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SOME ASPECTS OF THE CHEMISTRY OF ORGANOTIN HYDRIDES AND OF GROUP IB ARYLMETAL CLUSTER COMPOUNDS

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Introduction

The title of this article reflects the fact that over the years the topics of research in the area of organometallic and coordination chemistry studied at the Institute for Organic Chemistry TNO (Director: Prof. Dr. G.J.M. van der Kerk) have covered a wide range. This is because the organometallic research program of the Institute, which belongs to the Netherlands Organization for Applied Scientific Research (TNO), has been considerably influenced by external factors. The Institute had no specific interest in organometallic chemistry until it was approached in 1950 by the International Tin Research Council to embark upon an explorative study of organotin chemistry. The studies in the organotin field which were initiated by Van der Kerk and Luijten (for early reviews see refs.1,2) formed the basis for a rapid expansion of the Utrecht organometallic research program in the late 1950's and early 1960's, when studies dealing with a number of other metals were taken up following requests by international non-profit research organizations or by private industry. In 1959, organogermanium research was started on behalf of the Germanium Research Committee, Brussels. In 1960, the International Lead Zinc Research Organization, New York began sponsorship of an explorative program in organolead chemistry, and in 1962 this was extended with a program in organozinc chemistry. In the meantime, the field of transition metal chemistry had been entered in 1957, when an industrial sponsor requested a study of the synthesis and catalytic properties of novel organovanadium compounds. Since that time sponsored and non-sponsored, short- and long-term projects dealing with main group and transition metals including antimony, bismuth, boron, idium, copper silver, gold, palladium, manganese and cobalt, have been part of the organometallic research program.

In these studies much emphasis was given to the synthesis of new compounds, to developing new or improving existing synthetic methods, and finding new applications. Examples of the last named are *(i)* the discovery in Utrecht of the biocidal properties of triorganotin compounds [3] which now, in addition to other applications, are used as agricultural and industrial fungicides, as acaricides, as antifoulants in underwater coatings, or as preservatives of textiles and wood; *(ii)* research dealing with long-chain dialkyltins [4] which has led to the present day large-scale use of di-n-octyltin compounds as non-toxic stabilizers for PVC used as packaging materials; *(iii)* the discovery of various organozinc-catalyzed processes, including the polymerization of aldehydes [5,6], epoxides [7], episulphides [7], and lactones [8], the alkylation of aromatic compounds [9], and the cyclotrimerization of butadiene [10] and of isocyanates [11]. However, in addition to the application-oriented studies, fundamental research has been pursued throughout the years. Some of these studies arose naturally from application-directed studies, others were initiated on the basis of the view that the development of novel applications requires the development of novel chemistry.

The present paper deals exclusively with fundamental studies in organometallic chemistry in the author's laboratories. Attention will be focussed on some older work dealing with organotin hydrides which marked the author's first entry into the area of organometallic chemistry and on more recent work dealing with novel Group IB arylmetal cluster compounds. Space does not permit reference to other recent studies, such as those dealing with the coordination chemistry of organozinc [12] and organoantimony [13] compounds.

Synthetic and mechanistic studies into the chemistry of organotin hydrides

In the early organotin research at Utrecht, considerable attention had been given to developing improved methods for the formation of tin—carbon bonds [15,16]. In particular the cyclic Wurtz process for the manufacture of dibutyltin compounds [15] developed in 1954 may be mentioned in this connection. However, the methods for tin—carbon bond formation available at that time were unsuitable for the introduction of carbon-functional groups. Therefore, the observation in 1955 [17] that the Sn—H bond in organotin hydrides readily enters into a non-catalyzed addition reaction with reactive carbon—carbon unsaturated compounds which may contain functional groups constituted an important advance in synthetic organotin chemistry, the more so since the functionally substituted adducts obtained proved amenable to further chemical

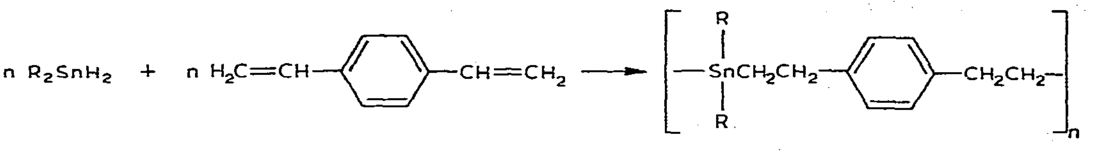
$$R_nSnH_{4-n} + (4-n)\ H_2C{=}CHY \rightarrow R_nSn(CH_2CH_2Y)_{4-n}$$

$$Y = CN,\ CH_2CN,\ COOMe,\ CONH_2,\ OCOMe,\ C_6H_5,\ \text{etc.}$$

transformations without cleavage of the functionally substituted organic groups from tin [18—21]. Following the first Utrecht papers dealing with preparative applications [17,22,23], organotin hydride chemistry developed in the 1960's into one of the most active areas of organotin research (for a review see ref. 24). Among the many contributors the groups of Neumann [25,26] and of Kuivila [29,30] deserve special mention.

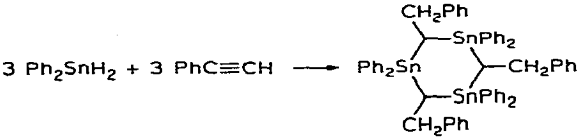
In addition to being eminently useful starting materials for the preparation of functionally substituted organotin compounds [18,22,23], organotin hydrides were shown to be applicable in a wide variety of organic as well as organometallic syntheses. In this paper only a few examples taken from the Utrecht work are briefly mentioned.

The 1/1 reaction of organotin dihydrides with bifunctionally unsaturated molecules provided a synthesis of a variety of organotin polymers containing tin atoms in the chain by hydrogen-transfer polymerization [30], e.g.:

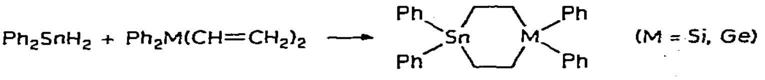


In addition to α,ω-diynes such as 1,5-hexadiyne or 1,4-diethynylbenzene [31], dienic reactants such as di-*p*-styrenyl derivatives of Ge, Sn and Pb or 1,4-divinylbenzene [32] were used, to give linear polymers with a variety of physical properties and with weight-average molecular weights ranging from 15,000 to 100,000. In addition to simple diorganotin dihydrides R_2SnH_2, more complex hydrides such as *p*-phenylene-bis(dimethyltin hydride) were also employed [33].

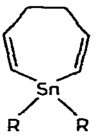
The 1/1 reaction of diphenyltin dihydride with phenylacetylene, which in principle might afford a polymer, instead gave a cyclic product [34], which we have shown more recently to fall into the novel 1,3,5-tristannacyclohexane class of compounds [35]:



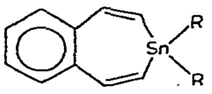
Similarly, the 1/1 reaction of Ph_2SnH_2 with divinylorganometallics instead of polymers afforded the novel 1-stanna-4-sila- and 1-stanna-4-germanacyclohexane ring systems [34]:



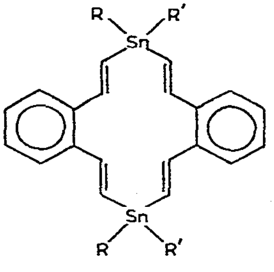
The 1/1 reaction of R_2SnH_2 with 1,5-hexadiyne in addition to linear polymer affords the 7-membered organotin heterocycle I [31]. Ring-formation is sterically favored in the reaction with *o*-diethynylbenzene resulting in the isolation of the 1/1 cyclic adduct II and the 2/2 cyclic adduct III [36,37]. The hetero-



(I)



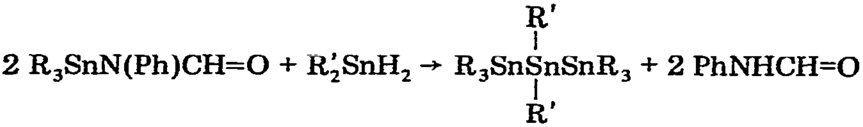
(II)



(III)

cycle (II, R = Me) has been converted by a simple substitution reaction with phenyldichloroborane into 3-phenyl-3-benzoborepin, which was shown by ^{1}H NMR and UV spectroscopic measurements to be the first example of a carbon—boron heterocycle with aromatic character [38]. It is worth noting that this method of synthesis has been used more recently for the synthesis of a variety of organometallic heterocycles [39,40], including the 1-phenylborabenzene anion [41] and phospha-, arsa- and stiba-benzene [42].

Although other methods have been employed in the Utrecht synthetic work concerned with metal—metal bonded compounds (see, e.g., the synthesis of alkylpolygermanes [43,44], $(Ph_3M')_4M$ [45] and $(Ph_3Pb)_4Pb$ [46]), the hydrostannolysis of metal—carbon or metal—heteroatom bonds provides the most versatile route to tin—metal bonded compounds [47]. Our observation that the tin—nitrogen bond is particularly susceptible to hydrostannolysis (see also ref. 48) has enabled us to synthesize a large variety of linear and branched poly-tin compounds [49,50], e.g.:

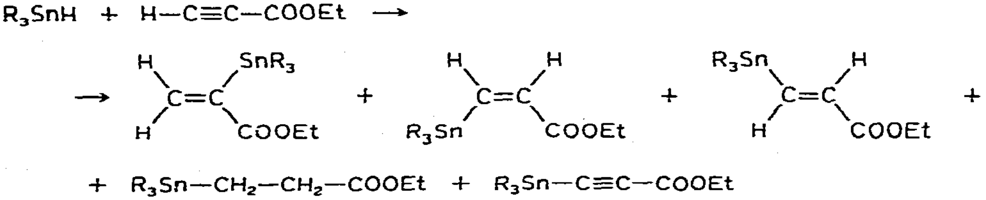


$$2\ R_3SnN(Ph)CH{=}O + R'_2SnH_2 \rightarrow R_3Sn\underset{R'}{\overset{R'}{Sn}}SnR_3 + 2\ PhNHCH{=}O$$

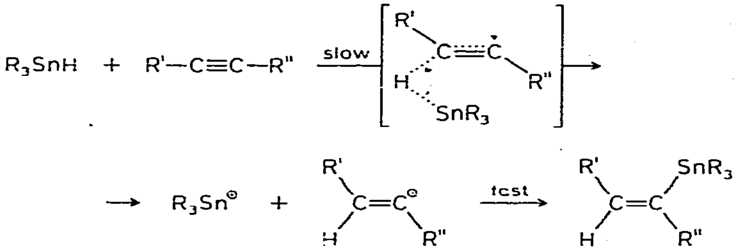
Appropriate combinations of hydrostannation (in particular the formation of Sn—N bonds starting from phenylisocyanate [51,52]) and hydrostannolysis reactions has enabled us to obtain linear stannanes containing up to six tin atoms [50]. Hydrostannolysis reactions have similarly been used by us for the synthesis of tin—germanium [53], tin—titanium and tin—zirconium [54], tin—magnesium [55,56] and tin—zinc and tin—cadmium [57,58] bonds.

In our early work on hydrostannation reactions we tentatively proposed a four-centre mechanism for the non-catalyzed hydrostannation of carbon—carbon double bonds [18]. Following the report by Neumann et al. that the hydrostannation of carbon—carbon double and triple bonds proceeds by a free radical chain mechanism [25,59] we embarked upon a more detailed study of the mechanistic and structural aspects of organotin hydride reactions [47,60] using instrumental techniques (NMR, GLC) not available at the time of the earlier studies.

An investigation of the structure of the addition products from trialkyltin hydrides and a variety of acetylenic compounds revealed that several products are obtained [61—63], e.g.:



The formation of these products could only be partly explained on the basis of a free radical mechanism. Further studies then revealed that the hydrostannation of carbon—carbon triple bonds can proceed by an ionic *trans*-mechanism as well as a free radical *trans*-mechanism. For electrophilic acetylenes such as cyanoethyne or methyl ethynecarboxylate the addition reaction involves *nucleophilic* attack of the hydride hydrogen on carbon as the first and rate-determining step, as shown by stereochemical data, kinetics, and substituent, solvent and isotope effects [64]:

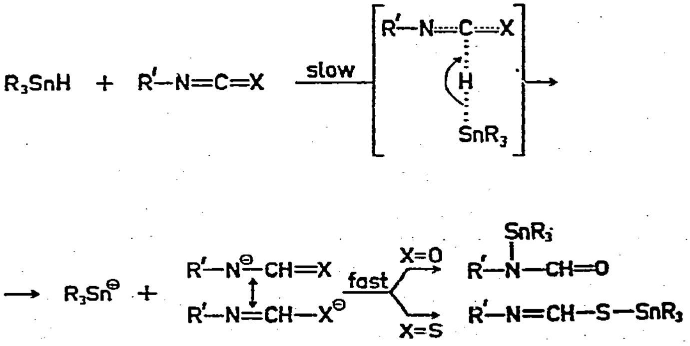


Hydrostannation of ethynes containing only an electron-releasing substituent (e.g. n-hexyne), or both an electron-withdrawing and an electron-releasing substituent (e.g. ethyl 1-propynecarboxylate), proceeds by a free radical *trans*-mechanism [65].

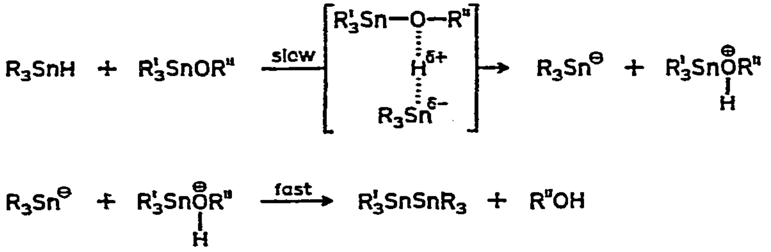
Whereas olefins normally react by a free radical chain mechanism [25], in addition to the usual β-adduct an α-adduct may be formed in a polar (nucleophilic) reaction if the olefin contains a strongly electrophilic substituent, as in acrylonitrile [66].

Hydrostannation of the C=O group of strongly electrophilic carbonyl compounds, such as pentafluorobenzaldehyde or chloral, similarly proceeds by *nucleophilic* attack of the organotin hydride hydrogen on the carbon atom of the carbonyl group, as indicated by the kinetics and solvent and substituent effects [67].

The hydrostannation of C=N and C=S double bonds in iso(thio)cyanates [51,52] provides a further example of the ability of organotin hydrides to react by a strictly polar mechanism. Kinetics, the influence of substituents attached to both the tin hydride and the iso(thio)cyanate, solvent and isotope effects revealed *nucleophilic* attack of the triorganotin hydride hydrogen on carbon to be the first and rate-determining step in the hydrostannation [68,69]:



As for the mechanism of tin—metal bond formation via hydrostannolysis, these reactions again are of a polar nature, as evidenced by the lack of activity of free radical generators or scavengers and by the influence of the polarity of the solvent on the rate of reaction. Kinetics, isotope effects, and the influence of substituents attached to tin and to nitrogen on the rate of hydrostannolysis of organotin—nitrogen derivatives showed *electrophilic* attack by the organotin hydride hydrogen at nitrogen to be the first and rate-determining step [70,71]. Substituent and solvent effects favor an identical mechanism for the hydrostannolysis of tin—oxygen bonds [71,72]:



$$R_3SnH + R'_3SnOR'' \xrightarrow{\text{slow}} \left[\begin{array}{c} R'_3Sn-O-R'' \\ \vdots \\ H^{\delta+} \\ \vdots \\ R_3Sn^{\delta-} \end{array}\right] \rightarrow R_3Sn^{\ominus} + R'_3Sn\underset{\substack{|\\ H}}{\overset{\oplus}{O}}R''$$

$$R_3Sn^{\ominus} + R'_3Sn\underset{\substack{|\\ H}}{\overset{\oplus}{O}}R'' \xrightarrow{\text{fast}} R'_3SnSnR_3 + R''OH$$

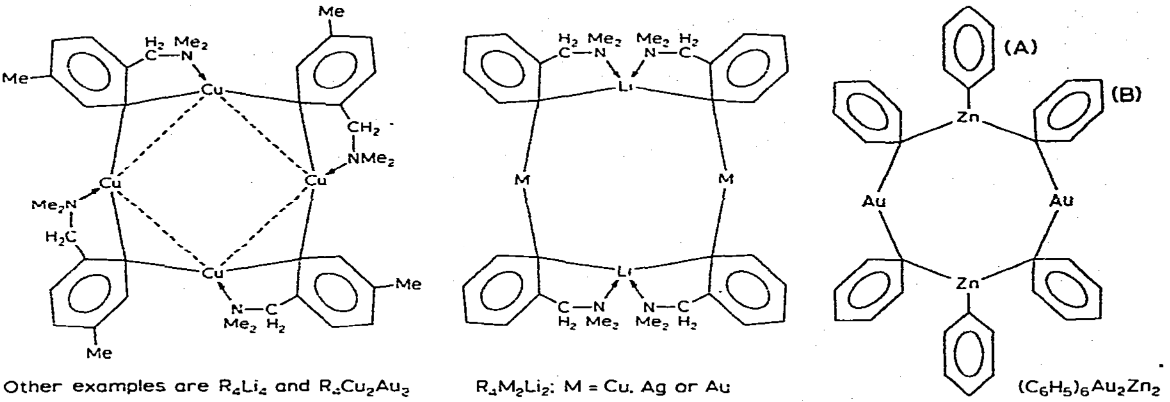
It is of interest to note that Kuivila has presented convincing evidence that the hydrostannolysis of carbon—halogen bonds proceeds by a free radical mechanism [28].

In summary, while organotin hydrides predominantly react by a *free radical* pathway, the Utrecht work has clearly established that depending on the electrophilicity or nucleophilicity of the substrate molecule organotin hydrides can also react by a *nucleophilic* or an *electrophilic* pathway, thus displaying a reaction pattern fully analogous to that of hydrocarbons.

Chemistry of aryl derivatives of the Group IB metals copper, silver and gold

Following earlier work at Utrecht in the area of organogold chemistry which had resulted in the isolation of quite stable dialkylgold(III) *N*,*N*-dialkyldithiocarbamates [73], we embarked in the late 1960's upon more extensive research in the area of the Group IB metals copper, silver and gold. At that time only a few σ-bonded organocopper and organosilver compounds were known, the majority of which, moreover, displayed thermal, oxidative and hydrolytic instability. Aiming at the isolation of more stable compounds, we set out to stabilize the metal—carbon bond by internal complexation, i.e., rather than coordinating to the metal and external ligand (e.g., pyridine or triphenylphosphine) we introduced a potentially coordinating group into the organic ligand bound to the metal (e.g., R = $2\text{-}Me_2NC_6H_4$ or $2\text{-}Me_2NCH_2C_6H_4$) [74,75]. This approach enabled us to isolate a series of arylcopper [74—77] and arylsilver [78] compounds having stabilities considerably exceeding those of the compounds previously reported. More recently, we have characterized similar type arylgold(I) triphenylphosphine complexes as well as ligand-free RAu^I compounds [79]. Very pure, uncomplexed phenylsilver C_6H_5Ag was obtained via the reaction of phenylsilver—silver nitrate complex with trialkylphenyl-tin or -lead compounds [80].

An X-ray structure determination of 5-methyl-2-[(dimethylamino)methyl]-phenylcopper which is tetrameric in solution, revealed a tetranuclear structure

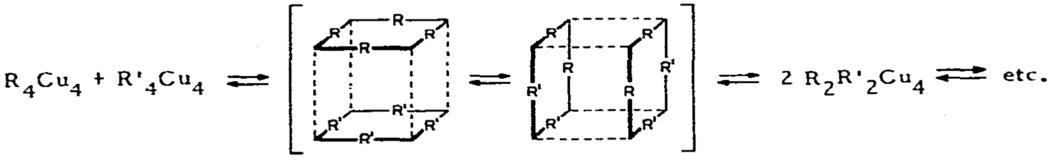


Other examples are R_4Li_4 and $R_4Cu_2Au_2$ $R_4M_2Li_2$: M = Cu, Ag or Au $(C_6H_5)_6Au_2Zn_2$

Fig. 1. Schematic structures of tetranuclear homo- and heterometallic Group IB cluster compounds.

with extremely short Cu—Cu distances (2.38 Å) and, perhaps as the most interesting feature, the presence of bridging aryl groups [81,82] (see Fig. 1).

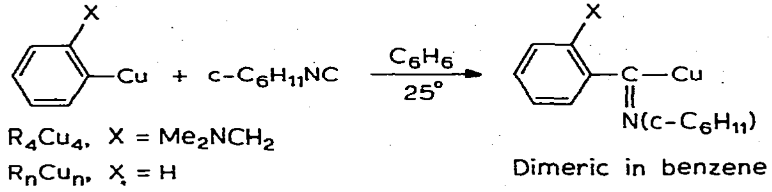
Mass spectroscopic studies revealed that the R_4Cu_4 cluster has considerable stability as evidenced by the high relative abundance of the $R_3Cu_4^+$ fragment which forms the base peak [82]. The tetranuclear arylcopper compounds readily undergo intercluster exchange reactions with formation of each of the three mixed cluster species $R_3R'Cu_4$, $R_2R'_2Cu_4$ and RR'_3Cu_4 probably via an octanuclear intermediate [82]:



Whereas molecular weight determinations and NMR studies have shown that strongly coordinating solvents or external ligands such as pyridine or triphenylphosphine leave the R_4Cu_4 structure unaffected, the 1/1 interaction with 1,2-bis(diphenylphosphine)ethane (Diphos) results in the break-down to a monomeric RCu·Diphos complex, while addition of excess of Diphos induces an unusual C_{Alk}—P bond cleavage reaction [83]:

$$\frac{1}{4}\,R_4Cu_4 \xrightarrow[C_6H_6;\,25^\circ]{2\,\text{Diphos}} Ph_2PCu\cdot\text{Diphos} + Ph_2PCH{=}CH_2 + RH \quad (R = 2\text{-}Me_2NCH_2C_6H_4)$$

In the presence of isocyanides, arylcopper compounds undergo insertion reactions into the Cu—C bond with the formation of novel types of organocopper



compounds [84]. Interestingly, the interaction of phenylsilver—silver nitrate complex with solid or gaseous carbon dioxide in ethanol, instead of resulting in insertion into the Ag—C bond, involves the formation of a carbon dioxide complex with the composition $[C_6H_5Ag \cdot CO_2 \cdot Ag]_n$ [85].

Aryl-copper and -silver compounds form complexes of well-defined stoichiometry with metal halides [75,78,86,87]; e.g., 2-$Me_2NC_6H_4Cu$ forms a 2/1 complex with copper(I) bromide which is dimeric in benzene. An X-ray structure determination of this hexanuclear complex revealed an octahedral cluster structure with very short Cu—Cu bonds and bridging aryl groups and bromine atoms [88]. Perhaps the most striking chemical property of these $R_4Cu_6X_2$ compounds is their ability to undergo ligand-substitution reactions (e.g., substitution of X by arylacetylide) with retention of the hexanuclear cluster structure [87]. The interesting thermolysis behavior of the resulting $R_4Cu_6R'_2$ compounds, i.e., exclusive formation of RR′ without a trace of RR and R′R′ formation, has been explained in terms of the arrangement of the organic ligands R and R′ around the Cu_6 cluster [87].

Whereas interaction of arylcopper compounds R_nCu_n with copper(I) halides results in the formation of new copper(I) cluster compounds, the 1/1 interaction of R_nCu_n with copper(II) halides results in the formation of RR, RX and RH, and this has been explained on the basis of intramolecular electron-transfer taking place in inner-sphere activated complexes of the type $R_nCu_{n-1}Cu\cdots X\cdots Cu^{II}X(Cu^{II}X_2)_{n-1}$, e.g.:

$$R_4Cu_4 + (CuX_2)_n \longrightarrow \left[R_4Cu^{I}_{3}Cu^{I}\cdots X\cdots Cu^{II}X(Cu^{II}X_2)_{n-1}\right] \longrightarrow \left[R^{\bullet}\ R_3Cu^{I}_{3}Cu^{I}X\cdot Cu^{I}X(Cu^{II}X_2)_{n-1}\right]$$

followed by intramolecular trapping of the $R^{\bullet}$ radical by Cu^{I}—R or by Cu^{II}—X bonds [89].

In addition to the R_4Cu_4 [76,82], R_nCu_n [77], R_nAg_n [78,80], R_nAu_n [79], R_2Cu_4 [86], $R_4Cu_6X_2$ [87,88], $R_4Ag_6X_2$ [78] and $R_4Cu_6R'_2$ [88] homometallic cluster species we have included Group IB heterometallic polynuclear compounds in our studies.

$[2\text{-}Me_2NCH_2C_6H_4]_2CuLi$ [86,90] and the corresponding silver-lithium compound [91] were obtained via intercluster metal exchange or lithium—halogen exchange reactions as thermostable, hydrocarbon-soluble, crystalline compounds. Molecular weight determinations and the results of ^1H and ^{13}C NMR spectroscopic studies revealed that these compounds have a tetranuclear, mixed-metal cluster structure containing aryl groups bridging one lithium and one copper (or silver) atom and the four dimethylamino groups being coordinated to lithium [86,90,91] (see Fig. 1). The NMR study of $R_4Ag_2Li_2$ permitted, in addition to lithium—carbon coupling, the observation for the first time of silver—proton and silver—carbon couplings [91]. More recently, the corresponding gold—lithium compound has been isolated, and this from molecular weight and NMR studies appears to be isostructural with the $R_4Cu_2Li_2$ and $R_4Ag_2Li_2$ clusters [92]. Compounds of this type are useful starting materials for the synthesis of uncomplexed arylgold(I) compounds R_nAu_n, as shown by the reaction with triorganotin halides which may well proceed via an Au^{III}—Sn intermediate [79]:

$$\underset{\text{(dimer)}}{R_2Au^{I}Li} + R'_3SnX \xrightarrow{-LiX} [R_2Au^{III}SnR'_3] \rightarrow R'_3SnR + RAu^{I}$$

The reaction with copper(I) halides provided the first example of a tetranuclear gold(I)-copper(I) cluster [92]:

$$R_4Au_2Li_2 + 2\ CuX \rightarrow R_4Au_2Cu_2 + 2\ LiX$$

Attempts to prepare arylgold(III) compounds by the reaction of $AuCl_3$ with diphenylzinc in benzene instead gave an orange-coloured compound with composition Ph_3AuZn, which, based on its dimeric molecular weight in benzene and on ^1H and ^{13}C NMR studies, has been assigned a tetranuclear $R_6Au_2Zn_2$ structure (Fig. 1) with four aryl groups bridging gold and zinc atoms [93], fully analogous to the aryl-Cu_2Li_2 [90], -Ag_2Li_2 [91], -Au_2Li_2 [92] and -Au_2Cu_2 [92] cluster species (see Fig. 1). It is clear that multi-centre bonded aryl groups, which had previously been uncommon in organometallic chemistry with the exception of arylaluminium dimers [94] and a few osmium trinuclear clusters [95], have emerged from the Utrecht studies as being a normal structural feature for aryl compounds of the Group IB metals.

Acknowledgements

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