COPPER, SILVER AND GOLD

ANNUAL SURVEY COVERING THE YEAR 1976

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CONTENTS

ABBREVIATIONS

acac = acetylacetonate
aq. = aqueous
BIPY = 2,2'—bipyridyl
COD = 1,5-cyclo-octadiene
COT = cyclo-octatetraene
Cp = cyclopentadienyl
DMF = dimethylformamide
DMSO = dimethylsulphoxide
DPE = 1,2-bis(diphenylphosphino)ethane

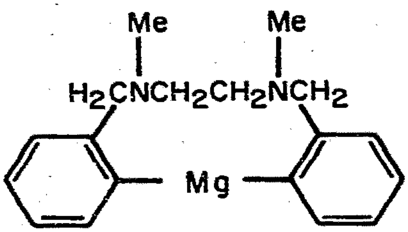
Copper, Silver and Gold, Annual Survey covering the year 1975 see J. Organometal. Chem., 138(1977)405-453.

LDC = lithium dimethylcuprate
PHEN = 1,10-phenanthroline
RT = room temperature
THF = tetrahydrofuran

I Organocopper compounds

Crystal and molecular structure data of Cu, Ag and Au coordination and organometallic compounds, as determined by X-ray diffraction methods, have been reviewed (124 refs.) [1].

Metathesis of 3,4-dichloro-2-thienyllithium and CuCl in THF gave the corresponding copper compound in high yield [2]. The reaction of 1,2-bis[N-{2-(bromomagnesio)benzyl}-N-methylamino]-ethane with $CuCl_2$ gave dimeric 1,2-bis[N-(2-cupriobenzyl)-N-methylamino]ethane and the product of the intramolecular ring closure 7,5-dihydrodibenzo-6,9-dimethyl[f,h][1,4]-diazecin. The formation of this latter product is explained in terms of a concerted electron transfer/carbon-carbon coupling reaction within a complex of the monomagnesium species (1) with $CuCl_2$. The interaction of 1,2-bis[2-(bromomagnesio)benzyloxy]ethane with $CuCl_2$ affords 7,8-dihydro-



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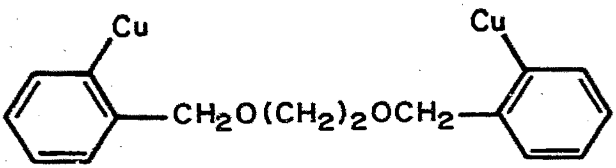

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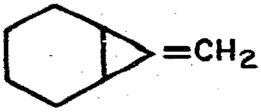

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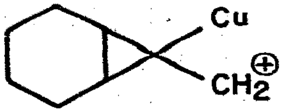

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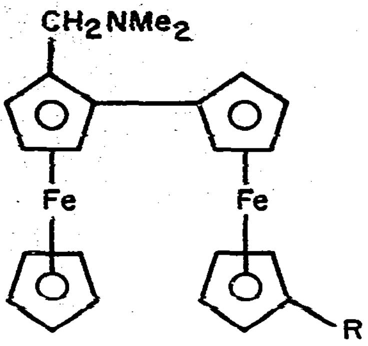
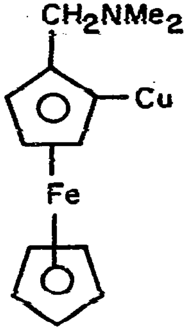


(5) R = Et, Cl



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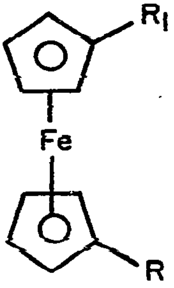
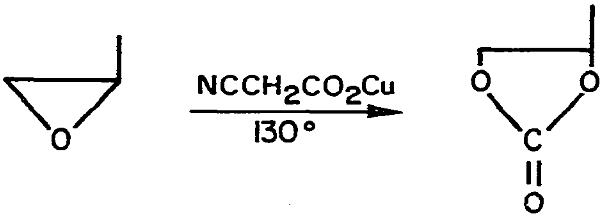


(7) R^1 = Br, I

dibenzo[f,h][1,4]dioxecin together with (2) [3]. The photorearrangement and photofragmentation of (3) in the presence of CF_3SO_3Cu to give cyclohexene, C_2H_2, bicyclo[4.2.0]oct-1(7)-ene, vinylidenecyclohexane and traces of 3- and 1-vinyl cyclohexene, is proposed to occur via the intermediate (4) [4]. The compound (5) was prepared by heating (6) and (7) at 120° [5].



(SCHEME I)

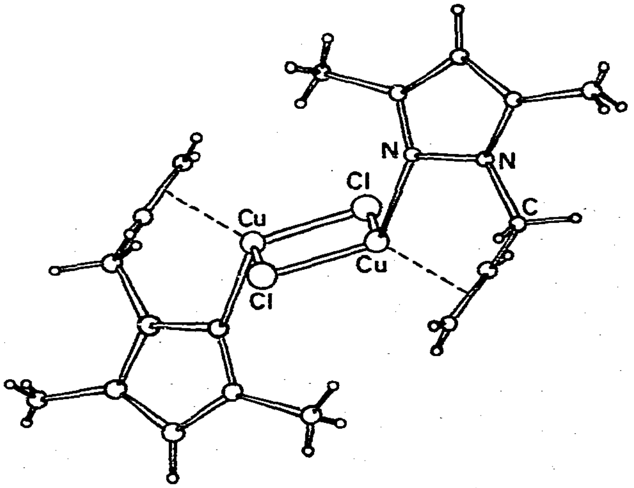
A number of insertion reactions into copper-carbon bonds with CO_2 [6-8] and SO_2 [9] have been reported. For example the alkylcopper(I) compounds $RCu(PPh_3)_2$ (R = Me, Et, Pr and $Me_2CH = CH_2$) and CX_2 (X = O,S) gave the carboxylato complexes $(RCX_2)Cu(PPh_3)_2$ together with the adducts $(RCO_2)Cu(CO_2)(PPh_3)_2$ and $Cu_2(CO_2)(PPh_3)_2(C_6H_4PPh_2)_2$. Similar reactions of $(RCu)_2(DPE)_3$ with CX_2 (X = O,S) also gave insertion products. Boiling $(RCS_2Cu)_2(DPE)_3$ in CS_2 effected P-C bond cleavage in the DPE ligand to give $Cu(CS_2)(PPh_2)(DPE)$ together with dithiocarboxylic acid and diphenylvinylphosphine [7]. $CuCH_2CN$ catalyses the production of propylene carbonate from CO_2 and propylene oxide via the inserted product $CuCO_2CH_2CN$ (Scheme 1) [8]. Alkyl and arylcopper compounds formed copper sulphinates with SO_2 which readily oxidised to sulphinic acid and sulphonyl bromides in high yields [9].

Chiral triorganotin halides R(Me)PhSnBr have been prepared from reactions of RCu (R = 2-$Me_2NCH_2C_6H_4$ and 2-$Me_2NCH_2C_6H_4CH_2$) with $(Me)PhSnBr_2$ [10].

A spectroscopic determination of the stability of $Cu(CN)_2^-$ by C. Kappenstein and R. Hugel {J. Inorg. Nucl. Chem., 36 (1974) 1821} has been criticised since the UV spectrum assigned to Cu^+ (aq.) is identical to that of Cu^{2+} (aq.). The observed reaction is suggested to be $2Cu(CN)_2^- + 4H^+ \longrightarrow Cu(0) + Cu^{2+} + 4HCN$ and not to give Cu^+ (aq.) as was previously proposed [11]. The ^{13}C NMR spectra of RNC (R = Me, Et, Pr, Me_2CH, Me_3C, $CH_2 = CHCH_2$, $CH_2 = CH$, <u>cis</u>-MeCH = CH and <u>p</u>-$R'C_6H_4$, {R' = H, Me, OMe, Cl}) and the complexes $[Cu(RNC)_4]BF_4$ in DMSO and $CDCl_3$ are reported. $J_{^{14}N-^{13}C}$ couplings were observed only in some complexes after heating and no Cu–C couplings were observed. The broad line observed for the isocyanide C resonance in the complexes was explained in terms of exchange of RNC ligands, together with quadrupole N and Cu relaxations. There is an upfield isocyano C resonance shift on complexation and $J_{^{14}N-^{13}C}$ is increased 3-fold due to larger excitation energies and higher effective charge on the C atom [12].

The deoxygenation of CO_2 by Me_3CNC promoted by $CuOCMe_3$ gave CO and Me_3CNCO [13]. The reaction of ethyl carbamate, Cu_2O, and Me_3CNC gave $Cu(NCO)(Me_3CNC)_{2.5}$ which further reacted with alkyl halides (RBr) in alcohols (R'OH), and with acyl halides (R"COCl) to form $RNHCO_2R'$ and R"CONCO respectively [14].

Cu_2O and Ag_2O absorbed CO under a CO atmosphere to form $Cu(CO)_n^+$



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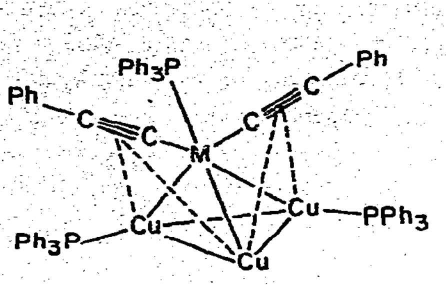
(n = 1,3,4) and $Ag(CO)_2$ respectively in H_2SO_4,$BF_3.H_2O$, FSO_3H, CF_3SO_3H and HF solutions. The ^{13}C NMR chemical shifts for the $Cu(CO)_n^+$ cations were approximately the same [15]. A suspension of Cu metal in aq. $Cu(ClO_4)_2$ solution reacted reversibly with CO, C_2H_4 and related olefins to give cuprous complexes. Two types of complexes were isolated, namely $CuL(H_2O)_2ClO_4$ (L = CO, C_2H_4 and ½ butadiene) and $Cu_2L_2(H_2O)_3(ClO_4)_2$ (L = CO, ½ allene) and equilibrium constants for the reactions were determined [16].

The crystal structure of (1-allyl-3,5-dimethylpyrazone)copper(I) chloride (8) has been determined. The complex is dimeric with copper atoms surrounded quasi-tetrahedrally by two bridging Cl's, a pyrazole N atom and the olefinic part of the allyl group. Relevant parameters observed were Cu-Cl 2.252 Å and 2.525 Å; C = C 1.338 Å; Cu-C 2.151 Å and 2.126 Å and Cu-N 2.045 Å [17]. The cocondensation reaction of Cu with pure C_2H_4 and C_2H_4-Ar mixtures at 10K was shown, by matrix IR spectroscopy, to give the first well-characterised examples of the binary zerovalent Cu-C_2H_4 complexes, $Cu(C_2H_4)_n$ (n = 1,2 or 3) [18]. Polyolefin copper(I) trifluoroacetate complexes $CuL(O_2CCF_3)$ {L = (Z,E,E)-1,5,9-cyclododecatriene, endo-dicyclopentadiene and COD}, $Cu_2L(O_2CCF_3)_2$(L = COD and COT), $Cu_4(COT)(O_2CCF_3)_4$ and Cu_3(1,3,5-cycloheptatriene)$(O_2CCF_3)_3$ have been prepared and shown by NMR to have only one olefinic bond bound to each Cu atom [19]. Thermodynamic data have been determined for the interaction of a series of liquid mono-olefins (C_5-C_{10}), including cyclic, linear and branched olefins, with CuCl and $AgNO_3$ in aq. medium. The effects of structural parameters of the olefins, nature of the metal ion, strain in cyclic olefins, etc., on the data obtained, were discussed [20].

The cationic π-acetylene complexes $[(RC{\equiv}CH)_2Cu]AlCl_4$ (R = Ph, Me_3C and H) were obtained from the arene complexes $[CuL_2]AlCl_4$ (L = C_6H_6 and Toluene) and the corresponding acetylene at -10° [21]. Cuprous acetylides have been used to synthesise $Pt(C_2R)_2(PPh_3)_2$ (R = Ph, p-MeC_6H_4, p-FC_6H_4 and C_6F_5) from $Pt(C_2H_4)(PPh_3)_2$ or from $PtCl_2(PPh_3)_2$ {for R = C_6F_5 only} [22]. The crystal structure determination of bis(triphenylphosphine)cyclopentadienylrutheniumphenylacetylidechlorocopper(I) acetone solvate has shown the molecule to contain a phenylethynyl group σ-bonded to the Ru atom and simultaneously π-bonded to a Cu-Cl moiety [23]. The preparations of the hexanuclear cluster complexes $M_2Cu_4(C_2R)_8(PR'Ph_2)_2$ (M = Rh and Ir; R = Ph, p-MeC_6H_4, p-FC_6H_4 and C_6F_5, R' = Ph; R = Ph and C_6F_5, R' = Me), $IrCu_3(C_2Ph)_2(PPh_3)_3$ (9) and $IrCu(C_2C_6F_5)_4(PPh_3)_3$ from $MCl(CO)(PPh_3)_2$ and CuC_2R have been reported. Further reactions of these clusters with $Fe_2(CO)_9$ gave the octanuclear compounds $Ir_2Cu_4Fe_2(C_2R)_8(CO)_8(PPh_3)_2$ (R = Ph and p-MeC_6H_4) [24].



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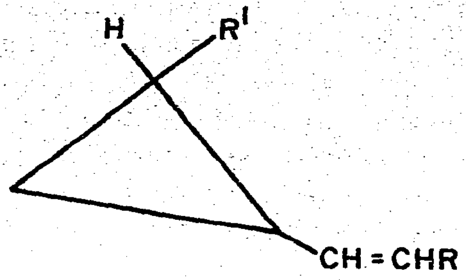


(10) R = Me, SPh; R¹ = Li, Cu

II Reactions of organocuprates and related reagents

A review has appearedon the use of organocopper reagents in organic synthesis [25].

1 Lithium-copper compounds

The functionalised 2-vinylcyclopropyllithium and -copper reagents (10) have been prepared by sequential metalations and alkylations of dibromovinylcyclopropane derivatives [26].

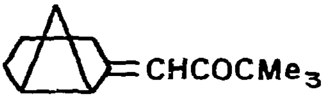
Evidence for the existence of $LiCu_2Me_3$ and Li_2CuMe_3 has been obtained from ^1H NMR signals observed from the system LiMe-CuMe in Me_2O at -136°. When the ratio of LiMe:CuMe was < 1, three signals were observed, but at a ratio of 1.021 only the signal due to $LiCuMe_2$ was seen. This suggests the successive equilibrium $LiMe + 2CuMe \rightleftharpoons LiCu_2Me_3$;
$LiCu_2Me_3 + LiMe \rightleftharpoons 2LiCuMe_2$ and $LiCuMe_2 + LiMe \rightleftharpoons Li_2CuMe$.
As the temperature was raised for LiMe:CuMe > 1 the three signals collapsed into a single peak due to $LiCuMe_2$. However the ratio between this signal and that for LiMe remained constant up to -40° and was the same as that between $Li_2CuMe_3 + LiCu_2Me_3$ and LiMe at -136°. In THF at $\leq 0^\circ$ Li_2CuMe_3, $LiCuMe_2$ and $LiCu_2Me_3$ were all observed [27]. From other evidence a dimeric structure was proposed for LDC having approximately D_{2h} symmetry [28]. The kinetics of reaction of LDC with MeI was found to involve a slow oxidative addition to copper, followed by a rapid concerted reductive-elimination step. The role of the dimeric structure in facilitating these steps was discussed [28].

2. Conjugate alkylation

Ketones which have sufficiently positive reduction potentials so that reduction by LDC to form an anion radical is energetically feasible undergo predominantly 1,2-additions. Thus, reaction of RCOR' (R = Ph; R' = cyclopropyl, 2,2-dimethyl-, and trans-2-phenylcyclopropyl, CMe$_2$OMe, CMe$_2$OAc, CMe$_2$Br and CMe$_3$) with LDC gave RCMeR'OH. This 1,2-addition reaction was significantly slower than the conjugate addition of LDC to α, β-unsaturated ketones. For R = 2-C$_{10}$H$_7$ and 1-C$_{10}$H$_7$ and R' = CMe$_3$, whose anion radicals are relatively unstable, reaction of LDC produced RCOCHMe$_2$ via a reductive elimination step [29].

In attempts to detect anion radicals as intermediates in conjugate addition reactions the cyclopropyl enone (11) was synthesised. This is an example of an enone whose anion radical (12) has a geometry very favourable for rearrangement to (13). The formation of a 72:28 ratio of rearranged product (14) and unrearranged product (15) from LDC and (11) provided compelling evidence that this reaction proceeds via an initial electron transfer step rather than direct nucleophilic addition [30].

When cold, colourless solutions of Ph$_2$CO and LDC were mixed an intermediate red-coloured solution, thought to arise from a charge-transfer absorption, was formed. Warming this red solution above 0° produced a deep blue solution containing a mixture of the blue ketyl Ph$_2$CO$^-$Li$^+$ and the salt of Ph$_2$C(OH)Me together with a precipitate of (CuMe)$_n$. Mixing



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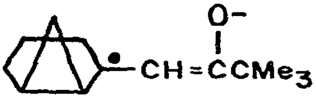

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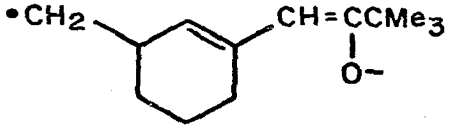

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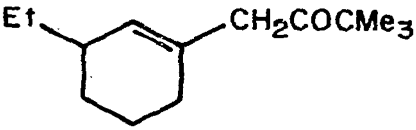

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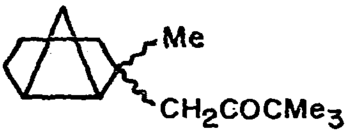

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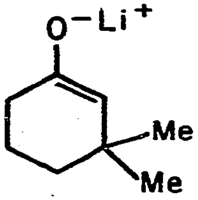
$2,4,6\text{-}Me_3C_6H_2COPh$ and LDC gave a yellow solution even up to 25°. Addition of LiMe to this cold yellow solution and warming above 0° gave a red solution containing a mixture of the red ketyl $2,4,6\text{-}Me_3C_6H_2CPhO^-Li^+$ and the salt of $2,4,6\text{-}Me_3C_6H_2CMePhOH$, and a precipitate of $(CuMe)_n$. This was taken to suggest the formation of some more powerful reducing agent such as Li_3CuMe_4 [31]. The intermediate formed from the conjugate addition of LDC to α,β-unsaturated carbonyl compounds has been shown to be the lithium enolate (16) with > 99% of the Cu precipitating as $(CuMe)_n$ [32].

The decomposition of m-trifluoromethylphenylcopper in the absence and presence of an enone has been studied. During the first phase of the decomposition 3,3'-bis(trifluoromethyl)biphenyl is produced in both cases together with conjugate addition when enone is present. When approximately half the organocopper has been consumed the above behaviour ceases and the remainder of the organocopper is converted into benzotrifluoride by removal of H from the solvent. The organocopper is suggested to exist in these solvents as a cluster compound which splits out aryl groups pairwise in competition with conjugate addition until an intermediate such as Ar_4Cu_8 is reached which then reacts with the solvent. The mechanisms of these processes were discussed [33]. Tetracyanoethylene decreases the rate of 1,4-addition of $MgCuPh_2$ to 1-mesityl-3-methyl-2-butenone and decomposes $LiCuPh_2$, whereas in the presence of PPh_3 the rate of 1,4-additions of $LiCuPh_2$ is increased and the magnesium organocuprates decompose [34]. The vinylcuprate $[CH_2 = C\{CH(OEt)_2\}Cu(SPh)]Li$ underwent 1,4-additions with α,β-unsaturated ketones to give for example (17) with cyclohexenone. The vinylcopper compound $CH_2 = C\{CH(OEt)_2\}Cu$ on the other hand gave 1,2-additions with cyclohexenone. Both organocopper compounds gave a variety of 1,4-dienes with allylic halides, but did not react with $Me(CH_2)_5CH = CHI$ or $PhCH_2Br$ [35]. The synthesis of prostaglandin analogues of (18) incorporating the (2-hydroxycyclo-octylidene)methyl moiety in place of the natural $C_{13}\text{-}C_{20}$ sidechain has been accomplished via copper-assisted conjugate addition of the (cyclo-octylidene)methyllithium (19) to the cyclopentenone intermediates [36]. Additions of LDC to the allenic ketone $CH_2 = C = CHCOCH_2Ph$ [37] and the allenic phosphine oxide $CH_2 = C = CHP(O)Ph_2$ [38] followed by protonations have given mixtures of $CH_2 = CMeCH_2R$ and $Me_2C = CHR$ ($R = COCH_2Ph$ and $POPh_2$). The results were explained in terms of a rapid 1,2-addition followed by an equilibrium slowly established between the intermediates $Li[CH_2 = CMeCH(CuMe)R]$ ($R = COCH_2Ph$ and $P(O)Ph_2$) and $Li[CH_2 = CMeCHR']$ ($R' = {:}C\{OCuMe\}CH_2Ph$ and $P(O)Ph_2$) [37,38]. The methoxyallene $CH_2 = C = CH(OMe)$ and $(RCuR')MgR^2$ ($R = R' =$ iso-Pr, CMe_3 and Bu; $R^2 = Cl$; $R = R' = Ph$, $R^2 = Br$; $R =$ iso-Pr, CMe_3, Bu and Ph; $R' = Br$, $R^2 = Cl$) produced mixtures of E- and Z-$RCH_2CH = CHOMe$. A mechanism is postulated involving attack by the cuprate on the α,β-double



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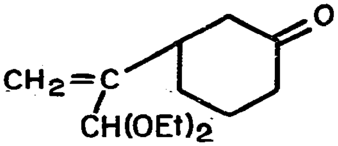

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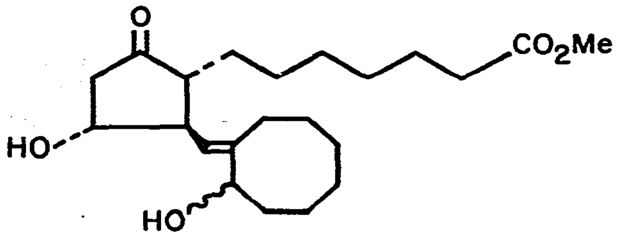

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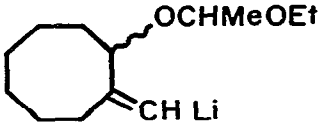


(19)

bond of the allene leading to a Cu(III) intermediate in which rotation to an allylic anion occurred. A subsequent 1,3-shift of the R radical from Cu to C_8 gave $[RCHC(CuR') = CHOMe]MgR^2$ which on protonation gave the product [39].

Homocuprates $LiCuR_2$ (R = alkyl) and heterocuprates LiCuR(SPh) or $LiCuR(OCMe_3)$ added regioselectively to $HC{\equiv}CCH(OEt)_2$ and regiospecifically to $MeC{\equiv}CCH(OMe)_2$ [40];

e.g. $MeC{\equiv}CCH(OMe)_2 + LiCuBu(OCMe_3) \xrightarrow{\text{methylation}} BuC(Me) = C(Me)CH(OMe)_2$

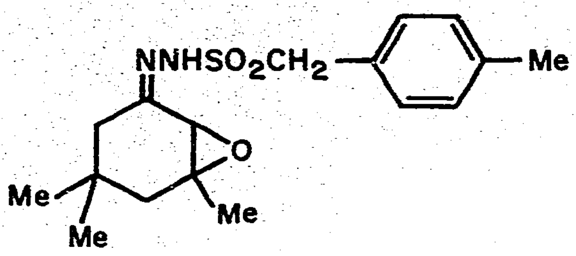
and $HC{\equiv}CCH(OEt)_2 + LiCuBu_2 \xrightarrow{\text{hydrol}} BuCH = CHCH(OEt)_2$

The reaction between RMgBr (R = Me_3C, cyclopentyl and Bu) and $HC{\equiv}CCH(OEt)_2$ in the presence of CuBr gave 78-80% RCH = C=CHOEt, the acidic hydrolysis of which gave RCH = CHCHO [41].

3. Reactions with epoxides, esters and halides

(i) Epoxides

Grignard reagents reacted in ether at RT with propargylic ethers to give allenic hydrocarbons in reasonable yields. The reactions required catalytic amounts of CuBr [42]. The sequential reaction of α-epoxytosyl-



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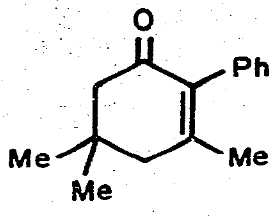

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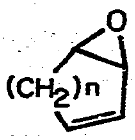

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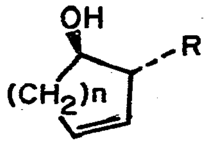

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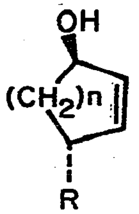

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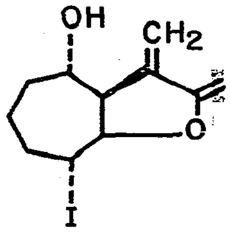


(25)

hydrazones (e.g.20) with LiBu and CuPh gave α-aryl-β-hydroxytosylhydrazones which could be dehydrated and hydrolysed to (21) [43]. The reactivity of several organo Cu reagents derived from 2-bromo-3,3-diethoxypropene with some simple epoxides and 3 activated epoxycycloalkenes has been studied. Thus treatment of (22) (n = 1,2,3) with (3,3-diethoxyisopropenyl)copper reagents gave the trans-1,2-adduct (23) and trans-1,4-adduct (24). A synthetic scheme was outlined for converting (23) (n = 3) into (25) [44]. Treatment of THF or 2-methyl-THF with LiR in the presence of CuI (10%) gave $R(CH_2)_3CHR'OH$ (R = Pr, Bu and $(CH_2)_7Me$, R' = H and Me). Similarly LiR(R = Bu, Ph, $CH_2 = CMe$ and $Me_2C = C = CH$) and CuI produced $R(CH_2)_3OH$ from oxetane [45].

A series of homo- and hetero-Z-vinylcuprates have been synthesised and condensed with epoxides to give unsaturated alcohols. Thus $LiCuBu_2$ and HC≡CH gave $(cis\text{-}BuCH{=}CH)_2CuLi$ whereas LiCuBu(SPh) and HC≡CH formed (cis-BuCH=CH)Cu(SPh)Li. With ethylene oxide the cuprates formed cis-$BuCH{=}CH(CH_2)_2OH$, with I_2 they gave 1-iodoalk-1-enes, and with CO_2 at -40° formed cis-$BuCH{=}CHCO_2H$ on hydrolysis [46].

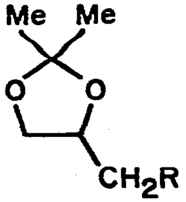
(ii) Esters

The controlled formation of allenes with organocuprates has been reported,e.g. $RC{\equiv}CCR'R^2OAc$ (R = H and Me, R' = H, R^2 = cyclopentyl; R = H,

$R',R^2 = (CH_2)_n$, n = 4,5) underwent reaction with LDC to give an organometallic intermediate which, under conditions favouring transfer of Me from the Cu to the C atom, gave $RCMe{=}C{=}CR'R^2$ as the major product. The inhibition of such a transfer followed by addition of a quenching reagent gave mainly $RCH{=}C{=}CR'R^2$ [47]. The conversion of _cis_- and _trans_-5-methyl-2-cyclohexenyl acetate to 3,5-dimethylcyclohexene with LDC is stereospecific e.g. _cis_-acetate converts to _trans_-hexene and _trans_-acetate gives _cis_-hexene. This substitution occurs on the side of the ring opposite from the replaced acetate group. The reaction involves a symmetrical intermediate e.g. an allyl radical or π-allyl complex in which the 2 allylic positions are equivalent [48]. The _tert_-ketones $(Me_3CCO)_2Z$ (Z = CH_2, CH=CH, 1,2- and 1,4-C_6H_4) and $Me_3CCO(CH_2)_2CO_2H$ were prepared by treating $Z(COCl)_2$ and succinic anhydride with 2 equivalents of $Me_3CCu(SPh)Li$. With maleic anhydride and $Me_3CCu(SPh)Li$ a mixture containing 19% $Me_3CCOCH_2CH(CMe_3)CO_2H$ and 44% $MeO_2CCH_2CH(CMe_3)CO_2H$ was formed. The cuprate underwent conjugate 1,4-addition to unsaturated aldehydes faster than 1,2-addition to the anhydride CO but at a rate slower than that for coupling with acid chlorides [49]. The coupling of the mono _p_-toluene sulphonates (26) and (27) (R = OTS) with $LiCuBu_2$ gave (26) and (27) (R = Bu), the latter being a precursor of (+)-prostaglandin A_2 [50]. Treatment of the cholenyl tosylate (28) (R = Me, R' = $4\text{-}MeC_6H_4SO_3$), with R'MgBr in the presence of Li_2CuCl_4 gave 78-85% (28) (R' = Bu, Me_2CH, Ph and cyclohexyl) [51]. The Claisen rearrangement of a triol cyclic carbonate (29), prepared from an erythrose derivative with $(MeO)_3C(CH_2)_2C{\equiv}C(CH_2)_3CO_2Me$, gave (30). Through a sequence of reactions involving hydrogenation, _o_-tosylation, protection with $EtOCH{=}CH_2$, coupling with $LiCuBu_2$, cyclising, hydrolysing etc. the (+)-prostaglandin A_2 was formed [52].

(iii) Halides

Treatment of $Me(CH_2)_7I$ with $(\underline{E}\text{-}MeCH{=}CH)_2CuLi$ at -35° in $(Me_2N)_3PO$ containing 3.75 equivalents of Et_2O gave 90-3% _E_-2-undecene The reaction of $RO_3SC_6H_4Me\text{-}\underline{p}$ (R = octyl, _sec_-octyl, Me_3CCH_2, cyclopentyl and cyclohexyl)



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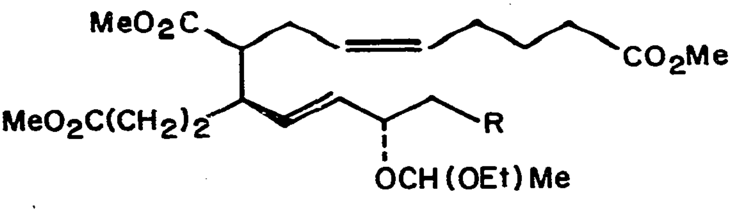

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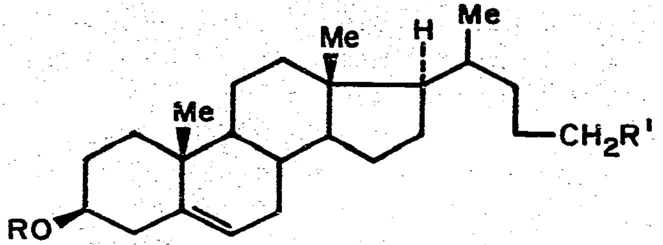

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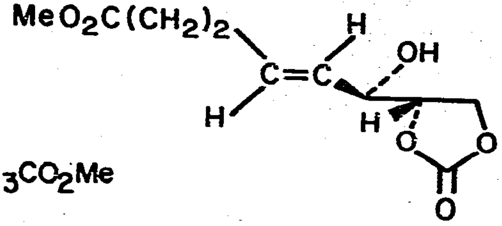

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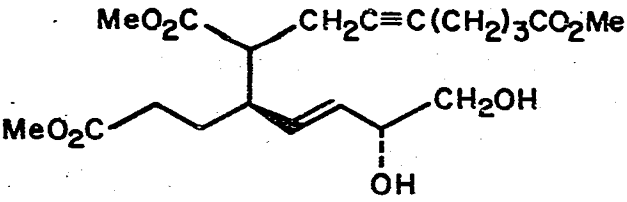
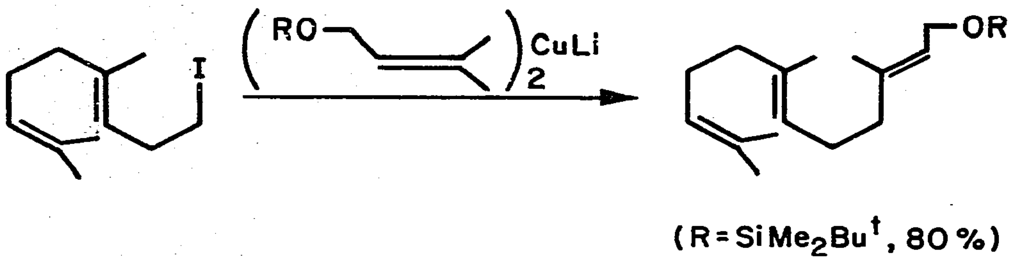


(30)

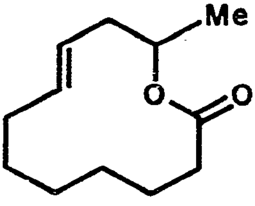
with $LiCuR'_2$ (R' = Me, EtCHMe and Ph) gave 20-95% RR' [53]. The synthesis of 3,11-dimethyl-2-nonacosanone, a sex pheromone of the german cockroach Blattella germanica, from $Me(CH_2)_{17}COSPh$ in 8 steps has been reported. The key step was Li_2CuCl_4-catalysed coupling of $Me(CH_2)_{17}CHMe(CH_2)_6Br$ with $LiCH_2(CHMe)_2OCHMeOEt$ to give, after hydrolysis, $Me(CH_2)_{17}CHMe(CH_2)_7(CHMe)_2OH$ [54]. Addition of an n-octyl halide or $HC{\equiv}CCO_2Me$ to the allenic cuprate $(Me_2C{=}C{=}CH)_2CuLi$ followed by hydrolysis gave 91% $Me_2C{=}C{=}CH(CH_2)_7Me$ and 91% trans-$Me_2C{=}C{=}CHCH{=}CHCO_2Me$ respectively. Corresponding reaction of $HC{\equiv}CCO_2Me$ with $CH_2{=}C{=}CH(CH_2)_7Me$ and Me_3CLi followed by addition of CuI gave 94% of trans-$Me(CH_2)_7CH{=}C{=}CH{-}CH{=}CHCO_2Me$, a pheromone of the parasitic bean weevil [55]. The double bond of cholesteryl- and 5-norbornen-2-yl p-toluene sulphonates and the cyclopropane ring of cyclopropylmethylcarbinyl p-toluenesulphonate underwent substitution reactions with organocuprates. Retention of configuration at the nucleophilic sp^3-C atom and skeletal rearrangements were observed. A mechanism for these reactions was discussed. One other application of this work was the coupling of homogeranyl iodide with a four-carbon functionalised vinylic cuprate reagent in a new isoprenoid synthesis to give trans-trans-farnesol (scheme 2) [56]. The stereoselective synthesis of (±)-11-hydroxy-trans-8-dodecenoic acid lactone (31), a naturally occurring macrolide from Cephalosporium recifei, has been reported. The preparation involved 5 steps, one of which involved treating trans-$Bu_3SnCH{=}CHCH_2CHMeOTHP$ (THP = tetrahydropyranyl)



SCHEME 2

with LiBu, 1-pentynylcopper and then I(CH$_2$)$_6$CN or I(CH$_2$)$_6$CO$_2$Et [57]. The stereoselective dialkylation of gem-dihalocyclopropanes has provided a simple route to dl-sesquicarene and dl-sirenin. For example treatment of (32) with Me$_2$C=CHCH$_2$CH$_2$Li and CuI at -20^o gave (33) [58]. A simple synthesis of E-4-bromo-3-methyl-2-buten-1-ol has been applied to the stereoselective synthesis of trisubstituted olefins from this alcohol and LiCuBu$_2$. Thus the reaction of E-ROCH$_2$CH=CMeCH$_2$Br (R = H and Ac) with LiCuBu$_2$ gave HOCH$_2$CH=CMeCH$_2$Bu and BuCH$_2$CH=CMeCH$_2$Bu respectively [59]. Treatment of R$_3$B with LiMe gave [R$_3$BMe]Li (R = Pr, Bu, Cl(CH$_2$)$_5$ and n-C$_6$H$_{13}$) which formed [R$_3$BMe]Cu with CuX (X = Br, Cl, I and CN). Addition of R'C$_6$H$_4$CH$_2$Br (R' = H, 3-Me, 4-Br and 4-CO$_2$Me) to the reaction solution gave R'C$_6$H$_4$CHR in 43-68% yield. A coupling mechanism based on a radical process involving a redox reaction of the copper ion was suggested [60].

The Grignard RCH = CR'MgBr(R = H, R' =H and Me; R = R'= Me) underwent CuI-catalysed alkylation with R^{2}X (R^2 = Me(CH$_2$)$_7$; X = I, Br and O$_3$SC$_6$H$_4$Me-4; R^2 = Me(CH$_2$)$_2$; X = I) to give 20-97% RCH = CR'R^2 [61]. The sulphones E-RSO$_2$CH = CR'I (R = Et, Ph and p-tolyl; R' = Bu, Me$_3$C and Ph) coupled stereospecifically with CuR^2 (R^2 = Me, Bu and Ph) to give E-RSO$_2$CH = CR'R^2 [62]. Treatment of 3-halo-2-acylaminoacrylic acids with LDC or LiCuBu$_2$ resulted in replacement of the vinylic halogen by the alkyl group. The reactions proceeded with complete or predominant retention of configuration; e.g. Z-RCH = C(CO$_2$H)NHCOCH$_2$Ph (R = Br) with LDC gave Z-RCH=C(CO$_2$H)NHCOCH$_2$Ph (R = Me and H), the latter being a small amount of reduction product [63].



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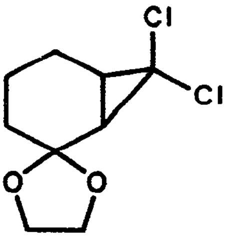

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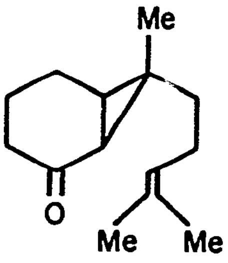

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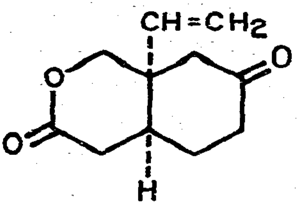
The 1,4-dienes $R(CH_2)_3CH=CR'CH_2CH=CH_2$ (R = Me and Cl; R'= H; R = R'= Me) and the mono-olefins $BuCH = CHR^2$ (R^2 = Bu and Me) were prepared in 42-95% yields with >99% stereochemical purity by the CuMe-induced cross-coupling of dialkenylchloroboranes. The boranes were formed from $R(CH_2)_3C\equiv CR'$ or $BuC\equiv CH$ and BH_2Cl with allyl halides or R^2I in the presence of $(EtO)_3PO$ [6 The benzopyrandione (34), an intermediate for the synthesis of vernolepin, was prepared by a number of steps, the final one involving coupling of (35) with $CH_2 = CHMgBr$ in the presence of CuI [65]. 2-Furylcopper couple with p-IC_6H_4R (R = $OSiMe_3$ and $N(SiMe_3)_2$) under standard Ullmann condition



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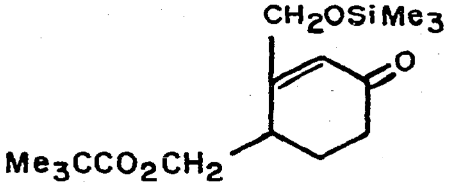


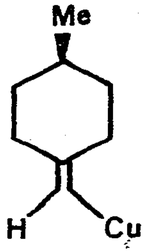
(35)

to give p-2-furylphenol and p-2-furylaniline respectively [66]. The react of $CuC\equiv CPh$ with BrCN gave 60% $PhC\equiv CCN$ and 28% $PhC\equiv CC\equiv CPh$. With $CuC\equiv CCMe_3$ and BrCN only $Me_3CC\equiv CC\equiv CCMe_3$ was formed [67].

Organocopper ate complexes were prepared in high yield from CuMe and aliphatic or aryl Grignard reagents. The resulting complexes were sufficient transfer reagents for primary, secondary, tertiary or aryl group in reactions with acyl chlorides to give ketones. These provided an alternative synthesis to cuprates from organolithium reagents [68]. Secondary and tertiary alkyl ketones (e.g. Me_3CCOPh) have been prepared from acid chlorides and $LiCu(CMe_3)SPh$ [69]. The acid chlorides $ClCO(CH_2)_nCO_2Me$ (n = 2,3 or 4) reacted with $CuC\equiv CPh$ and LiI to give $PhC\equiv CCO(CH_2)_nCO_2Me$. Similarly prepared were $R'C\equiv CCOCH_2CHRCO_2Me$ (R = H, Me and Ph; R' = Bu and Ph) [70].

4 General

The stereospecific addition of homo [71] and heterocuprates [72] to 1-alkynes has been studied. In both cases predominantly cis-additions occurred except for the reactions of $Me_3CCuMgCl$ with $PhC\equiv CH$ and $Me_3CC\equiv CH$. For the reactions of $Me_2CuMgCl$ and $(Me_3C)_2CuMgCl$ with $PhC\equiv CH$, evidence was obtained for accompanying proton abstraction from the terminal alkyne by the cuprate [71]. A kinetic study of the copper(I) induced homogeneous Ullmann



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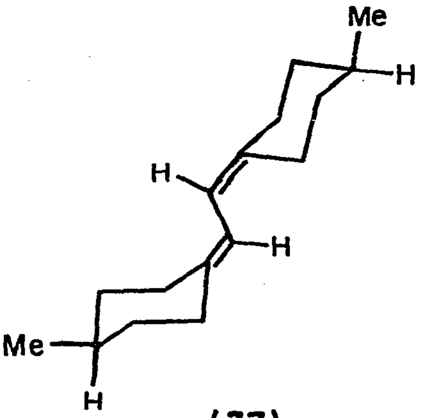

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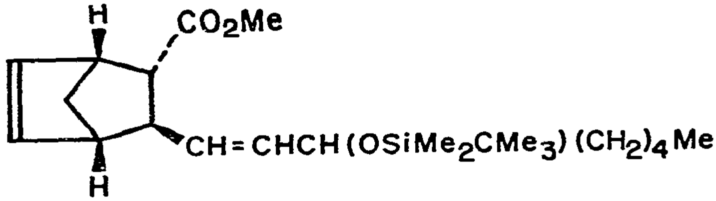

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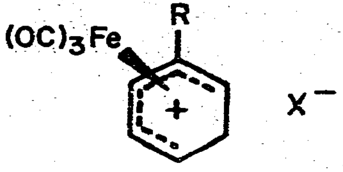
coupling of *o*-bromonitrobenzene has found the reaction to be second order in *o*-bromonitrobenzene and first order in Cu(I). The participation of free *o*-nitrophenyl radicals in the mechanism were excluded and an organocopper intermediate in the coupling was indicated. The mechanism proposed involves a reversible oxidative addition of the CBr bond to Cu(I) to form an organocopper(III) intermediate which may either displace a Br^- ion from a second aryl bromide or become protonated by the medium [73]. Treatment of (R)-(-)-4-methyl-1-bromomethylenecyclohexane with EtCHMeLi and CuI gave (36) which formed (37) with dioxygen [74]. The ester (38) was prepared by the reaction of the cyclopentadiene-methyl propiolate adduct with a mixed Gilman reagent prepared from (±)-*trans*-$BuCH_2CH(OSiMe_2CMe_3)CH{=}CHLi$ and $PrC{\equiv}CCu(Me_2N)_3PO$ [75]. Methylation of (39) (R = H, Me and OMe; X = BF_4 and PF_6) with LDC proceeded with stereospecificity and regioselectivity to give (40). Deuterium-labelled compounds established that alkylation occurred at the face of the dienyl system opposite to that occupied by $Fe(CO)_3$ [76]. The copper(I)-ylide complex of dimethylsulphoxonium methylide has been synthesised. It reacts with $PhCH = CMeNO_2$ to give (41), with $PhCH = CHNO_2$ to give 4-phenyl-2-isoxazoline N-oxide, and with PhCH = CHCOPh to give *trans*-benzoyl-2-phenylcyclopropane. The results were explained in terms of the relationship between reduction potential and reactivity [77].



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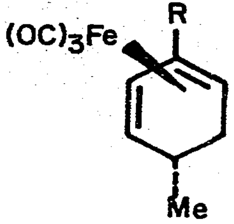

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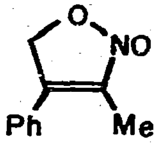
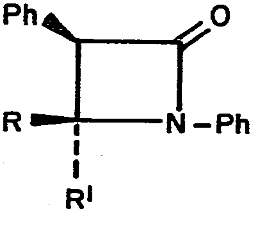


(41)

The reaction of R_2NNO (R = Me) and CuPh gave Me_2NH, Ph_2NOH, biphenyl, Ph_2NH, PhOH, Me_2NPh and PhNHOH. A mechanism was proposed involving initial formation of $R_2NN(OCu)Ph$ by nucleophilic attack of the organocopper cluster on the nitroso N. This then rearranged and subsequently reacted with a second molecule of CuPh to give a multicentre transition state which was followed by N-N bond cleavage. The reaction then proceeded along two paths; the major route involving formation of R_2NCu and Ph_2NOCu and giving R_2NH and Ph_2NOH respectively on hydrolysis, and the minor route involving form tion of R_2NPh and PhN(OCu)Cu, and giving R_2NPh and PhNHOH respectively on hydrolysis [78]. The C,N-diarylnitrone $PhCH = N^+(O^-)Ph$ reacted with CuC≡CPh to give 32% of a 5:3 mixture of (42) (R = Ph; R' = H) and (42) (R = H; R' = Ph). Deuteration and isomer studies showed that the trans-isomers are formed from the initially-produced cis-isomers and that the amounts of the latter are increased by using non-basic solvents. Lactams with aromatic, aliphatic and EtO_2C substituents were obtained from appropriately substituted acetylenes. Cyclic nitrones gave bicyclic azetidinones [79].

A series of papers on the carbonylation of organic compounds using copper or silver carbonyls and CO have appeared [80-82]. Saturated hydrocarbons such as hexane, cyclohexane and methylcyclopentane were found to carbonylate at -2^o to $+2^o$ at one atmosphere of CO in the presence of copper carbonyl in FSO_3H-SbF_5 mixtures to give secondary and tertiary carboxylic acids in high yields [80]. Corresponding reactions with olefins alcohols, dienes and diols produced tertiary carboxylic acids, monocarboxylic acids, dicarboxylic acids and lactones. No difference between Cu and Ag carbonyls in their catalytic behaviour was observed [81]. Dienes and diols having carbon numbers of 6 to 12 gave mixtures of lactones and mono- and dicarboxylic acids whereas those having carbon numbers >10 gave isomers of dicarboxylic acids, the main component of which was tetramethyl 1-substituted tertiary carboxylic acid. The yields for the reactions increased for an increase in the C number. All starting materials gave mixtures of 1,4- and 1,5-lactones, with larger amounts of lactones being obtained from diols than from dienes [82].

Examination of partial rate data for the decomposition of diazoacetic esters and dimethyldiazomalonate in the presence of soluble copper salts and cyclohexene revealed the existence of two paths to carbene dimer formation, one with a unimolecular dependence upon catalyst and the other with a bimolecular dependence. Assuming carbenoid formation this is taken as indicative of dimer formation occurring by carbenoid + diazo compound and carbenoid + carbenoid paths. Conformational analyses indicate a preference for diethyl maleate formation by the first path (carbenoid + diazo compound) for the case of diazoacetic ester and a preference for diethyl fumarate formation by the carbenoid + carbenoid path [83]. The addition of bis(methoxycarbonyl)carbene to a number of olefins employing homogeneous and heterogeneous catalysed decomposition of dimethyldiazomalonate by Cu and Ag salts has been studied. The cyclopropanations are stereospecific and are accompanied by appreciable amounts of allylic C-H insertion products, which could formally be derived from allylic radicals or ionic intermediates. Cyclopropanation with cis-2-heptene proceeds 5.2 times faster than with the trans-isomer and cyclohexene reacts 4-9 times faster than 1-methylcyclohexene when the catalyst is $CuIP(OMe)_3$ [84]. Thermolysis of Ph_2CN_2 and RCH_2OH ($R = CH_2=CH$, $MeCH=CH$ and $EtCH=CMeCH_2$) in benzene in the presence of copper acac gave 37-45% Ph_2CO and small amounts of $ROCHPh_2$ and $(Ph_2C=N)_2$ [85]. The compound (43), obtained by the $CuIP(OMe)_3$ catalysed decomposition of $N_2C(CO_2Et)_2$ in cyclohexene was used to prepare 5-spiro-7'-(bicyclo[4.1.0]-heptane)barbituric acid by condensing with urea [86]. The key step in the Meerwein reaction of p-$ClC_6H_4N_2^+$ salts in the presence of unsaturated compounds is the formation of aryl radicals; complexation of the Cu(I) salt with the unsaturated compound plays only a minor role. Thus, treatment of CuClCOD or $[Cu(COD)_2]BF_4$ with p-$ClC_6H_4\overset{+}{N_2}$ X^- ($X = Cl, BF_4$) gave no Meerwein products. Similarly treatment of $CH_2 = CHCH_2OH$, which complexes easily with Cu(I), with p-$ClC_6H_4\overset{+}{N_2}$ and a Cu(I) catalyst gave only 5% of the Meerwein product p-$ClC_6H_4CH_2CHClCH_2OH$. On the other hand $CH_2=CH(CH_2)_2CH_2OH$ and p-$ClC_6H_4\overset{+}{N_2}$ gave (44), via an aryl intermediate oxidised to a carbocation by Cu(I) [87]. The compound (45) (R = 1-methyl-cyclopropyl) was synthesised from (45) ($R = H_2C=CMe$) and CH_2N_2 in the presence of $CuBr/Cu(O_3SC_6H_4Me\text{-}4)_2$ [88].



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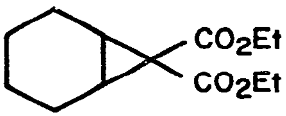

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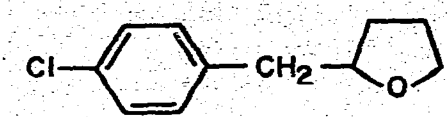

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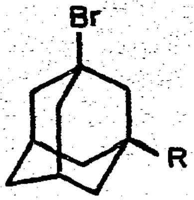

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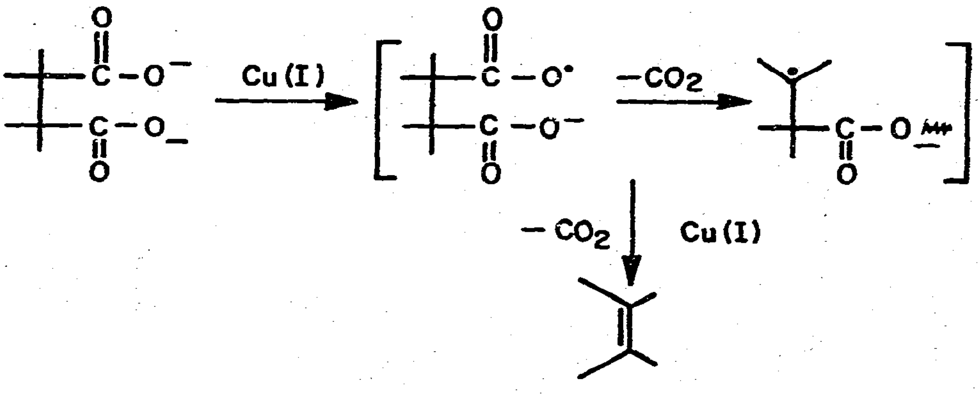
5. Catalysis

2-Arylbenzoxazoles (46) have been synthesised by heating (47) with R^2CHO in tetralin for 2-3 h [89]. The bis-copper(II) chelate complexes (48) (R_n = e.g. Me, Cl, Me_2N and CH = CHCHCN) readily underwent cycloaddition with $MeO_2CC{\equiv}CCO_2Me$ to give (49) in excellent yields. The role of the copper ion in these reactions is two-fold, namely (i) to polarize electron density in the ligand towards the termini of the heterodiene system and (ii) to create a coordinative template for the reaction [90]. The copper(I) catalysed oxidative decarboxylation of vicinal dicarboxylic acids has given good yields of the corresponding olefin. A mechanism for this reaction has been proposed (scheme 3) [91]. $RC{\equiv}CCO_2H$ (R = H and HO_2C) was decarboxylated to C_2H_2 and CO_2 at 20° in DMF containing CuCl [92].

Each of the olefins cis- and trans-p-menth-2-ene, 3-methylcyclohexene and 4-methylcyclohexene afforded a mixture of allylic benzoates with a high degree of stereo and regioselectivity when treated with $PhCO_2OCMe_3$ and cupric benzoate. The major products are those containing a disubstituted double bond and bearing a benzoate group in a trans position to an alkyl substituent. The mechanism involves a free-radical chain with preferential abstraction of allylic H atoms occupying quasi-axial positions, followed by ligand



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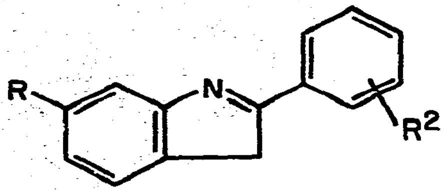

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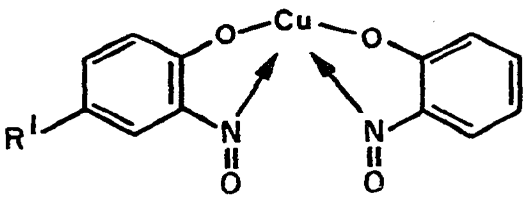

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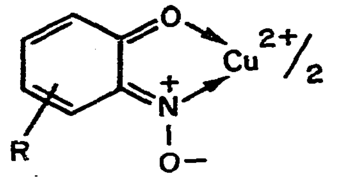
(R^1 = Cl, Me, Br; R^2 = 4-OMe, 4-OH, 2-OH, 3-Br)



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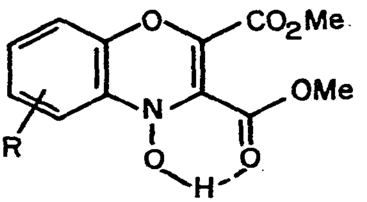


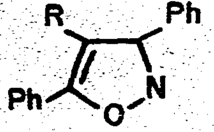
(49)

transfer from cupric carboxylate via a cyclic transition state [93]. The oxidation of phenol with O_2 and CuCl gave 44% cis-cis-$HO_2C(CH{=}CH)_2CO_2Me$ [94]. Anaerobic oxidation of o-$(HO)_2C_6H_4$ or 4-tert-butyl-1,2-benzoquinone by the pyridine complex of CuCl(OMe) gave monomethyl-cis-cis-muconate or a mixture of monomethyl-3- and 4-tert-butylmuconate respectively [95].

The compounds $Ph_2C{=}C{=}NC_6H_4R$-4 (R = MeO, Me, H, Br, Cl and F) with $CuCl_2$ and air formed 55-95% Ph_2CO, 9-40% 4-RC_6H_4NCO and 1-9% of 4-RC_6H_4NC [96]. The sodio-lithio derivative of acac reacted with methylene or ethylene dibromide using CuCl as a catalyst to give respectively 2,4,8,10-undecanetetrone and 2,4,9,11-dodecanetetrone [97].

The rather unusual loss of stereochemistry resulting from the facile cleavage of 3,3-dimethylbutyl-1,2-d_2 and tricyclo[2.2.1.$0^{2,6}$]heptyl groups from Pd, Zr and Hg complexes by CuBr rules out a concerted mechanism and favours alkyl radicals as intermediates [98].

Treatment of 1,2-diphenylcyclopropane with $Cu(NO_3)_2$ in dry Ac_2O at <10° gave 52% (50) (R = H) and 15% (50) (R = NO_2)[99]. Vinylpyrazolines (51) (R = H and Me) were obtained in 26% and 29% yields from $RCHClCH{=}CHC{\equiv}CH$



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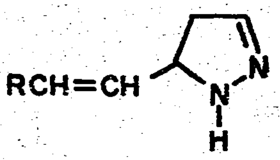

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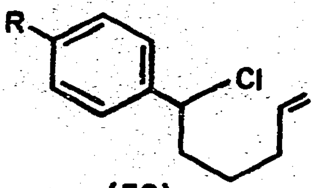

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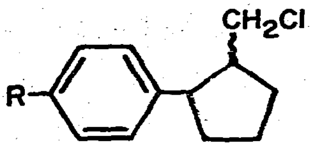

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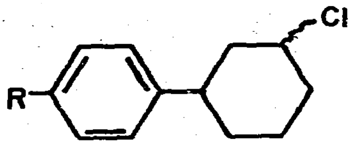
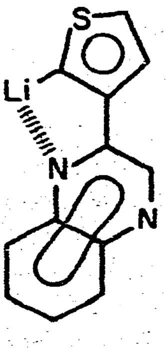


(54)

with N_2H_4 and $Cu-Cu_2Cl_2$ [100]. Treatment of (52) (R = NO_2) with $CuCl_2$ and $NHEt_2$ in MeCN gave (53) (R = NO_2) and (54) (R = NO_2). In the presence of BIPY or PHEN, cyclisation of (52) (R = NO_2) by CuCl in DMF produced 90-95% mixtures of 49% _trans_-(53) (R = NO_2) and 20% _cis_-(53) (R = NO_2), 21-3% _trans_-(54) (R = NO_2) and 8-9% _cis_-(54) (R = NO_2). Cyclisation of (52) (R = H) gave (53) (R = H) in high yields [101]. The lithio compound (55) gave open-chain oligomers on warming but in the presence of anhydrous CuF_2 gave the cyclic product (56) [102]. Metallic Sn reacted with organic halides in $PO(NMe_2)_3$ with CuI as a catalyst to give 55-95% of the corresponding diorganotin dihalide complexes [103]. Elimination of PhSH from $MeCH(SPh)CH_2CH(SPh)_2$, $PhSCH_2CH_2C(SPh)_2Me$ and $CH_2 = CHCH(OMe)CH(SPh)_2$, catalysed by $CF_3SO_3Cu-C_6H_6$, gave _E_-CH_2=CHCH=CHSPh, CH_2=CHC(SPh)=CH_2 and (_Z_)-CH_2=CHC(OMe)=CHSPh respectively [104]. A study on the conjugate



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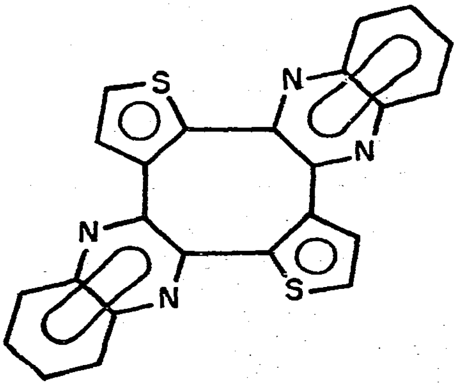
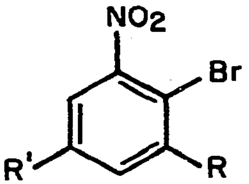


(56)

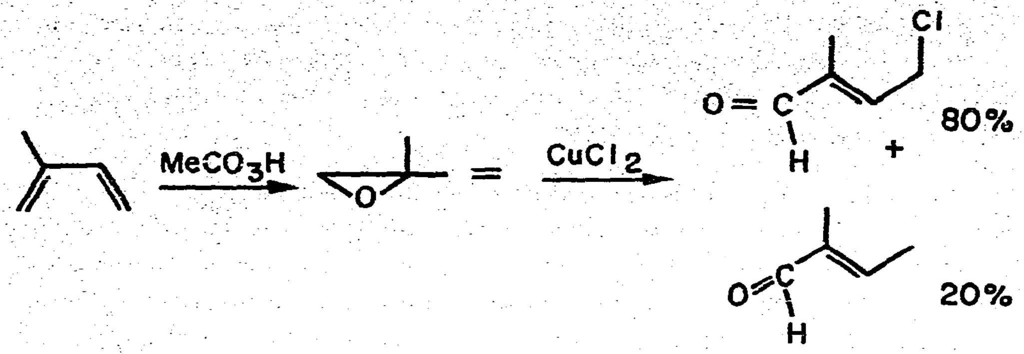
reduction of six α,β-unsaturated ketones by the new reagent $LiAlH_4$-CuI has shown the reduction to be sensitive to the $LiAlH_4$:CuI:enone ratio, temperature, solvent and reaction time involving contact of $LiAlH_4$ and CuI before the enone is added [105].

The halogen-halogen exchange between CuCl and $2\text{-}Me_2NC_6H_4I$ has been studied in an attempt to determine the nature of the intermediate. The results indicated that arylcopper complexes are not intermediates in these reactions [106]. The CuCl and $CuCl_2$ catalysed exchange reactions of $RCH{=}CHCH_2Cl$ (R = Me, Ph, Cl) $CH_2{=}CHCHMeCl$, $MeCCl{=}CHCH_2Cl$, $CH_2{=}CHCCl_3$ and $PhCH_2Cl$ with HX (X = Br and I) are reported [107]. Steric and some polar effects account for the activation of the substituent in the 3-position in the CuCl-catalysed bromine-chlorine exchange in (57). Activation parameters and mechanistic aspects of the results are given [108].

Primary amines coordinated with Cu(II) halides are oxidised to geminal dihalides by copper halide nitrosyls. Difunctional amines possessing a potentially reactive functional group underwent selective oxidation at the primary amine. In addition to geminal dihalides, however, nitrile, alkyl halide and alcohol products are formed in reactions of amines with Cu halide nitrosyls. Deaminations by copper nitrosyls leading to substitution products are remarkably free of rearrangments. α-Branched primary amines did not yield geminal dihalides in reactions with the copper nitrosyls. The results obtained suggest the occurrence of at least 3 separate reactions of the nitrosyl with amines; displacement of NO, deamination of the free amine and oxidative deamination of the Cu(II) halide-complexed amine [109]. An unprecedented oxidative chlorination of a 1,3-diene monoepoxide by cupric chloride has been reported during a two-step synthesis of (E)-4-chloro-2-methylcrotonaldehyde from isoprene (scheme 4) [110]. Ethanolic $CuCl_2$ has been found to be useful reagent for the efficient removal of the $Fe(CO)_3$ group from a variety of cyclohexadiene-iron tricarbonyl complexes, in some cases with the accompanying chlorination of the organic ligand [111].



(57) (R = F, Me, Et, t-Bu, R' = H,
R = H, R' = F, Me)



(SCHEME 4)

The 4-cyano-4'-halobiphenyls, 4-$NCC_6H_4C_6H_4R$ (R = Br and I) were prepared by reacting (4-$RC_6H_4)_2$ with equimolar amounts of CuCN in refluxing DMF. When R = Cl, an excess of CuCN was required and N-methylpyrrolidone was used as solvent [112].

III Silver-carbon bonds

A review on the noble metal complexes has appeared [113].

Condensation of Ag vapour with fluoralkyl iodides (e.g. CF_3I) at -196° followed by matrix warmup has given AgI and RAg. Matrix dilution experiments indicate that high RI/Ag ratios favour RAg formation [114].

The paramagnetic green complex $Ag(CO)_3$ has been prepared from cocondensing reactions and characterised by a variety of techniques. The carbonyl appears to adopt a distorted planar conformation in pure CO but has D_{3h} symmetry in Ar, Kr or Xe matrices. Unlike the Cu-CO reaction, $Ag_2(CO)_6$ could not be synthesised in the matrix. However $Ag(CO)_3$ was thermally and photochemically labile in pure CO and at 20-35°K underwent facile dimerisation to form $Ag_2(CO)_6$ [115]. The kinetics of this dimerisation appear to be diffusion controlled, with a diffusion coefficient of the mobile species being 7×10^{-16} cm^2sec^{-1} at 35°K. The activation energy for this process was 1900 cal/mole [116]. The syntheses and characterisation of $Ag(CO)_2$ and Ag(CO) were also described. Information from IR and UV-visible spectra was used, for the series $M(CO)_n$ (M = Cu, Ag; n = 1-3), to draw conclusions about their molecular and electronic structures, thermodynamic stabilities and bonding properties. Of special interest was the anomalous behaviour observed for the Cotton-Kraihanzel CO force constants, which were rationalised in terms of a very stable nd^{10} valence shell and the participation of energetically accessible valence p_π metal orbitals in the overall bonding scheme [115].

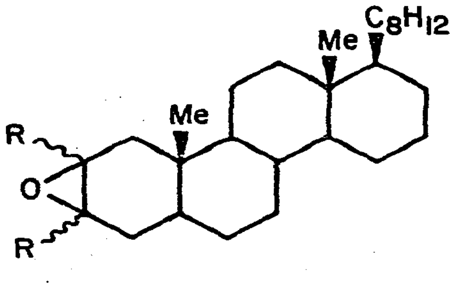
The reaction of $KAg(CN)_2$ with Me_3NBH_2I gave Me_3NBH_2NC, $(Me_3NBH_2)_2CNAg_2I_3$ (ratio 20:7) and Me_3NBH_2CN. AgCN and Me_3NBH_2NC formed $Me_3NBH_2NCAgCN$ which gave $Me_3NBH_2NCAgCNBH_3$ with B_2H_6 [117].

The crystal structure of the pseudo-Diels-Alder dimer complex of norbornadiene $Ag(C_{14}H_{16})NO_3$ has been resolved. Ag is equidistant from two olefinic C atoms with bond distances of 2.31 Å and 2.33 Å [118]. A series of 1:1 π-complexes of alkenes, dienes, trienes, alkynes and dienes has been prepared. The decrease in the chemical shift of the vinylic protons in the ^1H NMR of cyclohexene with increasing Ag(I) salt concentration indicates that the extent of olefin π-complexation to silver decreases in the order $AgO_3SCF_3 > AgSbF_6 > AgBF_4$. Stability constants from ^1H NMR for the alkyne complexes were found to decrease in the order: 1,8-cyclotetradecadiyne > 3-hexyne > 2-hexyne > 4-methyl-2-pentyne [119]. The complexing of Ag^+ with 2-methylpropene and NH_3 was studied potentiometrically at 15°, 25° and 40°. The equilibrium constants and standard thermodynamic functions of formation of the observed complex $[Ag(C_4H_8)(NH_3)]^+$ were calculated [120]. The compound η^5-$CpAgPPh_3$ has been synthesised from CpNa, PPh_3 and $AgSO_3CF_3$ in THF, and characterised by IR and NMR [121].

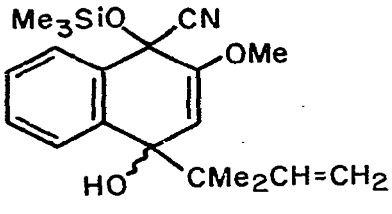
IV Catalysis by silver salts

C_2H_4 was oxidised to ethylene oxide in the presence of silver ketenide [122]. Steroidal alkenes, e.g. 5-α-cholest-2-ene, were found to undergo smooth epoxidation with I_2 and Ag_2O in 12:1 dioxane-H_2O solution, to give e,g, (58). The mechanism involved formation of an iodohydrin which rapidly lost HI to give the epoxide [123].

Treatment of (59) with aq.AgF in THF has given (60) via loss of MeOH from the intermediate (61). The formation of (61) from (59) occurred by loss of Me_3SiCN to form the quinol which then rearranged in a remarkably facile [3.3] sigmatropic Cope rearrangement [124].



(58) (R = α-H)



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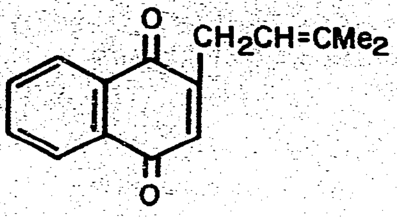

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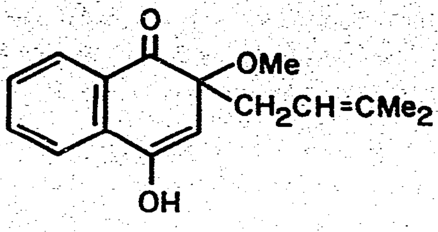

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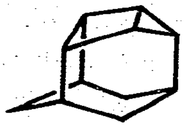

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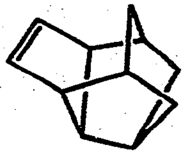

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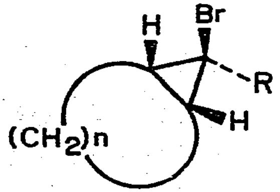

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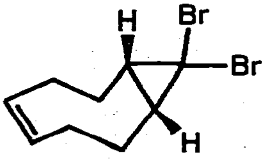

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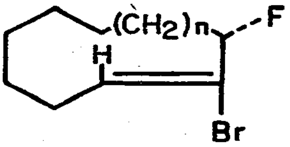

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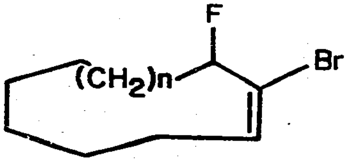

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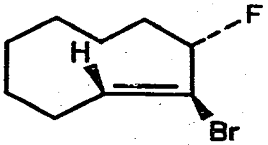

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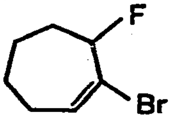
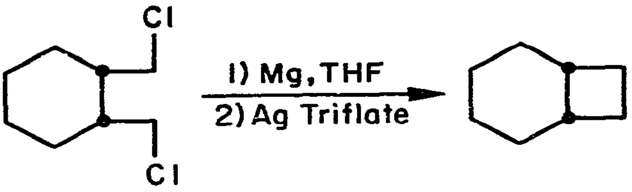


(69)

Treatment of (62) with 3.6 mole % of AgBF$_4$ in CHCl$_3$ gave 85% (63). Bicyclo[2.1.0]pentane was found to be inert to Ag$^+$ and though the strain energies of these two compounds are similar it appears that the reactivity of (62) may instead be due to the formation of a hyperconjugatively stabilized intermediate [125]. Ring opening of the geminal dibromocyclopropanes (64) (R = Br and Me; n = 6) and (65) by AgF in MeCN gave the allylic fluorides (66-68) in moderate yields, whereas (64) (R = I, n = 4) with AgF gave (69) [126]. Reactions of α -ω-alkane di-Grignard reagents with Ag(I)triflate has provided a practical synthesis for representative four-. five- and six-membered carbocyclic rings (scheme 5) [127].

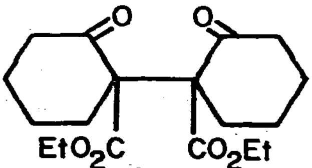


(SCHEME 5)

The Ag$^+$-assisted methanolyses of 9,9-dibromobicyclo[6.1.0]nonane and -non-4-ene showed both first and second order dependence on Ag$^+$. The rate of methanolysis of the latter ene was an order of magnitude greater than the former, while for both substrates the ratios of rate constants first and second order in Ag$^+$ are close to 1.1. A mechanism was discussed [128].

Alkylation of cyclopentanone and cyclohexanone with 1-octene or 1-decene in the presence of AgO or Ag$_2$O gave the appropriate 2-n-alkylcycloalkanes in 68-77% yields. The AgO initiated alkylation led to anti-Markovnikov 1:1 addition products [129]. The compounds $PhCO_2CH_2C{\equiv}CN{=}NC_6H_4R$ (R = H, p-Me and o-Me) were prepared from $PhCO_2CH_2C{\equiv}CAg$ and $[RC_6H_4N_2]Cl$ [130]. Condensation of 2,3-O-isopropylidene-5-O-trityl-D-ribofuranosyl chloride with the silver acetylide of methyl propiolate gave 34% β-D-ribofuranosyl propiolate [131].

Carboxylic acids e.g. acylacetates and monosubstituted malonates, were oxidatively dimerised by Ag$_2$O in DMSO without intervention of their carbanions. Thus 2-carbethoxycyclohexanone gave (70) [132]. A new



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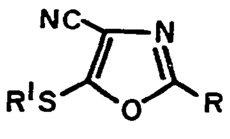


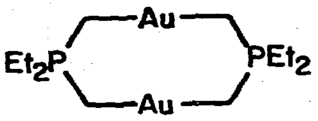
(71)

method for synthesising 5-(substitutedmercapto)oxazoles (71) from 3-mercapto-acrylic acid derivatives with Ag_2O, Ag_2CO_3 or AgOAc is described [133].

V Gold-carbon bonds

A review entitled "Is Gold Chemistry a Topical Field of Study?" has appeared [134] and recent advances in oxidative-addition and reductive-elimination reactions of organogold compounds have been surveyed [135].

$MeAuPPh_3$ and Me_3AuPPh_3 reacted with LiMe in the presence of $(Me_2NCH_2CH_2)_2NMe$ to give $[Li\{(Me_2NCH_2CH_2)_2NMe\}][AuMe_n]$ (n = 2 and 4) respectively [136]. A series of gold(III) salts of the type cis-$[Me_2AuL_2]^+X$[L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, $AsPh_3$, $SbPh_3$, $H_2NCH_2CH_2NH_2$, DPE, $(Ph_2AsCH_2)_2$ and o-$C_6H_4(AsMe_2)_2$, X = BF_4, PF_6, ClO_4 and CF_3SO_3], cis-$[Me(CD_3)Au(PPh_3)_2]O_3SCF_3$ and cis-$[R_2Au(PPh_3)_2]O_3SCF_3$ (R = Et and Bu) have been prepared. Reductive-elimination from these complexes gave only alkanes, no disproportionation products being observed. Elimination rates increased with increasing size of the alkyl groups and the neutral ligands and was inhibited by excess ligand. A small anion effect was observed. An intramolecular dissociative mechanism was proposed involving the rapid elimination of the alkane from an electron-deficient dialkylgold(III) complex with non-equivalent Au-C bonds [137]. The reductive elimination, but not isomerisation, of R_3AuL (R = Me and Et; L = PPh_3 and PMe_3) proceeds via two competing pathways. The intermolecular route predominates in non-polar solvents, whereas DMSO and DMF promote intramolecular reactions. R_3Au, formed by rate limiting dissociation of L, is a common intermediate in both cis- and trans-isomerisations and reductive eliminations. The capture of R_3Au by DMSO prevents its association with other alkylgold species to promote further intermolecular reactions and only intramolecular processes leading to isomers and reductive elimination are observed in this solvent. The intermediate Et_2MeAu undergoes isomerisation through a T-shaped configuration 100 times faster than reductive elimination. MO calculations indicate that the PE surface for Me_3Au is determined by the orbital degeneracy of the symmetrical C_{3h} geometry and favours distribution to T- and Y-shaped configurations of lower energies. The former represents minima and the Y-shaped configuration are saddle points for the cis-trans isomers of the T's, and serve as exit channels through which reductive elimination proceeds [138]. An examination of the electrophilic cleavage of Au-C bonds by the acids HX(X = ClO_4, CF_3SO_3, NO_3, I, Br, Cl, CF_3CO_2 and $MeCO_2$) for cis- and trans-$[RAuMe_2PPh_3]$ found that the Au-C bond trans to L is preferentially cleaved [139]. Cleavage of the methyl-metal bond in Pt(II), Au(I) and Au(III) complexes



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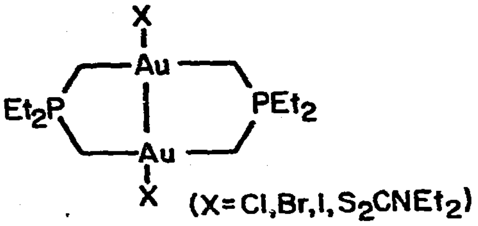

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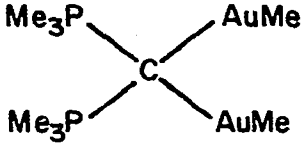

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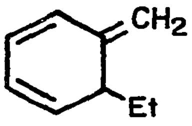

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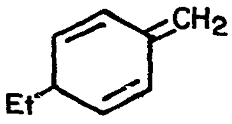


(76)

by PhSeH, Ph_2PH and Ph_2AsH has been effected [140]. $MeAuPPh_3$ reacted with $CHCl_3$ under UV irradiation to give methyl and solvent derived radicals in triplet pairs showing CIDNP. An S_H2 substitution by methyl radicals at the Au centre was observed [141].

The reaction of $AuClPPh_3$ with $MeEt_2P = CH_2$ gave (72) which formed the gold(II) product (73) with halogens [142] and $(Et_2NCS_2)_2$ [143]. The alkyl complex $AuMePMe_3$ and $Me_3P{=}C{=}PMe_3$ gave (74) [144]. ESCA and ^{197}Au Mössbauer spectra have been recorded for 7 ylide complexes of Au(I), Au(II) and Au(III). The results show significant trends in the various parameters and there is a correlation between the ESCA and Mössbauer data [145].

The complexes $RCOCH_2AuPPh_3$ (R = Me, Et, Ph and ferrocenyl) were prepared from $[(Ph_3PAu)_3O]MnO_4$ and RCOMe or from $AuBrPPh_3$, Ag_2O and acetone. Treatment of $[(Ph_3PAu)_3O]BF_4$ with $CH_2 = CHOBu$ or $CH_2 = CHOCOMe$ gave Ph_3PAuCH_2CHO [146]. Complexation of (75) or (76) with $[(Ph_3PAu)_3O]BF_4$ gave o- and p-$EtC_6H_4CH_2AuPPh_3$ [147].

The Grignard PhCH=CHMgBr and $AuXPPh_3$ (X = Cl and I) gave 16% cis and 60% trans-PhCH=CHAuPPh$_3$ [148].

Additions of CF_3I to AuMeL gave $AuMe_3(CF_3)L$ and AuIL (L = PMe_3 and PMe_2Ph) together with $Au(CF_3)L$ and MeI (L = PPh_3). A free-radical chain mechanism was suggested for these reactions [149]. Anionic aryl-gold complexes of the type $[Au(C_6F_5)_2]^-$, $[AuX(C_6F_5)]^-$ (X = Cl and Br), $[Au(C_6F_5)_4]^-$, $[AuBr(C_6F_5)_3]^-$ and $[AuBr_3(C_6F_5)]^-$ were obtained from

$[AuCl(tht)]$ (tht = tetrahydrothiophene), $[AuCl_3(tht)]$ or $K[AuCl_4]$ and LiC_6F_5 followed by displacement of tht with Bu_4NBr or Et_4NCl [150]. The oxidation of XAu(DPE)AuX with $TlBr(C_6F_5)_2$ gave for X = Cl, $Cl(C_6F_5)_2Au(DPE)Au(C_6F_5)_2Cl$. When X = C_6F_5, oxidations with halogens X'_2 (X'= Cl and Br) gave $X'_2(C_6F_5)Au(DPE)Au(C_6F_5)X'_2$ and with I_2, IAu(DPE)AuI [151]. Ligand-free monoarylgold compounds $[p\text{-}C_6H_4AuCl_2]_2$ (R = H, Me, Et, Me_2CH, Me_3C and Ph) have been synthesised from arenes and $AuCl_3$. The properties and reactions of these products were discussed [152].

The cocondensation of Au atoms with C_2H_4 and O_2 gave the single products $Au(C_2H_4)$ [153] and $Au(O_2)$ [154] respectively. The O_2 ligand was bonded 'side-on'. The electronic spectral data for $Au(O_2)$ indicates that the Au-dioxygen bonding interaction is more closely akin to the Dewar description of metal-olefin interactions in the complexes $M(C_2H_4)$ (M = Ag and Au) rather than the extreme case of ion-pair bonding found for $Ag^+(O_2)^-$ [154].

Quantitative yields of AuCOCl have been obtained from anhydrous $AuCl_3$ and CO in $SOCl_2$. The intermediate species Au_2COCl_4 in the reduction was characterised spectroscopically [155]. The CO group in AuCOCl has been displaced by pyridyl-, benzothiazolyl and benzimidazolylsilanes [156].

The crystal and molecular structure of Au(MeNC)CN has been determined. The Au atom is almost linearly coordinated with Au-C(CN) and Au-C(CNMe) bond lengths of 2.01 Å and 1.98 Å respectively [157].

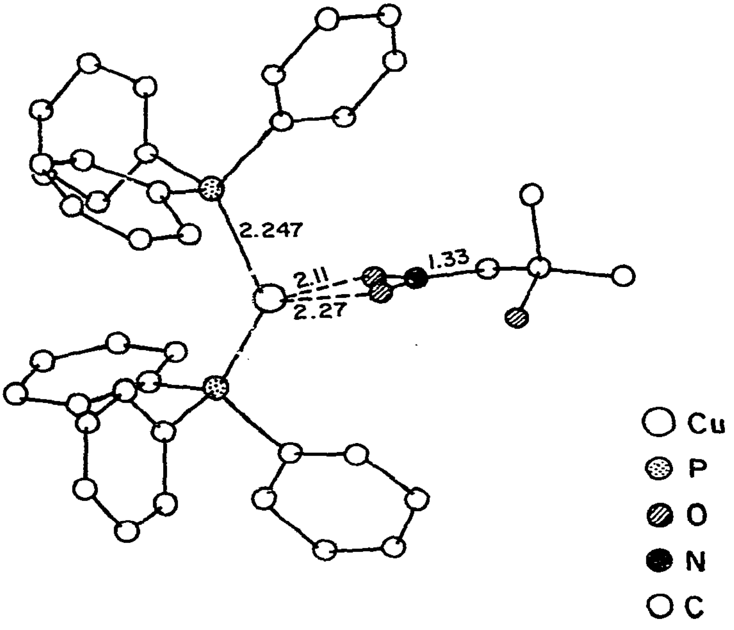
Some ionic bis(carbene) complexes of Au(III) were obtained by oxidation of the corresponding Au(I) derivatives with halogens. Complexes characterised were $[\{(RNH)(Y)C\}_2AuX_2]^+$ (R = *p*-tolyl, Y = RNH, MeNH and EtO; X = Br and I) [158]. The compounds $\{(4\text{-}RC_6H_4N)(OMe)C\}AuPPh_3$ (R = Me and NO_2) and $Hg[C(OEt)(NC_6H_4Me\text{-}4)]_2$ are basic and react with HF or picric acid to form salts. The gold complex was used as a monodentate N ligand to produce the compounds $[AgL_2]^+$, $AgL(NO_3)$ and *cis*-$[RhCl(CO)_2L]$ [L = $\{(4\text{-}RC_6H_4N)(OMe)C\}AuPPh_3$] [159].

The reaction of alkynes, cyclopropanes and benzene derivatives with Au(III) complexes has been studied. With alkynes and arenes, products are accounted for in terms of electrophilic attack by Au on the unsaturated centre. The reaction of $HAuCl_4$ with alkynes resembles the Hg(I)-catalysed hydration but gives better yields. Aromatic compounds and $AuCl_3$ give chloroarenes, the isomer distribution being consistent with initial metallation of the ring followed by displacement of the dichlorogold group by a Cl atom. Cyclopropanes and $HAuCl_4$ produced only 1,2-adducts [160].

VI Complexes and reactions of general interest

A review on chlorocuprates, covering crystal structures and spectral characteristics,has appeared [161].

The crystal structures of $CuClL_3$ (L = PPh_3 and $PMePh_2$), $[CuClAsMe_2Ph]_2$ and $Cu_2Cl_2(PPh_3)_3.C_6H_6$ have been determined [162]. The geometries of the four compounds were discussed in detail and compared with those of other $[CuX]_nL_m$ complexes [162]. The structure of $[CuBrP_2Et_4]_x$ is characterised by continuous chains; the Cu atoms are tetrahedrally coordinated and linked together by alternating double bridges of 2 Br atoms and 2 diphosphine molecules respectively [163]. The synthesis and structures of the complexes [MCl(PP)] (M = Cu(I), Ag(I) and Au(I); PP = 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene) are reported, and an increase in ionic character of the M-Cl bond is inferred along the series Cu>Ag>Au [164]. (aci-Nitromethanato)bis(triphenylphosphine)copper(I) reacted with acetone to give (aci-nitro-tert-butanolato)bis(triphenylphosphine)copper(I) whose structure (77) was determined by X-ray analysis [165].

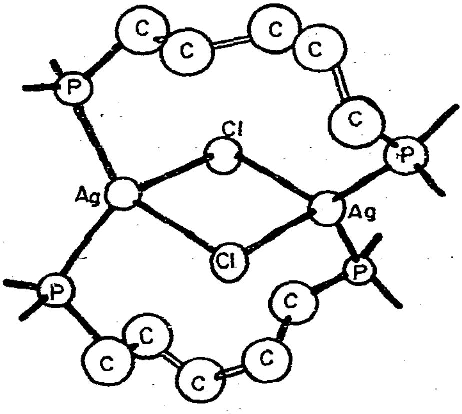


(77)

A series of crystal structure determinations of silver-halo-phosphine complexes have been completed [166-169]. In the dimeric chloro-[1,5-bis(diphenylphosphine)pentane]silver (78) the two Ag atoms are joined both by doubly-bridging Cl atoms and by two molecules of 1,5-bis(diphenylphosphine)-

pentane [166]. Cubane-type conformations have been found for [AgXL] (X = Cl and Br, L = PEt_3 [167]; X = Cl, L = PPh_3 [168]; X = I, L = PPh_3 [169]) e.g. (79). When $[AgIPPh_3]_4$ was allowed to crystallise slowly from CH_2Cl_2-Et_2O triclinic crystals were formed in which the Ag_4I_4 core defines a chair (80) conformation [169]. A detailed analysis of the stereochemical behaviour of these and other $M_4X_4(YR_3)_4$ (M = Cu and Ag; R = Ph and Et; Y = P and As; X = Cl, Br and I) molecules led to the unequivocal conclusion that their stereochemistries are to a significant extent dictated by intramolecular van der Waals repulsions [168,169]. Far IR spectral determinations of $MX(YPh_3)$ (M = Cu, Ag, Y = P, As, X = halogen), $M_2X_2(YPh_3)_4$, $M_2X_2(YPh_3)_3$ and $[MX(YPh_3)]_4$ have provided characteristic metal halogen stretching frequencies which have proved to be highly diagnostic of the different structural types [170]. The importance of steric effects in determining the s character of the Ag-P bond has been deduced from ^{107}Ag-^{31}P coupling constants and P-Ag-P angles obtained from the structural determination of $[Ag(PEtPh_2)_2]_2Ni\{S_2C_2(CN)_2\}_2$ [171].

The gold complexes $AuCl(PPh_3)$ [172], $[Au(PMePh_2)_2]PF_6$ [173] $[CpFe(\pi$-$C_5H_4)Au_2(PPh_3)_2]BF_4$ [174], $(1,2$-$C_2B_9H_{11})Au(S_2CNEt_2)$ [175] and



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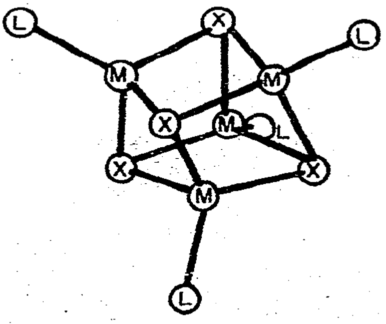

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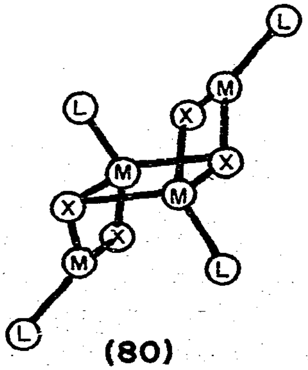
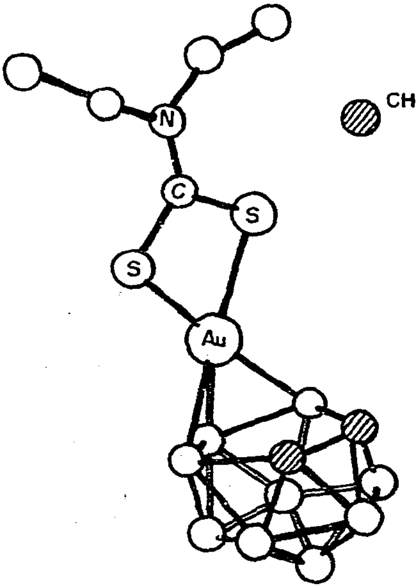


(80)

$[(Et_2NCS_2)_2Au]^+[(1,2\text{-}C_2B_9H_{11})_2Au]^-$ [175] have been structurally characterised. The neutral metallocarborane (81) is unusual in that it represents the first 'slipped' metal-cage structure for an 18 electron system. This nido-slipped configuration was rationalised in that a formal d^8/d^9 ion has either a filled d_{xz} or d_{yz} orbital which can donate electrons to a vacant cage antibonding orbital, and the asymmetry of such overlap is consistent with the observed distortions [175]. A series of metal sulphide arrays have been synthesised from $(Ph_2MeP)_2WO_2S_2$ and some suitable metal complex. Compounds prepared were $[(Ph_2MeP)_2M]_2WS_4$ (M = Cu and Ag) and $[(Ph_2MeP)M]_2WS_4$(M = Ag and Au), of which the gold product was characterised structurally as (82) [176].

A comparison of the ^1H NMR of $[(Ph_3P)_2Cu]_2B_{10}H_{10}$ and 2,3-μ-$[(Ph_3P)_2Cu]B_5H_8$ has shown the former to be fluxional and the latter to be static in solution [177]. An analysis of the ^1H NMR spectra of $L_2CuB_3H_8$ (L = $P(OPh)_3$ and $AsPh_3$) indicated that the rates of rearrangement of $B_3H_8^-$ in the complexes are very similar. The generally positive values of ΔS* are consistent with at least partial dissociation (e.g. Cu-H bond scission) in the rate determining step for $B_3H_8^-$ rearrangements [178].

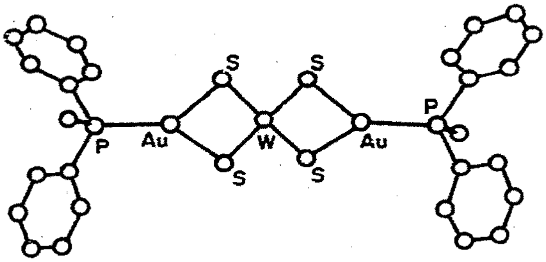
Complexes of Co, Ni and Cu with the tripod ligand 1,1,1-tris-(diphenylphosphinomethyl)ethane (p_3) e.g. Cup_3BH_4 [179], and the compounds $Cu(PPh_3)_nSO_3CF_3$ (n=1-4) have been synthesised [180]. In an effort to compare metal-P and metal -As bonding in normal and high formal oxidation



(81)

state complexes and to shed light on the possible 'non-innocent' behaviour of o-$C_6H_4(PMe_2)_2$ and o-$C_6H_4(AsMe_2)_2$ a detailed comparison of four-, five-, and six-coordinate $[M^{m+}X_nL_2]^{m-n}$ (X = Cl and Br; L = o-$C_6H_4(YMe_2)_2$ Y = P and As; m = 1-4, n = 0-2, M = transition metal) was made [181]. During this study the first trivalent Cu and Ag planar complexes $[ML_2]^{3+}$ and square pyramidal $[MClL_2]^{2+}$ were characterised [181]. The metal-metal bonded complexes (83) were synthesised by treating $MCl(CO)(PPh_3)_2$ (M = Rh and Ir) with the silver salt of the acetate (R=X=OC(CF_3)O [182], the perchlorate (R=X=OClO$_2$O) [182] or the triazene (R = NR'=N=NR"; X = Cl and Br; R = Me, R" = Me and p-tolyl) [183]. With silver isobutyrate (84) was formed [182]. The reaction of (83) (R = NR'=N=NR") with CO gave (85) [183].

NO reacted with a series of Pt and Au compounds to give, in the case of Au, cis-$AuMe_2NO_2L$ (L = PMe_2Ph) from $AuMe_3L$ [184]. ^{57}Fe Mössbauer spectra have been determined for 9 compounds in which the $Fe(CO)_2(NO)L$ (L = CO, PR_3 and AsR_3) groups were bonded to Hg, Pb or Au. The trends in the data were discussed in terms of the bonding characteristics of the ligands and σ-bonding effects were found to predominate [185]. MO calculations on $[Au_6(PPh_3)_6]^{2+}$, $[Au_9(PPh_3)_8]^{3+}$ and $[Au_{11}(PPh_3)_7X_3]$



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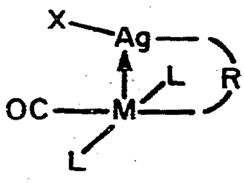

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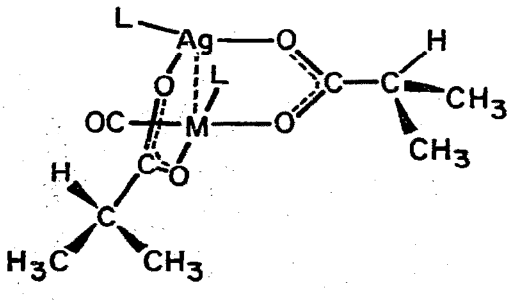

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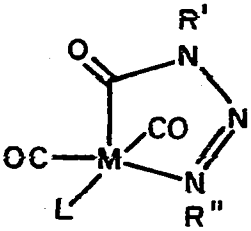

(85)

(X = SCN, I) cluster compounds showed that the overlap of the Au 6S orbitals makes a dominant contribution to the bonding. Coordination of ligands to the bare metal clusters encouraged a more favourable hybridisation of the metal orbitals and resulted in stronger metal-metal bonding. The electronic factors responsible for the breakdown of the Polyhedral Skeletal Electron Pair rules,when applied to the Au clusters,were discussed [186].

REFERENCES

1 W.S. McDonald, Mol. Struct. Diffr. Methods, 4 (1976) 319.
2 M.T.Rahman and H. Gilman, J. Ind. Chem., 53 (1976) 582.
3 G. van Koten and J.G. Noltes, J. Organometal. Chem. 104 (1976) 127.
4 R.G. Salomon and M.F. Salomon, J. Amer. Chem. Soc., 98 (1976) 7454.
5 A.N. Nesmeyanov, N.N. Sedova and Yu. V. Volgin, Izv. Akad. Nauk. SSSR, Ser. Khim. (1976) 2831. C.A. 86 (1977) 171570r.
6 A. Yamamoto, T. Ito, T. Yamamato, A. Miyashita, S. Komiya and T. Ikariya, Asahi Garasu Kogyo Gitutsu Shoreikai Kenkyu Hokoku, 27 (1975) 55 Publ. 1976.See C.A. 86 (1977) 5600.
7 A. Miyashita and A. Yamamoto, J. Organometal. Chem.113 (1976) 187.
8 T. Tsuda, Y. Chujo and T. Saegusa, Chem. Commun. (1976) 415.
9 G. Cahiez, D. Bernard, J.F. Normant and J. Villieras, J. Organometal. Chem., 121 (1976) 123.
10 G. van Koten, and J.G. Noltes, J. Amer. Chem. Soc., 98 (1976) 5393.
11 R.D. Hancock, N.P. Finkelstein and A. Evers, J. Inorg. Nucl. Chem. 38 (1976) 343.
12 D. Knol, N.J. Koole and M.J.A. De Bie, Org. Magn. Reson., 8 (1976) 213.
13 T. Tsuda, S. Sanada and T. Saegusa, J. Organometal. Chem., 116 (1976) C10.
14 Y. Ito, Y. Inubushi, S-i. Matsumura and T. Saegusa, Bull. Chem. Soc. Japan, 49 (1976) 573.
15 Y. Souma, J. Iyoda and H. Sano, Inorg. Chem., 15 (1976) 968.
16 T. Ogura, Inorg. Chem., 15 (1976) 2301.

17 K. Fukushima, A. Kobayashi, T. Miyamoto and Y. Sasaki, Bull. Chem. Soc., Japan, 49 (1976) 143.

18 H. Huber, D. McIntosh and G.A. Ozin, J. Organometal. Chem., 112 (1976) C50.

19 D.L. Reger and M.D. Dukes, J. Organometal. Chem., 113 (1976) 173.

20 G.S. Natarajan and K.A. Venkatachalam, J. Inst. Eng., 56(1976) 94. C.A. 85 (1977) 113334k.

21 G.A. Chukhadzhyan, G.A. Gevorkyan and V.P. Kukolev, Zh. Obshch. Khim., 46 (1976) 909. C.A. 85 (1977) 46829k.

22 O.M. Abu Salah and M.I. Bruce, Aust. J. Chem., 29 (1976) 73.

23 N.V. Raghavan and R.E. Davis, J. Cryst. Mol. Struct., 6 (1976) 73.

24 O.M. Abu Salah and M.I. Bruce, Aust. J. Chem., 29 (1976) 531.

25 R. Noyori, Yuki Gosei Kagaku Kyokai Shi, 34 (1976) 675. C.A. 86 (1977) 42527h.

26 J.P. Marino and L.J. Browne, Tetrahedron Letters (1976) 3241.

27 E.C. Ashby and J.J. Watkins, Chem. Commun. (1976) 784.

28 R.G. Pearson and C.D. Gregory, J. Amer. Chem. Soc., 98 (1976) 4098.

29 H.O. House, V.A. Prabhu, J.M. Wilkins and L.F. Lee, J. Org. Chem., 41 (1976) 3067.

30 H.O. House and K.A.J. Snoble, J.Org. Chem., 41 (1976) 3076.

31 H.O. House and C-Y. Chu, J. Org. Chem., 41 (1976) 3083.

32 H.O. House and J.M. Wilkins, J. Org. Chem., 41 (1976) 4031.

33 T. Cohen and M.D. Treblow, J. Org. Chem., 41 (1976) 1986.

34 C. Jallabert, H. Riviere and P.W. Tang, J. Organometal. Chem., 104 (1976) 1.

35 P.A. Grieco, C-L. Wang and G. Majetich, J. Org. Chem., 41 (1976) 726.

36 H.C. Arndt, W.G. Biddlecom, G.P. Peruzzotti and W.D. Woessner, Postaglandins, 11 (1976) 569.

37 J. Berlan, J.P. Battioni and K. Koosha, Tetrahedron Letters (1976) 3355.

38 J. Berlan, J.P. Battioni and K. Koosha, Tetrahedron Letters (1976) 3351.

39 H. Klein, H. Eijsinga, H. Westmijze, J. Meijer and P. Vermeer, Tetrahedron Letters (1976) 947.

40 A. Alexakis, A. Commercon, J. Villieras and J.F. Normant, Tetrahedron Letters (1976) 2313.

41 G. Tadema, P. Vermeer, J. Meijer and L. Brandsma, Rec. Trav. Chim. Pays-Bas, 95 (1976) 66.

42 J-L. Moreau and M. Gaudemar, J. Organometal. Chem., 108 (1976) 159.

43 P.L. Fuchs, J. Org. Chem., 41 (1976) 2935.

44 J.P. Marino and J.S. Farina, J. Org. Chem., 41 (1976) 3213.

45 J. Millon and G. Linstrumelle, Tetrahedron Letters (1976) 1095.

46 A. Alexakis, J. Normant and J. Villieras, Tetrahedron Letters (1976) 3461.

47 P. Crabbe, E. Barreiro, J.M. Dollat and J.L. Luche, Chem. Commun. (1976) 183.

48 H.L. Goering and V.D. Singleton Jr., J. Amer. Chem. Soc., 98 (1976) 7854.

49 G.B. Bennett, J. Nedelson, L. Alden and A. Jani, Org. Prep. Proced. Int., 8 (1976) 13. C.A. 85 (1977) 32369y.

50 S. Raucher, Tetrahedron Letters (1976) 1161.

51 J.E. Herz and E. Vazquez, Steroids, 27 (1976) 133.

52 G. Stork and S. Raucher, J. Amer. Chem. Soc., 98 (1976) 1583.

53 G. Linstrumelle, J.K. Krieger and G.M. Whitesides, Org. Synth., 55 (1976) 103.

54 D.L. Rosenblum, R.J. Anderson and C.A. Henrick, Tetrahedron Letters (1976) 419.

55 D. Michelot and G. Linstrumelle, Tetrahedron Letters (1976) 275.

56 G.H. Posner, J.S. Ting and C.M. Lentz, Tetrahedron, 32 (1976) 2281.

57 E.J. Corey, P. Ulrich and J.M. Fitzpatrick, J. Amer. Chem. Soc., 98 (1976) 222.

58 K. Kitatani, T. Hiyama and H. Nozaki, J. Amer. Chem. Soc., 98 (1976) 2362.

59 J.H. Babler and W.J. Buttner, Tetrahedron Letters (1976) 239.

60 N. Miyaura, M. Itoh and A. Suzuki, Synthesis (1976) 618.

61 F. Derguini-Boumechal and G. Linstrumelle, Tetrahedron Letters (1976) 3225.

62 W.E. Truce, A.W. Borel and P.J. Marek, J. Org. Chem., 41 (1976) 401.

63 K.D. Richards, A.J. Kolar, A. Srinivasan, R.D. Stephenson and K.R. Olsen, J. Org. Chem., 41 (1976) 3674.

64 Y. Yamamoto, H. Yatagai, A. Sonoda and S. Murahashi, Chem. Commun. (1976) 452.

65 P.M. Wege, R.D. Clark and H.C. Heathcock, J. Org. Chem., 41 (1976) 3144.

66 F.D. King and D.R.M. Walton, Synthesis (1976) 40.

67 P.L. Compagnon and B. Grosjean, Synthesis (1976) 448.

68 D.E. Bergbreiter and J.M. Killough, J. Org. Chem., 41 (1976) 2750.

69 G.H. Posner and C.E. Whitten, Org. Synth., 55 (1976) 122.

70 R. Robin, C.R. Hebd. Seances. Acad. Sci. Ser. C, 282 (1976) 281.

71 H. Westmijze, J. Meijer, H.J.T. Bos and P. Vermeer, Rec. Trav. Chim. Pays-Bas, 95 (1976) 304.

72 H. Westmijze, J. Meijer, H.J.T. Bos and P. Vermeer, Rec. Trav. Chim. Pays-Bas, 95 (1976) 299.

73 T. Cohen and I. Cristea, J. Amer. Chem. Soc., 98 (1976) 748.

74 B.R. Banks and H.M. Walborsky, J. Amer. Chem. Soc., 98 (1976) 3732.

75 E.J. Corey, M. Shibasaki, K.C. Nicolaou and C.L. Malmsten, Tetrahedron Letters (1976) 737.

76 A.J. Pearson, Aust. J. Chem., 29 (1976) 1101.

77 M. Clagett, A. Gooch, P. Graham, N. Holy, B. Main and J Strunk, J. Org. Chem., 41 (1976) 4033.

78 M.T. Rahman, I. Ara and A.F.M. Salahuddin, Tetrahedron Letters (1976) 959.

79 L.K. Ding and W.J. Irwin, J.C.S. Perkin, Trans. 1 (1976) 2382.

80 Y. Souma and H. Sano, Bull. Chem. Soc., Japan, 49 (1976) 3335.

81 Y. Souma and H. Sano, Bull. Chem. Soc., Japan, 49 (1976) 3296.

82 Y. Souma, J. Iyoda and H. Sano, Bull. Chem. Soc., Japan, 49 (1976) 3291.

83 D.S. Wulfman, B.W. Peace and R.S. McDaniel Jr., Tetrahedron, 32 (1976) 1251.

84 D.S. Wulfman, B.G. McGibboney, E.K. Steffen, V.T. Nguyen, R.S. McDaniel and B.W. Peace, Tetrahedron, 32 (1976) 1257.

85 Y. Kawai and M. Takebayashi, Kinki Daigaku Rikogakubu Kenkyu Hokoku, 10 (1975) 31. C.A. 84 (1976) 4081j.

86 R. Pellicciari, M. Curini, R. Moroni and E. Peppoloni, Farmaco. Ed. Sci., 31 (1976) 66. C.A. 84 (1976) 74218h.

87 Y.A. Al, B.S. Adeoti, J. Levisalles and H. Rudler, Bull. Soc. Chim. Fr. (1976) 934.

88 W. Fischer, C.A. Grob and H. Katayama, Helv. Chim. Acta, 59 (1976) 1953.

89 E. Yu Belyaev, M-S. Tovbis, T.P. Kononchuk and A.V. El'tsov, Khim. Geterotsikl Soedin (1976) 1338. C.A. 86 (1977) 72501n.

90 A. McKillop and T.S.B. Sayer, J. Org. Chem., 41 (1976) 1079.

91 L.A. Paquette, C.R. Degenhardt and R.A. Snow, Tetrahedron Letters (1976) 4447.

92 L.A. Akopyan, I.S. Tsaturyan and S.G. Matsoyan, Arm. Khim. Zh., 28 (1975) 998. C.A. 84 (1976) 135032s.

93 A.L. Beckwith and G. Phillipou, Aust. J. Chem., 29 (1976) 1277

94 J. Tsuji and H. Takayanagi, Tetrahedron Letters (1976) 1365.

95 M.M. Rogic, T.R. Demmin and W.B. Hammond, J. Amer. Chem. Soc., 98 (1976) 7441.

96 M.W. Barker and I.S. Perumal, Tetrahedron Letters (1976) 349.

97 G.K. Hampton and J.J. Christie, J. Org. Chem., 41 (1976) 2772.

98 R.A. Budnik and J.K. Kochi, J. Organometal. Chem., 116 (1976) C3.

99 L.D. Sychkova and Yu. S. Shabarov, Zh. Org. Khim, 12 (1976) 2630. C.A. 86 (1977) 106448t.

100 M.G. Voskanyan, G.G. Khudoyan and O. Sh. Badanyan, Ar. Khim. Zh., 28 (1975) 802. C.A. 84 (1976) 135539n.

101 M. Julia, B. Mansour and D. Mansuy, Tetrahedron Letters (1976) 3443.

102 T. Kauffmann and R. Otter, Angew. Chem. Int. Edn. Engl., 88 (1976) 500.

103 P. Fostein and J.C. Pommier, J. Organometal. Chem., 114 (1976) C7.

104 T. Cohen, A.J. Mura Jr., D.W. Shull, R.E. Fogel, R.J. Ruffner and J.R. Falck, J. Org. Chem., 41 (1976) 3218.

105 E.C. Ashby, J.J. Lin and R. Kovar, J. Org. Chem., 41 (1976) 1939.

106 G. van Koten, J.T.B.H. Jastrzebski and J.G. Noltes, Tetrahedron Letters (1976) 223.

107 N.M. Morlyan, A.G. Muradyan and Sh. O. Badanyan, Ar. Khim. Zh., 28 (1975) 633. C.A. 84 (1976) 16684w.

108 B. Liedholm, Acta. Chem. Scand. Ser. B. B30 (1976) 141.

109 M.P. Doyle, B. Siegfried and J.J. Hammond, J. Amer. Chem. Soc., 98 (1976) 1627.

110 G. Eletti-Bianchi, F. Centini and L. Re, J. Org. Chem., 41 (1976) 1648.

111 D.J. Thompson, J. Organometal. Chem., 108 (1976) 381.

112 J.M. McNamara and W.B. Gleason, J. Org. Chem., 41 (1976) 1071.

113 D.W. Clack, Inorg. Chem. Transition Elem., 4 (1976) 381.

114 K.J. Klabunde, J. Fluorine Chem., 7 (1976) 95.

115 D. McIntosh and G.A. Ozin, J. Amer. Chem. Soc., 98 (1976) 3167.

116 D. McIntosh, M. Moskovits and G.A. Ozin, Inorg. Chem., 15 (1976) 1669.

117 J.L. Vidal and G.E. Ryschkewitsch, Chem. Commun. (1976) 192.

118 C.N. Caughlan, G.D. Smith, P.W. Jennings and G.E. Voecks, Acta Cryst., Sect. B, 32 (1976) 1390.

119 G.S. Lewandos, D.K. Gregston and F.R. Nelson, J. Organometal. Chem., 118 (1976) 363.

120 E.A. Smirnova and M.I. Bogdanov, Zh. Fiz. Khim., 49 (1975) 2153. C.A. 84 (1976) 22843p.

121 H.K. Hofstee, J. Boersma and G.J.M. van der Kerk, J. Organometal. Chem., 120 (1976) 313.

122 M. Kobayashi, Kagaku Kogaku, 39 (1975) 607. C.A. 84 (1976) 42910m.

123 M. Parrilli, G. Barone, M. Adinolfi and L. Mangoni, Tetrahedron Letters (1976) 207.

124 A.D. Evans and J.M. Hoffman, J. Amer. Chem. Soc., 98 (1976) 1983.

125 T. Katsushima, R. Yamaguchi, M. Kawanisi and E. Osawa, Chem. Commun. (1976) 39.

126 H.J.J. Loozen, W.M.M. Robben and H.M. Buck, Recl. Trav. Chim. Pays-Bas, 95 (1976) 248.

127 G.M. Whitesides and F.D. Gutowski, J. Org. Chem., 41 (1976) 2882.

128 M.G. Blackburn and C.R.M. Ward, Chem. Commun. (1976) 79.

129 M. Hajek and J. Malek, Collect. Czech. Chem. Commun., 41 (1976) 746.

130 A.G. Makhsumov, K. Tillyaev and A. Shukurov, Zh. Vses. Khim O-va, 20 (1975) 585. C.A. 84 (1976) 58852e.

131 F.G. De las Heras, S.Y.K. Tam, R.S. Klein and J.J. Fox, J. Org. Chem 41 (1976) 84.

132 Y. Ito, S. Fujii, T. Konoike and T. Saegusa, Synth. Commun., 6 (1976) 429.

133 K. Matsumura, O. Miyashita, H. Shimadzu and N. Hashimoto, Chem. Pharm. Bull., 24 (1976) 948.

134 H. Schmidbaur, Angew. Chem. Int. Edn. Engl., 15 (1976) 728.

135 B.F.G. Johnson, Gold Bull., 9 (1976) 46.

136 G.W. Rice and S.R. Tobias, Inorg. Chem., 15 (1976) 489.

137 P.L. Kuch and R.S. Tobias, J. Organometal. Chem., 122 (1976) 429.

138 S. Komiya, T.A. Albright, R. Hoffmann and J.K. Kochi, J. Amer. Chem. Soc., 98 (1976) 7255.

139 S. Komiya and J.K. Kochi, J. Amer. Chem. Soc., 98 (1976) 7599.

140 R.J. Puddephatt and P.J. Thompson, J. Organometal. Chem., 117 (1976) 395.

141 P.W.N.M. van Leeuwen, R. Kaptein, R. Huis and C.F. Roobeek, J. Organometal. Chem., 104 (1976) C44.

142 H. Schmidbaur, J.R. Mandl, A. Frank and G. Huttner, Chem. Ber., 109 (1976) 466.

143 H. Schmidbaur and J.R. Mandl, Naturwiss., 63 (1976) 585.

144 H. Schmidbaur and O. Gasser, Angew. Chem. Int. Edn. Engl., 88 (1976) 502.

145 H. Schmidbaur, J.R. Mandl, F.E. Wagner, D.F. van de Vondel and G.P. van der Kelen, Chem. Commun. (1976) 170.

146 V.P. Dyadchenko, Vest. Mosk. Univ. Khim., 17 (1976) 358. C.A. 86 (1977) 5567.

147 V.I. Rozenberg, R.I. Gorbacheva, E.I. Smyslova, K.I. Grandberg, V.A. Nikanorov, Yu. G. Bundel and O.A. Reutov, Dokl. Akad. Nauk SSSR, 225 (1975) 1082. C.A. 84 (1976) 105708z.

148 A.N. Nesmeyanov, E.G. Peravalova, M.V. Ovchinnikov and K.I. Grandberg, Izv. Akad. Nauk SSSR, Ser Khim (1975) 2282. C.A. 84 (1976) 44297r.

149 A. Johnson and R.J. Puddephatt, J.C.S. Dalton (1976) 1360.

150 R. Uson, A. Laguna and J. Vincente, Chem. Commun. (1976) 353.

151 R. Uson, A. Laguna, J. Vincente and J. Garcia, J. Organometal. Chem., 104 (1976) 401.

152 P.W.J. de Graaf, J. Boersma and G.J.M. van der Kerk, J. Organometal. Chem., 105 (1976) 399.

153 D. McIntosh and G. Ozin, J. Organometal. Chem., 121 (1976) 127.

154 D. McIntosh and G.A. Ozin, Inorg. Chem., 15 (1976) 2869.

155 D.B. Dell'Amico, F. Calderazzo and F. Marchetti, J.C.S. Dalton (1976) 1829.

156 P. Jutzi and H. Heusler, J. Organometal. Chem., 114 (1976) 265.

157 S. Esperas, Acta Chem. Scand. Ser. A, 30 (1976) 527.

158 G. Minghetti, F. Bonati and G. Banditelli, Inorg. Chem., 15 (1976) 1718.

159 F. Bonati, G. Minghetti and G. Banditelli, Synth.-React. Inorg. Metal-Org. Chem., 6 (1976) 383.

160 R.O.C. Norman, W.J.E. Parr and C.B. Thomas, J.C.S. Perkin Trans I (1976) 1983.

161 D.W. Smith, Coord. Chem. Rev., 21 (1976) 93.

162 J.T. Gill, J.J.Mayerie, P.S. Welcker, D.F. Lewis, D.A. Ucko, D.J. Barton, D. Stowens and S.J. Lippard, Inorg. Chem., 15 (1976) 1155.

163 J. Kaiser, H. Hartung, E. Lengies, R. Richter and J. Sieler, Z. Anorg. Allg. Chem., 422 (1976) 149.

164 M. Barrow, H.B. Buergi, D.K. Johnson and L.M. Venanzi, J. Amer. Chem. Soc., 98 (1976) 2356.

165 A. Camus, N. Marsich, G. Nardin and L. Randaccio, Inorg. Chim. Acta, 17 (1976) L33.

166 A. Cassel, Acta Cryst. Sec. B 32 (1976) 2521.

167 M.R. Churchill, J. Donahue and F.J. Rotella, Inorg. Chem., 15 (1976) 2752.

168 B.-K. Teo and J.C. Calabrese, Inorg. Chem., 15 (1976) 2467.

169 B.-K. Teo and J.C. Calabrese, Inorg. Chem., 15 (1976) 2474.

170 B.-K. Teo and D.M. Barnes, Inorg. Nucl. Chem. Lett, 12 (1976) 681.

171 F.J. Hollander, Y.L. Ip and D. Coucouvanis, Inorg. Chem., 15 (1976) 2230.

172 N. C. Baenziger, W.E. Bennett and D.M. Soboroff, Acta Cryst. Sect. B, 32 (1976) 962.

173 J.J. Guy, P.G. Jones and G.M. Sheldrick, Acta Cryst. Sect. B 32 (1976) 1937.

174 G.G. Aleksandrov, V.G. Andianov, N.G. Bokii, N.I. Kirillova, L.G. Kuz' mina, T.N. Sal'nikova and T. Yu. Struchkov, Tezisy Dohl-Vses, Chugaevskoe Soveshch. Khim. Kompleksn. Soedin 12th, 2 (1975) 227. C.A. 86 (1977) 43764v.

175 H.M. Colquhoun, T.J. Creenhough and M.G.H. Wallbridge, Chem. Commun. (1976) 1019.

176 J.C. Huffman, R.S. Roth and A.R. Siedle, J. Amer. Chem. Soc., 98 (1976) 4340.

177 G.G. Outterson Jr., V.T. Brice and S.G. Shore, Inorg. Chem., 15 (1976) 1456.

178 H.C. Bushweller, H. Beall and W.J. Dewkett, Inorg. Chem., 15 (1976) 1739.

179 P. Dapporto, S. Midollini, A. Orlandini and L. Sacconi, Inorg. Chem., 15 (1976) 2768.

180 M.B. Dines, J. Inorg. Nucl. Chem., 38 (1976) 1380.

181 L.F. Warren and M.A. Bennett, Inorg. Chem., 15 (1976) 3126.

182 J. Kuyper and K. Vrieze, J. Organometal. Chem., 107 (1976) 129.

183 J. Kuyper, P.I. van Vliet and K. Vrieze, J. Organometal. Chem., 105 (1976) 379.

184 R.J. Puddephatt and P.J. Thompson, J.C.S. Dalton (1976) 2091.

185 C.A. McAuliffe, I.E. Niven and R.V. Parish, J.C.S. Dalton (1976) 2477.

186 D.M.P. Mingos, J.C.S. Dalton (1976) 1163.