (L = triarylphosphine, X = CN, SCN) have been prepared.

SILVER

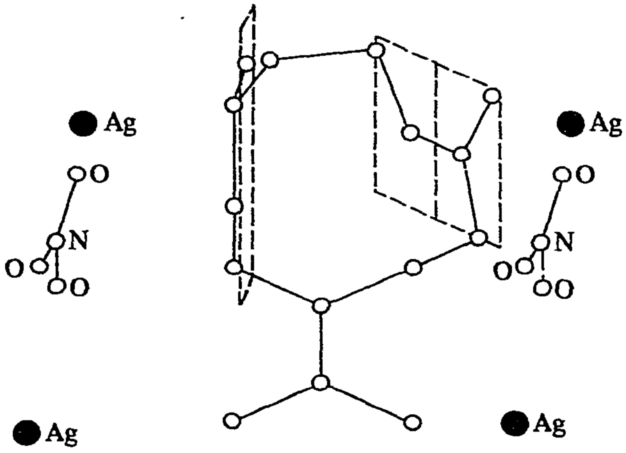
Ag–olefin complexes

In the crystal structure[116] of *exo*-tricyclo[3.2.1.0]oct-6-enesilver nitrate (23), the silver ion was found to be roughly tetrahedrally coordinated to the olefin and three nitrate groups.



(23)

Allen and Rogers[117] determined the molecular structure of the 1/1 adduct (24) of germacratriene with silver nitrate. All *trans* geometry for (24) was confirmed with each Ag^+ ion complexed to two double bonds in different molecules–this chain crosslinked by chains of nitrate and Ag^+ ions.



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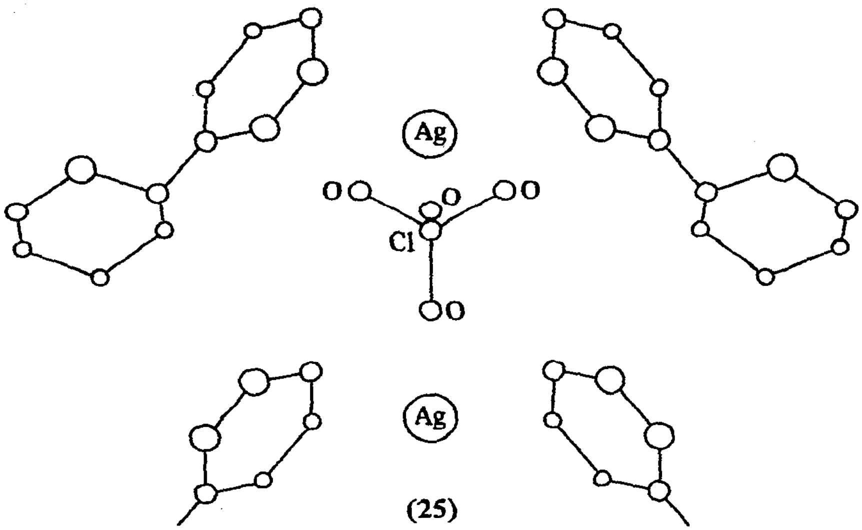


(25)

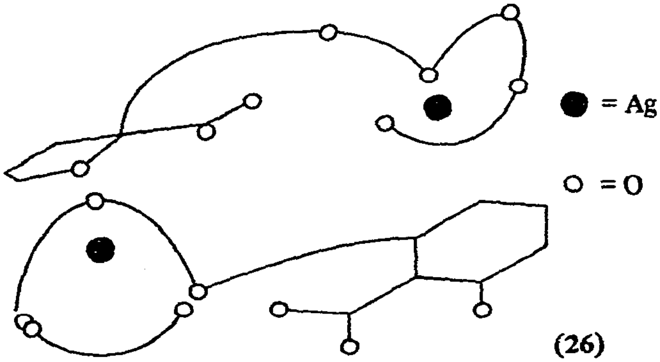
The relative arrangement of the Ag^+, NO_3^- ions and cyclo-olefin molecules was similar in the molecular structures[118] of *cis*-cyclodecene · 0.5 $AgNO_3$ and 1,1,4,4-tetramethyl-*cis*-7-cyclodecene · 0.5 $AgNO_3$, but the conformation of the ring skeletons was different.

In the structure[119] of di-*trans*-cyclododecenesilver nitrate, the non-planar distortion of the rings was attributed to electronic interaction with the metal.

The structure[120] of bis(cyclohexylbenzene)silver(I) perchlorate (25) resembled a half-open hinge with the leaves of the hinge being the organic groups. The Ag^I is three-coordinate: one bond with each aromatic ring and one bond to a perchlorate oxygen.

Analysis[121] of the crystal structure of the silver complex (26) of the antibiotic X-537A (27) revealed a dimeric cylindrical-like structure with a hydrophobic exterior and two Ag^I ions on the inside, each Ag^I complexed to five oxygen atoms and one phenyl ring.

Photolysis of the silver perchlorate-1-methylene cyclohexane complex in solid state or methanolic solution led[122] to isomerization to silver perchlorate-1-methylcyclohexene; further irradiation produced exclusively an *exo-trans-exo* dimer. Similar isomerization and less stereospecific dimerization were observed in the photolysis of the silver perchlorate β-pinene complex.



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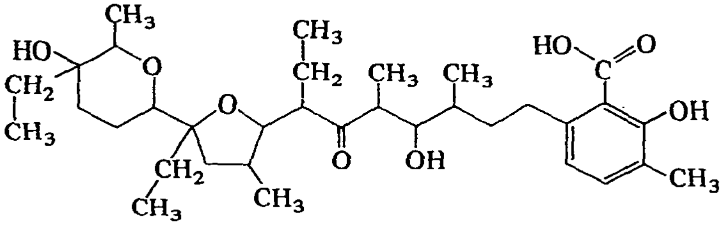


(27)

Tayim and Kharboush prepared[13] the $[Ag(1,4\text{-}COD)Ag]^{2+}(NO_3)_2^-$ complex with a 1,4-COD bridge between two silver ions. The novel π-complexes of 1,2,6-cyclodecatriene and 1,2,6,7-cyclodecatetraene with Ag^I were assigned[8] monomeric or polymeric and monomeric structures respectively. The products of the thermal decomposition of the 2-butenylsilver(I) complex discounted the possibility of a free radical mechanism.

In the calculation of thermodynamic parameters (0–40°C, $I = 0.20\,M$) for the formation of silver complexes Ag_2L, AgL, AgL_2 of saturated and unsaturated alkylthio and alkylseleno ($RXCH_2CO_2^-$, X = S, Se; R = butyl, 1-butenyl, 1-pentenyl) acetic acids, it was shown[123,124] that coordination of an olefin moiety to silver is strongly favored by enthalpy but disfavored by entropy. This difference was more pronounced for X = Se.

Solodar and Petrovich[125] have reported solvent dependent equilibrium constants for silver olefin complexes (olefin = norbornene, cyclohexene, 1-methylcyclohexene) measured essentially from the downfield shifts (Δδ) in ^1H NMR spectra of the olefinic protons with the addition of excess $AgBF_4$. The possibility of diolefin complexes was considered negligible. The order of thermodynamic stability for some $AgBF_4$ olefin complexes was found[126] to be $AgBF_4 \cdot 2C_3H_8 > AgBF_4 \cdot 2C_2H_4 > AgBF_4 \cdot C_2H_3Cl > AgBF_4 \cdot 2C_2H_3F$ and was rationalized on the basis of the lower basicity and the larger dipole of the haloolefins.

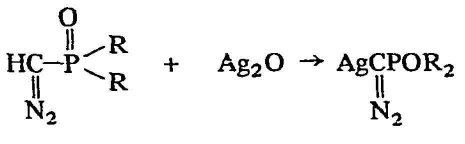
Petrov *et al.*[127] calculated the equilibrium constant for the complexation of butadiene with Ag^I to be 45.5–47.8.

Substituent effects on the equilibrium constant for the complexation of Ag^I with *endo*- and *exo*-5-substituted norbornene and ω-substituted 1-alkenes were investigated[128]. Comparison of the experimental results with those calculated from the Kirkwood–Westheimer–Tanford cavity method proved only marginally satisfactory.

Equilibrium measurements were made on the $AgNO_3\text{–}PhC{\equiv}CH$[129] ($5.4 \cdot 10^7$ l^3 $mole^{-3}$ at 25°C) and on the silver nitrate–isobutene[130] systems (polarographic 59.3 $mole^{-1}$ at 25°C).

ESR spectra of 1-methyl-cyclopentadienylsilver radical and of the radicals formed from the 1,3- and 1,4-cyclohexadiene-$AgClO_4$ and $-AgBF_4$ complexes, indicated[131] the presence of the 1-methyl-3-cyclopentyl radical and probably the same cyclopentadienylsilver radical.

Treatment of silver oxide with OPR_2CHN_2 resulted[132] in formation of a metal-carbon σ-bond.

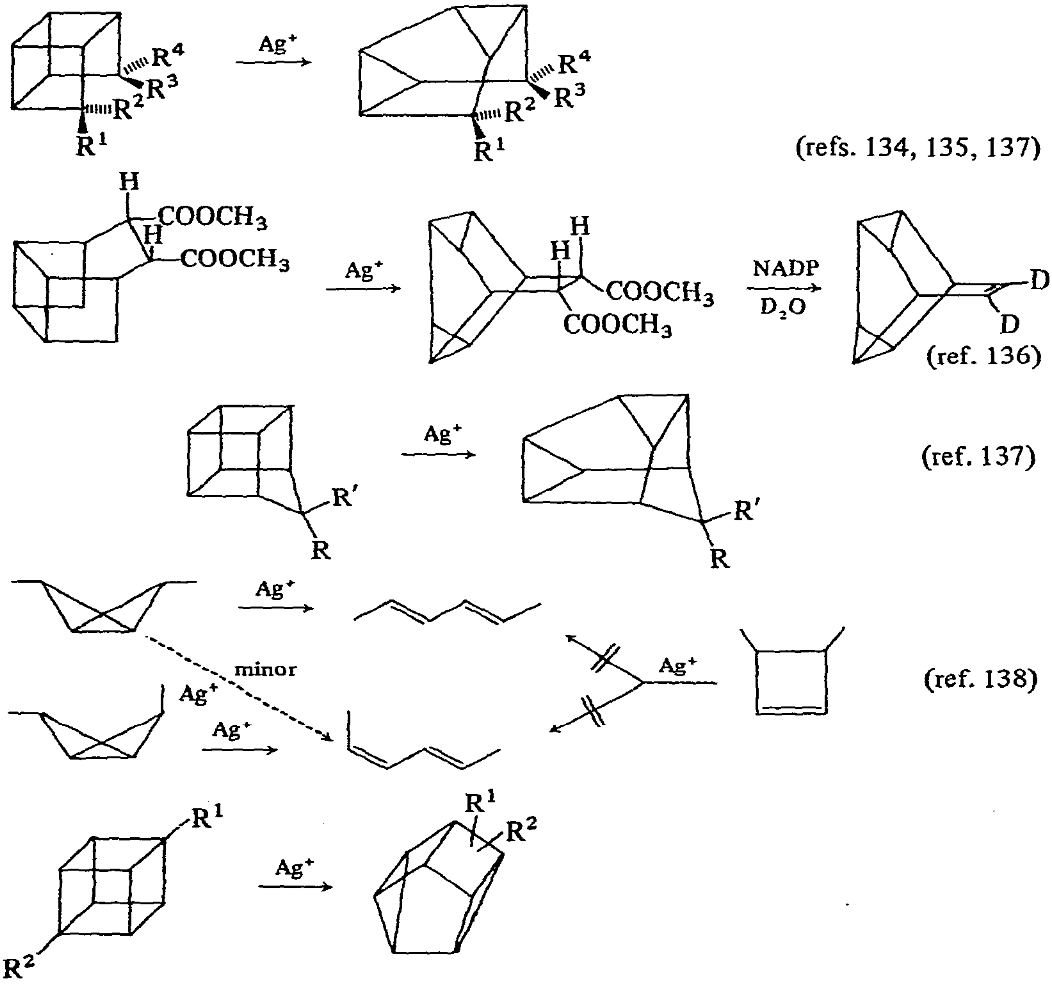


$$\underset{\underset{N_2}{\|}}{HC}\text{—}\overset{\overset{O}{\|}}{P}R_2 + Ag_2O \rightarrow Ag\underset{\underset{N_2}{\|}}{C}POR_2$$

Ag^I catalyzed rearrangements of strained hydrocarbons

A review of the Ag^I promoted steric rearrangements in saturated alicyclic molecules was published[133] (43 references).

Ag^I catalyzed rearrangements[134–140] of strained carbon σ-bonds of the general types reported are illustrated below:

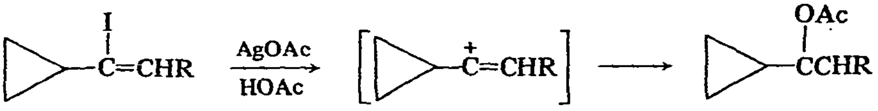


(28)

Since the rates of rearrangement of *endo–endo*, *endo–exo* and *exo–exo* substituted seco-cubanes[135] were comparable, the possibility of a concerted mechanism was discounted.

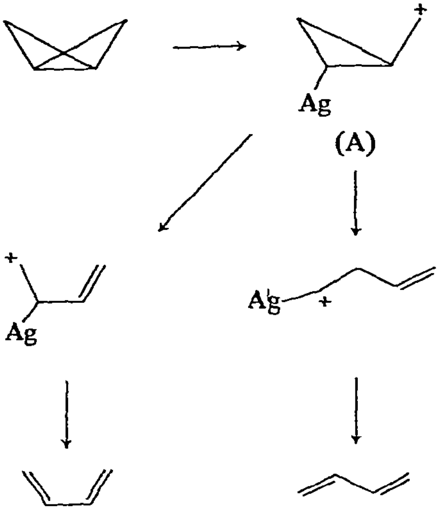
Koser[141] observed a linear free energy relationship between the reported rate constants for Ag^I catalyzed cubane (28)-cuneane rearrangements and the Taft σ* polar substituent constants.

Detailed product distribution and kinetic studies[139,140] on Ag^I promoted rearrangements of the *cis*- and *trans*-1-cyclopropyl-1-iodopropene, 1-cyclopropyl-1-iodoethylene, 3,4-pentadienyl iodide and 3,4-hexadienyl iodide have confirmed the existence of a cyclopropylvinyl type cationic intermediate.

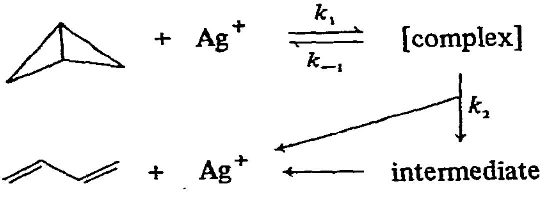


R = CH_3, H

Two mechanisms have been proposed for the Ag^I catalyzed rearrangements of bicyclobutane. Sakai suggested[142,143] that the initial one bond cleavage intermediate A, an argento carbonium ion, can lead to the various products formed.

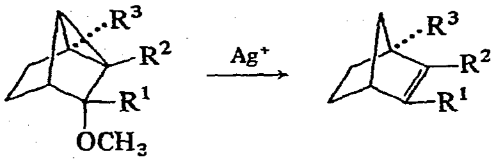


Paquette *et al.* [144-146] proposed a different mechanism on the basis of kinetic data. In some cases, this implies complexation of Ag^I to an sp^2 hybridized electron pair. Deuterium isotope effects in the rearrangements of tricyclo[4.1.0.$0^{2,7}$]heptanes failed to confirm the argento carbonium ion mechanism involving a 1-3 and 1-2 bond cleavage, while favoring a mechanism involving a cleavage of an edge bicyclobutane bond, if possible remote from bulky substituents.

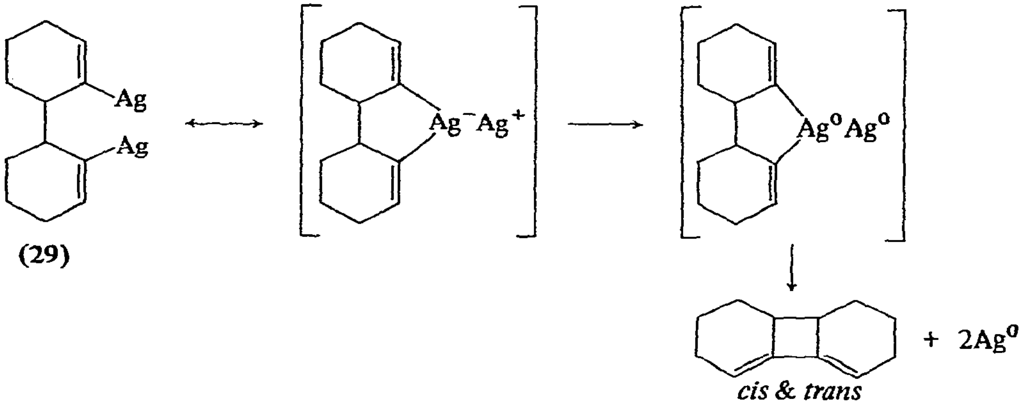


($k_{-1} > k_2$)

One rearrangement was caused[147] by ionization of a methoxyl substituent and not by an Ag^I strained σ-bond interaction.



Ag^{I} catalyzed intramolecular rearrangements of some non-strained systems have been reported. *dl*-2,2′-disilver-3,3′-bicyclohexenyl (29) rearranged[148] to *cis*- and *trans*-tricyclo-[6.4.0.0^{2,7}]dodeca-2,12-dienes, presumably through a transition state with the two carbon atoms coordinated to one Ag atom. A reexamination of the catalytic process has lead Warner to suggest[149] that two silver atoms are involved in the rearrangement of monohomotropylium ions (route a). Based on the catalytic action of the Ag^{I} ions on the cycloadditions of benzyne, Paquette has proposed[150] an alternate pathway involving solely a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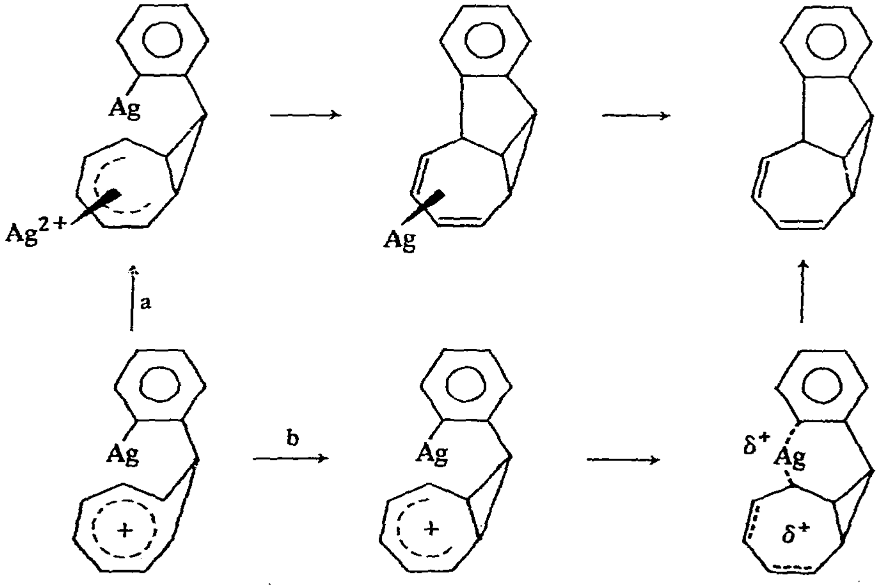
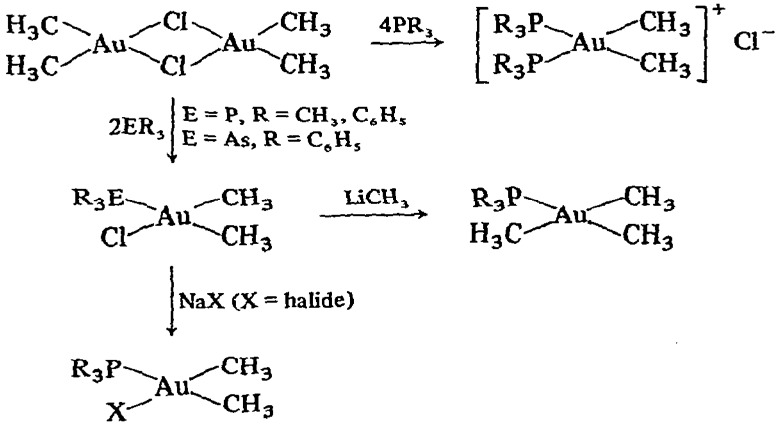
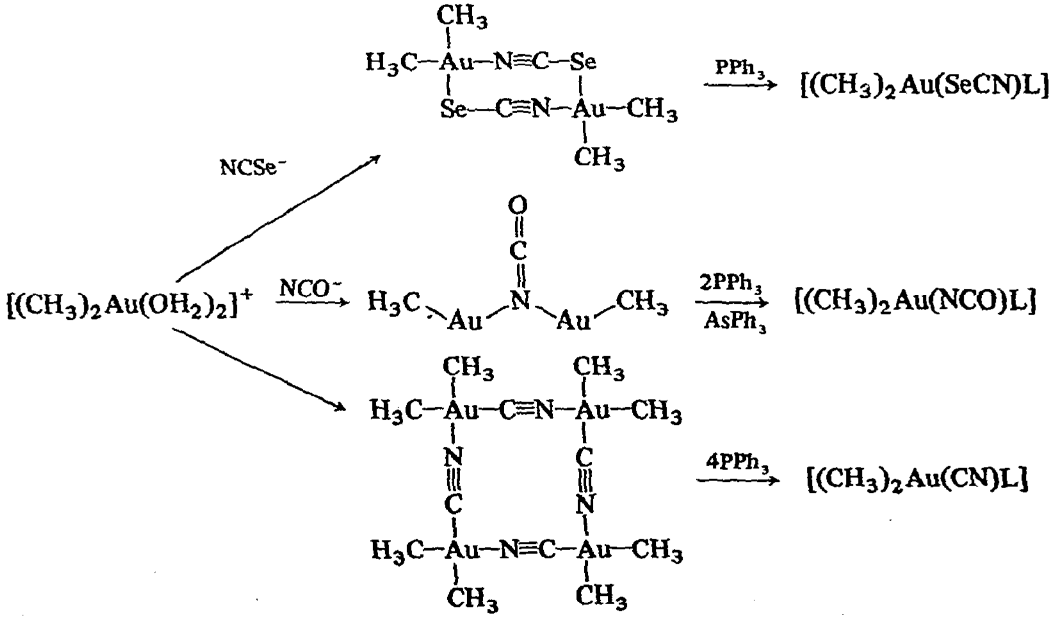


AuCl$_2$]$^-$. On the basis of line broadening in the ^{1}H NMR spectra, the exchange properties of these complexes were determined.

The synthesis and reactions of the dimethyl gold complexes [(CH$_3$)$_2$AuClX] (X = PR$_3$, AsR$_3$); and [(CH$_3$)$_2$ Au(PR$_3$)$_2$]$^+$Cl$^-$ were reported[163]. Structural information was obtained from IR and ^{1}H NMR spectra. By a similar bridgehead cleavage and a subsequent alkylation, [(σ-C$_5$H$_5$)(CH$_3$)$_2$AuPPh$_3$] has been prepared[164]. The stereochemically nonrigid cyclopentadienyl group is σ-bonded; no intermolecular exchange occurs. Replacement of Cl$^-$ in [(CH$_3$)$_2$AuCl(PR$_3$)] by CH$_3$$^-$or σ-C$_5H_5$$^-$ resulted in a decrease in the Au-C bond strength as indicated by a corresponding decrease in the Au-C stretching frequency.

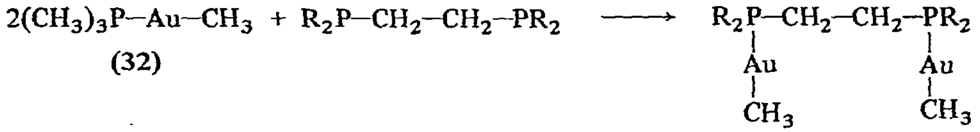


The dimeric pseudohalide complexes [(CH$_3$)$_2$AuX]$_2$ X = NCSe, NCO, have been synthesized[165] and characterized by laser Raman, IR and ^{1}H NMR spectra. The selenocyanate



was assigned C_{2h} symmetry, the cyanate D_{2h}. Bridge splitting reactions of these complexes and of the tetrameric dimethyl gold cyanide complex were described.

Schmidbaur *et al.*[166] on the basis of ^{1}H NMR spectra of $[CH_3Au^IPR_3]$ and $[(CH_3)_3Au^{III}PR_3]$ solutions containing free phosphine proposed an associative mechanism for the exchange process involving an *sp*^{2} hybridized Au^I intermediate and a *dsp*^{3} hybridized Au^{III} intermediate respectively. Thermodynamic parameters were computed[167] for the methyl gold phosphine complex but not for the Au^{III} complex since the exchange process was too slow. For the substitution of $[Me_3P\text{-}AuCH_3]$ (32) the following reactivity order was found[168]: $Ph_3P > (C_2H_5)_3P > (CH_3)_3P \gg Ph_3As$. With the phosphine $R_2P\text{-}CH_2\text{-}CH_2\text{-}PR_2$ ($R = CH_3$, Ph) a dimeric product (33) was formed with 2-coordinate Au^I. Substitution reactions of $(Me)_3Au(PMe_3)$ by PPh_3 were very slow.



$$2(CH_3)_3P\text{—}Au\text{—}CH_3 + R_2P\text{—}CH_2\text{—}CH_2\text{—}PR_2 \longrightarrow \begin{array}{c} R_2P\text{—}CH_2\text{—}CH_2\text{—}PR_2 \\ |\qquad\qquad\qquad | \\ Au \qquad\qquad\quad Au \\ |\qquad\qquad\qquad | \\ CH_3 \qquad\qquad CH_3 \end{array}$$

(32)

(33)

A Au^I acetate complex (34) has been prepared[169] in 90% yield.

$$\begin{tikzcd} \mathrm{PhLi} + \mathrm{ClAuPPh_3} \arrow[r, "\text{1 atm A}", "\text{THF 1 h}"'] & {} \arrow[r, "H_2O"] & \mathrm{PhAuPPh_3}\ (93\%) \arrow[d, "\text{HOAc}"] \\ & & \mathrm{AcOAuPPh_3}\ (90\%)\ (34) \end{tikzcd}$$

The preparation[170] and properties of bromo- and iodobis-pentafluorophenyltriphenylphosphinegold(III) were described.

$$\begin{tikzcd} (C_6F_5)_2AuClPPh_3 \arrow[d, "MX = KBr, LiBr, KI, NaI"] & \\ (C_6F_5)_2AuXPPh_3 & AuPPh_3 \arrow[l, "(C_6F_5)_2TlX"'] \end{tikzcd}$$

Su[171] combined energy correlation diagrams and a simple perturbation method to extend the Woodward–Hoffmann rules for sigmatropic reactions to stereochemically non-rigid organometallic compounds, *e.g.* $(C_5H_5)AuPPh_3$.

Observation of the ^{31}P–H coupling in the variable temperature ^{1}H NMR spectra of $[(C_5H_4R)(PPh_3)Au]$ ($R = H, CH_3$) led[172] to the conclusion that Au^I was σ-bonded. Further evidence of the lack of affinity of Au^I to π-bond was provided[173] by the failure of $[Cl(PPh_3)Au]$ to react with either di- or tetracyanoethylene.

σ-bonded silver atom (route b). Equimolar amounts of $AgBF_4$ have catalyzed[151] the 100% conversion of *cis,cis,trans*-tetramethylocta-2,4,6-triene to hexamethylbenzene.

Miscellaneous reactions

The coupling[152] of alkyl groups from the reaction of alkyl halides and Grignard reagents catalyzed by Ag^I halide is thought to operate via organosilver compound formation; the rate-determining step being the reoxidation of the Ag^0. Selective formation of alkyl radicals from the alkyl halide was confirmed by trapping experiments.

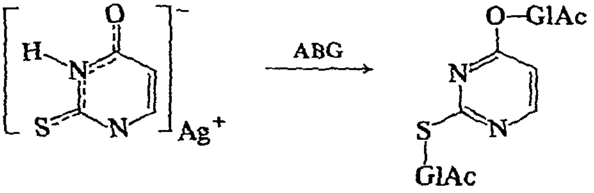
$$R'MgX + AgX \longrightarrow R'Ag + MgX_2$$

$$RAg, R'Ag \longrightarrow [R{-}R, R'{-}R, R'{-}R'] + 2Ag$$

$$Ag + R{-}X \xrightarrow{\text{slow}} R\cdot + AgX$$

$$R\cdot + Ag \longrightarrow RAg$$

Reaction of the silver salt of 2-thiouracil with 2,3,4,6-*O*-acetylglucopyranosylbromide (ABG) gave[153] only the *S*(2),*O*(4)-diglucoside (30).



(30)

An epoxide intermediate has been proposed[154] for the $AgClO_4$ catalyzed solvolysis of 2-chlorocyclohexanone-1-^{14}C in $EtOH$-H_2O to 2-(EtO)-cyclohexanone-x-^{14}C.

Tritium labelling of the acetyl groups in polyacetates has been achieved[155] by a T_2O/pyridine/AgF system.

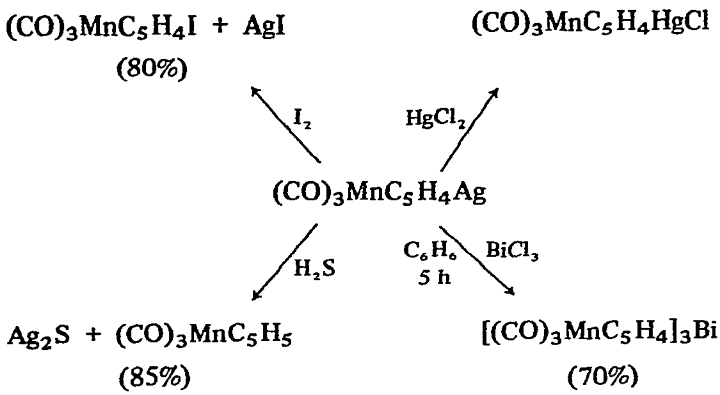
Silver-catalyzed oxidative decarboxylation of acids by peroxydisulphate has been used[157] as a source of alkyl radicals.

$$2Ag^+ + S_2O_8^= \longrightarrow 2Ag^{2+} + 2SO_4^{2-}$$

$$R{-}COOH + Ag^{2+} \longrightarrow R\cdot + CO_2 + H^+ + Ag^+$$

The preparation and reactions of a silver organomanganese complex were reported[158].

$$(CO)_3MnC_5H_4BO_2H_2 \xrightarrow[60°, H_2O]{AgNO_3} \underset{(32\text{–}40\%)}{(CO)_3MnC_5H_4Ag}$$



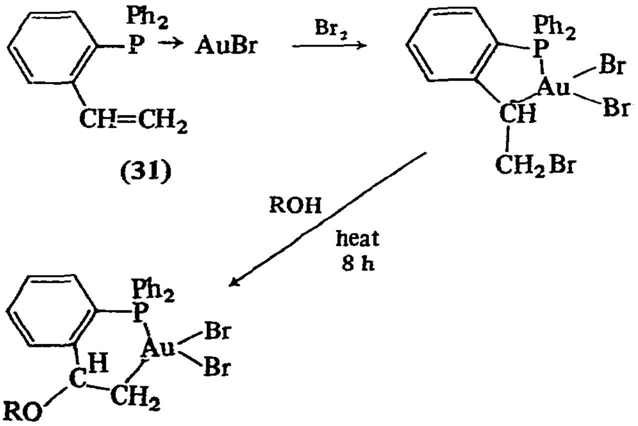
Ogden reported[19] evidence from IR spectra for the existence of silver carbonyl compounds.

Among various silver(I) salts tested, $AgBF_4$ and $AgClO_4$ were effective[88] catalysts in the conversion of hexamethyl Dewar benzene to hexamethylbenzene.

GOLD

A review[159] on $S_E1(N)$ mechanism in organometallic chemistry included considerations of organogold phosphine complexes.

Bennett *et al.*[160,161] have reported the bromination reactions of AuBr [o—CH_2=CH—C_6H_4—PPh_2] (**31**). The mechanism proposed involved a concerted attack on the metal complex by a polarized bromine molecule.



(31)

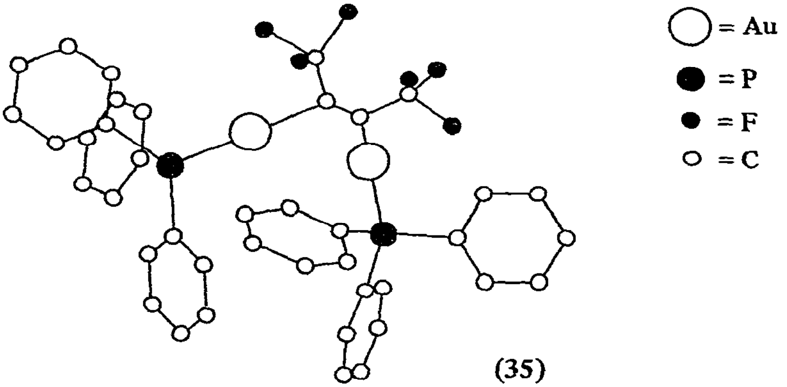
Stocco and Tobias[162] have prepared and characterized by Raman, IR and ^1H NMR spectra, the square planar complexes $[(CH_3)_2AuXY]$: X = Cl, Y = pyridine, PPh_3, $AsPh_3$; $SbPh_3$; X = SCN, Y = pyridine, PPh_3, $AsPh_3$; and the complexes $[(CH_3)_2AuX_2]Y$: Y = ClO_4, X = PPh_3, $AsPh_3$, $SbPh_3$; Y = Cl, X_2 = diphos; and $[(CH_3)_2Au(diphos)]^+[(CH_3)_2$-

Halide phosphinegold(I) complexes were prepared[174] by halogenation of $[Ph_3PAu(C_5H_4FeC_5H_5)]$.

$$Ph_3PAu(C_5H_4FeC_5H_5) \xrightarrow[CCl_4 \atop -20°]{X_2} \underset{(70\%)}{Ph_3PAuX} + \underset{(55\%)}{XH_4C_5FeC_5H_5}$$

$$(X = Br, Cl, I)$$

Gilmore and Woodward[175] have determined the molecular structure of $[(Ph_3P)Au(CF_3)C_2(CF_3)AuPPh_3]$ (35).



(35)

Waters *et al.*[176] have isolated and characterized the complexes $[Au(mnt)_2][(n\text{-}Bu)_4N]_2$ (36) mnt^{2-} = *cis*-1,2-dicyanoethylenedithiolate and $[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Au][Et_4N]_2$ using the mixed valence $[(PhCH_2)_2SAuX \cdot (PhCH_2)_2SAuX_3]$ X = Cl, Br for (36).

Indirect equilibrium studies on the halide exchange reaction of $[(CN)_3ClAu]^-$ with iodide indicated[177] that $k = 4.71 \cdot 10^4$ and that hydration of both the iodo and chloro complexes is less favored.

Negoiu and Baloiu[178] synthesized the linkage isomers of the $[Au(CN)_2(SCN)_2]^-$ complex (37).

$$[Au(CN)_2Cl_2]^- + 2SCN^- \rightarrow \underset{(37)}{[Au(CN)_2(SCN)_2]^-} + 2Cl^-$$

The isothiocyanate was isolated in methanolic solution (IR spectrum bands: 800, 2075 and 2145 cm^{-1}), the more stable thiocyanate from aqueous solution (IR spectrum bands: 705, 2135 and 2150 cm^{-1}).

The activity of $(Ph_3P)AuCl$ as a homogeneous catalyst for the oxidation of cyclohexene was found[179] to be low.

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