COPPER, SILVER AND GOLD

ANNUAL SURVEY COVERING THE YEAR 1973

E. SINGLETON and A. TUINMAN

National Chemical Research Laboratory, Council for Scientific and Industrial Research,
P.O. Box 395, Pretoria 0001 (Republic of South Africa)

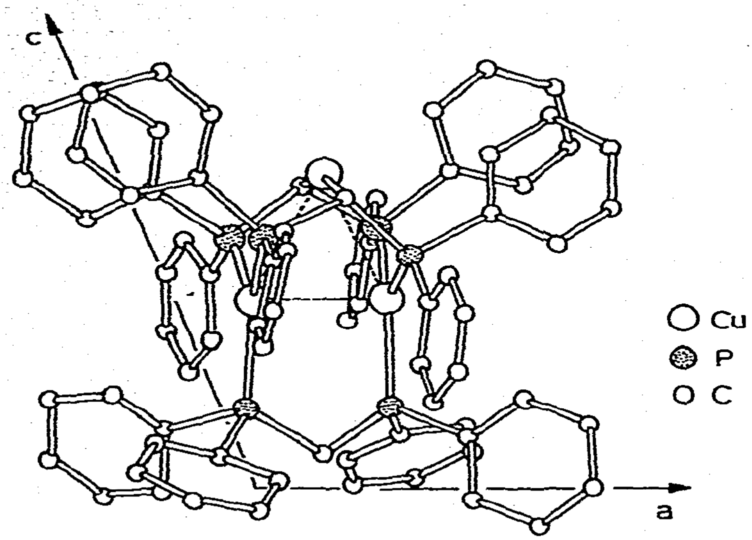
Contents

I. Organocopper compounds

The reaction of copper aryls with bis(diphenylphosphino)methane in toluene produced a complex of empirical formula $[\mathrm{Cu(Ph_2PCH_2PPh_2)}] \cdot \frac{2}{3}\mathrm{PhCH_3}$ (I) which was shown by X-ray analysis to be trimeric. The structural non-equivalence of the phosphine ligands favours the following scheme for the formation of the compound:

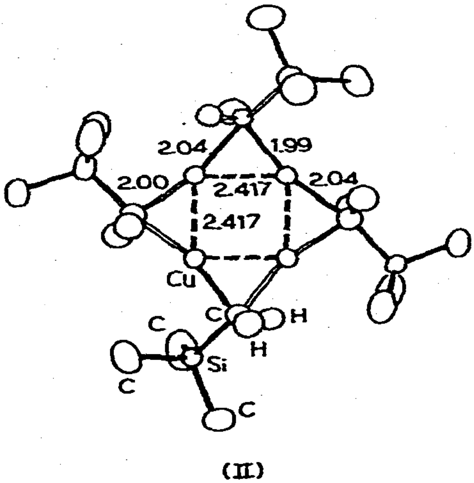
$$3\mathrm{Cu^{I}R} + 3\mathrm{Ph_2PCH_2PPh_2} \rightarrow 3\mathrm{RH} + [\mathrm{Cu^{II}(Ph_2P{\cdots}CH{\cdots}PPh_2)Cu^{\frac{1}{2}}_2(Ph_2P{\cdots}CH{\cdots}PPh_2)}]$$

in which the $\mathrm{Cu^{II}}$ atom is σ-bonded to two carbon atoms [1].



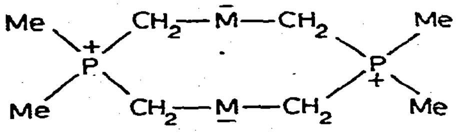
(I)

Preliminary structural analysis on $[Me_3SiCH_2Cu]_4$ (II) at −40° has shown the tetramer to contain a square plane of copper atoms and three centre two-electron alkyl bridges [2]. II prepared from Me_3SiCH_2Li and CuI [3] can be



(II)

used as an alkylating agent producing $(Me_3Si)_2CH_2$, $Me_3SiCH_2CH_2CH{=}CH_2$ and $PhCH_2SiMe_3$ with Me_3SiCl, $CH_2{=}CHCH_2Br$ and PhI, respectively. Increased stabilisation of copper, silver and gold alkyls compared with Me_3SiCH_2 alkyls has been achieved with the isoelectronic phosphonium group $Me_3P^+{-}CH_2^-$ which forms ylides of the type III on treating CuCl and $[Ph_3PAgCl]_4$ with an excess of $Me_3P{=}CH_2$ [4]. The electrophilic cleavage of tetraalkyllead by copper(I) acetate was found to be highly selective. In methylethyllead alkyls, for example, methyl cleavage occurs almost exclusively. A cyclic transition state is postulated with concomitant transfer of an alkyl group to the copper atom [5a]. An alkyl



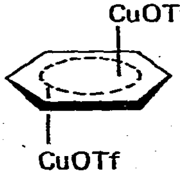
(III)

(M = Cu, Ag, Au)

transfer mechanism is also proposed for the facile reduction of copper(II) complexes by tetraalkyllead compounds. The reduction step is then a homolytic fission of the unstable alkylcopper(II) intermediate [5b].

Isocyanide complexes of copper(I) of stoichiometry $(p\text{-MeOC}_6\text{H}_4\text{NC})_n\text{CuX}$ ($n = 1$, X = Cl, Br, I; $n = 2$, X = Cl, Br), $(p\text{-MeOC}_6\text{H}_4\text{NC})\text{CuXY}$ (X = Cl, Y = Py, PPh_3, Phen; X = Br, Y = PPh_3, AsPh_3, Phen, DPE), $[(p\text{-MeOC}_6\text{H}_4\text{NC})\text{CuXY}]\text{PF}_6$ (X = PPh_3, Y = Phen; X = Y = PPh_3), $(\text{C}_2\text{H}_5\text{NC})\text{CuClPPh}_3$ and $[\text{C}_2\text{H}_5\text{NCCu}(\text{PPh}_3)_3]\text{PF}_6$ are reported [6]. The use of the anionic ligands HB(pz)_3 and $\text{HB(Me}_2\text{pz)}_3$ to increase electron density on copper led to a stabilisation of the copper carbonyls Cu(CO)L [L = HB(pz)_3 and $\text{HB(Me}_2\text{pz)}_3$]. The reactions of these carbonyls with other neutral ligands parallel those of CpCuCO, with the complexes $\text{HB(pz)}_3\text{CuL}$ [L = PPh_3, PMePh_2, P(OPh)_3, P(OMe)_3, DPE, AsPh_3, SbPh_3, CNBu-t] being isolated [7].

Cuprous oxide in aqueous BF_3 solution absorbs CO to produce a colourless solution, said to contain the cation Cu(CO)_4^+ from IR spectra [8]. Investigations into the activities of a series of transition metal ions, including copper zeolites, for CO oxidation by O_2 found that the activities increased exponentially with the increase in their standard oxidation potential [9]. The formation of carbonyl complexes in a $\text{Cu}^{\text{I}}\text{Y}$ zeolite was studied by means of IR spectroscopy [10]. Solutions of copper(II) chelates of (—)-ephedrine, ψ-ephedrine, *N*-ethylnorephedrine and *N*-n-butylnorephedrine in isooctane react with carbon dioxide producing 1/1 adducts which slowly lose CO_2 on standing in air [11]. The IR and laser Raman spectra of phenylethynylcopper(I) do not support the presence of two different types of C≡C bonds in the structure as suggested by X-ray analysis [12]. Cationic benzene and olefin complexes of the type $[\text{CuL}_2(\text{OTf})]$ (L = 1,5-COD, *endo*-dicyclopentadiene, OTf = trifluoromethanesulphonate), [CuL(OTf)] (L = 1,5-COD, 1,3,5,7-cyclooctatetraene, norbornylene, (*E*,*E*,*E*)-, (*Z*,*E*,*E*)- and (*Z*,*Z*,*Z*)-1,5,9-cyclododecatriene, 1,3-COD), $[\text{CuL}_3\text{OTf}]$ (L = *trans*-cyclooctene) and $[\text{Cu}_2\text{L(OTf)}_2]$ (L = 1,3,5-cycloheptatriene, C_6H_6) have now been fully characterised. Preliminary X-ray data on $[\text{Cu}_2(\text{C}_6\text{H}_6)(\text{OTf})_2]$ indicate structure IV for this complex. The dichotomy observed between vinyl proton shifts in the ^{1}H NMR of these olefin complexes is explained by variations in the nature



(IV)

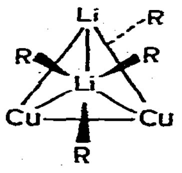
of the metal—olefin bond [13]. Copper(I) chloride dienes have been prepared by distilling olefins, e.g. butadiene, into aqueous NH_4Cl + CuCl solutions at 0°C under nitrogen. The structures are discussed with respect to the CuCl catalysed hydrochlorination of myrcene [14]. In the reactions of C_6-C_8 olefins, studied potentiometrically, with CuCl and $AgNO_3$ in aqueous medium, it was concluded that complex formation increased with the C number of the olefin, and that olefin branching decreased complex formation. Complexes of copper ions are considerably more stable than those of silver ions [15]. The single exchange-narrowed band recorded from ESR measurements on arene-Cu^{II} montmorillonite (arene = benzene, biphenyl, naphthalene and anthracene) are interpreted in terms of the d^9 Cu^{II} ion functioning as an electron acceptor for the transfer of π-arene electrons [16].

II. Reactions of organocuprates and related reagents

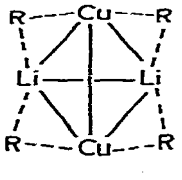
The use of organocuprates in synthesis has been reviewed by Normant [17]. Posner's very detailed and comprehensive survey covers the conjugate addition reactions of organocopper reagents [18].

1. Lithium—copper compounds

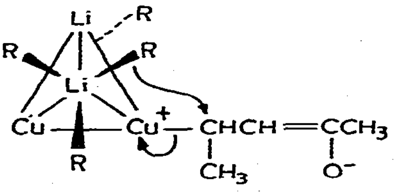
The decomposition of lithium dialkylcuprates was found to be catalysed by the presence of iron impurities, e.g. from imperfectly sealed teflon-coated stirring bars [19]. House [19] proposed a dimeric structure for dialkyllithium cuprates in which the alkyl groups would bind together at the faces (Va) or at the edges (Vb) of a tetrahedron formed by the four metal atoms. Conjugate alkylation is postulated to proceed via the intermediate (Vc) which could form either through electron transfer with subsequent recombination of ion radicals or by direct nucleophilic addition of Va to the enone. The saturated ketone pericyclocamphor reacts with LiR_2Cu (R = Me, n-Bu) producing VIa and VIb in high yields [20].



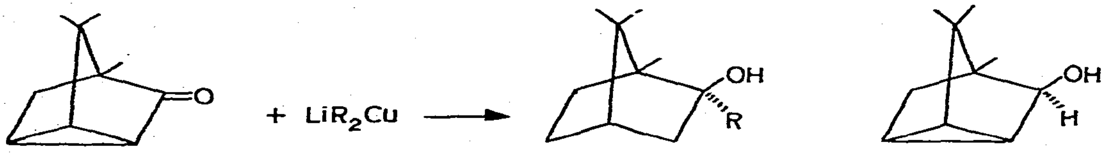
(Va)



(Vb)



(Vc)



(VIa)
(for R = Me only)

(VIb)
(for R = n-Bu only)

2. Mixed cuprates

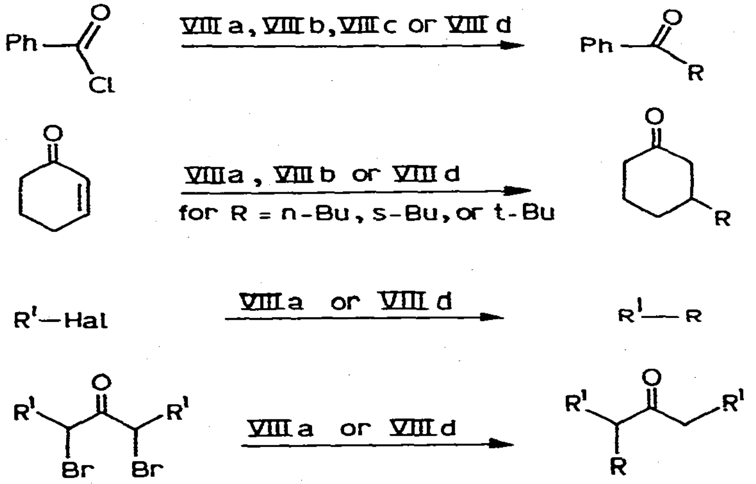
Unsymmetrical lithium organocuprates of the type LiRCuCN were prepared from RLi and CuCN, thus requiring only one equivalent of RLi to form the alkylating agent. The nitrile group displayed no tendency to transfer [21]. The newly developed mixed cuprates VII react with acid chlorides, alkyl halides or

$$t\text{-BuOCu} + \text{RLi} \longrightarrow \underset{(\text{VII})}{\text{Li}(t\text{-BuO})\text{RCu}}$$

(R = e.g. Me)

enones transferring only the R group. A reactivity gradient with the alkyl halides and enones for the different R groups of primary > secondary > tertiary ≫ vinyl was observed [22]. Posner et al. [23] synthesised and studied the reactions of 5 groups of alkylhetero(alkyl)lithium cuprates (VIIIa-VIIIe in Scheme 1). The cuprates (VIIId) were found to be most useful due to ease of preparation, thermal stability and high efficiency.

SCHEME 1

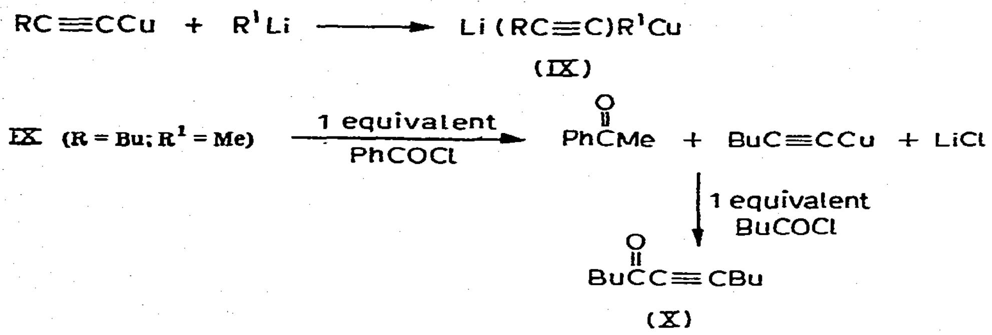


Li(Het)RCu

(VIIIa) Het = t-BuO
(VIIIb) Het = PhO
(VIIIc) Het = t-BuS
(VIIId) Het = PhS
(VIIIe) Het = Et_2N
(R = n-Bu, s-Bu or t-Bu)

The reactions of VIIIa or VIIId with the dibromoketone (Scheme 1) is said to proceed via a cyclopropanone intermediate [24]. Non-symmetrical ketones, e.g. 1,3-dibromo-2-heptanone, are alkylated preferentially at the least substituted α-position. Regioselectivity increases from methylation (1/1) to n-butylation (3/1) to s-butylation (7/1) to t-butylation (9/1) [24]. The selectivity of alkyl group transfer from the mixed dialkylcuprate IX was demonstrated by treating IX first with one equivalent of PhCOCl then with one equivalent of BuCOCl (Scheme 2). The reaction selectivity was indicated by the formation

SCHEME 2



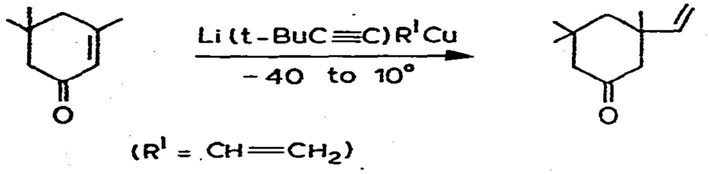
$$RC\equiv CCu + R^1Li \longrightarrow Li(RC\equiv C)R^1Cu \quad (IX)$$

$$IX\ (R = Bu; R^1 = Me) \xrightarrow[PhCOCl]{1\ equivalent} PhC(=O)Me + BuC\equiv CCu + LiCl$$

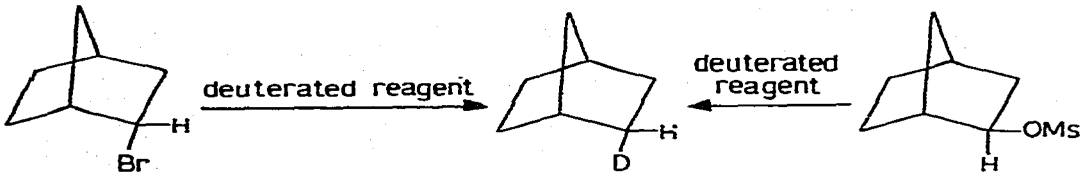
$$BuC\equiv CCu \xrightarrow[BuCOCl]{1\ equivalent} BuC(=O)C\equiv CBu \quad (X)$$

of X and the complete absence of any $PhC(=O)C\equiv CBu$ [25]. Ease of preparation and high reactivity made IX (R = t-Bu; R′ = $CH=CH_2$) the reagent of choice for the vinylation of isophorone [19] (Scheme 3). A reagent produced from $LiAlH(OMe)_3$ and $[CuI]_n$ promoted the reductive elimination (95-100%) of the hetero groups from a large variety of alkyl, allyl, vinyl or aryl bromides or mesylates. The reactions, which proceed with retention of configuration for the bromides but with 100% inversion for the mesylates (Ms) (Scheme 4), are postulated to occur via copper—bromide interaction and then ligand rearrangement and an S_N2 mechanistic pathway, respectively [26].

SCHEME 3



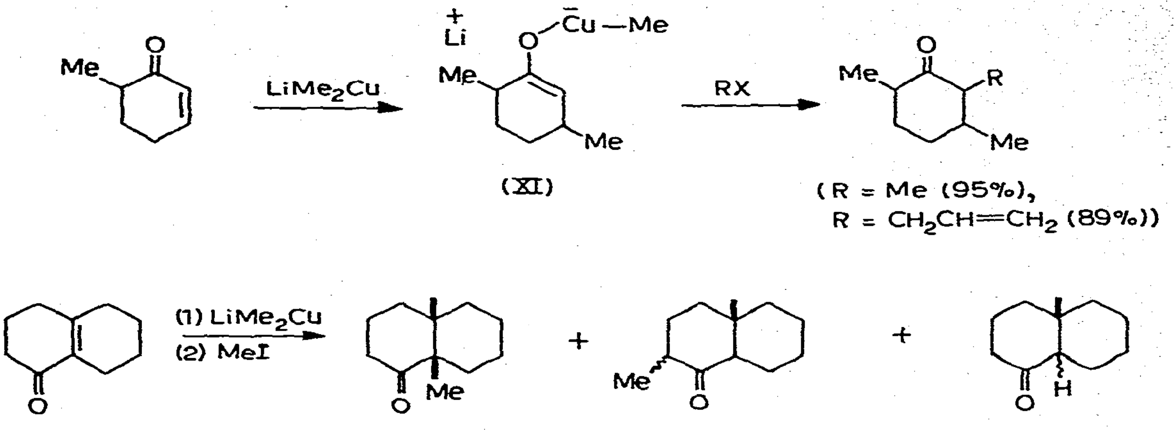
SCHEME 4



3. *Conjugate alkylation*

The primary product of enone alkylation with $LiMe_2Cu$ was reported as XI, which is readily alkylated in situ with alkyl or allyl halides in which this second alkylation is regiospecific if the enone β-carbon atom is not disubstituted

SCHEME 5



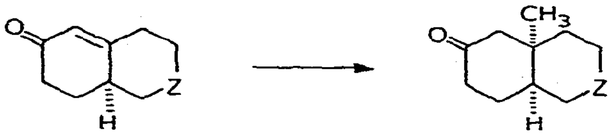
(XI)

(R = Me (95%),
R = $CH_2CH{=}CH_2$ (89%))

(XII) (47%) (XIII) (23%) (XIV) (30%)

[27] (Scheme 5). When enones with disubstituted β-carbon atoms are used (e.g. XII) steric hindrance becomes important, proton transfer becomes a competing reaction and non-specificity (XIII) as well as incomplete alkylation (XIV) result [27].

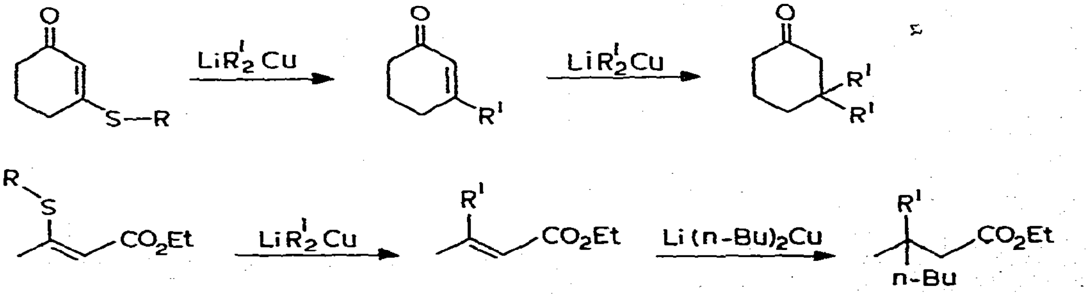
Carbocyclic and heterocyclic enones XV produced XVI with LiMe$_2$Cu [28] with β-thioethers of α,β-ethylenic esters and ketones, dialkyllithium cuprates initially replace the hetero group with an alkyl group [29]. LiMe$_2$Cu reacted further only with the enones, but the more reactive n-butyl reagent caused conjugate alkylation of the unsaturated esters as well (Scheme 6) [29]. Conjugate additions to cyclopropylenones proceed preferentially at the double bond regardless of whether the cyclopropyl or olefinic moiety was closer to the carbonyl



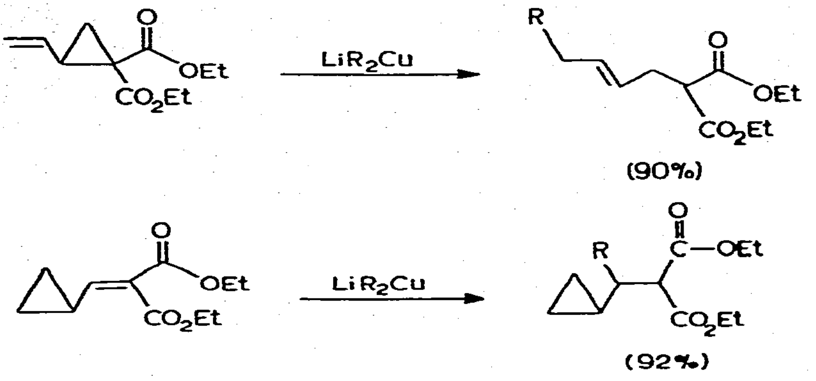
(XV) (XVI)

(Z = CH_2, NCH_3)

SCHEME 6



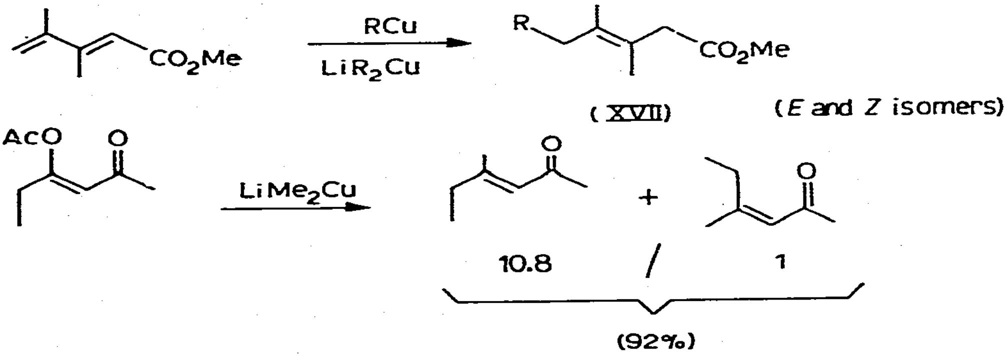
SCHEME 7



(R = Me, n-Bu)

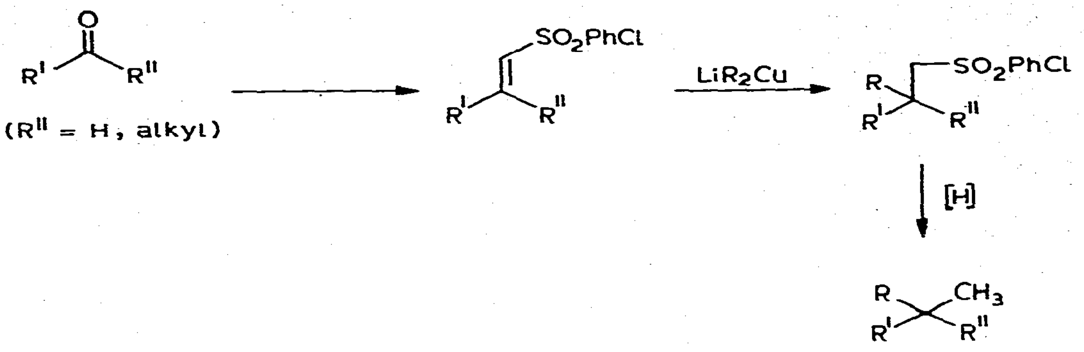
(Scheme 7) [30]. Reactions of LiR_2Cu with $\Delta^{2,4}$-dienoic esters readily produced approximately equal amounts of the *E* and *Z* isomers of XVII [31]. With vinyl- or alkyl-copper reagents, however, the reaction, though slower than that using LiR_2Cu compounds, occurs with a high degree of stereospecificity and produces a high yield of β,γ-unsaturated esters containing up to 99% of the *E* isomer [31]. With enol acetates of β-dicarbonyl compounds and one equivalent of LiR_2Cu the corresponding α,β-unsaturated carbonyl compounds in moderate to excellent yields are produced. The reaction proceeds via a stereoselective replacement of acetoxy by alkyl with predominant retention of configuration (Scheme 8) [32].

SCHEME 8

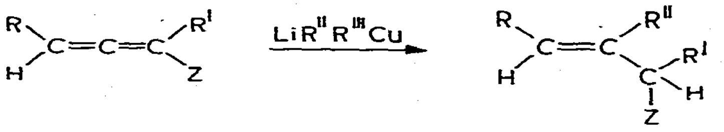


With two equivalents of the cuprate, saturated dialkylated ketones are formed [32]. Alkenyl-*p*-chlorophenyl sulphones were found to undergo organocopper addition β to sulphur. The resulting alkylaryl sulphones could then be selectively hydrogenolised at the alkyl—sulphur bond [33]. This reaction sequence (Scheme 9) allows the conversion of aldehydes to t-alkanes having three different alkyl groups, or of certain ketone carbonyls to quaternary alkanes [34]. LiR_2Cu and activated allenes form XVIII in a non-stereospecific manner. Unsymmetrical cuprates transferred predominantly the less anionic of the groups R″ and R‴ (Scheme 10) [35].

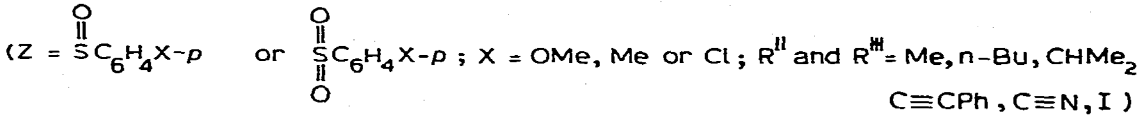
SCHEME 9



SCHEME 10



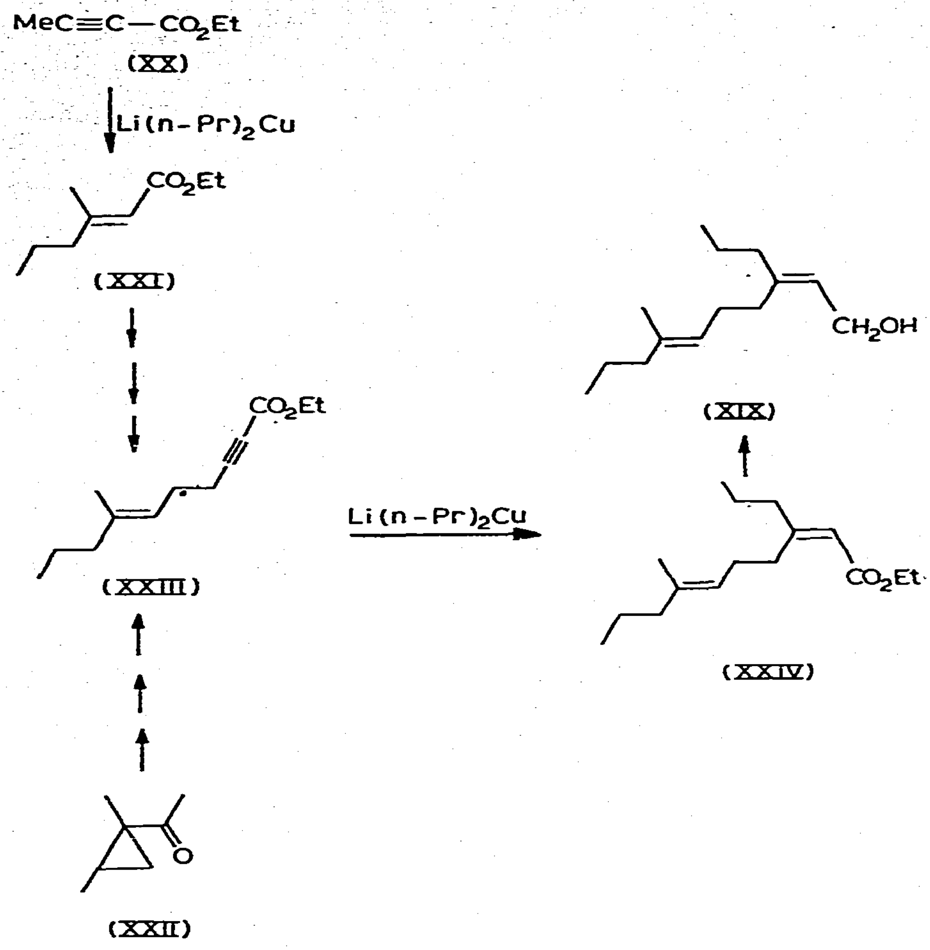
(XVIII) (58–89%)



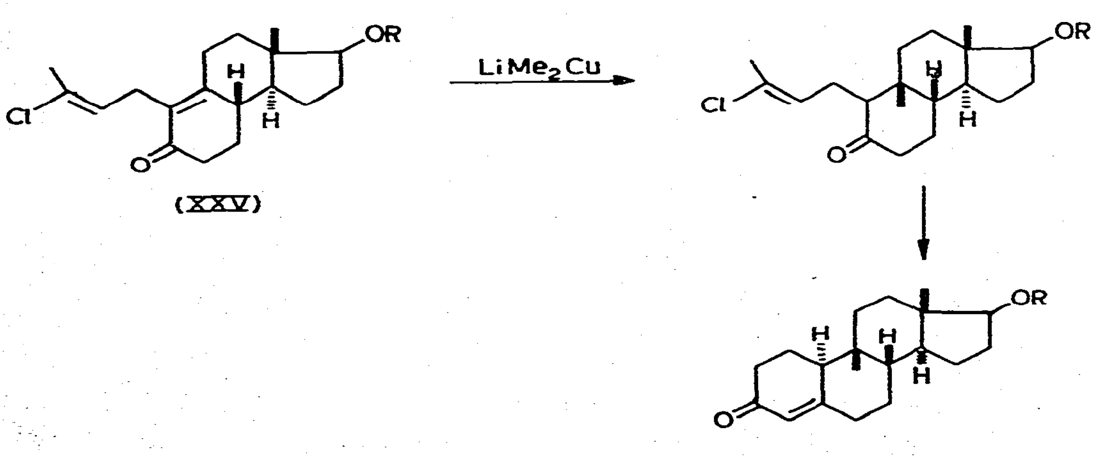
$(Z = \overset{\overset{\displaystyle O}{\|}}{S}C_6H_4X\text{-}p$ or $\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}C_6H_4X\text{-}p$; X = OMe, Me or Cl ; R^{II} and R^{III} = Me, n-Bu, $CHMe_2$, $C{\equiv}CPh$, $C{\equiv}N$, I)

4. Applications

Two syntheses of what was believed to be a sex pheromone of the Codling Moth (XIX) were reported simultaneously [36, 37]. Starting materials XX [36] and XXII [37] and synthetic routes were different but the key penultimate step was the same in each case, viz. conjugate alkylation of the 2-alkynoic ester XXIII with lithium di-n-propyl cuprate, which proceeded stereospecifically *cis* to give the 2*Z*-isomer XXIV. Reduction of the ester group afforded XIX. One group used the same *cis*-conjugate alkylation (XX → XXI) [36] to ensure *E*-stereochemistry at the 6-position. Unfortunately XIX was not identical with the natural product which is now believed to have 6*Z*-stereochemistry. Conjugate alkylation of the 4,5-*seco* steroid XXV with $LiMe_2Cu$ formed specifically the product with *B,C-cis* ring junctions, i.e. the introduction of a 9β-methyl group. Hydrolysis of the vinyl chloride and closure of the *A*-ring yielded 19(10→9β)-*abeo*-10α-testosterone (XXVI) [38, 39]. A number of compounds of general formula XXVIII have been prepared from the readily available XXVII, including 11α-methyl prostaglandin (XXVIIIb) formed from $LiMe_2Cu$ reduction of XXVIIb. Treatment of XXVIIa with an excess of $LiMe_2Cu$ gave 28% of the desired XXVIIIa. The major product XXIX was formed by methyl displacement of the 15-acetoxy group coupled with conjugate alkylation [40]. A report on the

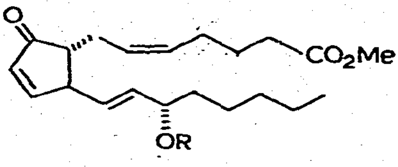


alkylation of the β-position of the prostaglandin precursor XXX utilising vinylcopper tributylphosphine complexes (XXXI and XXXII) has appeared. Protona-

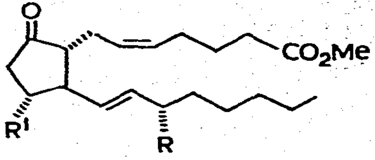


(XXV)

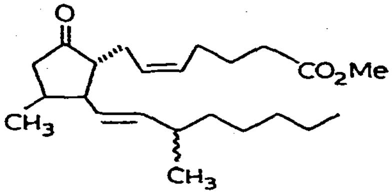
(XXVI)

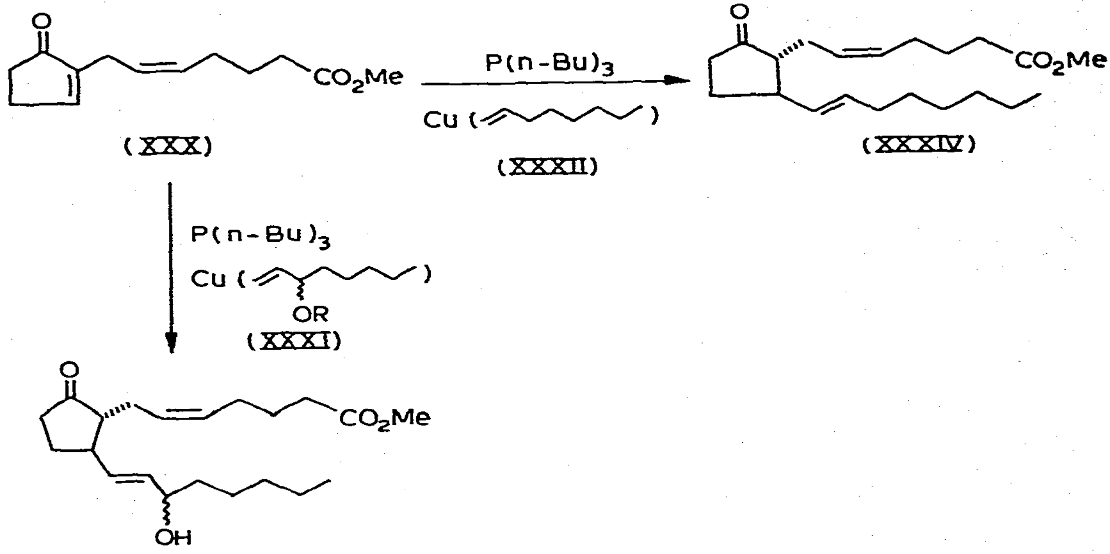

(XXVII)

(a, R = Ac; b, R = H)

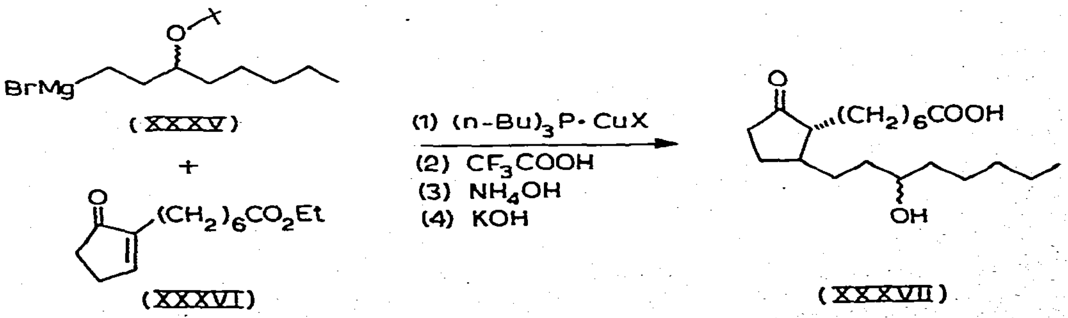

(XXVIII)

(A, R = Ac; R' = Me; b, R = H, R' = Me)


(XXIX)



(XXX) (XXXII) (XXXIV) (XXXI) (XXXIII)



(XXXV) (XXXVI) (XXXVII)

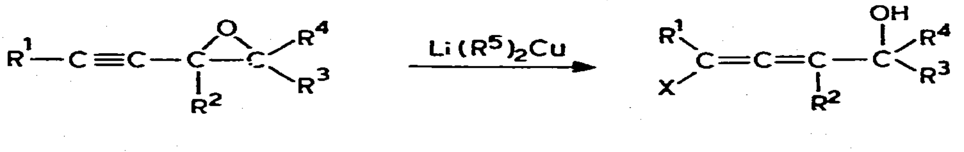
tion of the initial enolate afforded racemic mixtures of XXXIII and XXXIV [41]. The copper(I) catalysed reaction of XXXV with the enone XXXVI produced eventually racemic 11-deoxy-13-dihydroprostaglandin E_1 (XXXVII), with the thermodynamically more stable *trans*-configuration of the side chains predominating [42].

5. Reactions with epoxides, esters and halides

(i) Epoxides

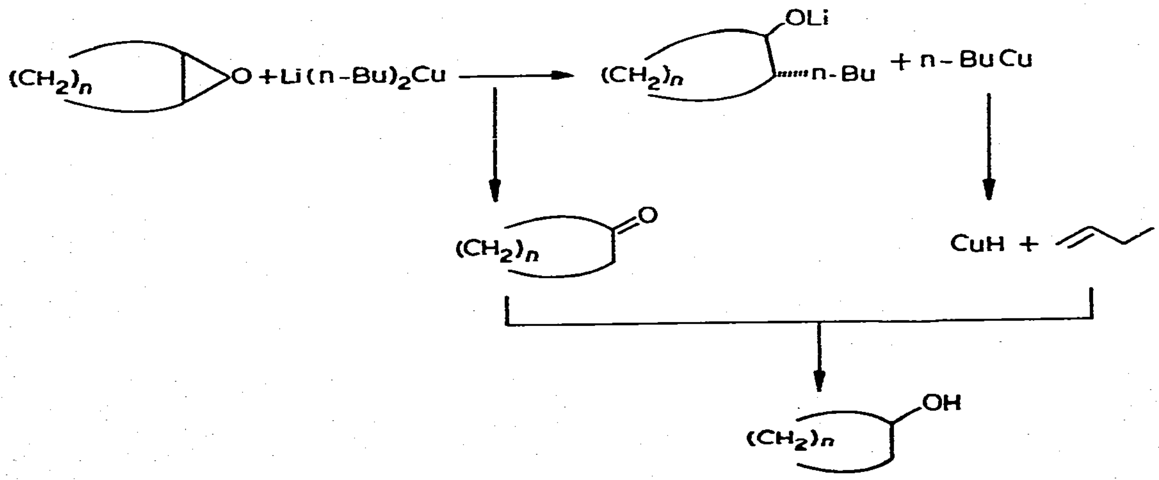
Allenic alcohols were generated in good yields by the reaction of dialkyllithio cuprates with α-acetylenic epoxides (Scheme 11). Non-alkylative reduction (to XXXVIII) was competitive in certain instances. Direct attack at the epoxide moiety was encountered only in one case and then only to about 10% [43]. Lithium organocuprates were found to be the best reagents for the reductive alkylation of oxiranes. Yields were significantly higher than with other organometallic reagents and could be carried out in the presence of unprotected carbonyls. When Li(n-Bu)$_2$Cu was used, the normally occurring side reaction to the ketone gave rise to non-alkylated alcohols via the butylcopper and copper halide reagent artefacts (Scheme 12) [44]. With LiMe$_2$Cu stereospecific anti-opening of the ether function in α-oxygen substituted epoxides was observed. The reaction was only slightly regioselective and no inductive or other

SCHEME 11

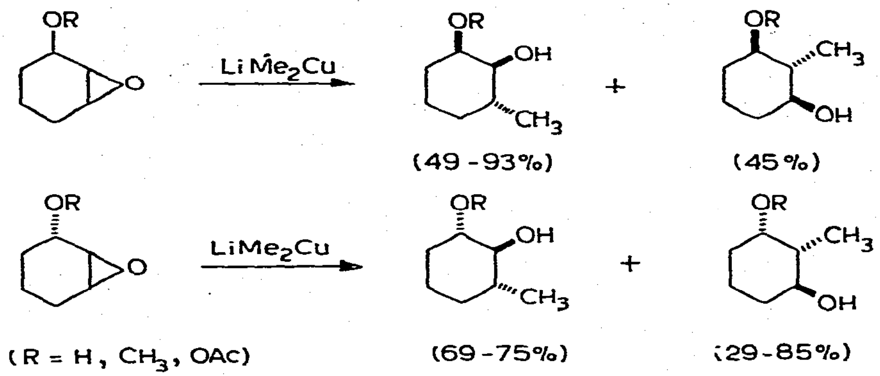


(XXXVIII) (X = R⁵, H)

SCHEME 12



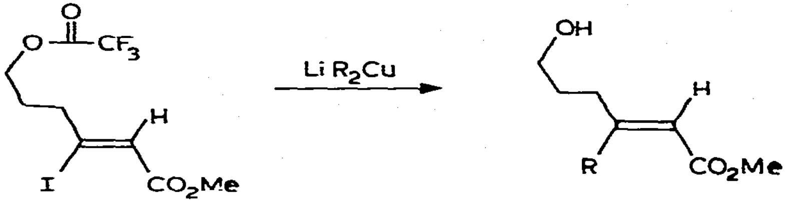
SCHEME 13



specific directive influence could be detected. Product distribution was found to be largely a result of conformational control (Scheme 13) [45].

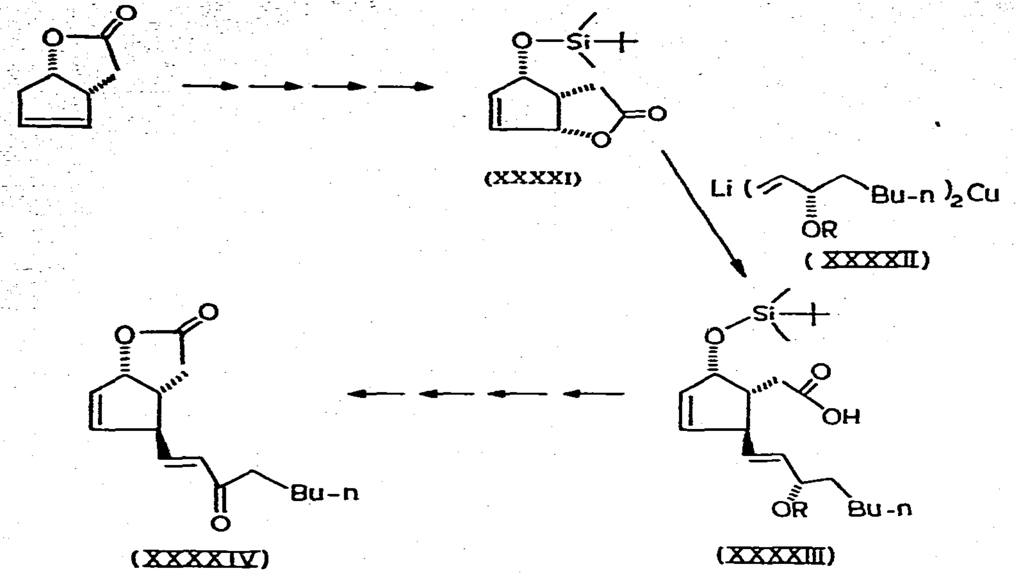
(ii) Esters

Reductive alkylation of the vinylic iodide XXXIX with LiR_2Cu gave XXXX, which is a building block for insect juvenile hormones [46]. The allylic lactone XXXXI underwent coupling with the enantiomerically pure vinylic cuprate XXXXII yielding the acid XXXXIII in high yield. The bulky silyloxy group prevented S_N2 product formation. Further transformation produced XXXXIV, an important intermediate in the synthesis of prostaglandins A_2, E_2 and $F_{2\alpha}$ [47]. The coupling reactions of a number of lithium diorganocuprates

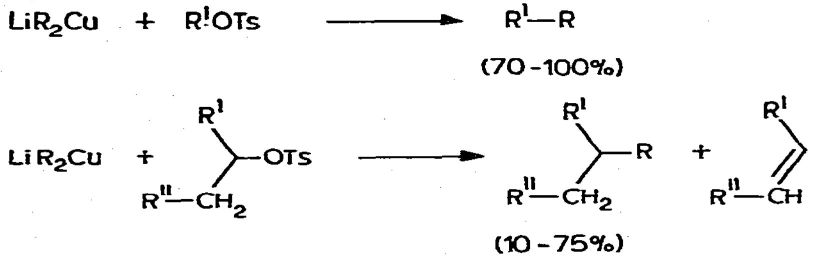


(XXXIX) (XXXX)

with tosylates is reported [48, 49]. With primary tosylates the reactions produced high yields of products [48], but secondary tosylates tended to form elimination products as a side reaction [49] (Scheme 14). Partial suppression of these side reactions was obtained at low temperatures and long reaction times [48]. The reactions with both the cuprates LiR_2Cu (R = Me, Ph) proceeded with inversion of configuration presumably via "S_N2-like" attack of cuprate copper on the tosyl carrying carbon, producing a square planar triorganocopper(III)

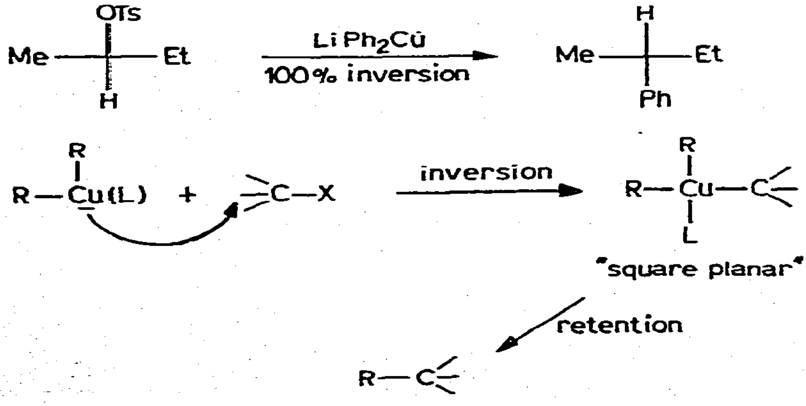


SCHEME 14



intermediate [49] (Scheme 15). Difunctional substrates react first at the tosyl group for halo- or keto-tosylates, but little selectivity is shown towards epoxy-

SCHEME 15

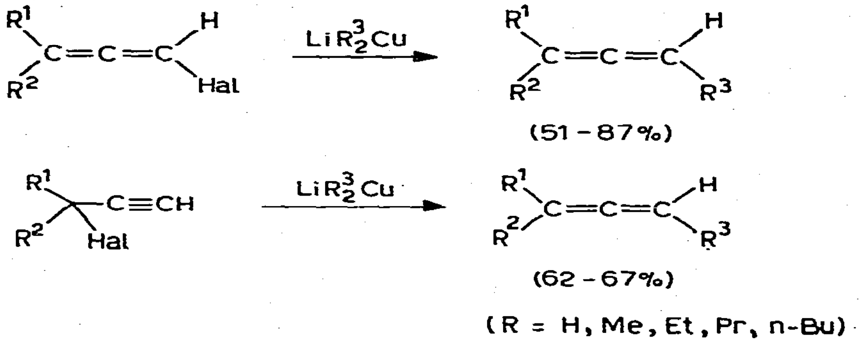


tosylates [48]. The order of effectiveness of the leaving group is OTs > I ~ Br > Cl [49].

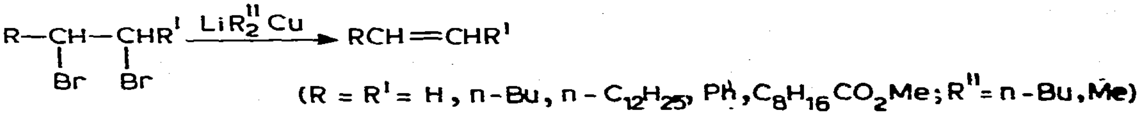
(iii) Halides

Alkylallenes were prepared in high yields by the reaction of either the halogenoallenes or halogenoalkylalkynes with LiR_2Cu (Scheme 16) [50]. An excess of LiR_2Cu (R = Me, n-Bu) with 1,2-dibromides produced olefins (Scheme 17). The presence of an ester group in the substrate did not affect the reaction [51]. Allylic halides formed three product types on exposure to Grignard reagents (Scheme 18). The effect of added metal salts, including $CuCl_2$, on the product distribution was studied [52]. The coupling reactions of various Grignards with α-chloroenamines produced two products (Scheme 19) whereas

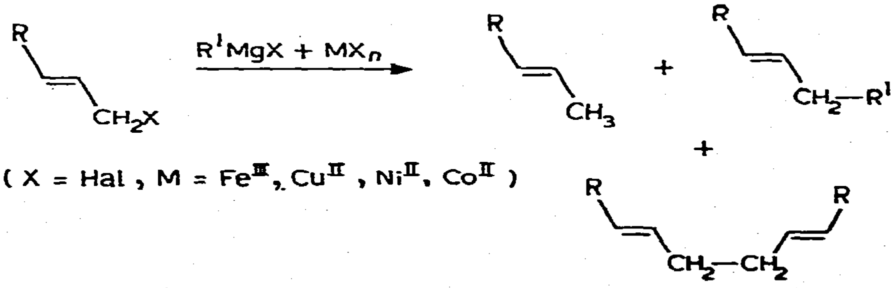
SCHEME 16



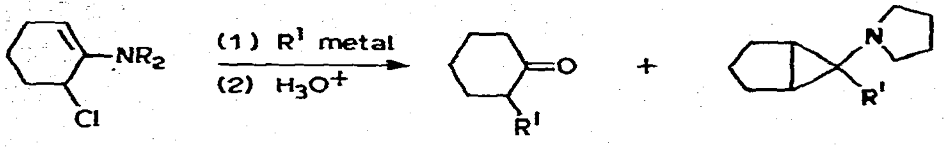
SCHEME 17



SCHEME 18



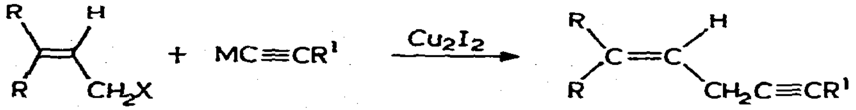
SCHEME 19



(XXXXV)

with LiR_2Cu only XXXXV was formed [53]. Cuprous salts catalysed the coupling of allyl chlorides and alkali acetylides [54] (Scheme 20). Alkynylcopper

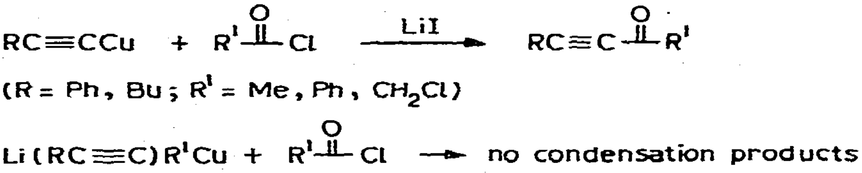
SCHEME 20



(M = Na, Li; R = H, Me; R^1 = Bu, CH_2OEt, Cl, OEt)

compounds reacted with acid chlorides in the presence of lithium iodide to give the corresponding ketones. Mixed dialkyl cuprates were reported not to condense with acid chlorides, however [55] (Scheme 21). The reactive species

SCHEME 21



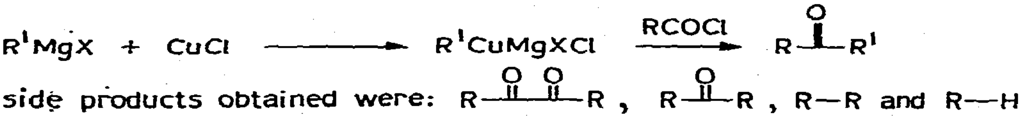
$$RC{\equiv}CCu + R^1\overset{O}{\overset{\|}{C}}Cl \xrightarrow{LiI} RC{\equiv}C\overset{O}{\overset{\|}{C}}R^1$$

(R = Ph, Bu; R^1 = Me, Ph, CH_2Cl)

$$Li(RC{\equiv}C)R^1Cu + R^1\overset{O}{\overset{\|}{C}}Cl \longrightarrow \text{no condensation products}$$

in the reductive alkylation of sterically hindered acid chlorides with Grignard reagent—cuprous chloride mixtures was found to be an alkylmagnesium copper compound. Though the major product of the reaction is a ketone, the radical decomposition of the intermediate produced a series of side products [56] (Scheme 22). Treatment of α,α-dichloro esters with $LiMe_2Cu$ at ambient

SCHEME 22



$$R^1MgX + CuCl \longrightarrow R^1CuMgXCl \xrightarrow{RCOCl} R\overset{O}{\overset{\|}{C}}R^1$$

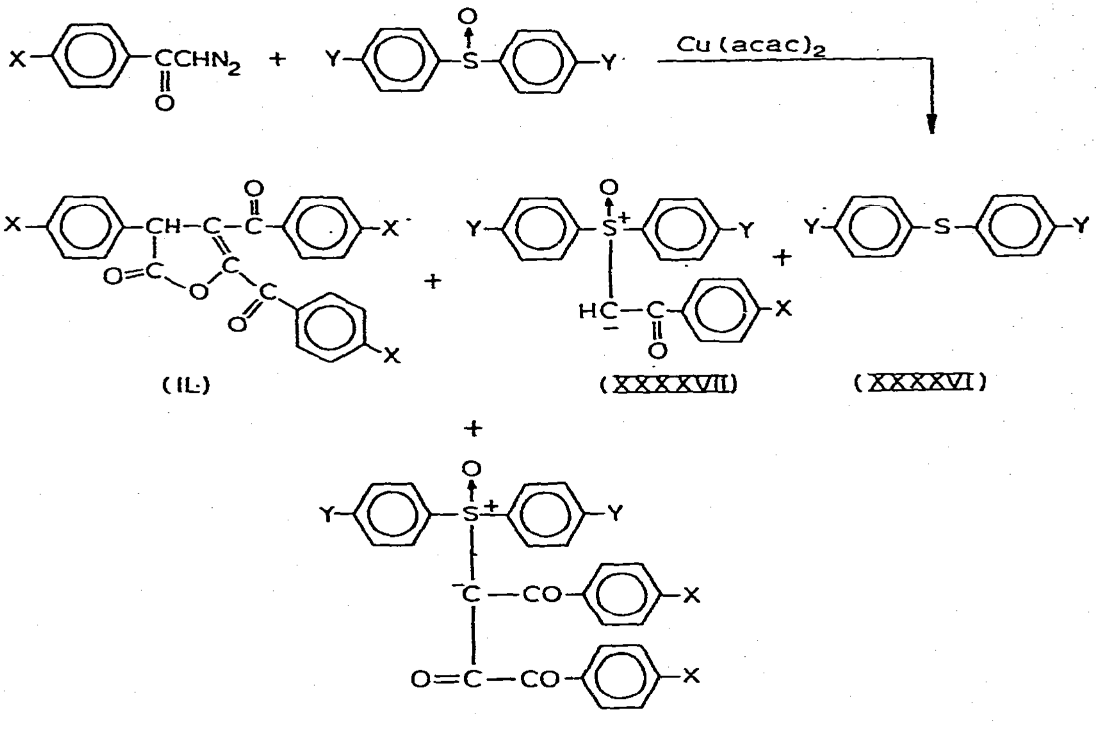
side products obtained were: $R\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}R$, $R\overset{O}{\overset{\|}{C}}R$, R—R and R—H

temperatures gave a mixture of α-chloro-α-methyl esters and non-chlorinated α-methyl esters. At —70°C the reaction produces α-chloroester enolates which gave α-methyl ester enolates on warming to room temperature [57].

6. *Catalysis*

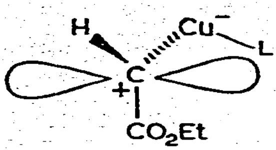
(i) Reactions of diazonium salts

The copper chelate catalysed reaction of α-diazoacetophenones with substituted diphenyl sulphoxides gave two types of products, diaryl sulphides (XXXXVI) and oxonium ylides (XXXXVII) in ratios depending upon the substituents of the α-diazoacetophenones and sulphoxide. The novel reaction of phenylglyoxal and oxosulphonium ylides in the presence of Cu(acac)$_2$ produces XXXXVIII, but with copper phthalocyanine as catalyst IL besides XXXXVI is formed [58]. Two studies [59, 60] on the cyclopropanations of olefins in the presence of copper salts have appeared. Regioselectivity in the copper(I) catalysed cyclopropanation results from the ability of various copper complexes to coordinate strongly to olefins, and is controlled by either the relative stabilities of the metal—olefin complexes or a combination of steric and electronic properties of the carbene and olefin [59]. Copper(I) triflate, a highly active catalyst for these reactions, promotes cyclopropanation of the least alkylated olefin [59]. Two reaction schemes were proposed depending upon the type of copper compound used: (a) Attack of the diazo compound on the metal—olefin complex [59, 60] or (b) coordination of the diazo compound to copper to form an inversion ylide (L), followed by electrophilic attack of the carbonium-ion centre in L on the olefin forming the three-membered cyclic transition state represented as LI [60]. Copper(I) perchlorates complexed by heterocyclic amines homolytically cleave 2-diazobenzophenone tetrafluoro-

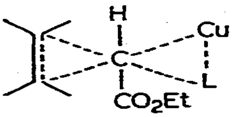


(IL) (XXXXVII) (XXXXVI)

(XXXXVIII)



(L)



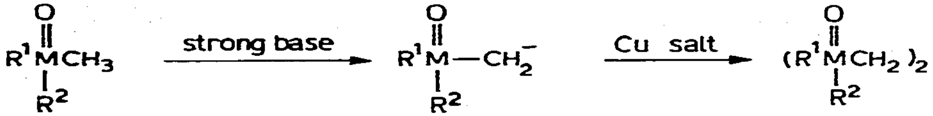
(LI)

borate in neutral solution to 2,2′-dibenzoylbiphenyl (~70%) and 9-fluorenone (~30%). With cupric ions 2-hydroxylbenzophenone is obtained, or benzophenone in the presence of hydrogen atom donors [61].

(ii) General reactions

Corresponding copper complexes have been utilised to introduce isocyanate [62], cyanide [63] and halogen [64] groups into aryl, porphyrin and aromatic compounds, respectively. The oxidations of PPh_3 [65] and PEt_3 [66] by $CuCl_2$ are reported. Binary systems of Cu_2O, CuCl or $Cu(acac)_2$ and an isocyanide were found to be effective catalysts for hydrosilylation of acrylonitrile by trichlorosilane and methyldichlorosilane [67]. Optically pure 1,2-ethano-bissulphoxides and -phosphine oxides have been prepared in a one step synthesis via copper promoted oxidative dimerisations of chiral sulphinyl and phosphinyl carbanions (Scheme 23) [68]. Reaction conditions have been optimised and utilised to convert aryl [69] and vinyl halides [70] (via the Gabriel reaction) to aryl and vinyl phthalimides (Scheme 24). Reductive removal of halo and mesyloxy groups has been effected by a reagent prepared from $LiAlH(OCH_3)_3$ + CuI [71].

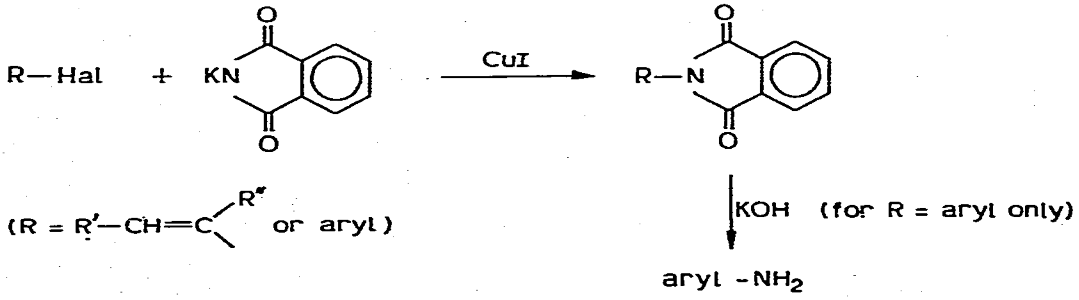
SCHEME 23



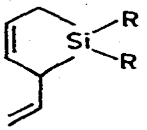
$$R^1\overset{O}{\overset{\|}{M}}(R^2)CH_3 \xrightarrow{\text{strong base}} R^1\overset{O}{\overset{\|}{M}}(R^2)-CH_2^- \xrightarrow{\text{Cu salt}} (R^1\overset{O}{\overset{\|}{M}}(R^2)CH_2)_2$$

(M = S (R² = electron pair) or P)

SCHEME 24

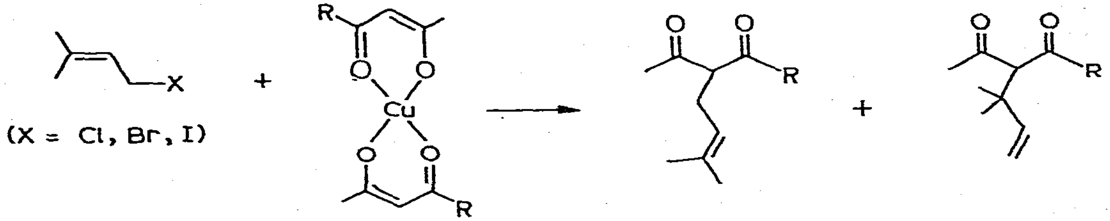


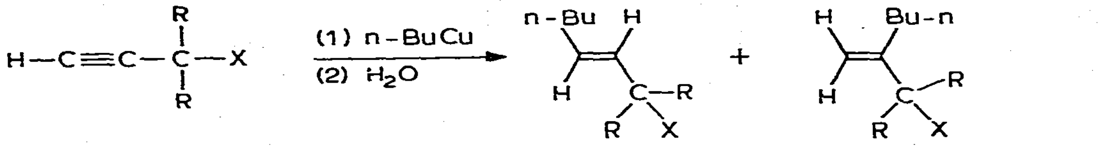
A preliminary communication on the preparation of LII from 1,3,5-hexatriene and SiR_2Cl_2 (R = Me, Ph) using Mg/Cu_2Cl_2 mixtures as catalyst, has appeared [72]. Oxidations of dihydrazones to substituted acetylenes occur smoothly in the presence of CuCl in pyridine solution at room temperature [73]. Cupric chloride is an effective coupling agent for lithiopyridine reagents allowing facile and high yield synthesis of substituted 2,2'-bipyridyls [74]. Aryl cyclopentadienes are formed from $CpCuPBu_3$ and iodobenzenes [75]. The alkylation of copper(II) chelates of acac and Me—acac by 3,3-dimethylallyl halides yields both 3,3-dimethylallyl and 1,1-dimethylallyl products from direct C-alkylation [76] (Scheme 25). The *syn* addition of butylcopper to various propargylic alcohols, ethers and amines was only moderately regioselective. Increasing the bulk of R and R' generally increased the ratio of LIIIa/LIIIb [77].



(LII) (R = Me, Ph)

SCHEME 25

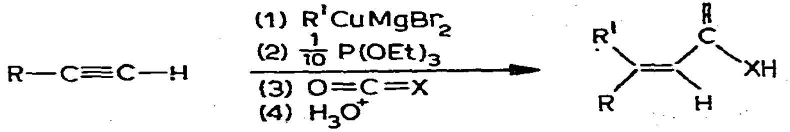




(X = OH, OR', NR_2) (LIIIa) (LIIIb)

Vinylcopper compounds, generated by the action of alkylcopper on terminal acetylenes inserted CO_2 or isocyanates into the Cu—C bond to give α,β-unsaturated acids or amides upon hydrolysis. The reaction was stereospecifically *trans* with respect to the original substituents and the addition of 0.1 equivalents of $P(OEt)_3$ proved to be an excellent ligand catalyst for the reaction (Scheme 26)

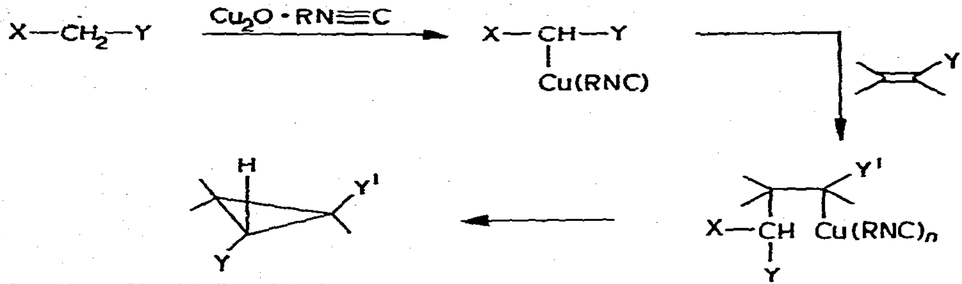
SCHEME 26



(X = O or N—Ph)

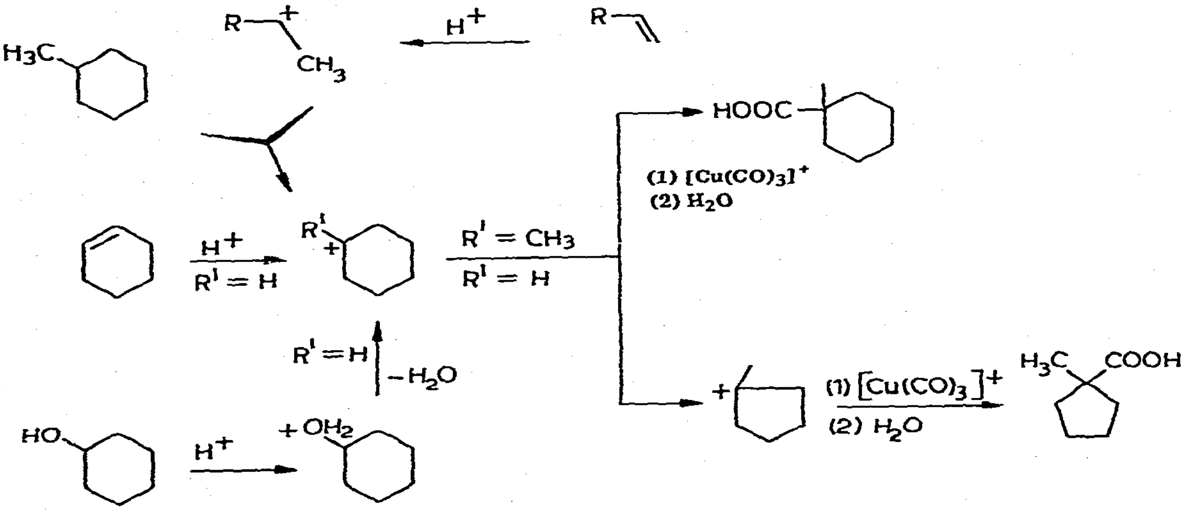
[78]. Disubstituted cyclopropanes are the major product of the reaction of α-halo-carbonyl and -nitrile compounds and electron deficient olefins using a Cu_2O-isonitrile complex as catalyst. The key step in the mechanism is postulated to be a copper carbenoid addition to the olefin (Scheme 27) [79]. Cu_2O-isonitrile complexes were also effective in esterifying carboxylic acids with alkyl halides. When optically-active alkyl halides were used ~75% of the activity was retained in the product [80]. Carbonylation of alcohols [81], olefins [82] and t-alkanes [83], respectively, by copper tricarbonyl in strongly acidic media to produce carboxylic acids, is reported. With olefins only t-carboxylic acids were formed due to acid-catalysed rearrangement [83]. In all cases the carbonylation reaction was preceded by carbonium ion formation (Scheme 28). Catalytic

SCHEME 27



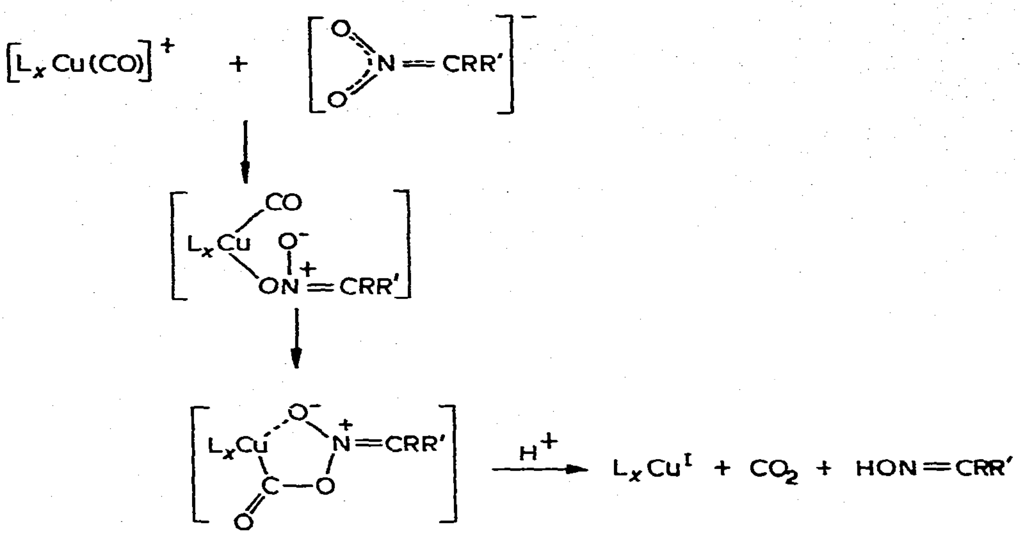
X = Cl, Br; Y = CO_2R, COR, CN

SCHEME 28

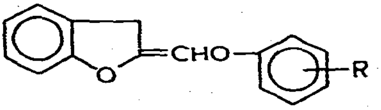


amounts of $[L_xCu(CO)_y]^+$ dissolved in alkyldiamines, reduce nitroalkanes to the corresponding oximes [84] (Scheme 29). Corresponding silver salts were not as efficient. Direct participation of Cu^{2+} ions in the acetoxylation of naphthalene by $Pd(CH_3COO)_2$ results in loss of selectivity [85]. Tertiary carboxylic acids were prepared by carbonylation and hydrolysis of olefins in the presence of Cu^I—CO catalysts, which were formed from Cu_2O + CO in 98% H_2SO_4 [86]. The

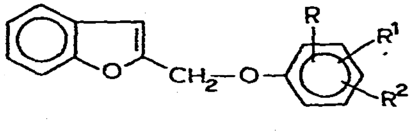
SCHEME 29



kinetics of hydration of C_2H_2 to MeCHO were examined at 50-110° in the presence of $Cu{-}CuSO_4{-}H_2SO_4$ mixtures [87]. Reaction of $RCuMgBr_2$ with $R^1C{\equiv}CH$ and $R^2CHXO(CH_2)_2Cl$ gave $RR^1C{=}CHCHR^2OCH_2CH_2Cl$ which with BuLi gave stereoselective $RR^1C{=}CHCHR^2OH$ (e.g. R = Et, R^1 = Me, X = Br, R^2 = H) [88]. $CCl_4 + Cl_3CCO_2Me + CH_2{=}CHCO_2Me$ or $CH_2{=}CHCN$ in the presence of copper salts and LiCl gave 1/1 and 1/2 adducts [89]. $PhC{\equiv}CR$ (R = Ph, p-BrC_6H_4CO, p-$O_2NC_6H_4CO$, m-$O_2NC_6H_4CO$, $PhCH{=}CHCO$) acetylenes were obtained in 40-58% yields by acylation of $PhC{\equiv}CCu$ with appropriate acyl chlorides. Also prepared were $PhC{\equiv}CXC{\equiv}CPh$ (X = p-OCC_6H_4CO, m-OCC_6H_4CO) [90]. LIVa and LIVb are readily formed by treating o-IC_6H_4OH with p-ClC_6H_4-$OCH_2C{\equiv}CCu$ [91] and $(R^2R^1RH_2C_6OCH_2C{\equiv}C)_2Cu$ (R = halo, R^1 = R^2 = H, halo) [92], respectively, in refluxing pyridine.



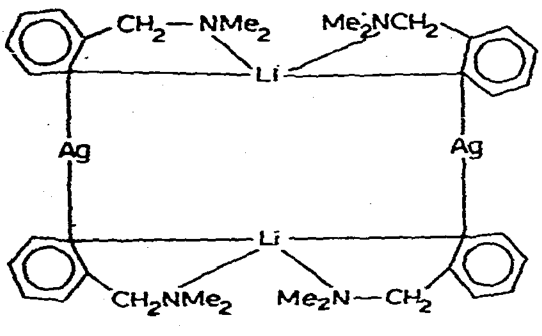
(LIVa)



(LIVb)

III. Silver—carbon bonds

New stable non-fluorinated σ-bonded silver complexes of the type $[AgC(OR){=}NR^1]_3$ (R = Me, Et, n-Pr; R^1 = p-MeC_6H_4) have been isolated from reactions of $(R^1NC)AgCl$ + ROH + KOH. The use of the complex as a synthetic reagent for preparing $[Ph_3PAuC(OR){=}NR^1]$, $[Hg\{C(OR){=}NR^1\}_2]$ and $[(Ph_3P)_2PtCl\{C(OR){=}NR^1\}]$ by metathesis is demonstrated [93]. A series of stable arylsilver compounds with dimethylamino, (dimethylamino)methyl or methoxy groups bonded to the phenyl ligand is reported. Thus treatment of AgBr with LiR (R = substituted phenyl group) produced complexes of stoichiometry RAg, RAg—AgBr, and $[RAg]_2 \cdot AgBr$ [94]. When {2-[(dimethylamino)-methyl]phenyl}silver is added to an equivalent amount of the corresponding organolithium compound in benzene, the tetranuclear mixed metal cluster bis{2-[(dimethylamino)methyl]phenyl}silver lithium (LV) is formed which contains bridging aryl groups between the silver and lithium [95]. Studies on the alkylation of silver(I) trifluoromethanesulphonate with $PbEt_4$ in protic and aprotic solvents have inferred that the formation of ethane (or butane depending upon the concentration of the reactants) in both solvents can be described to (i) protonation of the ethylsilver intermediate in the first case and (ii) reaction of ethyl radicals formed from homolytic cleavage of the ethylsilver in the second case. The reactions are not truly catalytic as with the corresponding copper(I) reductions [96]. AgC_6F_5 was used to prepare $[M(C_6F_5)(CO)(PPh_3)_2]$ (M = Rh, Ir), $[Rh(C_6F_5)COD(PPh_3)]$, $[Fe(C_6F_5)_2(CO)_4]$ and $[Pt(CF{=}CF_2)(C_6F_5)(PPh_3)_2]$ by metathesis with corresponding metal halides [97]. [Ag(thiourea)$_2$CN] has been isolated and characterised [98]. The unstable carbonyl cation $Ag(CO)_m{}^+$ was formed by treating Ag^+ in H_2SO_4 solution at −10 to 24° with CO at 1-20 atmospheres [99]. Preliminary measurements of ^{13}C resonances of some silver-alkenes and -arenes point to a correlation between mesomeric effects of substituents on the alkene or arene with the resonance shifts, $\Delta\delta$ [100]. The values obtained for heats of reactions for the reactions:



(LV)

$$[Ag(hfacac)(olefin)] + PPh_3 \xrightarrow{CH_2Cl_2} [Ag(hfacac)PPh_3] + olefin$$

$$[Ag(hfacac)] + PPh_3 \xrightarrow{CH_2Cl_2} [Ag(hfacac)(PPh_3)_2]$$

$$[Ag(hfacac)(olefin)] + olefin\ (excess) + PPh_3 \xrightarrow{CH_2Cl_2} [Ag(hfacac)PPh_3] + olefin$$

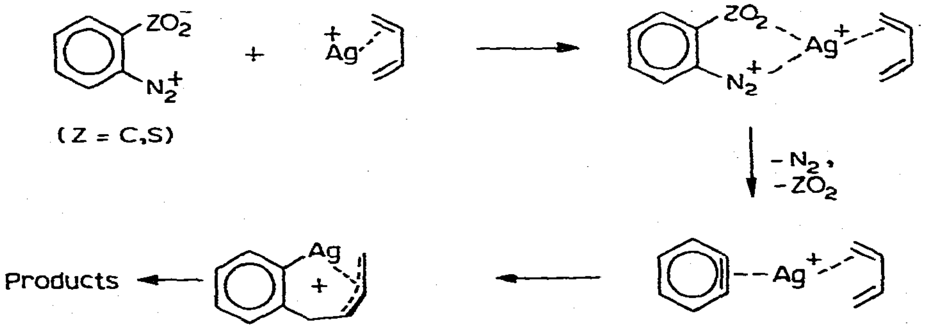
where hfacac is a conjugate base of hexafluoroacetylacetonate and olefin is cyclohexene, *cis*-cyclooctene, COD, and 1,3,5,7-cyclooctatetraene, are in disagreement with all other available thermodynamic silver olefin data which is said to be indicative of extensive solvation and entropic contribution in the previous values [101]. In a detailed study of the factors influencing the complexing of silver(I) ions with ethylene, it is suggested that the trends in the absorption efficiencies can be correlated with silver(I)—anion interactions in competition with silver ion—solvent interactions, and with the structure making influence of ions on the solvent [102]. Electronic structures of Ag^+ complexes with C_2H_4, propylene, *cis*- and *trans*-2-butene, 2-methyl-2-butene were studied by using the closed shell SCF-MO method with complete neglect of differential overlap for all valence electron systems [103]. Kinetic work on the $AgNO_3$ and $AgClO_4$ reactions with allyl halides in acetonitrile also seems to support the competitive anion—solvent interaction suggestion [104]. Treatment of silver trifluoroacetate with perfluoroisobutene, perfluoropropene, trifluorochloroethene and perfluorocyclobutene in DMF, acetonitrile or 1,2-dimethoxyethane utilising KF or CsF as a source of fluoride ion readily produced the corresponding perfluoroalkyl derivatives of silver. The products were not isolated but characterised by ^{19}F NMR. Elemental sulphur inserts into the silver—carbon bond in perfluoro-t-butyl and perfluorocyclobutyl compounds forming the corresponding thio complexes, which may be regarded as a convenient source of these products [105], e.g. $(CF_3)_3CSAg + CH_2{=}CHCH_2I \rightarrow (CF_3)_3CSCH_2CH{=}CH_2$.

Examinations of the localised interactions of silver ions with unsaturated hydrocarbons showed that hydrocarbons with isolated double bonds formed stronger complexed products than delocalised double bonds [106].

IV. Catalysis by silver salts

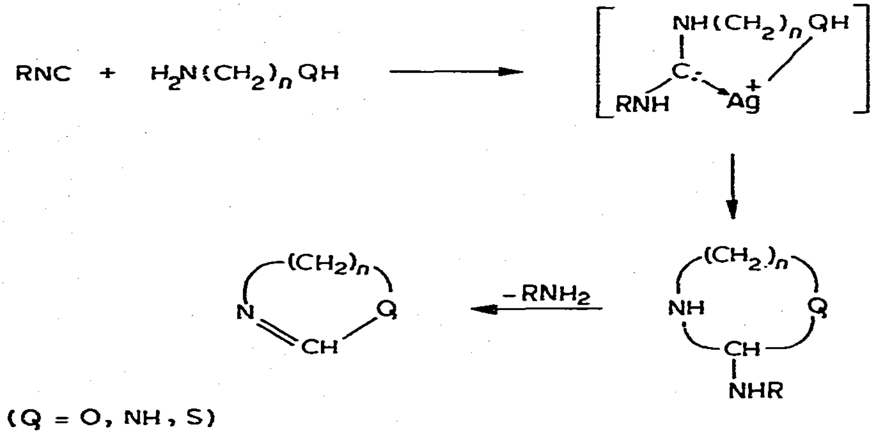
The effect of the addition of catalytic amounts of Ag^+ to benzyne additions of cyclic six- and seven-membered di- and tri-olefins to form exclusively 2 + 4 type products has been studied. The mechanism proposed (Scheme 30) accounts for both the catalytic effect and the observed product as a function of olefin type [107]. Oxidation reactions involving silver ions reported are: (i) Ag_2O reactions with ArNHNSO (Ar = Ph, *p*-tolyl, *p*-BrPh, α-$C_{10}H_7$, β-$C_{10}H_7$, 2-$C_6H_5C_6H_4$) producing a variety of products, many resulting from the formation of aryl radicals [108], (ii) the exclusive generation of nitriles RCN from

SCHEME 30



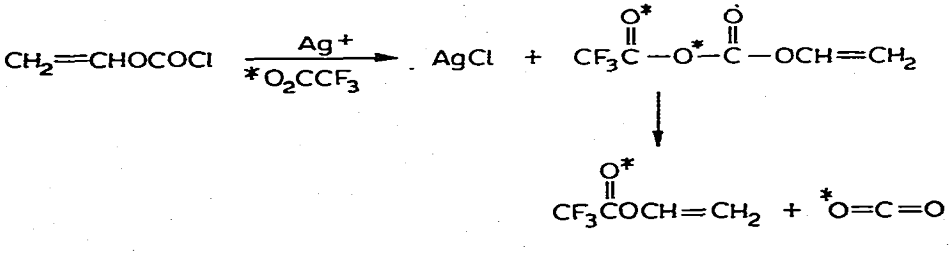
Ag^{II} picolinate oxidation of primary amines RCH_2NH_2 [109]. The single step synthesis of heterocycles containing the —N=CHQ— (Q = O, NH, S) unit from isonitriles + amino alcohol (or diamine or aminothiol) + AgCN is communicated. A carbene intermediate in the reaction is tentatively proposed (Scheme 31)

SCHEME 31

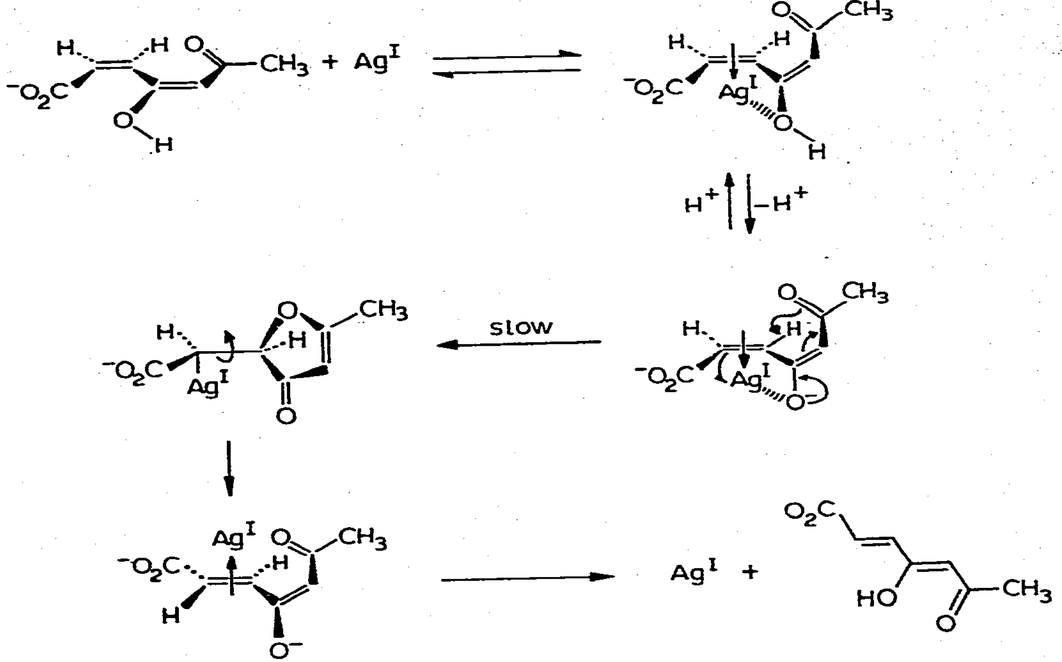


[110]. The reaction of vinyl chloroformate and oxime chloroformates with the silver salts AgO_2CCX_3 (X = H, F), $AgSbF_6$ and $AgBF_4$ has been studied. ^{18}O labelling experiments show that the reaction of the vinyl chloroformate occurs with retention of the carbon—oxygen bond and proceeds via a carbonate intermediate (Scheme 32) [111]. A study on the mechanism of *cis*—*trans* isomerisation about carbon—carbon double bonds in maleylacetone, maleylacetoacetone and similar compounds catalysed by Ag^I ions has appeared. Comparisons with enzymatic isomerisations are discussed, and for the Ag^I-maleylacetone system a proton loss from a π-complex in a preequilibrium step followed by intramolecular nucleophilic attack is proposed. The intermediate furanone then undergoes facile rotation about the isomerising C—C bond (Scheme 33) [112]. Treatment of 7-isopropylidene-2,3-bis(carbomethoxy)quadricyclane with $AgBF_4$ produced LVI and LVII in the ratio of 3/1. The rearrangement of a carbonium ion explains these products [113]. *trans*-Chlorovinylboronic acid

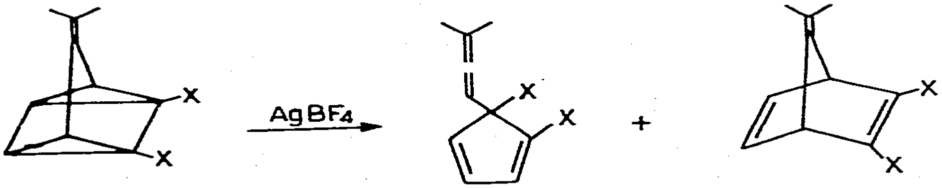
SCHEME 32


$$CH_2{=}CHOCOCl \xrightarrow[{*O_2CCF_3}]{Ag^+} AgCl + CF_3\overset{O^*}{\overset{\|}{C}}{-}O^*{-}\overset{O}{\overset{\|}{C}}{-}OCH{=}CH_2$$
$$\downarrow$$
$$CF_3\overset{O^*}{\overset{\|}{C}}OCH{=}CH_2 + {}^*O{=}C{=}O$$

SCHEME 33



and ammoniacal Ag_2O gave 2 $AgC{\equiv}CAg \cdot AgCl$, presumably by decomposition of an unstable chlorovinylsilver intermediate [114].



(X = CO_2CH_3)

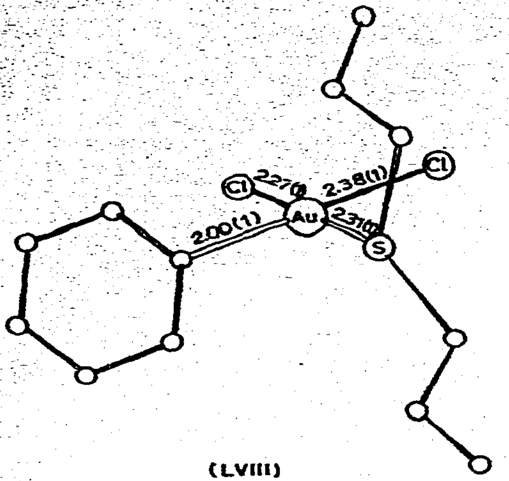
(LVI)

(XVII)

V. Gold—carbon bonds

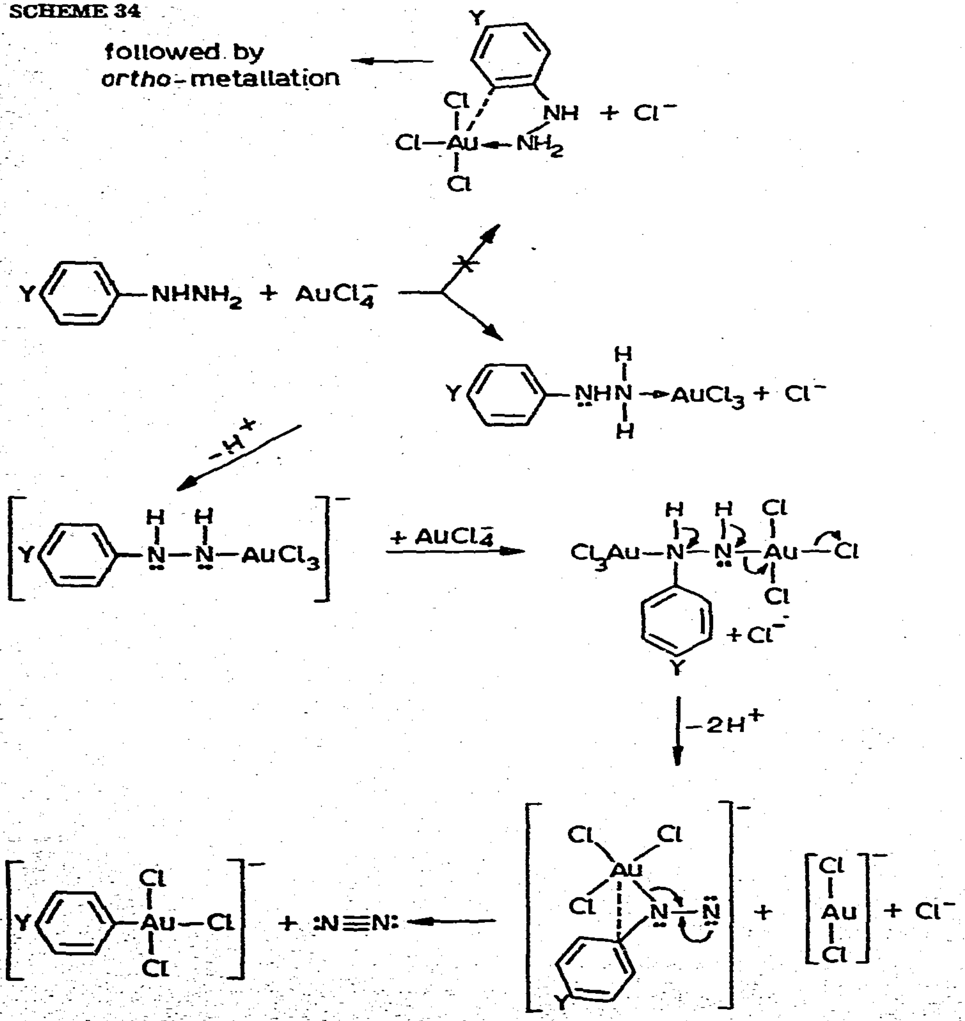
A preliminary X-ray crystallographic investigation of the complex $AuCl_2(C_6H_5)$-n-Pr_2S (LVIII) has confirmed the strong *trans*-influence of the σ-bonded phenyl group. Initial parameters (R = 0.086) observed are Au—C = 2.00(1) Å, Au—Cl = 2.27(1) Å (*trans* to S); 2.38(1) Å (*trans* to C) [115]. Treatment of AuX_4^- (X = Cl, Br) with phenyl- (or substituted phenyl)-hydrazine hydrochloride has afforded a novel route to aryl—gold complexes (Scheme 34) [116].

Alkyllithium reactions with alkylgold(I) species have been used to prepare a series of mixed alkyl ligand gold(III) complexes [117, 118]. The intermediates formed, namely $R^1R^2AuPR^3{}_3Li$ ($R^1 = R^2$ = Me, R^3 = Ph or Me), were not isolated but reacted directly in situ in ether solution with a series of the alkyl halides R^4X (R^4 = Me, CD_3, Et, i-Pr, n-Pr, i-Bu, n-Bu or Ph, X = Br or I) producing $R^1R^2R^4AuPR^4{}_3$.



(LVIII)

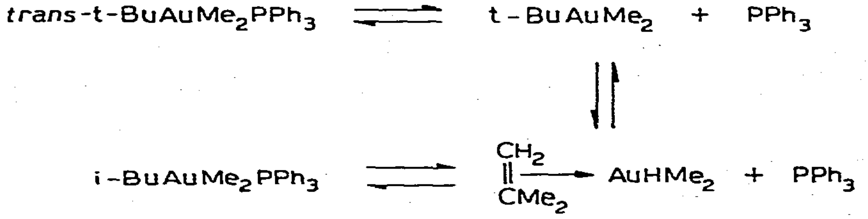
SCHEME 34



With this synthetic route stereospecific *trans*- and *cis*-alkyldimethyl(triphenylphosphine)gold compounds could be readily obtained [117, 118]. Lack of selectivity obtained by protonolysis of the mixed alkylmethylaurate(I) with HCl suggests that the reaction proceeds via an oxidative addition mechanism [118]. Grignard reagents on $ClAuPPh_3$ have been used to prepare the series of alkylgold(I) complexes $RAuPPh_3$ (R = Me, Et, n-Pr, n-Bu and neopentyl). The decomposition for these alkylgold products proceeds by either a reductive coupling (for methyl or primary alkyl) or disproportionation mechanism and was found to have first-order kinetics for $MeAuPPh_3$. The retardation of the rate on adding PPh_3 suggests a rate-limiting loss of phosphine which is probably followed by a rapid association with additional $MeAuPPh_3$ [119].

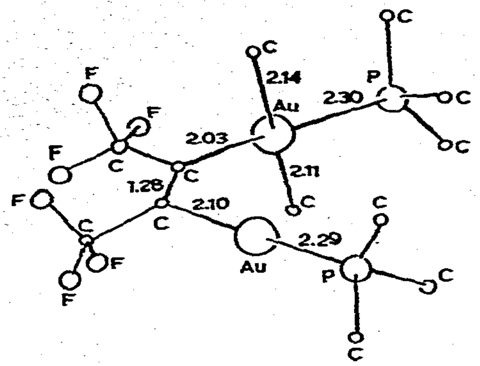
A similar mechanism is proposed [120] for the stereospecific *cis* eliminations observed in mixed alkylgold(III) complexes. Where *cis*- and *trans*-alkylgold(III) species give the same product, a rapid *cis*—*trans* isomerisation followed by preferential decomposition of the more labile *trans* isomer is postulated [120]. Kinetic studies on the spontaneous isomerisation of *trans*-[$t\text{-}BuMe_2AuPPh_3$] to *trans*-[$i\text{-}BuMe_2AuPPh_3$] suggest a dissociative intramolecular rearrangement involving a gold hydride (Scheme 35) [121].

SCHEME 35



No evidence was found for intra- or inter-molecular exchange in the system *cis*-[$(CH_3)_2(CD_3)AuPMe_3$] + CD_3Li. Vibrational analyses were also reported for $(CH_3)_3AuL$ (L = PMe_3, $AsMe_3$), *cis*-[$(CH_3)_2CD_3AuPMe_3$], $(CD_3)_3AuPMe_3$, CX_3AuPMe_3 (X = H, D) and $XAuPMe_3$ (X = Cl, Br, I) together with Raman and IR measurements [122]. The new cationic gold(III) compounds $[Me_2AuL_2]^+$ (L = PMe_3, PMe_2Ph, $PMePh_2$ and PPh_3) formed from $[Me_2AuX]_2$ (X = Cl, I) exchange faster with I^- than Cl^- suggesting nucleophilic attack on the cation. Evidence suggests that the reductive elimination step is enhanced by steric crowding [123].

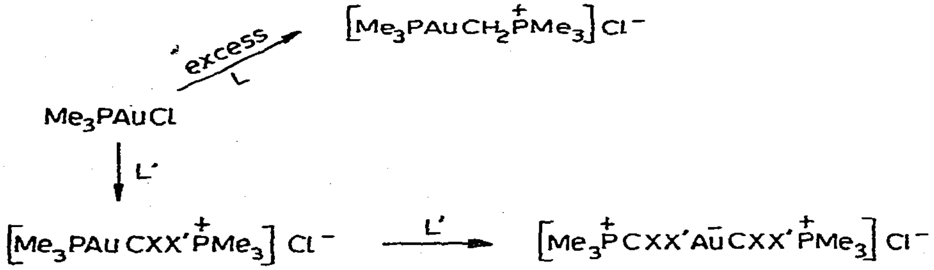
The cations of $[R(AuPPh_3)_2]BF_4$ (R = Ph, *p*-MeC_6H_4, $CH_2{=}CH$, ferrocenyl, $CpFeC_5H_3Cl$, $CpFeC_5H_3OMe$, $CpFeC_5H_4CH_2NMe_2$) were prepared from $RAuPPh_3$ by treatment with HBF_4. The structures of the complexes were determined by NMR, IR, UV and X-ray techniques [124]. The dimethylgold complexes with bidentate *N*-alkyl- and *N*-aryl-salicylaldimines, ($Me_2Ausal{=}N{-}R$), as well as bridged complexes of quadridentate ligands are reported [125]. Oxidative additions of CX_3I (X = H, F) to CH_3AuL (L = PMe_3, PPh_3) produced $(CH_3)_3AuL$, $(CH_3)_2AuIPMe_3$ and *cis*- and *trans*-[$(CH_3)_2(CF_3)AuPMe_3$] [126] and metathetical reactions with tricyclohexylphosphinegold chloride gave [$(C_6H_{11})_3PAuX$] (X = Br, I, $C{\equiv}CPh$, acac, $CO_2C_2F_5$) [127].



(LIX)

A series of novel organogold complexes has been characterised. Stabilization of the Au—C bond has been achieved with gold ylides (Scheme 36) [128].

SCHEME 36



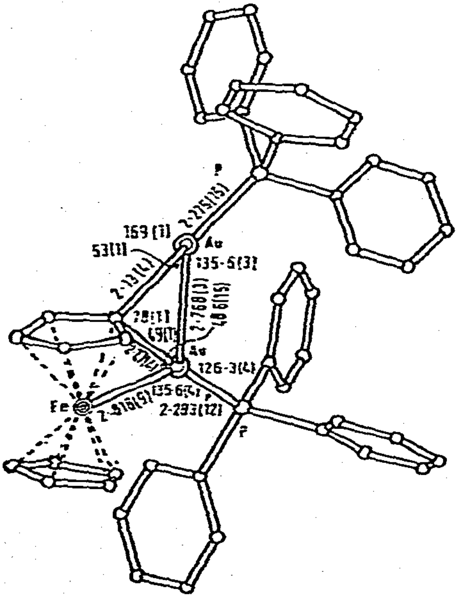
$[Me_3PAuCH_2\overset{+}{P}Me_3]Cl^-$

Me_3PAuCl

$[Me_3PAuCXX'\overset{+}{P}Me_3]Cl^-$

$[Me_3\overset{+}{P}CXX'\overset{-}{Au}CXX'\overset{+}{P}Me_3]Cl^-$

($L = Me_3P{=}CH_2$; $L' = L$, $X,X' = H$; $L' = Me_3P{=}CXX'$: $X = H$, $X' = SiMe_3$; $X,X' = SiMe_3$)

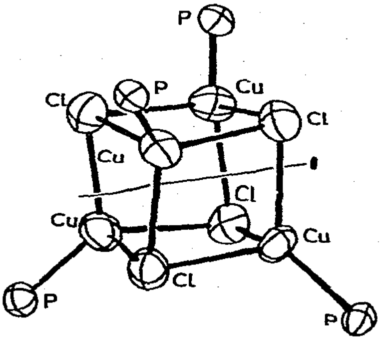


(LX)

The intermediate in the insertion of an acetylene into a methyl—gold bond has been characterised structurally (LIX) [129] as has the cation $[CpFe(\pi\text{-}C_6H_4)Au_2(PPh_3)_3]^+$ (LX) [130]. Grignard reagents and Ph_3PAuCl have produced Ph_3PAuL ($L = C_6H_4CH{=}CH_2\text{-}o$, $C_6H_4CH_2CH{=}CH_2$) which react with SO_2 to give the *o*-sulphinato inserted products [131]. $Ph_3PAuC(OMe){=}NAr$ ($Ar = p\text{-}MeC_6H_4$) can act as a monodentate ligand forming complexes of the type $[\{Ph_3PAuC(OMe){=}NAr\}_2Ag]^+ClO_4^-$, $Ph_3PAuC(OMe){=}N(Ar)\rightarrow AgNO_3$ and $Ph_3PAuC(OMe){=}N(Ar)RhCl(CO)_2$ [132]. The compounds $[Me_2AuNCSe]_2$, $[Me_2AuNCO]_2$ and $[Me_2AuCN]_4$ have been prepared and their vibrational and ^1H NMR spectra analysed. Bridge cleavage reactions produced $[Me_2Au(NCO)PPh_3]$, $[Me_2Au(NCO)AsPh_3]$ and $[Me_2Au(CN)PPh_3]$ [133].

A series of gold isocyanides has been reported. New products obtained were $(R^1NC)AuCl$ [134, 135] and $[(R^1NC)_2Au]X$ [134, 135] ($X = ClO_4$, PF_6) where R^1 is t-Bu, i-Pr, an aliphatic, cycloaliphatic, alkylaromatic or aromatic substituent. Reactions of certain of these compounds with alcohols or primary and secondary amines have produced carbene and dicarbene gold complexes of formulae $\{(R^1NH)(R^2O)C\}AuCl$, (R^2 = Me, $R^1 = CH_2Ph$, *p*-anisidino, $p\text{-}NO_2C_6H_4$; R^2 = i-Pr, $R^1 = p\text{-}NO_2C_6H_4$) [134], $[Au\{C(NHR^1)(NHR^2)(NH_2R^2)Cl]$ ($R^1 = R^2$ = t-Bu, R^1 = i-Pr, R^2 = t-Bu) [135], $\{(R^1NH)(R^3NH)C\}AuCl$ [135, 136], $[\{(R^1NH)(R^3NH)C\}_2Au]X$ ($X = ClO_4$ [137], PF_6 [135]), $[(C_6H_{11}NC)Au\{C(NHC_6H_{11})(NHC_6H_4CH_3\text{-}p)\}]ClO_4$ [137], $[\{(R^1NH)(R^4{}_2N)C\}_2Au]PF_6$ [135, 138], (R^1 = t-Bu, R^3 = t-Bu, i-Pr, n-Bu; R^1 = i-Pr, R^3 = t-Bu, i-Pr; R^1 = t-Bu, R^4 = Et, CH_2Ph; R^1 = i-Pr, R^4 = Et; R^2 = Me, i-Pr) and $[\{(RNH)(R^5NH)C\}_2(R^5NH_2)_2Au_2Cl_2]$ [136] (R = *p*-tolyl, R^5 = *p*-tolyl, $p\text{-}MeOC_6H_4$, $p\text{-}FC_6H_4$, $o,o'\text{-}Me_2C_6H_3$, $o,o'\text{-}(Me_2CH)_2C_6H_3$, $PhCH_2$, Me, Ph).

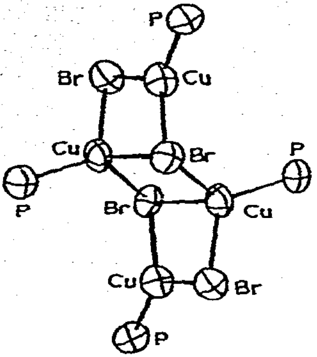
Treatment of specific dicarbene gold cations with PPh_3 [135], CN^- [138] or MeNC [138] gave formamides together with the corresponding gold—PPh_3, CN^- or MeNC salts. Geometrical isomers for $\{(p\text{-tolylNH})(RNH)C\}AuCl$ (R = *p*-tolyl, $p\text{-}MeOC_6H_4$) were identified from ^1H NMR spectroscopy, and this complex together with the gold dimer reacts with bases to give insoluble $[(ArN{=})(RNH)CAu]_x$ (*x* probably 3) [136]. Oxidation of $[\{(ArNH)_2C\}Au]^+$ with I_2 gave $[\{(ArNH)_2C\}_2AuI_2]^+$ [137].



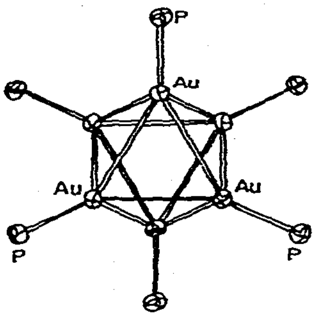
(LXI)

VI. Complexes of general interest

The structure of $CuBr(PPh_3)_3 \cdot \frac{1}{2}C_6H_6$ is essentially trigonal planar. Important parameters are Cu—Br = 2.346(2) Å, Cu—P = 2.272(3) Å [139]. Initial X-ray

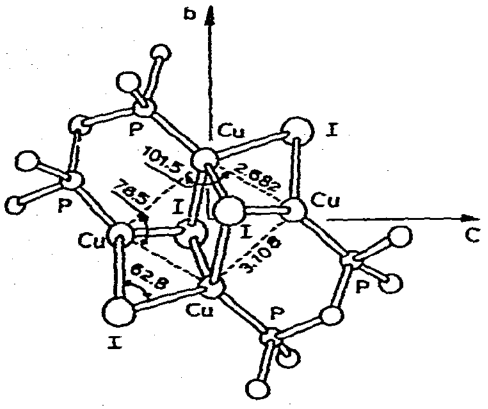


(LXII)



(LXIII)

evidence for the CuX_4 core of $[Ph_3PCuX]_4$ ($X = Cl, Br$) indicates a cubane structure for $X = Cl$ (LXI) and a step structure for $X = Br$ (LXII) [140]. Structural analysis showed $[Au_6\{P(p\text{-}MeC_6H_4)_3\}_6](BPh_4)_2$ to have an octahedron of gold atoms (LXIII) [141]. Addition of aqueous $[Me_4N]Cl$ solution to diglyme solutions of $Na[M^2(CO)_3Cp]$ ($M^2 = Mo, W$) and CuCl or $AgNO_3$ gave $Me_4N[M^1\{M^2(CO)_3Cp\}_2]$ ($M^1 = Cu, Ag$) salts which appear from IR evidence to have a linear $M^2—M^1—M^2$ bridge for Ag only [142]. The series LAgCNS ($L = PMe_3$, $P\text{-}n\text{-}Bu_3$, PEt_2Ph, $PEtPh_2$, PPh_3, $AsPh_3$, $SbPh_3$) have been characterised [143] and treatment of $(C_8H_{14})MCl$ ($M = Ag, Au$) with $P(OR)_3$, $P(OR)_2Ph$ and $P(OR)Ph_2$ (R = alkyl, aryl) produced the cations $[ML_4]^+$ isolated as the BPh_4 salts [144]. The reduction of $AuCl_4^-$ by L ($L = PPh_3, AsPh_3, SbPh_3$) to AuClL, $[AuL_2]^+$ and LCl_2 is first order in $AuCl_4^-$ and L, consistent with a reduction of $AuCl_4^-$ to $AuCl_2^-$, followed by equilibrium formation of AuClL [145]. In the complexes LAu(thiocyanate), the ratio of AuNCS/AuSCN in solution increases as the *trans*-effect of the ligand increases [146]. Metathetical replacement of Cl^- in PPh_3MCl ($M = Cu, Ag, Au$) by AgO_2SPh in the presence of PPh_3 gave the sulphinate complexes



(LXIV)

$PPh_3)_2MO_2SPh$ ($M = Cu, Ag, Au$) and PPh_3AuO_2SPh. Reactions of the copper roduct with O_2 to give the sulphate $(PPh_3)_2CuO_3SPh$ were reported [147]. The -ray determination of $[AuCl_3(PPh_3)]$ has shown a correlation between structural nd kinetic *trans*-effects. Bond distances were Au—Cl (*trans* to P) 2.347 Å, Au—Cl (*trans* to Cl) = 2.278 Å [148]. The preliminary crystal structure of $[Cu_2(DPM)I_2]_2$ (LXIV) has shown that one iodine atom bridges three copper atoms [149].

References

1 A Camus, N. Marsich, G. Nardin and L. Randaccio, J. Organometal. Chem., 60 (1973) C39.
2 J.A.J. Jarvis, B.T. Kilbourn, R. Pearce and M.F. Lappert, Chem. Commun., (1973) 475.
3 M.F. Lappert and R. Pearce, Chem. Commun., (1973) 24.
4 H. Schmidbaur, J. Adlkofer and W. Buchner, Angew. Chem. Intern. Ed. Engl., 12 (1973) 415.
5 (a) N.A. Clinton, H.C. Gardner and J.K. Kochi, J. Organometal. Chem., 56 (1973) 227.
(b) N.A. Clinton and J.K. Kochi, J. Organometal. Chem., 56 (1973) 243.
6 J. Bailey and M.J. Mays, J. Organometal. Chem., 47 (1973) 217.
7 M.I. Bruce and A.P.P. Ostazewski, J. Chem. Soc. Dalton, (1973) 2433.
8 Y. Matsushima, T. Koyano, T. Kitamura and S. Wada, Chem. Letters, (1973) 433.
9 T. Kubo, H. Tominaga and T. Kunugi, Bull. Chem. Soc. Japan, 46 (1973) 3549.
10 Y.-Y. Huang, J. Amer. Chem. Soc., 95 (1973) 6636.
11 J. Vlckova and J. Barton, Chem. Commun., (1973) 306.
12 I.A. Garbusova, V.T. Alexanjan, L.A. Leites, I.R. Golding and A.M. Sladkov, J. Organometal. Chem., 54 (1973) 341.
13 R.G. Salomon and J.K. Kochi, J. Amer. Chem. Soc., 95 (1973) 1889.
14 D.V. Banthorpe, M.R. Young and W.D. Fordham, Chem. Ind. (London), (1973) 743.
15 G.S. Natarajan and K.A. Venkatachalam, Indian Chem. Eng., 14 (1972) 31; Chem. Abstr., 79 (1973) 119062t.
16 J.P. Rupert, J. Phys. Chem., 77 (1973) 784.
17 J.F. Normant, Synthesis, (1972) 63.
18 G.H. Posner; Organic Reactions, (1972) 1.
19 H.O. House and M.J. Umen, J. Org. Chem., 38 (1973) 3893.
20 L.T. Scott and W.D. Cotton, Chem. Commun., (1973) 320.
21 J.P. Gorlier, L. Hamon, J. Levisalles and J. Wagnon, Chem. Commun., (1973) 88.
22 G.H. Posner and C.E. Whitten, Tetrahedron Lett., (1973) 1815.
23 G.H. Posner, C.E. Whitten and J.J. Sterling, J. Amer. Chem. Soc., 95 (1973) 7788.
24 G.H. Posner and J.J. Sterling, J. Amer. Chem. Soc., 95 (1973) 3076.
25 M. Bourgain, J. Villiéras and J.F. Normant, C.R. Acad. Sci. Paris, Sér. C, (1973) 1477.
26 S. Masamune, P.A. Rossy and G.S. Bates, J. Amer. Chem. Soc., 95 (1973) 6452.
27 R.K. Boeckman Jr., J. Org. Chem., 38 (1973) 4450.
28 S. Sicsic and N.T. Luang-Thi, Tetrahedron Lett., (1973) 169.
29 G.H. Posner and D.J. Brunelle, Chem. Commun., (1973) 907.
30 P.A. Grieco and R. Finkelhor, J. Org. Chem., 38 (1973) 2100.
31 E.J. Corey and R.H.K. Chen, Tetrahedron Lett., (1973) 1611.
32 C.P. Casey, D.F. Marten and R.A. Boggs, Tetrahedron Lett., (1973) 2071.
33 G.H. Posner and D.J. Brunelle, Tetrahedron Lett., (1973) 935.
34 G.H. Posner and D.J. Brunelle, J. Org. Chem., 38 (1973) 2747.
35 K. Koosha, J. Berlan and M.L. Capmau, C.R. Acad. Sci. Paris, Sér. C, 276 (1973) 1633; Chem. Abstr., 79 (1973) 53492z.
36 S.B. Bowlus and J.A. Katzenellenbogen, Tetrahedron Lett., (1973) 1277.
37 M.P. Cooke Jr., Tetrahedron Lett., (1973) 1281.
38 J.R. Bull and A. Tuinman, Chem. Commun., (1972) 921.
39 J.R. Bull and A. Tuinman, Tetrahedron, 29 (1973) 1101.
40 C.V. Grudzinskas and M.J. Weiss, Tetrahedron Lett., (1973) 141.
41 P.A. Grieco and J.J. Reap, J. Org. Chem., 38 (1973) 3413.
42 R.E. Schaub and M.J. Weiss, Tetrahedron Lett., (1973) 129.
43 P.R. Ortiz de Montellano, Chem. Commun., (1973) 709.
44 C.R. Johnson, R.W. Herr and D.M. Wieland, J. Org. Chem., 38 (1973) 4263.
45 B.C. Hartman, T.L. Livinghouse and B. Rickborn, J. Org. Chem., 38 (1973) 4346.
46 T.A. Bryson, Tetrahedron Lett., (1973) 4923.
47 E.J. Corey and J. Mann, J. Amer. Chem. Soc., 95 (1973) 6832.
48 C.R. Johnson and G.A. Dutra, J. Amer. Chem. Soc., 95 (1973) 7777.
49 C.R. Johnson and G.A. Dutra, J. Amer. Chem. Soc., 95 (1973) 7783.
50 M. Kalli, P.D. Landor and S.R. Landor, J. Chem. Soc. Perkin I, (1973) 1347.
51 G.H. Posner and J.-S. Ting, Syn. Commun., 3 (1973) 281.
52 Y. Ohbe and T. Matsuda, Tetrahedron, 29 (1973) 2989.
53 J.C. Blazejewski, D. Cantacuzene and C. Wakselman, Tetrahedron, 29 (1973) 4233.

54 M. Bourgain and J.F. Normant, Bull. Soc. Chim. Fr., (1973) 1777.
55 M. Bourgain and J.F. Normant, Bull. Soc. Chim. Fr., (1973) 2137.
56 J.E. Dubois and M. Boussu, Tetrahedron, 29 (1973) 3943.
57 J. Villieras, J.-R. Disnar, D. Masure and J.F. Normant, J. Organometal. Chem., 57 (1973) C95.
58 M. Takebayashi, T. Kashiwada, M. Hamaguchi and T. Ibata, Chem. Lett., (1973) 809.
59 R.G. Salomon and J.K. Kochi, J. Amer. Chem. Soc., 95 (1973) 3300.
60 T. Sato, T. Mori and J. Shinoda, Bull. Chem. Soc. Japan, 46 (1973) 1833.
61 A.H. Lewin and R.J. Michl, J. Org. Chem., 38 (1973) 1126.
62 S. Uemura, S. Uchida, M. Okano and K. Ichikawa, Bull. Chem. Soc. Japan., 46 (1973) 3254.
63 H.J. Callot, Tetrahedron Lett., (1973) 4987.
64 S.R. Bansal, D.C. Nonhebel and J.M. Mancilla, Tetrahedron, 29 (1973) 993.
65 G. Ondrejovic, D. Makanora, D. Valigura and J. Gazo, Z. Chem., 5 (1973) 193.
66 D.D. Axtell and T.J. Yoke, Inorg. Chem., 12 (1973) 1265.
67 P. Svoboda and J. Hetflejš, Coll. Czech. Chem. Commun., 38 (1973) 3834.
68 C.A. Maryanoff, B.E. Maryanoff, R. Tang and K. Mislow, J. Amer. Chem. Soc., 95 (1973) 5839.
69 R.G.R. Bacon and A. Karim, J. Chem. Soc. Perkin I, (1973) 272.
70 R.G.R. Bacon and A. Karim, J. Chem. Soc. Perkin I, (1973) 278.
71 S. Masamune, P.A. Rossy and G.S. Bates, J. Amer. Chem. Soc., 95 (1973) 6452.
72 L. Birkofer and D. Prustel, J. Organometal. Chem., 60 (1973) C1.
73 J. Tsuji, H. Takahashi and T. Kajimoto, Tetrahedron Lett., (1973) 4574.
74 J.E. Parkes, B.E. Wagner and R.H. Holm, J. Organometal. Chem., 56 (1973) 53.
75 R. Wahren, J. Organometal. Chem., 57 (1973) 415.
76 J.A. Miller, C.M. Scrimgeour, R. Black, J. Larkin, D.C. Nonhebel and H.C.S. Wood, J. Chem. Soc. Perkin I, (1973) 603.
77 J.F. Normant, A. Alexakis and J. Villieras, J. Organometal. Chem., 57 (1973) C99.
78 J.F. Normant, G. Cahiez, C. Chuit and J. Villieras, J. Organometal. Chem., 54 (1973) C53.
79 T. Saegusa, K. Yonezawa, I. Murase, T. Konoike, S. Tomita and Y. Ito, J. Org. Chem., 38 (1973) 2319.
80 T. Saegusa, I. Murase and Y. Ito, J. Org. Chem., 38 (1973) 1753.
81 Y. Souma and H. Sano, Bull. Chem. Soc. Japan, 46 (1973) 3237.
82 Y. Souma, H. Sano and J. Iyoda, J. Org. Chem., 38 (1973) 2016.
83 Y. Souma and H. Sano, J. Org. Chem., 38 (1973) 3633.
84 J.F. Knifton, J. Org. Chem., 38 (1973) 3296.
85 G.G. Arzoumanidis and F.C. Rauch, J. Org. Chem., 28 (1973) 4443.
86 Y. Souma and H. Sano, Kagaku Kogyu, 24 (1973) 1342; Chem. Abstr., 79 (1973) 125765.
87 D.V. Sokol'skii, B.Yu. Nogerbekov and Ya.A. Dorfman, Khim. Atsetilena, Tekhnol. Karbida Kal'tsuja, (1972) 371; Chem. Abstr., 79 (1973) 125455q.
88 J.F. Normant, G. Cahiez, C. Chuit and J. Villieras, Tetrahedron Lett., (1973) 2407.
89 Y. Mori and J. Tsuji, Tetrahedron, 29 (1973) 827.
90 A.M. Sladkov, and I.R. Gol'ding, Khim. Atsetilena, Tr. Vses. Konf. 3rd, (1968) 45; Chem. Abstr., 79 (1973) 5431g.
91 O.V. Afanas'eva, A.G. Makhsunov and Sh.U. Abdullaev, Dokl. Vses. Konf. Khim. Atsetilena, 4th, 1 (1972) 244; Chem. Abstr., 79 (1973) 31756m.
92 A.G. Makhsumov, O.V. Afanas'eva, Sh. U. Abdulaev and V.A. Abidov, Otkrytiya Izobret. Prom. Obraztsy, Tovarnyl, Znaki, 50 (1973) 90; Chem. Abstr., 79 (1973) 136978p.
93 G. Minghetti, F. Bonati and M. Massobrio, Chem. Commun., (1973) 260.
94 A.J. Leusink, G. van Koten and J.G. Noltes, J. Organometal. Chem., 56 (1973) 379.
95 A.J. Leusink, G. van Koten, J.W. Marsman and J.G. Noltes, J. Organometal. Chem., 55 (1973) 419.
96 N.A. Clinton and J.K. Kochi, J. Organometal. Chem., 61 (1973) 433.
97 R.L. Bennett, M.I. Bruce and R.C.F. Gardner, J. Chem. Soc., Dalton, (1973) 2653.
98 A.N. Sergeeva and D.I. Semenishin, Russ. J. Inorg. Chem., 18 (1973) 1101.
99 Y. Souma and H. Sano, Chem. Lett., (1973) 1059.
100 J.P.C.M. van Dongen and C.D.M. Beverwijk, J. Organometal. Chem., 51 (1973) C36.
101 W. Partenheimer and E.H. Johnson, Inorg. Chem., 12 (1973) 1274.
102 J.V. Crookes and A.A. Woolf, J. Chem. Soc. Dalton, (1973) 1241.
103 S. Sakaki, Theor. Chim. Acta, 30 (1973) 159.
104 D.N. Kevill and L. Held, J. Org. Chem., 38 (1973) 4445.
105 B.L. Dyatkin, B.I. Martynov, L.G. Martynova, N.G. Kizim, S.R. Sterlin, Z.A. Stumbrevichute and L.A. Fedorov, J. Organometal. Chem., 57 (1973) 423.
106 K.K. Deb, J.E. Bloor and T.C. Cole, J. Inorg. Nucl. Chem., 35 (1973) 1021.
107 P. Crews and J. Beard, J. Org. Chem., 38 (1973) 529.
108 C. Carpanelli, G. Leandri and G.P. Corallo, Gazz. Chim. Ital., 103 (1973) 469.
109 J.B. Lee, C. Parkin, M.J. Shaw, N.A. Hampson and K.I. MacDonald, Tetrahedron, 29 (1973) 751.
110 Y. Ito, Y. Inubushi, M. Zenbayashi, S. Tometa and T. Saegusa, J. Amer. Chem. Soc., 95 (1973) 4447.

111 P. Beak and J.A. Barron, J. Org. Chem., 38 (1973) 2771.
112 R.A. Johnson and S. Seltzer, J. Amer. Chem. Soc., 95 (1973) 5700.
113 S.F. Nelsen, J.P. Gillespie, P.J. Hintz and E.D. Seppanen, J. Amer. Chem. Soc., 95 (1973) 8380.
114 A.N. Nesmeyanov, A.K. Prokof'ev and A.E. Borisov, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 1922.
115 M. McPartlin and A.J. Markwell, J. Organometal. Chem., 5 (1973) C25.
116 P. Braunstein, Chem. Commun., (1973) 851.
117 A. Tamaki and J.K. Kochi, J. Organometal. Chem., 51 (1973) C39.
118 A. Tamaki and J.K. Kochi, J. Chem. Soc. Dalton, (1973) 2620.
119 A. Tamaki and J.K. Kochi, J. Organometal. Chem., 61 (1973) 441.
120 A. Tamaki, S.A. Magennis and J.K. Kochi, J. Amer. Chem. Soc., 95 (1973) 6487.
121 A. Tamaki and J.K. Kochi, Chem. Commun., (1973) 423.
122 C.F. Shaw and R.S. Tobias, Inorg. Chem., 12 (1973) 965.
123 C.F. Shaw, J.W. Lundeen and R.S. Tobias, J. Organometal. Chem., 51 (1973) 365.
124 A.N. Nesmeyanov, E.G. Perevalova, K.I. Grandberg, D.A. Lemenovskii, T.V. Baukova and O.B. Afanasova, Vestn. Mosk. Univ. Khim., 14 (1973) 387; Chem. Abstr., 79 (1973) 146613e.
125 K.S. Murray, B.E. Reichert and B.O. West, J. Organometal. Chem., 61 (1973) 451.
126 A. Johnson and R.J. Puddephatt, Inorg. Nucl. Chem. Letters, 9 (1973) 1175.
127 J. Bailey, J. Inorg. Nucl. Chem., 35 (1973) 1921.
128 H. Schmidbaur and R. Franke, Angew. Chem. Internat. Edit. Engl., 12 (1973) 416.
129 J.A.J. Jarvis, A. Johnson and R.J. Puddephatt, Chem. Commun., (1973) 373.
130 V.G. Andreanov, Yu.T. Struchkov and E.R. Rossinskaja, Chem. Commun., (1973) 338.
131 M. Aresta and G. Vasapollo, J. Organometal. Chem., 50 (1973) C51.
132 F. Bonati and G. Minghetti, J. Organometal. Chem., 60 (1973) C43.
133 G.C. Stocco, G.F. Stocco and R.S. Tobias, Atti. Accad. Sci. Lett., Arti. Palermo. Parte 1, 31 (1972) 199; Chem. Abstr., 79 (1973) 105364f.
134 F. Bonati and G. Minghetti, Gazz. Chim. Ital., 103 (1973) 373.
135 J.A. McCleverty and M.M.M. da Mota, J. Chem. Soc. Dalton, (1973) 2571.
136 F. Bonati and G. Minghetti, J. Organometal. Chem., 59 (1973) 403.
137 G. Minghetti and F. Bonati, J. Organometal. Chem., 54 (1973) C62.
138 J.E. Parks and A.L. Balch, J. Organometal. Chem., 57 (1973) C103.
139 P.H. Davis, R.L. Belford and I.C. Paul, Inorg. Chem., 12 (1973) 213.
140 M.R. Churchill and K.L. Kalra, J. Amer. Chem. Soc., 95 (1973) 5772.
141 P. Bellon, M. Manassero and M. Sansoni, J. Chem. Soc. Dalton, (1973) 2423.
142 P. Hackett and A.R. Manning, Chem. Commun., (1973) 71.
143 J.L. Cox and J. Howatson, Inorg. Chem., 12 (1973) 1205.
144 D.A. Couch and S.D. Robinson, J. Inorg. Nucl. Chem. Lett., 9 (1973) 1079.
145 R. Roulet, N.Q. Lan, W.R. Mason and G.P. Fenske, Jr., Helv. Chim. Acta, 56 (1973) 2405.
146 J.L. Burmeister and J.B. Melpolder, Chem. Commun., (1973) 613.
147 J. Bailey and M.J. Mays, J. Organometal. Chem., 63 (1973) C24.
148 G. Bandoli, D.A. Clemente, G. Marangoni and L. Cattalini, J. Chem. Soc. Dalton, (1973) 886.
149 N. Marsich, G. Nardin and L. Randaccio, J. Amer. Chem. Soc., 95 (1973) 4054.