reaction 1, and a related mechanism may apply. The reactivity of 1 with HCl (as with H_2) is in marked contrast to the reaction of $RuCl(COEt)(CO)(PPh_3)_2$ with HCl, which gives the hydroxycarbene complex $RuCl_2(CO)(C(OH)Et)(PPh_3)_2$;[30] i.e., protonation occurs at the acyl oxygen rather than carbon as seen with 1. Again, differences in electronegativity of the alkyl and alkenyl groups might account for the reactivity differences. Notably, en route to formation of 7 in reaction 10, a Ru intermediate with a ^{31}P singlet at 33.0 ppm was observed, this converting to the 17.0 ppm singlet characteristic of 7; however, we have been unable to detect any associated proton of a carbene hydroxide.[30]

Conclusions

The kinetics of the solution hydrogenolysis of the six-coordinate Ru(II) acyl complex $RuCl(COR)(CO)_2(PPh_3)_2$, where R = norbornenyl, to give $RuHCl(CO)_2(PPh_3)_2$ and RCHO reveal that the process occurs via dissociation of a PPh_3 ligand, followed by reaction of the resulting five-coordinate intermediate with H_2; the same pathways pertain to some cobalt acyl systems, studied previously because of their importance in hydroformylation. Activation parameters measured for the Ru system in DMA and toluene are very different; the former reflect a strongly solvated transition state, while the latter are consistent with little involvement of toluene in the transition state and then imply an upper value of 128 kJ mol^{-1} for the solution Ru–P bond dissociation energy (for mutually trans-disposed phosphines). Relative reactivities of the kinetic intermediates toward H_2 and PPh_3, and comparison with the behavior of a related Ru(II)–propionyl complex, reveal the importance of electronic effects in the hydrogenolysis step, although it is difficult to distinguish between an oxidative-addition/reductive-elmination ($+H_2$, $-RCHO$) pathway and a concerted four-center transition-state (heterolytic H_2 activation) pathway. The reaction of the norbornenoyl complex with HCl, to give $RuCl_2(CO)_2(PPh_3)_2$ and RCHO, contrasts with that of the propionyl species, which gives a hydroxycarbene derivative.

An incidental finding is that $RuHCl(CO)_2(PPh_3)_2$ catalyzes the H_2-hydrogenation of the norbornene aldehyde to the norbornane aldehyde, albeit slowly at 1 atm of H_2.

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New (Diarylgermyl)lithiums

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The new (diarylgermyl)lithiums R_2GeHLi (2; R = phenyl, mesityl) were prepared in good yields by hydrogermolysis reactions of *tert*-butyllithium in THF. The stability of compounds 2 depends on the nature of the R group and the solvent. For R = Ph, in the presence of an amine (Et_3N or Et_2NMe), the same reaction leads to the formation of the polygermanes $H(GePh_2)_nH$ (n = 2–4). The characterization of compounds 2 by IR and ^1H and ^{13}C NMR spectroscopy and their complexation with a crown ether are also reported. They are characterized by deuterolysis and alkylation reactions (with MeI and Me_2SO_4). Their germylation reactions with >Ge–Cl reagents constitute a convenient way for synthesizing organohydropolygermanes. Compounds 2 also react with acyl chlorides to give new germyl ketones, $R_2HGeCOR'$, and the unexpectedly stable β-germyl diketone $Ph_2Ge(COMes)_2$. They add easily to the carbonyl group of aromatic ketones or aldehydes, leading to the corresponding germylated alcohols.

Introduction

The organogermyl alkali-metal compounds R_3GeM (M = Li, Na, K) are very useful in organometallic synthesis, for example for the germylation of organic halides, metal halides, carbonyl compounds, etc.[1-4]

Among them, however, there are only a few reports regarding organogermyl alkali-metal compounds.[3-5] In the case of the lithium series, the only known (organogermyl)lithiums have been postulated in the reaction of organodihydrogermanes with RLi compounds (R = Me, Bu, Ph);[6] however, in these reactions the authors have always observed competition between metalation and alkylation reactions.[3]

In this paper, we report a modification of the hydrogermolysis procedure that allows a more specific synthesis of (diarylgermyl)lithium compounds stabilized by solvent and steric effects.

Results and Discussion

Preparation of R_2GeHLi. Recently, we have reported the synthesis in good yields of stable R_2GeHLi in THF solution from the reaction of R_2GeH_2 with t-BuLi:[7]

$$\underset{1}{R_2GeH_2} + t\text{-BuLi} \xrightarrow[\text{-BuH}]{\text{THF},\ T\ °\text{C}} \underset{2}{R_2GeHLi} \qquad (1)$$

2a, R = Ph (−40 °C, 95%);
2b, R = Mes (−20 °C, 84%)

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Table I. IR and ^{1}H NMR Data for (Diarylgermyl)lithiums and the Starting Organogermanes

compd	ν(Ge–H),[a] cm^{-1}	^{1}H NMR,[b] ppm: δ(Ge–H)	^{1}H NMR,[b] ppm: $\delta(C_6H_5)$ or $\delta(C_6H_2)$
Ph_2GeH_2 (**1a**)	2024	5.00	7.10–7.50
Ph_2GeHLi (**2a**)	2012	4.60	6.80–7.05, 7.45–7.60
Mes_2GeH_2 (**1b**)	2040	5.00	6.80
Mes_2GeHLi (**2b**)	2020	4.40	6.45
Mes_2GeH_2 (**1b**)	2060[c]		
Mes_2GeHLi (**2b**)	2000[c]		

[a] Spectra were recorded in THF/pentane solution unless otherwise noted. [b] In THF-d_8/pentane solution. [c] In Nujol mull.

These metalation reactions require the use of a slight excess of *t*-BuLi (20–40%) and a low-temperature procedure to avoid competitive alkylation reactions. In the case of (organosilyl)lithium, Tilley and co-workers have recently isolated $Mes_2HSiLi(THF)_2$[8] as off-white crystals. Compounds **2** are more difficult to crystallize from the solution but were completely characterized by ^{1}H and ^{13}C NMR spectroscopy and their reactivity. In solution, their stability depends on the solvent used and the nature of R. Compound **2b** is stable in such solvents as pentane, THF, and amines. Compound **2a** slowly decomposes in THF at 20 °C within 24 h. This decomposition is more effective in the presence of an amine (Et_3N or Et_2NMe) and gives di-, tri-, and tetragermyllithiums.[6,9] The nature of these polygermanes depends mainly on the reaction time. The selective synthesis of di-, tri-, and tetragermanes can be achieved and monitored by GC analysis.

$$Ph_2GeH_2 + t\text{-}BuLi \xrightarrow[\text{-BuH, -LiH}]{Et_3N} Ph_2HGe(GePh_2)_nGeLiPh_2 \xrightarrow{H_2O} \underset{\mathbf{3}}{Ph_2HGe(GePh_2)_nGeHPh_2} \quad (2)$$

$$n = 0\text{–}2$$

If a large excess of *t*-BuLi (>100%) is used, diphenylgermane gives (diphenylgermyl)dilithium in good yield:

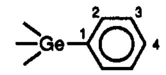
$$\underset{\mathbf{1a}}{Ph_2GeH_2} + 2t\text{-}BuLi \xrightarrow[\text{-BuH}]{\text{THF, -40 °C}} Ph_2GeHLi\ (37\%) + \underset{\mathbf{4}}{Ph_2GeLi_2}\ (56\%) \quad (3)$$

The yields were determined by alkylation of the Ge–Li bond with use of MeI.

The formation of **4** has been reported[10] only in the reaction of Ph_2GeH_2 with Li in HMPA, with use of a procedure similar to that described for the preparation of Ph_2GeK_2. Recently a new synthesis of Et_2GeLi_2 has been described in the literature.[11]

IR, ^{1}H, and ^{13}C NMR parameters of (diarylgermyl)lithiums are summarized in Tables I and II, together with those of the starting materials.

Table II. ^{13}C NMR Data for (Diarylgermyl)lithiums and Diarylgermanes

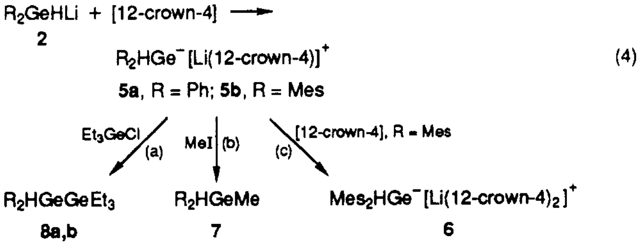


compd	solvent[a]	C_1	C_2	C_3	C_4	*o*-CH_3	*p*-CH_3
Ph_2GeH_2	THF	135.0	136.1	129.4	130.1		
Ph_2GeHLi	THF	159.4	137.6	127.0	124.1		
Ph_2GeHLi	TDA-1	164.9	136.9	125.9	122.3		
Mes_2GeH_2	THF	131.9	144.4	129.5	139.4	24.2	21.5
Mes_2GeHLi	THF	153.9	144.4	127.2	132.6	24.1	21.5
Mes_2GeHLi	TDA-1	159.3	143.9	125.9	130.3	25.7	21.1

[a] TDA-1 is $N(CH_2CH_2OCH_2CH_2OCH_3)_3$.

The IR data show a ν(Ge–H) displacement to high frequency due to the inductive effect (+I) of the alkali metal. However, the $\Delta\nu(M_{14}\text{–}H)$ value observed between R_2GeH_2 and R_2HGeLi (Nujol mull) is about half of that observed for the silicon series.[8] The chemical shifts of Ge–H and the aromatic protons in **2a** and **2b** in comparison with those of the corresponding diarylgermanes are shifted slightly to a lower field ($\Delta\delta \approx 0.4$–0.6 ppm). These observed shifts correlate with a negative charge at the germanium. The ^{13}C NMR values seem to confirm this result. The ipso ^{13}C resonance for **2a** and **2b** is shifted drastically to lower field while the para ^{13}C resonance is shifted slightly to lower field. The chemical shifts of the meta and para carbons are least affected by lithiation of the arylgermanes. These results are similar to those previously reported[5,10,12] for other organometallic compounds; they can be attributed to a polarization of the phenyl ring resulting in decreased electron density at the ipso carbon. Such polarization can be caused by a localized negative charge residing on the germanium center, which is consistent with a predominant inductive effect and the absence of a mesomeric (resonance) effect in the germyl anion. An additional feature is the influence of solvent on these chemical shifts (Table II). As previously noted, the chemical shift of the ipso carbon is the most sensitive to interaction with solvent. The dissociation of ion pairs is more effective in polar solvents, and so the negative charge at the germanium is increased.

Complexation of R_2GeHLi. The stabilization of **2** by a complexing reagent was examined with tris(3,6-dioxaheptyl)amine, abbreviated TDA-1, known to stabilize RMgX.[13] We observed only the decomposition of **2** with nucleophilic assistance as described above for R_3N. Treatment of **2** in THF solution with an excess of 12-crown-4 gives a new insoluble complex with 1/1 stoichiometry. When 12-crown-4 is used as solvent, a new ^{1}H NMR signal shifted to low field appears, which is probably due to the formation of a complex with 1/2 stoichiometry[14] (eq 4c).



Germyllithium complexes **5a,b** were isolated as powders sensitive toward hydrolysis. Compound **5b** seems less stable in solution than **5a**, which is probably due to steric

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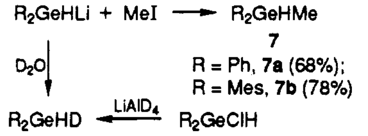
hindrance enhancing its lability. The characterization reactions (eq 4a and 4b) of **5a** occurred in high yields. When R = Mes (compound **5b**), the yields of reactions 4a and 4b were enhanced in comparison with the reactivity of **2** (eq 5).

Reactivity of (Diarylgermyl)lithium. Methyl iodide is a very effective alkylation reagent for the characterization of these organometallic compounds; the reactions proceed at room temperature and lead to the corresponding organogermanes (eq 5).



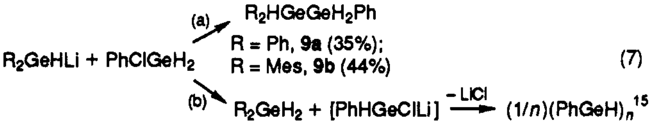
(5)

Deuterolysis of the germanium–lithium bond is effective but can be used only as a qualitative test since exchange reactions, Ge–H/Ge–D, occur.

Compounds **2** react immediately and almost quantitatively at 20 °C with dimethyl sulfate (eq 6).

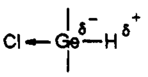
$$\underset{\mathbf{2}}{R_2GeHLi} \xrightarrow[(2)\ H_2O]{(1)\ Me_2SO_4} R_2GeHMe \quad R = Ph,\ \mathbf{7a}\ (95\%);\ R = Mes,\ \mathbf{7b}\ (95\%) \qquad (6)$$

(Organogermyl)lithiums are also very useful intermediates in organometallic synthesis, particularly for the preparation of asymetric hydropolygermanes, which are usually difficult to obtain (eq 7a).

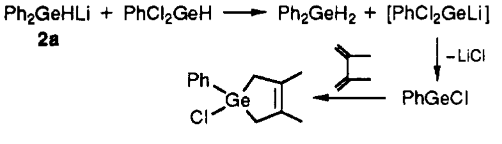


(7)

However, in the case of arylchlorogermanes, the acidic character of the hydrogen atom



leads to a competitive lithiation reaction (eq 7b). The transient (arylchlorogermyl)lithium gives germylene and polygermane through an α-elimination process.[15] This mechanism is supported by the characterization of stabilized phenylchlorogermylene in the reaction between **2a** and phenyldichlorogermane (eq 8).



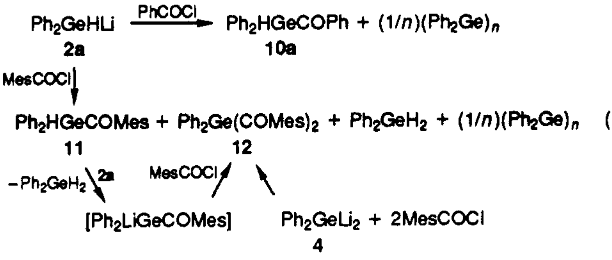
(8)

Phenylchlorogermylene was easily characterized by its 1,4-cycloaddition to 2,3-dimethylbuta-1,3-diene[16] (eq 8).

The reactions of (triorganogermyl)lithium, R_3GeLi, with carboxylic acid chlorides have been used to prepare acylgermanes.[17] The reaction of an excess of benzoyl chloride with **2a** at low temperature products the first-isolated diarylgermyl ketone **10b** (eq 9).

$$\underset{\mathbf{2b}}{Mes_2GeHLi} + PhCOCl \rightarrow \underset{\mathbf{10b}}{Mes_2HGeCOPh} + LiCl \qquad (9)$$

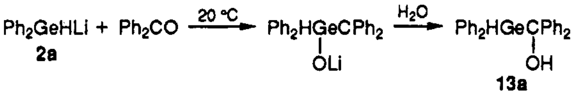
Within the phenyl series, the formation of $(Ph_2Ge)_n$ polymers probably results from partial decomposition of the germyl ketone **10a** (eq 10).



(10)

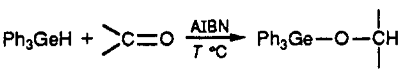
With the more sterically hindered 2,4,6-trimethylbenzoyl chloride, the expected reaction occurs in low yield. We also observed the formation of an unexpected germylated β-diketone, which was formed by diarylation of (diphenylgermyl)dilithium (eq 10) and may be due to the enhancement of the acidic character of the hydrogen attached to germanium in **11**. This results from an attractive effect of the acyl group, allowing a transmetalation reaction (eq 10).

Compound **2a** also adds to the carbonyl group of aromatic ketones, leading to the corresponding germylated alcohols (eq 11).



$$\underset{\mathbf{2a}}{Ph_2GeHLi} + Ph_2CO \xrightarrow{20\ °C} Ph_2HGe\underset{OLi}{C}Ph_2 \xrightarrow{H_2O} \underset{\mathbf{13a}}{Ph_2HGe\underset{OH}{C}Ph_2} \qquad (11)$$

We have not observed any interaction reaction between the germanium–hydrogen bond and the carbonyl group to form alkoxygermanes, which usually occurs through radical initiation or in thermolysis[18] (eq 12).



(12)

In the case of (dimesitylgermyl)lithium (**2b**), steric hindrance inhibits this addition reaction:

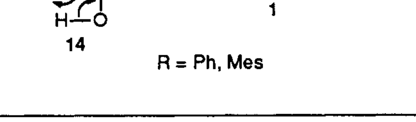
$$n\underset{\mathbf{2b}}{Mes_2GeHLi} + mPh_2CO \xrightarrow[(2)\ H_2O]{(1)\ -40\ °C} H(Mes_2Ge)_2H + (1/n)(Mes_2Ge)_n + Ph_2CHOH + Ph_2CO \qquad (13)$$

Formation of a germylated alcohol is not observed in eq 13, but instead, the unexpected diphenylcarbinol is obtained and also a small quantity of 1,1,2,2-tetramesityldigermane. The formation of these compounds can be explained by a mechanism involving radicals formed by a monoelectronic transfer from the germyllithium **2b** to the ketone as the first step.[4]

With benzaldehyde compounds **2** react at low temperature to form the corresponding germyl alcohols in good yield (eq 14).

$$\underset{\mathbf{2}}{R_2GeHLi} + PhCHO \xrightarrow[(2)\ H_2O]{(1)\ -30\ °C} R_2HGeCHOHPh \quad R = Ph,\ \mathbf{14a};\ R = Mes,\ \mathbf{14b} \qquad (14)$$

Compounds **14** are thermally unstable.[19] They decompose partially above 100 °C to give benzaldehyde and diorganogermanes **1**, according to eq 15.



(15)

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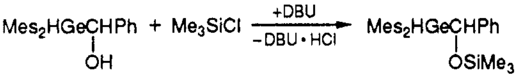
Table III

time	polygermane	yield, %
5 min	$H(GePh_2)_2H$[23]	26
9.5 h	$H(GePh_2)_3H$	46
14 h	$H(GePh_2)_4H$	69

The proposed mechanism (eq 15) is confirmed by the *O*-silylation of the OH group, which gives the stable distillable compound **15** (eq 16).



$$Mes_2HGeCH(OH)Ph + Me_3SiCl \xrightarrow[-DBU\cdot HCl]{+DBU} Mes_2HGeCH(OSiMe_3)Ph \tag{16}$$

15

Concluding Remarks

The presence of two functional sites in compounds **2** (germanium–lithium and germanium–hydrogen bonds) makes them very useful reagents in the synthesis of new organohydropolygermanes and functional organogermanes. Their germylation reactions produce intermediates with low-coordinate germanium, as we will describe in a future paper.[20]

Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen or argon by using standard Schlenk and high-vacuum-line techniques. NMR spectra were recorded on a Varian EM 360 A spectrometer at 60 MHz (^1H) and on a Bruker WP 90 spectrometer at 36.4 MHz (^{13}C). Infrared spectra were recorded on a Perkin-Elmer 457 infrared spectrometer. Mass spectra recorded on a Ribermag R 1010 or a Varian Mat 311 A spectrometer operating in the electron-impact mode at 70 eV. Gas-phase chromatography was done with a Varian Aerograph 1400 (SE 30) instrument, and yields were calculated by using an internal reference (Bu_4Ge). Elemental analyses were done by the "Service Central de Microanalyse du CNRS" (France). The compounds Ph_2GeH_2[21] and Mes_2GeH_2[22] were prepared according to literature procedures.

Ph_2GeHLi (2a). A solution of 4.8 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Ph_2GeH_2 (0.92 g, 4 mmol) in THF (4 mL) at −40 °C. The mixture was stirred for 15 min at −20 °C. Analysis by ^1H and ^{13}C NMR spectroscopy showed that **2a** had formed exclusively (~95%) (cf. Tables I and II).

Mes_2GeHLi (2b). A solution of 1.4 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Mes_2GeH_2 (0.31 g, 1.0 mmol) in THF (4 mL) at −20 °C. The mixture was stirred for 40 min at −20 °C. Analysis by ^1H and ^{13}C NMR spectroscopy showed that **2b** had formed in high yield (~84%) (cf. Tables I and II). Removal of the solvents under vacuum gave a yellow powder, which was washed three times with pentane (5 mL). Attempts to isolate pure **2b** in a solid state were not successful. Compound **2b** hydrolyzed rapidly to give **1b**.

In all manipulations, freshly prepared solutions of **2** were used.

Base-Catalyzed Decomposition of 2a. Synthesis of Polygermanes. A solution of 4.8 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Ph_2GeH_2 (0.92 g, 4 mmol) in Et_2NMe (4 mL) at −40 °C. After 5 min the solution was heated to 20 °C. The mixture was stirred for the times indicated in Table III. After hydrolysis, extraction, and concentration, the polygermanes were recovered by recrystallization from ether/methanol (4/1) (cf. Table III). $H(GePh_2)_3H$: mp 90–92 °C; ^1H NMR (C_6D_6) δ 5.65 (s, 2 H, GeH), 6.90–7.75 (m, 30 H, C_6H_5); mass spectrum m/z 682 ($M^{\bullet+}$); IR (Nujol, KBr) 2034 cm^{-1} (Ge–H). Anal. Calcd for $C_{36}H_{32}Ge_3$: C, 63.38; H, 4.69. Found: C, 63.15; H, 4.74. $H(GePh_2)_4H$: mp 130–135 °C; ^1H NMR (C_6D_6) δ 5.67 (s, 2 H, GeH), 6.85–7.75 (m, 40 H, C_6H_5); mass spectrum m/z 910 ($M^{\bullet+}$). IR (Nujol, KBr) 2000 cm^{-1} (Ge–H). This tetragermane was contaminated by small amounts of di- and trigermanes. Attempts to further purify $H(GePh_2)_4H$ were not successful.

Confirmation of the Formation of LiH. A solution of 4.8 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Ph_2GeH_2 (0.92 g, 4 mmol) in Et_3N (4 mL) at −40 °C. After 15 min at −40 °C and then 2 h at 20 °C, the mixture was concentrated under vacuum. The residue was washed with pentane (10 mL) and dried in vacuo. It was then treated with 3 mL of THF and a solution of Et_3GeCl (0.39 g, 2 mmol) in THF (2 mL). The reaction mixture was heated in a Carius tube for 15 h at 60 °C. Analysis of the solution by GC showed the quantitative formation of Et_3GeH.

Ph_2GeLi_2 (4). A solution of 4.8 mmol of *t*-BuLi (1.7 M) in pentane was added to a solution of Ph_2GeH_2 (0.46 g, 2 mmol) in THF (2 mL) at −40 °C. The mixture was stirred 40 min at −40 °C and then treated with an excess of MeI. After 15 min, the solution was allowed to warm to ambient temperature. After 1 h at 20 °C and hydrolysis, extraction, and concentration under vacuum, analysis of the residue showed the formation of Ph_2GeMe_2[24] (56%) and Ph_2GeHMe[25] (37%).

Solvation of 2a by 12-crown-4. 12-crown-4 (0.53 g, 3 mmol) was added to a solution of **2a** (3 mmol) in THF at −20 °C, giving an yellow oil. Analysis by NMR and GC methods showed the formation of crude **5a** (~90%): ^1H NMR (pure) δ 4.70 (s, 1 H, GeH), 3.35 (s, 16 H, OCH_2), 6.70–6.95 and 7.40–7.60 (m, 10 H, C_6H_5); ^{13}C NMR (pure) δ 163.2 (C_1), 137.1 (C_2), 126.5 (C_3), 123.1 (C_4); IR (Nujol, KBr, 1993 cm^{-1}) (Ge–H). The product was washed several times with pentane and dried under vacuum, giving the pale yellow solid **5a**, which hydrolyzed rapidly in air to give **1a**.

Reaction of 5a with Et_3GeCl. A solution of Et_3GeCl (0.20 g, 1 mmol) in THF (1.5 mL) was added to a suspension of **5a** (1 mmol) in pentane (0.5 mL) at 20 °C. The mixture was stirred 30 min at 20 °C. After hydrolysis, extraction, and concentration under vacuum, analysis of the residue by GC and ^1H NMR spectroscopy showed the formation of $Ph_2HGeGeEt_3$ (68%) and Ph_2GeH_2 (8%). The pure digermane **8a** was recovered by distillation: bp 70 °C (5×10^{-2} mmHg); yield 0.22 g (56%); ^1H NMR δ 1.00 (s, 15 H, C_2H_5), 5.17 (s, 1 H, GeH), 6.90–7.15 and 7.30–7.60 (m, 10 H, C_6H_5); IR (pure, KBr) 2000 cm^{-1} (Ge–H). Anal. Calcd for $C_{18}H_{26}Ge_2$: C, 55.77; H, 6.77. Found: C, 55.25; H, 6.92.

Reaction of 5a with MeI. **5a** (1.5 mmol) was treated with an excess of MeI at 20 °C. After hydrolysis, extraction, and concentration, nearly pure **7a**[25] (identified by ^1H NMR) was obtained in 82% yield (0.43 g).

Solvation of 2b by 12-crown-4. 12-crown-4 (0.49 g, 2.8 mmol) was added dropwise to a solution of **2b** (2 mmol) in THF (5 mL). The solution was stirred 1 h at 20 °C and then reduced in volume to 4 mL. Addition of 5 mL of pentane gave a precipitate, which was washed with pentane (10 mL) and dried in vacuo. **5b** was so obtained in 17% yield (0.23 g): mp 145–147 °C dec; ^1H NMR (THF-d_8) δ 2.05 (s, 6 H, *p*-CH_3), 2.25 (s, 12 H, *o*-CH_3), 3.50 (s, 16 H, OCH_2), 4.39 (s, 1 H, GeH), 6.38 (s, 4 H, C_6H_2); IR (THF, KBr) 1980 cm^{-1} (Ge–H). **5b** was very sensitive to moisture and always contained traces of Mes_2GeH_2. The same reaction was performed with an excess of 12-crown-4: a solution of **2b** (1 mmol) was added to a solution of 12-crown-4 (0.49 g, 2.8 mmol) in pentane (0.5 mL). With use of the same procedure, the precipitate so obtained was dissolved in 2 mL of THF and analyzed by ^{13}C NMR spectroscopy: $\delta(C_1)$, 157.9 and 159.4; $\delta(C_2)$, 144.3; $\delta(C_3)$, 126.5; $\delta(C_4)$, 131.4; δ(*o*-CH_3), 23.3; δ(*p*-CH_3), 21.2.

Reaction of 5b with Et_3GeCl. A solution of Et_3GeCl (0.20 g, 1 mmol) and **5b** (0.49 g, 1 mmol) in pentane (1 mL) was stirred at ambient temperature for 30 min. After hydrolysis, extraction, and concentration under vacuum, analysis of the residue by ^1H NMR spectroscopy showed that $Mes_2HGeGeEt_3$ (**8b**) had been formed in 98% yield. **8b** was then recovered by distillation: yield 0.30 g (64%); bp 198–200 °C (7×10^{-2} mmHg); ^1H NMR (C_6D_6) δ 1.07 (s, 15 H, C_2H_5), 2.10 (s, 6 H, *p*-CH_3), 2.40 (s, 12 H, *o*-CH_3), 5.40 (s, 1 H, GeH), 6.70 (s, 4 H, C_6H_2); IR (pure, KBr) 2010 cm^{-1} (Ge–H). Anal. Calcd for $C_{24}H_{38}Ge_2$: C, 61.09; H, 8.13. Found: C, 61.69; H, 8.15.

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Reaction of 5b with MeI. With use of the same procedure, a solution of **5b** (1 mmol) in pentane (0.5 mL) and MeI (excess) gave **7b** in 98% yield.

Reaction of 2a with MeI. An excess of MeI (100%) was added to a solution of **2a** (4 mmol) in THF at -40 °C. The mixture was heated to 20 °C. After 1 h and hydrolysis, extraction, and concentration, the residue was analyzed by ^{1}H NMR spectroscopy and showed that **7a**[25] had been formed in 68% yield.

Reaction of 2b with MeI. An excess of MeI (100%) was added to a solution of **2b** (1 mmol) in THF at -10 °C. The mixture was heated to ambient temperature. After 2 h at 20 °C and hydrolysis, extraction, and concentration under vacuum, a white solid identified as **7b** was obtained: yield 0.25 g (78%); mp 90–94 °C; ^{1}H NMR (C_6D_6) δ 0.80 (d, 3 H, CH_3), 2.10 (s, 6 H, p-CH_3), 2.30 (s, 12 H, o-CH_3), 5.50 (q, 1 H, GeH), 6.70 (s, 4 H, C_6H_2), J(HC–GeH) = 4 Hz; IR (Nujol, KBr) 2040 cm^{-1} (Ge–H); mass spectrum m/z 328 ($M^{\bullet+}$). Anal. Calcd for $C_{19}H_{26}Ge$: C, 69.77; H, 8.03. Found: C, 69.94; H, 8.07.

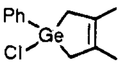
Reaction of 2a with D_2O. A solution of **2a** (1 mmol) in THF was hydrolyzed by D_2O at -40 °C and then extracted and concentrated under vacuum. Analysis of the residue by ^{1}H NMR spectroscopy showed the formation of Ph_2GeHD (C_6D_6): δ 5.10 (t, 1 H, GeH), 6.90–7.20 and 7.20–7.49 (m, 10 H, C_6H_5), J(H–Ge–D) = 0.9 Hz.

Ph_2GeHD was prepared by reduction, with use of $LiAlD_4$ (0.03 g, excess), of a solution of Ph_2GeHCl (0.26 g, 1 mmol) in ether (0.5 mL) at 0 °C. In solution, Ph_2GeHD slowly formed Ph_2GeH_2 over several days at 20 °C.

Reaction of 2 with Me_2SO_4. A solution of R_2GeHLi (1 mmol) in THF was added to an excess of Me_2SO_4 (R = Ph, 20%; R = Mes, 40%) in THF (0.5 mL) at 20 °C. An exothermic reaction was observed. After 3 h at 20 °C, the mixture was hydrolyzed, extracted, and concentrated under vacuum. Analysis of the residue by ^{1}H NMR spectroscopy showed the formation of **7a** in 95% yield and **7b** in 95% yield.

Reaction of 2 with $PhClGeH_2$. A solution of R_2GeHLi (2 mmol) in THF was added to a solution of $PhClGeH_2$ (0.37 g, 2 mmol) in THF (1 mL) at -20 °C. After 20 min at -20 °C, the mixture was heated to ambient temperature and stirred (2 h for **2a**, 14 h for **2b**) at 20 °C. After hydrolysis, extraction, and concentration under vacuum, analysis of the residue showed the formation of the following compounds: for **2a**, **1a** (20%), **9a** (35%), $H(Ph_2Ge)_2H$[23] (5%), $(PhHGe)_n$[15] (40%); for **2b**, **1a** (41%), **9b** (44%), $(PhHGe)_n$[15] (60%). **9a** and **9b** were identified by comparison with other samples prepared by a different route.[20] **9a**: bp 150 °C (0.2 mmHg); ^{1}H NMR (C_6D_6) δ 4.60 (d, 2 H, GeH_2), 5.50 (t, 1 H, GeH), J(HC–GeH) = 4 Hz, 6.90–7.60 (m, 15 H, C_6H_5); IR (pure, KBr) 2050 cm^{-1} (Ge–H); mass spectrum m/z 380 ($M^{\bullet+}$). **9b**: mp 85–86 °C; ^{1}H NMR (C_6D_6) δ 2.10 (s, 6 H, p-CH_3), 2.30 (s, 12 H, o-CH_3), 4.75 (d, 2 H, GeH_2), 5.50 (t, 1 H, GeH), J(HC–GeH) = 4 Hz, 6.65 (s, 4 H, C_6H_2), 6.85–7.40 (m, 5 H, C_6H_5); IR (Nujol, KBr) 2050–2060 cm^{-1} (Ge–H); mass spectrum m/z 464 ($M^{\bullet+}$). Anal. Calcd for $C_{24}H_{30}Ge_2$: C, 62.18; H, 6.48. Found: C, 61.99; H, 6.62.

Reaction of 2a with $PhCl_2GeH$. A solution of **2a** (4 mmol) in THF was added to a solution of $PhCl_2GeH$ (0.89 g, 4 mmol) in ether (2 mL) at -70 °C. After 1 h at -70 °C, the mixture was concentrated under vacuum. The oily residue was washed twice with pentane (4 mL). The pentane solution was evaporated, and the residue, analyzed by ^{1}H NMR spectroscopy, showed the presence of **1a** (43%), $H(GePh_2)_2H$[23] (33%), and $PhCl_2GeH$ (30%). The viscous oil was treated with an excess of 2,3-dimethylbuta-1,3-diene in benzene (1 mL). The reaction mixture was heated in a Carius tube for 2 h at 80 °C. After concentration, analysis by GC and ^{1}H NMR methods showed the formation of



in 30% yield.[16]

Reaction of 2b with PhCOCl. A solution of **2b** (2 mmol) in THF was added dropwise to a solution of PhCOCl (0.39 g, 2.8 mmol) in ether (1 mL) at -78 °C. After 30 min at -78 °C, the solution was heated to ambient temperature. The reaction was monitored by GC. After 30 min at 20 °C, the mixture was hydrolyzed ($NaHCO_3/H_2O$), extracted, dried over anhydrous sodium sulfate, and concentrated under vacuum. The residue was crystallized from a mixture of methanol (2 mL) and ether (3 mL) at -30 °C. A yellow solid precipitated, was isolated after decantation, and dried in vacuo, giving **10b**: yield 0.48 g (58%); mp 148–154 °C; ^{1}H NMR (C_6D_6) δ 2.10 (s, 6 H, p-CH_3), 2.40 (s, 12 H, o-CH_3), 6.50 (s, 1 H, GeH), 6.70 (s, 4 H, C_6H_2), 6.90–7.20 and 7.90–8.20 (m, 5 H, C_6H_5); IR (Nujol, KBr) 2048 (Ge–H), 1643 cm^{-1} (CO); mass spectrum m/z 418 ($M^{\bullet+}$). Anal. Calcd for $C_{25}H_{28}OGe$: C, 71.98; H, 6.78. Found: C, 71.53; H, 6.79.

Reaction of 2a with PhCOCl. A solution of **2a** (3 mmol) in THF was added dropwise to a solution of PhCOCl (0.51 g, 3.6 mmol) in ether (1 mL) at -78 °C. After 30 min at -78 °C, the mixture was heated to ambient temperature. After 1 h at 20 °C, hydrolysis with an aqueous solution of $NaHCO_3$, extraction, drying, and concentration in vacuo, analysis of the residue by ^{1}H NMR spectroscopy confirmed the formation of **10a** (55%) and $(Ph_2Ge)_n$ (~40%). **10a**: ^{1}H NMR (C_6D_6) δ 5.90 (s, 1 H, GeH), 7.00–7.10, 7.25–7.65, and 7.65–7.90 (m, 15 H, C_6H_5); IR (pure, KBr) 2052 (Ge–H), 1686 cm^{-1} (CO).

Reaction of 2a with MesCOCl. A solution of **2a** (2 mmol) in THF was added dropwise to a solution of MesCOCl[26] (0.44 g, 2.4 mmol) in ether (2 mL) at -78 °C. After 40 min at -78 °C, the mixture was heated to ambient temperature. After 3 h of stirring at 20 °C, it was hydrolyzed ($NaHCO_3/H_2O$), extracted, dried, over anhydrous sodium sulfate, and concentrated in vacuo. Analysis of the residue by ^{1}H NMR and GC/MS methods showed the presence of **11** (15%), **1a** (15%), **12** (19%), and $(Ph_2Ge)_n$ (~50%). **11**: ^{1}H NMR (C_6D_6) δ 2.00 (s, 6 H, p-CH_3), 2.10 (s, 12 H, o-CH_3), 5.75 (s, 1 H, GeH), 6.48 (s, 2 H, C_6H_2), 6.90–7.60 (m, 10 H, C_6H_5); IR (pure, KBr) 2048 (Ge–H), 1637 cm^{-1} (CO); mass spectrum m/z 376 ($M^{\bullet+}$). **12** was identified by comparison with a sample prepared by a different route (see below).

Synthesis of 12. A solution of MesCOCl (0.73 g, 4 mmol) in ether (2 mL) was added rapidly to a solution of **4** (2 mmol) in THF at -40 °C. After 15 min at -40 °C, the mixture was heated to ambient temperature. The reaction was monitored gy GC. After 3 h of stirring at 20 °C, the reaction mixture was hydrolyzed ($NaHCO_3/H_2O$), extracted, dried, and concentrated under vacuo. The residue was analyzed by ^{1}H NMR spectroscopy, which showed the presence of **12** (58%), **1a** (13%), and Ph_2GeHCl (14%). Pure compound **12** was recovered by distillation: yield 0.17 g (33%); bp 170 °C (0.2 mmHg); ^{1}H NMR (C_6D_6) δ 1.90 (s, 6 H, p-CH_3), 2.10 (s, 12 H, o-CH_3), 6.30 (s, 4 H, C_6H_2), 6.75–7.60 (m, 10 H, C_6H_5); IR (pure, KBr) 1637 cm^{-1} (CO); mass spectrum m/z 522 ($M^{\bullet+}$). Anal. Calcd for $C_{32}H_{32}O_2Ge$: C, 73.73; H, 6.20. Found: C, 73.32; H, 6.27.

Reaction of 2a with Ph_2CO. A solution of **2a** (2 mmol) in THF was added to a solution of Ph_2CO (0.44 g, 2.4 mmol) in ether (2 mL) at ambient temperature. The mixture was stirred for 4 h and then hydrolyzed, extracted, dried, and concentrated in vacuo. Addition of pentane (4 mL) gave a precipitate, which was isolated after eliminating pentane and drying in vacuo. The product was pure **13a**: yield 0.66 g (80%); ^{1}H NMR (C_6D_6) δ 5.70 (s, 1 H, GeH), 2.15 (s, 1 H, OH), 6.80–7.15 and 7.25–7.50 (m, 20 H, C_6H_5); IR (Nujol, KBr) 2033 (Ge–H), 3362 cm^{-1} (OH); mass spectrum m/z 412 ($M^{\bullet+}$). Anal. Calcd for $C_{25}H_{22}GeO$: C, 73.08; H, 5.35. Found: C, 72.70; H, 5.30.

Reaction of 2b with Ph_2CO. A solution of **2b** (1 mmol) in THF was added dropwise to a solution of Ph_2CO (0.25 g, 1.4 mmol) in THF (1 mL), and the mixture was refluxed for 2 h. After hydrolysis, extraction, drying, and concentration in vacuo, analysis of the residue by ^{1}H NMR, IR, and GC methods showed the presence of $(Mes_2HGe)_2$[27] (40%), $(Mes_2Ge)_n$ (~60%), Ph_2CHOH (~50%), and the remaining Ph_2CO.

Reaction of 2a with PhCHO. A solution of **2a** (3 mmol) in THF was added dropwise to a solution of PhCHO (0.38 g, 3 mmol) in ether (1 mL) at -30 °C. The mixture was stirred for 30 min at -30 °C and then heated to ambient temperature. After 1 h at 20 °C, it was hydrolyzed, extracted, dried, and concentrated in vacuo. Analyses by ^{1}H NMR spectroscopy showed that **14a**[19] had formed in good yield (87%). The presence of **1a** (traces) and $PhCH_2OH$ (13%) was also confirmed.

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Reaction of 2b with PhCHO. A solution of **2b** (1 mmol) in THF was added dropwise to a solution of PhCHO (0.15 g, 1.4 mmol) in ether (1 mL) at −20 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. The mixture was stirred for 30 min at −20 °C and then hydrolyzed, extracted, dried, and concentrated in vacuo. The residue was treated with pentane (2 mL) at −20 °C. After decantation and drying in vacuo, the resulting white powder was identified as pure **14b**: yield 0.26 g (62%); mp 78–80 °C; ^{1}H NMR (C_6D_6) δ 2.10 (s, 6 H, p-CH_3), 2.23 and 2.25 (s, 12 H, o-CH_3), 5.20 (d, 1 H, CH), 5.30 (d, 1 H, GeH), J(HC–GeH) = 3 Hz, 6.60 and 6.63 (s, 4 H, C_6H_2), 6.95 (s, 5 H, C_6H_5); IR (Nujol, KBr) 2060 (Ge–H), 3300 cm^{-1} (OH); mass spectrum m/z 420 ($M^{\bullet+}$). Anal. Calcd for $C_{25}H_{30}GeO$: C, 71.69; H, 7.16. Found: C, 71.76; H, 7.58.

The thermal decomposition of **14b** was monitored by ^{1}H NMR spectroscopy with use of a solution of **14b** in C_6D_6 that had been heated in a sealed tube for 4 h at 160 °C. The presence of **1b** (25%), PhCHO (25%), and **14b** (73%) was thereby confirmed.

A solution of **14b** (0.21 g, 0.5 mmol) in C_6H_6 (2 mL), Mes_3SiCl (0.06 g, 0.55 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.10 g, excess) was stirred for 15 h at 20 °C. After removal of DBU·HCl by filtration, the solution was concentrated in vacuo. **15** was then recovered by distillation: yield 0.11 g (44%); bp 95 °C (4 × 10^{-2} mmHg); ^{1}H NMR (C_6D_6) δ 0.05 (s, 9 H, $SiMe_3$), 2.05 (s, 6 H, p-CH_3), 2.30 (s, 12 H, o-CH_3), 5.50 (s, 2 H, GeH, CH),[28] 6.65 (s, 4 H, C_6H_2), 6.90–7.15 (m, 5 H, C_6H_5); IR (pure, KBr) 2050 cm^{-1} (Ge–H). Anal. Calcd for $C_{28}H_{38}OSiGe$: C, 68.50; H, 7.74. Found: C, 67.83; H, 7.96.

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[28] Using $CDCl_3$ as solvent, we observed the expected δ(CH) and δ(GeH) signals and their coupling: δ 5.20 (d, 1 H, CH) and 5.35 (d, 1 H, GeH), J(HC–GeH) = 3 Hz.

Synthetic Routes to Methylpalladium(II) and Dimethylpalladium(II) Chemistry and the Synthesis of New Nitrogen Donor Ligand Systems

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Convenient and widely applicable synthetic routes to methylhalogenopalladium(II), $PdXMe(L_2)$, and dimethylpalladium(II) complexes, $PdMe_2(L_2)$, have been developed, including complexes of triphenylphosphine and a wide range of bidentate nitrogen donor ligands. These routes involve either the generation of $Pd^{II}Me_n$ species at low temperature from methyllithium reagents and *trans*-$PdCl_2(SMe_2)_2$ followed by addition of ligand, PdIMe(2,2′-bipyridyl) being synthesized through the oxidative-addition reactivity of $Pd_2(dba)_3(CHCl_3)$, or the facile synthesis of complexes with the reagents $[PdIMe(SMe_2)]_2$ and $[PdMe_2(pyridazine)]_n$ in organic solvents at ambient temperature. These reagents are particularly suitable for ligands sensitive to MeLi reagents, and $[PdIMe(SMe_2)]_2$ is also a suitable substrate for the synthesis of chloro and bromo complexes, $PdXMe(L_2)$, including PPh_3 complexes. Several new nitrogen donor bidentate ligands are described, containing 1-methylimidazol-2-yl (mim) and pyridin-2-yl (py) groups in $(mim)_2C{=}CH_2$ and $(py)(mim)C{=}CH_2$ as relatives of planar ligands such as 2,2′-bipyridyl and mim, py, and pyrazol-1-yl (pz) groups in $(py)(mim)CH_2$, (py)(mim)CHMe, $(mim)_2CH_2$, $(mim)_2CHMe$, and $(pz)(mim)CH_2$ as relatives of ligands such as $(py)_2CH_2$ and $(pz)_2CH_2$. Methylpalladium(II) complexes of unsymmetrical bidentate ligands exhibit isomerism; e.g., isomers of PdIMe{(py)(mim)C=O} occur in the ratio 9:1, where the dominant isomer has the pyridine ring trans to methyl. The ligands with methane bridges, e.g. $(pz)(py)CH_2$, ethane bridges, e.g. $(pz)_2CHMe$, and propane bridges, e.g. $(py)_2CMe_2$, form complexes $PdMe_2(L_2)$ and $PdIMe(L_2)$ that exhibit variable-temperature NMR spectra indicating boat-to-boat inversion of the chelate ring, but complexes of $(mim)_2CHMe$ and (py)(mim)CHMe appear to adopt only the conformation with the methyl group axial and adjacent to palladium.

Introduction

Palladium and its compounds are widely used in catalysis and organic synthesis,[1–5] and the organometallic chemistry of palladium involving Pd–C σ bonds has been focused primarily on the divalent oxidation state with phosphine-based ligands.[1,6–8] Nitrogen donor complexes involve predominantly studies of cyclometalation and intramolecular coordination systems,[5,9] which also have applications for organic synthesis.[5,10] The intramolecular coordination systems usually involve Pd^{II}–C(sp^2) bonds,[5,9] although some Pd–C(sp^3) systems are known, e.g. four- and five-membered palladacycle rings in $[Pd(CHMeCHMeNMe_2)(NHMe_2)_2]^+$[11] and $[Pd(CH_2(C(CO_2Et)_2)CHCH_2NMe_2)(\mu\text{-}Cl)]_2$,[12] respectively. Palladacyclopentadiene complexes, e.g. $Pd[C(CO_2Me)]_5(bpy)$,[13] 2,2′-biphenyldiyl complexes, e.g. $PdC_{12}H_8(bpy)$,[14] and some

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