A weighted least-squares method[22] was used to fit the models to the extrapolated scattering curve. Theoretical scattering curves for models b and c were calculated by using the Debye formula.[33]

A small, constant background was also fitted to the experimental data to compensate for the difference in ionic medium of the scattering curve compared with the background curve. Of the three models, the sphere model a gave the best fit, with a fitting index *U* (cf. eq 5 in ref 18) equal to 0.71% and a sphere radius equal to 8.63 Å. The *U* values obtained for models b and c were 3.57% and 1.40%, respectively. Thus we can conclude that the best fit with scattering data is obtained for a single sphere model, but an acceptable fit is also obtained for the octamer ring, with the $Na(H_2O)_6$ unit in the center. A sphere of radius equal to 8.63 Å corresponds to a radius of gyration equal to 6.68 Å, which is in agreement with the value, 6.95 Å, obtained from Guinier plots after desmearing. From the forward scattering $I(0)$ obtained with the sphere model a, a molecular weight of 3.0×10^3 is calculated, which is also in good agreement with the value 3.1×10^3 obtained from Guinier plots after desmearing. It may seem surprising that such a good fit is obtained from such a simplified model. However, similar observations have been made before.[34]

C. Discussion. The structures of the copper(II)–uridine complex and its surrounding zeolitic framework are highly unusual. From the single-crystal structure determination it was not clear if the geometry of the complex is due to the unusual three-dimensional framework or if it is the geometry of the complex that determines the existence of the zeolitic framework. However, it seems chemically reasonable to expect such a structure for the copper(II)–uridine complex. In fact, the coordination of metal ions by the 2′ and 3′ hydroxy oxygens of the ribose group has been proposed several times,[7,8,12,23] and stacking of nucleosides in aqueous solutions is a well-known phenomena[28,35] that favors the overlap of pyrimidine rings. Furthermore, several examples may be found of complexes with head-to-tail arrangements of purine or pyrimidine type ligands.[4b,36]

The results from the emf titrations show unequivocally that the following complex formation reactions take place in aqueous solutions:

$$n\text{Cu}^{2+} + n\text{H}_3\text{urid} \rightleftharpoons \text{Cu}_n\text{urid}_n^{\;n-} + 3n\text{H}^+$$

Furthermore, the SAXS data can be adequately explained both with a sphere of radius 8.63 Å and with the molecular species $[\text{Cu}_8(\text{urid})_8\text{Na}(\text{H}_2\text{O})_6]^{7-}$, whose molecular weight, 2569, agrees fairly well with the value, 3.1×10^3, obtained from the SAXS data for the particles in solution. It is also interesting that the introduction of the $Na(H_2O)_6$ unit into the center of the octamer ring gives a more than 6-fold decrease in the error square sum, *U*. The slightly better fit for the solid sphere of radius 8.63 Å, as compared with the octamer ring, and the small difference in molecular weights might reflect either a certain degree of flexibility in the ring structure or, rather, the association of further Na^+ ions to compensate for the charge of the complex.

Thus, it should be concluded that the dominating Cu(II)–uridine complex in solution has either the same structure as the octamer ring found in the single crystal or a similar one and that, therefore, the peculiar zeolitic framework found in the crystal is due to the geometric properties of the complex.

This type of large polynuclear metal–nucleoside complex has not been reported previously, possibly due to the fact that they are difficult to detect in aqueous solution unless SAXS experiments are performed. Furthermore, single-crystal structure determinations of this kind of highly symmetrical and disordered solids are not a routine procedure.

Although the situation in the tunnels can be regarded as a model of zeolitic sorption because of the relatively large "windows", in fact, it results from a clathration process, since the liberation of the molecular species would induce a host–lattice breakdown. A related phenomena is the template synthesis of some zeolites with quaternary alkylammonium cations.[37]

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Some Aspects of the Reactivity of the First Stable Germaphosphene

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Contribution from the Laboratoire de Chimie des Organominéraux, U.A. du CNRS n° 477, Université Paul Sabatier, 31062 Toulouse Cedex, France. Received May 5, 1986

Abstract: Germaphosphene **1**, the first stable compound with a germanium–phosphorus double bond, is very reactive toward compounds with active hydrogens producing secondary phosphines with a high regiospecificity and toward halogens to give adducts **11** and halogermylphosphines **12**. Reaction with carbon tetrachloride allows, after addition followed by β-elimination, the quantitative synthesis of phosphaalkene **16**. **1** reacts easily with nucleophilic compounds such as lithio compounds and Grignard reagents and probably via a radical process with dimethyl disulfide. The germanium–phosphorus double bond of **1** is reduced by lithium aluminum hydride and by the complex $BH_3 \cdot SMe_2$ with formation of the germylphosphine **22**; in the last case, a competitive addition of borane to the double bond was also observed.

Compounds of groups 14 and 15 in low coordination state are of particular interest at the present time.[1] Until recently metallaphosphenes (>M═P—, M = Si, Ge, Sn) were postulated only as reactive intermediates and characterized by trapping reactions.

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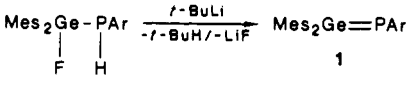
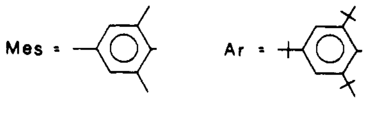
These highly reactive and short-lived species were obtained by two routes: (1) thermal decomposition of the four-membered heterocycles, 2-sila- or 2-germaphosphetanes (M = Si,[2a] Ge[2b]) and (2) exchange reactions between dialkyldichlorogermanes or -stannanes and disilylphosphines (M = Ge,[3] Sn[4]).

Owing to substituents having strong steric hindrance and electronic effects, such as mesityl, bis(trimethylsilyl)methyl, and 2,4,6-tri-*tert*-butylphenyl, the first stable silaphosphene[5] and stannaphosphene[6] were characterized, and the first stable germaphosphene **1** was isolated.[7] The best route to **1** is the nearly quantitative dehydrofluorination of the fluorogermylphosphine **2** by *tert*-butyllithium (eq 1). In a preliminary communication,[7] we have presented the characterization of **1** by its physicochemical data and by only a few reactions. We now describe in detail the behavior of germaphosphene **1** toward electrophilic reagents, such as compounds having active hydrogen or halogen, and toward nucleophilic compounds, such as lithio derivatives, Grignard reagents, metalhydrides, and boranes. The reaction of **1** with disulfides is also reported.

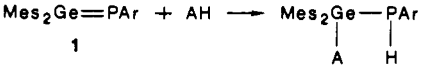


$$\underset{\mathbf{2}}{\mathrm{Mes_2Ge(F)-P(H)Ar}} \xrightarrow[-t\text{-BuH}/-\mathrm{LiF}]{t\text{-BuLi}} \underset{\mathbf{1}}{\mathrm{Mes_2Ge{=}PAr}} \quad (1)$$



Results and Discussion

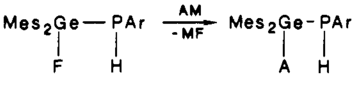
Germaphosphene **1** reacts very easily and quantitatively with numerous compounds having active hydrogen, such as water,[7] alcohols,[7] thiols, amines, mineral[7] and organic acids, phosphorus ylides,[7] and acetylenes. A secondary germylphosphine was obtained in each case (eq 2).



$$\underset{\mathbf{1}}{\mathrm{Mes_2Ge{=}PAr}} + \mathrm{AH} \longrightarrow \mathrm{Mes_2Ge(A)-P(H)Ar} \quad (2)$$

A = OH, **3** A = Cl, **7**
A = OMe, **4** A = CH_3COO, **8**
A = *i*-PrS, **5** A = $Me_3P{=}CH$, **9**
A = PhNH, **6** A = PhC≡C, **10**

The structure of derivatives **5**, **6**, and **10** was confirmed by their independent synthesis from **2** and the alkali derivatives *i*-PrSNa, PhN(H)Li, and PhC≡CNa, respectively (eq 3).

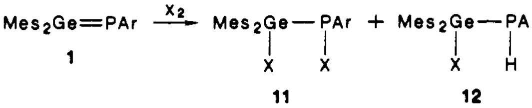


$$\underset{\mathbf{2}}{\mathrm{Mes_2Ge(F)-P(H)Ar}} \xrightarrow[-\mathrm{MF}]{\mathrm{AM}} \mathrm{Mes_2Ge(A)-P(H)Ar} \quad (3)$$

A = *i*-PrS, **5**; PhN(H), **6**; PhC≡C, **10**
M = Li or Na

These addition reactions are highly regiospecific producing only secondary phosphines. The regiochemistry is determined by polar effects arising from the fact that germanium (electronegativity: 2.0[8]) is more electropositive than phosphorus (2.1[8]) so that the germanium–phosphorus double bond is polarized with germanium as the more positive partner. This assumption and the reactivity of the Ge=P double bond are in good agreement with the polarity predictions arising from calculations made in collaboration with J. C. Barthelat (Laboratoire de Physique Quantique, Toulouse).[9] The same regiospecificity was previously observed by Bickelhaupt in the reaction between methanol and silaphosphene.[5] Even with a large excess of reagent having active hydrogen, only the germanium–phosphorus double bond reacts, and the single bond is unaffected, contrary to the behavior of acyclic germylphosphines[10] or germaphospholanes.[11] The difference is probably due to the large steric hindrance of the bulky substituents linked to the germanium and phosphorus atoms.

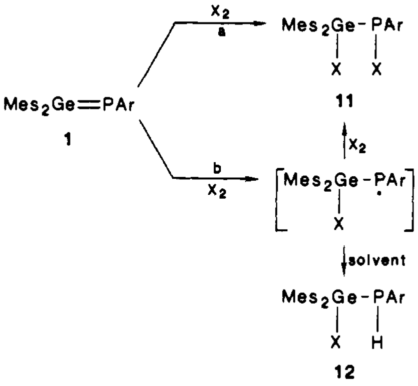
Bromine and iodine react with germaphosphene **1** to produce the expected adduct **11** and, surprisingly, halogermylphosphine **12** as major products (eq = 4).



$$\underset{\mathbf{1}}{\mathrm{Mes_2Ge{=}PAr}} \xrightarrow{X_2} \underset{\mathbf{11}}{\mathrm{Mes_2Ge(X)-P(X)Ar}} + \underset{\mathbf{12}}{\mathrm{Mes_2Ge(X)-P(H)Ar}} \quad (4)$$

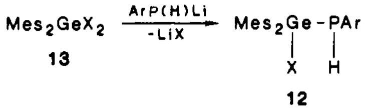
X = Br, **11a** and **12a**
X = I, **11b** and **12b**

Two competitive mechanisms probably occur: an electrophilic addition leading to **11** (route a) and a radical process (route b) forming the radical species $Mes_2Ge(X)-P^{\bullet}-Ar$ which reacts further to produce either **11** or **12** (eq 5).



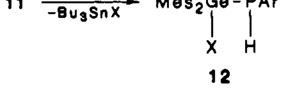
$$\begin{tikzcd} & \underset{\mathbf{11}}{\mathrm{Mes_2Ge(X)-P(X)Ar}} \\ \underset{\mathbf{1}}{\mathrm{Mes_2Ge{=}PAr}} \arrow[ru, "X_2", "a"'] \arrow[r, "b", "X_2"'] & \left[\mathrm{Mes_2Ge(X)-P^{\bullet}Ar}\right] \arrow[u, "X_2"'] \arrow[d, "\text{solvent}"] \\ & \underset{\mathbf{12}}{\mathrm{Mes_2Ge(X)-P(H)Ar}} \end{tikzcd} \quad (5)$$

Compound **12** was identified by an independent synthesis from dimesityldihalogermane and 2,4,6-tri-*tert*-butyllithiophosphide and by selective reduction of the P–X bond of **11** with a gentle reducing agent such as tributylstannane (eq 6).



$$\underset{\mathbf{13}}{\mathrm{Mes_2GeX_2}} \xrightarrow[-\mathrm{LiX}]{\mathrm{ArP(H)Li}} \underset{\mathbf{12}}{\mathrm{Mes_2Ge(X)-P(H)Ar}}$$

X = Br, **13a**
X = I, **13b**



$$\mathbf{11} \xrightarrow[-\mathrm{Bu_3SnX}]{\mathrm{Bu_3SnH}} \underset{\mathbf{12}}{\mathrm{Mes_2Ge(X)-P(H)Ar}} \quad (6)$$

Compounds **11** and **12** were identified by mass spectroscopy. Diphosphene ArP=PAr **14** and dihalodiphosphine ArP(X)–P(X)Ar **15** were observed as minor products in the reaction between germaphosphene and halogens. The mechanism of the reactions leading to **14** and **15** seems complex and has not yet been completely elucidated. Yoshifuji et al.[12] have also observed a

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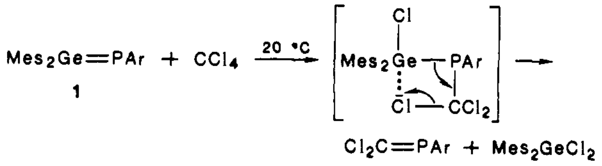
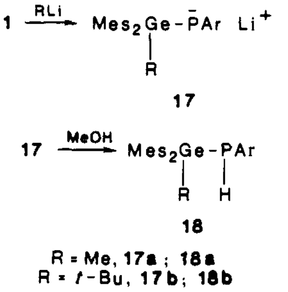
complicated reaction between halogens and diphosphenes.

The reaction of **1** with carbon tetrachloride is particularly interesting because it allows the quantitative synthesis of a compound with a phosphorus–carbon double bond from a compound having a germanium–phosphorus double bond (eq 7). The first


$$\underset{\mathbf{1}}{Mes_2Ge{=}PAr} + CCl_4 \xrightarrow{20\ ^\circ C} \left[Mes_2Ge(Cl)\text{—}PAr \cdots Cl\text{—}CCl_2 \right] \longrightarrow \underset{\mathbf{16}}{Cl_2C{=}PAr} + Mes_2GeCl_2 \quad (7)$$

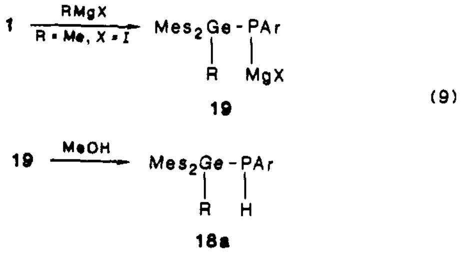
step of this reaction is probably the addition of carbon tetrachloride to the germanium–phosphorus double bond followed by a β-elimination initiated by the affinity of chlorine for germanium. The phosphaalkene **16** is the same as that previously prepared by Appel et al.[13] The study of the generalization of this method to the synthesis of various phosphaalkenes is now in progress.

The reactivity of germaphosphene **1** toward nucleophiles is clearly evident from its reactions with lithio compounds, Grignard reagents, and lithium aluminum hydride. Thus, methyllithium and *tert*-butyllithium react rapidly at room temperature with **1** affording deep red solutions characteristic of the presence of the phosphorus anions **17**. Quenching of **17** with methanol gives the new germylphosphines **18** (eq 8).

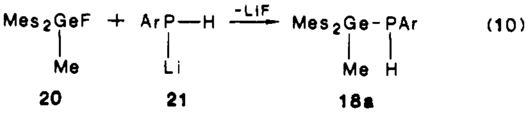

$$\mathbf{1} \xrightarrow{RLi} \underset{\mathbf{17}}{Mes_2Ge(R)\text{-}\bar{P}Ar\ Li^+} \quad (8)$$
$$\mathbf{17} \xrightarrow{MeOH} \underset{\mathbf{18}}{Mes_2Ge(R)\text{-}P(H)Ar}$$

R = Me, **17a**; **18a**
R = *t*-Bu, **17b**; **18b**

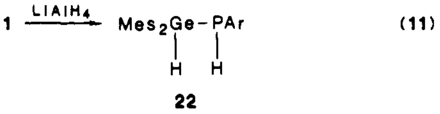
Grignard reagents, such as methylmagnesium iodide, react easily with **1** to afford adduct **19** which, after treatment of the solution with methanol, forms germylphosphine **18a** (eq 9).


$$\mathbf{1} \xrightarrow[R = Me,\ X = I]{RMgX} \underset{\mathbf{19}}{Mes_2Ge(R)\text{-}P(MgX)Ar} \quad (9)$$
$$\mathbf{19} \xrightarrow{MeOH} \underset{\mathbf{18a}}{Mes_2Ge(R)\text{-}P(H)Ar}$$

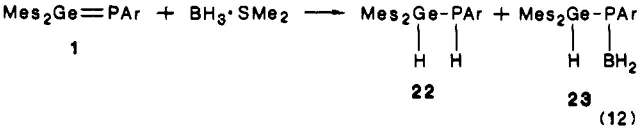
The composition of the germylphosphine **18a** was verified by its independent synthesis from methyldimesitylfluorogermane **20** and the lithio compound **21** (eq 10).


$$\underset{\mathbf{20}}{Mes_2Ge(Me)F} + \underset{\mathbf{21}}{ArP(Li)\text{—}H} \xrightarrow{-LiF} \underset{\mathbf{18a}}{Mes_2Ge(Me)\text{-}P(H)Ar} \quad (10)$$

The germanium–phosphorus double bond of **1** can be reduced by lithium aluminum hydride, leading to the germylphosphine **22** (eq 11).


$$\mathbf{1} \xrightarrow{LiAlH_4} \underset{\mathbf{22}}{Mes_2Ge(H)\text{-}P(H)Ar} \quad (11)$$

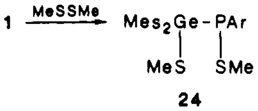
The same germylphosphine **22** has also been obtained as major product (80%), by reaction of **1** with the complex $BH_3{\cdot}SMe_2$; but besides **22** resulting from a simple reduction of the germanium–phosphorus double bond, we have also observed the formation of adduct **23**; **23** is a very air-sensitive compound not yet isolated in pure form but characterized by its physico-chemical data (eq 12).


$$\underset{\mathbf{1}}{Mes_2Ge{=}PAr} + BH_3{\cdot}SMe_2 \longrightarrow \underset{\mathbf{22}}{Mes_2Ge(H)\text{-}P(H)Ar} + \underset{\mathbf{23}}{Mes_2Ge(H)\text{-}P(BH_2)Ar} \quad (12)$$

The relative percentages of **23**/**22** (about 20/80) depend somewhat on experimental conditions. The regiospecific addition leading to **23** is the second example of addition of a borane to the double bond of metal–heteroelement compounds; recently McNamara et al. have described the addition of B_2H_6 or $BH_3{\cdot}THF$ to a Mo=P bond.[14]

Reactions of **1** with nucleophiles are quantitative and regiospecific in the case of lithio compounds and Grignard reagents; they involve only the germanium–phosphorus double bond. The fact that the Ge–P single bond, which is usually cleaved by lithio compounds,[10b] Grignard reagents,[15] and hydrides,[16] is unaffected is probably due to the very large steric hindrance of mesityl and tri-*tert*-butylphenyl groups. Reactions of lithio compounds and hydrides with diphosphenes, which also have trigonal planar phosphorus, have been described recently.[17,18]

Germaphosphene **1** reacts with dimethyldisulfide probably by a radical process (eq 13). Even with a large excess of dimethyldisulfide, cleavage of the germanium–phosphorus single bond of **24**, previously observed in the case of germaphospholanes,[11] does not occur.


$$\mathbf{1} \xrightarrow{MeSSMe} \underset{\mathbf{24}}{Mes_2Ge(SMe)\text{-}P(SMe)Ar} \quad (13)$$

In summary, germaphosphene **1** is a highly reactive compound toward both electrophilic and nucleophilic reagents leading, with high regioselective additions, to the formation of new functional substituted germylphosphines. The radical reactivity of the germanium–phosphorus double bond is also observed. One of the results of particular interest is the reaction with carbon tetrachloride with the formation of a phosphaalkene. It seems very interesting to extend this reaction to various halides of group 14 (C, Si, Ge, Sn). These studies are now in progress.

Experimental Section

Syntheses were performed under an atmosphere of dry nitrogen by using standard Schlenk and high-vacuum line techniques. Solvents were dried by distillation from sodium benzophenone ketyl immediately prior to use. ^1H NMR spectra were recorded on a Varian EM 360A at 60 MHz and Bruker WH 90 instruments at 90 MHz. ^{31}P NMR spectra were recorded on a Bruker WH 90 spectrometer at 36.44 MHz and ^{19}F on a Perkin Elmer instrument at 84.6 MHz. Chemical shifts are reported in ppm from internal Me_4Si for ^1H, from external 85% H_3PO_4 for ^{31}P, and external CF_3COOH for ^{19}F. Downfield shifts are noted positive in all cases. NMR spectra were measured on samples in C_6D_6 solution. Infrared spectra were recorded on a Perkin Elmer 457 grating spectrometer. Mass spectra were measured on a Varian MAT 311A spectrometer (EI) and a Ribermag R 1010 spectrometer (desorption). Experimental molecular peak patterns were assigned after comparison with

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theoretical peak patterns calculated on a Tektronics 4051.

Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were done by the "Service Central de Microanalyse du CNRS", Vernaison, France.

Reactions of 1 with Reagents Having Active Hydrogen. Equimolar amounts of the reagent (isopropylthiol, aniline, acetic acid, or phenylacetylene) were added by means of a syringe to a solution of **1** (0.80 g, 1.36 mmol) in 10 mL of pentane, at room temperature. Decoloration of the orange solution of **1** occurred immediately with isopropylthiol and acetic acid and after 10 min stirring with aniline and phenylacetylene. Removal of the solvent under reduced pressure afforded crude material which was recrystallized from pentane.

5: ^{1}H NMR δ 1.38 (d, ^{3}J(HH) = 7.0 Hz, 6 H, Me(*i*-Pr)), 1.42 (s, 9 H, *p*-*t*-Bu), 1.65 (s, 18 H, *o*-*t*-Bu), 2.13 (s, 6 H, *p*-Me), 2.63 (s, 12 H, *o*-Me), 6.77 (br s, 4 H, ArMes), 7.48 (d, ^{4}J(PH) = 2.0 Hz, 2 H, ArAr); ^{31}P δ -86.3, ^{1}J(PH) = 214.7 Hz; IR (pentane) ν(PH) 2345 cm^{-1}; MS (EI), (^{74}Ge) *m*/*e* 664 (M^{+}); yield (calcd from ^{31}P NMR) 85%. Anal. Calcd for $C_{39}H_{59}GePS$: C, 70.60; H, 8.96; S, 4.83. Found: C, 70.35; H, 8.60; S, 5.02.

6: ^{1}H NMR δ 1.40 (s, 9 H, *p*-*t*-Bu), 1.60 (s, 18 H, *o*-*t*-Bu), 2.10 (s, 6 H, *p*-Me), 2.37 (s, 12 H, *o*-Me), 6.68 (br s, 4 H, ArMes), 6.80–7.50 (m, 5 H, C_6H_5), 7.53 (d, ^{4}J(PH) = 2.0 Hz, 2 H, ArAr); ^{31}P –94.9, ^{1}J(PH) = 211.8 Hz; IR (pentane) ν(PH) 2350 cm^{-1}; ν(NH) 3360 cm^{-1}; MS (EI); (^{74}Ge) *m*/*e* 681 (M^{+}); yield (calcd from ^{31}P NMR) 60%. Anal. Calcd for $C_{42}H_{58}NGeP$: C, 74.13; H, 8.59; N, 2.06. Found: C, 74.28; H, 8.75; N, 1.99.

8: white crystals (0.54 g, yield 61%); mp 134–137 °C; ^{1}H NMR δ 1.37 (s, 9 H, *p*-*t*-Bu), 1.57 (s, 18 H, *o*-*t*-Bu), 1.80 (s, 3 H, CH_3CO), 2.10 (s, 12 H, *o*-Me), 2.43 (s, 6 H, *p*-Me), 5.97 (d, ^{1}J(PH) = 223.0 Hz, 1 H, PH), 6.70 (br s, 4 H, ArMes), 7.35 (br s, 2 H, ArAr); ^{31}P δ –98.6, ^{1}J(PH) = 223.0 Hz; IR (pentane) ν(PH) 2385 cm^{-1}, ν(CO) 1680 cm^{-1}. Anal. Calcd for $C_{38}H_{55}GeO_2P$: C, 70.49; H, 8.56. Found: C, 70.71; H, 8.58.

10: white crystals (0.74 g, yield 79%); mp 105 °C; ^{1}H NMR δ 1.30 (s, 9 H, *p*-*t*-Bu), 1.57 (s, 18 H, *o*-*t*-Bu), 2.10 (s, 6 H, *p*-Me), 2.57 (s, 12 H, *o*-Me), 6.72 (br s, 4 H, ArMes), 6.87–7.63 (m, 7 H C_6H_5 and 2 H ArAr); ^{31}P -106.3, ^{1}J(PH) 211.8 Hz. Anal. Calcd for $C_{44}H_{57}GeP$: C, 76.64; H, 8.33. Found: C, 76.41; H, 8.31.

Synthesis of 5, 6, and 10 from 2. Compounds **5**, **6**, and **10** were also prepared by the reaction of **2** with *i*-PrSNa, PhN(H)Li, and PhC≡CNa, respectively. In a typical experiment, a solution of lithioaniline (prepared from aniline (0.33 g, 3.6 mmol), an equimolar quantity of BuLi (1.6 M) in hexane, and 10 mL of diethyl ether) was added to a solution of **2** (2.10 g, 3.6 mmol) in diethyl ether (10 mL). The reaction mixture was heated at 35 °C for 1 h and then filtered. Removal of the solvent and recrystallization of the residue in pentane led to **6** previously described.

Reaction of 1 with Halogens. To a solution of **1** (2.28 g, 3.9 mmol) in diethyl ether was slowly added at -20 °C an equimolar amount of bromine (or iodine) in the same solvent. Analysis of the reaction mixture, done by ^{31}P NMR spectroscopy, showed the formation of **11** (**11a**: +46.4, **11b**: +24.0) and **12** as major products. Purification of **11** and **12** from this reaction mixture was impossible, but these compounds were identified by their independent synthesis and their chemical reactivity.

Synthesis of Dimesityldibromogermane (13a) and Dimesityldiiodogermane (13b). In a typical experiment, a solution (1 N) of hydrobromic (or hydroiodic) acid in water (11.3 mmol) was added to a solution of dimesityldimethoxygermane[7] (4.2 g, 11.3 mmol) in 30 mL of benzene. The reaction mixture was stirred for 2 h at 60 °C, extracted with pentane, and dried over Na_2SO_4. The solvents were removed at reduced pressure, and the residue was recrystallized in pentane to afford **13a**.

13a: white crystals (4.31 g, yield 81%); mp 136 °C; ^{1}H NMR δ 2.27 (s, 6 H, *p*-Me), 2.80 (s, 12 H, *o*-Me), 6.90 (s, 4 H, ArMes). Anal. Calcd for $C_{18}H_{22}GeBr_2$: C, 45.92; H, 4.71. Found: C, 46.08; H, 4.80.

13b: (5.23 g, yield 82%) mp 135 °C; ^{1}H NMR δ 2.08 (s, 6 H, *p*-Me), 2.67 (s, 12 H, *o*-Me), 6.57 (s, 4 H, ArMes). Anal. Calcd for $C_{18}H_{22}GeI_2$: C, 38.28; H, 3.93. Found: C, 39.31; H, 3.99.

Synthesis of 12a and 12b. A solution of 2,4,6-tri-*tert*-butylphenyllithiophosphide **21** (prepared from 2,4,6-tri-*tert*-butylphenylphosphine (2.28 g, 8.2 mmol), an equimolar quantity of butyllithium (1.6 M) in hexane, and 30 mL of diethyl ether) was slowly added to a solution of dimesityldibromogermane (**13a**) in pentane (20 mL). After 1 h at room temperature, removal of the solvents at reduced pressure afforded crude **12a**, which was recrystallized from pentane: white crystals (3.39 g, yield 62%); mp 117 °C; ^{1}H NMR 1.27 (s, 9 H, *p*-*t*-Bu), 1.53 (s, 18 H, *o*-*t*-Bu), 2.10 (s, 6 H, *p*-Me), 2.60 (s, 12 H, *o*-Me), 5.77 (d, ^{1}J(PH) = 217 Hz, 1 H, PH), 6.70 (s, 4 H, Ar Mes); ^{31}P{^{1}H} NMR δ –82.6. Anal. Calcd for $C_{36}H_{52}BrGeP$: C, 64.70; H, 7.84; Br, 11.96. Found C, 64.88; H, 7.91; Br, 11.99.

The same experimental procedure by using **13b** instead of **13a** led to **12b** in about 70% yield as calculated from ^{31}P NMR spectra: ^{31}P NMR δ –72.7, ^{1}J(PH) = 220.6 Hz; MS (EI), ^{74}Ge, *m*/*e* 716 (M^{+}).

Reduction of 11 to 12. To a mixture of **11** and **12** in solution in diethyl ether was added tributylstannane in solution in the same solvent until the disappearance of **11** as shown by ^{31}P NMR. Removal of the solvent led to a residue which was crystallized from pentane to afford **12a** (or **12b**) previously described.

Reaction of 1 with Carbon Tetrachloride. A mixture of **1** (1.40 g, 2.39 mmol), carbon tetrachloride (0.37 g, 2.39 mmol), and benzene (10 mL) was stirred 2 h at room temperature; during this time the color of the reaction mixture slowly turned from orange to light yellow. ^{1}H and ^{31}P NMR analysis showed the quantitative formation of **16** previously prepared by Appel et al.[13] Dimesityldichlorogermane was identified by gas chromatography and ^{1}H NMR as an authentic sample.[7]

16: ^{1}H NMR δ 1.33 (s, 9 H, *p*-Me), 1.57 (s, 18 H, *o*-Me), 7.53 (d, ^{4}J(PH) = 1.7 Hz, 2 H, ArAr); ^{31}P{^{1}H} δ +232.

Reaction of 1 with Methyllithium and *tert*-Butyllithium. Germaphosphene **1** (1.40 g, 2.39 mmol) in diethyl ether (10 mL) was treated with an equimolar quantity of MeLi (1.6 M) in the same solvent (or *t*-BuLi, 1.5 M in pentane) affording a deep red solution. The presence of the anion **17a** (or **17b**) was established by ^{31}P{^{1}H} NMR spectra [**17a**: –120.1 ppm (very br s); **17b**: –129.1 (very br s)]. Treatment of the solution of **17a** (or **17b**) with methanol led to an immediate decoloration. Evaporation of the solvents under reduced pressure, followed by recrystallization of the residue from pentane, afforded white crystals of **18a** (1.02 g, yield 71%) or **18b** (1.05, yield 68%).

18a: ^{1}H NMR δ 0.80 (d, ^{3}J(HP) = 2.4 Hz, 3 H, MeGe), 1.34 (s, 9 H, *p*-*t*-Bu), 1.52 (s, 18 H, *o*-*t*-Bu), 2.15 (s, 6 H, *p*-Me), 2.37 (s, 12 H, *o*-Me), 4.68 (d, ^{1}J(PH) = 211.9 Hz, 1 H, PH), 6.75 (s, 4 H, Ar Mes), 7.43 (d, ^{4}J(PH) = 2.2 Hz, 2 H, Ar Ar); ^{31}P{^{1}H} NMR -106.8; IR (pentane) ν(PH) 2380 cm^{-1}; MS (EI), (^{74}Ge) *m*/*e* 604 (M^{+}). Anal. Calcd for $C_{37}H_{55}GeP$: C, 73.65; H, 9.19. Found: C, 73.92; H, 9.33.

18b: ^{31}P{^{1}H} NMR -101.5 ^{1}J(PH) = 214.7 Hz; MS (EI), (^{74}Ge) *m*/*e* 646 (M^{+}). Anal. Calcd for $C_{40}H_{61}GeP$: C, 74.43; H, 9.53. Found C, 74.68; H, 9.51.

Synthesis of Methyldimesitylfluorogermane (20). Dimesityldifluorogermane (8.03 g, 23.0 mmol) in solution in diethyl ether (50 mL) was treated with 1 equiv of methyllithium (1.6 M in diethyl ether) at room temperature. The reaction mixture was stirred for 1 h, and then the solvents were removed under reduced pressure to give crude **20**. Recrystallization from pentane afforded **20**: white crystals (6.74 g, yield 85%); mp 115 °C; ^{1}H NMR δ 1.03 (d, ^{3}J(HF) = 7.6 Hz, 3 H, MeGe), 2.16 (s, 6 H, *p*-Me), 2.47 (s, 12 H, *o*-Me), 6.78 (s, 4 H, Ar Mes); ^{19}F NMR δ -112.4. Anal. Calcd for $C_{19}H_{25}FGe$: C, 66.14; H, 7.30; F, 5.51. Found: C, 66.38; H, 7.51; F, 5.56.

Synthesis of 18a from 20. A solution of the 2,4,6-tri-*tert*-butylphenyllithiophosphide (**21**) (prepared from 2,4,6-tri-*tert*-butylphenylphosphine (2.12 g, 7.6 mmol), an equimolar quantity of butyllithium (1.6 M) in hexane, and 20 mL of diethyl ether) was added to a solution of **20** (2.62 g, 7.6 mmol) in pentane (20 mL). The reaction mixture was stirred for 1 h at room temperature. Removal of the solvents led to **18a** previously obtained and identified according to its ^{1}H and ^{31}P NMR data.

Addition of Methylmagnesium Iodide to 1. A solution of methylmagnesium iodide (prepared from methyl iodide (0.35 g, 2.5 mmol), magnesium (0.06 g, 2.54 mat. g), and diethyl ether (15 mL)) was added slowly to a solution of **1** (1.34 g, 2.3 mmol) in the same solvent (20 mL). ^{31}P and ^{1}H NMR analysis showed the formation of **19** (δ –128.1 (br s)). Quenching with methanol followed by removal of the solvent under reduced pressure afforded the previously described germylphosphine **18a**.

Reduction of 1 by Lithium Aluminum Hydride. A solution of germaphosphene **1** (1.28 g, 2.18 mmol) in diethyl ether (5 mL) was added to a suspension of lithium aluminum hydride (0.15 g, 3.13 mmol) in the same solvent (10 mL). The reaction mixture was stirred for 1 h at 35 °C, hydrolyzed, extracted with pentane, and dried over Na_2SO_4. Removal of the solvent under reduced pressure afforded a crude product which was recrystallized from pentane to give **22**: white crystals (0.96 g, yield 74%); mp 79–82 °C; ^{1}H NMR δ 1.23 (s, 9 H, *p*-*t*-Bu), 1.47 (s, 18 H, *o*-*t*-Bu), 2.10 (s, 6 H, *p*-Me), 2.30 (s, 12 H, *o*-Me), 5.08 (dd, ^{1}J(PH) = 208.9 Hz, ^{3}J(HH) 2.5 Hz, 1 H, PH), 5.43 (dd, ^{2}J(PH) = 7.0 Hz, ^{3}J(HH) = 2.5 Hz, 1 H, GeH), 6.63 (s, 4 H, Ar Mes), 7.43 (d, ^{4}J(PH) = 2.2 Hz, 2 H, Ar Ar); ^{31}P{^{1}H} NMR δ –122.7; IR (pentane) ν(GeH) 2050, ν(PH) 2340 cm^{-1}. Anal. Calcd for $C_{36}H_{53}GeP$: C, 73.36; H, 9.06. found: C, 73.09; H, 8.88.

Reaction of 1 with $BH_3 \cdot SMe_2$. To a solution of **1** (1.92 g, 3.27 mmol) in pentane (15 mL) was slowly added a solution of $BH_3 \cdot SMe_2$ (0.25 g, 3.27 mmol) in the same solvent at room temperature. IR and NMR analysis showed the formation of **22** (80%) (see above) and **23** (20 %): ^{1}H NMR δ 1.40 (s, 9 H, *p*-*t*-Bu), 1.60 (s, 18 H, *o*-*t*-Bu), 2.10 (s, 6 H, *p*-Me), 2.50 (s, 12 H, *o*-Me), 6.73 (br s, 4 H, ArMes), 7.49 (d, ^{4}J(PH) ~ 2 Hz, 2 H, ArAr); ^{31}P -17.0 (s); ^{11}B -10.0 ($BF_3 \cdot Et_2O$ external ref); IR (thin film) ν(GeH) 2063, ν(BH) 2360, 2400 cm^{-1}.

Addition of Dimethyl Disulfide to 1. A mixture of 1 (1.20 g, 2.05 mmol), dimethyl disulfide (0.19 g, 2.05 mmol), and benzene (8 mL) was heated in a sealed tube at 80 °C for 4 h. After evaporation of the solvent at reduced pressure, the residue was recrystallized from pentane to afford 0.91 g of **24**: white crystals (yield 65%); mp 133–135 °C; ^{1}H NMR (C_6D_6) δ 1.40 (s, 9 H, *p*-*t*-Bu), 1.63 (s, 3 H, MeSGe), 1.77 (s, 18 H, *o*-*t*-Bu), 2.12 (s, 6 H, *p*-Me), 2.16 (d, ^3J(PH) = 12.7 Hz, 3 H, MeSP), 2.43 (s, 12 H, *o*-Me), 6.75 (s, 4 H, Ar Mes), 7.55 (d, ^4J(PH) = 2.6 Hz, 2 H, Ar Ar); ^{31}P{^{1}H} NMR (C_6D_6) δ 3.0. Anal. Calcd for $C_{38}H_{57}GePS_2$: C, 66.96; H, 8.43; S, 9.41. Found: C, 67.20; H, 8.58; S, 9.50.

Synthesis, Structure, and Spectroscopic Properties of Early Transition Metal η^2-Iminoacyl Complexes Containing Aryl Oxide Ligation

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Abstract: A total of twenty η^2-iminoacyl derivatives of the metals titanium, zirconium, hafnium, and tantalum have been synthesized by the migratory insertion of organic isocyanides into the metal–alkyl bonds of a series of mixed alkyl, aryl oxide compounds. For the group 4 metals reaction of the bis-alkyls $(ArO)_2M(R)_2$ (M = Ti, Zr, Hf; ArO = 2,6-diisopropyl, 2,6-diphenyl, or 2,6-di-*tert*-butylphenoxide; R = CH_3, CH_2Ph, or CH_2SiMe_3) with R′NC leads initially to the mono-iminoacyl derivatives $(ArO)_2M(\eta^2\text{-}R'NCR)(R)$ (I) and finally to the bis-insertion products $(ArO)_2M(\eta^2\text{-}R'NCR)_2$ (II). The tris-benzyl complex $(2,6\text{-}t\text{-}Bu_2ArO)Zr(CH_2Ph)_3$ yields the complex $(2,6\text{-}t\text{-}Bu_2ArO)Zr(\eta^2\text{-}R'NCCH_2Ph)_3$ (IV) with 3 equiv of R′NC via the isolated bis-iminoacyl intermediate (III). For tantalum, the complex $Ta(OAr\text{-}2,6\text{-}Me_2)_3(\eta^2\text{-}xyNCCH_2Ph)_2$ (V) ($OAr\text{-}2,6\text{-}Me_2$ = 2,6-dimethylphenoxide) is readily formed from the corresponding bis-benzyl complex and 2 equiv of 2,6-dimethylphenyl isocyanide (xyNC). With the tris-alkyls $Ta(OAr\text{-}2,6\text{-}Me_2)_2(R)_3$ (R = CH_3, CH_2Ph), however, only 2 equiv of xyNC were found to insert readily leading to $Ta(OAr\text{-}2,6\text{-}Me_2)_2(\eta^2\text{-}xyNCR)_2(R)$ (VI). The spectroscopic properties of all of these compounds is consistent with an η^2 coordination of the iminoacyl group. In order to confirm this and gain more insight into the structural parameters for this type of bonding, six single-crystal X-ray diffraction studies have been carried out on compounds of type I, II, IV, and VI. All compounds structurally characterized were found to have very similar M–N and M–C distances to the iminoacyl function with C–N distances being in the range 1.257 (6) to 1.285 (4) Å consistent with the presence of a double bond. Correlation of the observed solid-state structures of these complexes with their ^{1}H and ^{13}C NMR spectra indicate that the η^2-iminoacyl groups are fluxional. However, whether this fluxionality involves simple rotation while η^2 bound or an η^2-η^1-η^2 process could not be distinguished. The two mono-inserted compounds $Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(\eta^2\text{-}t\text{-}BuNCCH_2Ph)(CH_2Ph)$ (Ia) and $Ti(OAr\text{-}2,6\text{-}Ph_2)_2(\eta^2\text{-}PhNCCH_2SiMe_3)(CH_2SiMe_3)$ (Ib) adopt similar structures in which the η^2-iminoacyl and noninserted alkyl group are co-planar bisecting the plane of $(ArO)_2Ti$ unit with the carbon atoms mutually cis to each other. In the bis-iminoacyl derivatives $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2(\eta^2\text{-}t\text{-}BuNCCH_2Ph)_2$ (IId) and $Hf(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2(\eta^2\text{-}PhNCMe)_2$ (IIg) the η^2-R′NCR units lie parallel to each other in a head-to-tail fashion, aligned approximately along the O–M–O plane. The tris-insertion complex $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)(\eta^2\text{-}t\text{-}BuNCCH_2Ph)_3$ (IVa) contains three nonequivalent η^2-iminoacyls arranged about the metal center. All three types of group 4 metal complexes I, II, and IV can best be described as containing a 4-coordinate environment about the metal in which each η^2-R′NCR group occupies a single coordination site. The compound $Ta(OAr\text{-}2,6\text{-}Me_2)_2(\eta^2\text{-}xyNCMe)_2(Me)$ (VIa) was found to contain the η^2-iminoacyl groups co-planar with mutually cis-carbon atoms. The metal coordination sphere could best be described as pentagonal bipyramidal with trans, axial aryl oxide groups. The summary of the crystal data is as follows: for $Ti(OAr\text{-}2,6\text{-}i\text{-}Pr_2)_2(\eta^2\text{-}t\text{-}BuNCCH_2Ph)(CH_2Ph)$ (Ia) at −154 °C, a = 18.678 (7) Å, b = 11.724 (4) Å, c = 9.053 (3) Å, α = 111.99 (2), β = 74.23 (2)°, γ = 101.96 (2)°, Z = 2, d_{calcd} = 1.148 g cm^{-3} in space group $P\bar{1}$; for $Ti(OAr\text{-}2,6\text{-}Ph_2)_2(\eta^2\text{-}PhNCCH_2SiMe_3)(CH_2SiMe_3)$ (Ib) at −160 °C, a = 23.086 (9) Å, b = 11.100 (4) Å, c = 10.122 (3) Å, α = 95.94 (2)°, β = 107.38 (2)°, γ = 78.51 (2)°, Z = 2, d_{calcd} = 1.178 g cm^{-3} in space group $P\bar{1}$; for $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2(\eta^2\text{-}t\text{-}BuNCCH_2Ph)_2$ (IId) at −157 °C, a = 23.612 (8) Å, b = 11.198 (4) Å, c = 21.243 (8) Å, β = 123.52 (2)°, Z = 4, d_{calcd} = 1.206 g cm^{-3} in space group $C2/c$; for $Hf(OAr\text{-}2,6\text{-}t\text{-}Bu_2)_2(\eta^2\text{-}PhNCMe)_2$ (IIg) at 22 °C, a = 13.203 (3) Å, b = 15.150 (3) Å, c = 21.213 (6) Å, β = 103.33 (2)°, Z = 4, d_{calcd} = 1.328 g cm^{-3} in space group $C2/c$; for $Zr(OAr\text{-}2,6\text{-}t\text{-}Bu_2)(\eta^2\text{-}t\text{-}BuNCCH_2Ph)_3$ (IVa) at −155 °C, a = 14.031 (5) Å, b = 15.788 (7) Å, c = 10.918 (4) Å, α = 108.89 (2)°, β = 97.01 (2)°, γ = 94.30 (2)°, Z = 2, d_{calcd} = 1.207 g cm^{-3} in space group $P\bar{1}$; for $Ta(OAr\text{-}2,6\text{-}Me_2)_2(\eta^2\text{-}xyNCMe)_2(Me)$ (VIa) at −160 °C, a = 10.881 (2) Å, b = 18.154 (5) Å, c = 9.188 (2) Å, α = 99.07 (1)°, β = 108.80 (1)°, γ = 75.36 (1)°, Z = 2, d_{calcd} = 1.465 g cm^{-3} in space group $P\bar{1}$.

The migratory insertion of carbon monoxide into metal–carbon bonds is an organometallic reaction that has deservedly received considerable study.[2] However, it is the structure and reactivity of the ensuing metal–acyl functional group that determines the organic products that one might expect from transition metal mediated utilization of CO.[3] For high valent, electron deficient (oxophilic) metals such as the early d-block,[4–6] lanthanides and[7]

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