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Electron-Rich Trichlorogermyl Complexes of Molybdenum and Tungsten Bearing a Cyclopentadienyl Ligand: Synthesis, Crystal Structures, and Cyclic Voltammetric Studies

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Oxidative decarbonylation of *cis*-(η^5-C_5R_5)M(CO)$_2$(PMe$_3$)Cl (**1a**−**1d**) (**a**, R = H, M = Mo; **b**, R = H, M = W; **c**, R = Me, M = Mo; **d**, R = Me, M = W) with 1 equiv of PhICl$_2$ yields selectively the M(IV) complexes (η^5-C_5R_5)M(CO)(PMe$_3$)Cl$_3$ (**2a**−**2d**). Complex **1c** reacts with 1.5 equiv of PhICl$_2$ and complex **2d** with 0.5 equiv of PhICl$_2$ to give respectively Cp*Mo(PMe$_3$)Cl$_4$ (**3c**) and Cp*W(PMe$_3$)Cl$_4$ (**3d**) (Cp* = C_5Me_5) in quantitative yield. Complex **2d** can also be prepared from Cp*W(CO)$_3$Cl (**4d**) in two steps. The first step involves an oxidation of **4d** with 1 equiv of PhICl$_2$ to yield selectively Cp*W(CO)$_2$Cl$_3$ (**5d**) followed by a CO ligand exchange reaction of **5d** with PMe$_3$. Reduction of **2a**−**2d** with Na/Hg affords in the presence of PMe$_3$ the M(II) chloro complexes *trans*-(η^5-C_5R_5)M(CO)(PMe$_3$)$_2$Cl (**6a**−**6d**) in high yield. Complexes **6a**−**6d** rapidly insert GeCl$_2$ into the metal−chlorine bond to give selectively the “electron-rich” trichlorogermyl complexes *trans*-(η^5-C_5R_5)M(CO)(PMe$_3$)$_2$GeCl$_3$ (**7a**−**7d**). The crystal structures of CpW(CO)(PMe$_3$)Cl$_3$·MeCN (Cp = C_5H_5) (**2b-1**), CpW(CO)(PMe$_3$)Cl$_3$·0.5THF (**2b-2**), **6d**, and **7b** are presented, and the cyclic voltammetric data of the complexes **6b**−**6d** and **7a**−**7d** are compared.

Introduction

Trichlorogermyl complexes of transition metals have a high synthetic potential bearing reactive Ge−Cl bonds.[1] Several methods have been employed for the synthesis of these compounds, the most common ones involving the salt elimination reaction of GeCl$_4$ with a carbonyl metalate,[2] the oxidative addition of HGeCl$_3$ or GeCl$_4$ to a transition-metal center,[3] and the thermal or photochemical substitution of a carbonyl or arene ligand by the GeCl$_3^-$ ion.[4] However, the applicability of these methods depends strongly on the metal substrate, and their use can be severely restricted by side reactions such as the chlorination of the metal complex by GeCl$_4$. In these cases a different route involving the insertion of GeCl$_2$ into a transition-metal chlorine bond offers a valuable solution.[5] We have recently demonstrated the advantages of the GeCl$_2$ insertion method with the high-yield synthesis of various group 6 trichlorogermyl and dichlorogermyl complexes of the formula (η^5-C_5R_5)M(CO)$_{3-m}$L$_m$(GeCl$_{3-n}$H$_n$) (R = H, Me; M = Mo, W; L = EtNC, PMe$_3$; m, n = 0, 1).[6] In the present work we provide further evidence for the broad scope of the GeCl$_2$ insertion method describing the synthesis, crystal structures, and cyclic voltammetric studies of the trichlorogermyl complexes *trans*-(η^5-C_5R_5)M(CO)(PMe$_3$)$_2$GeCl$_3$ (**7a**−**7d**).

Results and Discussion

A multistep route was developed that allows the synthesis of the trichlorogermyl complexes *trans*-(η^5-

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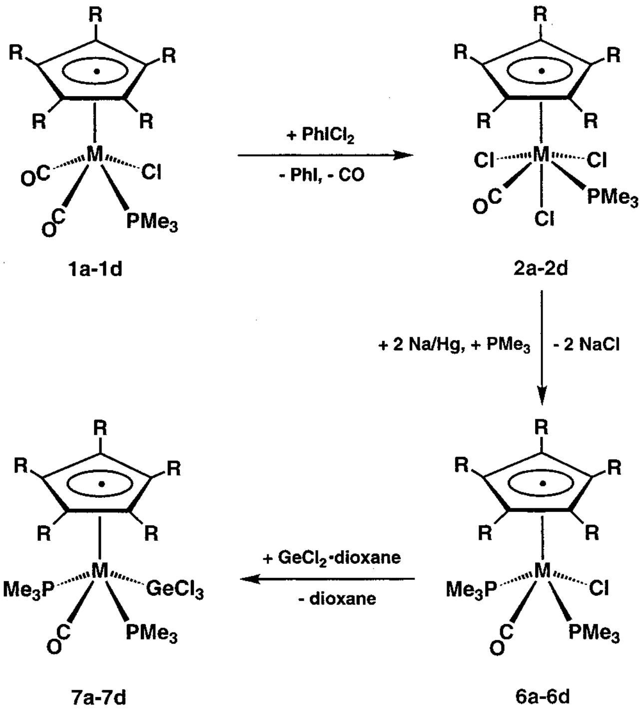
Scheme 1



a: M = Mo, R = H; b: M = W, R = H; c: M = Mo, R = Me; d: M = W, R = Me

$C_5R_5)M(CO)(PMe_3)_2GeCl_3$ (**7a**−**7d**) in large scale and high overall yield (Scheme 1).

Starting materials in this route are the chloro complexes *cis*-(η^5-C_5R_5)M(CO)$_2$(PMe$_3$)Cl (**1a**−**1d**), which were obtained in quantitative yield from the hydrido complexes *cis/trans*-(η^5-C_5R_5)M(CO)$_2$(PMe$_3$)H after chlorination with CCl_4. This reaction leads first to a mixture of the cis and trans isomers of (η^5-C_5R_5)M(CO)$_2$(PMe$_3$)-Cl; the trans isomer then isomerizes in solution at ambient temperature to the cis isomer.[6c]

Treatment of the chloro complexes **1a**−**1d** with 1 equiv of $PhICl_2$ in CH_2Cl_2 at −78 °C followed by warming of the solutions to room temperature was accompanied by vigorous gas evolution (CO) and a color change from red to orange (**1a**, **1b**) or brown (**1c**, **1d**) and resulted in the selective formation of the trichloro complexes **2a**−**2d** (Scheme 1). In addition, precipitation of the less soluble Cp derivatives **2a** and **2b** was observed during the reactions of **1a** and **1b** with $PhICl_2$. Evidence for the selective oxidation of **1a**−**1d** to **2a**−**2d** was given by the IR spectra of the reaction solutions, which revealed that the two ν(CO) absorptions of the starting materials had been replaced within a short period of time by the ν(CO) absorption of the products at 2032 (**2a**), 2011 (**2b**), 1956 (**2c**), and 1936 cm^{-1} (**2d**) (see Experimental Section). Complexes **2a**−**2d** were isolated as orange (**2a**, **2b**) and brown (**2c**, **2d**) microcrystalline solids in 94−99% yields. The Cp derivatives **2a** and **2b** are sparingly soluble in CH_2Cl_2 and acetone and insoluble in THF, Et_2O, and pentane. The molybdenum compound **2a** decomposes slowly in acetone solution at ambient temperature, as evidenced by the solution IR spectrum, which reveals a gradual decrease in intensity of the ν(CO) absorption at 2025 cm^{-1}. In comparison, the analogous tungsten compound **2b** is stable in acetone solution over a period of at least 5 h. However, both compounds are thermally quite stable in the solid state, decomposing upon heating in a sealed capillary under argon at 150 and 180 °C, respectively. In comparison, the Cp* complexes **2c** and **2d** show a higher solubility in organic solvents, being soluble in CH_2Cl_2, acetone, and THF, and are thermally more robust than **2a** and **2b,** decomposing upon heating at 179 and 188 °C, respectively.

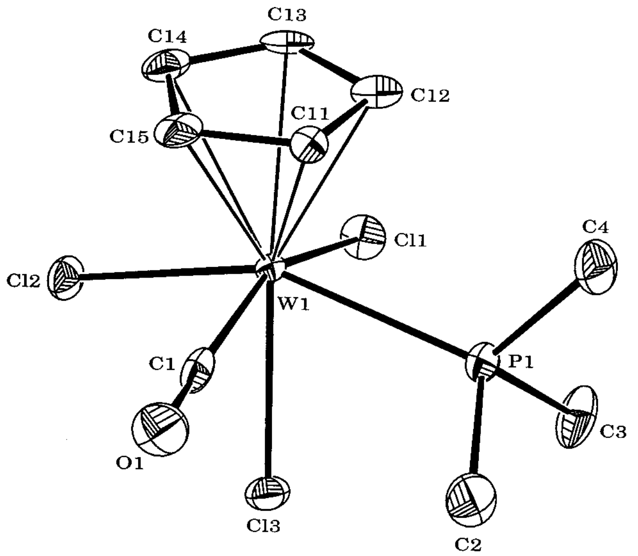


Figure 1. ZORTEP plot of a $CpW(CO)(PMe_3)Cl_3$ molecule in the crystal lattice of **2b-1**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity reasons.

Complexes **2a**−**2d** were fully characterized (see Experimental Section). Thus, the solution IR spectra of **2a**−**2d** display only one ν(CO) absorption. In addition, the ^1H NMR spectra show one doublet resonance for the methyl protons of the PMe_3 ligand and one doublet resonance for the Cp ring protons (**2a**, **2b**), or one singlet resonance for the Cp* ligand (**2c**, **2d**). Furthermore, one singlet resonance is observed in the $^{31}P\{^1H\}$ NMR spectra of **2a**−**2d**, which in the case of the tungsten complexes **2b** and **2d** is accompanied by satellites due to $^{183}W-^{31}P$ coupling, and the $^{13}C\{^1H\}$ NMR spectra of **2a**−**2d** display one carbonyl−carbon resonance, which is split to a doublet due to $^{31}P-^{13}C$ coupling. All these data suggest the presence of only one stereoisomer in solution. The structure of this isomer was determined in the case of the Cp complex **2b** by a single-crystal X-ray diffraction study. Suitable crystals were obtained upon slow cooling of a saturated solution of **2b** in MeCN or THF from room temperature to −30 °C. The crystals contain one molecule of MeCN per molecule of **2b** (**2b-1**) and one molecule of THF per two molecules of **2b** (**2b-2**), respectively. The molecular parameters of **2b** are similar in both crystal structures, and therefore the discussion is based on the more precise data of **2b-1**. A ZORTEP plot of one of the $CpW(CO)(PMe)Cl_3$ molecules in the crystal lattice of **2b-1** with the atom-labeling scheme adopted is shown in Figure 1. Selected bond lengths and angles are listed in Table 1.

The coordination geometry of complex **2b** can be described as distorted octahedral, considering that the Cp ligand occupies one coordination site. The distortion results from the steric bulk of the Cp ligand, which pushes the trimethylphosphane, carbonyl, and the equatorial chloro ligands Cl(1) and Cl(2) away from it

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations for 2b-1

W(1)−Cl(1)	2.4755(11)	W(1)−C_f[a]	1.987
W(1)−Cl(2)	2.4980(13)	Cl(1)−W(1)−Cl(2)	84.20(4)
W(1)−Cl(3)	2.4607(13)	Cl(1)−W(1)−Cl(3)	81.60(4)
W(1)−P(1)	2.5489(13)	Cl(2)−W(1)−Cl(3)	78.45(4)
W(1)−C(1)	2.016(4)	Cl(1)−W(1)−P(1)	86.20(4)
W(1)−C(11)	2.268(4)	Cl(2)−W(1)−P(1)	151.89(4)
W(1)−C(12)	2.276(5)	Cl(3)−W(1)−P(1)	74.03(4)
W(1)−C(13)	2.375(4)	Cl(1)−W(1)−C(1)	155.36(13)
W(1)−C(14)	2.398(5)	Cl(2)−W(1)−C(1)	91.28(15)
W(1)−C(15)	2.314(4)	Cl(3)−W(1)−C(1)	73.76(13)
W(1)−C_g[a]	1.993	P(1)−W(1)−C(1)	86.56(14)

[a] C_g and C_f denote the center of gravity of the Cp* ring and the foot of the tungsten-to-ring normal, respectively.

and toward the axial chloro ligand Cl(3). This is reflected in the angles Cl(1)−W(1)−Cl(3), Cl(2)−W(1)−Cl(3), Cl(3)−W(1)−P(1), and Cl(3)−W(1)−C(1), which are smaller than 90°, ranging from 73.76° to 81.60° (Table 1). The chloro ligands adopt a *facial* arrangement, with the axial W−Cl bond [W(1)−Cl(3) = 2.4607(13) Å] being slightly shorter than the two equatorial W−Cl bonds [W(1)−Cl(1) = 2.4755(11) Å; W(1)−Cl(2) = 2.4980(13) Å]. The W−Cl bond lengths of **2b** have an average value of 2.478 Å, which is close to those found in related pseudo-octahedral M(IV) cyclopentadienyl complexes [e.g., $CpMo(dppe)Cl_3$ $(Mo{-}Cl)_{av} = 2.476(3)$ Å;[7] $CpMo(PMe_2Ph)_2Cl_3$ $(Mo{-}Cl)_{av} = 2.505(1)$ Å].[8] The W−P bond of **2b** [W(1)−P(1) = 2.5489(13) Å] compares well with the M−P bonds of M(IV) cyclopentadienyl phosphane complexes having either a pseudo-octahedral coordination geometry, such as $CpMo(PMe_2Ph)_2Cl_3$ $[(Mo{-}P)_{av} = 2.554(1)$ Å],[8] or a "four-legged piano-stool" coordination geometry, such as *trans*-$[CpMo(PMe_3)_2Cl_2]^+$ $[(Mo{-}P)_{av} = 2.531(3)$ Å][9] and *trans*-$[CpMo(PMe_3)_2I_2]^+$ $[(Mo{-}P)_{av} = 2.545(5)$ Å].[10] However this bond is considerably longer than those found in various "four-legged piano-stool" M(III) and M(II) cyclopentadienyl phosphane complexes, e.g., *trans*-$CpMo(PMe_3)_2Cl_2$ $[(Mo{-}P)_{av} = 2.483(2)$ Å],[9] *trans*-$CpMo(PMe_3)_2I_2$ $[(Mo{-}P)_{av} = 2.501(2)$ Å],[9] *trans*-$CpW(CO)(PMe_3)_2GeCl_3$ (**7d**) $[(W{-}P)_{av} = 2.476(2)$ Å], *trans*-$CpMo(CO)_2(PMe_3)GeCl_3$ $[(Mo{-}P)_{av} = 2.4701(13)$ Å],[6a] and *trans*-$CpW(CO)_2(PMe_3)GeCl_3$ $[(W{-}P)_{av} = 2.464(3)$ Å],[11] although the metal center of **2b** is in a higher oxidation state (+IV). All these data indicate a decrease of M−P π back-bonding on going from M(II) and M(III) to M(IV) cyclopentadienyl phosphane complexes.[9,10,12] The W−CO bond of **2b** is 2.016(4) Å, slightly shorter than those of $(\eta^5\text{-}C_5H_4{}^iPr)W(CO)_2Br_3$ $[(W{-}CO)_{av} = 2.041(9)$ Å],[13] indicating a stronger metal(dπ)−CO(π^*) back-bonding in **2b** in full agreement with the IR spectra of these compounds. Finally, the Cp ligand shows a distortion from an η^5 toward an η^3 coordination, the more distant carbon atoms C(13) and C(14) occupying approximately a trans position relative to the carbonyl and the PMe_3 ligand, respectively. This distortion results probably from the strong trans influence of these ligands.[14]

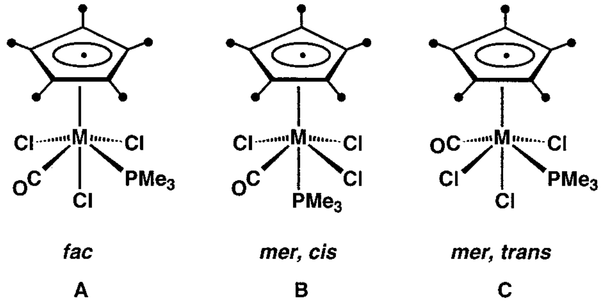


Figure 2. Possible stereoisomers for **2c** and **2d** with a cis arrangement of the Cp* and the CO ligand.

The Cp* complexes **2c** and **2d** might have a different configuration from that of the Cp derivatives **2a** and **2b** taking into consideration their spectroscopic data. Thus, the ν(CO) absorption of **2c** and **2d** in CH_2Cl_2 is observed at lower wavenumbers (1956 and 1936 cm^{-1}, respectively) than that of the corresponding Cp complexes [**2a**, $\nu(CO) = 2032$ cm^{-1}; **2b**, $\nu(CO) = 2011$ cm^{-1}]. This might be explained at first glance by the stronger electron-releasing ability of the Cp* ligand. However, the difference in the ν(CO) frequencies between the Cp and Cp* derivatives of 75−76 cm^{-1} is considerably larger than one would expect for a series of Cp and Cp* complexes of the same configuration. This is evidenced by a comparison with the ν(CO) absorptions of the analogous ethyl isocyanide complexes $CpM(CO)(EtNC)Cl_3$ and $Cp^*M(CO)(EtNC)Cl_3$, which like **2b** adopt in the solid-state a *facial* coordination geometry according to single-crystal X-ray diffraction studies. In this case, the ν(CO) absorptions of the Cp* complexes [$Cp^*Mo(CO)(EtNC)Cl_3$, ν(CO) in $CH_2Cl_2 = 2026$ cm^{-1}; $Cp^*W(CO)(EtNC)Cl_3$, ν(CO) in $CH_2Cl_2 = 2006$ cm^{-1}] are shifted by only 27−29 cm^{-1} to lower wavenumbers relative to those of the Cp complexes [$CpMo(CO)(EtNC)Cl_3$, ν(CO) in $CH_2Cl_2 = 2055$ cm^{-1}; $CpW(CO)(EtNC)Cl_3$, ν(CO) in $CH_2Cl_2 = 2033$ cm^{-1}].[11] In addition, the ${}^1J$(WP) coupling constant of the Cp* complex **2d** is 121.0 Hz, considerably smaller than that of the Cp derivative **2b** (221.2 Hz).

Three stereoisomers can be envisaged for **2c** and **2d**, in which the Cp* ligand and the carbonyl ligand are cis oriented (Figure 2). One isomer has a *facial* arrangement of the three chloro ligands (**A**), as observed for **2a** and **2b**, and two isomers have a *meridional* arrangement of the three chloro ligands (**B**, **C**). The *meridional* isomers **B** and **C** differ in the relative position of the carbonyl and the PMe_3 ligand (**B**, cis; **C**, trans). A fourth stereoisomer with a trans arrangement of the Cp* and the carbonyl ligand is also conceivable for **2c** and **2d**. However, this isomer should be less stable than **A**, **B**, or **C**, because of the weaker metal(dπ)−CO(π^*) back-bonding expected for such an isomer, and is therefore not depicted in Figure 2.

Both stereoisomers **B** and **C** are reasonable for **2c** and **2d** given the low ${}^1J$(WP) coupling constant of **2d**, which indicates a weak W−P bond and might be explained by

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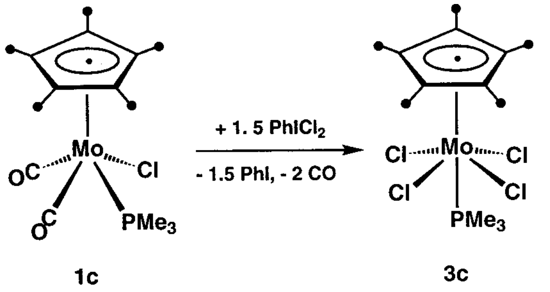
the trans influence of the Cp* ligand in **B** and of the carbonyl ligand in **C**. Therefore, the Mo−$P_{ax.}$ bond (trans to the Cp ligand) is in general longer than the Mo−$P_{eq.}$ bond in pseudo-octahedral Mo(IV) cyclopentadienyl complexes with a *mer, cis* configuration (**B**).[7,15] Unfortunately, suitable single crystals of **2c** or **2d** could not be grown so far. Therefore, an unambiguous assignment of the stereochemistry in **2c** and **2d** is not possible at the moment.

The oxidation of **1a**−**1d** with $PhICl_2$ offers a very convenient route to the reactive M(IV) compounds **2a**−**2d** (Scheme 1) considering the high selectivity of this reaction and the easy, large-scale and high-yield synthesis of **1a**−**1d** starting from $M(CO)_6$. However, an excess of $PhICl_2$ must be avoided in the chlorination of **1a**−**1d**; otherwise the products **2a**−**2d** are contaminated with the M(V) complexes $(\eta^5\text{-}C_5R_5)M(PMe_3)Cl_4$. In fact, treatment of **1c** with 1.5 equiv of $PhICl_2$ in CH_2Cl_2 results in the selective formation of $Cp^*Mo(PMe_3)Cl_4$ (**3c**) (eq 1), and oxidation of **2d** with 0.5 equiv of $PhICl_2$ affords selectively the analogous W(V) complex $Cp^*W(PMe_3)Cl_4$ (**3d**) (eq 2). Both products are easily isolated in essentially quantitative yields. In addition, these reactions can be carried out in large scale, providing therefore a convenient route to **3c** and **3d**. Complexes **3c** and **3d** were previously obtained by addition of PMe_3 to Cp^*MCl_4,[16] the latter complexes providing an entry to a variety of pentamethylcyclopentadienyl complexes of molybdenum and tungsten[17] as well as permethyltungstenocene derivatives.[18]



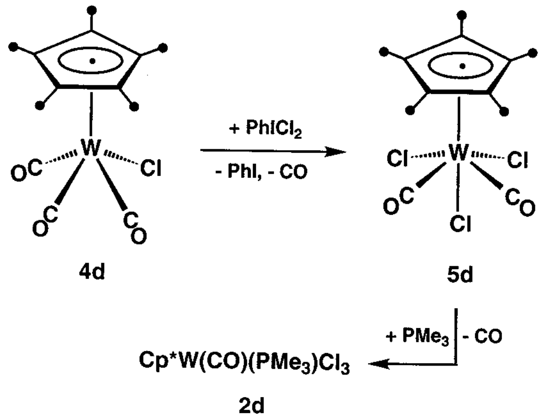
(1)

$$Cp^*W(CO)(PMe_3)Cl_3 \xrightarrow[\text{- 0.5 PhI, - CO}]{\text{+ 0. 5 PhICl}_2} Cp^*W(PMe_3)Cl_4 \quad (2)$$

2d **3d**

An alternative two-step route to **2d** involves oxidation of $Cp^*W(CO)_3Cl$ (**4d**) with 1 equiv of $PhICl_2$ in CH_2Cl_2 to give selectively the W(IV) complex $Cp^*W(CO)_2Cl_3$ (**5d**), which then undergoes a CO ligand exchange reaction with PMe_3 to give **2d** (Scheme 2). Complex **2d** was thereby obtained in 90% overall yield.

Scheme 2



In comparison, the analogous triiodo complexes $Cp^*M(CO)_2I_3$ (M = Mo, W) are reduced by PMe_3 to afford the M(II) trimethylphosphane complexes $Cp^*M(CO)_2(PMe_3)I$.[11,17h]

Oxidative decarbonylation of low oxidation-state molybdenum and tungsten cyclopentadienyl complexes such as **1a**−**1d** with halogens was previously shown to be a valuable route to M(IV) derivatives. For example, using this method, we have prepared the Mo(IV) and W(IV) isocyanide complexes $(\eta^5\text{-}C_5R_5)M(CO)(R'NC)I_3$ (R = H, Me; R′ = Et, ^{t}Bu) and have demonstrated that these compounds are useful starting materials for the synthesis of various isocyanide complexes of molybdenum and tungsten in low and high oxidation states.[19] Furthermore, the M(IV) dicarbonyl complexes $CpM(CO)_2X_3$ (M = Mo, W; X = Cl, Br, I) were obtained over 30 years ago by the oxidation of $CpM(CO)_3X$ or $[CpM(CO)_3]_2$ with X_2,[20] and the analogous molybdenum pentamethylcyclopentadienyl complexes $Cp^*Mo(CO)_2X_3$ (X = Cl, Br, I) were prepared recently by identical procedures.[21] In addition, the Mo(IV) dicarbonyl complexes were shown to undergo a thermal decarbonylation to give the Mo(IV) trihalides $[(\eta^5\text{-}C_5R_5)MoX_3]_n$ (R = H, Me; X = Cl, Br, I), which are valuable starting materials for a variety of 16-electron and 18-electron Mo(IV) complexes of the general formula $(\eta^5\text{-}C_5R_5)Mo(L)_mX_3$ (L = phosphane; m = 1, 2).[8,21,22] Similarly, halogenation of $CpMo(CO)_2(L)X$ (L = $P(OMe)_3$, PEt_3, PMe_2Ph; X = Cl, Br, I) was previously shown to give the Mo(IV) monocarbonyl complexes $CpMo(CO)(L)X_3$, whereas the triphenylphosphane derivatives $CpMo(CO)_2(PPh_3)X$ react with X_2 to afford the Mo(IV) dicarbonyl complexes $CpMo(CO)_2X_3$.[23] Chlorination of the

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Mo(II) compound CpMo(CO)(dppe)Cl (dppe = 1,2-bis(diphenylphosphino)ethane) was also reported to give the Mo(IV) complex CpMo(dppe)Cl$_3$.[7] Other less practicable methods for the synthesis of M(IV) cyclopentadienyl complexes include the oxidation of the W(II) methyl complex Cp*W(CO)$_3$Me with iodine to give Cp*W(CO)$_2$I$_3$,[24] the reaction of M(IV) bis(cyclopentadienyl) complexes with nucleophiles,[25] the oxidative cleavage of the metal−metal bond in Cp*(CO)$_3$W−W(O)$_2$Cp* with X$_2$ (X = Cl, Br, I) leading to a mixture of the complexes Cp*W(CO)$_2$X$_3$ and Cp*W(O)$_2$X,[26] the photooxidation of the carbyne complex Cp(CO)[P(OMe)$_3$]W≡C(c-C$_3$H$_5$) in CHCl$_3$, which affords the trichloro complex CpW(CO)[P(OMe)$_3$]Cl$_3$,[27] and the oxidation of the carbene complexes Cp*(CO)$_2$(SnPh$_3$)M=C(OEt)Ph (M = Mo, W) with I$_2$ to give among other products also Cp*M(CO)$_2$I$_3$.[28]

The chlorination of **1a**−**1d** with PhICl$_2$ offers a very convenient access to **2a**−**2d**. This has enabled us to study some reactions of these compounds. Thus, reduction of **2a**−**2d** in THF with Na/Hg leads in the presence of PMe$_3$ to the “electron-rich” M(II) complexes **6a**−**6d** (Scheme 1). IR monitoring of these reactions revealed a selective transformation of the starting materials to the products, which were isolated as orange-red (**6a**, **6c**) or red solids (**6b**, **6d**) in 78−94% yields. All compounds are air-sensitive, thermally stable solids, which are soluble in CH$_2$Cl$_2$, THF, and Et$_2$O and sufficiently soluble in pentane. Complexes **6a**, **6b,** and **6c** melt without decomposition at 152, 176, and 212 °C, respectively, whereas complex **6d** remains unchanged upon heating to 230 °C. Complexes **6a** and **6b** were previously isolated in low yield on attempts to purify the methyl complexes *trans*-CpM(CO)(PMe$_3$)$_2$Me (M = Mo, W) by column chromatography on silica,[29] and complex **6c** was obtained by carbonylation of Cp*Mo(PMe$_3$)$_2$Cl.[17k] The procedure reported here for the preparation of **6a**−**6d** (Scheme 1) is distinguished by a sequence of high-yield reactions, which can be carried out in large scale. It is therefore a very convenient method for the synthesis of **6a**−**6d**.

Complexes **6a**−**6d** were fully characterized (see Experimental Section). The spectroscopic data of these compounds indicate the presence of only the trans stereoisomer in solution, which in the case of **6d** was also confirmed by a single-crystal X-ray diffraction study (vide infra). Thus, the ^{31}P{^{1}H} NMR spectra of **6a**−**6d** display a singlet resonance for the chemically equivalent PMe$_3$ ligands. The ^{1}H NMR spectra show one resonance for the PMe$_3$ protons with the multiplicity pattern expected for a X$_9$AA'X$_9$' spin system.[30] The IR spectra of the M(II) complexes **6a**−**6d** display in THF a ν(CO) absorption at 1788, 1774, 1780, and 1770 cm^{-1}, respectively. This absorption is shifted by 160−250 cm^{-1} to lower frequency than that of the M(IV) complexes **2a**−**2d**, indicating a considerable increase of the electron density at the metal center. In fact, the ν(CO) absorption of **6a**−**6d** appears in the same frequency range as those of Cp/Cp*-substituted group VI carbonyl metalates [e.g., ν(CO) in THF: Na[CpMo(CO)$_2$(CNEt)] = 1766, 1727 cm^{-1}; Na[CpW(CO)$_2$(CNEt)] = 1762, 1713 cm^{-1}; Na[Cp*Mo(CO)$_2$(CNEt)] = 1753, 1703 cm^{-1}; Na[Cp*W(CO)$_2$(CNEt)] = 1750, 1697 cm^{-1}],[31] suggesting, in full agreement with the cyclic voltammetric data (vide infra), the presence of an electron-rich metal center in these compounds. This is also supported by the ^{13}C{^{1}H} NMR spectra of **6a**−**6d**, which display a triplet resonance for the carbonyl ligand at very low field (δ 258.3−275.1), indicating a strong metal(dπ)−CO(π*) back-bonding.[32]

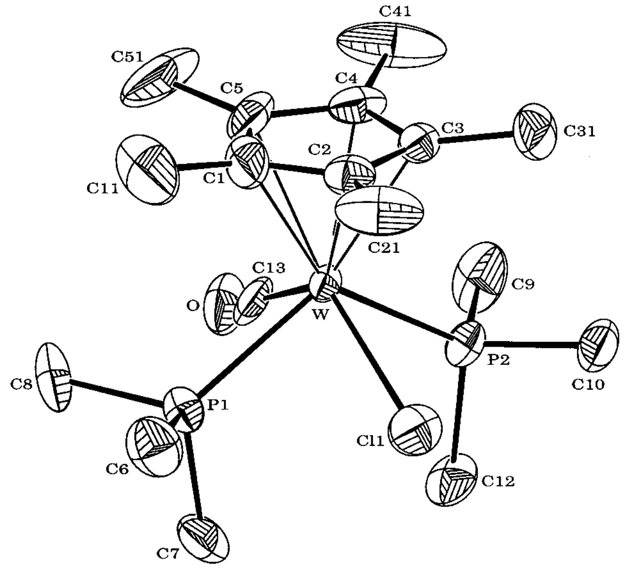

Figure 3. ZORTEP plot of the molecular structure of **6d** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity reasons.

The solid-state structure of **6d** was determined by a single-crystal X-ray diffraction study. Suitable crystals were obtained after slow evaporation of a pentane solution of **6d** containing some CH$_2$Cl$_2$ and Et$_2$O at ambient temperature. A ZORTEP plot of the molecular structure of **6d** with the atom-labeling scheme adopted is depicted in Figure 3. Selected bond lengths and angles are given in Table 2.

Complex **6d** shows the expected “four-legged piano-stool” coordination geometry with a trans *(diagonal)* arrangement of the trimethylphosphane ligands.[6,12c,33] The angles about the tungsten center including those between the W−C$_g$ vector and the W−L bonds (C$_g$ denotes the center of gravity of the pentamethylcyclopentadienyl ring) are similar to those of the related

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations for 6d

W−Cl(1)	2.560(2)	Cl(1)−W−P(1)	76.57(8)
W−P(1)	2.449(2)	Cl(1)−W−P(2)	77.07(8)
W−P(2)	2.455(2)	Cl(1)−W−C(13)	126.3(3)
W−C(1)	2.401(9)	P(1)−W−P(2)	116.35(7)
W−C(2)	2.397(6)	P(1)−W−C(13)	76.1(3)
W−C(3)	2.335(7)	P(2)−W−C(13)	75.1(3)
W−C(4)	2.287(7)	Cl(1)−W−C_g	114.1
W−C(5)	2.312(9)	P(1)−W−C_g	120.3
W−C_g[a]	2.012	P(2)−W−C_g	123.3
W−C_f[a]	2.007	C(13)−W−C_g	119.6
W−C(13)	2.082(14)		

[a] C_g and C_f denote the center of gravity of the Cp* ring and the foot of the tungsten-to-ring normal, respectively.

Mo(II) compound *trans*-Cp*Mo(CO)(PMe_2Ph)$_2$Cl.[34] The W−P bonds have an average length of 2.452(2) Å, which is close to those found in other "electron-rich" W(II) pentamethylcyclopentadienyl complexes, e.g., spy-5-52-Cp*W(CO)(CNEt)(PMe_3)$GeCl_3$ [W−P = 2.453(3) Å][11] and spy-5-52-Cp*W(CO)(CNEt)(PMe_3)($GeBr_2$Mes) [W−P = 2.464(6) Å][11] [(W−P)$_{av}$ = 2.489(2) Å],[11] suggesting extensive W−P π back-bonding. A 2-fold disorder superposes the chloro and the carbonyl ligand; therefore the W−CO bond of **6d** appears considerably longer than expected for an "electron-rich" carbonyl complex.

Complexes **6a**−**6d** react fast with $GeCl_2$(1,4-dioxane) in CH_2Cl_2 to give the trichlorogermyl complexes **7a**−**7d** (Scheme 1). Evidence for the selective and fast insertion of $GeCl_2$ into the metal−chlorine bond of **6a**−**6d** was provided by the IR spectra of the reaction solutions. These revealed that the ν(CO) absorption of the starting materials was replaced very quickly by the ν(CO) absorption of the products **7a**−**7d** at 1847, 1835, 1831, and 1820 cm^{-1}, respectively (see Experimental Section). Complexes **7a**−**7d** were isolated as yellow, slightly air-sensitive solids in 87−98% yields. All compounds are soluble in CH_2Cl_2 and THF, the Cp* derivatives **7c** and **7d** showing also considerable solubility in Et_2O. The cyclopentadienyl complexes **7a** and **7b** are thermally more robust than the pentamethylcyclopentadienyl complexes **7c** and **7d,** decomposing, when heated in a sealed capillary under argon, at 175 and 215 °C (**7c** and **7d** decompose at 165 °C). IR spectra of the decomposed samples of **7c** and **7d** in CH_2Cl_2 reveal the formation of the chloro complexes **6c** and **6d** and the dicarbonyl complexes *trans*-Cp*M(CO)$_2$(PMe_3)$GeCl_3$ (M = Mo, W), indicating that one decomposition pathway of **7c** and **7d** involves extrusion of $GeCl_2$.

Complexes **7a**−**7d** were fully characterized. Thus, the IR spectra of **7a**−**7d** in CH_2Cl_2 show one ν(CO) absorption, which is shifted by 63−76 cm^{-1} to higher energy than that of the chloro complexes **6a**−**6d**. This shows, in full agreement with the cyclic voltammetric data of **6b**−**7d** (vide infra), that insertion of $GeCl_2$ into the metal−chlorine bond reduces the electron density at the metal center and weakens thereby the metal (dπ)−CO-(π*) back-bonding. The observed shift can be explained by the different electronic properties of the chloro and the trichlorogermyl ligand, the first one being a potential π-donor ligand[35] and the latter one a π-acceptor ligand.[4] Evidence for a weaker metal (dπ)−CO(π*) back-bonding in the trichlorogermyl complexes **7a**−**7d** is also given by the $^{13}C\{^1H\}$ NMR spectra, which display a triplet resonance for the carbonyl ligand at higher field (δ 239.6−260.1) than that of the corresponding chloro complexes **6a**−**6d** (δ 258.3−275.1).[6a,c,d,32] In addition, the ^1H and $^{31}P\{^1H\}$ NMR spectra of **7a**−**7d** suggest the presence of only the trans stereoisomer in solution, which was also verified for **7b** by a single-crystal X-ray diffraction study. Suitable single crystals were obtained upon slow evaporation of a CH_2Cl_2 solution of **7b** at room temperature. A ZORTEP drawing of one of the four independent molecules in the asymmetric unit with the atom-labeling scheme adopted is depicted in Figure 4. The bonding parameters of the four independent molecules are very similar. Therefore only the bond lengths and angles of one molecule are listed in Table 3, and the following discussion is based on the average values.

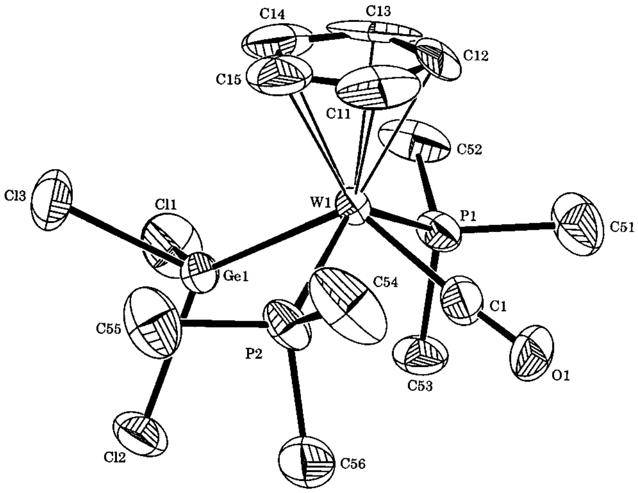

Figure 4. ZORTEP plot of one of the four independent molecules of **7b** in the crystallographic asymmetric unit**.** Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity reasons. The other three molecules contain the atoms: W(2)−W(4), Ge(2)−Ge(4), P(3)−P(8), Cl(4)−Cl(12), C(2)−C(4) and O(2)−O(4) (carbonyl ligand), C(21)−C(25), C(31)−C(35) and C(41)−C(45) (cyclopentadienyl ligand), and C(61)−C(66), C(71)−C(76) and C(81)−C(86) (trimethylphosphane ligands).

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) with Estimated Standard Deviations for One of the Four Independent Molecules of 7b in the Asymmetric Unit

W(1)−Ge(1)	2.5305(10)	Ge(1)−W(1)−P(1)	83.18(6)
Ge(1)−Cl(1)	2.222(2)	Ge(1)−W(1)−P(2)	81.26(6)
Ge(1)−Cl(2)	2.244(2)	P(1)−W(1)−P(2)	133.47(8)
Ge(1)−Cl(3)	2.250(3)	Ge(1)−W(1)−C(1)	117.9(3)
W(1)−P(1)	2.472(2)	P(1)−W(1)−C(1)	75.3(3)
W(1)−P(2)	2.470(2)	P(2)−W(1)−C(1)	74.0(2)
W(1)−C(1)	1.926(9)	Ge(1)−W(1)−C_g	117.1
W(1)−C(11)	2.269(8)	P(1)−W(1)−C_g	112.8
W(1)−C(12)	2.286(8)	P(2)−W(1)−C_g	113.4
W(1)−C(13)	2.344(8)	C(1)−W(1)−C_g	125.0
W(1)−C(14)	2.356(11)	Cl(1)−Ge(1)−Cl(2)	93.73(10)
W(1)−C(15)	2.303(10)	Cl(1)−Ge(1)−Cl(3)	93.95(12)
W(1)−C_g[a]	2.001	Cl(2)−Ge(1)−Cl(3)	96.32(10)

[a] C_g denotes the center of gravity of the Cp* ring.

Complex **7b** has, like **6d,** the expected square-pyramidal coordination geometry of a "four-legged piano-stool" complex.[6,12c,33] The trimethylphosphane ligands

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are trans positioned, as deduced from the NMR spectroscopic data of this compound. The W−CO bond of **7b** [$(W-CO)_{av} = 1.928(9)$] is shorter than that of the related trichlorogermyl complexes $CpW(CO)_3GeCl_3$ [$(W-CO)_{av} = 1.994(9)$ Å],[11] *trans*-$CpW(CO)_2(PMe_3)GeCl_3$ [$(W-CO)_{av} = 1.961(10)$ Å],[11] *cis*-$Cp^*W(CO)_2(PMe_3)GeCl_3$ [$(W-CO)_{av} = 1.955(5)$ Å],[6c] *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3$ [$(W-CO)_{av} = 1.974(10)$ Å],[6c] and spy-5-53-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$ [$(W-CO)_{av} = 1.958(7)$ Å],[11] indicating the presence of an electron-rich metal center and a strong metal($d\pi$)−CO(π^*) back-bonding in **7b**. The tetrahedral environment of the germanium atom is strongly distorted, as shown by the Cl−Ge−Cl bond angles with an average value of 95.1(1)° and the W−Ge−Cl bond angles with an average value of 121.66(7)°. A similar distortion was previously observed in other tungsten trichlorogermyl complexes.[6] In addition, a comparison of the structures of $GeCl_4$,[36] $CpW(CO)_3GeCl_3$,[11] *trans*-$CpW(CO)_2(PMe_3)GeCl_3$,[11] *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3$,[6c] spy-5-52-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$,[11] and **7b** reveals the following trends as a chloro group is replaced successively by a more electropositive substituent: (a) the mean Cl−Ge−Cl bond angles decrease [$GeCl_4$, 109.5°; $CpW(CO)_3GeCl_3$, 101.3(1)°; *trans*-$CpW(CO)_2(PMe_3)GeCl_3$, 98.9(2)°; *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3$, 98.6(2)°; spy-5-52-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$, 97.6(2)°; **7b**, 95.1(1)°] and (b) the mean Ge−Cl bond lengths increase [$GeCl_4$, 2.113(3) Å; $CpW(CO)_3GeCl_3$, 2.178(3) Å; *trans*-$CpW(CO)_2(PMe_3)GeCl_3$, 2.192(4) Å; *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3$, 2.199(3) Å; spy-5-52-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$, 2.221(4) Å; **7b**, 2.233(2) Å]. These trends can be rationalized assuming a stronger tungsten−trichlorogermyl π back-bonding, when the electron density on the metal center is enhanced. Such an assumption is reasonable given the isoelectronic relationship of a $GeCl_3^-$ ion with $AsCl_3$ and the π-acceptor character of $AsCl_3$.[35] These structural data can be also rationalized using the atom rehybridization model of Bent.[6c,d,37] The same arguments would let one predict a shortening of the W−Ge bond in the series **7b** > spy-5-52-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$ > *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3$ > *trans*-$CpW(CO)_2(PMe_3)GeCl_3$ > $CpW(CO)_3GeCl_3$, if steric effects are negligible. In fact, the mean W−Ge bond of **7b** is 2.531(1) Å, shorter than that of $CpW(CO)_3GeCl_3$ [W−Ge: 2.5437(9) Å], but longer than that of the other trichlorogermyl complexes [*trans*-$CpW(CO)_2(PMe_3)GeCl_3$, $(W-Ge)_{av} = 2.517(1)$ Å; *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3$, W−Ge = 2.516(1) Å; spy-5-52-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$, 2.493(2) Å],[6c,11] indicating an overcompensation of the electronic effect of the ligand sphere on the W−Ge bond of **7b** by the steric repulsion between the trichlorogermyl and the PMe_3 ligands. Experimental evidence for such a repulsion is given by the Ge−W−P bond angles of **7b**, which are 82.33(6)° (average value), larger than the cis $Cl_3Ge-W-L$ bond angles of *trans*-$CpW(CO)_2(PMe_3)GeCl_3$ [$(Ge-W-CO)_{av} = 75.7(3)°$], *trans*-$Cp^*W(CO)_2(PMe_3)GeCl_3$ [$(Ge-W-CO)_{av} = 74.8(3)°$], and spy-5-52-$Cp^*W(CO)(CNEt)(PMe_3)GeCl_3$ [Ge−W−CO = 75.0(5)°; Ge−W−CNEt = 72.0(3)°].[6c,11]

Table 4. Cyclic Voltammetric Data of the Complexes 6b−7d[a]

complex	$E_{p,a}$ (V)[b]	$E_{p,c}$ (V)[b]	$(E_{p,a} + E_{p,c})/2$ (V)	$E_{p,a} - E_{p,c}$ (mV)	I_a/I_c[c]
6b	−0.46 0.42	−0.62	−0.54	160	1.04
6c	−0.49 0.65	−0.59	−0.54	100	1.03
6d	−0.54 0.61	−0.74	−0.64	200	0.93
7a	0.25 1.09	0.09	0.17	160	0.93
7b	0.19 1.10	0.02	0.11	170	1.05
7c	0.02 1.07	−0.12	−0.05	140	0.98
7d	0.00 1.04	−0.13	−0.06	130	1.01

[a] Measurements in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ at 25 °C with a scan rate of 0.1 V s^{-1} or 0.2 V s^{-1} (**6d** and **7d**); concentration of the complex approximately 10^{-4} M. [b] Anodic and cathodic peak potentials are given in volts vs the ferrocene/ferrocenium redox couple. [c] Ratio of anodic to cathodic peak current.

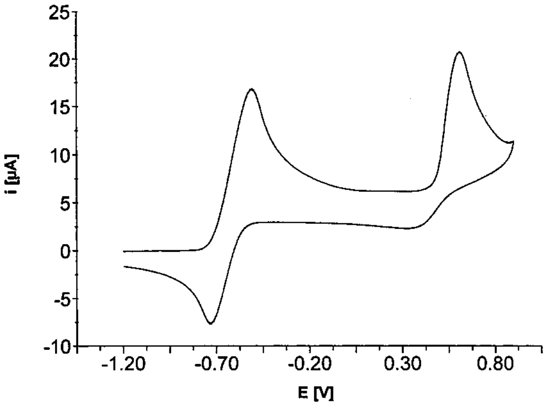

Figure 5. Cyclic voltammogram of **6d** in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ at 25 °C and a scan rate of 0.2 V s^{-1}. $Fc/Fc^+ = 0$ V.

Cyclic voltammetric studies of the complexes **6b**−**7d** were conducted in CH_2Cl_2 at 25 °C in order to determine the influence of substitution of a chloro by a trichlorogermyl ligand on the redox potentials. All the complexes studied were electrochemically active, and the data are summarized in Table 4.

The cyclic voltammograms of all complexes display common features showing a quasi-reversible one-electron oxidation at anodic peak potentials ranging from −0.52 V (**6d**) to 0.25 V (**7a**) followed by an irreversible oxidation at more positive potentials. The cyclic voltammograms of a chloro complex (**6d**) and the corresponding trichlorogermyl complex (**7d**) are depicted in Figures 5 and 6 to illustrate these features.

The chloro complex **6d** displays one peak on the anodic wave at −0.52 V and a corresponding cathodic peak at −0.73 V ($v = 0.2$ V s^{-1}) (Figure 5). As the scan rate was changed from 0.4 to 0.05 V s^{-1}, the difference of the anodic and cathodic peak potential for this process varied from 300 to 170 mV, while the ratio of anodic to cathodic peak current remained close to unity. The electrochemical behavior of the other chloro complexes was similar, suggesting a quasi-reversible process, which involves a moderately slow one-electron transfer compared to the rate of potential change.[38] Oxidation of **6c** with $[Cp_2Fe][PF_6]$ has been recently shown to give

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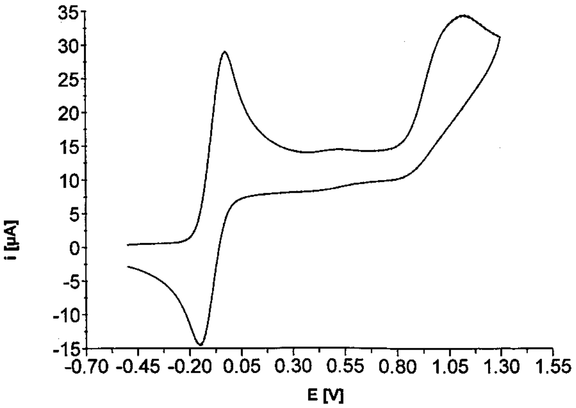

Figure 6. Cyclic voltammogram of **7d** in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ at 25 °C and a scan rate of 0.05 V s^{-1}. $Fc/Fc^+ = 0$ V.

selectively the Mo(III) complex $[Cp^*Mo(CO)(PMe_3)_2Cl][PF_6]$, giving additional evidence for the reversibility of this one-electron-transfer step.[17k] Furthermore, all chloro complexes display an irreversible response on the anodic wave at more positive potentials (**6d**: $E_{p,a} = 0.61$ V, Figure 5), indicating further oxidation of the formed M(III) complexes *trans*-$[(\eta^5\text{-}C_5R_5)M(CO)(PMe_3)_2Cl]^+$. The cyclic voltammogram of the trichlorogermyl complex **7d** is similar to that of **6d,** displaying a quasi-reversible one-electron redox process at −0.06 V $[(E_{p,a} + E_{p,c})/2]$ followed by an irreversible response on the anodic wave at 1.04 V (Figure 6). A comparison of the electrochemical data of the chloro and the corresponding trichlorogermyl complexes reveals a decrease of the potential for the first electron-transfer step $[(E_{p,a} + E_{p,c})/2]$ by 490−630 mV (Table 4), indicating a considerable decrease in electron density at the metal center upon replacement of a chloro ligand by a trichlorogermyl group.

Conclusion

A three-step route to the molybdenum and tungsten trichlorogermyl complexes *trans*-$(\eta^5\text{-}C_5R_5)M(CO)(PMe_3)_2GeCl_3$ (R = H, Me) was developed starting from the easily accessible chloro complexes *cis*-$(\eta^5\text{-}C_5R_5)M(CO)_2(PMe_3)Cl$. This route is distinguished by a sequence of high-yield reactions, which can be carried out in large scale. The spectroscopic, structural, and cyclovoltammetric data of the trichlorogermyl complexes indicate the presence of an electron-rich metal center, which causes a strong deformation of the tetrahedral environment of the germanium atom and an elongation of the Ge−Cl bonds. This suggests the trichlorogermyl complexes to be suitable precursors for functionalized metallagermanes using the reactivity of the Ge−Cl bonds.

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (pentane over CaH_2, diethyl ether and THF over Na/benzophenone, CH_2Cl_2 over P_2O_5 and Na/Pb alloy, and acetone over $CaCl_2$/moleculare sieve 3 Å) and distilled under argon prior to use. The compounds *cis/trans*-$(\eta^5\text{-}C_5R_5)M(CO)_2(PMe_3)H$,[39] $PhICl_2$,[40] PMe_3,[41] and $GeCl_2$(1,4-dioxane)[42] were prepared according to literature procedures.

Elemental analyses were obtained from the Zentrale Analytische Gruppe des Instituts für Chemie der Humboldt-Universität zu Berlin. Solution IR spectra were recorded on a Bruker IFS-55 spectrometer using a NaCl cell. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-300 spectrometer in dry deoxygenated benzene-d_6, acetone-d_6, chloroform-d_1, and methylene-d_2 chloride. The ^1H and $^{13}C\{^1H\}$ NMR spectra were calibrated against the internal residual proton or natural abundance ^{13}C resonances of the deuterated solvent (benzene-d_6, δ_H 7.15 and δ_C 128.0 ppm; acetone-d_6 δ_H 2.04 and δ_C 206.0 ppm; chloroform-d_1 δ_H 7.24 and δ_C 77.0 ppm; methylene chloride-d_2, δ_H 5.32 and δ_C 53.8 ppm) and the $^{31}P\{^1H\}$ NMR spectra against an external 85% H_3PO_4 aqueous solution. Mass spectra were obtained with a Hewlett-Packard 5995A spectrometer; *m*/*z* values are given relative to the ^{184}W, ^{98}Mo, ^{74}Ge, and ^{35}Cl isotopes. Melting points were determined using a Büchi 530 melting point apparatus and are not corrected. The samples were sealed under argon in capillary tubes and heated with a rate of 1 K/min. IR spectra of the heated samples were recorded and compared with those of authentic samples to determine whether the compounds had decomposed. Cyclic voltammetric measurements were carried out using an Autolab PGSTAT 20 potentiostat (Metrohm) and a commercially available electrochemical cell. The cell was purged with nitrogen prior to use and then charged with the freshly prepared CH_2Cl_2 solution of the sample (0.1 mmol/L) containing tetrabutylammonium hexafluorophosphate (0.1 mol/L) as the supporting electrolyte. The solution resistance was not compensated. Sweep rates were usually varied from 0.05 to 0.80 V s^{-1}. A glassy carbon electrode was used as the working electrode and a $Ag/AgCl//CH_3CN$/0.1 M $[NBu_4]Cl$ electrode as the reference electrode, which was separated from the solution by a double-fritted cartridge system (Metrohm). Following IUPAC recommendations[43] all potentials are given against the ferrocene/ferrocenium redox couple (Fc/Fc^+), which was used as external standard ($E_{p,a} = 0.76$ V; $E_{p,c} = 0.64$ V).

1. Preparation of $CpMo(CO)(PMe_3)Cl_3$ (2a). A 497 mg (1.51 mmol) sample of **1a** was dissolved in 20 mL of CH_2Cl_2, and the red solution was cooled to −78 °C (dry ice/acetone bath). To this solution was added slowly through a stainless steel cannula a solution of 415 mg (1.51 mmol) of freshly prepared $PhICl_2$ in 20 mL of CH_2Cl_2, and the reaction mixture was allowed to warm to room temperature. Evolution of gas was observed, and the major amount of complex **2a** precipitated out of the solution as an orange solid. After 1 h stirring at ambient temperature an IR spectrum of the supernatant solution was recorded in the region 2200−1800 cm^{-1} to confirm the complete conversion of **1a** to **2a**. The suspension was then concentrated in vacuo to a few milliliters, and diethyl ether was added to complete precipitation of **2a**. The supernatant solution was discarded, and the precipitate was washed twice with 15 mL of diethyl ether and dried in vacuo to give **2a** as orange solid: yield 530 mg (94%); mp 150 °C (dec). Anal. Calcd for $C_9H_{14}Cl_3MoOP$ (371.48): C, 29.10; H, 3.80. Found: C, 28.54; H, 3.71. IR (CH_2Cl_2): ν(CO) 2032 (s) cm^{-1}. IR (acetone): ν(CO) 2025 (s) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 1.72 (d, $^2J(PH) = 10.4$ Hz, 9H, PMe_3), 5.68 (d, $^3J(PH) = 3.7$ Hz, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 2.0.

2. Preparation of $CpW(CO)(PMe_3)Cl_3$ (2b). To a solution of 497 mg (1.19 mmol) of **1b** in 20 mL of CH_2Cl_2 was added

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dropwise at −78 °C (dry ice/acetone bath) a solution of 328 mg (1.19 mmol) of freshly prepared $PhICl_2$ in 20 mL of CH_2Cl_2. The reaction mixture was then allowed to warm to room temperature and stirred for 2 h. The resulting orange suspension was worked up as described above for **2a** to afford complex **2b** as an orange solid: yield 540 mg (99%); mp 180 °C (dec). Anal. Calcd for $C_9H_{14}Cl_3OPW$ (459.39): C, 23.53; H, 3.07; Cl, 23.15. Found: C, 23.77; H, 3.00; Cl, 23.08. EI-MS (70 eV), *m*/*e*: 430 $[M - CO]^+$, 354 $[M - CO - PMe_3]^+$, 319 $[M - CO - PMe_3 - Cl]^+$, 318 $[M - CO - PMe_3 - HCl]^+$, 282 $[M - CO - PMe_3 - 2\ HCl]^+$. IR ($CH_2Cl_2$): ν(CO) 2011 (s) cm^{-1}. IR (acetone): ν(CO) 2005 (s) cm^{-1}. ^1H NMR (300 MHz, acetone-d_6, 293 K): δ 1.85 (d, $^2J(PH) = 10.5$ Hz, 9H, PMe_3), 5.77 (d, $^3J(PH) = 3.5$ Hz, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6, 293 K): δ 16.5 (d, $^1J(PC) = 35.6$ Hz, PMe_3), 97.1 (C_5H_5) (the resonance of the carbonyl-carbon nucleus was not observed due to the low solubility of **2b** in acetone-d_6). $^{31}P\{^1H\}$ NMR (121.5 MHz, acetone-d_6, 293 K): δ −23.0 ($^1J(WP) = 221.2$ Hz).

3. Preparation of Cp*Mo(CO)(PMe$_3$)Cl$_3$ (2c). To a solution of 740 mg (1.86 mmol) of **1c** in 20 mL of CH_2Cl_2 was added slowly at −78 °C (dry ice/acetone bath) a solution of 510 mg (1.86 mmol) of freshly prepared $PhICl_2$ in 10 mL of CH_2Cl_2. The reaction mixture was then allowed to warm to room temperature and stirred for 1 h. Evolution of gas was observed, and the color of the solution changed from red to brown. After 1 h an IR spectrum of the solution was recorded in the region of 2200−1800 cm^{-1}, showing complete conversion of **1c** to **2c**. The solution was then evaporated to dryness, and the residue was washed twice with 15 mL of a diethyl ether/pentane mixture (1/1) to afford **2c** as a brown solid: yield: 790 mg (96%); mp 179 °C (dec). Anal. Calcd for $C_{14}H_{24}Cl_3MoOP$ (441.62): C, 38.08; H, 5.48; Cl, 24.08; P, 7.01. Found: C, 37.08; H, 5.35; Cl, 24.29; P, 6.78. EI-MS (70 eV), *m*/*e*: 338 $[M - CO - PMe_3]^+$, 302 $[M - CO - PMe_3 - HCl]^+$, 266 $[M - CO - PMe_3 - 2HCl]^+$. IR ($CH_2Cl_2$): ν(CO) 1956 (s) cm^{-1}. IR (THF): ν(CO) 1949 (s) cm^{-1}. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 1.83 (s, 15H, C_5Me_5), 1.84 (d, $^2J(PH) = 11.9$ Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 293 K): δ 11.0 (C_5Me_5), 15.8 (d, $^1J(PC) = 33.8$ Hz, PMe_3), 112.3 (C_5Me_5), 233.6 (d, $^2J(PC) = 45.7$ Hz, CO). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 12.2.

4. Preparation of Cp*W(CO)(PMe$_3$)Cl$_3$ (2d) from 1d and PhICl$_2$. Following the procedure described above for **2c**, complex **2d** was obtained as a dark brown solid after treatment of 3.19 g (6.56 mmol) of **1d** with 1.80 g (6.55 mmol) of freshly prepared $PhICl_2$: yield 3.26 g (94%); mp 188 °C (dec). Anal. Calcd for $C_{14}H_{24}Cl_3OPW$ (529.53): C, 31.76; H, 4.57; Cl, 20.09. Found: C, 31.42; H, 4.83; Cl, 20.17. EI-MS (70 eV), *m*/*e*: 500 $[M - CO]^+$, 424 $[M - CO - PMe_3]^+$, 389 $[M - CO - PMe_3 - Cl]^+$, 388 $[M - CO - PMe_3 - HCl]^+$, 352 $[M - CO - PMe_3 - 2HCl]^+$. IR ($CH_2Cl_2$): ν(CO) 1936 (s) cm^{-1}. IR (THF): ν(CO) 1930 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 1.85 (d, $^2J(PH) = 11.3$ Hz, 9H, PMe_3), 1.98 (s, 15H, C_5Me_5). ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 1.82 (d, $^2J(PH) = 11.3$ Hz, 9H, PMe_3), 1.96 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 293 K): δ 11.2 (C_5Me_5), 15.1 (d, $^1J(PC) = 35.9$ Hz, PMe_3), 108.2 (C_5Me_5), 228.2 (d, $^2J(PC) = 35.9$ Hz, CO). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 293 K): δ 2.1 ($^1J(WP) = 121.0$ Hz). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 1.3 ($^1J(WP) = 121.0$ Hz).

5. Preparation of Cp*Mo(PMe$_3$)Cl$_4$ (3c) from 1c and PhICl$_2$. A solution of 2.89 g (7.25 mmol) of **1c** in 80 mL of CH_2Cl_2 was cooled to −78 °C (dry ice/acetone bath) and treated with a solution of 3.00 g (10.91 mmol) of freshly prepared $PhICl_2$ in 60 mL of CH_2Cl_2. The mixture was then allowed to warm to room temperature and stirred for 4 h. Evolution of gas was observed, and the color of the solution changed from red to purple. After 4 h an IR spectrum of the solution was recorded in the region of 2200−1800 cm^{-1}, confirming the absence of any CO-containing compounds. The solution was then evaporated to dryness, and the residue was washed four times with 30 mL of a diethyl ether/pentane mixture (1/1) and dried in vacuo. Purple solid: yield 3.04 g (93%). Anal. Calcd for $C_{13}H_{24}Cl_4MoP$ (449.06): C, 34.77; H, 5.39; Cl, 31.58. Found: C, 33.94; H, 5.10; Cl, 31.86.

6. Preparation of Cp*W(PMe$_3$)Cl$_4$ (3d) from 2d and PhICl$_2$. A solution of 3.21 g (6.06 mmol) of **2d** in 60 mL of CH_2Cl_2 was cooled to −78 °C (dry ice/acetone bath). To this solution was added through a stainless steel cannula a solution of 838 mg (3.05 mmol) of freshly prepared $PhICl_2$ in 40 mL of CH_2Cl_2, and the mixture was allowed to warm to room temperature. Evolution of gas was observed, and the color of the solution changed from brown to green. Completion of the reaction after stirring for 3 h at ambient temperature was confirmed by IR spectroscopy (disappearance of the ν(CO) absorption of **2d** at 1936 cm^{-1}). The solution was then evaporated to dryness, and the residue was washed three times with 30 mL of a diethyl ether/pentane mixture (1/2) and dried in vacuo to afford complex **3d** as a green solid: yield 3.17 g (97%). Anal. Calcd for $C_{13}H_{24}Cl_4PW$ (536.97): C, 29.08; H, 4.51; Cl, 26.41. Found: C, 28.36; H, 4.29; Cl, 25.96.

7. Preparation of Cp*W(CO)$_2$Cl$_3$ (5d) from Cp*W(CO)$_3$Cl (4d) and PhICl$_2$. A solution of 890 mg (2.03 mmol) of Cp*W(CO)$_3$Cl (**4d**) in 30 mL of CH_2Cl_2 was cooled to −78 °C (dry ice/acetone bath). To this solution was added slowly through a stainless steel cannula a solution of 556 mg (2.03 mmol) of freshly prepared $PhICl_2$ in 10 mL of CH_2Cl_2. The reaction mixture was then allowed to warm to room temperature and stirred for 1 h. During this time evolution of gas was observed, the color of the solution changed from red to orange-yellow, and the major portion of the product precipitated. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorptions of **4d** at 2032, 1942, and 1930 cm^{-1} by those of **5d** at 2077 and 2024 cm^{-1}). The suspension was then concentrated in vacuo to a few milliliters, and diethyl ether was added to complete precipitation of **5d**. The supernatant solution was decanted off and the precipitate washed twice with 15 mL of diethyl ether and dried in vacuo. Orange-yellow solid: yield 950 mg (97%). Anal. Calcd for $C_{12}H_{15}Cl_3O_2W$ (481.46): C, 29.94; H, 3.14; Cl, 22.09. Found: C, 29.49; H, 3.09; Cl, 22.11. IR (CH_2Cl_2): ν(CO) 2077 (vs), 2024 (vs) cm^{-1}.

8. Preparation of Cp*W(CO)(PMe$_3$)Cl$_3$ (2d) from 5d and PMe$_3$. A suspension of 560 mg (1.16 mmol) of **5d** in 20 mL of CH_2Cl_2 was treated at ambient temperature with 0.24 mL (2.36 mmol) of PMe_3. IR monitoring of the reaction revealed a gradual decrease in intensity of the two ν(CO) absorptions of **5d** at 2077 and 2024 cm^{-1} and a simultaneous increase in intensity of the ν(CO) absorption of **2d** at 1936 cm^{-1}. After 20 h the insoluble orange-yellow solid (**5d**) had disappeared, the color of the solution had changed to brown, and the starting material had been completely consumed (IR detection). The solution was then concentrated in vacuo, and a few milliliters of diethyl ether was added. The brown solution was filtered from some insoluble material through a filter cannula, and the filtrate was evaporated to dryness to afford **2d** as a brown, microcrystalline solid: yield 570 mg (93%). The IR ^1H and ^{31}P NMR spectra of the product were identical to those of an analytically pure sample of **2d** obtained upon oxidation of **1d** with $PhICl_2$ as described above.

9. Preparation of *trans*-CpMo(CO)(PMe$_3$)$_2$Cl (6a). A 185 mg (0.50 mmol) sample of **2a** was suspended in 20 mL of THF, the suspension was cooled to −60 °C (dry ice/acetone bath) and treated with 0.057 mL (0.56 mmol) of PMe_3 and 0.41 mL (2.48 mmol Na) of Na/Hg (6.05 mmol Na/mL). The mixture was warmed to −10 °C and stirred for 23 h at this temperature. The gray precipitate consisting of NaCl and Na/Hg was then allowed to settle, and an IR spectrum of the supernatant red-brown solution was recorded in the region 2200−1800 cm^{--1}, which confirmed the selective formation of **6a**. The solution was filtered with a filter cannula, and the filtrate was evaporated to dryness. The residue was separated from some insoluble material by extraction with 50 mL of a diethyl ether/

pentane mixture (1/1) and filtration of the solution. The filtrate was evaporated to dryness to give **6a** as an orange-red solid: yield 150 mg (80%); mp 152 °C. $C_{12}H_{23}ClMoOP_2$ (376.65). EI-MS (70 eV), *m/e*: 378 $[M]^+$, 350 $[M - CO]^+$, 274 $[M - CO - PMe_3]^+$, 198 $[M - CO - 2PMe_3]^+$. IR (CH_2Cl_2): ν(CO) 1778 (s) cm^{-1}. IR (THF): ν(CO) 1788 (s) cm^{-1}. IR (pentane): ν(CO) 1803 (s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 1.30 (m, $N = {}^2J(PH) + {}^4J(PH) = 9.1$ Hz, 18H, 2 P*Me$_3$*), 4.67 (t, $^3J(PH) = 1.1$ Hz, 5H, C$_5$*H$_5$*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 293 K): δ 17.2 (m, $N = {}^1J(PC) + {}^3J(PC) = 28.1$ Hz, P*Me$_3$*), 90.8 (*C$_5$*H$_5$), 265.0 (t, $^2J(PC) = 35.3$ Hz, *C*O). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 293 K): δ 21.3.

10. Preparation of *trans*-CpW(CO)(PMe$_3$)$_2$Cl (6b). A suspension of 1.62 g (3.53 mmol) of **2b** in 50 mL of THF was treated at −30 °C with 0.40 mL (3.93 mmol) of PMe$_3$ and 1.77 mL (10.71 mmol Na) of Na/Hg (6.05 mmol Na/mL). Afterward the mixture was allowed to warm to room temperature and stirred for 16 h. The resulting suspension was worked up in an analogous way to that followed for **6a**, to give complex **6b** as a light red solid: yield 1.27 g (78%); mp 176 °C. Anal. Calcd for $C_{12}H_{23}ClOP_2W$ (464.56): C, 31.03; H, 4.99. Found: C, 31.40; H, 5.28. EI-MS (70 eV), *m/e*: 464 $[M]^+$, 436 $[M - CO]^+$, 388 $[M - PMe_3]^+$, 360 $[M - CO - PMe_3]^+$, 284 $[M - CO - 2PMe_3]^+$. IR (CH_2Cl_2): ν(CO) 1759 (s) cm^{-1}. IR (THF): ν(CO) 1774 (s) cm^{-1}. IR (pentane): ν(CO) 1792 (s) cm^{-1}.^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 1.56 (m, $N = {}^2J(PH) + {}^4J(PH) = 9.3$ Hz, 18H, 2P*Me$_3$*), 5.12 (t, $^3J(PH) = 0.9$ Hz, 5H, C$_5$*H$_5$*). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 293 K): δ 17.4 (m, $N = {}^1J(PC) + {}^3J(PC) = 32.4$ Hz, P*Me$_3$*), 89.4 (*C$_5$*H$_5$), 258.3 (t, $^2J(PC) = 25.0$ Hz, *C*O). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 293 K): δ −10.5 ($^1J(WP) = 264.3$ Hz).

11. Preparation of *trans*-Cp*Mo(CO)(PMe$_3$)$_2$Cl (6c). A solution of 390 mg (0.88 mmol) of **2c** in 25 mL of THF was treated at −30 °C with 0.10 mL (0.97 mmol) of PMe$_3$ and 0.58 mL (3.51 mmol Na) of Na/Hg (6.05 mmol Na/mL) and then was allowed to warm to room temperature and stirred for 7 h. The resulting suspension was worked up in an analogous way to that followed for **6a**, to give complex **6c** as an orange-red solid: yield 370 mg (94%); mp 212 °C. Anal. Calcd for $C_{17}H_{33}ClMoOP_2$ (446.79): C, 45.70; H, 7.44. Found: C, 44.49; H, 7.56. EI-MS (70 eV), *m/e*: 448 $[M]^+$, 420 $[M - CO]^+$, 372 $[M - PMe_3]^+$, 344 $[M - CO - PMe_3]^+$, 268 $[M - CO - 2PMe_3]^+$, 266 $[M - CO - 2PMe_3 - H_2]^+$. IR ($CH_2Cl_2$): ν(CO) 1776 (s), 1768 (sh) cm^{-1}. IR (THF): ν(CO) 1780 (s) cm^{-1}. IR (pentane): ν(CO) 1794 (s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 1.28 (m, $N = {}^2J(PH) + {}^4J(PH) = 8.6$ Hz, 18H, 2P*Me$_3$*), 1.65 (s, 15H, C$_5$*Me$_5$*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 293 K): δ 11.7 (C$_5$*Me$_5$*), 16.6 (m, $N = {}^1J(PC) + {}^3J(PC) = 26.0$ Hz, P*Me$_3$*), 102.7 (*C$_5$*Me$_5$), 275.1 (t, $^2J(PC) = 33.9$ Hz, *C*O). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 293 K): δ 18.6.

12. Preparation of *trans*-Cp*W(CO)(PMe$_3$)$_2$Cl (6d). Following the procedure described above for **6a**, complex **6d** was isolated as a red solid after treatment of 730 mg (1.38 mmol) of **2d** with 0.16 mL (1.57 mmol) of PMe$_3$ and 0.46 mL (2.78 mmol Na) of Na/Hg (6.05 mmol Na/mL) in THF for 4 h at room temperature: yield 630 mg (85%); mp >230 °C. Anal. Calcd for $C_{17}H_{33}ClOP_2W$ (534.70): C, 38.19; H, 6.22; Cl, 6.63. Found: C, 37.30; H, 6.38; Cl, 5.81. EI-MS (70 eV), *m/e*: 534 $[M]^+$, 458 $[M - PMe_3]^+$, 430 $[M - CO - PMe_3]^+$, 428 $[M - CO - PMe_3 - H_2]^+$, 352 $[M - CO - 2PMe_3 - H_2]^+$. IR ($CH_2Cl_2$): ν(CO) 1766 (sh), 1752 (s) cm^{-1}. IR (THF): ν(CO) 1770 (s) cm^{-1}. IR (pentane): ν(CO) 1783 (s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 293 K): δ 1.37 (m, $N = {}^2J(PH) + {}^4J(PH) = 8.8$ Hz, 18H, 2P*Me$_3$*), 1.73 (s, 15H, C$_5$*Me$_5$*). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 293 K): δ 12.1 C$_5$*Me$_5$*), 16.9 (m, $N = {}^1J(PC) + {}^3J(PC) = 30.2$, P*Me$_3$*), 101.0 (*C$_5$*Me$_5$), 267.1 (t, $^2J(PC) = 22.5$ Hz, *C*O). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 293 K): δ −12.8 ($^1J(WP) = 289.9$ Hz).

13. Preparation of *trans*-CpMo(CO)(PMe$_3$)$_2$GeCl$_3$ (7a). A 140 mg (0.37 mmol) sample of **6a** and 93 mg (0.40 mmol) of GeCl$_2$(1,4-dioxane) were weighed in a Schlenk tube and dissolved at −78 °C (dry ice/acetone bath) in 20 mL of CH$_2$Cl$_2$. The suspension was allowed to warm to room temperature and stirred for 10 min. During this time the red solution brightened and turned to yellow. An IR spectrum was recorded in the region 2200−1800 cm^{-1} to confirm the complete consumption of **6a**. The slightly cloudy solution was then filtered, and the filtrate was concentrated to approximately 3 mL and treated with 20 mL of pentane to precipitate complex **7a**. The supernatant solution was rejected, and the precipitate was washed three times with 10 mL of a diethyl ether/pentane mixture (1/3) and dried in vacuo to give **7a** as yellow solid: yield 172 mg (89%); mp 175 °C (dec). Anal. Calcd for $C_{12}H_{23}Cl_3GeMoOP_2$ (520.15): C, 27.71; H, 4.46; Cl, 20.45. Found: C, 26.67; H, 4.66; Cl, 20.88. EI-MS (70 eV), *m/e*: 522 $[M]^+$, 487 $[M - Cl]^+$, 378 $[M - GeCl_2]^+$, 350 $[M - GeCl_2 - CO]^+$, 274 $[M - GeCl_2 - CO - PMe_3]^+$, 198 $[M - GeCl_2 - CO - 2PMe_3]^+$. IR ($CH_2Cl_2$): ν(CO) 1847 (s) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 1.72 (m, $N = {}^2J(PH) + {}^4J(PH) = 8.9$ Hz, 18H, 2 P*Me$_3$*), 5.00 (t, $^3J(PH) = 1.4$ Hz, 5H, C$_5$*H$_5$*). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 293 K): δ 22.4 (m, $N = {}^1J(PC) + {}^3J(PC) = 31.5$ Hz, P*Me$_3$*), 89.5 (*C$_5$*H$_5$), 249.0 (t, $^2J(PC) = 33.2$ Hz, *C*O). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 13.1.

14. Preparation of *trans*-CpW(CO)(PMe$_3$)$_2$GeCl$_3$ (7b). A solution of 462 mg (0.99 mmol) of **6b** in 20 mL of CH$_2$Cl$_2$ was treated at 0 °C with 232 mg (1.00 mmol) of GeCl$_2$(1,4-dioxane), then warmed to room temperature, and stirred for 30 min. The slightly cloudy solution was worked up in an analogous way to that followed for **7a** to afford complex **7b** as a yellow solid: yield 590 mg (98%); mp 215 °C (dec). Anal. Calcd for $C_{12}H_{23}Cl_3GeOP_2W$ (608.06): C, 23.70; H, 3.81; Cl, 17.49. Found: C, 23.59; H, 3.97; Cl, 17.68. EI-MS (70 eV), *m/e*: 608 $[M]^+$, 573 $[M - Cl]^+$, 464 $[M - GeCl_2]^+$, 436 $[M - GeCl_2 - CO]^+$, 388 $[M - GeCl_2 - PMe_3]^+$, 360 $[M - GeCl_2 - CO - PMe_3]^+$. IR ($CH_2Cl_2$): ν(CO) 1835 (s) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 1.83 (m, $N = {}^2J(PH) + {}^4J(PH) = 9.0$ Hz, 18H, 2P*Me$_3$*), 5.13 (t, $^3J(PH) = 1.3$ Hz, 5H, C$_5$*H$_5$*). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 293 K): δ 22.8 (m, $N = {}^1J(PC) + {}^3J(PC) = 36.8$ Hz, P*Me$_3$*), 87.5 (*C$_5$*H$_5$), 239.6 (t, $^2J(PC) = 25.4$ Hz, *C*O). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 293 K): δ −24.9 ($^1J(WP) = 217.0$ Hz).

15. Preparation of *trans*-Cp*Mo(CO)(PMe$_3$)$_2$GeCl$_3$ (7c). A solution of 308 mg (0.69 mmol) of **6c** in 20 mL of CH$_2$Cl$_2$ was treated at 0 °C with 160 mg (0.69 mmol) of GeCl$_2$(1,4-dioxane), then warmed to room temperature, and stirred for 1 h. The resulting slightly cloudy solution was worked up in analogous way to that followed for **7a** to afford complex **7c** as a dark yellow solid: yield 354 mg (87%); mp 165 °C (dec). Anal. Calcd for $C_{17}H_{33}Cl_3GeMoOP_2$ (590.28): C, 34.59; H, 5.63; Cl, 18.02; P, 10.49. Found: C, 34.06; H, 5.63; Cl, 18.42; P, 11.04. EI-MS (70 eV), *m/e*: 448 $[M - GeCl_2]^+$, 372 $[M - GeCl_2 - PMe_3]^+$, 344 $[M - GeCl_2 - PMe_3 - CO]^+$, 266 $[M - GeCl_2 - CO - 2PMe_3 - H_2]^+$. IR ($CH_2Cl_2$): ν(CO) 1831 (s) cm^{-1}. IR (Et$_2$O): ν(CO) 1833 (s) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 1.59 (m, $N = {}^2J(PH) + {}^4J(PH) = 8.4$ Hz, 18H, 2 P*Me$_3$*), 1.90 (s, 15H, C$_5$*Me$_5$*). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 293 K): δ 11.7 (C$_5$*Me$_5$*), 22.1 (m, $N = {}^1J(PC) + {}^3J(PC) = 29.5$, P*Me$_3$*), 102.8 (*C$_5$*Me$_5$), 260.1 (t, $^2J(PC) = 36.8$ Hz, *C*O). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 293 K): δ 8.1.

16. Preparation of *trans*-Cp*W(CO)(PMe$_3$)$_2$GeCl$_3$ (7d). Following the procedure described above for **7a**, complex **7d** was isolated as a dark-yellow solid after treatment of 424 mg (0.79 mmol) of **6d** with 183 mg (0.79 mmol) of GeCl$_2$(1,4-dioxane) in CH$_2$Cl$_2$ for 1 h at room temperature: yield 494 mg (92%), mp 165 °C (dec). Anal. Calcd for $C_{17}H_{33}Cl_3GeOP_2W$ (678.19): C, 30.11; H, 4.90; Cl, 15.68. Found: C, 29.78; H, 5.24; Cl, 15.13. EI-MS (70 eV), *m/e*: 534 $[M - GeCl_2]^+$, 458 $[M - GeCl_2 - PMe_3]^+$, 430 $[M - GeCl_2 - PMe_3 - CO]^+$, 352 $[M - GeCl_2 - CO - 2PMe_3 - H_2]^+$. IR ($CH_2Cl_2$): ν(CO) 1820 (s) cm^{-1}. IR (Et$_2$O): ν(CO) 1823 (s) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 293 K): δ 1.71 (m, $N = {}^2J(PH) + {}^4J(PH) = 8.7$ Hz, 18H, 2 P*Me$_3$*), 2.00 (s, 15H, C$_5$*Me$_5$*). ^{13}C{^{1}H} NMR (75.5 MHz, CD$_2$-

Table 5. Summary of Crystallographic Data for the Complexes 2b-1, 2b-2, 6d, and 7b

	2b-1	**2b-2**	**6d**	**7b**
empirical formula	$C_{11}H_{17}Cl_3NOPW$	$C_{11}H_{18}Cl_3O_{1.5}PW$	$C_{17}H_{33}ClOP_2W$	$C_{12}H_{23}Cl_3GeOP_2W$
M_t	500.43	495.42	534.67	608.05
crystal color	orange	orange	dark red	orange
crystal size (mm)	0.18 × 0.15 × 0.08	0.38 × 0.17 × 0.04	1.14 × 0.80 × 0.46	0.38 × 0.38 × 0.15
temp (K)	160(2)	293(2)	293(2)	200(2)
cryst syst	triclinic	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
a (Å)	6.8057(10)	6.864(2)	8.9250(9)	15.135(2)
b (Å)	9.1413(15)	12.892(5)	14.599(2)	17.016(3)
c (Å)	14.300(3)	18.664(3)	16.4380(10)	17.503(2)
α (deg)	105.81(2)	75.51(2)		86.18(2)
β (deg)	94.75(2)	79.28(2)		64.975(14)
γ (deg)	109.615(15)	86.91(3)		76.94(2)
V (Å^3)	791.3(2)	1571.0(8)	2141.7(4)	3976.7(11)
Z	2	4	4	8
ρ_{calcd} (g/cm^3)	2.100	2.095	1.658	2.031
$\mu_{Mo\ K\alpha}$ (mm^{-1})	7.610	7.665	5.457	7.564
$F(000)$	476	944	1056	2320
2θ min/max (deg)	5.0/52.5	2.3/50.0	3.8/50.0	4.4/52.4
hkl range	−8, 8/−11, 10/0,17	−7, 8/−14, 15/ −16, 22	−6, 10/−17, 17/0, 19	−16, 18/−20, 21/0, 21
tot. no. of data	5655	6686	3770	28802
no. of unique data ($I > 2\sigma I$)	2905 [R(int) = 0.0961]	5518 [R(int) = 0.0403]	2159 [R(int) = 0.0279]	14725 [R(int) = 0.1605]
abs corr.		ψ-scan	ψ-scan	
min, max		0.274, 0.423	0.193, 0.961	
min/max density (e Å^{-3})	−1.561/1.436	−1.536/1.680	−0.504/0.793	−2.940/1.733
no. of params refined	164	316	201	740
absolute structure param χ^a			0.01(2)	
extinction coeff^b			0.0063	
$R_1{}^c$ ($I > 2\sigma I$)	0.0250	0.0367	0.0223	0.0437
$wR_2{}^d$ ($I > 2\sigma I$)	0.0565	0.0848	0.0581	0.1157
GOF^e	1.015	1.053	1.085	0.782

[a] Flack, H. D. *Acta Crystallogr. A* **1983**, *39*, 876. [b] $F_c{}^* = kF_c[1 + 0.001F_c{}^2\lambda^3/\sin(2\theta)]^{-1/4}$. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$. [e] GOF $= S = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/(n - p)\}^{1/2}$.

Cl_2, 293 K): δ 12.1 (C_5*Me*$_5$), 22.9 (m, $N = {}^1J(PC) + {}^3J(PC) = 34.4$, P*Me*$_3$), 101.3 (*C*$_5Me_5$), 250.5 (t, $^2J(PC) = 28.7$ Hz, *C*O). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 293 K): δ −29.1 ($^1J(WP) = 247.3$ Hz).

17. Crystal Structure Determinations of 2b-1, 2b-2, 6d, and 7b. A summary of the crystal data, data collection, and refinement for **2b-1, 2b-2, 6d,** and **7b** is given in Table 5.Data collection for **2b-1** and **7b** was performed on a STOE IPDS area detector equipped with a low-temperature device and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Lattice parameters were refined from 2000 reflections after data collection. The crystal of **2b-1** was rotated in 1.6° steps to yield 113 exposures, and each of them was exposed for 6 min, whereas the crystal of **7b** was rotated in 1.2° steps to yield 150 exposures, which were each exposed for 2.7 min. Intensity data were integrated and converted into a SHELX *hkl*-file with the STOE IPDS software.[44] Data collection for **2b-2** and **6d** was performed on a STOE STADI4 four-circle diffractometer at ambient temperature using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Lattice parameters were determined from the setting angles of 36 reflections in the range of $27° \leq 2\theta \leq 32°$ for **2b-2** and of 26 reflections in the range of $32° \leq 2\theta \leq 36°$ for **6d**. Data were collected in the $\omega-2\theta$ scan mode. After every 2 h three standard reflections were monitored, and the crystal was reoriented in case of deviation between 0.1° and 0.15°. Intensity data were corrected for Lorentz and polarization effects. The input files for the SHELX programs were prepared with the program UTILITY.[45] Structure solution was performed with Patterson methods (SHELXS-86)[46] and subsequent difference Fourier synthesis (SHELXL-93).[47] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model with d(C−H) = 0.96 Å and $U_{iso} = 0.08$ Å^2. Geometrical calculations were performed with PLATON[48] and illustrations with ZORTEP.[49]

In the final stages of refinement, data for **6d** were corrected for secondary extinction effects. Complex **2b-2** crystallizes with two independent molecules in the asymmetric unit and complex **7b** with four independent molecules. A split atom model was successfully employed in the third independent molecule of complex **7b** for atoms Cl(7) and Cl(8) attached to atom Ge(3) leading to a ratio of 1/1. Atoms Cl(7), Cl(8), Cl(7A), and Cl(8A) could be refined anisotropically.

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Supporting Information Available: Further details of the crystal structure determination including tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and thermal parameters for **2b-1**, **2b-2**, **6d,** and **7b.** This material is available free of charge via the Internet at http://pubs.acs.org.

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