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Halide Substitution Reactions of the Germylidyne Complexes *trans*-[X(dppe)$_2$W≡Ge(η^1-Cp*)] (X = Cl, I; dppe = $Ph_2PCH_2CH_2PPh_2$; Cp* = C_5Me_5)

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The first reactions of the germylidyne complexes *trans*-[X(dppe)$_2$W≡Ge(η^1-Cp*)]·[toluene] (**1-Cl**·C_7H_8, X = Cl; **1-I**·C_7H_8, X = I) with nucleophiles and electrophiles are reported. Treatment of **1-I**·C_7H_8 with KBH_4 in refluxing THF affords selectively the hydrido−germylidyne complex *trans*-[H(dppe)$_2$W≡Ge(η^1-Cp*)] (**2**). Similarly, metathetical exchange of **1-I**·C_7H_8 with an excess of MY (M = Na, K; Y = NCO, N_3, NCS, CN) gives the pseudohalide complexes *trans*-[Y(dppe)$_2$W≡Ge(η^1-Cp*)]·x(toluene) (**3a**, Y = NCO, $x = 0$; **3b**, Y = N_3, $x = 0$; **3c**·C_7H_8, Y = NCS, $x = 1$; **3d**·0.5C_7H_8, Y = CN, $x = 0.5$). Chloride abstraction from **1-Cl**·C_7H_8 with Li[B(C_6F_5)$_4$]·2.5Et_2O yields in the presence of acetonitrile the first cationic germylidyne complex, *trans*-[(MeCN)(dppe)$_2$W≡Ge(η^1-Cp*)][B(C_6F_5)$_4$] (**4**). All new complexes were well characterized. The molecular structures of **2**·1.5C_6D_6, **3a**·THF, **3d**·0.5C_7H_8, and **4** were determined by single-crystal X-ray diffraction studies. The germylidyne complexes reveal very short W−Ge distances (d_{W-Ge} = 229.91(9)−231.84(6) pm), an almost linear geometry at the triply bonded germanium atom (W−Ge−C_{Cp*} = 172.0(1)−176.8(1)°) and a η^1-bonded Cp* substituent.

Introduction

Compounds featuring a triple bond to Si, Ge, Sn, or Pb are very attractive targets in main-group chemistry.[1] These compounds are expected to be very reactive, given the reluctance of main-group elements with principal quantum numbers ≥ 3 to participate in multiple bonding,[2] as documented in the classical double-bond rule.[3] In fact, compounds containing a triple bond to a heavier group 14 element were elusive until recently, when the first germylidyne complexes [(η^5-C_5H_5)(CO)$_2$M≡GeR] (M = Cr, Mo, W; R = C_6H_3-2,6-Mes$_2$, C_6H_3-2,6-Trip$_2$, where Mes = C_6H_2-2,4,6-Me$_3$ and Trip = C_6H_2-2,4,6-*i*Pr$_3$)[4] and *trans*-[X(dppe)$_2$M≡Ge(η^1-Cp*)] (X = Cl, Br, I; dppe = $Ph_2PCH_2CH_2PPh_2$; M = Mo, W; Cp* = C_5Me_5)[5] were isolated and structurally characterized.[6] The cyclopentadienyl complexes [(η^5-C_5H_5)(CO)$_2$M≡GeR] were prepared by salt elimination from Na[M(η^5-C_5H_5)(CO)$_3$] and {Ge^{II}(Cl)R}$_n$ (R = C_6H_3-2,6-Mes$_2$, $n = 2$; R = C_6H_3-2,6-Trip$_2$, $n = 1$).[7] The reaction afforded the V-shaped metallogermylenes [(η^5-C_5H_5)(CO)$_3$M−GeR], which upon heating or photolysis eliminated CO to yield the triply bonded germanium compounds.[4] In comparison, the germylidyne complexes *trans*-[X(dppe)$_2$M≡Ge(η^1-Cp*)] were obtained directly from *trans*-[M(dppe)$_2$(N_2)$_2$] (M = Mo, W)[8] upon thermal elimination of dinitrogen in the presence of {Ge^{II}(Cp*)X}$_n$ (X = Cl, $n = 1$; X = Br, $n = 2$; X = I, $n = \infty$).[5,9] Application of the "salt elimination method" to analogous tin(II) and lead(II) halides afforded only the ylenes [(η^5-C_5H_5)(CO)$_3$M−ER] (E = Sn, Pb; R = C_6H_3-2,6-Mes$_2$, C_6H_3-2,6-Trip$_2$), displaying a V-shaped coordination geometry at the E atom and an M−E single bond.[10] Attempts to transform the tricarbonyl complexes [(η^5-C_5H_5)(CO)$_3$M−ER] into triply bonded tin and lead compounds failed.[10] In comparison,

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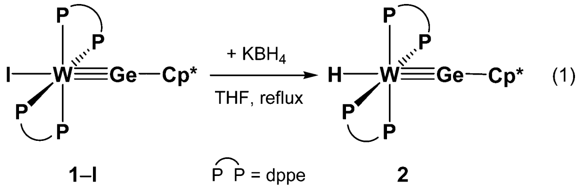
the "dinitrogen elimination method" proved to be straightforward and very efficient for the formation of the first triple bonds to tin and lead, as demonstrated recently by the syntheses and full characterizations of the stannylidyne and plumbylidyne complexes *trans*-$[Cl(PMe_3)_4W{\equiv}SnR]$ ($R = C_6H_3$-2,6-Mes_2) and *trans*-$[Br(PMe_3)_4Mo{\equiv}PbR]$ ($R = C_6H_3$-2,6-$Trip_2$).[11,12] The electronic structures of the germylidyne, stannylidyne, and plumbylidyne complexes were analyzed with various quantum-chemical methods, which revealed a bonding situation similar to that in Fischer-type carbyne complexes.[5a,12,13] Numerous stoichiometric and catalytic reactions of carbyne complexes have been uncovered since the synthesis of the first carbyne complex in 1973.[14] In comparison, reactivity studies of the heavier group 14 element ylidyne complexes have not been carried out to date. We set out to explore the chemistry of the new ylidyne complexes and report here first nucleophilic and electrophilic substitution reactions of the germylidyne complexes *trans*-$[X(dppe)_2W{\equiv}Ge(\eta^1\text{-}Cp^*)]\cdot$(toluene) (**1-Cl**$\cdot C_7H_8$, X = Cl; **1-I**$\cdot C_7H_8$, X = I). Detailed spectroscopic and structural features of the substitution products are also presented.

Results and Discussion

Synthesis and Characterization of *trans*-$[H(dppe)_2W{\equiv}Ge(\eta^1\text{-}Cp^*)]$ (2). The reaction of **1-I**$\cdot C_7H_8$ with an excess of KBH_4 in refluxing THF afforded selectively the hydrido–germylidyne complex *trans*-$[H(dppe)_2W{\equiv}Ge(\eta^1\text{-}Cp^*)]$ (**2**), which was isolated as a red-orange, air-sensitive solid in 95% yield (eq 1).



(1)

1–I **2**

Monitoring of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy revealed a slow but selective conversion of the starting material to the product, which was completed in ca. 50 h. The chloro complex **1-Cl**$\cdot C_7H_8$ was found to be much less reactive than **1-I**$\cdot C_7H_8$. For example, only a very small amount of the hydrido complex **2** was formed after heating of **1-Cl**$\cdot C_7H_8$ with an excess of KBH_4 in refluxing THF for 7 days. Complex **2** is more soluble in THF and toluene than **1-Cl**$\cdot C_7H_8$ to give red solutions, which discolor rapidly upon exposure to air. It is also decomposed by CD_2Cl_2 to give a mixture of unknown products, whereas the ^1H and $^{31}P\{^1H\}$ NMR spectra of the chloro complex **1-Cl**$\cdot C_7H_8$ in CD_2Cl_2 show no sign of decomposition after 18 h.

Table 1. W–H Stretching Frequencies in cm^{-1} of Selected Tungsten Hydrides in Different Oxidation States

compd	ν(W–H)	medium	ref
trans-$[H(dppe)_2W{\equiv}GeCp^*]$ (**2**)	1812	Nujol	this work
trans-$[H(dmpe)_2W{\equiv}CMes]$	1600	*a*	15b
trans,trans-$[W(H)(CO)_2(NO)(PEt_3)_2]$	1671	hexane	16
trans,trans-$[W(H)(CO)_2(NO)\{P(OPh)_3\}_2]$	1721	hexane	16
$[CpW(CO)_3H]$	1845	hexane	18
$[Cp^*W(CO)_3H]$	1827	hexane	18
WH_2 ($^5B_2$, C_{2v})	1832^b	neon matrix	19
WH_3 ($^4A_1$, C_{3v})	1895^c	neon matrix	19
$W(H)_2(SiH_3)_2(PMe_3)_4$	1860	Nujol	20
$[Cp_2WH_2]$	1918	Nujol	21
$[Cp^*_2WH_2]$	1919	Nujol	22
$[Cp^*_2W(H)Me]$	1900	Nujol	23
$[Cp^*_2W(H)Cl]$	1940	Nujol	23
WH_4 ($^3A_1$, T_d)	1921^d	neon matrix	19
WH_6 ($^1A_1$, C_{3v})	2021, 2004, 1954, 1928^e	neon matrix	19

[a] Solid-state Raman spectrum. [b] Only the antisymmetric (b_2) stretching mode was detected. [c] Only the antisymmetric degenerate (e) stretching mode was detected. [d] Only the antisymmetric (t_2) stretching mode was detected. [e] The distorted-trigonal-prismatic WH_6 displays two a_1 (2021 and 1954 cm^{-1}) and two e stretching modes (2004 and 1928 cm^{-1}).

Complex **2** was fully characterized. The IR spectrum of **2** in Nujol shows a broad and weak absorption band at 1812 cm^{-1}, which is assigned to the ν(W–H) stretching vibration. It is noteworthy that the W–H stretching modes of the electronically related carbyne complexes *trans*-$[H(dmpe)_2W{\equiv}CR]$ (dmpe = $Me_2PCH_2CH_2PMe_2$; R = *t*Bu, Mes) could not be observed in the IR spectra.[15] The W–H stretching mode of **2** has a considerably higher frequency (1812 cm^{-1}) than those of the carbyne complex *trans*-$[H(dmpe)_2W{\equiv}CMes]$ (1600 cm^{-1}, detected by solid-state Raman spectroscopy)[15b] and the related nitrosyl complexes *trans,trans*-$[W(H)(CO)_2(NO)(PR_3)_2]$ (R = Et, Me, Ph, O*i*Pr, OMe, OPh: ν(W–H) = 1671–1721 cm^{-1}) (Table 1).[16] This reflects the weaker trans influence of the germylidyne ligand compared with the carbyne and nitrosyl ligands, which display a strong trans influence.[14a,15b,16,17] A comparison with the W–H stretching modes of various tungsten hydrides in the oxidation states II–VI reveals, however, a rather low frequency of the W–H stretching vibration of **2**, indicating a rather polarized W–H bond in the electron-rich germylidyne complex (Table 1).[18–23] The ^1H NMR spec-

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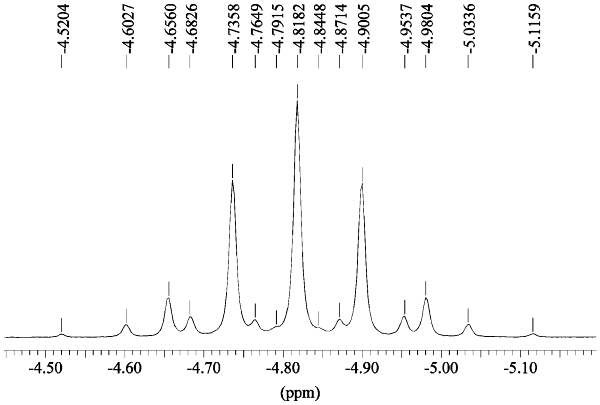

Figure 1. Hydride signal in the ^1H NMR spectrum of **2** in THF-d_8 at 298 K.

trum of **2** (THF-d_8, 298 K) displays a characteristic high-field-shifted 1:4:6:4:1 quintet resonance for the hydrido ligand at δ −4.82 ppm,[24] indicating the presence of four chemically equivalent phosphorus nuclei ($^2J(H,P) = 24.7$ Hz). Each individual line of the quintet signal is flanked by a pair of satellites, arising from coupling with the ^{183}W nucleus ($^1J(H,W) = 81.0$ Hz) (Figure 1). The hydride resonance of **2** appears at lower field as compared to those of the carbyne complexes *trans*-[H(dmpe)$_2$W≡CR] (R = *t*Bu, δ −6.2 ppm, $^2J(H,P) = 30$ Hz, $^1J(H,W) = 30$ Hz; R = Mes, δ −6.58 ppm, $^2J(H,P) = 32$ Hz, $^1J(H,W) = 32$ Hz)[15] and *trans*-[H{P(OMe)$_3$}$_4$W≡C-Mes] (δ −5.58 ppm, $^2J(H,P) = 35.7$ Hz, $^1J(H,W) = 20.4$ Hz).[17c] The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a singlet resonance for the chemically equivalent dppe ligands, which appears at lower field (δ_P in C_6D_6 64.7 ppm) than that of **1-Cl**·C_7H_8 (δ_P in C_6D_6 48.3 ppm) and of **1-I**·C_7H_8 (δ_P in C_6D_6 40.6 ppm). The $^1J(P,W)$ coupling constant of **2** (261.8 Hz) has a value between those of **1-Cl**·C_7H_8 (264.6 Hz) and **1-I**·C_7H_8 (258.0 Hz).[5b]

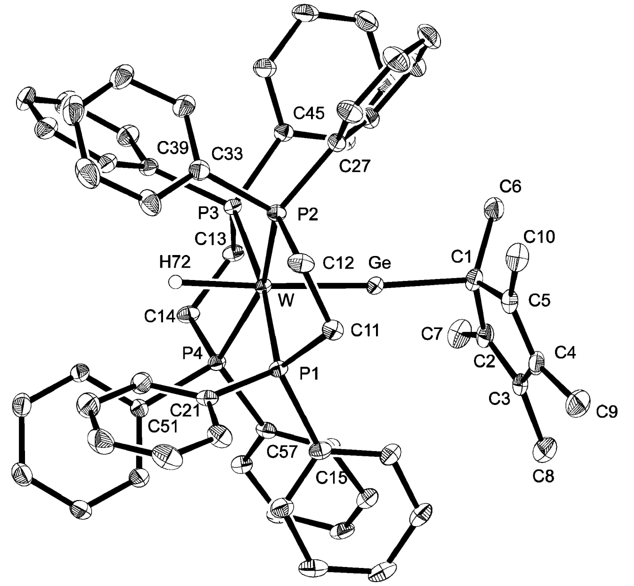

Figure 2. Illustration of the molecular structure of *trans*-[H(dppe)$_2$W≡Ge(η^1-Cp*)] (**2**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity, except for that bonded to tungsten.

Table 2. Selected Bond Lengths (pm) and Bond Angles (deg) of the Germylidyne Complexes *trans*-[Y(dppe)$_2$W≡Ge(η^1-Cp*)] (2, Y = H; 3a, Y = NCO; 3d, Y = CN) and *trans*-[(MeCN)(dppe)$_2$W≡Ge(η^1-Cp*)][B(C_6F_5)$_4$] (4)[a]

	2·1.5C_6D_6	**3a**·THF	**3d**·0.5C_7H_8	**4**
W−Ge	231.0(1)	229.91(9)	231.84(6)	230.30(8)
W−Y	179(3)	216.6(5)	218.3(5)	214.4(2)
C63−N		109.6(6)	113.0(5)	114.0(3)
C63−O1		123.8(7)		
W−P1	242.8(2)	245.2(1)	245.4(1)	246.25(9)
W−P2	243.3(2)	245.1(1)	246.7(1)	246.7(1)
W−P3	243.5(2)	250.0(1)	250.8(1)	248.27(9)
W−P4	244.2(2)	249.8(1)	248.3(1)	248.8(1)
$(W-P)_{av}$	243.2	247.5	247.8	247.5
Ge−C1	203.7(4)	203.1(5)	200.8(4)	200.4(2)
C1−C2	148.9(6)	149.5(7)	151.2(6)	150.2(3)
C2−C3	134.6(7)	137.5(7)	135.6(6)	135.5(3)
C3−C4	146.3(7)	143.0(7)	146.3(6)	146.1(3)
C4−C5	136.3(6)	136.0(8)	135.5(6)	135.5(3)
C5−C1	147.8(7)	151.5(7)	151.1(6)	150.0(3)
W−Ge−C1	176.8(1)	172.0(1)	172.2(1)	174.31(7)
Ge−W−Y	176.5(11)	174.6(1)	170.0(1)	177.63(5)
Ge−W−P1	93.95(5)	90.67(4)	90.76(3)	92.55(3)
Ge−W−P2	95.62(5)	85.93(4)	92.08(3)	90.03(3)
Ge−W−P3	92.95(5)	103.00(4)	88.82(3)	94.77(3)
Ge−W−P4	100.92(4)	101.58(4)	103.12(3)	96.44(3)
Y−W−P1	89.4(11)	87.5(1)	97.9(1)	87.81(6)
Y−W−P2	84.2(12)	88.8(1)	84.7(1)	87.74(6)
Y−W−P3	83.7(12)	78.6(1)	83.2(1)	84.91(6)
Y−W−P4	79.4(12)	83.7(1)	81.4(1)	85.82(6)
Ge−C1−C_g[b]	113.1(3)	104.6(3)	115.4(3)	112.2(2)
W−N−C63		179.2(4)		179.4(2)
W−C63−N			178.5(4)	
N−C63−O1		177.0(6)		

[a] Estimated standard deviations are given in parentheses. [b] C_g denotes the center of the Cp* ring.

The solid-state structure of **2**·1.5C_6D_6 was determined by single-crystal X-ray diffraction. The molecular structure of **2** is depicted in Figure 2, and selected bond lengths and angles are listed in Table 2. Complex **2** reveals a distorted-octahedral coordination geometry at tungsten and a trans arrangement of the germylidyne and the terminal hydrido ligand (Ge−W−H72 = 176.5(11)°). The hydride ligand could be located in the difference Fourier synthesis map. The W−H72 bond length (179(3) pm) is close to those found in other tungsten hydrides by neutron diffraction ($d(W-H)_{terminal}$ = 171.5(4)−177.8(3) pm).[25] The W−Ge triple-bond length of **2**·1.5C_6D_6 at 231.0(1) pm compares well with those of **1-Cl**·C_7H_8 (230.2(1) pm)[5a] and **1-I**·C_7H_8 (230.60(9) pm),[5b] despite the presence of a trans-positioned hydrido ligand, which is known to exert a strong trans influence.[26] This suggests that the σ-bonding part of the W−Ge bond, which is expected to be weakened by the trans-disposed hydrido ligand, has a minor influence on the W−Ge bond length of **2**·1.5C_6D_6 and provides evidence for the strong π-bonding contributions to the W−Ge covalent bond energy of *trans*-[X(dppe)$_2$W≡Ge(η^1-Cp*)] (X = H, Cl, I), in full agreement with the

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Table 3. ν_{as}(NCO), ν_{as}(NNN), ν_{as}(NCS), and ν(CN) Absorption Bands (cm^{-1}) of the Germylidyne Complexes 3a−3d·0.5C$_7$H$_8$ and Other Isocyanato, Azido, Isothiocyanato, and Cyano Complexes of Tungsten

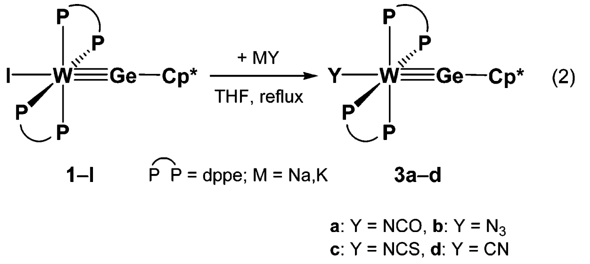
isocyanato complex	ν_{as}(NCO)	medium	ref	azido complex	ν_{as}(NNN)	medium	ref
trans-[(OCN)(dppe)$_2$W≡GeCp*]	2221	THF	this work	*trans*-[(N$_3$)(dppe)$_2$W≡GeCp*]	2098	THF	this work
[N(PPh$_3$)$_2$]NCO	2141	CH$_2$Cl$_2$	28, 29	[N(PPh$_3$)$_2$]N$_3$	2005	CH$_2$Cl$_2$	28, 37
trans-[(OCN)(CO)$_4$W≡CNEt$_2$]	2226	*a*	31	(AsPh$_4$)[W(CO)$_5$(N$_3$)]	2048	CHCl$_3$	38
[(OCN)(dppe)(CO)$_2$W≡CR][b]	2209	KBr	32	[CpW(CO)$_3$(N$_3$)]	2072	CH$_2$Cl$_2$	34
(NEt$_4$)[W(CO)$_5$(NCO)]	2235	CH$_2$Cl$_2$	33	*cis*-[CpW(CO)$_2$(PMe$_3$)(N$_3$)]	2064	CH$_2$Cl$_2$	34
[CpW(CO)$_3$(NCO)]	2248	CH$_2$Cl$_2$	34	[Cp*W(CO)$_3$(N$_3$)]	2066	CH$_2$Cl$_2$	34
cis-[CpW(CO)$_2$(PPh$_3$)(NCO)]	2241	CH$_2$Cl$_2$	35	*cis*-[Cp*W(CO)$_2$(PMe$_3$)(N$_3$)]	2059	CH$_2$Cl$_2$	34
(NBu$_4$)$_2$[W$_6$Cl$_8$(NCO)$_6$]	2217	CH$_2$Cl$_2$	36	(PPh$_4$)(*cis*-[WCl$_4$(NCl)(N$_3$)])	2070	Nujol	39

isothiocyanato complex	ν_{as}(NCS)	medium	ref	cyano complex	ν(CN)	medium	ref
trans-[(SCN)(dppe)$_2$W≡GeCp*]	2066	Nujol	this work	*trans*-[(NC)(dppe)$_2$W≡GeCp*]	2082	THF	this work
(NBu$_4$)NCS	2056	CH$_2$Cl$_2$	29	(NEt$_4$)CN	2054	CH$_2$Cl$_2$	this work
trans-[(SCN)(CO)$_4$W≡CNEt$_2$]	2078	CH$_2$Cl$_2$	31	*trans*-[(NC)(CO)$_4$W≡CNEt$_2$]	2126	CH$_2$Cl$_2$	31
[(SCN)(dppe)(CO)$_2$W≡CR][b]	2057	KBr	32	[(NC)(CO)$_2$(dppe)W≡CR][b]	2111	KBr	43
[(SCN)(dmpe)(CO)$_2$W≡CR′][c]	2067	CH$_2$Cl$_2$	40	(NBu$_4$)[W(CN)(N$_2$)(dppe)$_2$]	2030	Nujol	44
trans-[(SCN)(dppe)$_2$W(μ-N$_2$)TiCp$_2$Cl]	2049	KBr	41	[N(PPh$_3$)$_2$][W(CO)$_5$(CN)]	2098	CH$_2$Cl$_2$	45
trans-[(SCN)(dppe)$_2$W(μ-N$_2$)BCy$_2$)]	2056	KBr	42	Tp′W(CN)(CO)(HC≡CH)[d]	2114	KBr	46

[a] 1,1,2-Trichloroethane. [b] R = C(H)=C(CH$_2$)$_4$. [c] dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$, R′ = C$_6$H$_4$-4-Me. [d] Tp′ = hydridotris(3,5-dimethylpyrazol-1-yl)borate.

results of quantum-chemical studies.[5a,13b,d] The complex **2**·1.5C$_6$D$_6$ features an almost linear coordination geometry at the germanium atom (W−Ge−C1 = 176.8(1)°) and an η^1-bonded Cp* substituent, which displays bonding parameters similar to those of the tungsten germylidyne complexes **1-Cl**·C$_7$H$_8$,[5a] **1-I**·C$_7$H$_8$,[5b] **3a**·THF, **3d**·0.5C$_7$H$_8$, and **4** (Table 2). All these structural data provide additional support for the presence of a tungsten−germanium triple bond in **2**.

Synthesis and Characterization of *trans*-[Y(dppe)$_2$W≡Ge(η^1-Cp*)]·*x*(toluene) (**3a**, Y = NCO, *x* = 0; **3b**, Y = N$_3$, *x* = 0; **3c**·C$_7$H$_8$, Y = NCS, *x* = 1; **3d**·0.5C$_7$H$_8$, Y = CN, *x* = 0.5). Nucleophilic substitution of iodide in **1-I**·C$_7$H$_8$ occurs also by a variety of pseudohalides to give the tungsten germylidyne complexes **3a**−**d** (eq 2). Thus, prolonged heating of **1-I**·C$_7$H$_8$ with a large excess of KNCO in refluxing THF afforded the isocyanato complex **3a**. Monitoring of the reaction by IR and ^{31}P{^{1}H} NMR spectroscopy revealed a selective but slow conversion of the starting material to the product. Completion of the reaction after ca. 120 h was confirmed by ^{31}P{^{1}H} NMR spectroscopy, and the reaction solution was worked up to afford the germylidyne complex **3a** in 85% yield as an orange, moderately air-sensitive solid of remarkable thermal stability (mp 237−238 °C). The iodo complex **1-I**·C$_7$H$_8$ is much more reactive than the chloro complex **1-Cl**·C$_7$H$_8$ toward KNCO, as observed in the reaction with KBH$_4$. Indicative of the very low reactivity of **1-Cl**·C$_7$H$_8$ was the observation in one case when a contaminated sample of **1-I**·C$_7$H$_8$ with 3% of **1-Cl**·C$_7$H$_8$ was treated with KNCO under the conditions given above. Complete conversion of **1-I**·C$_7$H$_8$ to the product **3a** was observed by ^{31}P{^{1}H} NMR spectroscopy (**3a**, δ_P in C$_6$D$_6$ 48.9 ppm; **1-I**·C$_7$H$_8$, δ_P in C$_6$D$_6$ 40.6 ppm), whereas the contaminant **1-Cl**·C$_7$H$_8$ had not been consumed (**1-Cl**·C$_7$H$_8$, δ_P in C$_6$D$_6$ 48.3 ppm).



Similarly, the reactions of **1-I**·C$_7$H$_8$ with a large excess of NaN$_3$ and KNCS in refluxing THF afforded selectively the germylidyne complexes **3b** and **3c**, respectively (eq 2). The azido complex **3b** was isolated as an orange solid in 96% yield, and the isothiocyanato complex **3c** was obtained after crystallization from toluene as an orange-brown toluene solvate in 84% yield. Both compounds are soluble in THF and toluene, the solubility of **3c** in both solvents being lower than that of **3a** and **3b**. The complex **1-I**·C$_7$H$_8$ reacts also with an excess of NaCN in refluxing THF to give the cyano complex **3d** (eq 2). The reaction is, however, less selective than those with KNCO, NaN$_3$, and KNCS. The germylidyne complex **3d** was isolated in 33% yield as a green toluene hemisolvate, which decomposes upon melting at 196−197 °C. Complexes **3a**−**d**·0.5C$_7$H$_8$ were characterized by elemental analyses and IR and ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy, and the solid-state structures of **3a**·THF and **3d**·0.5C$_7$H$_8$ were determined by single-crystal X-ray diffraction (Tables 2−5, Figures 3 and 4, Experimental Section).

The IR spectrum of **3a** in THF displays a characteristic, intense ν_{as}(NCO) absorption band at 2221 cm^{-1} (Table 3), which appears as in other transition-metal isocyanato complexes[27] at higher energy than that of the cyanate anion ([N(PPh$_3$)$_2$]NCO, ν_{as}(NCO) in CH$_2$Cl$_2$ 2141 cm^{-1};[28,29] KNCO, ν_{as}(NCO) 2165 cm^{-1}).[30] The ν_{as}(NCO) frequency of **3a** compares well with those of the electronically related carbyne complexes *trans*-[(OCN)(CO)$_4$W≡CNEt$_2$][31] and [(OCN)(dppe)(CO)$_2$W≡CC(H)=C(CH$_2$)$_4$][32] and of other tungsten isocyanato complexes

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Table 4. Cp* Proton Chemical Shifts of the Germylidyne Complexes 1-Cl·C_7H_8 through 3d·0.5C_7H_8 and the Germanium(II) Halides $\{Ge^{II}(Cp^*)X\}_n$ in Different Solvents

compd	δ (ppm) in CD_2Cl_2	 in THF-d_8	 in C_6D_6	ref
trans-[Cl(dppe)$_2$W≡Ge(η^1-Cp*)] (**1-Cl**)	1.38	1.42	1.53	5a, this work
trans-[Br(dppe)$_2$W≡Ge(η^1-Cp*)] (**1-Br**)		1.37	1.47	5b
trans-[I(dppe)$_2$W≡Ge(η^1-Cp*)] (**1-I**)		1.31	1.40	5b
trans-[H(dppe)$_2$W≡Ge(η^1-Cp*)] (**2a**)		1.52	1.69	this work
trans-[(OCN)(dppe)$_2$W≡Ge(η^1-Cp*)] (**3a**)		1.48	1.59	this work
trans-[(N$_3$)(dppe)$_2$W≡Ge(η^1-Cp*)] (**3b**)			1.56	this work
trans-[(SCN)(dppe)$_2$W≡Ge(η^1-Cp*)] (**3c**)	1.46	1.49	1.57	this work
trans-[(NC)(dppe)$_2$W≡Ge(η^1-Cp*)] (**3d**)		1.44	1.52	this work
Ge(Cp*)Cl	2.02	2.00	1.65	5b
{Ge(Cp*)Br}$_2$	2.00		1.65	5b
{Ge(Cp*)I}$_\infty$	2.05		1.59	this work

Table 5. Selected Crystallographic and Structure Refinement Data of the Germylidyne Complexes 2·1.5C_6D_6, 3a·THF, 3d·0.5C_7H_8, and 4

	2·1.5C_6D_6	**3a**·THF[a]	**3d**·0.5C_7H_8	**4**
empirical formula	$C_{71}H_{73}GeP_4W$	$C_{67}H_{71}GeNO_2P_4W$	$C_{66.5}H_{67}GeNP_4W$	$C_{88}H_{66}BF_{20}GeNP_4W$
fw	1306.61	1302.57	1260.53	1908.55
cryst color	dark red	reddish	dark green	dark red
cryst dimens (mm)	0.48 × 0.48 × 0.20	0.44 × 0.32 × 0.12	0.32 × 0.20 × 0.10	0.64 × 0.64 × 0.44
cryst syst	triclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$I2/a$	$P\bar{1}$
a (Å)	14.406(5)	13.358(4)	24.601(4)	11.655(4)
b (Å)	14.792(6)	17.610(4)	13.466(3)	17.604(6)
c (Å)	16.554(6)	25.160(8)	34.549(5)	20.121(6)
α (deg)	97.65(4)	90	90	104.17(4)
β (deg)	104.64(4)	95.18(3)	97.56(2)	97.74(3)
γ (deg)	112.72(4)	90	90	90.75(3)
V (Å^3)	3041.0(19)	5894(3)	11346(3)	3962(2)
Z	2	4	8	2
ρ_{calcd} (g cm^{-3})	1.427	1.468	1.476	1.600
temp (K)	180(2)	180(2)	180(2)	180(2)
μ(Mo Kα) (mm^{-1})	2.531	2.614	2.711	2.006
F(000)	1330	2648	5112	1904
2θ scan range (deg)	$5.10 < 2\theta < 50.50$	$4.90 < 2\theta < 50.50$	$4.32 < 2\theta < 50.50$	$3.54 < 2\theta < 51.98$
no. of rflns collected	20 208	35 846	36 306	23 286
no. of unique rflns	10 323 ($R_{int} = 0.0387$)	10 164 ($R_{int} = 0.0766$)	10 259 ($R_{int} = 0.0613$)	15 508 ($R_{int} = 0.0209$)
abs cor	refinement of ΔF^2	refinement of ΔF^2	refinement of ΔF^2	empirical (ψ scan)
no. of restraints/params refined	0/698	6/665	6/673	0/1052
R1 ($I > 2\sigma(I)$)	0.0316	0.0363	0.0306	0.0206
wR2 (all data)	0.0790	0.0531	0.0591	0.0494
goodness of fit	1.000	1.564	0.900	1.069

[a] The C atoms of the poorly defined solvent molecule were only refined isotropically.

(Table 3).[33-36] The azido−germylidyne complex **3b** displays in THF an intense IR absorption band for the ν_{as}(NNN) vibration at 2098 cm^{-1}, which appears at higher frequency than that of the azide anion ([N(PPh$_3$)$_2$]-N$_3$, ν_{as}(NNN) in CH_2Cl_2 2005 cm^{-1})[28,37] and other tungsten azido complexes,[34,38,39] suggesting the presence of a less polar W−N bond (Table 3). The complex **3c**·C_7H_8 is identified by an IR absorption band at 2066 cm^{-1}, which is assigned to the ν_{as}(NCS) mode (Table 3).[27] This band appears at a position close to that of related carbyne complexes[32,40] and other tungsten dppe complexes (Table 3),[41,42] for which N-bonding of the SCN group has been confirmed by single-crystal X-ray diffraction. This lets us suggest that the SCN ligand is also N-bonded to tungsten in **3c**·C_7H_8. The presence of a terminal cyano ligand in **3d**·0.5C_7H_8 is indicated by a weak ν(CN) IR absorption band in THF at 2082 cm^{-1} and was confirmed by X-ray crystallography (vide infra). The ν(CN) band of **3d**·0.5C_7H_8 appears between those of the carbyne complexes *trans*-[(NC)(CO)$_4$W≡CNEt$_2$][31] and [(NC)(CO)$_2$(dppe)W≡CC(H)=C(CH$_2$)$_4$][43] and that of the dinitrogen complex (NBu$_4$)[W(CN)(N$_2$)(dppe)$_2$] (Table 3),[44] reflecting the increasing π-acceptor/σ-donor ratio of the cyano ligand in the series dinitrogen complex > germylidyne complex > carbyne complex.

The ^{1}H NMR spectra of **3a**−**d**·0.5C_7H_8 display two resonance signals for the diastereotopic methylene protons of the dppe ligands, and the ^{13}C{^{1}H} NMR

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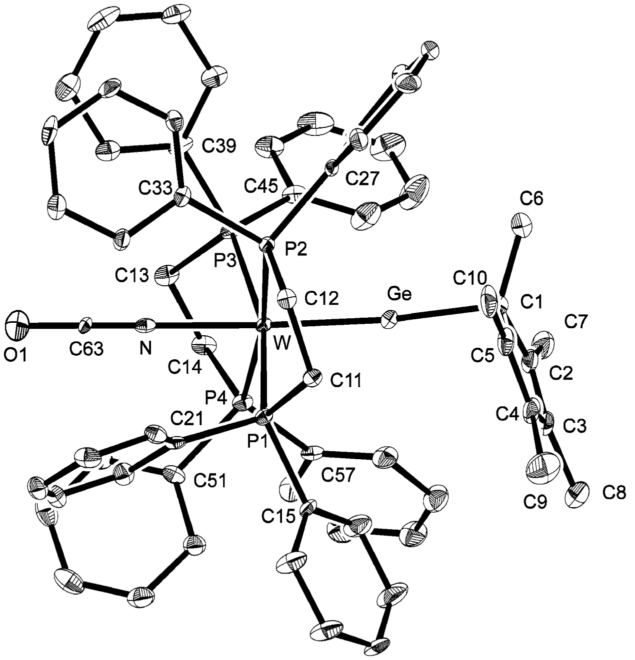

Figure 3. Illustration of the molecular structure of *trans*-[(OCN)(dppe)$_2$W≡Ge(η^1-Cp*)] (**3a**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

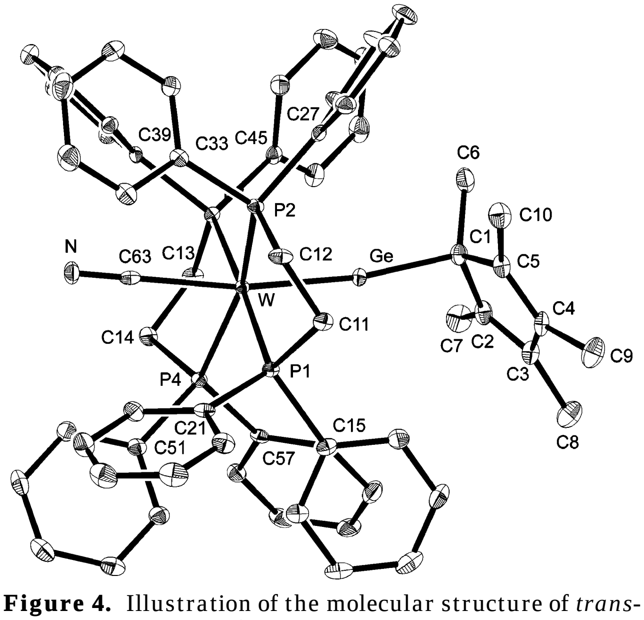

Figure 4. Illustration of the molecular structure of *trans*-[(NC)(dppe)$_2$W≡Ge(η^1-Cp*)] (**3d**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

spectra show double sets of signals for the ring carbon nuclei of the diastereotopic phenyl groups, as expected for diamagnetic complexes of the general formula *trans*-[W(dppe)$_2$(L)(L′)]. Furthermore, the NMR spectra of **3a**–**d**·0.5C$_7$H$_8$ reveal, as do those of **1-Cl**·C$_7$H$_8$,[5] **1-I**·C$_7$H$_8$,[5] and **2**, a fast haptotropic shift of the Cp* group. This gives rise to only one singlet resonance for the methyl protons in the ^{1}H NMR spectra and two singlet resonances in the ^{13}C{^{1}H} NMR spectra, one for the methyl carbon and one for the ring carbon nuclei of the Cp* group. The Cp* proton resonances of **1-Cl**·C$_7$H$_8$ through **3d**·0.5C$_7$H$_8$ appear in THF-d_8 or CD$_2$Cl$_2$ at considerably higher field than those of {Ge^{II}(Cp*)X}$_n$ (X = Cl, n = 1; X = Br, n = 2; X = I, n = ∞) (Table 4).[5b,9] It is also characteristic that a solvent change from THF-d_8 or CD$_2$Cl$_2$ to C$_6$D$_6$ has an opposite effect on the chemical shift of the Cp* protons in the germylidyne complexes **1-Cl**·C$_7$H$_8$ through **3d**·0.5C$_7$H$_8$ and the germanium(II) halides {Ge^{II}(Cp*)X}$_n$ (Table 4). All these observations indicate that the Cp* methyl protons of **1-Cl**·C$_7$H$_8$ through **3d**·0.5C$_7$H$_8$ are shielded intramolecularly by the phenyl groups of the dppe ligands, this shielding effect being diminished through intermolecular interactions with the benzene solvent, whereas the Cp* methyl protons of the germanium(II) halides {Ge^{II}(Cp*)X}$_n$ experience an intermolecular shielding by the benzene solvent.

The molecular structures of **3a**·THF and **3d**·0.5C$_7$H$_8$ are depicted in Figures 3 and 4, respectively, and selected bond lengths and angles are listed in Table 2. The germylidyne ligand displays in both complexes the three characteristic structural parameters, which are also found in the germylidyne complexes **1-Cl**·C$_7$H$_8$,[5a] **1-I**·C$_7$H$_8$,[5b] **2**·1.5C$_6$D$_6$, and **4** (Table 2). These are the very short W–Ge bond (**3a**·THF, 229.91(9) pm; **3d**·0.5C$_7$H$_8$, 231.84(6) pm), the almost linear coordination geometry at germanium (**3a**·THF, W–Ge–C1 = 172.0(1)°; **3d**·0.5C$_7$H$_8$, W–Ge–C1 = 172.2(1)°), and the η^1 bonding mode of the Cp* substituent (Table 2). The OCN group in **3a**·THF is bound through the nitrogen atom to the tungsten center. The W–N distance of 216.6(5) pm is slightly longer than those found in other tungsten isocyanato complexes such as [CpW(CO)$_3$(NCO)] (d(W–N)$_{av}$ = 213.4(6) pm, W–N–C = 169.6(6) and 162.7(7)° for the two crystallographically independent molecules),[34] [Cp*W(CO)$_3$(NCO)] (d(W–N) = 213.1(6) pm, W–N–C = 166.1(8)°),[34] [Cp*W(CO)$_2$(PMe$_3$)(NCO)] (d(W–N) = 212.1(6) pm, W–N–C = 173.4(8)°),[34] and (NBu$_4$)$_2$[W$_6$Cl$_8$(NCO)$_6$] (d(W–N) = 210.4(9)–212.9(8) pm, W–N–C = 157.5(8)–168.1(9)°).[36] The isocyanato ligand is essentially linear with a N–C–O bond angle of 177.0(6)° and a W–N–C angle of 179.2(4)° (Table 2). The W–N–C bond angles of the few structurally characterized tungsten isocyanato complexes range from 157.5(8) to 173.4(8)°, suggesting a rather flat energy profile for bending the isocyanato ligand at the nitrogen atom.[34–36] The W–C63 bond length of the cyano ligand in **3d**·0.5C$_7$H$_8$ at 218.3(5) pm lies in the range observed for other tungsten cyano complexes (212.9(10)–227.7(3) pm).[46,47]

Synthesis and Characterization of *trans*-[(MeCN)(dppe)$_2$W≡Ge(η^1-Cp*)][B(C$_6$F$_5$)$_4$] (4). Previously we have shown that cationic carbyne complexes can be prepared straightforwardly from neutral pre-

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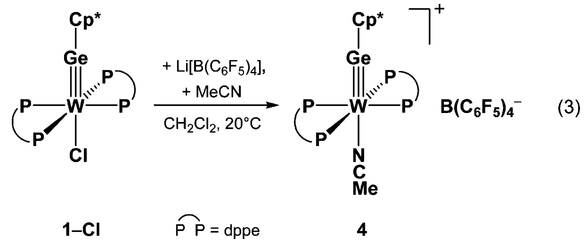
cursors upon halide abstraction in the presence of neutral two-electron-donor ligands. Representative examples include the reactions of the low-oxidation-state carbyne complexes *trans*-[I(*t*BuNC)$_4$W≡CPh] and [Br(*t*BuNC)$_2$(CO)$_2$Cr≡CR] (R = Ph, N*i*Pr$_2$) with TlPF$_6$ and *t*BuNC to give the cationic carbyne complexes [(*t*BuNC)$_5$W≡CPh](PF$_6$)[48] and *fac*-[(*t*BuNC)$_3$(CO)$_2$Cr≡CR](PF$_6$),[49,50] respectively, or the reaction of the high-oxidation-state tungsten aminocarbyne complexes [(η^5-C$_5$R$_5$)(I)$_2$(CO)W≡CNEt$_2$] (R = H, Me) with TlPF$_6$ and EtNC to afford [(η^5-C$_5$R$_5$)(I)(EtNC)(CO)W≡CNEt$_2$](PF$_6$).[51] In case of strongly activated metal−halogen bonds, halide substitution occurs even in the absence of a halide abstraction reagent, as demonstrated by the reactions of [I(CO)$_2$L$_2$W≡CNEt$_2$] (L$_2$= 2,2′-bipy, *o*-phen) with PR$_3$ (R = Me, Et) and of *trans*-[I(*t*BuNC)$_{4-n}$(CO)$_n$W≡CNEt$_2$] (n = 0, 1) with *t*BuNC to yield the cationic aminocarbyne complexes [(CO)$_2$L$_2$(PR$_3$)W≡CNEt$_2$]I[52] and [(*t*BuNC)$_{5-n}$(CO)$_n$W≡CNEt$_2$]I (n = 0, 1),[53,54] respectively. The same methodology has been used recently by other groups to obtain cationic carbyne complexes.[17b,d] Following the electronic analogy of carbyne and germylidyne complexes,[5a] we decided to follow a similar approach to cationic germylidyne complexes. However, initial attempts were unsuccessful. Thus, treatment of **1-Cl**·C$_7$H$_8$ with TlPF$_6$ in toluene afforded only the adduct *trans*-[Cl(dppe)$_2$W≡Ge(η^1-Cp*)]·TlPF$_6$·3(toluene), featuring a Cl−Tl donor−acceptor bond (d(Tl−Cl) = 290.6(2) pm), and chloride abstraction from **1-Cl**·C$_7$H$_8$ by TlPF$_6$ in the presence of isocyanides was accompanied by oxidative degradation of the W−Ge triple bond to afford germanium-free products.[34] These results suggested that a nonoxidizing halide abstraction reagent might be necessary to achieve the goal. In fact, treatment of a solution of **1-Cl**·C$_7$H$_8$ in CH$_2$Cl$_2$ with 1 equiv of Li[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O in the presence of acetonitrile afforded selectively the cationic germylidyne complex *trans*-[(MeCN)(dppe)$_2$W≡Ge(η^1-Cp*)][B(C$_6$F$_5$)$_4$]-(**4**) (eq 3). Complex **4** was isolated as an amber-colored solid in 98% yield and was fully characterized. The ^{1}H NMR spectrum of **4** in CD$_2$Cl$_2$ displays a characteristic quintet resonance for the methyl protons of the acetonitrile ligand at δ 0.81 ppm, the multiplicity of the signal indicating a long-range coupling of the methyl protons with the four chemically equivalent ^{31}P nuclei of the dppe ligands (^5J(H,P) = 2.6 Hz). In addition, a singlet resonance is observed for the Cp* methyl protons of **4** at lower field (δ 1.62 ppm) than that of **1-Cl**·C$_7$H$_8$ (δ(Cp*) in CD$_2$Cl$_2$ 1.38 ppm) (Table 4). The ^{13}C{^{1}H} NMR spectrum of **4** shows one methyl carbon singlet resonance for the acetonitrile ligand at δ 4.2 ppm. Furthermore, two singlet resonances are found for the methyl and ring carbon nuclei of the Cp* group at δ 12.6 and 128.4 ppm, indicating the fast haptotropic shift of the η^1-bonded Cp* group on the NMR time scale. Finally, the ^{31}P{^{1}H} NMR spectrum of the trans-configured complex **4** displays expectedly a singlet resonance for the dppe ligands at lower field (δ_P in CD$_2$Cl$_2$ 54.0 ppm) than that of **1-Cl**·C$_7$H$_8$ (δ_P in CD$_2$Cl$_2$ 48.3 ppm).[55] The structure of **4** was determined by X-ray crystallography. It verifies the trans-configuration of the germylidyne complex cation, in full agreement with the NMR spectroscopic data (Figure 5).



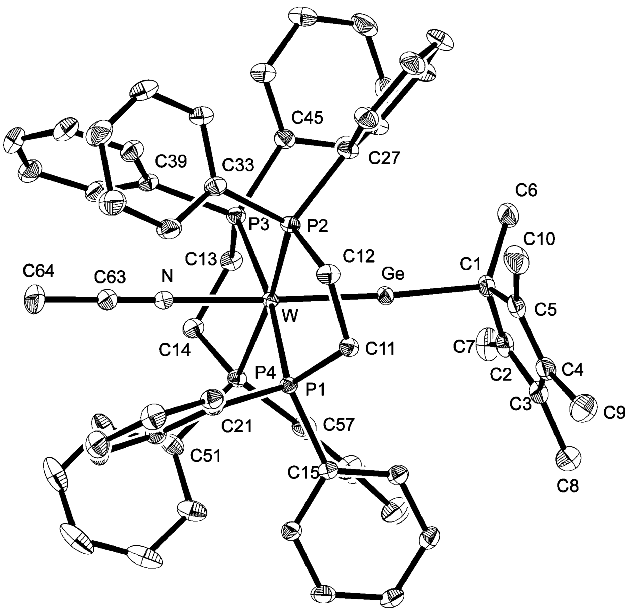


Figure 5. Illustration of the molecular structure of the cation *trans*-[(MeCN)(dppe)$_2$W≡Ge(η^1-Cp*)]$^+$ in **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

The acetonitrile ligand features a linear atom array (W−N−C63 = 179.4(2)°; N−C63−C64 = 179.5(3)°), and the W−N and C−N bond lengths of 214.4(2) and 114.0(3) pm compare well with those of the stannylidyne complex *trans*-[(MeCN)(dppe)$_2$W≡SnC$_6$H$_3$-2,6-Mes$_2$](PF$_6$) (W−N = 213.2(3) pm; C−N = 114.2(5) pm).[34] The structural parameters of the germylidyne ligand in **4** are similar to those of the other germylidyne complexes (Table 2).

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[55] NMR spectroscopic data of *trans*-[Cl(dppe)$_2$W≡Ge(η^1-Cp*)]·toluene (**1-Cl**·C$_7$H$_8$) are as follows. ^{1}H NMR (300.1 MHz, C$_6$D$_6$, 298 K; δ (ppm)): 1.53 (s, 15H, C$_5$*Me*$_5$), 2.10 (s, 3H, Ph*Me*), 2.35 (m, br, 4H, 4 × C*H*^{1}H^2), 2.84 (m, br, 4H, 4 × CH^1*H*^{2}), 6.92−7.06 (m, 37H, (*o-H*, 4 × Ph), (*m-H* + *p-H*, 8 × Ph) and *Ph*Me), 7.79 (m, br, 8H, *o-H*, 4 × Ph). ^{1}H NMR (300.1 MHz, CD$_2$Cl$_2$, 298 K; δ (ppm)): 1.38 (s, 15H, C$_5$*Me*$_5$), 2.34 (s, 3H, Ph*Me*), 2.40 (m, 4H, 4 × C*H*^{1}H^2), 2.85 (m, 4H, 4 × CH^1*H*^{2}), 6.82 (m, br, 8H, *o-H*, 4 × Ph), 6.94 (t, ^3J(H,H) = 7.5 Hz, 8H, *m-H*, 4 × Ph), 7.10 (t, ^3J(H,H) = 7.3 Hz, 4H, *p-H*, 4 × Ph), 7.16−7.24 (m, 13H, (*m-H*, 4 × Ph) and *Ph*Me), 7.27 (t, ^3J(H,H) = 7.3 Hz, 4H, *p-H*, 4 × Ph), 7.62 (m, br, 8H, *o-H*, 4 × Ph). ^{31}P{^{1}H} NMR (121.5 MHz, C$_6$D$_6$, 298 K; δ (ppm)): 48.3 (s, ^1J(P,W) = 264.6 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$, 298 K; δ (ppm)): 48.3 (s, ^1J(P,W) = 265.2 Hz).

Conclusion

Halide displacement reactions of the germylidyne complexes *trans*-[X(dppe)$_2$W≡Ge(η^1-Cp*)]·(toluene) (X = Cl, I) with various nucleophiles and electrophiles lead straightforwardly to neutral and cationic germylidyne complexes with variable ligand spheres. The ionic products are promising candidates for studying addition reactions at the tungsten−germanium triple bond. The presented reactions provide the first experimental evidence for the electronic analogy of the germylidyne complexes with Fischer-type carbyne complexes.

Experimental Section

1. General Considerations. All experiments were carried out under an atmosphere of argon using a combination of Schlenk and glovebox techniques. The glassware was oven-dried at approximately 110 °C, assembled hot, and baked in vacuo prior to use. The solvents were dried by standard methods (pentane over CaH_2, toluene, Et_2O, and THF over sodium/benzophenone, CH_2Cl_2 over Sicapent (Merck) and Na/Pb alloy, and CH_3CN over Sicapent (Merck) and K_2CO_3) and distilled under argon. The solvents were stored over $LiAlH_4$ (CH_2Cl_2 over CaH_2), trap-to-trap condensed, and deoxygenated by two freeze−pump−thaw cycles immediately prior to use. The germylidyne complexes **1-Cl**·C_7H_8 and **1-I**·C_7H_8 and the germanium(II) halides {Ge(Cp*)X} ((X = Cl, n = 1; X = I, n = ∞) were prepared as described previously.[5,55] Li[B(C_6F_5)$_4$]·2.5Et_2O was prepared as reported in the literature[56] and shown by ^{1}H and ^{19}F{^{1}H} NMR spectroscopy and elemental analysis to be pure.[57] KBH_4 and NaN_3 were dried overnight at 90 °C under fine vacuum. KNCS and NaCN were dried under vacuum for several days. KNCO was prepared by ethanol extraction of a commercially available sample and dried under vacuum.

The C, H, N analyses were performed on a Leco CHNS-932 elemental analyzer, and the halogens were determined using Schöniger's method followed by titration with Hg(ClO_4)$_2$.[58] IR spectra of solutions were recorded on a Bruker IFS-55 spectrometer in the spectral range of 2300−1500 cm^{-1} using a cell of NaCl windows. IR spectra of solids were recorded either as Nujol mulls between KBr or NaCl plates (Nujol/KBr, Nujol/NaCl) or as dispersions in pressed KBr disks in the spectral range of 4000−600 cm^{-1} (**3c**), 4000−500 cm^{-1} (**2**, **3b**), or 4000−400 cm^{-1} (**3a**, **3d**·0.5C_7H_8). Nujol was dried with sodium and stored in the glovebox. The following abbreviations were used for the intensity and shape of the IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{19}F{^{1}H} NMR spectra were recorded on a Bruker AM-300 or a DPX-300 spectrometer in dry deoxygenated benzene-d_6, tetrahydrofuran-d_8, or dichloromethane-d_2. The ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated against the internal residual proton and natural-abundance ^{13}C resonances of the deuterated solvent (benzene-d_6, δ_H 7.15 ppm and δ_C 128.0 ppm; tetrahydrofuran-d_8, δ_H 1.73 ppm and δ_C 25.3 ppm; methylene-d_2 chloride, δ_H 5.32 ppm and δ_C 53.8 ppm). The ^{31}P{^{1}H} NMR spectra were calibrated against an external 85% aqueous H_3PO_4 solution and the ^{19}F{^{1}H} NMR spectra against external $CFCl_3$. The standards were filled in capillaries and measured in 5 mm NMR tubes containing the deuterated solvent. The following abbreviations were used for the signal multiplicities: s = singlet, t = triplet, quint = quintet, m = multiplet, dm = doublet of multiplets. Diastereotopic methylene protons were designated as H^1 and H^2, respectively. Coupling could not be resolved for the methylene and ortho phenyl proton NMR signals of the dppe ligands, the ortho and meta phenyl carbon NMR signals of the dppe ligands, and the ortho fluorine NMR signal of the C_6F_5 groups in **4**, resulting in signal broadening. The abbreviations m, br and s, br were used for the multiplicity and form of these signals. The ^{1}H and ^{13}C NMR signals of **2** were assigned by a combination of H,H-COSY, C,H-COSY, and HMBC experiments. The diastereotopic phenyl groups in **2** were labeled with the subscript letters X and Y, respectively. The ^{1}H and ^{13}C NMR signals of the dppe ligands in **1-Cl**·C_7H_8 through **3d**·0.5C_7H_8 and **4** were assigned on the basis of their relative intensities, their multiplicities, and the correlated NMR spectroscopic results of **2**. The assignment of the toluene signals in the ^{1}H and ^{13}C{^{1}H} spectra of the solvates **1-Cl**·C_7H_8, **3c**·C_7H_8, and **3d**·0.5C_7H_8 was confirmed by a comparison with the NMR data given in ref 59.

The thermal behavior of the products was studied with a Büchi SMP 530 melting point apparatus (Dr. Tottoli, Patent 320338). The samples were sealed under vacuum in capillary tubes and heated until melting had occurred.

2. Preparation of *trans*-[H(dppe)$_2$W≡Ge(η^1-Cp*)] (2). A Schlenk tube was charged with the complex **1-I**·C_7H_8 (380 mg, 0.27 mmol) and KBH_4 (167 mg, 3.10 mmol). THF (45 mL) was added to the mixture, and the red-orange suspension was heated under reflux in an oil bath for ca. 50 h. The resulting red-orange suspension was cooled to room temperature, and the solution was separated from the white solid by filtration through a filter cannula. The solid was washed with THF (2 × 15 mL), and the washings were combined with the filtrate, evaporated to dryness, and dried in vacuo at 50 °C for 1 h. The resulting red-orange solid was washed at −78 °C with few milliliters of Et_2O and dried in vacuo to give complex **2**. Yield: 305 mg (95%) of a red-orange solid. Anal. Calcd for $C_{62}H_{64}GeP_4W$ (1189.52): C, 62.60; H, 5.42. Found: C, 62.13; H, 5.38. IR (Nujol/KBr; ν (cm^{-1})): 3051 (m, br), 1812 (w, br, ν(W−H)), 1583 (w), 1572 (w), 1483 (m), 1432 (s), 1306 (w), 1275 (vw), 1252 (w), 1186 (w), 1154 (w), 1095 (m), 1085 (m), 1068 (w), 1027 (w), 1000 (vw), 973 (vw), 872 (m), 801 (m), 738 (s), 692 (vs), 648 (m), 629 (m), 613 (m), 528 (vs), 509 (s). ^{1}H NMR (300.1 MHz, C_6D_6, 298 K; δ (ppm)): −4.52 (quint, ^2J(H,P) = 24.3 Hz, W−*H*), 1.69 (s, 15H, C_5Me_5), 2.34 (m, br, 4H, 4 × CH^1H^2), 2.50 (m, br, 4H, 4 × CH^1H^2), 6.88 (m, 12H, *m-H* + *p-H*, 4 × Ph), 7.03 (m, 12H, *m-H* + *p-H*, 4 × Ph), 7.31 (m, br, 8H, *o-H*, 4 × Ph), 7.49 (m, br, 8H, *o-H*, 4 × Ph). ^{1}H NMR (300.1 MHz, THF-d_8, 298 K; δ (ppm)): −4.82 (quint, ^2J(H,P) = 24.7 Hz, ^1J(H,W) = 81.0 Hz, W−*H*), 1.52 (s, 15H, C_5Me_5), 2.23−2.50 (m, br, 8H, 4 × CH^1H^2), 6.85 (t, ^3J(H,H) = 7.3 Hz, 8H, *m-H*, 4 × Ph$_X$), 6.98 (t, ^3J(H,H) = 7.3 Hz, 4H, *p-H*, 4 × Ph$_X$), 7.03 (t, ^3J(H,H) = 7.3 Hz, 8H, *m-H*, 4 × Ph$_Y$), 7.07 (m, br, 8H, *o-H*, 4 × Ph$_X$), 7.14 (t, ^3J(H,H) = 7.3 Hz, 4H, *p-H*, 4 × Ph$_Y$), 7.34 (m, br, 8H, *o-H*, 4 × Ph$_Y$). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K; δ (ppm)): 64.7 (s, ^1J(P,W) = 261.8 Hz). ^{31}P{^{1}H} NMR (121.5 MHz, THF-d_8, 298 K; δ (ppm)): 64.8 (s, ^1J(P,W) = 261.2 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8, 298 K; δ (ppm)): 12.6 (s, C_5Me_5), 38.6 (m, 4 × CH_2), 125.7 (s, C_5Me$_5$), 127.4 (s, br, *m-C*, 4 × Ph$_X$), 127.8 (s, br, *m-C*, 4 × Ph$_Y$), 128.2 (s, *p-C*, 4 × Ph$_X$), 128.4 (s, *p-C*, 4 × Ph$_Y$), 133.8 (s, br, *o-C*, 4 × Ph$_Y$), 134.1 (s, br, *o-C*, 4 × Ph$_X$), 144.5 (m, *ipso-C*, 4 × Ph$_X$), 149.2 (m, *ipso-C*, 4 × Ph$_Y$).

3. Preparation of *trans*-[(OCN)(dppe)$_2$W≡Ge(η^1-Cp*)] (3a). A Schlenk tube was charged with 245 mg (0.174 mmol)

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(57) NMR spectroscopic data of Li[B(C_6F_5)$_4$]·2.5Et_2O are as follows. ^{1}H NMR (300.1 MHz, CD_2Cl_2, 298 K; δ (ppm)): 1.20 (t, ^3J(H,H) = 7.1 Hz, 15H, CH$_2$CH_3), 3.57 (q, ^3J(H,H) = 7.1 Hz, 10H, CH_2CH$_3$). ^{19}F{^{1}H} NMR (282.4 MHz, CD_2Cl_2, 298 K; δ (ppm)): −167.7 (t, ^3J(F,F) = 17.7 Hz, *m-F*, C_6F_5), −163.7 (t, ^3J(F,F) = 20.6 Hz, *p-F*, C_6F_5), −133.7 (m, br, *o-F*, C_6F_5).

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of the complex **1-I**·$\mathrm{C_7H_8}$ and 940 mg (11.6 mmol) of KNCO, and the mixture was degassed. THF (45 mL) was then added via a double-ended needle to the mixture, and the red-orange suspension was heated under reflux. Monitoring of the reaction by IR spectroscopy and $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy revealed a slow conversion of the starting material to the product. Completion of the reaction after heating under reflux for ca. 120 h was confirmed by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. The suspension was cooled to room temperature and filtered through a filter cannula. The filter cake was washed with THF (3 × 10 mL), the washings were combined with the filtrate, and the solvent was removed under reduced pressure. The obtained substance was dried in vacuo at 50 °C for 1.5 h and then extracted with toluene until the extracts were colorless (ca. 25 mL in total). The combined extracts were concentrated in vacuo to a few milliliters and treated with 20 mL of pentane. The resulting precipitate was allowed to settle, separated from the slight orange supernatant solution by filtration, washed with 10 mL of $\mathrm{Et_2O}$, and dried under fine vacuum to give complex **3a** as an orange solid. Yield: 182 mg (85%). Mp: 237−238 °C. Anal. Calcd for $\mathrm{C_{63}H_{63}GeNOP_4W}$ (1230.53): C, 61.49; H, 5.16; N, 1.14. Found: C, 61.31; H, 5.46; N, 1.12. IR (THF; ν (cm^{-1})): 2221 (vs, ν_{as}(NCO)). IR (toluene; ν (cm^{-1})): 2221 (vs, ν_{as}(NCO)). IR (KBr; ν (cm^{-1})): 3052 (m, br), 2984 (w), 2965 (m, br), 2918 (m, br), 2855 (m), 2220 (vs, ν_{as}(NCO)), 1585 (vw), 1569 (vw), 1483 (m), 1432 (s), 1380 (vw), 1307 (vw), 1263 (vw), 1239 (vw), 1186 (vw), 1154 (vw), 1091 (m), 1069 (w), 1027 (w), 999 (vw), 864 (w), 803 (w), 739 (m), 696 (s), 658 (w), 634 (w), 594 (w), 527 (s), 509 (m), 482 (m), 418 (m). ^{1}H NMR (300.1 MHz, $\mathrm{C_6D_6}$, 298 K; δ (ppm)): 1.59 (s, 15H, $\mathrm{C_5}Me_5$), 2.27 (m, br, 4H, 4 × $\mathrm{C}H^{1}\mathrm{H}^{2}$), 2.70 (m, br, 4H, 4 × $\mathrm{CH}^{1}H^{2}$), 6.86 (m, br, 8H, *o-H*, 4 × Ph), 7.03 (m, 24H, *m-H* + *p-H*, 8 × Ph), 7.72 (m, br, 8H, *o-H*, 4 × Ph). ^{1}H NMR (300.1 MHz, THF-d_8, 298 K; δ (ppm)): 1.48 (s, 15H, $\mathrm{C_5}Me_5$), 2.39 (m, br, 4H, 4 × $\mathrm{C}H^{1}\mathrm{H}^{2}$), 2.76 (m, br, 4H, 4 × $\mathrm{CH}^{1}H^{2}$), 6.67 (m, br, 8H, *o-H*, 4 × Ph), 6.91 (t, ^{3}J(H,H) = 7.5 Hz, 8H, *m-H*, 4 × Ph), 7.07 (t, ^{3}J(H,H) = 7.3 Hz, 4H, *p-H*, 4 × Ph), 7.17 (t, ^{3}J(H,H) = 7.3 Hz, 8H, *m-H*, 4 × Ph), 7.25 (t, ^{3}J(H,H) = 7.2 Hz, 4H, *p-H*, 4 × Ph), 7.64 (m, br, 8H, *o-H*, 4 × Ph). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{C_6D_6}$, 298 K; δ (ppm)): 48.9 (s, ^{1}J(P,W) = 266.9 Hz). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, THF-d_8, 298 K; δ (ppm)): 48.8 (s, ^{1}J(P,W) = 267.3 Hz).$^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.5 MHz, THF-d_8, 298 K; δ (ppm)): 12.8 (s, $\mathrm{C_5}Me_5$), 36.1 (m, 4 × CH_2), 127.1 (s, $C_5\mathrm{Me}_5$), 128.2 (s, br, *m-C*, 8 × Ph), 128.5 (s, *p-C*, 4 × Ph), 129.3 (s, *p-C*, 4 × Ph), 134.1 (s, br, *o-C*, 4 × Ph), 134.8 (s, br, *o-C*, 4 × Ph), 138.9 (m, *ipso-C*, 4 × Ph), 146.4 (m, *ipso-C*, 4 × Ph); the ^{13}C NMR signal of the isocyanato ligand was not detected.

4. Preparation of *trans*-[($\mathrm{N_3}$)(dppe)$_2$W≡Ge(η^1-Cp*)] (3b). The complex **1-I**·$\mathrm{C_7H_8}$ (100 mg, 0.071 mmol) and $\mathrm{NaN_3}$ (910 mg, 14.0 mmol) were placed in a Schlenk tube, and THF (ca. 20 mL) was condensed onto the mixture via vacuum transfer. The suspension was heated under reflux. Monitoring of the reaction by IR spectroscopy and $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy revealed a slow conversion of the starting material to the product (after 60 h the ratio of **1-I** to **3b** was 1/9). Completion of the reaction after heating for ca. 120 h was confirmed by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. The suspension was cooled to room temperature and filtered through a filter cannula. The red filtrate was evaporated to give an oily residue, which was dried in vacuo at ambient temperature overnight and then treated with 40 mL of toluene. The resultant red solution was filtered, and the filtrate was evaporated to give an oil. Addition of pentane (5 mL) and stirring at low temperature resulted in the precipitation of a solid, which was separated after decantation of the supernatant solution and dried in vacuo at ambient temperature overnight to afford **3b** as an orange solid. Yield: 84 mg (96%). Anal. Calcd for $\mathrm{C_{62}H_{63}GeN_3P_4W}$ (1230.53): C, 60.52; H, 5.16; N, 3.41. Found: C, 59.46; H, 5.29; N 2.91. IR (THF; ν (cm^{-1})): 2098 (vs, ν_{as}(NNN)). IR (Nujol/KBr; ν (cm^{-1})): 3431 (w), 3054 (m, br), 3020 (w), 2091 (vs, ν_{as}(NNN)), 1585 (w), 1571 (w), 1482 (m), 1432 (m), 1407 (w), 1306 (w), 1271 (vw), 1241 (w), 1182 (w), 1158 (w), 1090 (m), 1069 (w), 1028 (w), 1000 (w), 873 (w), 863 (w), 806 (m), 787 (m), 756 (w), 743 (m), 736 (m), 695 (s), 655 (m), 636 (w), 628 (w), 614 (w), 526 (s), 515 (m), 508 (s), 502 (m). ^{1}H NMR (300.1 MHz, $\mathrm{C_6D_6}$, 298 K; δ (ppm)): 1.56 (s, 15H, $\mathrm{C_5}Me_5$), 2.33 (m, br, 4H, 4 × $\mathrm{C}H^{1}\mathrm{H}^{2}$), 2.71 (m, br, 4H, 4 × $\mathrm{CH}^{1}H^{2}$), 6.94 (m, br, 8H, *o-H*, 4 × Ph), 7.04 (m, 24H, *m-H* + *p-H*, 8 × Ph), 7.69 (m, br, 8H, *o-H*, 4 × Ph). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{C_6D_6}$, 298 K; δ (ppm)): 48.4 (s, ^{1}J(P,W) = 268.8 Hz). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, THF-d_8, 298 K; δ (ppm)): 48.3 (s, ^{1}J(P,W) = 268.9 Hz).

5. Preparation of *trans*-[(SCN)(dppe)$_2$W≡Ge(η^1-Cp*)]·(toluene) (3c·$\mathrm{C_7H_8}$). The complex **1-I**·$\mathrm{C_7H_8}$ (200 mg, 0.142 mmol) was heated with an excess of KNCS (2.45 g, 25.2 mmol) in refluxing THF for ca. 62 h. Completion of the reaction was confirmed by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. The resulting suspension was filtered through a filter cannula, the filtrate was evaporated, and the obtained substance was dried in vacuo at ambient temperature. The product was extracted with 40 mL of warm toluene (50 °C), the extract was filtered, and the red-brown filtrate was concentrated to incipient crystallization and cooled in a −30 °C freezer. The supernatant solution was decanted off, and the crystalline solid was washed with $\mathrm{Et_2O}$ (10 mL) and pentane (10 mL) to afford, after drying in vacuo at ambient temperature for 0.5 h, **3c**·$\mathrm{C_7H_8}$ as an orange-brown solid. Yield: 158 mg (84%). Anal. Calcd for $\mathrm{C_{70}H_{71}GeNP_4SW}$ (1338.77): C, 62.80; H, 5.35; N, 1.05; S, 2.40. Found: C, 63.39; H, 5.62; N, 1.04; S, 2.40. IR (Nujol/NaCl; ν (cm^{-1})): 3048 (m, br), 3021 (w), 2066 (vs, ν_{as}(NCS)), 1606 (w), 1584 (w), 1570 (w), 1497 (w), 1483 (m), 1431 (s), 1417 (w), 1306 (w), 1264 (w), 1182 (w), 1157 (w), 1091 (m), 1068 (w), 1026 (w), 1000 (w), 876 (w), 864 (w), 852 (vw), 827 (w), 806 (m), 777 (m), 744 (m), 739 (m), 728 (m), 695 (s), 665 (w), 654 (m), 631 (m), 614 (w). ^{1}H NMR (300.1 MHz, $\mathrm{C_6D_6}$, 298 K; δ (ppm)): 1.57 (s, 15H, $\mathrm{C_5}Me_5$), 2.22 (m, br, 4H, 4 × $\mathrm{C}H^{1}\mathrm{H}^{2}$), 2.73 (m, br, 4H, 4 × $\mathrm{CH}^{1}H^{2}$), 6.86 (m, br, 8H, *o-H*, 4 × Ph), 7.03 (m, 12H, *m-H* + *p-H*, 4 × Ph), 7.08 (m, 12H, *m-H* + *p-H*, 4 × Ph), 7.73 (m, br, 8H, *o-H*, 4 × Ph). ^{1}H NMR (300.1 MHz, $\mathrm{CD_2Cl_2}$, 298 K; δ (ppm)): 1.46 (s, 15H, $\mathrm{C_5}Me_5$), 2.35 (s, 3H, Ph*Me*), 2.39 (m, 4H, 4 × $\mathrm{C}H^{1}\mathrm{H}^{2}$), 2.77 (m, 4H, 4 × $\mathrm{CH}^{1}H^{2}$), 6.66 (m, br, 8H, *o-H*, 4 × Ph), 6.99 (t, ^{3}J(H,H) = 7.5 Hz, 8H, *m-H*, 4 × Ph), 7.14−7.25 (m, 17H, (*m-H* + *p-H*, 4 × Ph) and *Ph*Me), 7.30 (t, ^{3}J(H,H) = 7.3 Hz, 4H, *p-H*, 4 × Ph), 7.60 (m, br, 8H, *o-H*, 4 × Ph). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{C_6D_6}$, 298 K; δ (ppm)): 50.4 (s, ^{1}J(P,W) = 268.3 Hz). $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{CD_2Cl_2}$, 298 K; δ (ppm)): 50.0 (s, ^{1}J(P,W) = 268.5 Hz). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{CD_2Cl_2}$, 298 K; δ (ppm)): 12.5 (s, $\mathrm{C_5}Me_5$), 21.5 (s, Ph*Me*), 35.7 (m, 4 × CH_2), 125.6 (s, *p-C*, *Ph*Me), 127.1 (s, $C_5\mathrm{Me}_5$), 127.8 (s, br, *m-C*, 4 × Ph), 128.3 (s, br, *m-C*, 4 × Ph; s, *p-C*, 4 × Ph), 128.5 (s, *m-C*, *Ph*Me), 129.2 and 129.3 (s each, (*o-C*, *Ph*Me) and (*p-C*, 4 × Ph)), 133.5 (s, br, *o-C*, 4 × Ph), 133.9 (s, br, *o-C*, 4 × Ph), 138.0 (m, *ipso-C*, 4 × Ph), 145.4 (m, *ipso-C*, 4 × Ph); the ^{13}C NMR signal of the isothiocyanato ligand was not detected.

6. Preparation of *trans*-[(NC)(dppe)$_2$W≡Ge(η^1-Cp*)]·0.5(toluene) (3d·0.5$\mathrm{C_7H_8}$). The complex **1-I**·$\mathrm{C_7H_8}$ (171 mg, 0.12 mmol) was heated with an excess of NaCN (301 mg, 6.14 mmol) in refluxing THF for 69 h. Completion of the reaction was confirmed by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. The resulting suspension was filtered through a filter cannula, and the filtrate was evaporated to dryness. The obtained substance was dried in vacuo at ambient temperature and extracted with toluene (20 mL in total). The combined extracts were filtered, and the filtrate was stored for 15 min at −40 °C. During this time a yellowish green solid deposited, which was filtered off at −40 °C. The orange-red filtrate was evaporated to dryness, and the residue was dissolved in 45 mL of toluene. The orange-red solution was filtered from some insoluble material, the filtrate was concentrated in vacuo to 1−2 mL and treated at −20 °C with cold pentane to precipitate complex **3d**. The precipitate was isolated by filtration and washed with diethyl ether (3 × 10 mL). The slightly orange washings were discarded, and the precipitate was dried in vacuo at 50 °C for 2 h to give the complex **3d**·$0.5C_7H_8$ as a green solid. Yield: 51 mg (33%), Mp: 196−197 °C dec. Anal. Calcd for $C_{66.5}H_{67}GeNP_4W$ (1260.63): C, 63.36; H, 5.36; N, 1.11. Found: C, 63.27; H, 5.74; N, 1.17. IR (THF; ν (cm^{-1})): 2082 (ν(CN)). IR (toluene; ν (cm^{-1})): 2082 (ν(CN)). IR (KBr; ν (cm^{-1})): 3049 (m, br), 2956 (w, br), 2913 (m, br), 2854 (w, br), 2077 (m, ν(CN)), 1585 (w), 1573 (w), 1484 (m), 1432 (vs), 1413 (w), 1380 (vw, br), 1306 (vw), 1276 (vw), 1236 (vw), 1190 (w, br), 1156 (vw), 1121 (vw), 1088 (m, br), 1069 (w), 1026 (w), 1000 (vw), 960 (vw, br), 871 (w), 822 (w), 804 (w), 739 (s), 730 (m), 695 (vs), 671 (w), 658 (m), 633 (w), 615 (vw), 528 (vs), 511 (s), 484 (m), 465 (w), 424 (m), 415 (m). ^{1}H NMR (300.1 MHz, C_6D_6, 298 K; δ (ppm)): 1.52 (s, 15H, C_5Me_5), 2.10 (s, 1.5H, 0.5Ph*Me*), 2.23 (m, 4H, 4 × CH^1H^2), 2.91 (m, 4H, 4 × CH$^1H^2$), 6.91−7.03 (m, 26.5 H, (*m-H* + *p-H*, 8 × Ph) and 0.5*Ph*Me), 7.27 (m, br, 8H, *o-H*, 4 × Ph), 7.71 (m, br, 8H, *o-H*, 4 × Ph). ^{1}H NMR (300.1 MHz, THF-d_8, 298 K; δ (ppm)): 1.44 (s, 15H, C_5Me_5), 2.31 (s, 1.5H, 0.5Ph*Me*), 2.33 (m, 4H, 4 × CH^1H^2), 2.90 (m, 4H, 4 × CH$^1H^2$), 6.88 (t, ^3J(H,H) = 7.4 Hz, 8H, *m-H*, 4 × Ph), 7.04 (m, 12H, *o-H* + *p-H*, 4 × Ph), 7.11−7.26 (m, 14.5 H, (*m-H* + *p-H*, 4 × Ph) and 0.5*Ph*Me), 7.62 (m, br, 8H, *o-H*, 4 × Ph). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 298 K; δ (ppm)): 51.1 (s, ^1J(P,W) = 257.2 Hz). ^{31}P{^{1}H} NMR (THF-d_8, 121.5 MHz, 298 K; δ (ppm)): 50.9 (s, ^1J(P,W) = 257.6 Hz). ^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz, 298 K; δ (ppm)): 12.5 (s, C_5Me_5), 21.5 (s, Ph*Me*), 38.0 (m, 4 × CH_2), 126.0 (s, *p-C*, *Ph*Me), 127.1 (s, C_5Me$_5$), 127.5 (s, br, *m-C*, 4 × Ph), 128.1 (s, br, *m-C*, 4 × Ph), 128.5 (s, *p-C*, 4 × Ph), 128.9 (s, *m-C*, *Ph*Me), 129.2 (s, *p-C*, 4 × Ph), 129.7 (s, *o-C*, *Ph*Me), 134.4 (s, br, *o-C*, 4 × Ph), 134.8 (s, br, *o-C*, 4 × Ph), 138.4 (s, *ipso-C*, *Ph*Me), 141.3 (m, *ipso-C*, 4 × Ph), 148.1 (m, *ipso-C*, 4 × Ph); the ^{13}C NMR signal of the cyano ligand was not detected.

7. Preparation of *trans*-[(MeCN)(dppe)$_2$W≡Ge(η^1-Cp*)]-[B(C_6F_5)$_4$] (4). A Schlenk tube was charged with the complex **1-Cl**·C_7H_8 (158 mg, 0.12 mmol) and Li[B(C_6F_5)$_4$]·2.5Et$_2$O (104 mg, 0.12 mmol). The mixture was treated at −25 °C with 20 mL of CH_2Cl_2 containing 20 μL of MeCN. The orange solution was warmed slowly to ambient temperature and stirred for 2 h. During this time the solution became cloudy and its color changed to amber. The solution was filtered, and the filtrate was evaporated to dryness to give a foamy, amber-colored solid, which was washed twice with 5 mL of a Et$_2$O−pentane mixture (1:1) and dried in vacuo for 5 h. Yield: 225 mg (98%). Empirical formula: $C_{88}H_{66}BF_{20}GeNP_4W$ (1908.61). ^{1}H NMR (300.1 MHz, CD_2Cl_2, 298 K; δ (ppm)): 0.81 (quint, ^5J(H,P) = 2.6 Hz, 3H, *Me*CN), 1.62 (s, 15H, C_5Me_5), 2.35 (m, br, 4H, 4 × CH^1H^2), 2.86 (m, br, 4H, 4 × CH$^1H^2$), 6.52 (m, br, 8H, *o-H*, 4 × Ph), 7.04 (t, ^3J(H,H) = 7.5 Hz, 8H, *m-H*, 4 × Ph), 7.24 (t, ^3J(H,H) = 7.3 Hz, 4H, *p-H*, 4 × Ph), 7.25 (t, ^3J(H,H) = 7.5 Hz, 8H, *m-H*, 4 × Ph), 7.38 (t, ^3J(H,H) = 7.3 Hz, 4H, *p-H*, 4 × Ph), 7.55 (m, br, 8H, *o-H*, 4 × Ph). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): 54.0 (s, ^1J(P,W) = 270.5 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 298 K; δ (ppm)): 4.2 (s, *Me*CN), 12.6 (s, C_5Me_5), 35.9 (m, 4 × CH_2), 128.4 (s, C_5Me$_5$), 128.5 (s, *m-C*, 4 × Ph), 128.6 (s, *m-C*, 4 × Ph), 129.5 (s, *p-C*, 4 × Ph), 130.2 (s, *p-C*, 4 × Ph), 132.7 (s, br, *o-C*, 4 × Ph), 133.4 (s, br, *o-C*, 4 × Ph), 135.7 (m, *ipso-C*, 4 × Ph), 136.7 (dm, ^1J(C,F) = 239.7 Hz, *o*-C, C_6F_5), 138.6 (dm, ^1J(C,F) = 240.1 Hz, *p*-C, C_6F_5), 143.1 (m, *ipso-C*, 4 × Ph), 148.5 (dm, ^1J(C,F) = 237.8 Hz, *m*-C, C_6F_5); the Me*C*N NMR signal and the *ipso-C* NMR signals of the C_6F_5 groups were not detected. ^{19}F{^{1}H} NMR (282.4 MHz, CD_2Cl_2, 298 K): −167.9 (t, ^3J(F,F) = 18.0 Hz, *m-F*, C_6F_5), −164.1 (t, ^3J(F,F) = 20.3 Hz, *p-F*, C_6F_5), −133.5 (m, br, *o-F*, C_6F_5).

8. Crystal Structure Determination of 2·1.5C_6D_6, 3a·THF, 3d·0.5C_7H_8, and 4. Suitable dark red single crystals of **2**·1.5C_6D_6 were obtained upon slow diffusion of pentane into a benzene-d_6 solution of **2** at 6 °C and reddish single crystals of **3a**·THF upon slow diffusion of pentane into a THF solution of **3a**. Dark green single crystals of **3d**·0.5C_7H_8 were grown upon slow evaporation of a toluene/THF (3:1) solution in the glovebox and dark red single crystals of **4** upon slow diffusion of pentane into a benzene-d_6 solution of **4** at 6 °C. The data collection of **2**·1.5C_6D_6, **3a**·THF, and **3d**·0.5C_7H_8 was performed on a STOE IPDS diffractometer (area detector) equipped with a low-temperature device (Cryostream, Oxford Cryosystems) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The data collection of **4** was performed on a STOE STADI-4 diffractometer (NaI(Tl) scintillation counter) equipped with the same temperature device as mentioned above. Unit cell parameters of **2**·1.5C_6D_6, **3a**·THF, and **3d**·0.5C_7H_8 were determined from least-squares analyses using 5000 reflections (4.4° < 2θ < 50.4°). Intensities were measured by φ-oscillation scans and corrected for background, polarization, and Lorentz effects. ABSCOR was applied for absorption correction of the data sets of **2**·1.5C_6D_6, **3a**·THF and **3d**·0.5C_7H_8.[60]

Unit cell dimensions of **4** were obtained by a least-squares fit of 48 centered reflections in the range of 28.0° < 2θ < 34.2°. The scan width, $\Delta\omega$, for each reflection ranged from 1.25 to 1.50°. Intensities were corrected for Lorentz, polarization, and absorption effects (based on the ψ scans of 10 reflections). The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system.[61] The hydrogen atoms were included isotropically using the riding model on the bound carbon atoms, except for the hydrido ligand in **2**·1.5C_6D_6, which was found in the difference Fourier synthesis map. The identities of the N and O atoms in the isocyanato complex **3a**·THF were proven by free optimization of the site-occupancy factors, the chosen model correlating well with the observed bond lengths.

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Supporting Information Available: Crystallographic data as CIF files for **2**·1.5C_6D_6, **3a**·THF, **3d**·0.5C_7H_8, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. These data have been also deposited with the Cambridge Crystallographic Data Centre under the file numbers CCDC-239416, CCDC-239417, CCDC-239418, and CCDC-239419, respectively, and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, via e-mail to data_request@ccdc.cam.ac.uk, or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44)1223 336033.

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