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A novel synthesis of metallogermacyclopropane and molybdenum bis(iminophosphorano)carbene complexes from bisgermavinylidene

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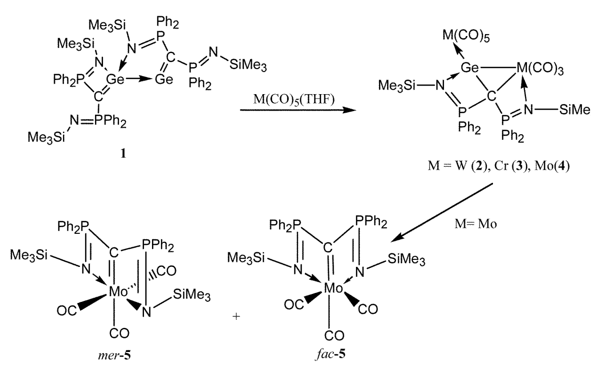
The reaction of bisgermavinylidene [(Me$_3$SiN=PPh$_2$)$_2$C=Ge→Ge=C(PPh$_2$=NSiMe$_3$)$_2$] (1) with M(CO)$_5$(THF) (M = Cr, W, Mo) afforded the metallagermacyclopropane [(Me$_3$SiN=PPh$_2$)$_2$CGeM(CO)$_3${M(CO)$_5$}] [M = W (2), Cr (3), Mo (4)]; in one of the reactions, compound 4 reacts further to give a "pincer" carbene complex [(CO)$_3$Mo{C(Ph$_2$P=NSi Me$_3$)$_2$}] (5); the X-ray structures of compounds 2 and 5 have been determined.

We have recently reported the synthesis and structure of bis(germavinylidene) [(Me$_3$SiN=PPh$_2$)$_2$C=Ge→Ge=C-(PPh$_2$=NSiMe$_3$)$_2$] (**1**).[1] As **1** may serve as a synthon for the preparation of metal-germavinylidene complexes, we have investigated the reactivity of **1**. We now report the synthesis of a series of Group 6 metallagermacyclopropanes and novel molybdenum carbene complexes derived from the reaction of **1** with M(CO)$_5$(THF) (M = Cr, W, Mo). The results have demonstrated that bis(germavinylidene) **1** provides the source of synthetic equivalent of germavinylidene for subsequent reactions. It has also shown that **1** can play the role of a transfer reagent in the synthesis of a novel molybdenum carbene complex.

The reaction of [(Me$_3$SiN=PPh$_2$)$_2$C=Ge→Ge=C(PPh$_2$=N-SiMe$_3$)$_2$] (**1**) with M(CO)$_5$(THF) (M = W and Cr) in THF afforded the metallagermacyclopropanes [(Me$_3$SiN=PPh$_2$)$_2$C-GeM(CO)$_3$(M(CO)$_5$)] [M = W (**2**) and Cr (**3**)] in 37% and 43% yields, respectively.† The structures of the products as confirmed by X-ray structure analysis have shown that the M(CO)$_5$ moiety generated *in-situ* by UV light (254 nm) added across the germanium–carbon double bond of the germavinylidene moiety with concomitant displacement of two CO molecules and formed the three-member C–Ge–M ring (Scheme 1). The structure has also shown that the germanium atom of the metallagermacyclopropane coordinated to another M(CO)$_5$ fragment. The valence electron counts for the W centers in **2** are 18 for W(1) and 16 for W(2).

Similar reaction of **1** with Mo(CO)$_5$(THF) for a longer reaction time of 3 days afforded the molybdenum carbene complex [(OC)$_3$Mo{C(Ph$_2$P=NSiMe$_3$)$_2$}] (**5**) in 48% yield together with a small amount of molybdenum-germacyclopropane [(Me$_3$SiN=PPh$_2$)$_2$CGeMo(CO)$_3$(Mo(CO)$_5$)] (**4**).† The structure of **5** as determined by X-ray structure analysis is a 'pincer' type carbene complex with the imino nitrogens displaced two CO ligands and coordinated to molybdenum. Similar Group 4 transition metal bis(iminophosphorano)methanediide complexes [MCl$_2${C(Ph$_2$P=NSiMe$_3$)$_2$-κ^3*C,N,N′*}] (M = Ti, Zr and Hf) prepared from the dilithium methanediide compound have been reported by Cavell and coworkers. The alkylidene compounds are stabilized by two phosphorano groups.[2] The current result suggests that the carbene ligand [**:**C(Ph$_2$P=NSiMe$_3$)$_2$] is being transferred from the germavinylidene to form the metallagermacyclopropane which rearranges with elimination of '[GeMo(CO)$_5$]'. However, this by-product has not been isolated or characterised.

The molecular structure of **2** as shown in Fig. 1 features a three-membered tungsten-germacyclopropane ring with W(2) bonded to C(9) and Ge(1), and subtended at an angle of 48.93(10)°.‡ The Ge(1)–C(9) bond distance of 2.046(4) Å is similar to the Ge–C single bond distances in germylenes [Ge{CH(SiMe$_3$)$_2$}{C(SiMe$_3$)$_3$}] (2.067 Å, 2.012 Å)[3] and [Ge{CPh(SiMe$_3$)C$_5$H$_4$N-2}$_2$] (2.116 Å),[4] but slightly longer than the Ge–C distance of 1.905(8) Å in **1**. The Ge(1)–W(2) bond distance of 2.6133(5) Å is similar to the Ge–W distance of 2.58 Å in (CO)$_5$WGe[W(CO)$_5$]$_2$.[5] The comparatively shorter Ge(1)–W(1) bond distance of 2.6001(5) Å suggested that the Ge(1)–W(1) bonding in **2** is more appropriately described as a donor–acceptor interaction with bond order slightly exceeding one.



Scheme 1 Synthesis of complexes **2**, **3**, **4** and **5**.

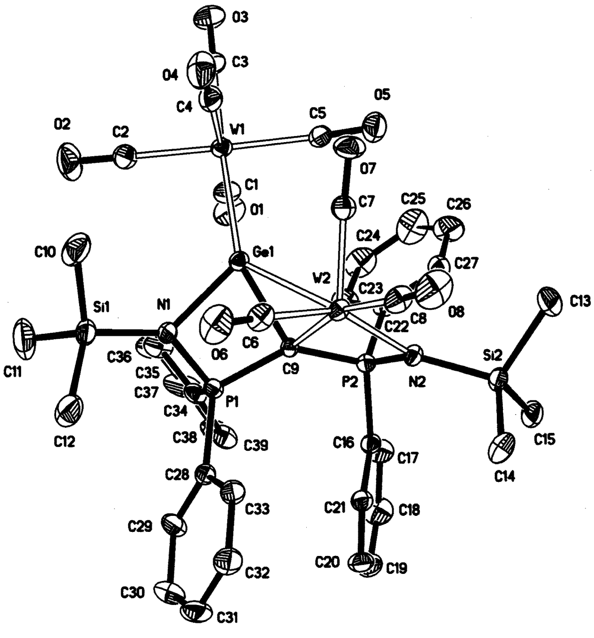


Fig. 1 ORTEP drawing of **2**; hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Ge(1)–W(1) 2.6001(6), Ge(1)–W(2) 2.6133(5), Ge(1)–C(9) 2.046(4), W(2)–C(9) 2.267(4), Ge(1)–N(1) 2.013(4), W(2)–N(2) 2.149(3), N(2)–P(2) 1.603(4), P(2)–C(9) 1.730(4), C(9)–P(1) 1.755(4), P(1)–N(1) 1.626(4); W(1)–Ge(1)–W(2) 132.513(19), W(2)–Ge(1)–C(9) 56.67(11), Ge(1)–W(2)–C(9) 48.93(10), W(2)–N(2)–P(2) 97.51(15), N(2)–P(2)–C(9) 100.30(19), C(9)–P(1)–N(1) 97.42(18), P(1)–N(1)–Ge(1) 93.19(17), N(1)–Ge(1)–W(1) 103.39(11).

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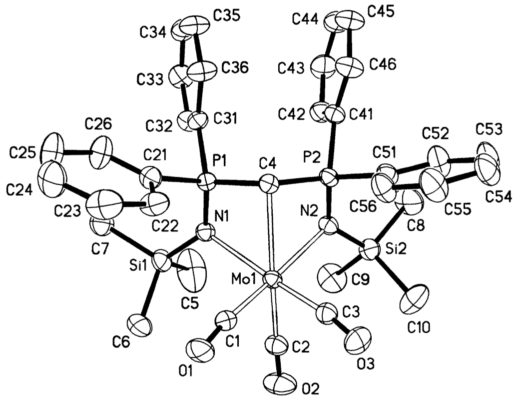

Fig. 2 ORTEP drawing of *fac*-**5**; hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Mo–C(4) 2.419(2), P(1)–C(4) 1.749(2), P(2)–C(4) 1.749(2), P(1)–N(1) 1.579(2), P(2)–N(2) 1.582(2), N(1)–Mo(1) 2.376(2), N(2)–Mo(1) 2.363(2); P(1)–C(4)–P(2) 120.05(13), P(1)–C(4)–Mo(1) 87.75(9), P(2)–C(4)–Mo(1) 86.86(10), N(1)–Mo(1)–N(2) 82.93(7), C(4)–Mo(1)–N(2) 67.41(8), C(4)–Mo(1)–N(1) 67.76(7), P(1)–N(1)–Mo(1) 93.41(9), P(2)–N(2)–Mo(1) 92.79(10).

The molecular structure of **5** as shown in Fig. 2 is comprised of the "pincer" carbene ligand bonded to molybdenum in a tridentate manner through coordination of the carbene atom and two imino nitrogens.† The Mo–C distance of 2.419(2) Å is relatively longer than similar Mo–C bond distances of 2.262 Å in the N-heterocyclic carbene complexes $[(CO)_5Mo\{CNH(CH_2)_3NH\}]$ and *cis*-$[Mo(CO)_4\{CN(Me)CH_2CH_2NMe\}_2]$ (2.293 Å).[6] It is also longer than the Mo–C bond distances in Schrock alkylidenes $[Mo(NAd)(CHCMe_2Ph)\{OCH(CF_3)_2\}_2(2,4\text{-lutidene})]$ (1.880 Å), [*syn*-$Mo(CH\text{-}t\text{-}Bu)(NAr)\{OCMe(CF_3)_2\}_2(PMe_3)]$ (1.878 Å) and $[Mo(CH\text{-}t\text{-}Bu)(NAr)(OSO_2CF_3)_2(dme)]$ (1.93 Å).[7] The structural data within the N–P–C–P–N skeleton when compared with the free ligand,[8] suggested that delocalization of electron within the four membered ring which would arise from the conjugation of the P=N and Mo–C bonds. As a result, Mo–C bond in **5** is lengthened. This result shows that **5** is structurally comparable to the metal alkylidene complexes. The geometry at the molybdenum is octahedral with the three carbonyl groups at the facial positions. The Mo–CO distance of 1.950(3) Å at the *trans*-position is longer than the other two Mo–CO distances of 1.906(3) Å and 1.901(3) Å. The existence of geometrical isomers of **5** is conceivable. The ^{31}P NMR spectrum of **5** showed two signals at 10.70 and 35.97 ppm with intensity ratio of 3:2, respectively. This is probably due to the geometrical isomers of the *fac*- and *mer*-complexes of **5** in solution.

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Notes and references

† *Selected spectroscopic data* for **2**: ^1H NMR (300 MHz, d-THF, 25 °C): δ = −0.05 (s, 9H, $SiMe_3$), 0.05 (s, 9H, $SiMe_3$), 7.12–7.71 (m, 20H, Ph); $^{13}C\{^1H\}$ NMR (75.47 MHz, d-THF, 25 °C): δ = 1.88 ($SiMe_3$), 4.14 ($SiMe_3$), 129.48, 129.66, 129.75, 129.83, 129.92, 130.78, 131.41, 131.56, 132.09, 132.35, 132.50, 132.80, 132.94, 133.01, 133.16, 133.44, 134.08, 134.24 (Ph), 198.97 (PCP), 201.76 (CO), 224.60 (CO). $^{31}P\{^1H\}$ NMR (161.90 MHz, d-THF, 25 °C): δ = 52.48, 62.85.

For **3**: ^1H NMR (300 MHz, d-THF, 25 °C): δ = 0.03 (s, 9H, $SiMe_3$), 0.11 (s, 9H, $SiMe_3$), 3.92–7.72 (m, 20H, Ph); $^{13}C\{^1H\}$ NMR (75.47 MHz, d-THF, 25 °C) δ = 2.04 ($SiMe_3$), 3.95 ($SiMe_3$), 129.23, 129.38, 129.55, 129.70, 129.85, 131.89, 132.55, 132.68, 132.95, 133.41, 133.74, 134.45, 134.61, 134.76 (Ph), 218.02 (PCP), 224.89 (CO); $^{31}P\{^1H\}$ NMR (161.90 MHz, d-THF, 25 °C): δ = 56.32.

For **5**: ^1H NMR (300 MHz, d-THF, 25 °C): δ = −0.15 (s, 9H, $SiMe_3$), 0.06 (s, 9H, $SiMe_3$), 1.12 (t, 3H, Et_2O), 3.40 (q, 2H, Et_2O), 6.83 (t, 3H, Ph), 7.00–7.13 (m, 3H, Ph), 7.29–7.35 (m, 8H, Ph), 7.61–7.73 (m, 3H),7.85–7.94 (m, 3H,, Ph); $^{13}C\{^1H\}$ NMR (75.47 MHz, d-THF, 25 °C): δ = 5.28 ($SiMe_3$), 15.69 ($SiMe_3$), 15.69, 66.33 (Et_2O), 127.50, 127.58, 127.65, 128.01, 128.09, 128.16, 128.58, 129.55, 130.42, 131.14, 131.90, 131.97, 132.04, 132.23, 132.30, 132.37, 138.72 (Ph), 231.24 (CO). $^{31}P\{^1H\}$ NMR (161.90 MHz, d-THF, 25 °C): δ = 10.70, 35.97; IR (Nujol), ν(CO) = 1819.2, 1896.8, 1956.6, 2018.6, 2149.3 cm^{-1}.

‡ *Crystal data* for **2** ($C_{39}H_{38}N_2O_8GeP_2Si_2W_2$): M = 1221.12, crystal size 0.28 × 0.22 × 0.20 mm, a = 10.921(2), b = 19.945(3), c = 20.951(3) Å, α = 90, β = 90, γ = 90°, V = 4563.3(11) $Å^3$, ρ_{calcd} = 1.77 g cm^{-3}, μ = 5.855 cm^{-1}, Z = 4, orthorhombic, space group $P2_12_12_1$, λ = 0.71073 Å, T = 294(2) K, $2\theta_{max}$ = 27.54°, 31 134 measured reflections, 10 521 independent reflections, 505 refined parameters, $R1$ = 0.0277, $wR2$ = 0.0628, largest diff. peak and hole 1.149 and −1.099 e $Å^{-3}$. CCDC 188276.

Crystal data for **5** ($C_{34}H_{38}MoN_2O_3GeP_2Si_2.2Et_2O$): M = 885.97, crystal size 1.50 × 0.72 × 0.65 mm (a large crystal was used as cutting would cause it to shatter or deform), a = 11.128(1), b = 14.245(1), c = 16.201(2) Å, α = 98.922(2), β = 95.369(2), γ = 110.193(2)°, V = 2350.9(4) $Å^3$, ρ_{calcd} = 1.252 g cm^{-3}, μ = 0.439 mm^{-1}, Z = 2, triclinic, space group $P1$, λ = 0.71073 Å, T = 293(2) K, $2\theta_{max}$ = 28.03°, 15832 measured reflections, 11098 independent reflections, 487 refined parameters, $R1$ = 0.0429, $wR2$ = 0.1222, largest diff. peak in the intermolecular region and hole 3.780 and −0.340 e $Å^{-3}$. CCDC 188277.

See http://www.rsc.org/suppdata/cc/b2/b210598e/ for crystallographic files in CIF or other electronic format.

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