

5.6. Formation of Bonds between Elements of Group IVB (C, Si, Ge, Sn, Pb) and Group IB (Cu, Ag, Au)

5.6.1. Introduction

In this chapter are found the reactions used to prepare the coinage-metal (Cu, Ag and Au) derivatives of the main fourth-group elements. Few compounds containing group-IB bonds to the lower congeners of group IVB (Si, Ge, Sn or Pb) can be isolated except for the binaries, and the preparations of these compounds are mentioned together with those of the organic derivatives. Organocopper reagents play an important role in organic synthesis.

(J. J. ZUCKERMAN, ED.)

5.6.2. from the Elements.

Little work on intermetallic phases has relevance for inorganic chemistry.

Nineteenth-century chemists produced binary Si-Cu alloys by heating together carbon (C), Silicon (Si), and copper (Cu) to white heat in closed crucibles to obtain an alloy containing 2.3 wt % Si (the proportion of Si could be increased by heating the elements together at 1200°C for 2 h); or by reductive processes, such as the electrolysis of potassium fluorosilicate with molten Cu metal as the cathode; or by heating together elemental Si and CuO or from $\text{CuO} + \text{CaO} + \text{C} + \text{SiO}_2$. The freezing curve for the Cu-Si system shows a maximum at ca. 13 wt % Si (855°C) corresponding to the compound CuSi and two eutectic points at 825° (9.8 % Si) and 800°C (18.3 % Si). Other binary compounds identified are SiCu_5 , SiCu_6 and $\text{Si}_4\text{Cu}_{15}$, all of which melt between 800° and 855°C and have a metallic appearance^{1,2}. With Ag and Au, Si forms eutectics, but no binary compounds. The solubility of elementary Si in molten Ag metal is ca. 30 % at 1400°C. Gold metal and elementary Si are totally miscible when liquid; the eutectic, containing 6 % Si, melts at 370°C.

Like Si, Ge forms a compound GeCu_3 . Germanium-metal compounds and alloys are listed in ref. 3. Gaseous molecules of the Au-Ge systems are found using a high-T cell in a single-focusing mass spectrometer⁴. Knowledge of metal-cluster geometry leads to predictions of catalytic effects. The vaporization enthalpies and equilibrium pressures of elementary Ge and Au metal are similar and hence likely to lead to large intermetallic clusters. Ionic species observed for this system are: $[\text{AuGe}]^+$, $[\text{Au}_2\text{Ge}]^+$, $[\text{AuGe}_2]^+$, $[\text{Au}_2\text{Ge}_2]^+$, $[\text{AuGe}_3]^+$ and $[\text{AuGe}_4]^+$, and thermal functions for these ions can be calculated. A symmetrical structure is proposed for Au_2Ge , and AuGe_2 has an asymmetric structure. A similar range of ions is observed for the Sn-Au⁵ and Ge-Cu⁶ systems at 1525°C.

The Cu-Sn system shows only one compound, SnCu_3 , mp ca. 720°C , which is dark- or bluish-grey and is only slowly attacked by HCl and other mineral acids. Melting together Sn and Cu metals forms the 2:1 alloy, after treatment with conc HCl. The molten metals Sn and Ag are soluble in all proportions, but only one compound, SnAg_3 , is formed. The Sn-Au system shows a eutectic at 20% Sn, mp 280°C , and the compound SnAu (mp 418°C), which is silver grey, is only slowly attacked by aqua regia and is resistant to other mineral acids. Other Sn-Au compounds are Sn_2Au and SnAu_4 .

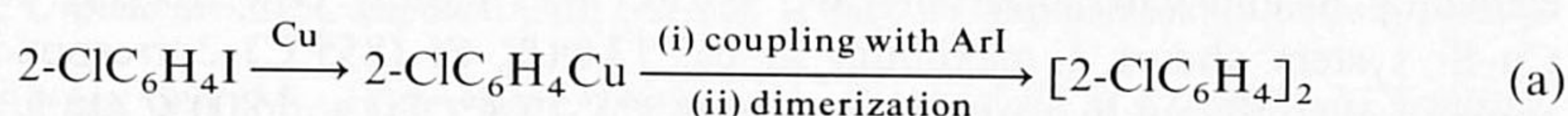
The Cu-Pb system gives a eutectic at 969°C (60% Pb), but with no evidence for binary compounds. Liquid Ag and Pb metals are miscible in all proportions, but no compounds are identified. By contrast, Au and Pb metals form PbAu_2 and Pb_2Au , the latter as brittle white crystals.

(F. GLOCKLING)

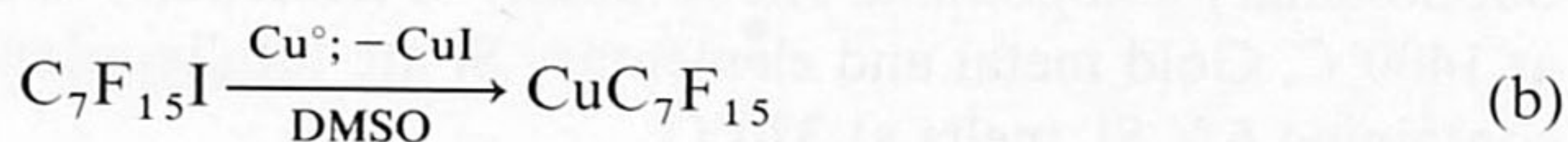
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5.6.3. from the Group-IB Metals and Alloys.

General synthetic methods for preparing group-IB compounds containing a group-IB-carbon bond directly from the group-IB metals and organic compounds are not available. An obvious reason for Cu and Ag is the low intrinsic stability of the Cu-C and Ag-C bonds¹, which contrasts with the often forcing conditions required for such reactions. However, synthetically important reactions are known that are based on the use of metallic Cu. In these reactions organocopper compounds are formed as intermediate or transient species that react further with other substrates present in the reaction mixture. Examples include the synthesis of biaryls² from aryl halides and Cu metal:



and the synthesis of perfluoroalkyl or -arylcopper compounds in dipolar aprotic solvents such as dimethylsulfoxide (DMSO)^{3,4}:



Highly reactive Cu metal from $\text{Cu}(\text{PEt}_3)\text{I}$ and $\text{Li}^+[\text{C}_{10}\text{H}_8]^-$ in tetrahydrofuran (THF) can oxidatively add to non-fluorinated organic halides, e.g., to $\text{PhCH}=\text{CHBr}$ or $o\text{-O}_2\text{NC}_6\text{H}_4\text{I}$ to give the corresponding Cu derivatives⁵.

Organic halides react with metallic Ag, e.g., Ph_3CCl with Ag foil⁶, but the organosilver compounds cannot be isolated.

(G. VAN KOTEN)

1. G. van Koten, J. G. Noltes, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Vol. 1, Pergamon Press, Oxford, 1982, Ch. 14, p. 709.

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5.6.4. from the Metal Salts

For the preparation of pure organometallic-IB compounds, the following points¹ should be considered:⁷

1. Of the various possibilities for the group IB-group IVB bond, only the synthesis of compounds containing a σ or η^2 bond between the group-IB metal and the one-electron (e.g., Me, Ph, $C\equiv CR$) or two-electron (e.g., CO, olefin) carbon ligands is known in detail. The synthesis of η^2 -metal IB-carbon-containing compounds is discussed in §5.6.2.3.6.
2. Organocopper compounds are known for Cu(I) but not for Cu(II); organosilver compounds contain Ag(I), whereas organogold compounds are synthesized for both Au(I) and Au(III).
3. The stability of the σ -metal IB-carbon bond follows the order alkyl-M < aryl-M ~ alkenyl-M < alkynyl-M [M = Cu(I), Ag(I), Au(I)L]. However, for Cu(I) and Ag(I), most alkyl, aryl and alkenyl compounds are only stable at $<0^\circ\text{C}$ ¹. Furthermore, the stable organogold(I) species, with a few exceptions, have the general formula RAu(I)L, in which L is a neutral two-electron donor ligand.
4. Organocopper and -silver compounds are susceptible to hydrolysis and oxidation, whereas organogold(I) and -gold(III) compounds have good hydrolytic and oxidative stability. The Ag compounds, moreover, are often light sensitive². The organocopper(I) and -silver(I) compounds often have low solubility. This adds to the problem of obtaining pure compounds.
5. Despite their limited thermal stability, organocopper compounds are reagents in organic synthesis and have advantages over the usually applied organolithium and organomagnesium-halide reagents¹. In these syntheses the organocopper compounds are reacted further without prior isolation. These reactions are not discussed here. Reviews are available³⁻⁷.
6. Reviews that contain pertinent information concerning the synthesis and structures of organometal-IB compounds are available. For σ -M—C-containing compounds, see refs. 1-3, 7-13, and for η^2 -M—C compounds, refs. 2, 8, 14-16. Examples of stable, well-characterized organometal-IB compounds are given in Table 1. **Solid alkylcopper and -silver compounds, although stable as suspensions at -80°C , may decompose spontaneously or even explode. Handling should be carried out only by an experienced person.**

(G. VAN KOTEN)

1. G. van Koten, J.G. Noltes, in *Comprehensive Organometallic Chemistry*, G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Vol. 1, Pergamon Press, Oxford, 1982, Ch. 14, p. 709. Recommended reading for the synthesis and structure relationship of organocopper and -silver compounds.
2. *Gmelin Handbuch der Anorganischen Chemie, Silber*, Teil B5, Springer-Verlag, Berlin, 1974. Excellent review.

TABLE 1. STABLE, WELL-DEFINED ORGANOMETAL-IB COMPOUNDS^a

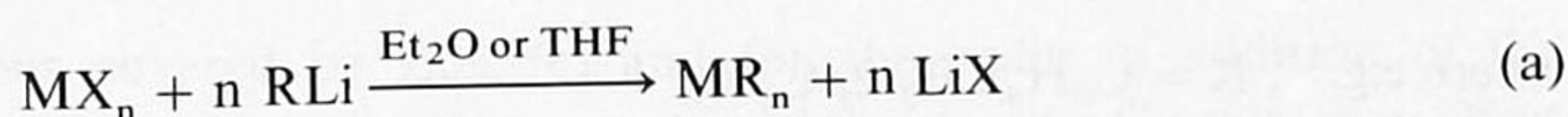
Compound	Synthetic route	Decomposition T (°C)	Ref.
$[\text{CuCH}_2\text{SiMe}_3]_4$	$\text{CuI/LiCH}_2\text{SiMe}_3$	78–79 (mp)	17
$\text{AgCF}(\text{CF}_3)_2 \cdot \text{MeCN}$	$\text{AgF/CF}_3\text{CF} = \text{CF}_2$ in MeCN	> 60	18
$\text{Au(I)Me}(\text{PPh}_3)$	$\text{AuCl}(\text{PPh}_3)/\text{LiMe}$	175 (mp)	19
$\text{Au(III)Me}_3(\text{PPh}_3)$	$\text{AuCl}_3/\text{LiMe/PPH}_3$	23 (mp)	19
$[\text{CuC}_6\text{H}_4\text{Me-n}]_4$	$\text{CuBr/LiC}_6\text{H}_4\text{Me-n}$ (n = 2 or 4)	≈ 100	20,21
	$\text{CuCl/Zn}(\text{C}_6\text{H}_4\text{Me-2})_2$		22
$[\text{M}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)]_n$	$\text{MBr/LiC}_6\text{H}_4\text{CH}_2\text{NMe}_2-2$	≈ 160–185	23
n = 4; M = Cu(I), Ag(I)	$\text{Au}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4/\text{Me}_3\text{SnBr}$	117	24
n = 2; M = Au(I)			
$\text{Au(I)Ph}(\text{PPh}_3)$	$\text{AuCl}(\text{Ph}_3\text{P})/\text{LiC}_6\text{H}_5$	152	25
$\text{Au(III)}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{PPh}_3)$	$\text{AuCl}(\text{Ph}_3\text{P})/(\text{C}_6\text{H}_5)_2\text{TIBr}$	150	26,27
$\text{Ag}_4\text{Au}_2(\text{O}_3\text{SCF}_3)_2-(\text{C}_6\text{H}_4\text{NMe}_2-2)_4$	$\text{Au}_2\text{Li}_2(\text{C}_6\text{H}_4\text{NMe}_2-2)_4/4 \text{ Ag}(\text{O}_3\text{SCF}_3)$	130 (decomp)	28
$\text{M}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)_4$	$\text{MX}/2\text{LiR}$ M = Cu(I), Ag(I)	140–200	29
M = Cu(I), Ag(I) or Au(I)	MR/LiR M = Cu(I), Ag(I)		
$\text{h}^5\text{-C}_5\text{H}_5\text{M}(\text{PPh}_3)$	$\text{Au}(\text{PPh}_3)(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2-2)/\text{LiR}$		29
M = Cu(I), Ag(I), Au(I)	$\text{Cu}_2\text{O}/\text{C}_5\text{H}_6/\text{PPh}_3$		See §5.6.2.3
	$\text{MCl}/\text{NaC}_5\text{H}_5/\text{PPh}_3$		
	$[(\text{AuPPh}_3)_3\text{O}][\text{BF}_4]/\text{C}_5\text{H}_6/\text{NaH}$		
$\text{Cu}_4\text{R}'_2\text{Br}_2$, R = $\text{C}(\text{C}_6\text{H}_4\text{NMe}_2-2) = \text{C}(\text{Me})(\text{C}_6\text{H}_4\text{Me-4})$	CuBr/LiR	155	30
$\text{AgCH} = \text{CHC}_6\text{H}_5$	$\text{AgNO}_3/\text{Et}_3\text{PbCH} = \text{CHPh}$	> 60 (decomp)	31

^a The compounds are isolated pure in > 60% yields.

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5.6.4.1. by Metal–Metal Exchange with Another Organometallic.

(i) Via Reaction with Organolithium and Organomagnesium-Halide Reagents. The most widely used method for synthesizing σ -group IB–carbon bonds involves reaction of a group-IB metal salt with an organolithium reagent in a coordinating solvent, e.g., Et₂O or tetrahydrofuran (THF). Via this route alkyl, aryl, alkenyl, alkynyl and ferrocenyl IB-metal compounds can be prepared¹:

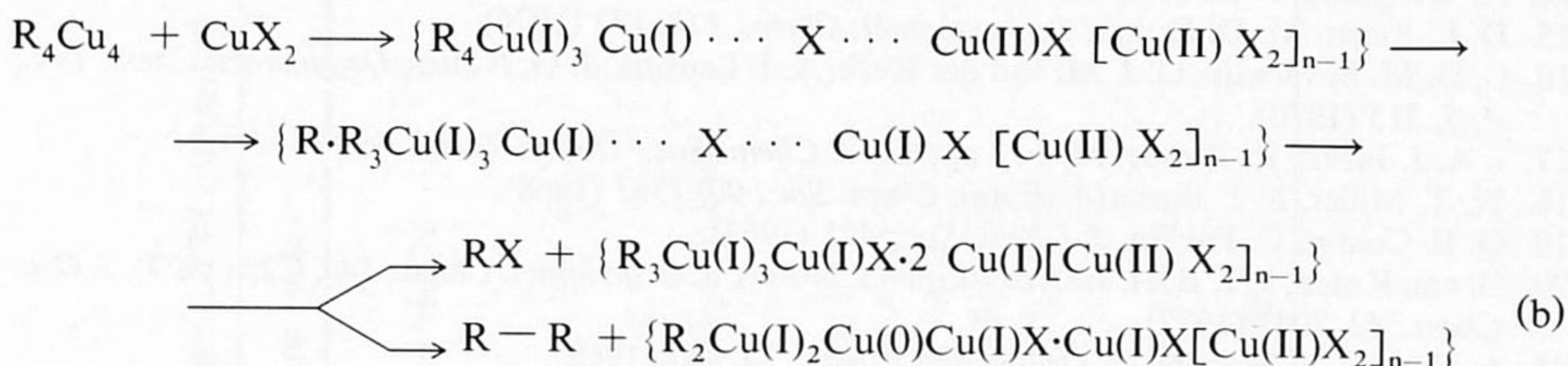


where $n = 1$; $M = \text{Cu(I)}$, Ag(I) , LAu(I) ($L =$ neutral two-electron donor ligand); or $n = 3$; $M = \text{Au(III)}$. These reactions are carried out at $<0^\circ\text{C}$ with exclusion of moisture, O₂ and light (for organosilver compounds) (see Table 1, §5.6.2.3). Although RMgX reagents also can be applied, the use of organolithium compounds is recommended because these provide the organometallic-IB compounds in better yields and higher purity. Exceptions are the perhaloaryl and the 2,6-disubstituted arylmetal-IB compounds, which proceed well via the RMgX route (vide infra).

For the preparation of the organocopper compounds, RCu, Cu(I) halides (preferably the bromide) are employed, although Cu(I)CN¹, Cu(I)SCN¹, Cu(I)O₃SCF₃ (soluble in benzene!)² or the ether-soluble phosphine complexes of these salts [e.g., Cu(I)I[P(Bu-n)₃]-tetramer]³ can be used also.

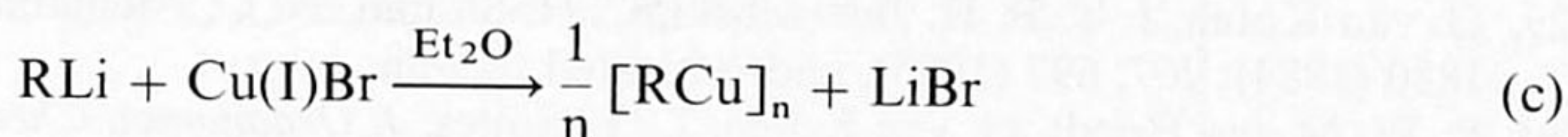
The use of Cu(II) salts is not recommended because transmetallation, Eq. (c), is then preceded by reduction of Cu(II) to Cu(I), which requires an extra equivalent of organolithium or RMgX reagent. Moreover, the oxidation products of the organo group and the interaction of the newly formed organocopper with unreacted Cu(II)X₂ can hamper the isolation of pure products. The 1-norbornylcopper which is prepared from Cu(II) acac₂ and 1-norbornyllithium is an exception⁴.

The Cu(II)X₂-CuR reaction results in formation of oxidative coupling and ligand-transfer oxidation products, R-R and R-X, respectively, e.g.⁵:

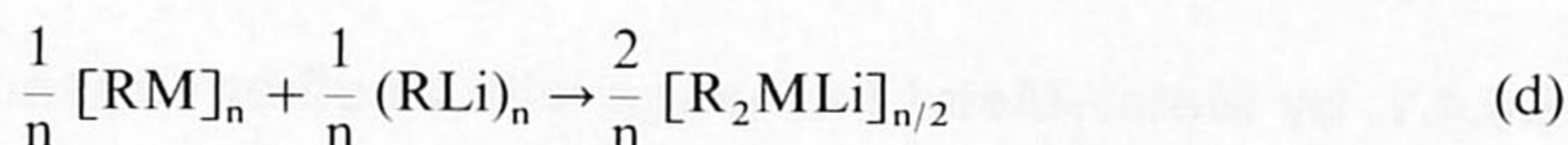


The reaction of RCu with Cu(II)X₂ is useful for the oxidative dimerization of functionalized organo groups^{1,6-10}.

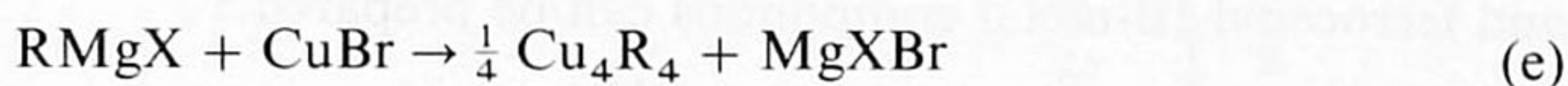
For the synthesis of pure organocopper compounds vs organolithium or RMgX reagents, as well as of Cu salts, must be avoided. The former give rise to cuprate complexes⁵:



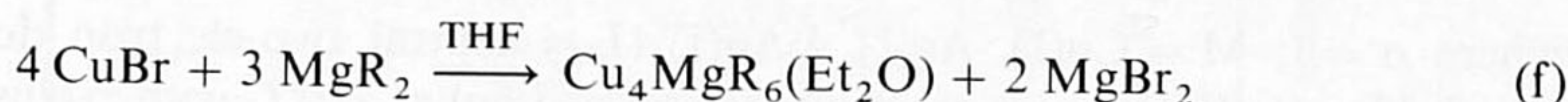
where, e.g., R = Ph¹¹, C₆H₄OMe-2¹², C₆H₄CH₂NMe₂-2¹³, C₅H₄CH(SiMe₃)₂¹⁴;



where, e.g.¹³, for R = C₆H₄CH₂NMe₂-2 and M = Cu(I) or Ag(I), n = 4. Whereas, e.g., pure Cu₄(C₆H₄CF₃-2)₄ can be obtained¹⁵ from the reaction of the corresponding RMgX reagent with CuBr, similar reactions of phenylmagnesium halides with CuBr give mixtures of products with complex Ph : Cu : MgX₂ ratios¹⁶:



where e.g.¹⁵, R = C₆H₄CF₃-2, C₆F₅;



where R = Ph, C₆H₄Me-4. The cuprate species in Eq. (f) is identified by using xs R₂Mg reagent^{17,18}.

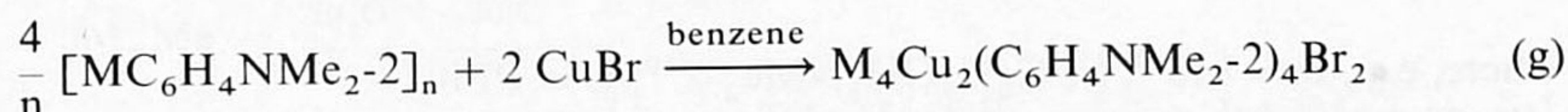
The cuprate complexes have better thermal stability and solubility than the parent organocopper compounds. They can be prepared directly in high yields from the 2 : 1 reaction of RLi with CuBr [Eqs. (c) + (d)]^{5,13} or quantitatively via the 1 : 1 reaction of

5.6.4. from the Metal Salts

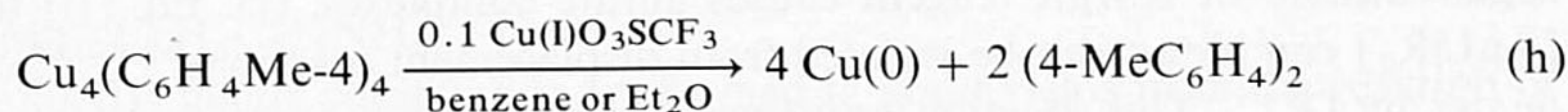
5.6.4.1. by Metal-Metal Exchange with Another Organometallic.

pure RLi with the pure RCu species [Eq. (d)]¹³. The alkylcopperlithium species, $\text{Alk}_4\text{-Cu}_{4-n}\text{Li}_n$, are synthetic intermediates for mediating new C—C bonds, often in a stereoselective and regioselective coupling manner (see refs. 1–16, §5.6.2.3). The solution structures of $\text{M}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\text{-2})_4$ [$\text{M} = \text{Cu(I), Ag(I) or Au(I)}$], which are isolated pure, are studied by ^1H , ^{13}C , ^7Li and ^{109}Ag NMR spectroscopy^{15,19}. Phenyllithium reacts with CuBr in THF to give low yields of $[\text{Cu}_5\text{Ph}_6]^-$ anionic clusters and $[\text{Li}(\text{THF})_4]^+$ cations²⁰. Mononuclear [bis(alkyl)copper]Li⁺ complexes are formed²¹ with bulky alkyl groups, e.g., $[\text{Li}(\text{THF})_4][\text{Cu}\{\text{C}(\text{SiMe}_3)_3\}_2]$. Reactions of polynuclear arylcoppers, in which the aryl group is substituted in both ortho positions (e.g., mesityl), with bidentate ligands (e.g., diphos) may lead²² to mononuclear bisaryl copper anion-bis(ligand)copper cation complexes (e.g., $[\text{Cu}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2][\text{Cu 2 diohos}]$). With terdentate phosphine ligands, mononuclear arylcopper compounds are formed, e.g., Cu(triphos)Cl with PhLi in THF provides Cu(triphos)Ph in 60% yield²³.

Reactions of the organolithium compounds with xs Cu(I) salts may lead either to formation of polynuclear organocopper-copper salt complexes²⁴:



where $\text{M} = \text{Cu(I), Ag(I)}$, or to catalytic decomposition²⁵:



The organocopper-copper salt complexes synthesized via Eq. (g) are stable, have a well-defined stoichiometry and can be isolated in high yields²⁴. With 2 equiv of $\text{LiC}_6\text{H}_4\text{NMe}_2\text{-2}$, the compound [$\text{M} = \text{Cu(I)}$] can be converted²⁴ into pure $\text{CuC}_6\text{H}_4\text{NMe}_2\text{-2}$ (see also §5.6.2.3.1.ii). However, in the reaction of ViLi [Vi is (E)-(2-Me₂NCH₂C₆H₄)C=C(Me)(C₆H₄Me-4)] with CuBr, this alkenylcopper-copper salt complex, $[\text{Cu}_4\text{Br}_2\text{Vi}_2]$, is the stable end product²⁶ (see also §5.6.2.3.1.ii). However, complex formation with metal salts (also MgX_2) is often less specific and leads to mixtures of inseparable products.

The counteranion can determine the stability of the organocopper formed. p-Tolylcopper tetramer synthesis via the RLi–CuO₃SCF₃ route is impossible²⁵; whereas it can be accomplished in 50% yield when CuBr is used²⁵. This difference is ascribed to the p-tolylcopper-copper trifluoromethane sulfonate intermediates, which are unstable. Stable, mixed (organo)(organic)Cu species, e.g., $\text{Cu}_3(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})(\text{O}_2\text{CPh})_2$, can be prepared via the interaggregate exchange between mesitylcopper pentamer²⁷ and copper benzoate dimer.

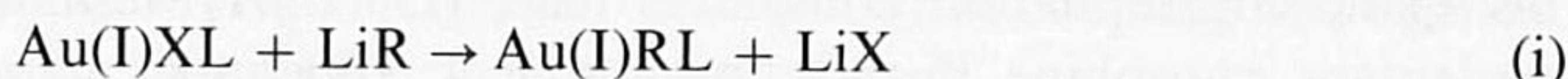
For those reactions covered by Eqs. (c) and (e), the order of addition of the organolithium or organomagnesium-halide reagents and the starting Cu salts may affect the nature and purity of the organocopper products (cf. ref. 4 for a discussion and examples).

Treatment of CuCl with LiC_5Me_5 in THF at -78°C affords a $\text{CuC}_5\text{Me}_5\text{-h}^5$ reagent that is used for the synthesis of transition-metal cluster species containing the $\text{CuC}_5\text{Me}_5\text{-h}^5$ fragment^{28–30}.

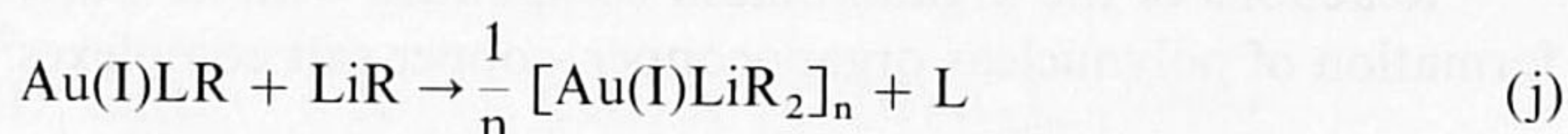
The metal-metal exchange reaction (a) also can be applied to the synthesis of pure organosilver compounds¹. The available AgNO₃ should not be used as a starting

material because of its complex formation with the organosilver product [e.g., $\text{AgMe} \cdot \text{AgNO}_3$, $(\text{AgPh})_n(\text{AgNO}_3)_m$, $n/m = 2$ or $5/2$; see ref. 2, §5.6.2.3]. Instead, reactions of the organolithium compound with AgBr give better yields and pure products³¹. The problems mentioned above concerning possible complexation of organosilver species with either silver salts [Eq. (g) and, e.g., formation³¹ of $[\text{AgC}_6\text{H}_4\text{CH}_2\text{NMe}_2 \cdot 2 \cdot \text{AgBr}]$ or with xs organolithium reagent [cf. Eq. (d), e.g., preparation³² of $[\text{Ag}_3\text{Li}_2\text{Ph}_6]^-$ and of³³ $[\text{Ag}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$ are valid not only for the synthesis of organocoppers, but for the preparation of pure organosilver compounds as well.

The pure and stable organogold (I) compounds, RAuL , can be prepared starting from a gold(I) halide–ligand complex^{34–42}:



where, e.g., $\text{R} = \text{Me}$, Ph , $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2 \cdot 2$; $\text{L} = \text{PPh}_3$, tetrahydrothiophene (THT);



where, e.g., $\text{R} = \text{Me}^{40,41}$, $\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2 \cdot 2^{19}$; $\text{L} = \text{PPh}_3$.

These reactions can be carried out at RT. Isolation of the RAuL complexes is easier than for the corresponding RCu or RAg complexes because of the better solubility of the Au(I) derivatives in organic solvents and their better thermal stability. However, use of xs organolithium or RMgX reagent causes aurate complexes, [cf. Eq. (j)] to form. Pure $[\text{AuLiR}_2]$ complexes can be isolated from displacement reactions^{15,40,41} of the neutral ligand by $[\text{R}]^-$. This reaction sequence also provides a route for the preparation of ligand-free RAu(I) complexes³⁹, vide infra, e.g., Eq. (n).

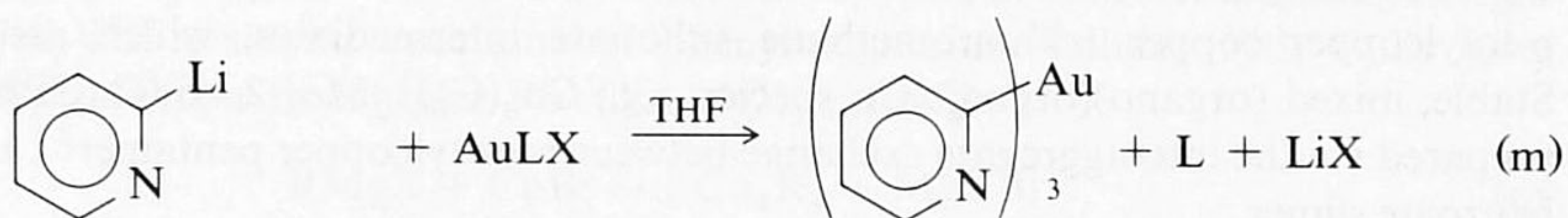
When weak coordinating ligands, L , such as Ph_3As or THT are used, anionic haloarylgold(I) compounds can be synthesized starting from AuRL complexes^{42,43}:



or from the Au(I) –halide complex⁴³:



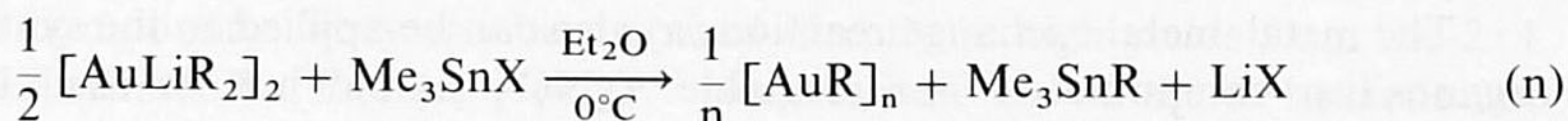
Stable complexes $(\text{AuR})_n$ are obtained when the aryl group R contains a suitably positioned heteroatom from which intermolecular coordination to Au(I) can occur^{39,42}:



where $\text{L} = \text{AsPh}_3$ ⁴⁴, THT⁴².

A prerequisite for the occurrence of this reaction is the use of weakly coordinating ligands in the starting AuLX complex.

An alternative route makes use of the different reactivity of the metal IB—C and Li—C bonds toward the arylation of triorganotin halides; reaction (j), in which the ligand L is removed, is then followed by:



5.6.4. from the Metal Salts

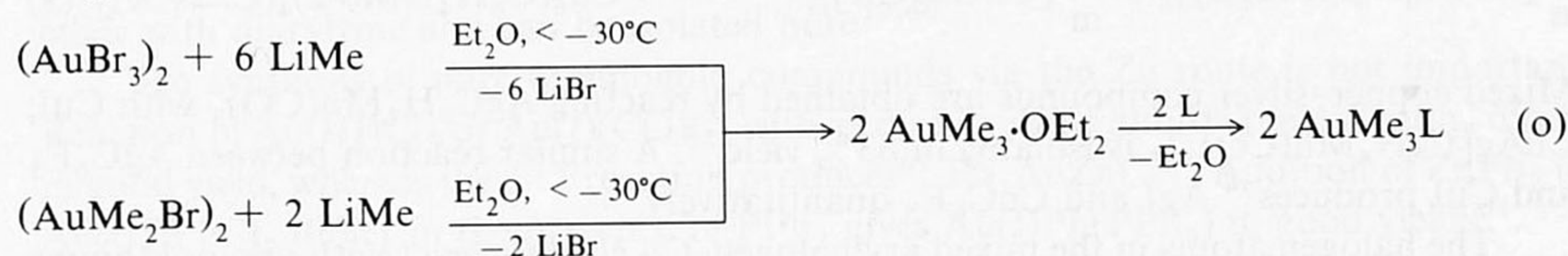
5.6.4.1. by Metal-Metal Exchange with Another Organometallic.

where, e.g., $R = C_6H_4NMe_2-2$, $C_6H_4CH_2NMe_2-2$ ($n = 2$) or $C_6H_3(OMe)_2-2,6$, affording pure $[AuR]$ compounds quantitatively³⁹. Subsequent reaction of $[AuR]$ with L (e.g., CNR)^{39,42,44} gives rise to quantitative formation of the corresponding $[AuRL]$ complexes.

When aryl groups having bulky ortho substituents, e.g., mesityl, are used, ligand-free arylgold(I) compounds can be prepared directly from the reaction of $Au(CO)Cl$ with the arylmagnesium-halide reagent⁴⁵.

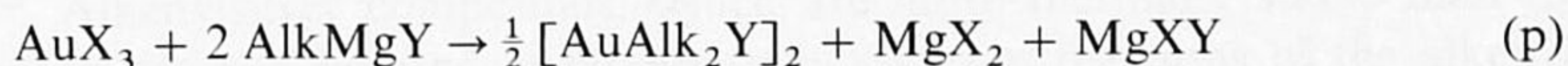
The organogold(III) complexes are neutral, anionic and cationic species, $[AuRX_2]_2$, $[AuRX_2L]$, $[AuRX_3]^-$, $[AuR_2LX]$, $[AuR_2LL']$, $[AuR_3]$, $[AuR_3L]$, $[AuR_3X]^-$ and $[AuR_4]^-$. Metal-metal exchange reactions of Au(III) starting materials with organolithium or $RMgX$ reagents are not important for the preparation of these Au(III) species owing to the easy reduction of Au(III) by these electropositive metal reagents.

Reaction of $LiMe$ with $(AuBr_3)_2$ in ether must be accomplished at low T, and the Et_2O species formed reacted further with other ligands to give stable $AuMe_3L$ complexes^{46,47}:

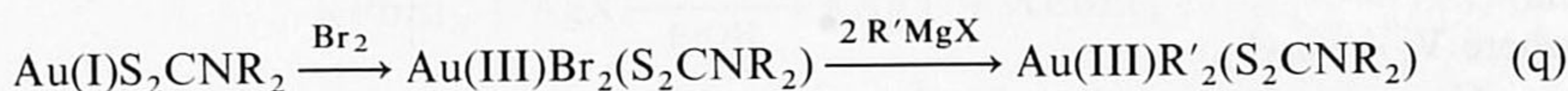


where $L = PMe_3, C_6H_5CH_2NH_2$.

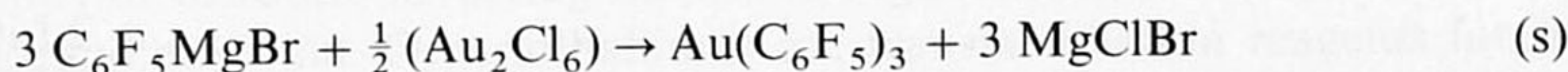
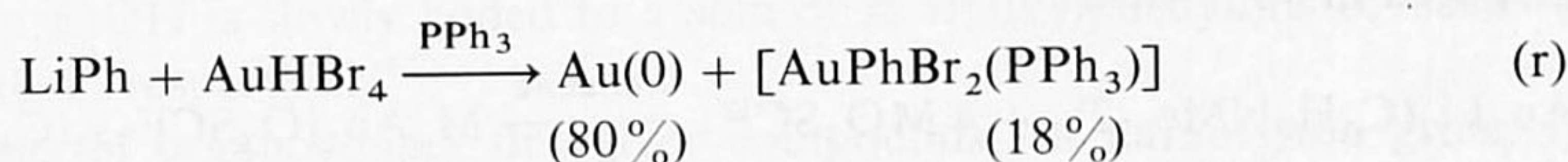
Dialkylgold(III) halide compounds are formed in good yields from the reaction of $AuCl_3$, $AuHCl_4$ or $AuCl_3py$ with alkylmagnesium halides in ether^{44,48}:



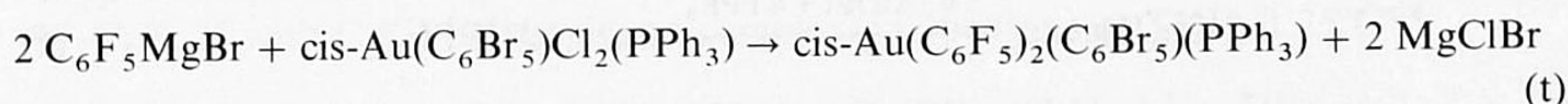
where Alk = alkyl. The $Au(III)R_2Y$ compounds can be prepared for anions, Y, directly from the $Au(I)Y$ compounds⁴⁴:



Arylations of gold(III) halides can proceed in different ways and are not important:



Whereas the reaction with $LiPh$ results in reduction to $Au(0)$, the reaction with the perhalophenylmagnesium halides produces in excellent yields the triarylgold(III) compound⁴⁹. This $RMgX$ reagent is used also for the synthesis of mixed arylgold(III) complexes⁴³:

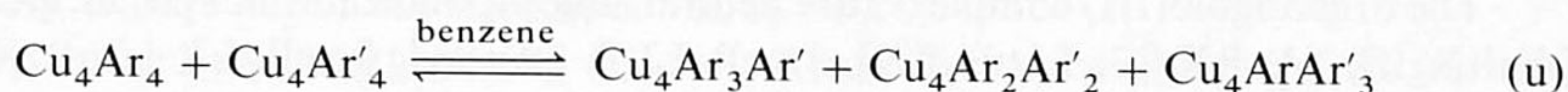


However, this reaction is not generally applicable.

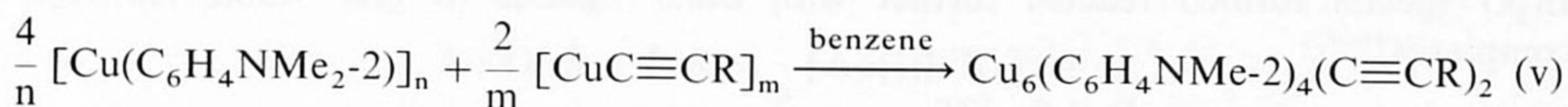
Treatment of $[AuCl_4][NMe_4]$ with R_2Mg derivatives ($R = C_6H_4NO_2-2$ or $C_6H_3Me-2-NO_2-6$) gives the aromatic Au(III) complexes⁴³ $[cis-AuR_2Cl_2][NMe_4]$.

(ii) Via Interaggregate Exchange and Ligand Substitution. These two routes are important for the synthesis of polynuclear organometallic-IB compounds. Interaggregate exchange between tetranuclear organocopper or -silver compounds and the corresponding tetranuclear organolithium compound leads to quantitative formation of the mixed Cu-Li and Ag-Li species, respectively [see Eq. (d), §5.6.2.3.i.^{13,50,51}].

Mixed arylcopper compounds can be prepared via reaction of two pure organocopper compounds^{51,52}:

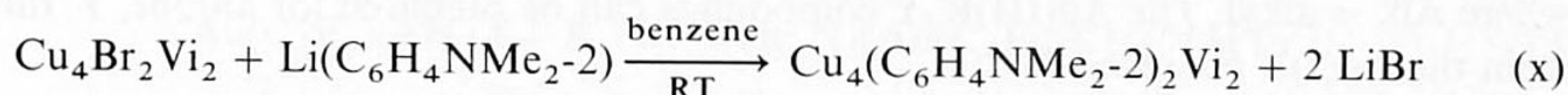
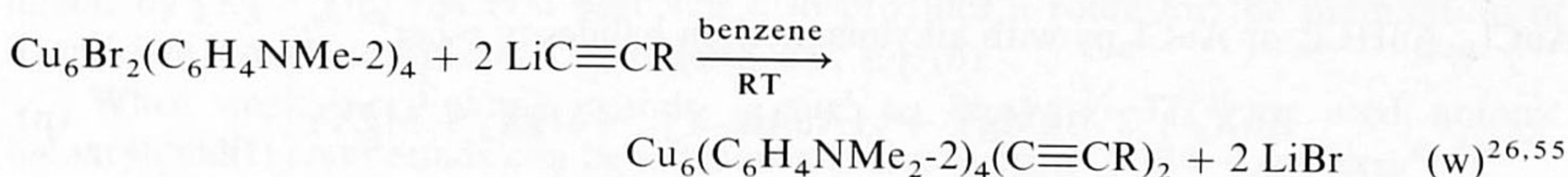


where Ar = C₆F₅ or C₆H₄CH₂NMe₂-2; Ar' = C₆H₄CF₃-2 or C₆H₃CH₂NMe₂-2-Me-5. However, the tetrameric species cannot be separated. A pure mixed-copper species is formed by reacting an aryl and an alkynylcopper compound^{51,52}:



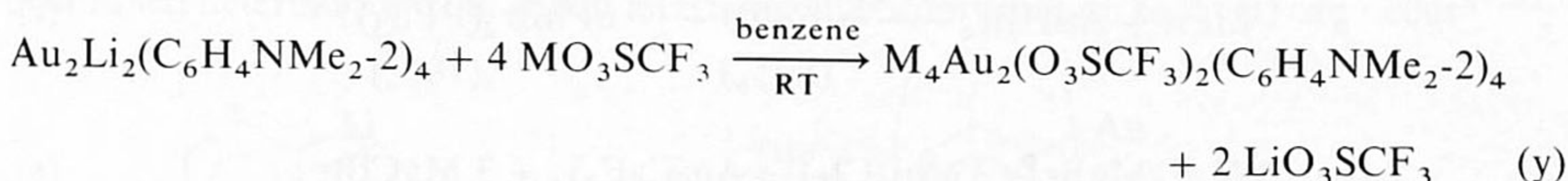
Mixed copper-silver compounds are obtained by reacting AgC₅H₄Mn(CO)₃ with CuI; CuAg[C₅H₄Mn(CO)₃]₂ is isolated in 63% yield⁵³. A similar reaction between AgC₆F₅ and CuI produces⁵⁴ AgI and CuC₆F₅ quantitatively.

The halogen atoms in the mixed arylhalogen-Cu clusters react with organolithiums with the formation of Cu-C bonds. These substitutions take place with retention of the cluster structure:



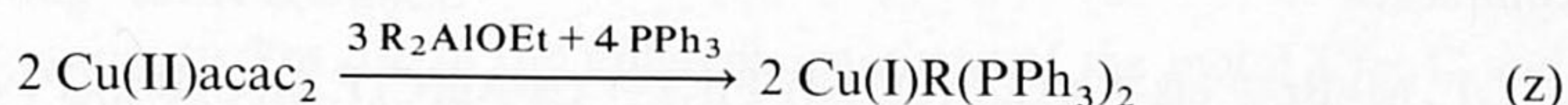
where Vi = vinyl.

Compounds consisting of aryl groups and anionic atoms (Br, I) or groups (O₃SCF₃) bound to a polynuclear array of Ag(I) and Au(I) or Au(I) and Cu(I) atoms can be prepared in 90% yield^{2,24,39}:

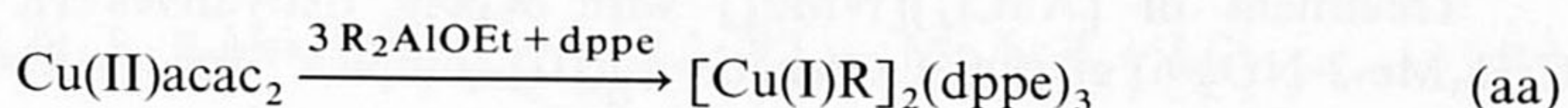


where M = Cu(I), Ag(I).

(iii) Via Organoaluminiums. Organoaluminium reagents react with Cu(II) acetylacetonate in the presence of phosphines to give the corresponding alkylcopper(I) phosphine complexes⁵⁶:



where R = Me, Et, n-Pr, i-Bu;

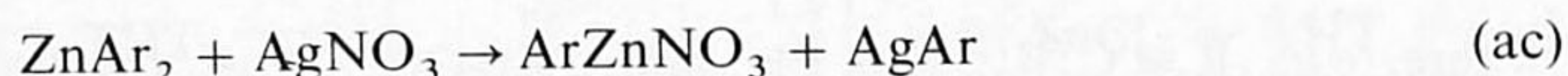
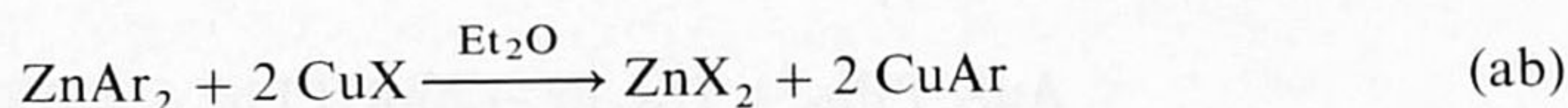


5.6.4. from the Metal Salts

5.6.4.1. by Metal-Metal Exchange with Another Organometallic.

where R = Me, Et, n-Pr, i-Bu and dppe is bis(diphenylphosphino)ethane, $\text{Ph}_2\text{P}(\text{CH}_2\text{CH}_2)\text{PPh}_2$.

(iv) Via Reaction with Organozincs. Dialkylzinc compounds can be used to prepare pure alkylcoppers. Although the method starts from Cu(II) halides⁵⁷, better yields and higher purity of the insoluble alkylcoppers are obtained when Cu(I) halides are used. The synthesis of arylcoppers via diarylzincs is claimed as a route to pure compounds⁵⁸:

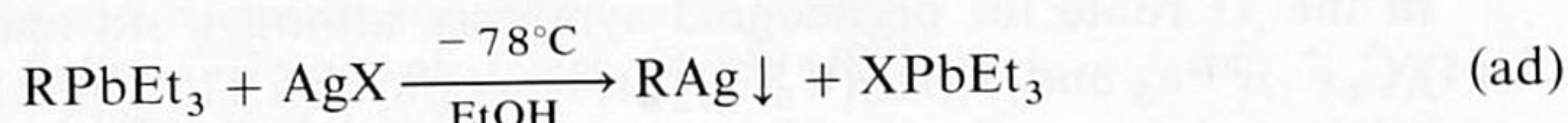


where Ar = Ph, $\text{C}_6\text{H}_4\text{Me}_n$ (n = 2, 3, 4), $\text{C}_6\text{H}_3\text{Me}_{2-2,6}$. However, when the aryl group contains coordinating substituents, purification of the arylcopper from the zinc halides formed is difficult [see §5.6.2.3.1.i, synthesis via the organolithium route (above)].

Arylsilvers are quantitatively formed in the 1 : 1 reaction of finely divided AgNO_3 in ether with diarylzinc and can be isolated pure^{59,60}.

The synthesis of pure organogold compounds via the Zn route is not important. Reaction of Au(III)Cl_3 or Au(I)(CO)Cl with xs diphenylzinc affords the AuZnPh_3 dimer in good yield, whereas the 1 : 1 reaction produces⁶¹ Ph_2AuZnCl ⁶¹. Addition of ZnPh_2 to Au(III)PhCl_2 dimer in the presence of PPh_3 gives $\text{Au(I)Ph(PPh}_3)$ in good yields⁶¹.

(v) Via Tetraorgano Group-IV Compounds. The synthesis of alkylcoppers via reaction of tetraalkylleads with Cu(II) salts is possible but impracticable when pure products are wanted^{62,63}. Likewise, alkylsilvers are formed in the 1 : 1 reaction of AgNO_3 with tetraalkylleads in MeOH at low T. However, isolation of the alkylsilver derivative is impossible^{64,65}. Alkenylsilver compounds, which are more thermally stable than the alkylsilver compounds, are isolated in moderate yields from reactions of the alkenyl-triethylleads with AgNO_3 at -78°C in EtOH^{64,65}:



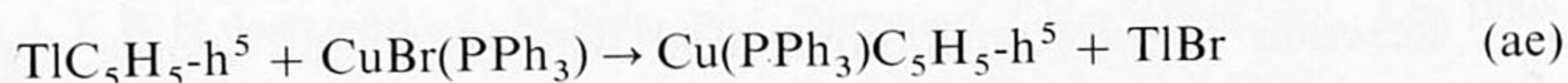
where, e.g., R = isobutenyl, styryl⁶⁶.

Pure, uncomplexed phenylsilver can be isolated in good yields from the reaction in which AgNO_3 in EtOH is slowly added to a soln of xs trialkylphenyltins or -leads at $>15^\circ$ and $>-10^\circ\text{C}$, respectively⁶⁷.

The synthesis of organocopper or -silver compounds via tetraorgano group-IV compounds is inferior to routes involving the use of organolithiums.

(vi) Via Organothalliums. Organothalliums are transmetallation reagents for the synthesis of organocopper and -silver compounds. However, their potential is for organogold synthesis, and the derivatization of these compounds, in particular the making of organogold(III) compounds.

Examples in organocopper chemistry are the synthesis of h^5 -cyclopentadienyl-copper complexes with phosphite, phosphine or isocyanide ligands via the reaction of $h^5\text{-C}_5\text{H}_5\text{Tl}$ with Cu(I) halide-ligand complexes in pentane or THF at 25°C ⁶⁸.

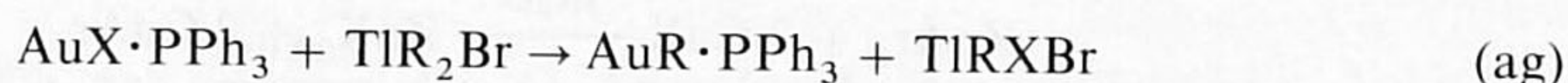


Correspondingly $\text{Ag(PPh}_3)\text{C}_5\text{H}_5\text{-}h^5$ can be isolated from the 1:1 reaction of AgO_3SCF_3 with NaC_5H_5 in THF⁶⁹.

Organothalliums transfer aryl groups to Au(I) or Au(III) centers. An exception is the synthesis of C-bonded acetylacetonate via^{40,70,71}:

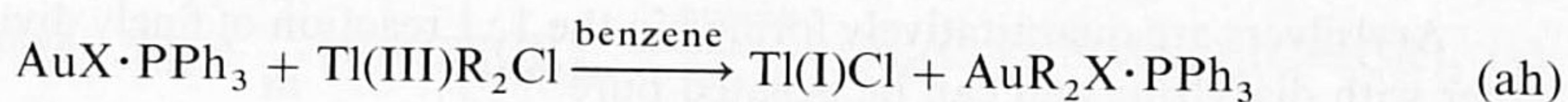


Transfer of perhaloaryl groups from Tl(III) (either as R_3Tl or as R_2TlCl) to Au(I) is possible without oxidation^{72,73}:



where, e.g., $\text{R} = \text{C}_6\text{F}_5$; $\text{X} = \text{Ph}, \text{NO}_3, \text{MeCO}_2$. For $\text{X} = \text{Ph}$ this reaction involves exchange of aryl groups. The monoarylthalliums formed in Eq. (ag) are further converted to the more stable diarylthallium halides.

The influence of the counterion in the starting Au(I) complex is demonstrated by:



where $\text{X} = \text{Cl}$; $\text{R} = \text{C}_6\text{F}_5, 2,4,6\text{-F}_3\text{H}_2\text{C}_6$. When reaction (ag), $\text{X} = \text{Cl}$, is carried out in refluxing benzene, oxidation occurs and the diaryl Au(III) complexes are obtained⁷⁴. However, no reaction occurs⁷⁴ with $\text{R} = \text{C}_6\text{H}_4\text{F-4}$ and $\text{C}_6\text{H}_4\text{CF}_3\text{-3}$.

The use of weak coordinating ligands opens up a route to mixed triaryl gold(III) derivatives, which for various R groups can be isolated in high yields⁷⁴:

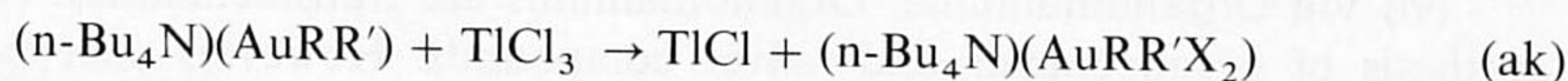
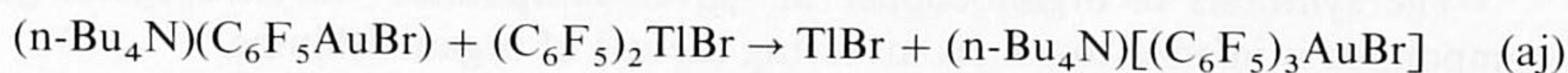


where $\text{R} = \text{C}_6\text{H}_2\text{F}_3\text{-2,4,6}$. These complexes react readily with neutral ligands, such as $\text{PPh}_3, \text{AsPh}_3$ or bis(diphenylphosphine)methane, to give the corresponding Au(III) R_3L complexes⁷⁵.

In the Tl route for organogold synthesis, although no reaction occurs between $\text{Au}(\text{I})(\text{C}_6\text{F}_5)\text{PPh}_3$ and $\text{Tl}(\text{III})(\text{C}_6\text{F}_5)_2\text{Br}$, reaction with TlCl_3 results in electron transfer and halide exchange, affording⁷⁶ $\text{cis-C}_6\text{F}_5\text{Au}(\text{III})\text{Cl}_2 \cdot \text{PPh}_3$.

In this reaction it is advisable to use Au and Tl species containing similar anions because, otherwise, mixtures of products with different anions can be obtained.

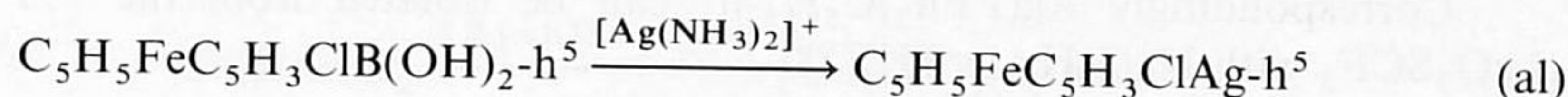
A series of organogold compounds can be made starting from anionic Au(I) complexes and reacting these with diarylthallium bromides^{43,77}:



where $\text{R} = \text{R}' = \text{C}_6\text{F}_5, \text{C}_6\text{H}_2\text{F}_3\text{-2,4,6}$; $\text{R} = \text{C}_6\text{F}_5, \text{R}' = \text{C}_6\text{H}_2\text{F}_3\text{-2,4,6}$.

(vii) Via Other Organometallics. Organometal-IB compounds are formed by using organometallics other than the previously mentioned Li, Mg or Tl derivatives. Although these reactions are isolated examples, they are described briefly here because they may have wider applicability.

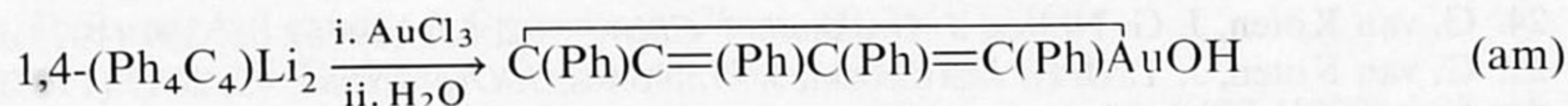
Reaction of ferrocenylboronic acid with Ag^+ ions affords the corresponding ferrocenylsilver complex⁷⁸:



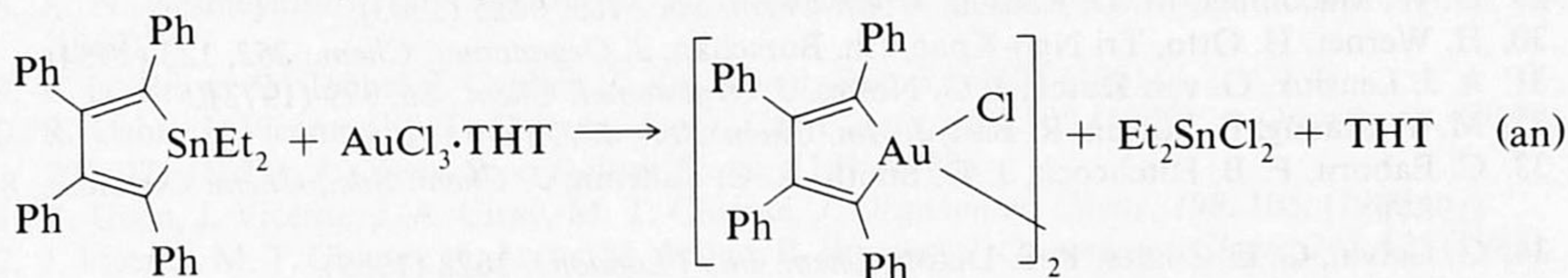
5.6.4. from the Metal Salts

5.6.4.1. by Metal-Metal Exchange with Another Organometallic.

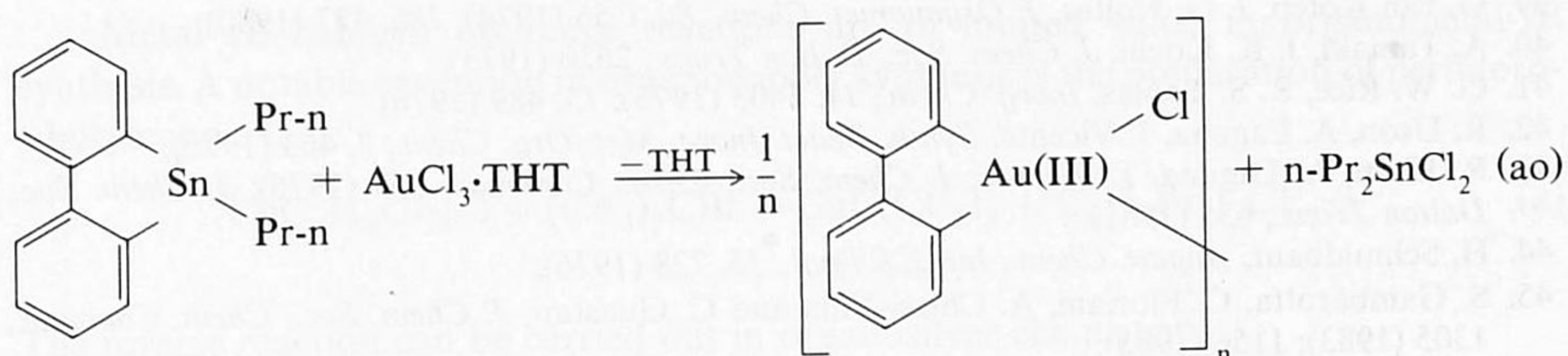
A 1-auracyclopentadiene complex can be prepared via the organolithium route⁷⁹:



However, similar 1-auracyclopentadiene complexes are synthesized (75% yield) by reaction of the diethylstannole derivative with $\text{AuCl}_3 \cdot \text{THT}$ in ether⁸⁰:



Other metallocyclic tin compounds react similarly, producing the metallocyclic Au(III) derivatives^{81,82}:



(G. VAN KOTEN)

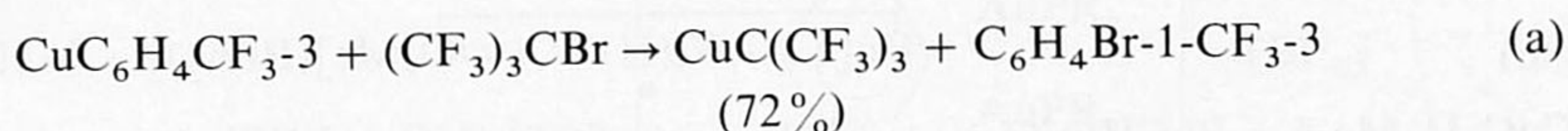
1. See refs. 1-3, 7-10 of §5.6.2.3.
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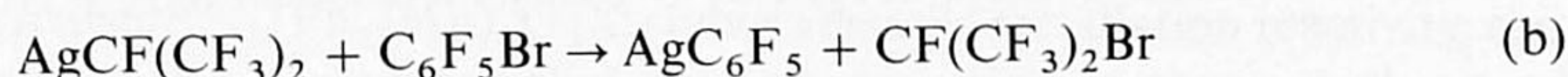
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5.6.4.2. by Metal-Halogen Exchange.

Metal IB-halogen exchange reactions are of limited value in organometal-IB synthesis. A notable exception in organocopper synthesis is the preparation of perfluoro-*t*-butylcopper¹:



The reverse reaction can be carried out in organosilver chemistry²:



These metal-halogen exchange reactions, i.e.:



where X = Br, I, follow the order²: $\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)$ displaces C_6F_5 , which displaces $(\text{CF}_3)_2\text{CF}$.

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5.6.4.3. by Metallation.

Alkynylmetal-IB compounds are more stable than the alkyl- or arylmetal-IB compounds. The Cu compounds can be prepared via a reaction of the alkyne with ammoniacal Cu(I) chloride:



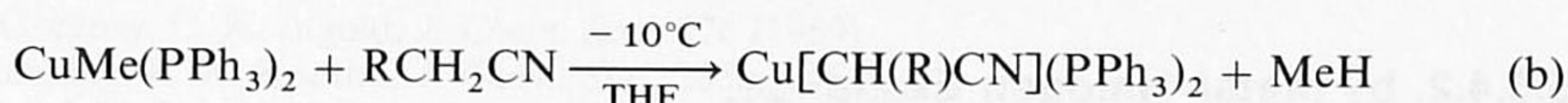
These compounds are formed quantitatively and are obtained pure because of their insolubility¹⁻³.

Preparation of $\text{CuC}\equiv\text{CPh}\cdot\text{L}$ (L=1,10-phen, bipy) occurs by oxidation of $\text{HC}\equiv\text{CPh}$ in acetone or CH_3CN at a Cu anode⁴. Treatment of $\text{CuBH}_4(\text{PPh}_3)_2$ with $\text{HC}\equiv\text{CPh}$ and KOH affords tetranuclear $[\text{CuC}\equiv\text{CPh}(\text{PPh}_3)]_4$ in high yield⁵.

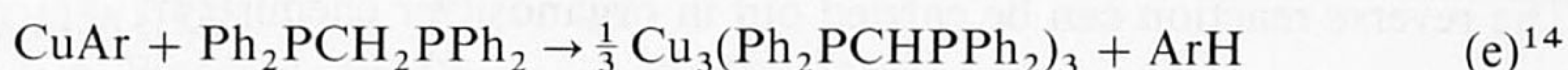
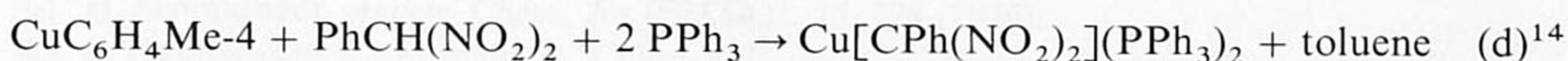
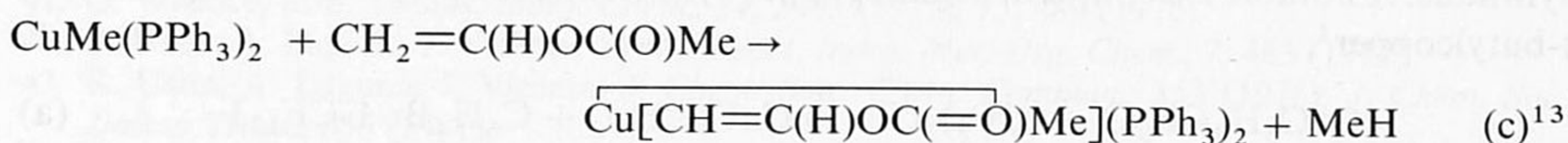
Reaction of alkynes with AgNO_3 or AgClO_4 in alcohols or H_2O in the presence of NH_3 results similarly in alkynylsilver(I) compounds quantitatively. When *xs* AgNO_3 is used and the reaction is performed in neutral solution, complex formation between alkynylsilver and AgNO_3 takes place. The ratio $\text{AgNO}_3 : \text{AgC}\equiv\text{CR}$ in these complexes depends on the AgNO_3 concentration during the reaction^{2,3,6,7}.

The alkynylgold(I) compounds $\text{AuC}\equiv\text{CR}$ cannot be prepared via metallation [e.g., the reaction of Au with KC_2H in liq NH_3 gives⁸ $\text{K}[\text{Au}(\text{C}\equiv\text{CH})_2]$], but they are synthesized via the reaction of freshly reduced AuCl_3 with the corresponding alkynylsodium or -potassium. The resulting insoluble products are reacted further with donor ligands, such as amines, phosphines, or isocyanides, affording alkynylgold(I)-ligand complexes that have better solubility than the parent compounds^{9,10}.

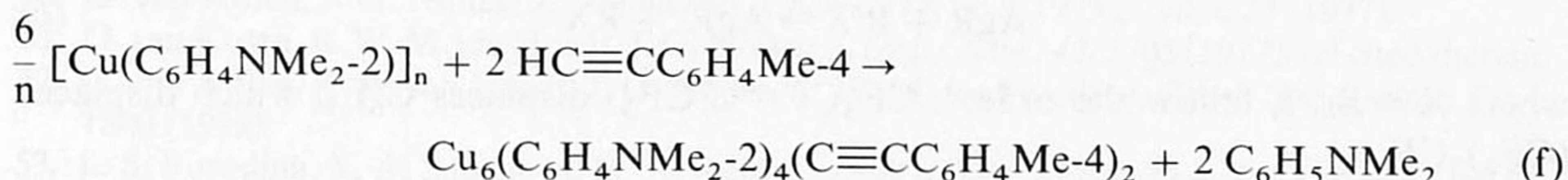
Metallation reactions are used for quantitatively converting a CH-acidic compound with methylcopper or phenylcopper into an organocopper complex:



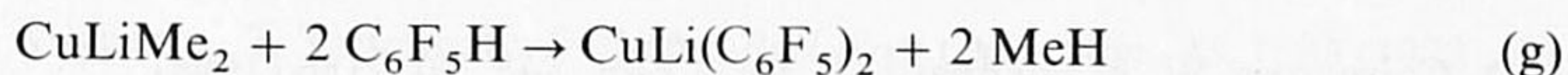
where $\text{R} = \text{H}, \text{CH}_3$ ¹¹, CN ¹² and THF is tetrahydrofuran;



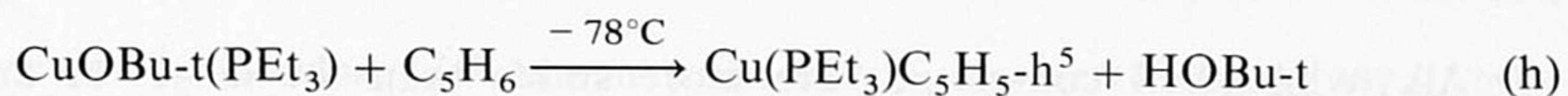
Insoluble $\text{CuC}_6\text{H}_4\text{NMe}_2\text{-2}$ reacts with 4-tolylacetylene to give a soluble mixed-aryl-alkynylcopper species in 58% yield^{15,16}:



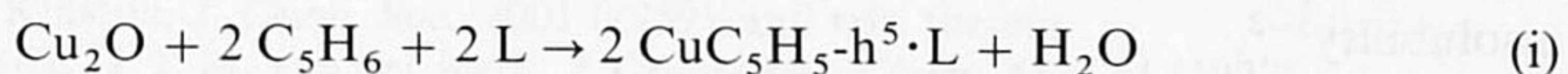
Also, diarylcuprate compounds, $\text{CuLi}(\text{C}_6\text{F}_5)_2$, can be prepared via metallation¹⁷:



Terminal acetylenes, cyclopentadiene (at -78°C), indene and other CH-acidic compounds can be metallated under extremely mild conditions by Cu(I) *t*-butoxide, e.g.¹⁷⁻¹⁹:



A less convenient route for the preparation of cyclopentadienylcopper-ligand complexes involves the use of Cu(I) oxide. Purification of the organocopper complexes is difficult because of the decomposition products formed by subsequent hydrolysis by H_2O produced in the metallation reaction, e.g.^{20,21}:



where $\text{L} = \text{t-BuNC}, \text{PEt}_3$.

Metallation is rare in organogold chemistry. Low yields are obtained by direct auration of arenes^{22,23}:



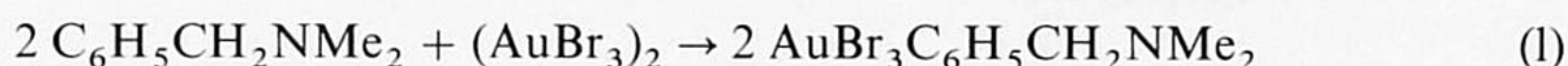
where R = H, Me, Ph.

Under somewhat different conditions auration proceeds via²⁴:

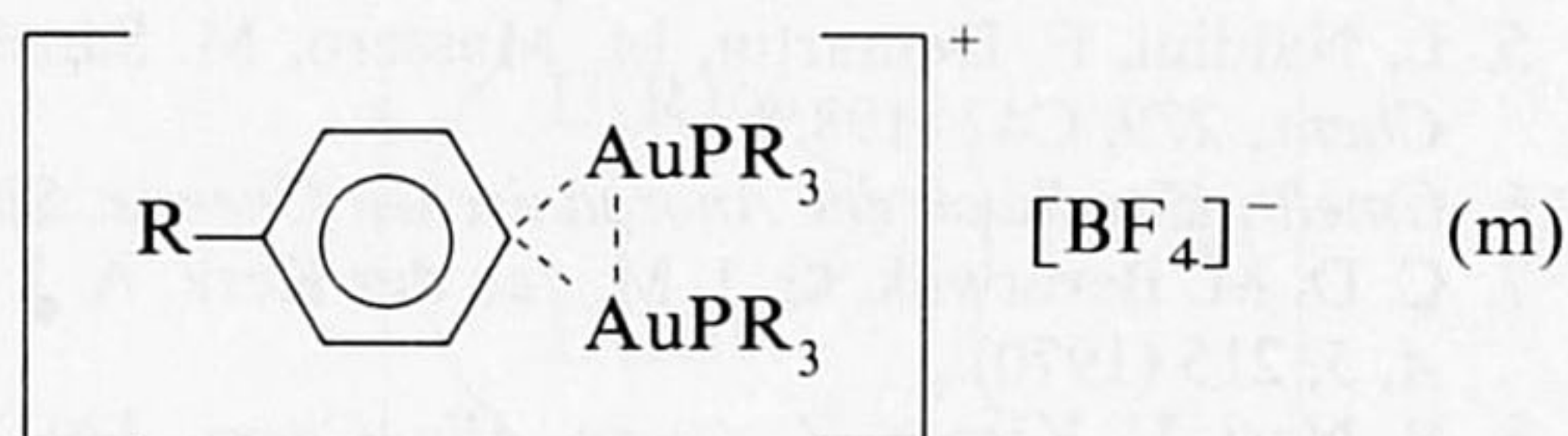
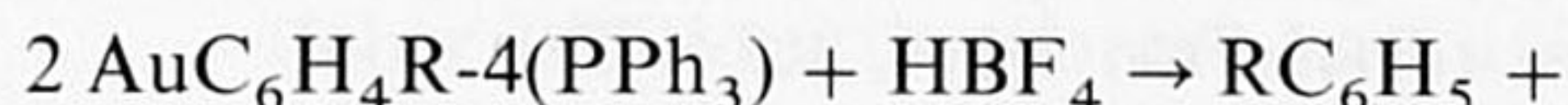


where R = H, Me, Et, i-Pr, t-Bu, Ph. The side products and the low yields make these reactions impracticable for monoarylgold(III) halides.

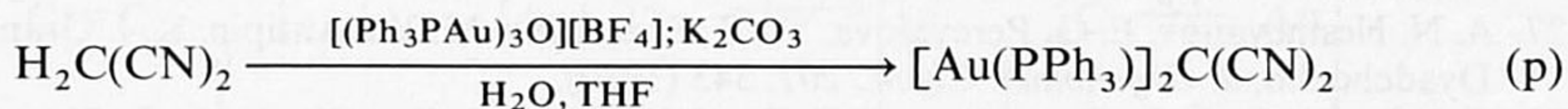
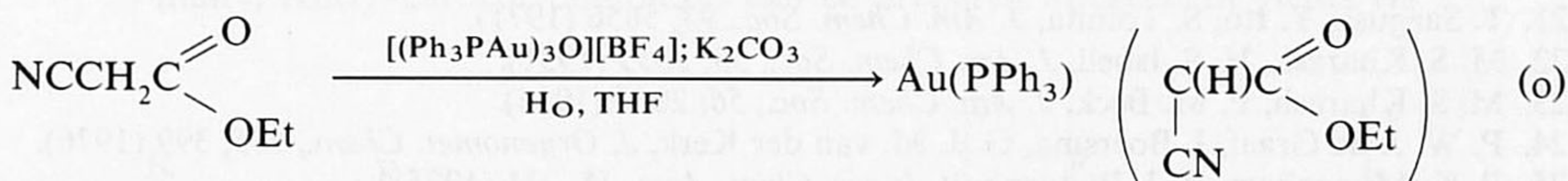
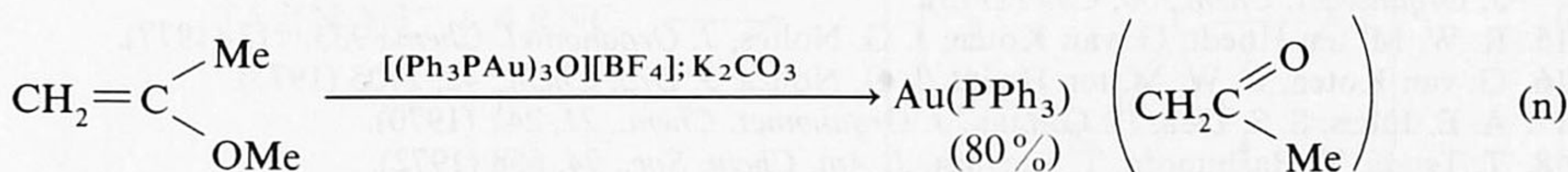
When R contains a coordinating group, single complexes instead of auration products form, e.g.²³:



The 1 : 1 reaction of arylgold(I) complexes with HBF_4 proceeds quantitatively²⁶:

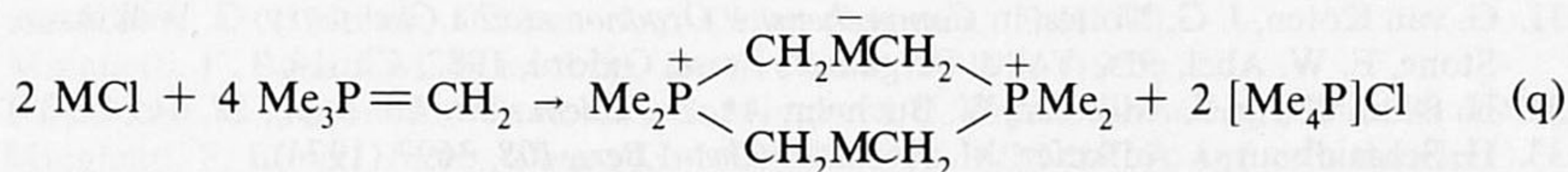


The auration reagent²⁵, $[(\text{Ph}_2\text{PAu})_3\text{O}]\text{X}$, shows versatile metallation reactivity; e.g., CH-acidic molecules, such as ferrocenes, aliphatic and aromatic ketones, enol ethers and esters, are aured under mild conditions, affording the corresponding organogold(I) compounds in excellent yields:

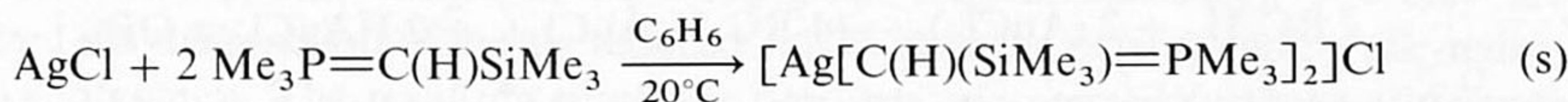
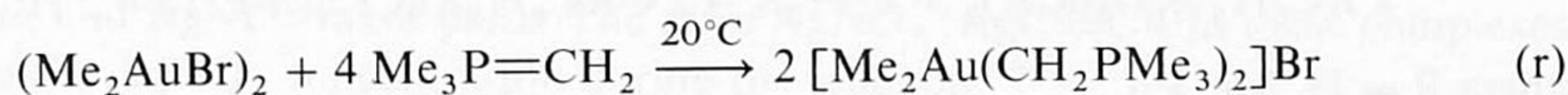


The presence of bases, e.g., sodium hydride or potassium carbonate is essential²⁶.

Metal(II)-ylid complexes can be prepared for all three metals^{3,29,31}, e.g.:



where M = Cu, Ag or Au(I). Metal-IB-ylid complexes are synthesized via direct coordination of the ylid to the IB-metal salt or compound^{3,29-33}:

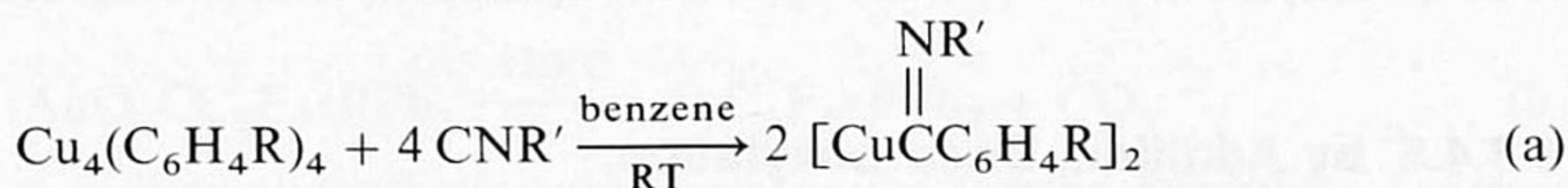


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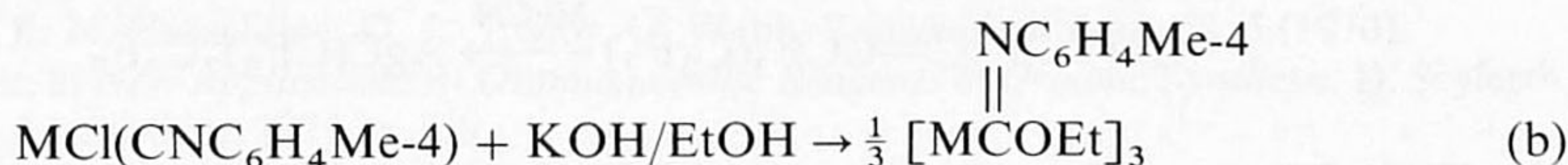
5.6.4.4. by Insertion.

Isonitriles insert into the Cu-C bond of arylcoppers. These reactions, which afford new Cu-carbon bonds, proceed quantitatively at RT¹:



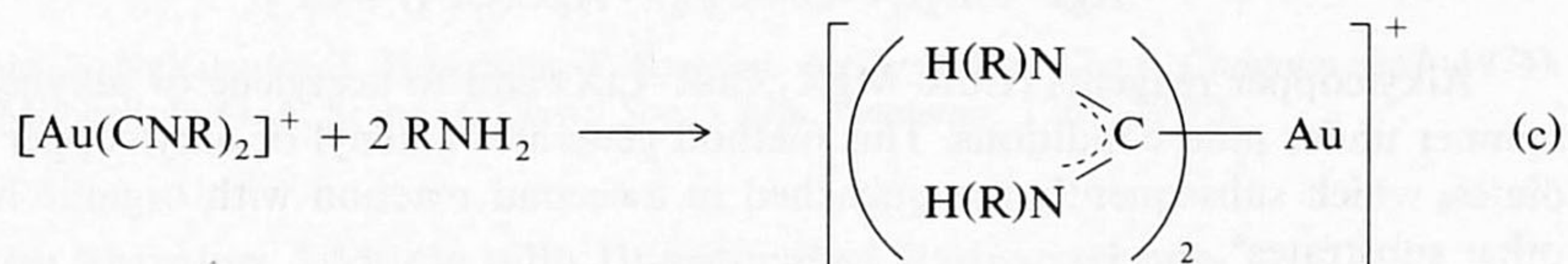
where R = CH₂NMe₂-2, NMe₂-2, Me-2; R' = Me, t-Bu, c-Hex.

Similar insertion reactions into the Ag- or Au-C bond are not known. However, for these metals related products can be synthesized via addition²⁻⁴:

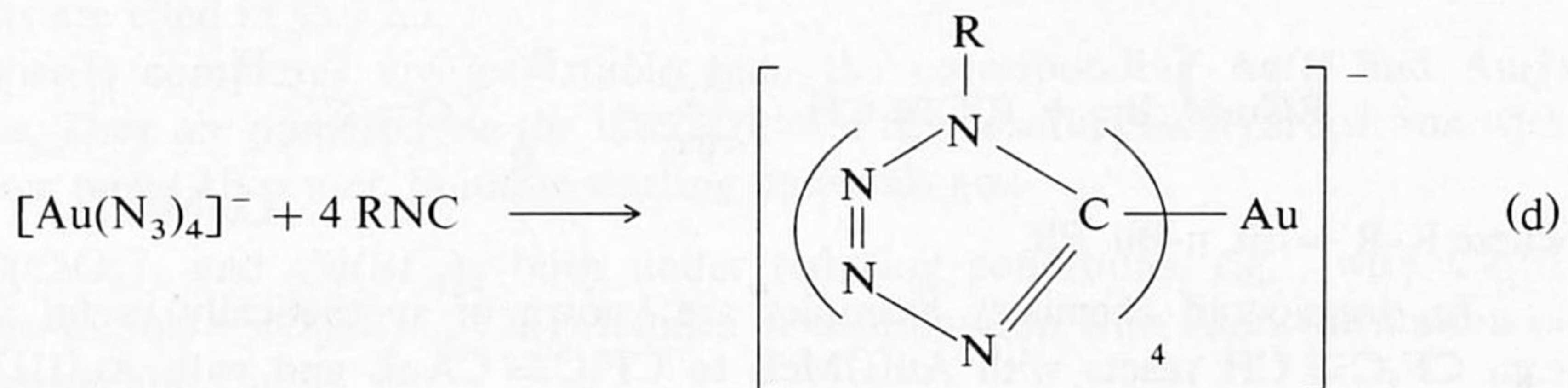


where M = Ag(I), Au(I).

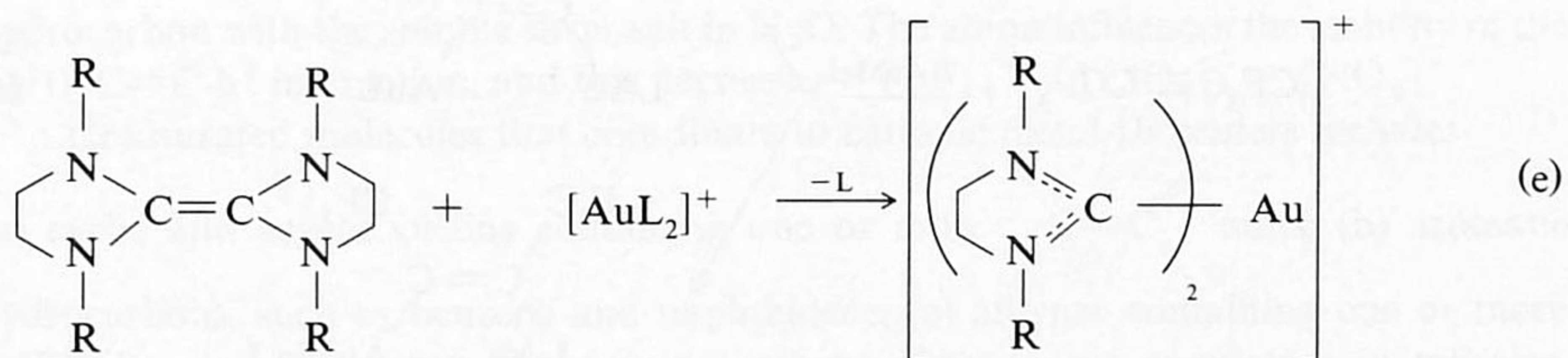
Other additions that form new Au-C bonds involve coordinated isocyanides^{5,6}:



where R = Me as well as⁷:



Finally, Au(I)-carbene complexes can be prepared in excellent yields via⁸:



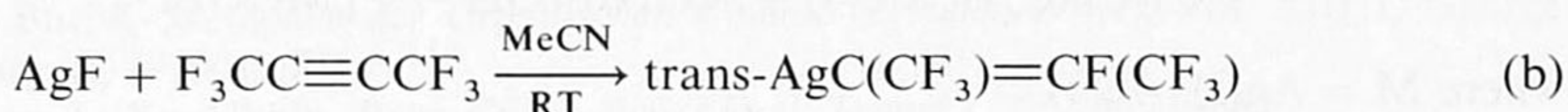
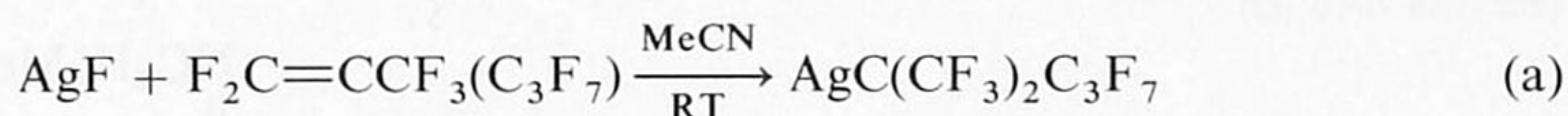
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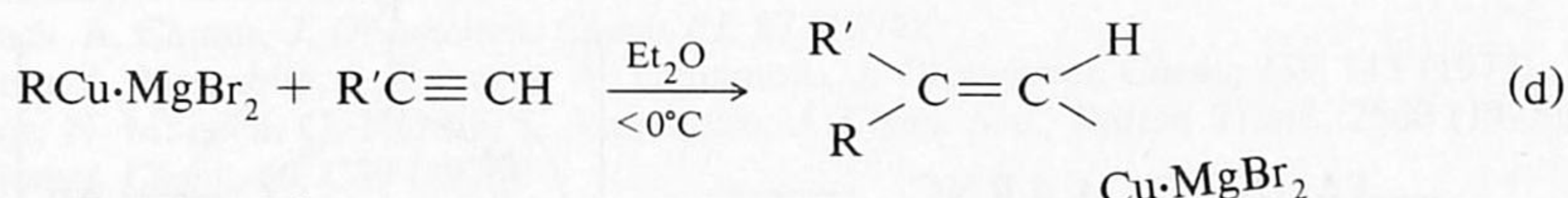
5.6.4.5. by Addition, Decarboxylation.

A unique route is available for the synthesis of alkyl- and alkenylcopper and silver compounds. Addition reactions of AgF to alkenes¹, alkynes² or allenes³ proceed (in 50–70% yield) under mild conditions:



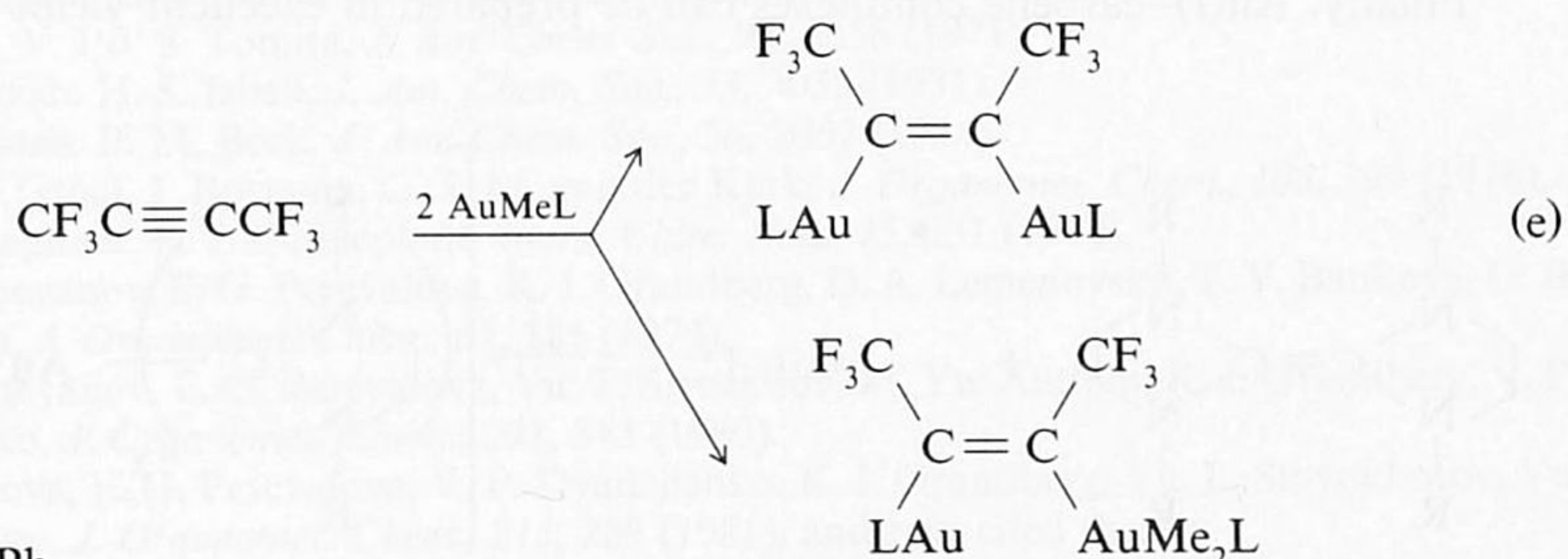
Alkylcopper reagents ($\text{CuR-MgX}_2, \text{CuR-LiX}$) add to acetylene or alkynes in a cis manner under mild conditions. This method generates alkenyl or alkylcopper intermediates, which subsequently are quenched in a second reaction with organic halides or other substrates⁴:

Pure organocoppers are not isolated:



where R, R' = Et, n-Bu, Ph.

In organogold chemistry examples are known of synthetically useful additions; e.g., $\text{CF}_3\text{C}\equiv\text{CH}$ reacts with Au(I)MeL to $\text{CF}_3\text{C}\equiv\text{CAuL}$ and with $\text{Au(III)Me}_3\text{L}$ to *cis*- $\text{AuMe}_2\text{L}(\text{C}\equiv\text{CCF}_3)$. However, with⁵ $\text{CF}_3\text{C}\equiv\text{CCF}_3$:



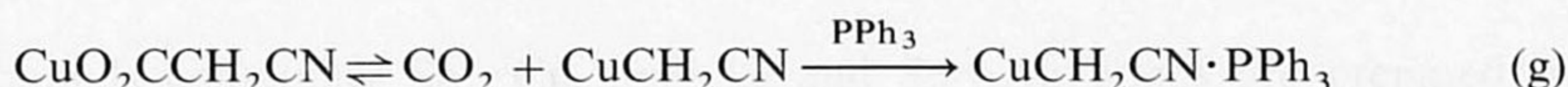
where L = PPh_3 .

Moreover, alkylgold(I) compounds are formed⁶:

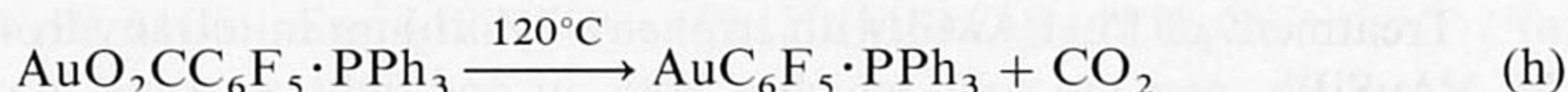


Examples of useful decarboxylations include the preparation of the quinoline complex of CuC_6F_5 in good yield by heating to 60°C $\text{Cu(I)O}_2\text{CC}_6\text{F}_5$ in quinoline⁷.

Reversible decarboxylation is known⁸ for $\text{CuO}_2\text{CCH}_2\text{CN}$:



An Au-C bond is formed in the decarboxylation reaction⁹:



Decarboxylation is of limited synthetic value because the forcing conditions contrast with the limited thermal stability of the metal IB-carbon bond.

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5.6.4.6. by Forming Adducts with Unsaturated Hydrocarbons.

Reviews of coordination of unsaturated and aromatic compounds with group-IB metal salts are cited in §5.6.2.3.

Copper(I) complexes are less stable than the corresponding Ag(I) and Au(I) complexes. They are prepared via the interaction of the unsaturated hydrocarbon with the cationic metal-IB center. Suitable starting materials are:

1. $\text{Cu(II)(ClO}_4)_2$ and $\text{Cu(BF}_4)_2$ both under reducing conditions, e.g.¹, with Cu(0), benzene-soluble CuO_3SCF_3 , Cu(I) halides in combination with AlX_3 (formation of AlX_4^- anion and Cu^+),
2. AgBF_4 , AgNO_3 , AgO_3SCF_3 , AgO_2CCF_3 , or
3. AuCl_3 (formation of $[\text{AuCl}_4]^-$ anion and Au^+).

Typical examples are the Ag(I) complexes that are synthesized by mixing the hydrocarbon with the soluble silver salt in H_2O . The anion influences the stability of the Ag(I)-C=C-h² interaction, and this decreases^{2,3} $[\text{BF}_4]^- < [\text{ClO}_4]^- < [\text{NO}_3]^-$.

Unsaturated molecules that coordinate to cationic metal-IB centers include:

- (a) cyclic and acyclic olefins containing one or more $\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$ units; (b) aromatic hydrocarbons, such as benzene and naphthalene; (c) alkynes containing one or more $-\text{C}\equiv\text{C}-$ units, but not the terminal alkynes because of competing metallation reactions (see §5.6.2.3.3). In addition, each of these hydrocarbons may contain heteroatoms or groups.

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