75%). The 1-ether-2-ester-glycerophosphocholines (**6**–**10**) were synthesized starting with *R*-(–)-1,2-isopropylideneglycerol. The obtained 1-*O*-alkyl-2-*O*-benzyl-*sn*-glycerophosphocholines were in the last step debenzylated and immediately acylated with the desired acid anhydride (recovered yields between 60–75%). Purification was performed by column chromatography.

2: $C_{56}H_{112}NO_8P$ ($M_r = 958.48$); calcd: P 3.23; found: P 3.40; ES-MS (*m*/*z*): 959.1 [M+H$^+$], 981.0 [M+Na$^+$]. **3**: $C_{43}H_{86}NO_8P$ ($M_r = 776.13$); calcd: P 3.99; found: P 4.15; ES-MS (*m*/*z*): 777.9 [M+H$^+$], 799.6 [M+Na$^+$], 815.9 [M+K$^+$], 1552.3 [2M+H$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.51$ (m, 2H; glycerol-*sn*-1-CH_2), 3.75–3.79 (s, 2H; NCH_2), 4.10 (m, 2H; glycerol-*sn*-3-CH_2), 5.00 (m, 1H, glycerol-*sn*-2-CH). **4**: $C_{45}H_{90}NO_8P$ ($M_r = 804.18$); calcd: P 3.85; found: P 3.71; ES-MS (*m*/*z*): 805.6 [M+H$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.5$ (m, 2H; glycerol-*sn*-1-CH_2), 3.75–3.80 (s, 2H; NCH_2), 4.02 (m, 2H; glycerol-*sn*-3-CH_2), 5.03 (m, 1H; glycerol-*sn*-2-CH). **5**: $C_{58}H_{116}NO_8P$ ($M_r = 986.53$); calcd: P 3.14; found: P 3.29; ES-MS (*m*/*z*): 987.5 [M+H$^+$], 1010.4 [M+Na$^+$], 1026.6 [M+K$^+$]. **6**: $C_{42}H_{86}NO_7P$ ($M_r = 748.12$); calcd: P 4.14; found: P 4.02); ES-MS (*m*/*z*): 749.5 [M+H$^+$], 771.3 [M+Na$^+$], 787.3 [M+K$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.6$ (m, 2H; glycerol-*sn*-1-CH_2), 3.75–3.80 (s, 2H; NCH_2), 4.02 (m, 2H; glycerol-*sn*-3-CH_2), 5.07 (m, 1H; glycerol-*sn*-2-CH). **7**: $C_{56}H_{114}NO_7P$ ($M_r = 944.49$); calcd: P 3.28; found: 3.21; ES-MS (*m*/*z*): 945.4 [M+H$^+$], 967.4 [M+Na$^+$], 983.3 [M+K$^+$]. **8**: $C_{43}H_{88}NO_7P$ ($M_r = 762.14$); calcd: P 4.06; found: 3.99; ES-MS (*m*/*z*): 763.0 [M+H$^+$], 785.0 [M+Na$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.6$ (m, 2H; glycerol-*sn*-1-CH_2), 4.05 (m, 1H; OCH_2CH), 4.15 (m, 2H; glycerol-*sn*-3-CH_2), 4.55 (s, 2H; CH_2CH_2N), 5.05 (m, 1H; glycerol-*sn*-2-CH). **9**: $C_{43}H_{88}NO_7P$ (762.24); calcd: P 4.06; found: 3.99); ES-MS (*m*/*z*): 763.3 [M+H$^+$], 1525.2 [2M+H$^+$]; ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 3.6$ (m, 2H; glycerol-*sn*-1-CH_2), 3.75–3.80 (s, 2H; NCH_2), 4.1 (m, 2H; glycerol-*sn*-3-CH_2), 4.54 (s, 2H; CH_2CH_2N), 5.10 (m, 1H; glycerol-*sn*-2 CH). **10**: $C_{56}H_{114}NO_7P$ (944.49); calcd: P 3.28; found: 3.35; ES-MS (*m*/*z*): 945.2 [M+H$^+$], 967.2 [M+Na$^+$], 983.0 [M+K$^+$].

Monolayer experiments: A buffer of NaCl (150 mM), $CaCl_2$ (5 mM), and Tris (10 mM) at a pH of 8.9 was utilized as the subphase. The film balance (R&K ,Wiesbaden, Germany) was equipped with an Wilhelmy-type pressure measuring system. Phospholipase A_2 of the venom from *Crotalus Atrox* was used for hydrolysis (660 units per mg protein, Sigma, Germany). The enzyme was dissolved in buffer, at 40 mN m^{-1} injected underneath the monolayer (6 ng protein per mL subphase) and carefully stirred. The hydrolysis was monitored at a constant lateral pressure of 8 mN m^{-1}. After 60, 120, or 180 min the monolayer was compressed to 40 mN m^{-1} and a spectrum was recorded. All experiments were performed at 20 °C.

PM-IRRAS experiments: The IR beam was decoupled from a Bruker IFS66 spectrometer (Bruker, Karlsruhe, Germany), linearly polarized (KRS5, Specac, Orpington, UK) and passed through a photoelastic modulator (ZnSe, Type II, Hinds). The beam was then reflected from the water surface and focused with a ZnSe lense on the nitrogen-cooled MCT detector (Figure 1). With the polarization modulation one can nearly fully delete the influence of isotropic water absorption since the parallel (R_p) and the normal (R_s) to the plane of incidence polarized reflectivity was determined simultaneously. With the electronic setup one can obtain (bandpassfilter: 300–1200 Hz, Stanford Research System, model SR 650; EG&G lock-in amplifier, model 5209) the differential signal $(R_p - R_s)/(R_p + R_s)$, with a contribution from only the anisotropic absorption of the monolayer.

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Synthesis and Structure of the Germylyne Complexes *trans*-[X(dppe)$_2$W≡Ge(η^1-Cp*)] (X = Cl, Br, I) and Comparison of the W≡E Bonds (E = C, Ge) by Density Functional Calculations **

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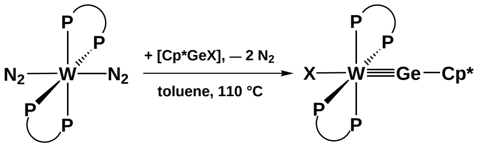
A large number of transition metal carbyne complexes have been described and their reactions investigated in depth.[1] However, complexes containing a triple bond between a transition metal and a heavier element of the fourth main group (E = Si, Ge, Sn, Pb) are very rare. To the best of our knowledge silylyne,[2] stannylyne and plumbylyne complexes are unknown, and for germylyne complexes there are only the compounds [(η^5-C_5H_5)(CO)$_2$M≡GeR] (M = Cr, Mo, W) containing a sterically very demanding substituent R (R = 2,6-$Trip_2C_6H_3$, 2,6-$Mes_2C_6H_3$; Trip = 2,4,6-$i$$Pr_3C_6H_2$; Mes = 2,4,6-$Me_3C_6H_2$).[3] Here we report a new route to germylyne complexes carrying a pentamethylcyclopentadienyl group on the germanium atom. Our route exploits the thermal elimination of N_2 from *trans*-[W(dppe)$_2$(N$_2$)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) (**1**).[4]

The reaction of **1** with the germylenes [Cp*GeX] **2a–c** (X = Cl, Br, I)[5] in boiling toluene leads smoothly to the germylyne complexes **3a–c**, respectively [Eq. (a)]. The complexes **3a–c** which each contain one equivalent of



(a)

1 **3a-c**

X = Cl, Br, I; P⌒P = dppe; Cp* = C_5Me_5

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toluene were isolated as orange–brown to red–brown solids of remarkable thermal stability in 65–80 % yields and fully characterized. The molecular structure of **3a**·toluene was determined by X-ray diffraction of dark red single crystals obtained upon slow cooling of a toluene solution of **3a** to −30 °C (Figure 1).[6] The structure shows a distorted octahedral complex with C_1 symmetry and a *trans* orientation of the chloro and germylyne ligands (Figure 1). The W–Ge bond (2.302(1) Å) is significantly shorter than W–Ge single bonds (2.493(2)–2.681(3) Å)[3b, 7] and slightly longer than the W–Ge triple bond in $[(\eta^5\text{-}C_5H_5)W(CO)_2{\equiv}Ge\text{-}2,6\text{-}Mes_2C_6H_3]$ (2.277(1) Å).[3b] The angle of 172.2(2)° at the Ge atom indicates a nearly linear W-Ge-C(Cp*) atom sequence. Furthermore, the Cp* substituent is η^1 bound as shown by the Ge–C1 bond (2.038(5) Å) which is in the range expected for Ge–C σ bonds. Additionally this bond is shorter than the Ge–C2/C5 bonds (2.739/2.812 Å) and shorter than the average Ge–C bond in **2a** (2.217(3) Å), which contains a η^2-bound Cp* ligand.[5] Finally the bond angles indicate sp^3 hybridization of the C1 atom, and the different C–C bond lengths within the five-membered Cp* ring point to localized π bonds (C2–C3 and C4–C5).[8]

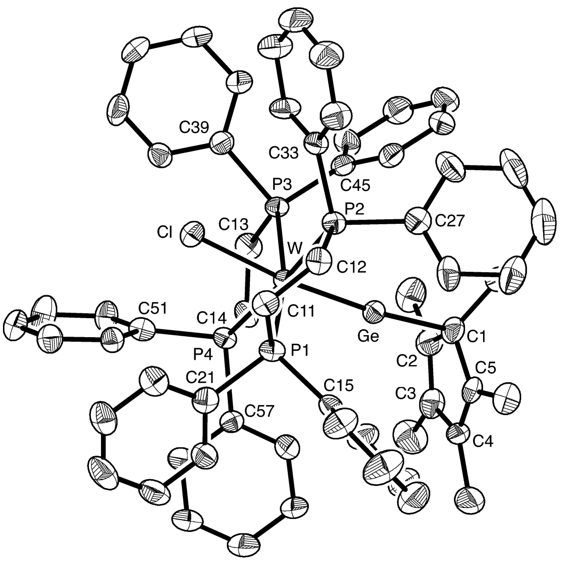

Figure 1. ZORTEP plot of the molecular structure of **3a**. The thermal ellipsoids are set at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: W-Ge 2.302(1), W-Cl 2.486(1), W-P1 2.469(1), W-P2 2.489(1), W-P3 2.455(1), W-P4 2.446(1), Ge-C1 2.038(5), C1-C2 1.500(8), C2-C3 1.367(8), C3-C4 1.451(8), C4-C5 1.372(7), C1-C5 1.477(8); Ge-W-Cl 174.04(3), Ge-W-P1 101.81(4), Ge-W-P2 94.16(5), Ge-W-P3 87.80(4), Ge-W-P4 92.11(5), Cl-W-P1 81.85(5), Cl-W-P2 81.87(5), Cl-W-P3 88.91(5), Cl-W-P4 92.17(5), W-Ge-C1 172.2(2), Ge-C1-C2 100.3(3), Ge-C1-C5 105.2(3), Ge-C1-C6 111.7(4), C2-C1-C5 104.7(4), C2-C1-C6 117.1(5), C5-C1-C6 116.1(4).

The structural analogy of the complexes **3a–c**·toluene is demonstrated by the following properties: the IR spectra in KBr are practically identical and the ^{31}P NMR spectra display a singlet for the chemically equivalent diphosphane ligands that is flanked by tungsten satellites (see Experimental Section). In addition the ^1H and $^{13}C\{^1H\}$ NMR spectra of **3a–c**·toluene display the signals expected for complexes of the type *trans*-[W(dppe)$_2$LL′], that is doublets for the diastereotopic methylene protons and the phenyl groups of the dppe ligands and a singlet each for the methyl groups and ring carbon atoms of the Cp* substituent. The latter finding in conjunction with the solid-state structure of **3a** and density functional theory (DFT) calculations on **5a–7a** (see below) suggest a haptotropic shift of the Cp* group, which is fast on the NMR time scale, [9] and occurs via a transition state with an η^2-bound Cp* substituent.

To clarify the bonding in the germylyne complexes **3a–c** density functional calculations were performed (Table 1) on

Table 1. Bonding parameters, dissociation energies, CDA, and NBO results for the complexes *trans*-[Cl(L)$_4$W≡ECp] (**4**/**5**: L = CO, E = C/Ge; **6**/**7**: L = PH_3, E = C/Ge) (BP86/II).[11]

Complex[a]			Length/angle			BDE[b]	CDA[c]			Charge (NPA[d])				W–E bond (NBO[d])			
	symm.	*n*	W–E [Å]	E–Cp [Å]	W-E-Cp [°]	[kJ mol^{-1}]	*d*	*b*	*b*/*d*	W	E	ECp	occ.[e]	*x*(W) [%]	hybrid	*x*(E) [%]	hybrid
4a	C_1	0	1.855	1.476	178.9	468.1	0.509	0.652	1.28	−0.33	0.06	0.08	σ: 1.95	32.6	$sd^{2.27}$	67.4	$sp^{0.75}$
													π1: 1.80	62.4	d	37.6	p
													π2: 1.80	62.2	$sd^{91.5}$	37.8	p
4b	C_s	1	1.911	1.625	152.3	391.2	0.506	0.534	1.06	−0.27	−0.08	0.07					
5a	C_s	0	2.374	2.091	178.5	273.2	0.371	0.617	1.66	−0.87	1.04	0.71	σ: 1.70	37.8	$sd^{1.17}$	62.2	$sp^{1.05}$
													π1: 1.70	79.9	d	20.1	p
													π2: 1.67	82.8	$sd^{56.1}$	17.2	p
5b	C_s	1	2.385	2.222	160.6	269.5	0.376	0.608	1.62	−0.86	1.04	0.72					
6a	C_s	0	1.831	1.495	178.6	466.1	0.570	0.767	1.35	−0.80	−0.05	−0.10	σ:1.94	33.7	$sd^{3.02}$	66.3	$sp^{0.71}$
													π1: 1.91	59.8	d	40.2	p
													π2: 1.90	59.5	$sd^{80.0}$	40.5	p
6b	C_s	1	1.864	1.646	153.0	370.8	0.582	0.657	1.13	−0.72	−0.13	−0.20					
7a	C_s	0	2.335	2.087	177.7	228.9	0.306	0.778	2.54	−1.47	0.92	0.50	σ: 1.76	38.3	$sd^{1.92}$	61.7	$sp^{0.81}$
													π1: 1.87	77.9	d	22.1	p
													π2: 1.85	75.6	$sd^{98.3}$	24.4	p
7b	C_s	1	2.347	2.262	160.9	218.1	0.311	0.749	2.41	−1.49	0.93	0.52					

[a] Symmetry of the complex and number *n* of the imaginary vibrational frequencies. [b] Bond dissociation energy ($L_nW{\equiv}ECp \rightarrow L_nW + ECp$) (BP86/III//BP86/II) plus ZPE(BP86/II);[11] the fragments L_nW and ER have doublet ground states. [c] Donation *d* ($[ECp]^+ \rightarrow [L_nW]^-$) and back donation *b* ($[L_nW]^- \rightarrow [ECp]^+$) in elemental charges; the residual term (interaction of unoccupied fragment orbitals) is in every case near to zero, the repulsive polarization *r* has values from −0.171 to −0.327. [d] NBO analysis (natural bond orbital) and NPA (natural population analysis) are integrated into the Gaussian program. [e] Occupancies.

the model complexes *trans*-[Cl(L)$_4$W≡ECp] (Cp = C_5H_5; **4**/**5**: L = CO, E = C/Ge; **6**/**7**: L = PH_3, E = C/Ge).[10, 11] All complexes have a minimum structure with an η^1-bound Cp substituent (**4a**–**7a**). In contrast, the structures with η^2 coordination of the Cp unit (**4b**–**7b**) are transition states for the haptotropic shift of the Cp ring.[9] Calculated and experimentally determined bond lengths and angles are in good agreement, as shown, for example, by the similar W–Ge, W–Cl, and Ge–C bond lengths of **3a** · toluene and **7a** (W–Ge 2.302(1) and 2.335 Å, W–Cl 2.486(1) and 2.485 Å, Ge–C 2.038(5) and 2.087 Å, respectively). A change in the hapticity of the Cp substituent from η^1 (**4a**–**7a**) to η^2 (**4b**–**7b**) leads to significant bending of the carbyne/germylyne ligand at the E atom, which is more pronounced in the carbyne complexes (compare for example **6a**/**6b** with **7a**/**7b**). Accordingly the barrier for the haptotropic shift of the Cp ring is significantly higher for the carbyne complexes **4a**/**6a** (76.9/95.3 kJ mol^{-1}) than for the germylyne complexes **5a**/**7a** (3.7/10.8 kJ mol^{-1}).

In all the complexes the W≡E triple bond is composed of a σ and two π bonds. The σ is polarized towards the ligand, whereas the π bonds are polarized towards the metal. The dissociation energies of the W–C bonds are significantly higher. The strength of the W–E bond is also reflected in the occupancies of the σ and π orbitals. These are higher for the carbyne complexes than for the germylyne complexes and higher for the phosphane complexes than for the carbonyl complexes.

The results of the charge–decomposition analysis (CDA) indicate that the germylyne ligand is a poorer σ donor than the carbyne ligand but an equally good π acceptor. The acceptor capability of the germylyne ligand is weakened by the presence of other π-acceptor ligands (for example CO). Accordingly the acceptor/donor ratio (*b*/*d*; see Table 1) of the germylyne ligand is greater than that of the carbyne ligand and increases on going from the carbonyl to the phosphane complexes. Finally the NPA results (Table 1) indicate a positive partial charge on the germanium atom, while the carbyne carbon is almost electroneutral. This charge distribution could be the basis for targeted reactivity studies of germylyne complexes.

Considering the large number of dinitrogen complexes that are known of the Group 6 transition metals and the possibility of utilizing the Cp* substituent as a leaving group,[12] then the synthetic method described here opens up very promising opportunities for developing the chemistry of germylyne complexes.

Experimental Section

NMR spectra were recorded at room temperature in [D$_8$]THF (Bruker AM 300 Spectrometer); the δ_H values are calibrated against the residual proton signal of the deuterated solvent at $\delta_H = 1.73$ and the δ_C values against the ^{13}C signal of the solvent at $\delta_C = 25.3$.

3a · toluene: compound **1** (0.464 g, 0.448 mmol) and **2a** (0.119 g, 0.489 mmol) were weighed into a Schlenk tube and suspended in toluene (50 mL). The orange suspension was heated, in an oil bath preheated to 120 °C, so that the reaction mixture boiled gently. On boiling the reaction mixture a clear orange solution was obtained that over the course of the reaction turned dark red–brown. Completion of the reaction (after ca. 20 min) was indicated by the disappearance of the $\nu(N_2)$ absorption bands of **1** at 2010 and 1949 cm^{-1} from the IR spectrum of the reaction mixture. The mixture was cooled to room temperature, filtered, and the volume of the filtrate was reduced to about 10 mL. Crystals of **3a** · toluene formed overnight at −78 °C. The supernatant solution was decanted, and the crystals were washed with pentane (2 × 20 mL) and dried under high vacuum at room temperature for 1 h. Yield 0.396 g (67 % from **1**) as an orange–brown powder, m.p. 248 °C (decomp). Elemental analysis calcd (%) for $C_{69}H_{71}ClGeP_4W$ (1316.11): C 62.97, H 5.44, Cl 2.69; found: C 62.64, H 5.58, Cl 2.83; ^{1}H NMR: $\delta = 1.42$ (s, 15 H; C_5Me_5), 2.31 (s, 3 H, Ph*Me*), 2.42 (m, 4 H, 4 × H_ACH_B), 2.86 (m, 4 H, 4 × H_ACH_B), 6.86–7.67 (m, 45 H, 4 × PPh_2 and *Ph*Me); $^{31}P\{^1H\}$ NMR: $\delta = 46.3$ (^1J(W,P) = 264.7 Hz); $^{13}C\{^1H\}$ NMR: $\delta = 12.7$ (C_5Me_5), 21.5 (Ph*Me*), 36.6 (m, 4 × CH_2), 126.0 (*p*-C, *Ph*Me), 127.1 (C_5Me_5), 127.2 and 128.0 (m, *m*-C, 4 × Ph_APPh_B), 128.3 and 129.1 (*p*-C, 4 × Ph_APPh_B), 128.9 (*m*-C, *Ph*Me), 129.7 (*o*-C, *Ph*Me), 134.8 and 135.2 (m, *o*-C, 4 × Ph_APPh_B), 138.4 (*ipso*-C, *Ph*Me), 138.9 and 147.6 (m, *ipso*-C, 4 × Ph_APPh_B).

3b · toluene: Yield 78 % as an orange–brown powder, m.p. 236 °C (decomp). Elemental analysis calcd (%) for $C_{69}H_{71}BrGeP_4W$ (1360.57): C 60.91, H 5.26, Br 5.87; found: C 60.54, H 5.48, Br 6.49; selected spectroscopic data: ^{1}H NMR: $\delta = 1.37$ (s, 15 H, C_5Me_5), 2.31 (s, 3 H, Ph*Me*), 2.46 (m, 4 H, 4 × H_ACH_B), 2.95 (m, 4 H, 4 × H_ACH_B), 6.89–7.70 (m, 45 H, 4 × PPh_2 and *Ph*Me); $^{31}P\{^1H\}$ NMR: $\delta = 43.9$ (^1J(W,P) = 262.3 Hz).

3c · toluene: Yield 65 % as a red–brown powder, m.p. 221 °C (decomp). Elemental analysis calcd (%) for $C_{69}H_{71}GeIP_4W$ (1407.56): C 58.88, H 5.08, I 9.02; found: C 58.79, H 5.20, I 9.23; ^{1}H NMR: $\delta = 1.31$ (s, 15 H, C_5Me_5), 2.31 (s, 3 H, Ph*Me*), 2.54 (m, 4 H, 4 × H_ACH_B), 3.09 (m, 4 H, 4 × H_ACH_B), 6.89–7.72 (m, 45 H, 4 × PPh_2 and *Ph*Me); $^{31}P\{^1H\}$ NMR: $\delta = 38.7$ (^1J(W,P) = 258.8 Hz); $^{13}C\{^1H\}$ NMR: 12.6 (C_5Me_5), 21.5 (Ph*Me*), 38.4 (m, 4 × CH_2), 127.0 (C_5Me_5).

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[6] Crystal structure determination of **3a** · toluene ($C_{69}H_{71}ClGeP_4W$): $M_r = 1316.03$; triclinic, space group $P\bar{1}$, $a = 10.524(3)$, $b = 16.117(4)$, $c = 17.875(5)$ Å, $\alpha = 96.86(3)$, $\beta = 96.67(3)$, $\gamma = 102.86(3)°$, $V = 2902.4(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.506$ g cm^{-3}, STOE-IPDS diffractometer with area detector, $T = 180(2)$ K, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 2.697$ mm^{-1}, $F(000) = 1336$, 24 651 measured reflections, 10 539 independent reflections, 686 parameters, GOF = 0.951, $R_1 = 0.0508$ [$I > 2\sigma(I)$], $wR2 = 0.1225$, min./max. residual electron density −2.046/1.916 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142852. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[10] The DFT calculations indicate no fundamental electronic differences between the complexes *trans*-[Cl(L)$_4$W≡EMe] and **4a–7a**.

[11] The gradient corrected functionals BP86 were used (A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822). For the W atom and the elements Ge, Cl, and P the pseudo potentials (W: P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299; Ge, Cl, P: G. Igel-Mann, H. Stoll, H. Preuss, *Mol. Phys.* **1988**, *65*, 1321) and corresponding valence basis sets were used (W: 441/2111/21 and 441/2111/111/1; Ge, Cl, P: 31/31/1 and 211/211/11). Together with the standard basis sets 6-31G(d) (P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213) and 6-311G(2d,p) (R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650) for the remaining elements the combinations II and III were obtained (Table 1). The calculations were performed with Gaussian 98 (Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Lui, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**) and CDA 2.1 (charge decomposition analysis; S. Dapprich, G. Frenking, CDA 2.1, Marburg, **1994**).

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Isolation of a Kinetically Stabilized 1,3,6-Triphosphafulvene**

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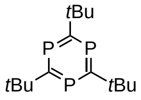
Masaaki Yoshifuji*

Substitution of some of the sp^2-hybridized carbon atoms in conjugated systems with heavier main-group elements, such as phosphorus atoms, is of interest but requires kinetic stabilization with bulky substituents. In 1995, 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**) was first reported, prepared through the trimerization of *tert*-butylphosphaacetylene (or 3,3-dimethyl-1-phospha-1-butyne), together with its valence isomer **2**;[1] the structure of **1** was established in 1998.[2, 3] Oligomerization of *tert*-butylphosphaacetylene has been utilized for the construction of various types of five-membered heterocyclic systems containing polycyclic systems.[4] We now report one of the valence isomers of triphosphabenzene, utilizing the 2,4,6-tri-*tert*-butylphenyl group (Mes*). 2,4,6-Tris(2,4,6-tri-*tert*-butylphenyl)-1,3,6-triphosphafulvene (**3**) was formed by the trimerization of lithium phosphanylidene carbenoid **4** (Scheme 1).[5–7]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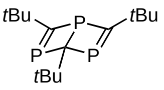
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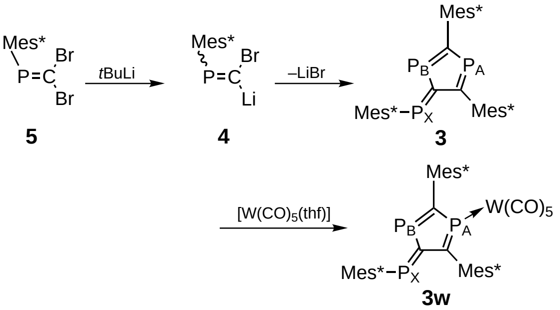
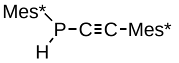


Scheme 1. Preparation of **3** and **3w**. Mes* = 2,4,6-tBu$_3$C$_6$H$_2$.

Dibromophosphaethene **5**[8] was allowed to react with two equivalents of *tert*-butyllithium at −78 °C to afford the phosphanylidene carbenoid **4**, after which the reaction mixture warmed gently to 25 °C. After purification (silica-packed column chromatography), **3** was obtained as a deep red solid together with trace amounts of 2-(2,4,6-tri-*tert*-butylphenyl)-1-(2,4,6-tri-*tert*-butylphenylphosphanyl)acetylene (**6**), 1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaacetylene (**7**),[5–7, 9] and 6,8-di-*tert*-butyl-4,4-dimethyl-1-phospha-3,4-dihydronaphthalene (**8**).[5, 6, 10] The ^{31}P NMR spectrum of **3** shows an ABX system. The signal of the exocyclic phosphorus atom P$_X$ ($\delta_{P_X} = 313.8$) is positioned downfield compared to ring atoms P$_A$ and P$_B$ but similar to that found for **9** ($\delta = 321.5$),[11] due to the electron-withdrawing effects of the 1,3-diphosphacyclopentadiene moiety.[12] The chemical shifts of the ring phosphorus atoms in **3** ($\delta_{P_A} = 291.3$, $\delta_{P_B} = 264.7$) are close to those for 1,2,4-selenadiphosphole **10** (Mch = 1-methylcyclohexyl).[13] Their coupling constant, J(P$_A$,P$_B$), is 32 Hz, which is also similar to that found for **10**;[13] values of the exocyclic coupling constants are 120 and 44 Hz for J(P$_A$,P$_X$) and J(P$_B$,P$_X$), respectively. The UV/Vis spectrum of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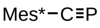
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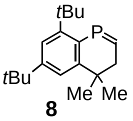
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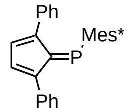
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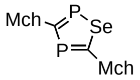
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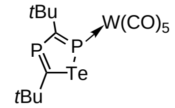
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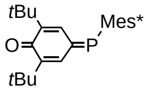
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