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THE REGIO- AND STEREOSPECIFIC SYNTHESIS OF DIARYLPROPENYLLITHIUM COMPOUNDS FROM DIMETHYLAMINO- AND DIMETHYLAMINOMETHYL-SUBSTITUTED DIARYLACETYLENES VIA TRANSMETALLATION REACTIONS INVOLVING DIARYLPROPENYLMAGNESIUM AND -TIN COMPOUNDS

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Summary

Dimethylamino- and dimethylaminomethyl-substituted diarylacetylenes were prepared by the $Pd(PPh_3)_4$-catalyzed coupling reaction of dimethylamino- and dimethylaminomethyl-substituted aryl halides with arylacetylenes.

Reaction of the asymmetric diarylacetylenes with methylmagnesium bromide in the presence of $NiCl_2(PPh_3)_2$ gave stereo- and regio-selectively *cis* addition products in which the aryl group bearing the built-in ligand (Me_2N or Me_2NCH_2) and the magnesium atom are bonded to the same unsaturated carbon atom. The *E*-diarylpropenylmagnesium bromides were converted in two successive transmetallation steps into the corresponding *E*-triphenyltin and *Z*-lithium compounds with retention of configuration. Depending on the type of solvent, complete inversion of configuration was observed for the *Z*-diarylpropenyllithium compounds. From the *E*-lithium compounds the corresponding *Z*-diarylpropenyltriphenyltin compounds were prepared (Scheme 1).

Retention of configuration in the series of transmetallation reactions has unambiguously been established by comparison of the $^{119}Sn—^{1}H$, $^{13}C—^{1}H$ and $^{119}Sn—^{13}C$ coupling constants observed in the ^{1}H and ^{13}C NMR spectra of the configurationally pure stereoisomeric pairs.

Introduction

Although vinylcopper compounds and vinylcuprates are widely used in organic synthesis [1], it is surprising that little is known about their structures. This lack of information can be attributed to the thermal instability of these

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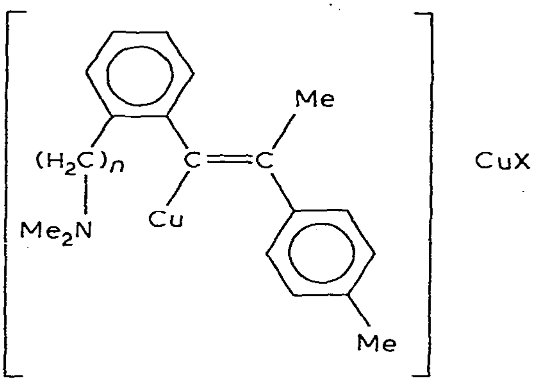
compounds, which prevents their isolation and characterization. Recent studies have shown that intramolecular copper—hetero atom coordination, as well as steric crowding near the copper—carbon bond enhances to a considerable extent the thermal stability of arylcopper compounds [2—4].

Recently, we have successfully applied these principles to the synthesis of the thermally stable (1,2-diaryl-1-propenyl)copper compounds I, II and III [5].



(I, n = 0, X = Br ; II, n = 0, X = OTf* ; III, n = 1, X = Br)

These compounds were synthesized via transmetallation reactions of organolithium reagents with copper(I) halides. The latter reaction provides a generally useful route for the synthesis of alkyl- [6], ethynyl- [7] and aryl-copper [3,4,8] compounds.

For our study of thermally stable vinylcopper compounds the isolation of chemically and configurationally pure vinyllithium compounds containing both bulky substituents and a potentially coordinating ligand was required. The isolation of configurationally pure organolithium compounds of this type, to the best of our knowledge, has not been attempted. Vinyllithium compounds generally are obtained via lithiation of vinyl halides [9] or via transmetallation reactions involving organotin [10] or organomercury [11] compounds.

The recently reported $NiCl_2(PPh_3)_2$-catalyzed regio- and stereo-selective addition of Grignard reagents to the acetylenic triple bond [12] seems to offer an excellent starting point for a planned synthesis of configurationally pure vinyllithium compounds. The transformation of the resulting vinylmagnesium halides into vinyltin compounds, which are then converted by a second transmetallation step into the vinyllithium reagents, completes the reaction sequence.

In the present paper we report on: (i) the synthesis of the *E*- and *Z*-isomers of unsubstituted and Me_2N- and Me_2NCH_2-substituted (1,2-diaryl-1-propenyl)-lithium compounds (ViLi) by the above mentioned synthetic routes; (ii) the influence of built-in ligands, such as 2-Me_2N or 2-Me_2NCH_2, on the regio- and stereo-specific behaviour of the $NiCl_2(PPh_3)_2$-catalyzed addition of MeMgBr

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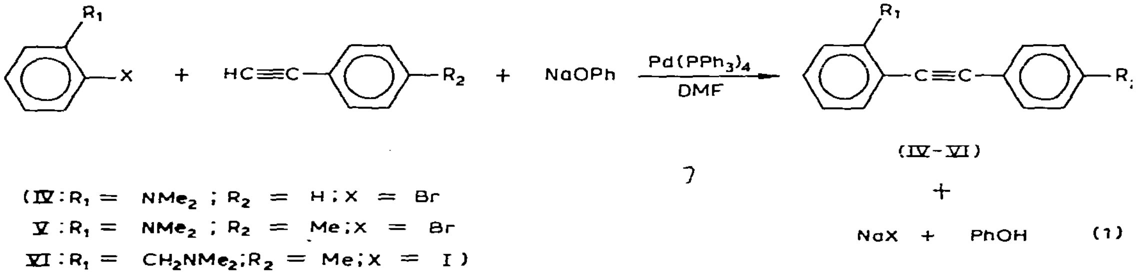
* *OTf = triflate = trifluoromethanesulphonate.*

to 2-Me_2N- or 2-Me_2NCH_2-substituted diarylacetylenes; and (iii) the synthesis and configurational assignment based on ^1H and ^{13}C NMR spectral data for a series of $ViPh_3Sn$ and ViH compounds.

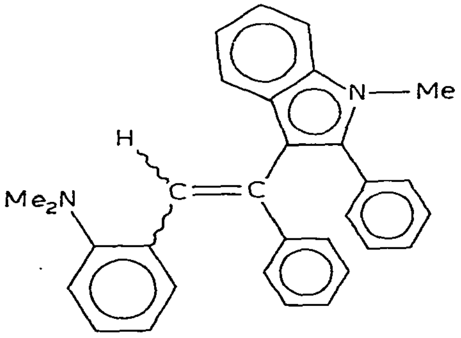
Details on the synthesis and characterization of thermally stable (1,2-diaryl-1-propenyl)copper compounds starting from *E*-ViLi will be reported separately [5].

Results

Diarylacetylenes, IV—VI, in which one of the aryl groups bears a Me_2N or Me_2NCH_2 substituent in the 2 position, have been prepared in 78—82% yield via a Pd(0)-catalyzed coupling reaction of the 2-substituted aryl halide and an arylacetylene following the procedure of Cassar [13] (eq. 1). Moreover, we



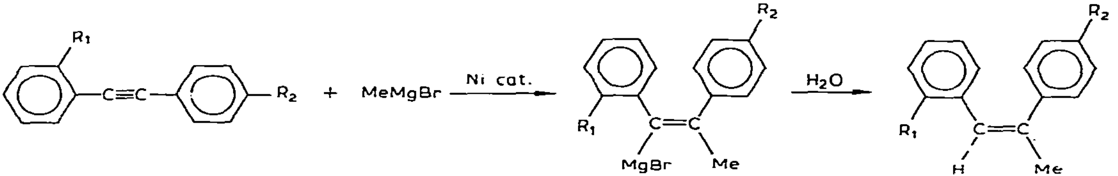
obtained IV and V via the selective asymmetric coupling of phenylethynylcopper and 4-tolylethynylcopper respectively with 2-dimethylaminophenylcopper [14]. When sodium methoxide was used instead of sodium phenoxide (eq. 1) in addition to compound IV (41% yield) a further product was isolated in 26% yield. From the elemental analysis, ^1H and ^{13}C NMR and mass spectral data of this new product we have tentatively assigned it the structure VII depicted in Fig. 1.



(VII)

FIG. 1.

Initial attempts to obtain vinyl iodides, which could be precursors to vinyllithium compounds, by addition of HI or I_2 to the diarylacetylenes IV and V were unsuccessful. For example, with V, these addition reactions resulted in the formation of the ring-closed products *N*-methyl-2-(4-tolyl)indole and its 3-iodo derivative, respectively [15]. Likewise, attempts to obtain vinyllithium compounds by direct addition of MeLi (room temperature, diethyl ether solution, 65 h) or of Me_2CuLi (—20°C, diethyl ether solution, 1 h) to the acetylenes IV—VI were unsuccessful. An organoaluminium route [16] (reaction of i-Bu_2AlH with V) also failed because the reaction was non-specific (NMR analysis of the products obtained upon hydrolysis of the reaction mixture shows the presence of two stereoisomeric 1,2-diarylethenes in a 1/3 ratio). In contrast, the $NiCl_2(PPh_3)_2$-catalyzed addition reaction [13] of MeMgBr with IV—VI proceeded in a regio- and stereo-selective manner, to give the *E*-(1,2-diaryl-1-propenyl)magnesium bromide compounds IX—XI by *cis* addition (eq. 2) *. Similarly, the addition of MeMgBr to diphenylacetylene (VIII) results in the exclusive formation of the *cis* addition product [12].



(

(IV-VI, VIII)

(*E*-IX – *E*-XII)

(*Z*-XIII – *Z*-XVI)

(IV, IX, XIII : R_1 = NMe_2; R_2 = H
V, X, XIV : R_1 = NMe_2; R_2 = Me
VI, XI, XV : R_1 = CH_2NMe_2; R_2 = Me
VIII, XII, XVI : R_1 = R_2 = H)

Hydrolysis of IX—XII affords the corresponding *Z*-1,2-diaryl-1-propene compounds XIII—XVI (eq. 2) **. The location of the methyl group in the adducts X and XI has been determined by the oxidative cleavage of the carbon—carbon double bond of the corresponding hydrolysis products XIV and XV with potassium permanganate (see Experimental). The product consisted of 4-methylacetophenone, and 4-methylbenzoic acid and *N*,*N*-dimethyl-2-acetylbenzenamine were shown to be absent (NMR analysis, comparison with authentic samples). This indicates that the addition across the carbon—carbon triple bond had occurred in the regioselective fashion shown in eq. 2.

Reaction of the *E*-(1,2-diaryl-1-propenyl)magnesium bromides, IX—XII, with Ph_3SnCl afforded the *E*-(1,2-diaryl-1-propenyl)triphenyltin compounds XVII—XX (eq. 3).

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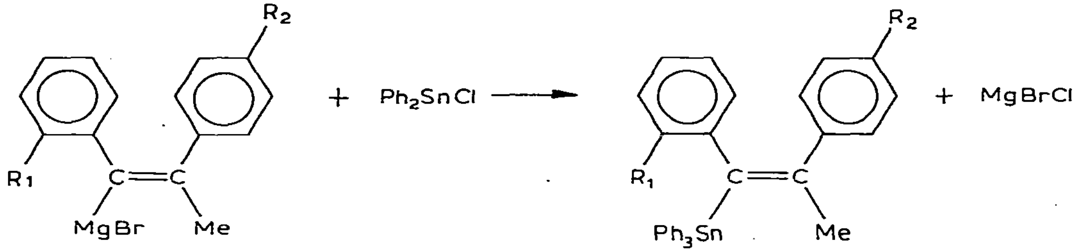
* For the discussion of the configurational assignment of the various 1,2-diaryl-1-propenyl derivatives reported in this paper, see Discussion.

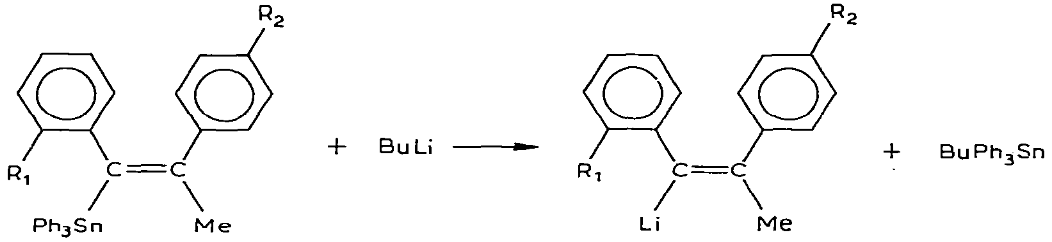
** The configuration of *E*-IX—*E*-XII are the same as those of *Z*-XIII—*Z*-XVI, because the *E*- and *Z*-conventional rules are based on atomic weights [17].



(E-IX – E-XII) (E-XVII – E-XX) (3)

(IX, XVII : R_1 = NMe_2; R_2 = H
X, XVIII : R_1 = NMe_2; R_2 = Me
XI, XIX : R_1 = CH_2NMe_2; R_2 = Me
XII, XX : R_1 = R_2 = H)

The *E*-(1,2-diaryl-1-propenyl)triphenyltin compounds, XVII—XX, react with n-butyllithium in pentane/hexane solution to give quantitative yields of the *Z*-(1,2-diaryl-1-propenyl)lithium compounds * XXI—XXIV (eq. 4).



(E-XVII – E-XX) (Z-XXI – Z-XXIV) (4)

(XVII, XXI : R_1 = NMe_2; R_2 = H
XVIII, XXII : R_1 = NMe_2; R_2 = Me
XIX, XXIII : R_1 = CH_2NMe_2; R_2 = Me
XX, XXIV : R_1 = R_2 = H)

Butyltriphenyltin is soluble in pentane/hexane while compounds XXI and XXII are insoluble in this mixture, and thus can be readily isolated. Addition of diethyl ether or benzene to a suspension of the *Z* isomers XXI or XXII in pentane/hexane or to pure *Z*-XXI or XXII results in a clear yellow solution containing only the *E*-(1,2-diaryl-1-propenyl)lithium compounds XXV and XXVI. In contrast, the *Z* isomers XXIII and XXIV are soluble in pentane/hexane and configurationally unstable in this solvent system. Complete inversion of configuration takes place in approximately 4 h, giving the pentane-insoluble *E*-(1,2-diaryl-1-propenyl)lithium compounds XXVII and XXVIII (eq. 5).

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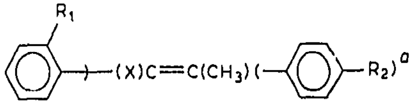
* Cf. footnote 2 on page 134.

TABLE 1

^{1}H NMR SPECTRAL DATA FOR THE COMPOUNDS (



)^a

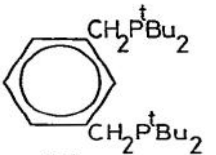
X	R_1	R_2	Comp. (config.)	$N(CH_3)_2$	NCH_2	$PhCH_3$	$C{=}CCH_3$
H	$N(CH_3)_2$	H	XXIX (*E*)	2.50	—	—	2.15 (^4J(H—H) 1.3 Hz ^{b})
	$N(CH_3)_2$	CH_3	XXX (*E*)	2.53	—	2.15	2.18 (^4J(H—H) 1.3 Hz ^{b})
			XIV (*Z*)	2.63	—	2.07	2.17 (^4J(H—H) 1.4 Hz ^{b})
	$CH_2N(CH_3)_2$	CH_3	XXXI (*E*)	2.10	3.35	2.17	2.05 (^4J(H—H) 1.4 Hz ^{b})
			XV (*Z*)	2.14	3.40	2.02	2.14 ^{c}
	H	H	XXXII (*E*)	—	—	—	2.08 (^4J(H—H) 1.3 Hz ^{b})
			XVI (*Z*)	—	—	—	2.17 ^{d} (^4J(H—H) 1.4 Hz ^{b})
$SnPh_3$	$N(CH_3)_2$	H	XVII (*E*)	2.23 ^{e}	—	—	2.40 ^{e} (^4J(Sn—H) 12.8 Hz)
			XXXIII (*Z*)	2.40	—	—	2.13 (^4J(Sn—H) 8.8 Hz)
	$N(CH_3)_2$	CH_3	XVIII (*E*)	2.27	—	2.00	2.43 (^4J(Sn—H) 12.6 Hz)
			XXXIV (*Z*)	2.27	—	2.00	2.07 (^4J(Sn—H) 8.7 Hz)
	$CH_2N(CH_3)_2$	CH_3	XIX (*E*)	1.90	δ_1 2.92 δ_2 3.50 *J* 14.0 Hz	1.90	2.37 (^4J(Sn—H) 12.8 Hz)
			XXXV (*Z*)	2.00	δ_1 3.28 ^{f} δ_2 3.46 *J* 13.2 Hz	2.00	1.97 (^4J(Sn—H) ^{g})
	H	H	XX (*E*)	—	—	—	2.30 (^4J(Sn—H) 12.8 Hz)
			XXXVI (*Z*)	—	—	—	2.03 (^4J(Sn—H) 8.8 Hz)
Li	$N(CH_3)_2$	H	XXV (*E*)	2.13	—	—	2.18
	$N(CH_3)_2$	CH_3	XXVI (*E*)	2.01	—	2.18	2.18

[a] δ(H) (C_6D_6 unless otherwise stated, TMS, internal, δ(ppm)). [b] For X = D, one resonance line. [c] Coincides with $N(CH_3)_2$ resonance line, coupling not observable. [d] In $CDCl_3$, see also ref. 38. [e] In CCl_4. [f] One resonance line in $CDCl_3$ solution (δ(NCH_2) 3.25 ppm). [g] Obscured by δ(NMe_2); in $CDCl_3$, ^4J(Sn—H) 8.4 Hz.

reaction of C_3F_7I with cobalt(II) acetate, in the presence of pyridine and sodium diethyldithiocarbamate [4].

The five coordinate cobalt(I) perfluoroalkyl compounds $[RCo(PF_3)_x(CO)_{4-x}]$ ($R = CF_3, C_2F_5, C_3F_7; x = 1$—$4$) are stereochemically non-rigid at room temperature. ^{19}F NMR studies reveal two types of dynamic processes, one occurring between different isomers and the other between nonequivalent sites in a single isomer. The data are consistent with a trigonal bipyramidal structure with an axial perfluoroalkyl group. In the complex $[CF_3Co(PF_3)(CO)_3]$ there are nearly equal proportions of isomers having axial and equatorial PF_3 groups, however, the equatorial isomer is increasingly favoured for $x = 2$ and 3. In the perfluoroethyl and perfluoropropyl compounds $[RCo(PF_3)(CO)_3]$ the isomer with an axial PF_3 group is strongly favoured over the equatorial while for the di- and trisubstituted compounds the isomer with all PF_3 groups equatorial is not observed [5].

Novel *ortho*-metallation reactions continue to produce a variety of rhodium and iridium metal—carbon σ-bonded complexes. The bulky diphosphine **5** undergoes metallation very readily to give a new type of tridentate chelating system. Thus reaction of **5** with hydrated rhodium(III) chloride gives the five coordinate hydride **6** (M = Rh) and an analogous iridium complex can similarly be prepared. Treatment of **6** (M = Ir) with carbon monoxide gives the octahedral complex **7**. A similar reaction with the rhodium complex gave an analogous adduct but this readily loses hydrogen chloride to give **8** and possibly other products. Attempts to obtain an analogous iridium(I) carbonyl complex failed. Thus treatment of **6** (M = Ir) with sodium ethoxide and carbon monoxide gives only impure **7** [6].



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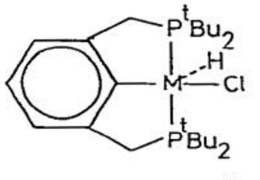
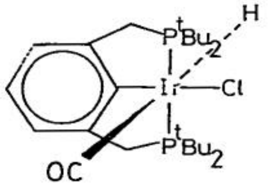


(M = Rh, Ir)

(6)



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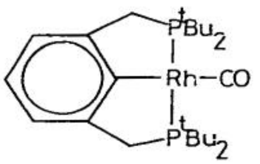

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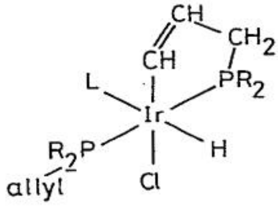
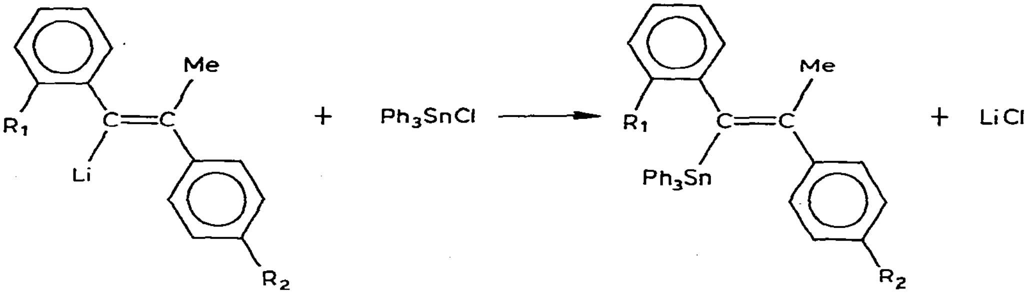


(L = γ-picoline ;
R = ^tBu , cyclohexyl)

(9)

The reactions of the allylic phosphines, $R_2P(allyl)$ (R = t-Bu, cyclohexyl) with $[IrCl(cyclooctene)_2]_2$ in the presence of γ-picoline at room temperature yield the octahedral metallated complexes **9**.

A five coordinate metallated complex can be obtained with $t\text{-}Bu_2P$-allyl in the absence of γ-picoline. The ease of metallation of these unsaturated ligands may



(6)

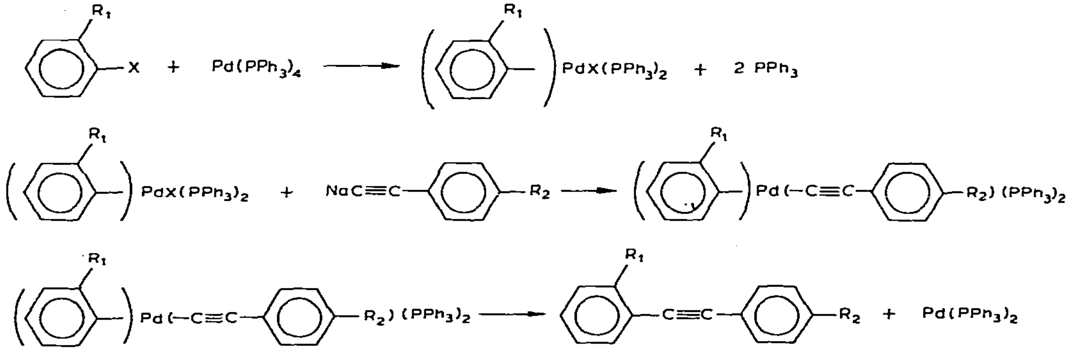
(*E*-XXV–*E*-XVIII) (*Z*-XXXIII–*Z*-XXXVI)

(XXV, XXXIII : R_1 = NMe_2 ; R_2 = H
XXVI, XXXIV : R_1 = NMe_2 ; R_2 = Me
XXVII, XXXV : R_1 = CH_2NMe_2 ; R_2 = Me
XXVIII, XXXVI : R_1 = R_2 = H)

Discussion

The palladium-catalyzed coupling reaction

The $Pd(PPh_3)_4$-catalyzed coupling reaction of an aryl halide and an acetylene in the presence of a base (sodium methoxide or phenoxide) has been previously described [13]. This reaction was thought to occur by an oxidative addition of the aryl halide to a palladium(0) species (eq. 7), followed by reaction of the resulting palladium(II) species with sodium arylacetylide (obtained from the reaction of the arylacetylene with sodium methoxide or phenoxide). The mixed aryl—arylacetylide palladium species then yields the asymmetric coupling product by reductive elimination (eq. 9).

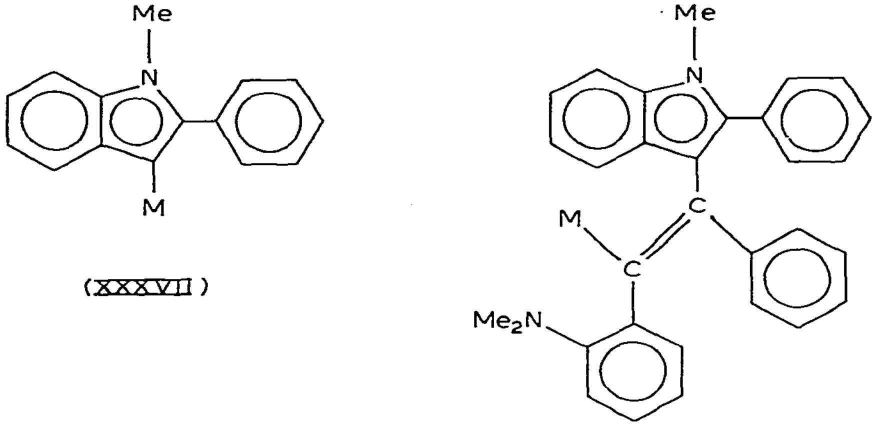


(7)

(8)

(9)

An interesting aspect of the coupling reactions reported in this paper is the formation of the novel cyclization product VII (see Fig. 1) in the reaction where $R_1 = Me_2N$ and R_2 = H. The formation of this product probably involves two discrete stages, the first of these being the formation of an indole fragment XXXVII (see Fig. 2). A possible explanation for the formation of this fragment involves intramolecular nucleophilic attack of the dimethylamino group on the acetylenic bond, which has become electrophilic by coordination to a Pd species.



(XXXVII)

(XXXVIII)

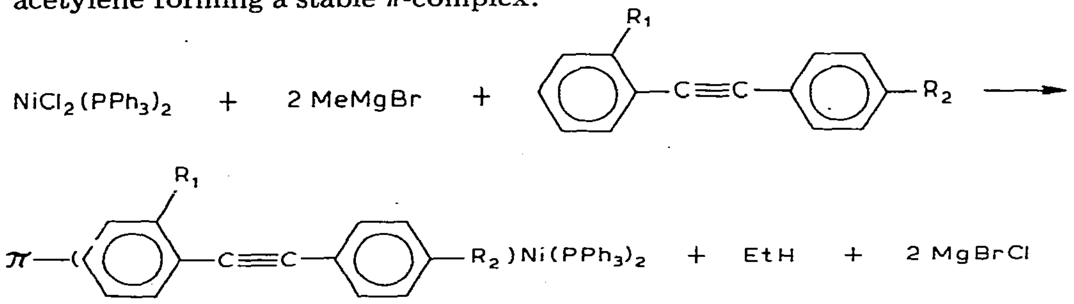
Fig. 2.

In this connection it is relevant to mention the synthesis of *N*-methyl-2-phenylindole and its 3-iodo-derivative by the reaction of *N*,*N*-dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine with HI or I_2, respectively. This reaction also proceeds by the intramolecular nucleophilic attack of the dimethylamino group on an activated acetylenic bond [15].

In the second stage the indolylpalladium species adds across the triple bond of the diarylacetylene, yielding the intermediate XXXVIII shown in Fig. 2. The specific formation of only one product, as evidenced by the ^{13}C NMR spectrum of VII (Fig. 1), can be explained by the directing effect of Pd—N coordination, which results in the formation of a vinylpalladium species containing a five-membered chelate ring. Formation of VII from the species XXXVIII can occur by hydrogen abstraction from sodium methoxide, as has been described by Helquist et al. for the $Pd(PPh_3)_4$-catalyzed formation of arenes from an aryl halide and sodium methoxide [18].

The nickel-catalyzed addition reaction

The Ni-catalyzed addition of MeMgBr to the diarylacetylenes, IV—VI, proceeds not only with complete stereospecificity (*cis* addition [12]) but also with complete regiospecificity. The reaction is thought to occur via the initial formation of a nickel(0) species [19] (eq. 10), which coordinates to the diarylacetylene forming a stable π-complex.



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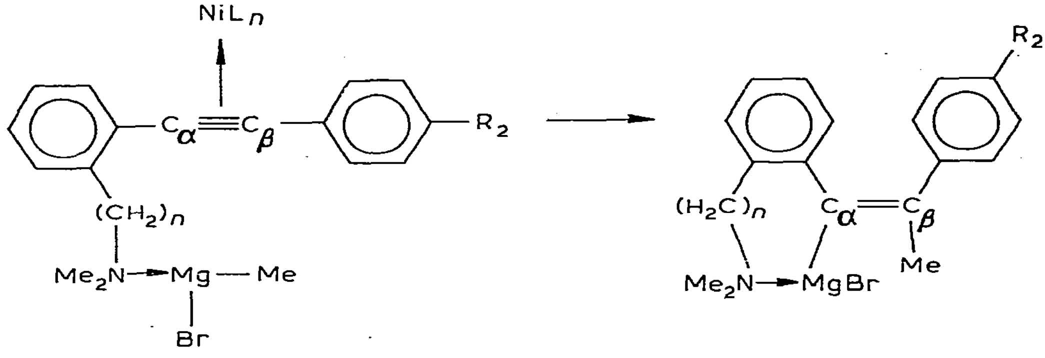


(XXXIX)

Fig. 3.

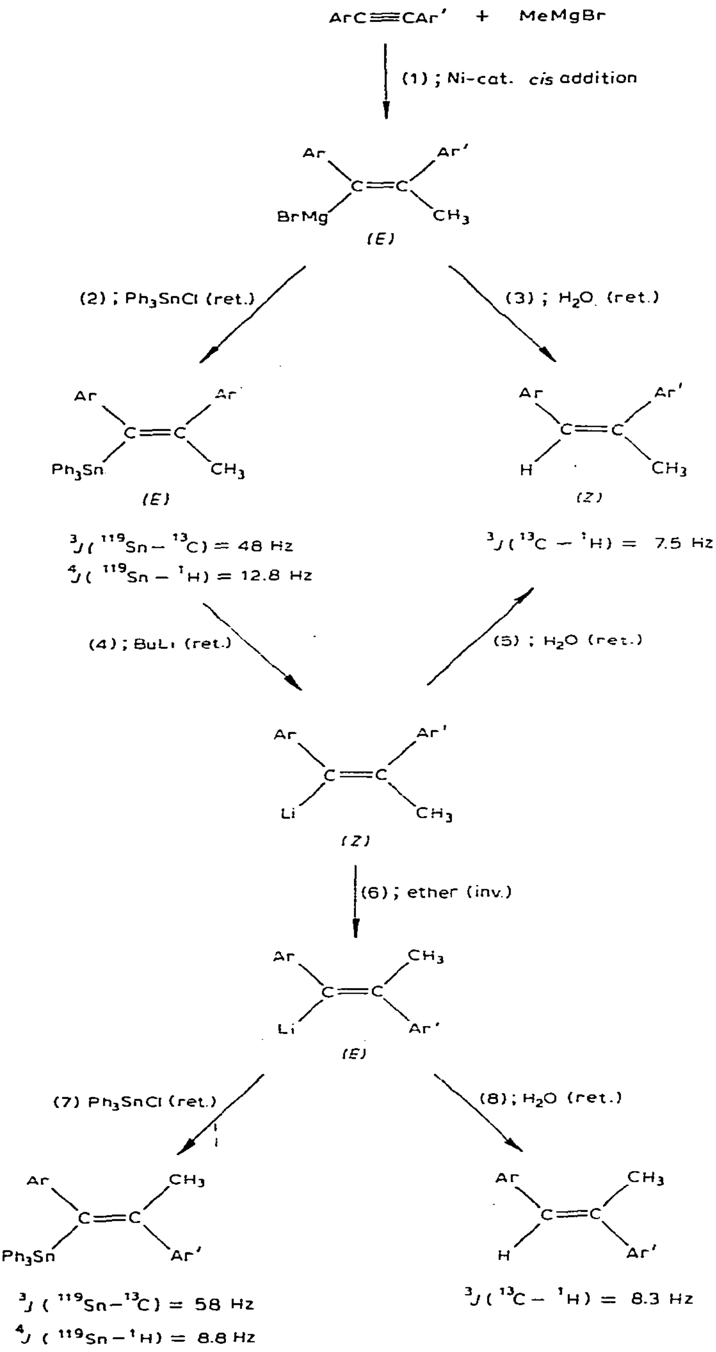
Attack of MeMgBr may proceed via an intermediate of the type XXXIX, where both the acetylenic bond and the Mg—C bond are activated as result of complex formation. Such an intermediate accounts for the observed regiospecificity. A study of models clearly shows that in the intermediate complex the orientation of the Mg—C and C≡C bond favours nucleophilic attack of the methyl group on the C_β atom. Moreover, formation of a five ($n = 0$) or six ($n = 1$) membered chelate ring, resulting from the attachment of Mg to C_α, will be favoured over the alternative formation of a six- or seven-membered chelate ring resulting from attachment of Mg to C_β.

The transmetallation reactions

In our work, we started with the configurationally pure *E*-(1,2-diaryl-1-propenyl)magnesium bromide compounds IX—XII obtained by the *cis* addition of MeMgBr to the diarylacetylenes (cf. previous section). The *Z*-(1,2-diaryl-1-propenyl)lithium compounds were obtained in two subsequent transmetallation steps 2 and 4 (see Scheme 1), which in analogy with other transmetallations of vinylmetal compounds reported in the literature (e.g. Zr → Cu [20], Hg → Li [11], Sn → Li [10]) are expected to occur with retention of configuration. Indeed, hydrolysis of the *E*-(1,2-diaryl-1-propenyl)magnesium bromide and the *Z*-(1,2-diaryl-1-propenyl)lithium compound provided the configurationally pure *Z*-1,2-diaryl-1-propene compound (route 3, 5 respectively). Complete inversion of configuration of the *Z*-(1,2-diaryl-1-propenyl)lithium isomers occurred in ether (route 6). The transmetallation reaction of the *E*-(1,2-diaryl-1-propenyl)lithium isomers with Ph_3SnCl (route 7) yielded the *Z*-(1,2-diaryl-1-propenyl)triphenyltin compounds with retention of configuration, while hydrolysis (route 8) gave the *E*-1,2-diaryl-1-propenes with retention of configuration.

In principle, the conversion of the *E*-(1,2-diaryl-1-propenyl)magnesium bromide into the *Z*-(1,2-diaryl-1-propenyl)lithium compounds might proceed by two successive steps involving inversion of configuration [9]. However, this possibility is excluded by a comparison of the spectroscopic data for the *E*-

SCHEME 1



and *Z*-(1,2-diaryl-1-propenyl)triphenyltin isomers and the *Z*- and *E*-1,2-diaryl-1-propenes. We found that $^3J(^{119}Sn—^{13}C)$ for the *E*-isomers, in which the tin atom and the methyl group are in a *cis* position, is smaller than for the *Z*-isomers, which have the tin atom and the methyl group in the *trans* position (see Scheme). Similarly, for the Z-1,2-diaryl-1-propenes, in which the coupling nuclei are in the *cis* position, $^3J(^1H—^{13}C)$ is smaller than $^3J(^1H—^{13}C)$ for the E-1,2-diaryl-1-propenes having the coupling nuclei in *trans* position.

The opposite order is observed when the coupling between the nuclei takes place over four bonds: i.e., $^4J(^{119}Sn—^1H)$ for the E-isomers > $^4J(^{119}Sn—^1H)$ for the Z-isomers. The observed sequence ^3J *cis* < ^3J *trans* and ^4J "*cis*" > ^4J "*trans*" is in accordance with the stereochemical assignments based on NMR spectroscopy previously reported in the literature {$^3J(^1H—^{13}C)$ [21], $^3J(M—^1H)$ for alkenyl derivatives of Sn, Hg, Tl and Pb [22] and $^3J(^{119}Sn—^{13}C)$ [23] as well as $^4J(^{199}Hg—^1H)$ [24,25]}.

The present results show that the Me_2N- and Me_2NCH_2-substituted (1,2-diaryl 1-propenyl)lithium compounds have been obtained configurationally pure. Moreover, unambigious stereochemical assignments have been made.

Structural aspects of the E-(1,2-diaryl-1-propenyl)lithium compounds

A cryoscopic molecular weight determination points to pure E-XXVI being a dimer in benzene. The ^1H NMR spectrum at room temperature is surprisingly simple, with a sharp singlet for the NMe_2 group at 2.01 ppm. However, this does not allow any conclusions to be drawn about N—Li coordination (cf. the strong N—Li coordination in 5-Me-2-$Me_2NCH_2C_6H_3Li$ tetramer [26]). Table 3 shows the change in chemical shift for the NMe_2 protons (for XXV) upon addition of increasing amounts of diethyl ether. The CH_2 and CH_3 resonances of diethyl ether are shifted upfield as a result of the coordination to lithium. Comparable values for δ CH_2 [2.72 (Cu); 2.85 (Au) ppm] and δ CH_3 [0.64 (Cu); 0.75 (Au) ppm] have been observed for coordinated diethyl ether in the complexes $(4\text{-}MeC_6H_4)_4M_2Li_2 \cdot 2\ Et_2O$ (M = Cu, Au) [27].

A complex in which half a mole of diethyl ether is coordinated to one mole of E-XXVI has been isolated from a diethyl ether solution. The observed composition points to a polynuclear structure $(Vi_2Li_2 \cdot OEt_2)_n$.

Although conclusive structural evidence is not available we propose for compound E-XXVI a binuclear structure with bridging propenyl groups (see Fig. 4). This proposal is supported by structural information which is available

TABLE 3

^1H NMR SPECTRAL DATA (C_6D_6, TMS INTERNAL, δ (ppm)) FOR E-[1-(2-N,N-DIMETHYLAMINOPHENYL)-2-PHENYL-1-PROPENYL]LITHIUM (XXV) IN THE PRESENCE OF VARIOUS AMOUNTS OF DIETHYL ETHER

Mol. ratio XXV/diethyl ether	δ (ether)		δ (XXV)	
	CH_3	CH_2	NCH_3	$C{=}CCH_3$
Pure XXV [a]			2.13	2.17
1/0.4	0.58	2.83	2.22	2.22
1/0.75	0.73	2.95	2.28	2.25
1/1.2	0.87	3.05	2.30	2.27
Pure ether [a]	1.01	3.25		

[a] In C_6D_6.

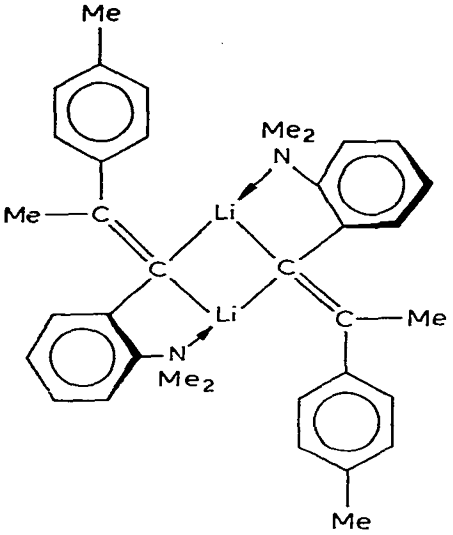


Fig. 4.

for organolithium compounds. The presence of multicenter bonded organo groups has, for example, been confirmed by X-ray crystallography for Me_4Li_4 [28], Et_4Li_4 [29] and for cyclohexyllithium hexamer [30]. Oliver et al. have recently shown the presence of bridging butenyl ligands in $(t\text{-}BuCHCH)_2Al_2(i\text{-}Bu)_4$ [31].

The lack of solubility of *E*-XXVII in organic solvents prevents it from being studied by spectroscopic techniques and molecular weight determinations.

Experimental

General

All reactions were carried out under dry oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled under nitrogen before use.

The following compounds were prepared according to literature methods: cuprous bromide [32], tetrakis(triphenylphosphine)palladium(0) [33], bis(triphenylphosphine)nickel dichloride [34], 2-bromo-*N*,*N*-dimethylaniline [35], sodium phenolate [36] and 4-methylphenylacetylene [37]. 2-Bromoaniline, *N*,*N*-dimethylbenzylamine, phenylacetylene, diphenylacetylene, sodium methanolate and n-butyllithium in hexane were commercially available.

Melting points were determined on a Reichert melting point microscope and are uncorrected. Mass spectra were obtained from a Finnigan 3100 D gaschromatograph/mass spectrometer. ^1H NMR spectra were recorded on a Varian Associates T-60 spectrometer, ^{13}C and ^7Li NMR spectra on a Bruker WH-90 spectrometer.

Elemental analyses were carried out in this Institute under the supervision of Mr. W.J. Buis.

Synthesis of 2-iodo-N,N-dimethylbenzylamine

n-Butyllithium (300 mmol, 1.5 *N* in hexane) was added to a solution of *N*,*N*-dimethylbenzylamine (311 mmol) in diethyl ether (500 ml), resulting in the precipitation of 2-lithio-*N*,*N*-dimethylbenzylamine. Upon slow addition (after 20 h) of solid iodine (300 mmol) to the suspension a clear solution was obtained. Washing with water, drying over $MgSO_4$ and evaporation of the solvent gave a liquid residue. Distillation in vacuo afforded pure 2-iodo-*N*,*N*-dimethylbenzylamine in 66% yield. B.p. 107°C/8 mmHg. NMR spectrum (CCl_4, TMS internal, δ(ppm)): 3.40 (NCH_2), 2.25 (NCH_3).

Synthesis of the diarylacetylenes IV—VI

N,N-Dimethyl-2-[phenylethynyl]benzenamine (IV). A mixture of 2-bromo-*N*,*N*-dimethylaniline (53.5 mmol), phenylacetylene (58.7 mmol), sodium phenolate (60.3 mmol) and tetrakis(triphenylphosphine)palladium (2.6 mmol) in *N*,*N*-dimethylformamide (200 ml) was heated at 100°C for 2 h. After removal of the solvent by vacuum evaporation, the residue was extracted with diethyl ether. A yellow solid remained. The extract was thoroughly washed with water, dilute NaOH and water, followed by extraction with dilute HCl (400 ml, 4 *N*, 3 times). After neutralization with dilute NaOH, the mixture was extracted with diethyl ether. This extract was washed with water, dried over $MgSO_4$ and evaporated, giving a yellow oil, which solidified on standing. Recrystallization from methanol/water gave yellow crystals of IV (80% yield). M.p. 45—48°C. NMR (C_6D_6, TMS internal, δ (ppm)): 2.73 (NCH_3).

N,N-Dimethyl-2-[(4-methylphenyl)ethynyl]benzenamine (V). The same procedure was followed as described above for IV, starting with 2-bromo-*N*,*N*-dimethylaniline (433 mmol), 4-methylphenylacetylene (433 mmol), sodium phenolate (431 mmol) and tetrakis(triphenylphosphine)palladium (6.9 mmol) in *N*,*N*-dimethylformamide (700 ml), with a reaction temperature of 75°C and a reaction time of 26 h. V was isolated as a faintly red oil (82% yield). NMR (C_6D_6, TMS internal, δ (ppm)): 2.00 (CH_3), 2.75 (NCH_3).

N,N-Dimethyl-2-[(4-methylphenyl)ethynyl]benzylamine (VI). The reaction of 2-iodo-*N*,*N*-dimethylbenzylamine (191 mmol), 4-methylphenylacetylene (263 mmol), sodium phenolate (264 mmol) and tetrakis(triphenylphosphine)-palladium (3.5 mmol) in *N*,*N*-dimethylformamide (500 ml) was carried out at 100° C with a reaction time of 4 h. The work-up procedure was the same as described above for IV. Destillation gave VI as a colourless oil (78% yield). B.p. 152°C/0.27 mmHg. NMR (C_6D_6, TMS internal, δ (ppm)): 3.73 (NCH_2), 2.20 (NCH_3), 2.00 (CH_3).

Synthesis of 1-methyl-2-phenyl-3-[1-phenyl-2-(2-N,N-dimethylaminophenyl)-ethenyl]indole (VII)

A mixture of 2-bromo-*N*,*N*-dimethylaniline (123 mmol), phenylacetylene (128 mmol), sodium methanolate (157 mmol) and tetrakis(triphenylphosphine)-palladium (7.5 mmol) in *N*,*N*-dimethylformamide (500 ml) was heated at 100°C for 3.5 h. After addition of water at room temperature, the mixture was extracted with diethyl ether. The combined ether layers were washed with water and extracted with acid (100 ml 4 *N* HCl, 4 times). Evaporation of the remaining diethyl ether solution afforded an oil which solidified partly on standing.

Recrystallization of the solid from light petroleum (60—80°C) afforded 1-methyl-2-phenyl-3-[1-phenyl-2-(2-*N*,*N*-dimethylaminophenyl)ethenyl]indole (VII) as a white powder in 25% yield. M.p. 147—148°C. Anal.: Found: C, 86.97; H, 6.72; N, 6.55. $C_{31}H_{28}N_2$ calcd.: C, 86.88; H, 6.59; N, 6.56%. ^{1}H NMR (CCl_4, TMS internal, δ (ppm)): 2.75 ($C{=}CCH_3$), 3.63 (NCH_3). ^{13}C NMR ($CDCl_3$, TMS internal, δ (ppm)): 31.0 [NCH_3]; 44.1 [$N(CH_3)_2$]. Quantitative analysis of the ^{13}C NMR spectrum, recorded after addition of chromium(III) acetylacetonate for promoting the relaxation, gives a total number of carbon atoms which agrees with the proposed structure *. Mass spectral data (*m/e*): 428 (M^+), 308, 296, 220, 132, 120, 118, 91, 77 (high intensity fragment ions); calcd. for $C_{31}H_{28}N_2$: 428.

Synthesis of the E-(1,2-diaryl-1-propenyl)triphenyltin compounds XVII—XVIII

E-[1-(2-N,N-Dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]triphenyltin (XVIII). The synthesis of XVIII is given as a typical example. A solution of methylmagnesium bromide in diethyl ether (302 ml, 1.35 *N*) was added to II (340 ml) and $NiCl_2(PPh_3)_2$ (33.6 mmol) in THF (500 ml). The catalyst dissolves with liberation of heat and evolution of gas and the initially colourless solution became brown-red. After stirring at room temperature for 18 h and at reflux temperature for 5 h the diarylacetylene (II) had been consumed (according to NMR analysis). A solution of triphenyltin chloride (521 mmol) in THF (500 ml) was added and stirring was continued for 8 h at reflux temperature. Thereafter the solvent was removed by vacuum evaporation. Addition of a small amount of diethyl ether to the residue afforded a first crop of impure XIV. A second amount was obtained after addition of methanol. Further amounts were obtained by repeating the process of evaporation, diethyl ether and methanol addition. Recrystallization of the crude material from acetone/methanol afforded XVIII as white crystals (36%). M.p. 176—177°C. Anal.: Found: C, 72.11; H, 6.06; N, 2.33; Sn, 19.07. $C_{36}H_{35}NSn$ calcd.: C, 72.02; H, 5.88; N, 2.33; Sn, 19.77%. For NMR data see Table 1.

E-[1-(2-N,N-Dimethylaminophenyl)-2-phenyl-1-propenyl]triphenyltin (XVII). White crystalline solid. M.p. 129—132°C. Anal.: Found: C, 71.49; H, 5.77; N, 2.43; Sn, 20.05. $C_{35}H_{33}NSn$ calcd.: C, 71.70; H, 5.67; N, 2.39; Sn, 20.24%. For NMR data see Tables 1 and 2.

E-[1-(2-N,N-Dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propenyl]-triphenyltin (XIX). White crystalline solid. M.p. 125—126.5°C. Anal.: Found: C, 72.26; H, 6.05; N, 2.29; Sn, 19.60. $C_{37}H_{37}NSn$ calcd.: C, 72.33; H, 6.07; N, 2.28; Sn, 19.32%. For NMR data see Table 1.

E-[1,2-Diphenyl-1-propenyl]triphenyltin (XX). White crystalline solid. M.p. 135—136.5°C. Anal.: Found: C, 72.98; H, 5.29; Sn, 21.27. $C_{33}H_{28}Sn$ calcd.: C, 72.96; H, 5.20; Sn, 21.85%. For NMR data see Table 1.

Synthesis of the Z-(1,2-diaryl-1-propenyl)lithium compounds XXI and XXII

Z-[1-(2-N,N-Dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]lithium (XXII). The synthesis of XXII is given as a typical example. A solution of n-butyllithium in hexane (4.0 ml, 1.3 *N*) was added to solid XVIII (5.25 mmol)

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* We thank Mr. J. Marsman for this measurement.

in pentane (40 ml). The mixture was stirred for 4 h after which XVIII had disappeared and a yellow suspension had formed. This suspension was centrifuged, the supernatant was removed by decantation. The residue was washed with pentane (50 ml), and after centrifugation and removal of the solvent by decantation the precipitate was dried in high vacuum to give XXII as a yellow solid in quantitative yield. The isomeric purity (>98%) was determined by hydrolysis (see below).

Z-[1-(2-N,N-Dimethylaminophenyl)-2-phenyl-1-propenyl]lithium (XXI). Starting from XVII this compound was obtained as a yellow pentane-insoluble solid.

Hydrolysis of the Z-(1,2-diaryl-1-propenyl)lithium compounds XXI and XXII. Synthesis of the diarylpropenes XIII and XIV

Z-1-(2-N,N-Dimethylaminophenyl)-2-(4-methylphenyl)-1-propene (XIV). The synthesis of XIV is given as a typical example. Dilute HCl (1 *N*, 10 ml) was added to a suspension of XXII (5.25 mmol) in 30 ml of pentane. The precipitate disappeared immediately after addition, while the pentane solution became colourless. The solution was neutralized with dilute NaOH (4 *N*). The organic layer was washed with water, dried over $MgSO_4$ and evaporated, yielding XIV as an oil. Isomeric purity >98% (according to NMR analysis). Similarly deuterolysis afforded 1-D-XIV. For NMR data see Tables 1 and 2.

Z-1-(2-N,N-Dimethylaminophenyl)-2-phenyl-1-propene (XIII). Using the same method as described above for XIV, hydrolysis of XXI gave XIII as a colourless oil. For NMR data see Tables 1 and 2.

XIII and XIV have also been obtained by hydrolysis of the appropriate *E*-(1,2-diaryl-1-propenyl)magnesium bromides IX and X, by the same procedure as described for the synthesis of XIV from XXII.

Synthesis of the E-(1,2-diaryl-1-propenyl)lithium compounds XXV—XXVI

E-[1-(2-N,N-Dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]lithium (XXVI). The synthesis of XXVI is given as a typical example. Benzene (70 ml) was added to XXII (3.8 mmol). The resulting suspension was stirred for 4 h when a clear solution was obtained. Benzene was removed by vacuum evaporation. The yellow residue was washed with pentane and dried in high vacuum, affording pure XXVI. For NMR data see Table 1. Mol. weight (cryoscopic in benzene): 447 (mean), *n*: 1.74.

Addition of diethyl ether to XXII results similarly in the quantitative formation of XXVI. However, isolation by evaporation of the diethyl ether yields a product containing 0.5 mol equivalent of diethyl ether. NMR (C_6D_6, TMS internal, δ (ppm)): 2.30 (NCH_3 and 4-CH_3 or $C{=}CCH_3$), 2.22 (4-CH_3 or $C{=}CCH_3$), 0.68 (CH_3-ether), 2.05 (CH_2-ether).

The isomeric purity of the compound XXVI (>98%) has been determined by NMR analysis of the hydrolysis products (see below).

E-[1-(2-N,N-Dimethylaminophenyl)-2-phenyl-1-propenyl]lithium (XXV). Prepared by addition of benzene or diethyl ether to XXI in the same way as described above for XXVI. For NMR data see Table 1.

Synthesis of the E-1,2-diaryl-1-propenes XXIX and XXX

E-1-(2-N,N-Dimethylaminophenyl)-2-(4-methylphenyl)-1-propene (XXX). Addition of water (7 ml) to a solution of XXVI (4.8 mmol) in diethyl ether (50 ml) results in immediate discolouration of the solution. After stirring for 15 min the ether layer was separated, washed with water and dried over $MgSO_4$. Removal of the solvent by vacuum evaporation afforded XXX (83%) as a colourless oil. Isomeric purity >98% (according to NMR). For NMR data see Tables 1 and 2.

E-1-(2-N,N-Dimethylaminophenyl)-2-phenyl-1-propene (XXIX). XXIX was prepared by addition of water to a diethyl ether solution of XXV by the same procedure as described above for XXX. For NMR data see Tables 1 and 2.

Reaction of E-[1-(2-N,N-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propenyl]triphenyltin (XIX) with n-BuLi. Synthesis of the Z- and E-(1,2-diaryl-1-propenyl)lithium compounds XXIII and XXVII, respectively, and the corresponding Z- and E-1,2-diaryl-1-propenes XV and XXXI, respectively

A solution of n-butyllithium in hexane (2.9 ml, 1.3 *N*) was added to solid XIX (3.74 mmol) in the presence of pentane (50 ml). After three minutes the reaction with XIX was complete and a clear solution was obtained. Hydrolysis of a sample gave pure *Z*-1-(2-*N*,*N*-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propene (XV) resulting from pure pentane-soluble *Z*-[1-(2-*N*,*N*-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propenyl]lithium (XXIII). For NMR data of XV see Table 1. XV has similarly been obtained by hydrolysis of the *E*-(1,2-diaryl-1-propenyl)magnesium bromide compound XI.

The 1,2-diaryl-1-propenyllithium compound XXIII is configurationally unstable in pentane. Inversion of configuration has been followed by NMR spectroscopy. Aliquots of the above mentioned pentane solution were taken at different time intervals and hydrolyzed. The following XV/XXXI ratios were measured: 7.5/1 (after 15 min); 3.8/1 (32 min); 2.1/1 (45 min); 1/9.3 (2.5 h). After 1 h a precipitate was formed. After 4 h this precipitate was isolated after centrifugation, washed with pentane and finally dried in high vacuum giving pure *E*-1-(2-*N*,*N*-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propenyllithium (XXVII) as a yellow pentane- and ether-insoluble solid. Addition of water to XXVII in the presence of pentane afforded pure *E*-1-(2-*N*,*N*-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propene (XXXI) as a colourless oil. For NMR data see Table 1.

Reaction of E-(1,2-diphenyl-1-propenyl)triphenyltin (XX) with BuLi. Synthesis of E-(1,2-diphenyl-1-propenyl)lithium (XXIV) and E-1,2-diphenyl-1-propene (XXXII)

n-Butyllithium in hexane (5.46 mmol) was added to *E*-(1,2-diphenyl-1-propenyl)triphenyltin (XX) suspended in 50 ml of pentane. After 4 h with continuous stirring a yellow precipitate appears, while XX is still present. After 24 h the mixture was centrifuged (2000 c/s, 20 min). After decantation of the supernatant the yellow solid was washed with 50 ml of pentane. After centrifugation and decantation of the washing liquid, the precipitate was high-vacuum dried, yielding XXIV as a yellow solid.

Addition of diethyl ether gives a clear yellow solution, which discolours on addition of water. The resulting ether solution gives after washing with water, drying over $MgSO_4$ and evaporation *E*-1,2-diphenyl-1-propene (XXXII), which according to NMR analysis is configurationally pure. NMR (CCl_4, TMS, internal, δ (ppm)): 2.29 (d, *J* (C=CMe) 1.3 Hz) (see ref. 12).

Oxidative cleavage of the C=C double bond in XIV and XXXI

The reaction of XXXI with potassium permanganate is given as a typical example. A solution of potassium permanganate (12.7 mmol) in water (50 ml) was added to a solution of *E*-1-(2-*N*,*N*-dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propene (XXXI, 3.77 mmol) in acetone (20 ml). After stirring for 2 h the mixture was acidified and extracted with diethyl ether. The diethyl ether solution was washed with water, dried over $MgSO_4$ and evaporated. NMR and mass spectral analysis showed the exclusive presence of 4-methylacetophenone. NMR (C_6D_6, TMS internal, δ (ppm)): 2.03, 2.15, 6.84(d) and 7.66(d).

The same result was obtained when XIV was used instead of XXXI.

Synthesis of the Z-(1,2-diaryl-1-propenyl)triphenyltin compounds XXXIII—XXXVI

Z-[1-(2-N,N-Dimethylaminomethylphenyl)-2-(4-methylphenyl)-1-propenyl]-triphenyltin (XXXV). The synthesis of XXXV is given as a typical example. A solution of triphenyltin chloride (2.59 mmol) in diethyl ether (20 ml) was added to a suspension of XXVII (2.4 mmol) in diethyl ether (50 ml) (XXV and XXVI are soluble in ether). After stirring for 3 h the ether solution was washed with water and extracted with acid (4 *N* HCl). The acid extract was neutralized with dilute NaOH and extracted with diethyl ether. The diethyl ether solution was washed with water, dried over $MgSO_4$ and evaporated giving XXXV as a white solid (62% yield). M.p. 140—142°C. Anal.: Found: C, 72.31; H, 6.10; N, 2.13; Sn, 19.29. $C_{37}H_{37}NSn$ calcd.: C, 72.33; H, 6.07; N, 2.28; Sn, 19.32%. For NMR data see Table 1.

Z-[1-(2-N,N-dimethylaminophenyl)-2-phenyl-1-propenyl]triphenyltin (XXXIII). White crystals. M.p. 136.5—137.5°C. Anal.: Found: C, 71.61; H, 5.67; N, 2.36; Sn, 20.31. $C_{35}H_{33}NSn$ calcd.: C, 71.70; H, 5.67; N, 2.39; Sn, 20.24%. For NMR data see Tables 1 and 2.

Z-[1-(2-N,N-Dimethylaminophenyl)-2-(4-methylphenyl)-1-propenyl]triphenyltin (XXXIV). White crystals. M.p. 128—130°C. Anal.: Found: C, 72.17; H, 5.79; N, 2.36; Sn, 19.94. $C_{36}H_{35}NSn$ calcd.: C, 72.02; H, 5.88; N, 2.33; Sn, 19.77. For NMR data see Table 1.

Z-(1,2-Diphenyl-1-propenyl)triphenyltin (XXXVI). White crystals. M.p. 107—109°C. Anal.: Found: C, 71.95; H, 5.36; Sn, 21.33. $C_{33}H_{28}Sn$ calcd.: C, 72.96; H, 5.20; Sn, 21.85%. For NMR data see Table 1.

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