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Aryl Oligogermanes as Ligands for Transition Metal Complexes

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Abstract: The ligand properties of a series of aryl oligogermanes R_3Ge-$GeAr_3$, **3-7** (Me_3Ge-$GePh_3$ (**3**), Me_3Ge-$Ge(pTol)_3$ (**4**), Ph_3Ge-$GePh_3$ (**5**), $(C_6F_5)_3Ge$-$GePh_3$ (**6**), Ph_3Ge-$GeMe_2GePh_3$ (**7**)), for the synthesis of transition metal carbonyl complexes such as R_3Ge-$GeAr_2(R'C_6H_4$-$\eta^6)M(CO)_3$ (M = Cr, **3a-7a**; M = Mo, **3b**; M = W, **3c**) were investigated. The complexes were obtained, using several different synthetic approaches, in moderate yields. The physicochemical properties of these newly synthesised complexes were investigated by IR, UV/vis, NMR spectroscopy, electrochemistry and DFT calculations. The molecular structures of **3c**, **4a** and **5a** were studied by single crystal X-ray diffraction analysis. A comparative analysis of the donor- and acceptor properties of aryl oligogermanes, as ligands for transition metal carbonyl complexes, is reported.

Introduction

Recently, derivatives of Group 14 bearing element – element bonds (E(IV) = Si, Ge, Sn, Pb) have attracted significant attention due to their unique physical properties (conductivity, light absorbance, luminescence *etc.*). These unique properties are due to the presence of a σ-conjugation between the E atoms within the framework of the molecule (Scheme 1).[1] The number of E atoms in the chain, their nature, the electronic properties of their substituents and the conformation of the molecule significantly affect on the σ-conjugation. The ability to finely tune the electronic properties of these new catenated derivatives

would open the door to the preparation materials displaying new physical properties. Biding transition metals (M) to catenated Group 14 derivatives should impact on the σ-delocalisation and therefore, also on the physical properties of the complex.[2] In addition, several possible modes of bonding between the metal and the Group 14 ligand could be expected, each of them having a different impact on the σ-conjugation. A few compounds, containing a covalent bond between the E atom and a transition metal, have been reported in the literature (leading references for Si derivatives with M = rare earth metals;[3] Ti, Zr, Hf;[4] Ta;[5] Cr, Mo, W;[6] Fe;[7] Pd;[8] Pt;[9] Au;[10] for special interest to Ge derivatives for Hf, Zr;[4] W, Cr;[11] Pt;[9b, 12] Pd;[13] Au;[14] for Sn derivatives with Ti;[4, 15] Mo, W;[16] Fe[17] *etc.*). In the present study, we are reporting the impact of the different types of bonding, including when the metallic fragment is connected to an organic group (η^n-coordination), on the physical properties of the new compounds. Only a few studies on η^5-C_5R_5 (Cp) catenated Ge derivatives[18] and $Cr[\eta^6$-$C_6H_5GeMe_2]_2$[19] have been reported to date while molecular oligostannanes ($Cp^{[28]}$ derivatives). Polysilanes[29] and oligosilane[20] complexes have been extensively studied (complexed with η^4-butadiene,[21] η^5-half-sandwich,[6c, 22] ferrocenyl[23] or other Cp ligands,[24] (η^6-aryl)$M(CO)_3$,[25] sandwich Cr complexes,[26] η^7-derivatives[27]). Only molecular oligogermanium complexes bearing transition metals remain to be studied to complete the series. To the best of our knowledge, only 6 articles describing complexes of arylmonogermanes with $M(CO)_3$ have been reported up to this day.[19, 30]

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        Supporting information for this article (Crystallographic data, NMR
        and UV/vis spectra of the compounds obtained, and data of DFT
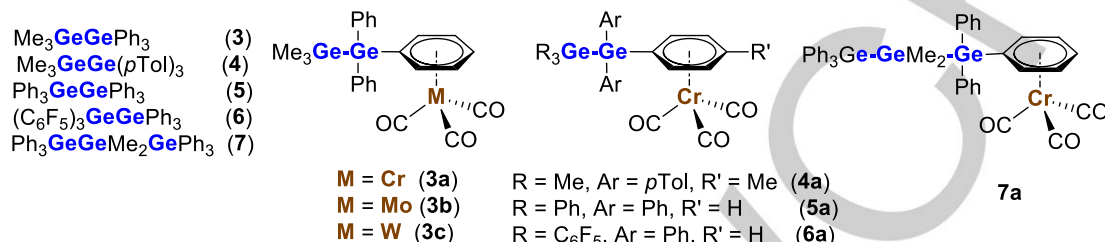   calculations) is given via a link at the end of the document.
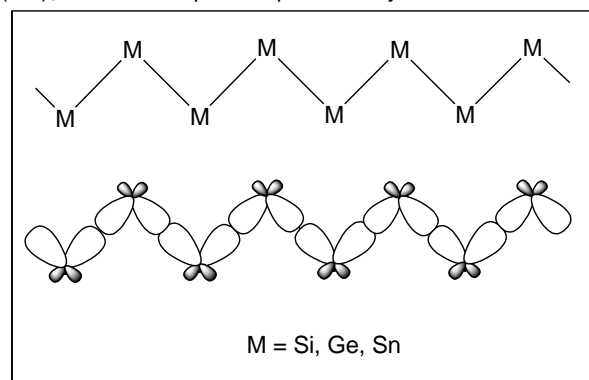
**Scheme 1.** Schematic representation of σ-conjugation between Group 14 E atoms.

Arene chromium tricarbonyl complexes are valuable compounds that are used in organic synthesis and catalysis,[31] the preparation of materials with non-linear properties,[32] *etc.* In general, a $Cr(CO)_3$ group, coordinated to an arene, acts as a strong electron withdrawing substituent which reduces the electron density of the aryl group. A priori, $M(CO)_3$ would exhibit similar electron-withdrawing properties with a magnitude

comparable to that of a nitro group.[33] When the arene bears a functional group Y, such as in (η6-C6H5Y)Cr(CO)3, the extent of the charge transfer to the metal strongly depends on the electron donating or electron withdrawing properties of the group Y. This has been shown by infrared spectroscopy and is supported by theoretical calculations. In this work, we are reporting the synthesis of the aryloligogermane carbonyl complexes **3a-c**, **4a-7a** (Scheme 2) as well as an investigation about their structure – physical properties relationships. Oligogermanes Me3Ge-GePh3 (**3**), Me3Ge-Ge(pTol)3 (**4**), Ph3Ge-GePh3 (**5**), (C6F5)3Ge-GePh3 (**6**), and [Ph3Ge]2GeMe2 (**7**) were used as simple and easily available model-compounds, differing in their number of Ge atoms and in the steric and electronic properties of the substituents on their Ge centers.

Me3**GeGe**Ph3   (**3**)
Me3**GeGe**(pTol)3   (**4**)
Ph3**GeGe**Ph3   (**5**)
(C6F5)3**GeGe**Ph3   (**6**)
Ph3**GeGe**Me2**Ge**Ph3 (**7**)

M = **Cr** (**3a**)
M = **Mo** (**3b**)
M = **W** (**3c**)

R = Me, Ar = pTol, R' = Me (**4a**)
R = Ph, Ar = Ph, R' = H   (**5a**)
R = C6F5, Ar = Ph, R' = H   (**6a**)

Scheme 2. Structures of the compounds under investigation.
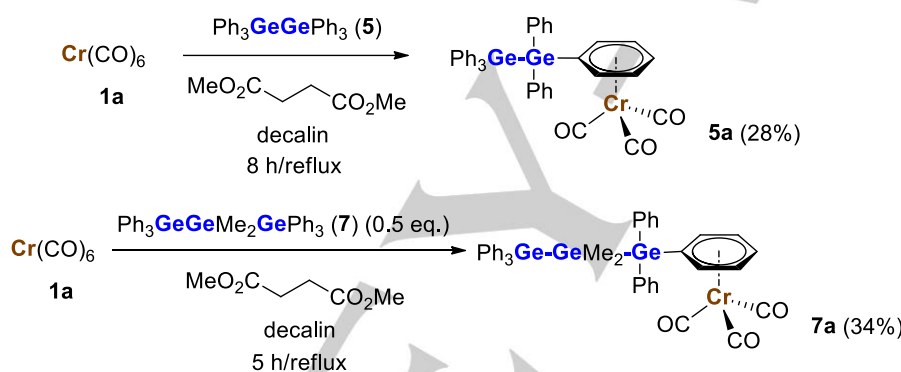
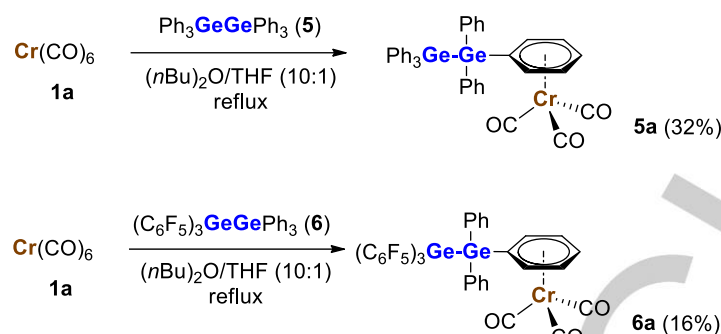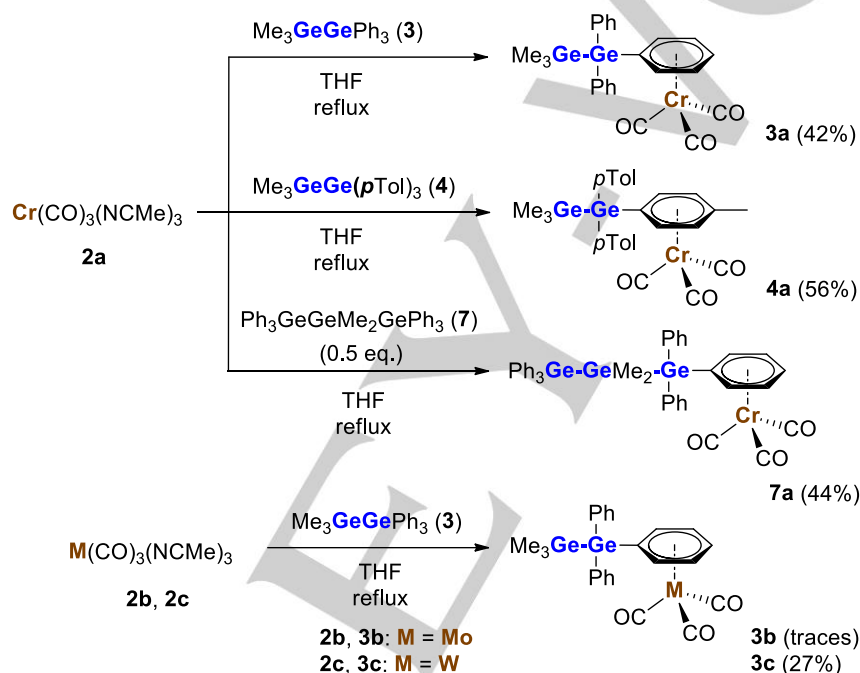**Scheme 3.** Synthesis of **5a** and **7a** using Cr(CO)6 (**1a**) in decalin.

Results and Discussion

Synthesis. The synthesis of the new organometallic complexes required the use of different metallic precursors, Cr(CO)6 (**1a**) and M(CO)3(NCMe)3 (M = Cr (**2a**), M = Mo (**2b**), M = W (**2c**)).

As a first attempt to prepare the new compounds, the thermolysis of Cr(CO)6, in a solvent with a high boiling point such as decalin,[34] in the presence of the corresponding arene (aryloligogermane **5** and **7**) and dimethyl succinate as an agent promoting the abstraction of the CO the chromium center,[35] was investigated (Scheme 3).
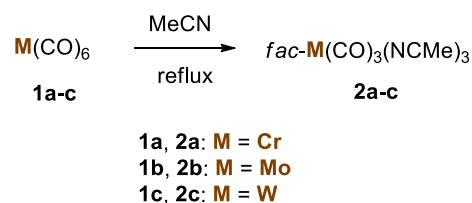
Unfortunately, a significant amount of unreacted starting material was recovered at the end of the reaction, even when the reaction time was extended to 12h and only a low conversion was achieved (29-33%) resulting in low yields in **5a** and **7a**. Using an excess of **1a** did not improve the yield either. The thermolysis approach has shown the have serious drawbacks. In addition to giving low yields in **5a** and **7a**, harsh reaction conditions have to be used to overcome the low reactivity of Cr(CO)6 and tedious chromatographic separations are often needed to get the pure compounds.

In order to improve the yields and simplify the isolation of the desired compounds, a new set of conditions was investigated. Cr(CO)6 (**1a**) was reacted with Ph3GeGePh3 (**5**) and (C6F5)3GeGePh3 (**6**) in a refluxing mixture of (nBu)2O/THF (10:1)[34, 36] (Scheme 4). Similar conditions have been reported before for the synthesis of Group 14 derivatives using DME[37] or dyglime.[38] When the unsymmetrical donor-acceptor digermane **6** was used, the product **6a** was exclusively formed, where the Cr(CO)3 coordinates to the electron-rich aromatic ring. The isolation of pure **5a** and **6a** were easily performed by column chromatography (for details, see Experimental part). Unfortunately, once again, the target compounds were isolated in low yields. When benzene was used as the eluent for the chromatographic separation of **6a**, a transmetallation was observed leading to the formation of (η6-C6H6)Cr(CO)3; therefore, a mixture of ether and petroleum ether should be used instead of benzene for the isolation of the pure complexes. The yield of the desired complex also depends on the structure of the oligogermane used in the complexation reaction. The use of an oligogermane bearing at least one electron withdrawing group generally results in even lower yields.

Cr(CO)$_6$ $\xrightarrow[\text{reflux}]{\substack{\text{Ph}_3\textbf{GeGe}\text{Ph}_3 \ (\textbf{5})\\(n\text{Bu})_2\text{O/THF (10:1)}}}$ Ph$_3$**Ge-Ge** [Cr(CO)$_3$ complex] **5a** (32%)

1a

Cr(CO)$_6$ $\xrightarrow[\text{reflux}]{\substack{(\text{C}_6\text{F}_5)_3\textbf{GeGe}\text{Ph}_3 \ (\textbf{6})\\(n\text{Bu})_2\text{O/THF (10:1)}}}$ (C$_6$F$_5$)$_3$**Ge-Ge** [Cr(CO)$_3$ complex] **6a** (16%)

1a

Scheme 4. Synthesis of **5a** and **6a** using Cr(CO)$_6$ (**1a**) in (nBu)$_2$O.

Cr(CO)$_3$(NCMe)$_3$ **2a**

$\xrightarrow[\substack{\text{THF}\\\text{reflux}}]{\text{Me}_3\textbf{GeGe}\text{Ph}_3 \ (\textbf{3})}$ Me$_3$**Ge-Ge** [Cr(CO)$_3$ complex] **3a** (42%)

$\xrightarrow[\substack{\text{THF}\\\text{reflux}}]{\text{Me}_3\textbf{GeGe}(p\text{Tol})_3 \ (\textbf{4})}$ Me$_3$**Ge-Ge** [Cr(CO)$_3$ complex] **4a** (56%)

$\xrightarrow[\substack{\text{THF}\\\text{reflux}}]{\substack{\text{Ph}_3\text{GeGeMe}_2\text{GePh}_3 \ (\textbf{7})\\(0.5 \text{ eq.})}}$ Ph$_3$**Ge-Ge**Me$_2$**-Ge** [Cr(CO)$_3$ complex] **7a** (44%)

M(CO)$_3$(NCMe)$_3$ **2b**, **2c**

$\xrightarrow[\substack{\text{THF}\\\text{reflux}}]{\text{Me}_3\textbf{GeGe}\text{Ph}_3 \ (\textbf{3})}$ Me$_3$**Ge-Ge** [M(CO)$_3$ complex]

2b, **3b**: **M = Mo**   **3b** (traces)
2c, **3c**: **M = W**   **3c** (27%)

Scheme 6. Synthesis of complexes **3a-c**, **4a** and **7a** using M(CO)$_3$(NCMe)$_3$ (**2a-c**).

When W(CO)$_6$ was subjected to the same reaction conditions, in the presence of Me$_3$GeGePh$_3$ (**3**), the desired complex Me$_3$GeGePh$_2$(η^6-Ph)Cr(CO)$_3$ (**3c**) was isolated only in a trace amount; the major compound being the initial ligand **3**. A possible reason would be the decomposition of the W complex under high-temperature conditions. Therefore, in order to perform the reaction at lower temperatures, **2a-c**, M(CO)$_3$(NCMe)$_3$M(CO)$_6$, in which three carbonyl groups have been substituted by more labile MeCN were used instead of **1a-c** (M = Cr, Mo, W).[30b, 35b, 39]

The compounds **2a-c** are easy to prepare (Scheme 5) and can either be isolated in high yields or used without isolation.[40]

M(CO)$_6$ **1a-c** $\xrightarrow[\text{reflux}]{\text{MeCN}}$ fac-M(CO)$_3$(NCMe)$_3$ **2a-c**

1a, **2a**: **M = Cr**
1b, **2b**: **M = Mo**
1c, **2c**: **M = W**

Scheme 5. Synthesis of **2a-c**.

As expected, using M(CO)$_3$(NCMe)$_3$ as more reactive starting materials, allowed to prepare the desired complexes, with improved yields, by refluxing **2a-c,** in THF for 1 h, in the

presence of aryl oligogermanes (Scheme 6). For these reactions, the conversion of the starting material proved to be much higher (54-68 %). Increasing the reaction time (up to 3 h) resulted only in a decrease of the yields, most probably, again, due to the thermal instability of Cr complexes. No conversion was observed when the reaction was carried out either in MeCN (under reflux for 12 h) or in THF at room temperature (for up to 3 days), indicating that acetonitrile is a strong donating ligand than the arenes (see below).

Using an excess of **2a** (up to 2 eq.) resulted in the sole formation of mono-Cr complexes (in the case of **7a**) without any traces of di-Cr complexes. In the case of Mo, the complex **3b** has shown to be unstable and to decompose quickly during the various attempts to isolate it. Mo derivatives are known for their low stability.[41] When other derivatives, such as $M(CO)_3(Py)_3$[35b] were used as starting materials, under the same conditions, in the presence of $Ph_3GeGeMe_3$ (**3**), only traces of the desired compounds were observed.

When comparing the three methods used for the synthesis of **3a-c** and **4a-7a**, namely thermolysis of $M(CO)_6$ in decalin/dimethyl succinate, reflux of $M(CO)_6$ in (nBu)$_2$O/THF and reflux of $M(CO)_3(NCMe)_3$ in THF. Among these three options, the latest one seems to be the most successful, leading to the formation of the desired complexes in higher yields.

All studied the complexes, **3a**, **3c**, **4a-7a**, are yellow powders, which are stable under an inert atmosphere, but get slowly oxidised (and become greenish) upon exposure to air for several months. In stark contrast, solutions of these compounds have shown to be much more air-sensitive. All of the newly synthesized derivatives are soluble in aromatic hydrocarbons (benzene, toluene), acetone, ethers (THF, diethyl ether) but are insoluble in n-hexane and decompose very quickly in chloroform (or CDCl$_3$). Among the possible decomposition pathways, the rupture of the Cr-Ar bond is the most probable, especially under harsh conditions. The rupture of the Ge-Ge bond was also observed when NMR was used to monitor the stability of the solutions of **6a** in C_6D_6. After 3 days, the formation of **6**, $(C_6F_5)_3GeGePh_3$, and $(C_6F_5)_3GeH$ was observed.

All compounds were characterized by elemental analysis, IR and NMR spectroscopy, mass-spectrometry[42] and in the case of **3c**, **4a** and **5a** by single crystal X-ray diffraction (XRD) analysis. The deviations in elemental analysis data are explained by the sensitivity of the compounds and by the partial combustion due to the presence of transition metals.

Solid state structure. A search in the CSD (Cambridge Structural Database) (June 2018) for structures of aryloligogermanes coordinated with $M(CO)_3$ returned no result. Therefore, the structural investigation of **3c**, **4a** and **5a** by XRD reported in this work (Figures 1-3; Supporting Information, Table S1) represents a significant contribution to the chemistry of Group 14 derivatives. Moreover, only one structure of monogermanium compound, $N(CH_2CH_2O)_3Ge(\eta^6$-Ph)Cr(CO)$_3$,[30d] has ever been studied by XRD to date.

For all of the structures studied in this work, the metal-ligand core shown to adopt the well-known "piano stool" geometry.[43]
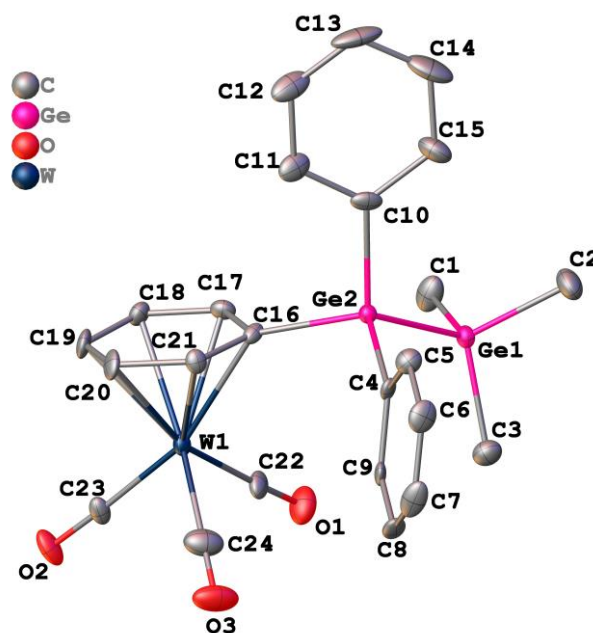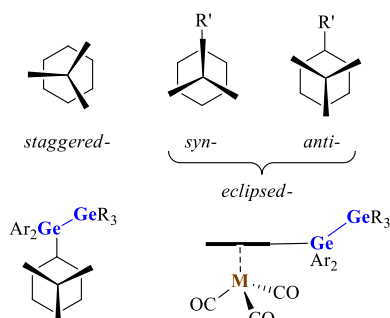

Figure 1. Molecular structure of $Me_3GeGePh_2(\eta^6$-Ph)W(CO)$_3$ (**3c**). Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge(1)-Ge(2) 2.4266(9), W-C$_{av}$(arene) 2.341(6), W-C$_{av}$(centroid) 1.867(6), W-CO$_{av}$ 1.967(7), Ge(1)-C$_{av}$ 1.949(6), Ge(2)-C$_{av}$ 1.957(6), Ge(2)-C(16) 1.972(6), C-O$_{av}$ 1.155(8); C-W-C$_{av}$(CO) 87.4 (3), C-Ge(1)-Ge(2)$_{av}$ 110.8(2), C-Ge(1)-C$_{av}$ 108.1(3), C-Ge(2)-Ge(1)$_{av}$ 112.64(19), C-Ge(2)-C$_{av}$ 106.2(2).

In **3c**, the W(CO)$_3$ group in relation to the coordinated C_6H_5 ring adopts an *anti-eclipsed*-conformation (Scheme 6; torsion angles C$_{Ge}$-C$_{centroid}$-W-C$_O$ are 55.4(7) and 71.1(7)°; 60° for ideal *anti*- and 0° for ideal *syn*-). Due to the electronic interactions, a *syn-eclipsed*-conformation is typical for monosubstituted bearing an electron donating group R' (η^6-R'C$_6H_5$)M(CO)$_3$,. An electron-donating R' increases the electron density in *ortho*- and *para*-positions of the η^6-Ar ring, where the octahedral set of Cr orbitals are overlapping.[44] Usually, an *anti-eclipsed* conformation is due to steric reasons, but in our case, additional orbital interactions between the *d* orbitals of the Cr and the σ-orbital of Ge-Ar and Ge-Ge bonds may be observed (Scheme 7). The maximal overlapping (torsion angle M-C$_{ArGe}$-Ge-Ge 180° is the most profitable) is observed in **5a** (see below); in **3c** a torsion angle of 55.2(7)° is found, indicating that they are electronic interactions between all parts of the molecule. The conformation along the Ge-Ge bond is staggered (torsion angles C-Ge-Ge-C$_{av}$ are 78.27/41.71°).

In **4a**, the conformation of the Cr(CO)$_3$ group in relation to the coordinated C_6H_5 ring is close to be *anti-eclipsed* (torsions C$_{ArGe}$-C$_{centroid}$-Cr-C$_O$ are 52.9(8) and 68.7(8)°). The torsion angle of Cr-C$_{ArGe}$-Ge-Ge is 46.5(8)°, indicating weak interactions between Cr and Ge2. DFT calculations for **4a** (see below) showed that in the gas phase this torsion angle is 155°, indicating an effect of the crystal packing on the conformation. The conformation along the Ge-Ge bond is staggered (torsion angles C-Ge-Ge-C$_{av}$ are 70.5(8)/49.5(8)°).

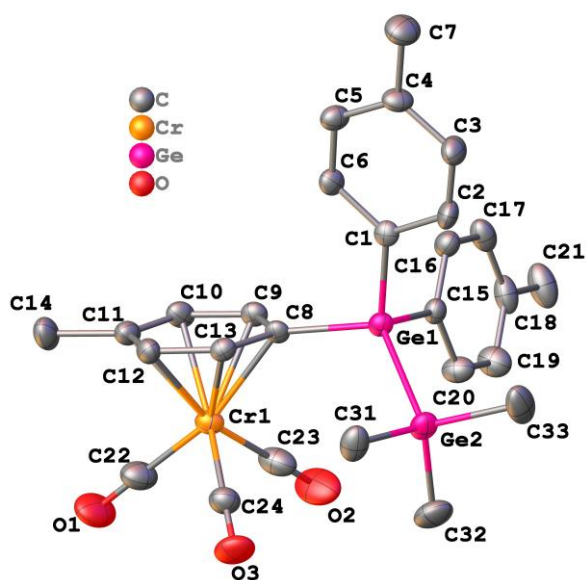Scheme 7. Conformations of substituents in relation to η⁶-benzene.

Figure 2. Molecular structure of compound Me₃GeGe(pTol)₂(η⁶-pTol)Cr(CO)₃ (4a). Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge(1)-Ge(2) 2.4284(6), Ge(1)-C$_{av}$ 1.952(5), Ge(1)-C(8) 1.970(4), Ge(2)-C$_{av}$ 1.932(7), Cr(1)-CO$_{av}$ 1.828(9), Cr(1)-C$_{av}$(arene) 2.212(5), Cr-C$_{av}$(centroid) 1.715(5), C-O$_{av}$ 1.163(8); C-Cr-C$_{av}$(CO) 88.2(3), C-Ge(1)-Ge(2)$_{av}$ 112.66(13), C-Ge(1)-C$_{av}$ 106.1(2), C-Ge(2)-Ge(1)$_{av}$ 110.49(19), C-Ge(2)-C$_{av}$ 108.5(3).

The structure of the complex 5a differs from the ones of 3c and 4a. The conformation of the Cr(CO)₃ group in relation to the coordinated C₆H₅ ring is distorted and *staggered* (torsion angles C$_{ArGe}$-C$_{centroid}$-Cr-C$_O$ are 27.6(9) and 95.6(9)°), indicating electron interactions between Cr(CO)₃ and Ge2. The torsion angles Cr-C$_{ArGe}$-Ge-Ge is 159.7(9)°, showing a very high interaction between Cr, η⁶-Ph and Ge2. This significant observed difference, in 5a, may be explained by the presence of Ph groups at both Ge atoms, what is known to affect the electronic structure of the molecule strongly.[45], [46] The conformation along the Ge-Ge

bond is *staggered* (torsion angles C-Ge-Ge-C$_{av}$ are 59.6(9)/60.4(9)°).

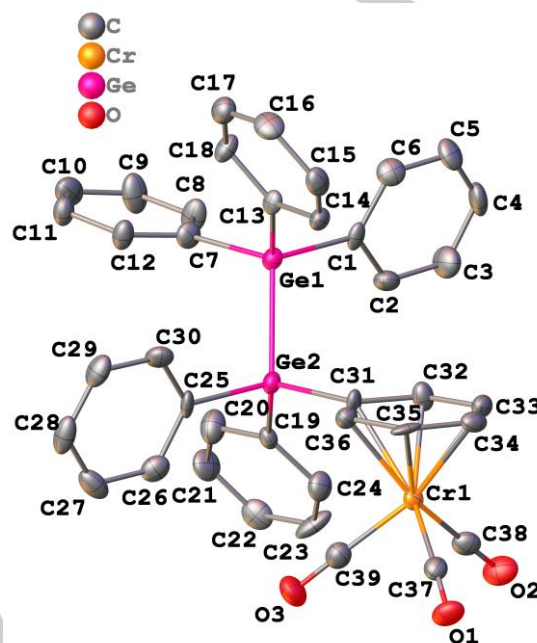Figure 3. Molecular structure of compound Ph₃GeGePh₂(η⁶-Ph)Cr(CO)₃ (5a). Displacement ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ge(1)-Ge(2) 2.4316(13), Ge(1)-C$_{av}$ 1.955(9), Ge(2)-C$_{av}$ 1.953(10), Ge(2)-C(31) 1.974(9), Cr(1)-C$_{av}$(arene) 2.209(11), Cr-C$_{av}$(centroid) 1.698(11), Cr-CO$_{av}$ 1.842(11), C-O$_{av}$ 1.157(13); C-Cr-C$_{av}$(CO) 88.1(5), C-Ge(1)-Ge(2)$_{av}$ 110.0(3), C-Ge(1)-C$_{av}$ 108.9(4), C-Ge(2)-Ge(1)$_{av}$ 109.0(3), C-Ge(2)-C$_{av}$ 109.9(4).

In all of the structures studied, 3c, 4a, and 5a, the η⁶-coordinated arene ring is almost planar (the maximal deviations from the mean square plane are 0.022(9) Å in 3c (C(19)-*para* to Ge toward to W), 0.008(9) Å in 4a (C(8)-*ipso* and C(9)-*ortho* to Ge out of Cr) and 0.012(9) Å in 5a (C(35)-*meta* to Ge out of Cr).[43] In every case, the nearest Ge atom is slightly moved out of the plane of the η⁶-Ar in the direction above M(CO)₃ (0.228(9) Å for 3c, 0.131(9) Å for 4a, 0.101(9) Å for 5a; the angles of deviation α are 6.4(7), 3.6(8), 3.0(9)°, respectively) due to the electronic effects (Scheme 7), indicating a π-donor effect of the oligogermyl substituent. In 4a, the methyl group of the *p*-tolyl ring is almost in the plane of aryl group (the deviation is only 0.001(9) Å).

The presence of the M(CO)₃ increases the nonequivalence of the aryl C-C bonds (approaching a hexadienyl character) and leads tp an elongation of C1-C2 bond (Scheme 8), whereas the electron density is partially transferred from the Ge-Ge bond (HOMO-3, HOMO-4, HOMO-5; Figs. S26-S28, ESI) to the η⁶-arene ring (LUMO+3, LUMO+4, LUMO+5; Figs. S32-S34, ESI). This was observed for each of the new complexes studied (Scheme 9), indicating that the presence of a M(CO)₃ moiety

lowers the bond order of the aromatic ring due to its acceptor properties.

Furthermore, a deviation from the ideal sp^2 hybridization for the arene carbon atoms bonded to Ge is observed.

Table 1. Comparison structural parameters of complexes **3c**, **4a**, **5a** with parent oligogermanes **3**, **4** and **5**.

Compound [a]	d(Ge-Ge)	d(Ge-C)	d(Ge$_M$-C)	C-Ge-Ge$_M$	C-Ge-C	C-Ge$_M$-Ge	C-Ge$_M$-C
Me$_3$GeGePh$_3$ (**3**) [47]	2.418(1)	1.943(4)	1.957(2)	110.2(1)	108.7(1)	110.3(1)	108.6(1)
3c	2.4266(9)	1.949(6)	1.972(6)	110.8(2)	108.1(3)	112.64(19)	106.2(2)
Me$_3$GeGe(pTol)$_3$ (**4**) [48]	2.4292(7)	1.936(7)	1.948(4)	115.6(2)	107.2(4)	110.90(12)	107.97(17)
4a	2.4284(6)	1.932(7)	1.970(4)	110.49(19)	108.5(3)	112.66(13)	106.1(2)
Ph$_3$GeGePh$_3$ (**5**) [49]	2.437	1.959	1.959	110.80	108.10	110.80	108.10
5a	2.4316(13)	1.955(9)	1.974(9)	110.0(3)	108.9(4)	109.0(3)	109.9(4)

[a] Bond lengths (Å) and bond angles (deg); Ge$_M$ is a nearest to M(CO)$_3$ germanium atom; average values are used
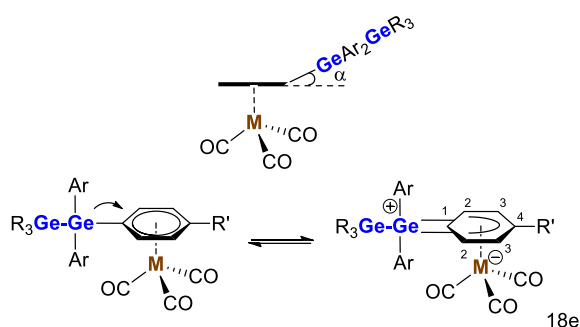
Scheme 8. Donor effects of oligogermyl substituent.
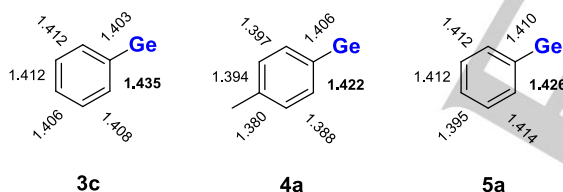
Scheme 9. Values of d(C-C) bond lengths in η^6-arene for **3c**, **4a** and **5a**.

The Ge-Ge bond is *cisoid*- in relation to the M(CO)$_3$ group in **3c** (the value of the torsion angle for Ge-Ge-C(16)$_{Ar}$-W is 55.2(7)°) and **4a** (torsion Ge-Ge-C(8)$_{Ar}$-Cr is 46.5(8)°), whereas in **5a** this same bond is *transoid*- (torsion Ge-Ge-C(31)$_{Ar}$-Cr is 159.6(9)°). These data, along with the conformation of M(CO)$_3$ along the Ar group, indicate that there is a stronger electron interaction between the octahedrally directed metal's orbitals and the η^6-arene in **5a**. The values of the torsion angles for Ge-Ge-C$_{Ar}$-C$_{Ar}$ and Ge-Ge-C$_{Ar}$-M (-39.2(7)/55.2(7)° for **3c**; 46.0(8)/-46.5(8)° for **4a**; -67.1(9)/-159.6(9)° for **5a**) indicate the presence of a σ-π-conjugation between the Ge-Ge bond and the η^6-Ar fragments (90° for an ideal conjugation).

In all of the structures **3c**, **4a** and **5a** the values of d(C-O) are very similar (1.155(8) *vs*. 1.163(8) *vs*. 1.157(13) Å), showing acceptor properties across the different oligogermanes and metals. The values of d(Cr-C$_O$) in **4a** and **5a** are almost identical

(1.828(9) *vs*. 1.842(11) Å). Variation of the substituents on the Ge atom or of the nature of M resulted only in small changes of the main structural parameters, i.e. Ge-Ge bond length (2.4266(9) *vs*. 2.4284(6) *vs*. 2.4316(13) Å in **3c**, **4a**, **5a**, respectively) and Ge-C bond length (for example, Ge-C$_{ArM}$ 1.972(6) *vs*. 1.970(6) *vs*. 1.974(9) Å). The length of d(Ge-C$_{ArM}$) is longer than the other Ge-C bonds; this could be due to steric reasons (introduction of a more voluminous M(CO)$_3$) and electronic effects similar to what has been earlier observed for donor-acceptor oligogermanes.[46, 50] In general, the geometry at each of Ge atom may be described as a slightly distorted tetrahedral.

A comparison between the structural parameters of complexes **3c**, **4a**, **5a** and the ones of the parent oligogermanes **3**,[47] **4**[48] and **5**,[49] respectively (Table 1), shows minimal differences, indicating a strong mutual influence of the Ge2, aryl and M(CO)$_3$ fragments in the molecule, where the acceptor properties of M(CO)$_3$ fragments are counterbalanced by a Ge2 donation.

Structure in solution. The NMR spectra of complexes **3a-3c** and **4a-7a** were recorded in C$_6$D$_6$ or acetone-d6. Due to the weaker π-acceptor properties of the η^6-coordinated arene ligand in comparison with CO, a quenching of the ring current is observed in such compounds. The electron density is transferred from arene to the M(CO)$_3$. This phenomenon is reflected in the NMR spectra by upfield shifts of the coordinated aryl group signals in comparison with the parent oligogermanes **3-7**. In ^{1}H NMR (C$_6$D$_6$) the signals of the η^6-coordinated Ar appeared between δ 4.0-5.3 ppm (an upfield shift of ca. 2 ppm), and the signals of the uncoordinated Ar were shifted toward downfield by ca. 0.2 ppm in comparison with the free oligogermane (for details, see Experimental Part and Supporting Information, Figs. S1-S16). A comparison with the parent (η^6-C$_6$H$_6$)Cr(CO)$_3$ (*vs*. δ 4.31 ppm)[51] showed that for oligogermanes **3a-7a** the proton signals are shifted toward lower fields. Furthermore, the signals for each position of the coordinated Ar group (*ortho*-, *para*- and *meta*-) appeared as well resolved multiplets (doublets, triplets *etc*., $^3J_{H-H}$ = 6.6 Hz, $^4J_{H-H}$ = 1.0 Hz). The weakest upfield shifts were observed for Mo and the largest ones for W (**3b** *vs*. **3a** *vs*. **3c**).

The ^{13}C NMR spectra of Cr compounds have shown a single signal for *C*O (δ 232.1-234.1 ppm), indicating the rapid (on the

NMR time scale) rotation along the M-Ar$_{centroid}$ axis resulting in the equivalence of the 3 carbonyls. The ^{13}C NMR spectra are characterized by the presence of 4 signals typical for coordinated carbon arene at δ 110.6-90.8 ppm (upfield shift of ca. 35 ppm in comparison with non-coordinated Ar); *ipso-*,

Table 2. Data of the UV/vis spectra according to experiment and DFT Calculations for the compounds **4**, **4'**, **4''**, **4'''** and **4a**.

compound	λ_{exp}, nm [a]	λ_{calc}, nm [b]	transition
Me$_3$GeGe(pTol)$_3$ (**4**) [c]	232 (2.3)	229 (0.282)	HOMO→LUMO+2
(η^6-pTol)Cr(CO)$_3$ (**4'**)	**220 (1.74)**	-	-
	253 (0.76)	**286 (0.2228)**	HOMO→LUMO+1, HOMO-1→LUMO
		321 (0.0017)	HOMO-2→LUMO+1
	317 (0.95) [d]	**327 (0.0030)**	HOMO-2→LUMO
		343 (0.0010)	HOMO-1→LUMO+1
(η^6-Me$_3$Ger)Cr(CO)$_3$ (**4''**)	-	**288 (0.2091)**	HOMO→LUMO+1, HOMO-1→LUMO
		322 (0.0022)	HOMO-2→LUMO+1
		327 (0.0019)	HOMO→LUMO+1, HOMO-2→LUMO
MeGe(pTol)$_2$(η^6-pTol)Cr(CO)$_3$ (**4'''**)	-	**295 (0.1044)**	HOMO→LUMO+1
		318 (0.0037)	HOMO-2→LUMO+2
		323 (0.0032)	HOMO-1→LUMO+2
		333 (0.0028)	HOMO-1→LUMO+1
		337 (0.0027)	HOMO-2→LUMO+1
		350 (0.0025)	HOMO→LUMO+2
		382 (0.0025)	HOMO-1→LUMO
		391 (0.0071)	HOMO→LUMO
Me$_3$GeGe(pTol)$_2$(η^6-pTol)Cr(CO)$_3$ (**4a**)	233 (4.55)	-	-
		279 (0.0132)	HOMO-3→LUMO
	267 (0.80)	**298 (0.1452)**	HOMO-1→LUMO+1
		326 (0.0029)	HOMO-2→LUMO+1
	321 (0.87)	**328 (0.0156)**	HOMO-1→LUMO+2
		336 (0.0092)	HOMO-2→LUMO+1
		357 (0.0016)	HOMO→LUMO+1
		383 (0.0024)	HOMO-1→LUMO
		394 (0.0107)	HOMO→LUMO

[a] Absorptivity ε (10^4 M^{-1} cm^{-1}) in parentheses; data in CH$_2$Cl$_2$. [b] Oscillator strength in parentheses. [c] Data from [48]. [d] Data from [52].

ortho-meta- and *para-*carbon signals are easily distinguished. In general these signals are shifted toward lower fields in comparison with the parent C$_6$H$_6$Cr(CO)$_3$ (*vs.* δ 92.36 ppm).[51]

DFT calculations. Theoretical investigation has been performed for the model compounds Me$_3$GeGe(pTol)$_2$(η^6-pTol)Cr(CO)$_3$ (**4a**), (η^6-TolH)Cr(CO)$_3$ (**4'**), Me$_3$Ge(η^6-pTol)Cr(CO)$_3$ (**4''**), MeGe(pTol)$_2$(η^6-pTol)Cr(CO)$_3$ (**4'''**) and Me$_3$GeGe(pTol)$_3$ (**4**) (Supporting Information, Figs. S17-S62, Tables S2-S4); the results obtained are typical for all series of compounds **3a-7a**.

According to the calculations using B3LYP/6-311+G(2d,p) in THF, **4a** has three bands, active in IR for the carbonyl groups, 1960 and 1884/1855 cm^{-1}. This correlates well with the experimental results (1961, 1887 cm^{-1}, see below), confirming the validity of the model used. In the gas phase, using 6-31G(d), a different set of values (2107, 2056/2052 cm^{-1}) was obtained, showing the high dependence of these values on the solvent used. These calculations have also shown that the presence of a Ge2 fragment increases the donor properties of the aryl group (*vs.* 2117, 2066/2060 cm^{-1} for (η^6-TolH)Cr(CO)$^{-1}$ (**4'**)).

For **4a**, due to the presence of the metal, an electron acceptor, the HOMO is mainly localised on the Cr(CO)$_3$ fragment (bonding Cr-CO), whereas the HOMO-1, HOMO-2 are mainly localised on the TolCr(CO)$_3$. The lower energy HOMO-3 orbital is bonding and localised on the Ge-Ge fragment; the other bonding orbitals, HOMO-4, HOMO-5, HOMO-6, HOMO-7 are all located on the non-coordinated Tol rings. Furthermore, the LUMO as well as the LUMO+1, are π-antibonding orbitals are localised on the non-coordinated Tol rings. The LUMO+2 is characterised by a contribution to the antibonding orbital on TolCr(CO)$_3$. The higher energy orbital LUMO+3 is mainly

localised on the (Tol)Cr(CO)$_3$ fragment. All of this indicates a full conjugation between the different parts of the molecule and a distribution of the electron density over the whole molecule. This situation differs significantly from what is observed for the parent aryloligogermanes, where the HOMO is mainly localised on the Ge-Ge bond and the LUMO on Ar substituents,[45], [46] as it was confirmed for **4**. It means that the electron density is transferred from Ge2 to ArCr(CO)$_3$ through an intramolecular conjugation.

Calculations of the UV/vis spectra were performed for **4**, **4'**, **4''**, **4'''** and **4a** (Table 2).

The UV/vis spectra of (η^6-C$_6$H$_6$)Cr(CO)$_3$[25c, 52-53] exhibits 3 bands, corresponding respectively to a π-π* transition (~ 220 nm with ε~1-3x10^4 M^{-1} cm^{-1}), a M→ArH charge transfer (~250 nm with ε<10^4 M^{-1} cm^{-1}) and a M→π* CO charge transfer (~ 315 nm with ε~10^4 M^{-1} cm^{-1}).[38a, 53c]

The most hypsochromic bands of the UV/vis absorption spectrum (220 nm for **4'**; 233 nm for **4a**) correspond to an intraligand charge transfers (ILCT) for Ar, where the transition is occurring from a low HOMO (such as HOMO-4 and lower) to a higher LUMO (such as LUMO+5 and higher), which are located on the Ar groups. Due to DFT restrictions, these transitions have not been taken into account during the calculations.

The data obtained for **4a** show an orbital mixing and all bands are significantly bathochromically shifted in comparison with the model compounds. The following bands attributions could be made: 267 nm (metal-to-arene charge transfer, MACT, from Ge2 to Ar, and MACT from TolCr(CO)$_3$ to the antibonding orbital of Tol; in general from a lower HOMO to LUMO and near) and 321 nm (metal-to-carbonyl charge transfer, MCCT,[54] from TolCr(CO)$_3$ to the antibonding orbital of Cr(CO)$_3$; in general from a lower HOMO to higher LUMO orbitals).

UV/vis spectroscopy. UV/vis spectroscopy is an important method for the characterization of catenated Group 14 compounds and for the estimation of their HOMO-LUMO transitions gap. For the compounds **3a-7a**, one might expect a shift on the bands compared to the parent compounds. The introduction of aromatic groups within an oligogermane framework is known to lead to a bathochromic shift of the UV/vis absorbance bands due to the σ-π-conjugation. The effect of the insertion of transitional metal fragments remains less evident to predict.

The σ-σ* transition in the Ge-Ge bonds is usually observed around 230-250 nm for di- and trigermanes with a very high absorptivity ($ε$~2-5x10^4 M^{-1} cm^{-1}).

Table 3. UV/vis spectroscopy data for **3a-7a** and related compounds.

compound [a]	$λ$ (nm), σ→σ* [b]	$λ$ (nm), ILCT [b]	$λ$ (nm), MACT [b]	$λ$ (nm), MCCT [b]	reference
($η^6$-EtO$_2$CC$_6$H$_5$)Cr(CO)$_3$		223 (2.23)	255 (0.82)	323 (1.00)	[52]
($η^6$-C$_6$H$_6$)Cr(CO)$_3$		213 (3.00)	256 (0.75)	317 (1.06)	[52]
($η^6$-MeC$_6$H$_5$)Cr(CO)$_3$		220 (1.74)	253 (0.76)	317 (0.95)	[52]
($η^6$-Et$_3$SiC$_6$H$_5$)Cr(CO)$_3$		212 (2.17)	256 (0.71)	317 (1.03)	[52]
Me$_3$SiSiMe$_2$($η^6$-C$_6$H$_5$)Cr(CO)$_3$		231 (1.9)	256	318 (1.1)	[25c]
Me$_3$SiSiMe$_2$($η^6$-C$_6$H$_5$)Mo(CO)$_3$		232 (1.9)	286 (4.1)	326 (2.1)	[25c]
Me$_3$SiSiMe$_2$($η^6$-C$_6$H$_5$)W(CO)$_3$		232 (2.1)	278 (5.1)	321 (1.9)	[25c]
PhSiMe$_2$SiMe$_2$($η^6$-C$_6$H$_5$)Mo(CO)$_3$ [c]		213 (2.87)		327 (1.56)	[53d]
Me$_3$GeGePh$_3$ (**3**)	230				[55]
Me$_3$GeGePh$_2$($η^6$-C$_6$H$_5$)Cr(CO)$_3$ (**3a**)		232 (2.47)	263 (0.53)	320 (0.67)	this work
Me$_3$GeGePh$_2$($η^6$-C$_6$H$_5$)W(CO)$_3$ (**3c**)		233 (1.96)	291 (0.38)	322 (0.46)	this work
Me$_3$GeGe(pTol)$_3$ (**4**)	232 (2.3)	-	-	-	[48]
Me$_3$GeGePh$_2$($η^6$-C$_6$H$_5$)Cr(CO)$_3$ (**4a**)		233 (4.55)	267 (0.80)	321 (0.87)	this work
Ph$_3$GeGePh$_3$ (**5**)	241	-	-	-	[56]
Ph$_3$GeGePh$_2$($η^6$-C$_6$H$_5$)Cr(CO)$_3$ (**5a**)		238 (3.57)	267 (1.64) (sh)	322 (0.64)	this work
(C$_6$F$_5$)$_3$GeGePh$_3$ (**6**)	226 (3.70)	-	-	-	[46]
(C$_6$F$_5$)$_3$GeGePh$_2$($η^6$-C$_6$H$_5$)Cr(CO)$_3$ (**6a**)		234 (2.15)	261 (0.78)	322 (0.41)	this work
Ph$_3$GeGeMe$_2$GePh$_3$ (**7**) [d]	245 (3.02)	-	-	-	[57]
Ph$_3$GeGeMe$_2$GePh$_2$($η^6$-C$_6$H$_5$)Cr(CO)$_3$ (**7a**)		244 (3.60)	261 (2.10) (sh)	321 (0.38)	this work

[a] Performed in solution in CH$_2$Cl$_2$ unless otherwise stated. [b] $ε$ (10^4 M^{-1} cm^{-1}) in parentheses. [c] Solution in THF. [c] Solution in cyclohexane.

Table 4. IR spectroscopy data for arene chromium tricarbonyl complexes.

Compound	$ν_{CO}$, cm^{-1}	solvent	reference	Compound	$ν_{CO}$, cm^{-1}	solvent	reference
Cr(CO)$_6$	1987	hydrocarbons	[58]	Cr(CO)$_3$($η^6$-C$_6$H$_5$Cl)	1991, 1929, 1925	cyclohexane	[34]
fac-Cr(CO)$_3$(PF$_3$)$_3$	2062, 1998	not given	[59]	Cr(CO)$_3$($η^6$-C$_6$H$_5$NMe$_2$)	1969, 1894, 1888	cyclohexane	[34]
fac-Cr(CO)$_3$[(MeO)$_3$P]$_3$	1962, 1875	CS$_2$	[60]	Cr(CO)$_3$($η^6$-C$_6$H$_5$COOMe)	1990, 1927	cyclohexane	[34]
	1966, 1888/1879	hexadecane	[61]	Cr(CO)$_3$($η^6$-C$_6$H$_5$COOMe)	1992, 1929	heptane	[54]
fac-Cr(CO)$_3$[Me$_3$P]$_3$	1939, 1849	not given	[62]	Cr(CO)$_3$($η^6$-PhSiMe$_3$)	1987, 1911	cyclohexane	[30a]
	1935, 1842	hexadecane	[61]	Cr(CO)$_3$($η^6$-PhGeMe$_3$)	1985, 1911	cyclohexane	[30a]
fac-Cr(CO)$_3$[NH$_3$]$_3$	1911, 1887	MeCN	[63]	Cr(CO)$_3$($η^6$-PhGeMe$_2$Ph)	1980, 1915/1870	nujol	[30c]
fac-Cr(CO)$_3$[NCMe]$_3$	1910, 1782	nujol	[40b]	Cr(CO)$_3$($η^6$-PhSnMe$_3$)	1984, 1908	cyclohexane	[30a]
fac-Cr(CO)$_3$[Py]$_3$	1910, 1778	not given	[64]	Cr(CO)$_3$($η^6$-PhSiMe$_2$SiMe$_3$)	1977, 1911	isooctane	[25c]
Cr(CO)$_3$($η^6$-C$_6$H$_5$CH$_3$)	1983, 1914	cyclohexane	[53b]	Cr(CO)$_3$($η^6$-PhSiMe$_2$SiMe$_2$C≡CPh)	1972, 1906	hexane	[25d]
	1962, 1893	nujol	[65]	Cr(CO)$_3$($η^6$-PhSiMe$_2$SiMe$_2$SiMe$_2$C≡CPh)	1975, 1909	hexane	[25d]
Cr(CO)$_3$($η^6$-C$_6$H$_5$OCH$_3$)	1980, 1908	cyclohexane	[34]	Cr(CO)$_3$($η^6$-PhGePh$_2$GeMe$_3$) (**3a**)	1974, 1897	nujol	this work
	1975/1945, 1903/1857	nujol	[66]	Cr(CO)$_3$($η^6$-pTol)Ge(pTol)$_2$GeMe$_3$) (**4a**)	1970, 1894	nujol	this work
Cr(CO)$_3$($η^6$-C$_6$H$_6$)	1982, 1915	cyclohexane	[34]	Cr(CO)$_3$($η^6$-PhGePh$_2$GePh$_3$) (**5a**)	1975, 1900	nujol	this work
	1978, 1910	nujol	[67]	Cr(CO)$_3$($η^6$-PhGePh$_2$Ge(C$_6$F$_5$)$_3$) (**6a**)	1976, 1901	nujol	this work
Cr(CO)$_3$($η^6$-C$_6$H$_5$F)	1990, 1929, 1926	cyclohexane	[34]	Cr(CO)$_3$($η^6$-PhGePh$_2$GeMe$_2$GePh$_3$) (**7a**)	1972, 1896	nujol	this work
fac-Mo(CO)$_3$(NCMe)$_3$	1915, 1783	nujol	[40b], [68]	Mo(CO)$_3$($η^6$-C$_6$H$_5$SiMe$_3$)	1983, 1913	petroleum ether	[53d]
fac-Mo(CO)$_3$(PMe$_3$)$_3$	1927, 1828	not given	[69]	Mo(CO)$_3$($η^6$-PhSiMe$_2$SiMe$_3$)	1981, 1912	isooctane	[25c]
Mo(CO)$_3$($η^6$-C$_6$H$_6$)	1987, 1916	heptane	[70]	Mo(CO)$_3$($η^6$-PhSiMe$_2$SiMe$_2$Ph)	1953, 1871	KBr	[53d]
	1985, 1912	nujol	[30e]	Mo(CO)$_3$($η^6$-C$_6$H$_5$GeMe$_3$)	1986/1958, 1909/1867	nujol	[30e]
Mo(CO)$_3$($η^6$-C$_6$H$_5$Me)	1980, 1910	nujol	[30e]	Mo(CO)$_3$($η^6$-C$_6$H$_5$SnMe$_3$)	1979/1951, 1909/1862	nujol	[30e]
Mo(CO)$_3$($η^6$-C$_6$H$_5$SiMe$_3$)	1986/1944, 1916/1874	nujol	[30e]	Mo(CO)$_3$($η^6$-PhGePh$_2$GeMe$_3$) (**3b**)	1978, 1900	nujol	this work
fac-W(CO)$_3$(NCMe)$_3$	1885, 1778	nujol	[40b]	W(CO)$_3$($η^6$-C$_6$H$_6$)	1968, 1886	CH$_2$Cl$_2$	[71]
fac-W(CO)$_3$[(MeO)$_3$P]$_3$	1973, 1894/1880	hexadecane	[61]	W(CO)$_3$($η^6$-MeC$_6$H$_5$)	1985, 1910	heptane	[72]
fac-W(CO)$_3$[Me$_3$P]$_3$	1940, 1845	hexadecane	[61]	W(CO)$_3$($η^6$-PhSiMe$_2$SiMe$_3$)	1980, 1909	isooctane	[25c]

W(CO)$_3$(η^6-PhGePh$_2$GeMe$_3$) **(3c)**	1980, 1904	nujol	this work

Due to solubility reasons, all UV/vis spectra in this work were recorded in CH$_2$Cl$_2$ which allows getting data at λ>230 nm. For oligogermane **3a-7a**, three major bands were observed. Other bands were presents but were either weak or overlapped with the main absorptions or with the solvent.

The comparison of UV/vis spectra of the compounds obtained within this study with the spectra of the initial oligogermanes shows that the introduction of a Cr(CO)$_3$ group has a strong influence on the absorption (Table 3; DFT section above). The bands corresponding to the σ→σ* transition in the parent oligogermanes did not appear due to a mixing of the MO. The two bands corresponding to an ILCT and a MACT in the parent chromium complexes are significantly bathochromically shifted in **3a-7a**; at the same time, the bands located at λ 320-322 nm (MCCT) are weakly redshifted. This indicates an increase of the donor properties of the η^6-Ar ligand (HOMO increase) due to the presence of a Ge2 group. The weak bands at 260-270 nm (MACT) appeared as a shoulder for Cr and as a distinct peak for the heavier Mo[25c] and W analogues.[73] This indicates an orbital mixing of the Ge-Ge σ-bond, π-aryl and π-CO, where Ge-Ge acts as a strong electronic donor. This band may be attributed to a transfer of electronic density from Ge-Ge to Ar.

For the complexes studied, the nature of the metal M (compare **3a** and **3c**) has shown to have little effect on the UV properties; only the MACT is significantly bathochromically shifted when replacing Cr by Mo or W.[74]

In contrast with the free molecular oligogermanes[75], [48] all complexes showed a total absence of luminescence both in solution and in solid form. The presence of transition metal fragments, M(CO)$_3$ (M = Cr, Mo, W), within the complexes, results in a quenching of the emissive properties. The electronic conjugation between Ge2, η^6-arene and M(CO)$_3$ occurs through direct interaction between a filled Cr d-orbitals and a σ* of Ge2 bond, metal-ring σ-π-delocalization (π-conjugation) and a back-donation from Cr d-orbitals to a π*-orbitals of the arene and a donation from Ar to Cr (due to the withdrawing effect of Cr(CO)$_3$). This resulted in a bathochromic shift of the metal absorption bands (at 220 nm) with a small increase in absorbance.

IR spectroscopy and donor properties. For each of the compounds studied, the IR spectrum contains the expected 2 bands in the carbonyl region: a non-degenerate symmetric A$_1$ (at higher wave numbers, v_{CO} ~2000-1970 cm^{-1}) and a doubly-degenerated asymmetric E (v_{CO} ~1950-1900 cm^{-1}) vibration (local C_{3v} symmetry)[76] (Table 4). Experimentally, there is no possible splitting of the E bands, which may be observed due to a small perturbation of the general symmetry of the arene substituent[77] (compared with DFT calculations, see above). The analysis of the IR data (mainly, A$_1$ band) could be used to assess the donor (a decrease of the IR value) or the acceptor (an increase of the IR value) properties of a ligand. A strong dependence of the IR bands on the solvent has also been observed. Broadened red shifted bands are observed in polar solvents due to Lewis acidic interaction between the solvent and the carbonyl ligands.[51]

Comparing the IR data for the compounds **3a-c**, **4a-7a** with the parent compound (η^6-C$_6$H$_6$)Cr(CO)$_3$ shows a decrease of the stretching absorption due to the electron donating properties of the catenated Group 14 fragment; its insertion within the Ar framework results in a small increase in the σ-donating properties and a decrease of the π-acceptor ability. Using data from the literature and the ones obtained through this work (Table 4) helps to place the aryloligogermanes among ligands that increase the π-back acceptor properties: [Py]$_3$ < [MeCN]$_3$ < [NH$_3$]$_3$ < [PMe$_3$]$_3$ < [P(OMe)$_3$]$_3$ < **ArGeAr$_2$GeR$_3$** < [CO]$_3$ < [PF$_3$]$_3$. The catenated germanium fragment may be considered as a donor group: NMe$_2$ < **Ar$_3$GeGeR$_2$GeR$_3$** < Ar$_3$GeGeR$_3$ ≤ Ar(SiR$_2$)$_2$SiR'$_3$ < OMe < ArSiR$_2$SiR'$_3$ < Ar$_2$GeMe$_2$ < Me < H < PhSnMe$_3$ < PhGeMe$_3$ < PhSiMe$_3$ < CO$_2$Me < F< Cl. Also, the Ge atoms have shown to exhibit greater electron donating abilities than Si. Increasing the length of the Ge chain increased the donor properties of the aryloligogermane. This suggests that Ge2 fragments have σ- as well as π-donating properties.

In comparison, it is known that the introduction of disilane fragment decreases the donor properties of the Ar ligand (Me$_3$Si(η^6-Ph)Mo(CO)$_3$ and PhSiMe$_2$SiMe$_2$(η^6-Ph)Mo(CO)$_3$ in KBr: 1946, 1865 $vs.$ 1953, 1871 cm^{-1}).[53d]

The comparison of the IR data between **3a-7a** (a weak increase of the donor properties in **6a**<**5a**<**3a**<**7a**<**4a**) shows a similar trend as the one observed in other spectroscopies. A similar trend could be observed when comparing the NMR chemical shifts of the ^{13}CO groups, where increased donor properties correspond to a deshielding.[78] Increasing the donor properties in η^6-coordinated Ar groups results to a decrease of the acceptor properties (**4a** in Tol $vs.$ Ph in **3a**); the same effect is observed when increasing the Ge chain length (Ge3 in **7a** $vs.$ Ge2 **3a**) and during the metal transition W<Mo<Cr. Varying the nature of the substituent on the Ge atom, neighbouring the η^6-coordinated Ar group also influence on the donor properties, but this effect remains relatively weak; therefore, the introduction of an electron withdrawing groups resulted only in a small decrease of the donor properties (**3a** $vs.$ **5a**; **5a** $vs.$ **6a**). Changing the nature of substituent on the central Ge atom has a more significant effect (when comparing PhGeMe$_3$ with Ph$_2$GeMe$_2$, Table 3). Therefore, in order to maximise the donor properties of the complex, one has to use long chained oligogermane, containing aryl groups bearing electron donating groups.

Electrochemistry. In this work, compound **4a** was studied as a typical example of the new complexes (Figure 4).

Compound **4a** displays a reversible one-electron oxidation of the organometallic centre Cr(0)→Cr(1+)[44, 79] that leads to the formation of a stable cation-radical (on the voltammetric experiment timescale);[80] the presence of the a Ge-Ge donor group offer an additional stabilization to the cationic oxidized product;[81] no further oxidation has been observed. This differs from the parent oligogermanes, where an irreversible Ge-Ge oxidation is observed usually. The oxidation of the chromium center into a cationic specie is pushing any possible further oxidation towards higher potentials, making a second oxidation

of the compound much more difficult. The oxidation of **4a** has the shape of a typical slow electron transfer and occurs at $E_{1/2}$ = 0.32 V *vs.* Fc/Fc+. The oxidation of the parent compound (η^6-MeC$_6$H$_5$)Cr(CO)$_3$ has been reported to occur at $E_{1/2}$ = 0.38 V *vs.* Fc/Fc+,[53b, 78-79] indicating that the presence of the Ge2 fragment in conjugation with (η^6-MeC$_6$H$_5$)Cr(CO)$_3$ framework resulted in a slight HOMO destabilization.[82] This decrease of the oxidation potential differs only slightly from what was observed for monogermanium fragments ($E_{1/2}$ 0.827 V *vs.* Ag/AgCl (0.377 V *vs.* Fc/Fc+) for Me$_2$Ge[(η^6-Ph)Cr(CO)$_3$]).[44] Based on the electrochemical data, the effect of a Ge2 fragment is comparable to the introduction of four methyl groups on the η^6-benzene ring (for (η^6-Me$_4$C$_6$H$_2$-1,2,4,5)Cr(CO)$_3$ $E_{1/2}$ = 0.33 V *vs.* Fc/Fc+). Furthermore, these data indicate that the HOMO orbitals of Cr(CO)$_3$ are located on of the whole molecule. The parent digermane **4** is oxidized, irreversibly, at a much higher potential E_{ox} 1.65 V *vs.* Ag/AgCl[48] (1.20 V *vs.* Fc/Fc+).
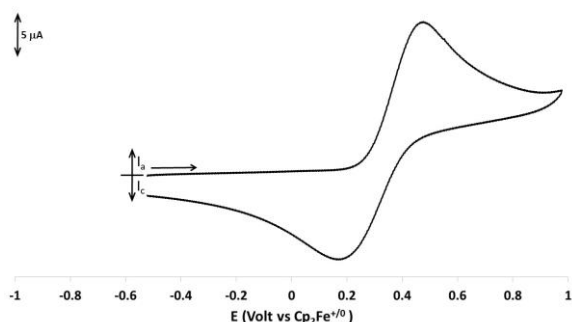

Figure 4. Electrochemical data for Me$_3$GeGe(*p*Tol)$_2$(η^6-*p*Tol)Cr(CO)$_3$ (**4a**) 1.00 mM in [TBA][PF$_6$] in CH$_2$Cl$_2$. Sweeping rate: 250 mV/s.

Conclusions

Several synthetic routes for the synthesis **3a-3c**, **4a-7a**, R$_3$Ge-GeAr$_2$(R'C$_6$H$_4$-η^6)M(CO)$_3$, were developed and studied. Among them, the reaction between aryloligogermane and M(CO)$_3$(NCMe)$_3$ was found to be the most efficient one. The analysis of the experimental and literature data for (η^6-arene)M(CO)$_3$ complexes, including derivatives of catenated Group 14 compounds, has shown that electronic interactions (π-, d- and σ-interactions) between all parts of the molecule (Ge-Ge, arene, M(CO)$_3$) are observed and affect the physical properties of the whole molecule even though it remains weak. Oligogermanyl substituents on the aromatic ring have shown to behave similarly to usual electron donating substituents. Therefore complexes such as R$_3$Ge-GeAr$_2$(R'C$_6$H$_4$-η^6)M(CO)$_3$ are typical donor-acceptor compounds. Introduction of oligogermanyl groups bathochromically shifted UV/vis absorption bands, due to a significant mixing of the atomic orbitals. The electrochemical oxidation of (η^6-ArGe$_2$R$_5$)M(CO)$_3$ is reversible since to the oxidation is happening on the metallic centre M rather than on the Ge-Ge bond.

Experimental Section

Experimental Details. All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. ^{1}H NMR (400.130 MHz), ^{13}C NMR (100.613 MHz) and ^{19}F (376.498 MHz) spectra were recorded with a Bruker 400 or Agilent 400MR spectrometers at 298 K. Chemical shifts are given in ppm relative to internal Me$_4$Si (^{1}H and ^{13}C NMR spectra) or external CFCl$_3$ (^{19}F NMR spectra). Mass spectra (EI-MS, 70 eV) were recorded on a quadrupole mass spectrometer FINNIGAN MAT INCOS 50 with direct insertion; all assignments were made with reference to the most abundant isotopes. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). Elemental analyses were carried out in the Microanalytical Laboratory of the Chemistry Department of the Moscow State University using HeraeusVarioElementar instrument. UV/visible spectra were obtained using two ray spectrophotometer Evolution 300 «Thermo Scientific» with cuvette of 1.00 cm long. The IR spectra were recorded by using a 200 Thermo Nicolet apparatus. Flash chromatography was performed using SiO$_2$ (0.015-0.040 mm).

Solvents were dried by standard methods and distilled prior to use. Tetrahydrofuran, diethyl ether were stored under solid KOH and then distilled over sodium/benzophenone. Toluene and *n*-hexane were refluxed and distilled over sodium. Dichloromethane and acetonitrile were distilled over CaH$_2$. C$_6$D$_6$ was distilled over sodium under argon.

Starting materials, Me$_3$GeGePh$_3$ (**3**),[56b] Me$_3$GeGe(*p*Tol)$_3$ (**4**),[48] Ph$_3$GeGePh$_3$ (**5**),[56b, 83] (C$_6$F$_5$)$_3$GeGePh$_3$ (**6**)[46] were synthesized according to the literature procedures. Metal carbonyls, M(CO)$_6$ (M = Cr (**1a**), M = Mo (**1b**), M = W (**1c**)), were sublimed under vacuum before using. Other reagents were used as supplied.

Attention! The work with metal carbonyl compounds should be performed under special conditions (under fume hood) due to volatility and formation of CO.

X-Ray crystallography. Crystal data for **3c**, **4a** and **5a** are given in Table S1. These data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. 1865890 (**3c**), 1865473 (**4a**), 1865889 (**5a**). They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry. Electrochemical measurements were carried out using an Autolab 302N potentiostat interfaced through Nova 2.0 software to a personal computer. Electrochemical measurements were performed in a glovebox under oxygen levels of less than 5 ppm using solvent that had been purified by passing through an alumina-based purification system. Diamond-polished glassy carbon electrodes of 3 mm diameter were employed for cyclic voltammetry (CV) scans. CV data were evaluated using standard diagnostic criteria for diffusion control and for chemical and electrochemical reversibility. The experimental reference electrode was a silver wire coated with anodically deposited silver chloride and separated from the working solution by a fine glass frit. The electrochemical potentials in this article are referenced to ferrocene/ferrocenium couple. The ferrocene potential was obtained by its addition to the analyte solution.

Data for initial compounds

Me$_3$GeGePh$_3$ (3). ^{1}H NMR (400.130 MHz, C$_6$D$_6$): δ = 7.55-7.50 (m, 6H), 7.16-7.10 (m, 9H) (aromatic protons), 0.36 (s, 9H, GeMe$_3$) ppm. ^{13}C NMR

(100.613 MHz, C$_6$D$_6$): δ = 138.49 (ipso-C$_6$H$_5$), 135.61 and 128.67 (o- and m-C$_6$H$_5$), 128.84 (p-C$_6$H$_5$), -0.88 (GeMe$_3$) ppm.

Ph$_3$GeGePh$_3$ (5). ^{1}H NMR (400.130 MHz, C$_6$D$_6$): δ = 7.60-7.56 (m, 12H), 7.09-7.01 (m, 18H) (aromatic protons) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): δ = 137.92 (ipso-C$_6$H$_5$), 135.98 and 128.74 (o- and m-C$_6$H$_5$), 129.19 (p-C$_6$H$_5$) ppm.

(C$_6$F$_5$)$_3$GeGePh$_3$ (6). ^{1}H NMR (400.130 MHz, C$_6$D$_6$): δ = 7.41-7.33 (m, 6H), 7.06-6.98 (m, 3H), 6.95-6.87 (m, 6H) (aromatic protons) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): δ = 135.08 and 128.73 (o- and m-C$_6$H$_5$), 133.21 (ipso-C$_6$H$_5$), 130.13 (p-C$_6$H$_5$) ppm. ^{19}F NMR (376.498 MHz, C$_6$D$_6$): δ = -124.52 – (-124.60) (2F), 149.03 – (-149.13) (1F), -159.68 – (-159.78) (2F) ppm.

Synthesis of Ph$_3$GeGeMe$_2$GePh$_3$ (7). At -78 the solution of nBuLi in hexane (2.5 M, 2.0 mL, 5.00 mmol) was added dropwise to the solution of Ph$_3$GeH (1.52 g, 5.00 mmol) in ether (50 mL). After stirring at the same temperature for 2 h the solution of Ph$_3$GeLi generated in situ was used further without isolation. Then Me$_2$GeCl$_2$ (0.43 g, 2.50 mol) was added to the solution of Ph$_3$GeLi obtained as described above, reaction mixture was slowly warmed to room temperature and stirred overnight. Then water (50 mL) was added, aqueous phase was extracted with ether (3x20 mL), combined organic phases were dried over MgSO$_4$, and then all volatile materials were removed under reduced pressure. After recrystallization from toluene/n-heptane mixture compound **7** (1.49 g, 84 %) was isolated as white crystals. ^{1}H NMR (400.130 MHz, C$_6$D$_6$): δ = 7.46-7.39 (m, 12H), 7.14-7.03 (m, 18H) (aromatic protons), 0.70 (s, 6H, GeMe$_2$) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): δ = 138.10 (ipso-C$_6$H$_5$), 135.85 and 128.61 (o- and m-C$_6$H$_5$), 128.84 (p-C$_6$H$_5$), -2.00 (GeMe$_2$) ppm. The ^{13}C NMR data in CDCl$_3$ corresponds to known from the literature.[84] HRMS (ESI), m/z [M-H]$^+$, calcd. 709.6045, found 709.6036.

Synthesis of the initial complexes

Synthesis of fac-(MeCN)$_3$M(CO)$_3$ (M = Cr (2a), Mo (2b), W (2c)). Synthesis was performed using literature procedure,[40] by refluxing corresponding M(CO)$_6$ in MeCN, what allows to obtain (MeCN)$_3$M(CO)$_3$ (72 % for **2a**; 67 % for **2b**; 76 % for **2c**) as a yellow powder.

Synthesis of the target aryloligogermane carbonyl complexes

Me$_3$GeGePh$_2$(Ph-η^6)Cr(CO)$_3$ (3a). Solid (MeCN)$_3$Cr(CO)$_3$ (**2a**) (0.34 g, 1.31 mmol) was added to the solution of Me$_3$GeGePh$_3$ (**3**) (0.46 g, 1.09 mmol) in THF (20 mL), the mixture obtained was refluxed for 1 h. Then all volatile materials were removed under reduced pressure and the residue was purified by flash-chromatography (SiO$_2$, petroleum ether/toluene 4:1) giving target compound **3a** (R_f 0.3, 0.25 g, 42 %) as a yellow powder. ^{1}H NMR (400.130 MHz, C$_6$D$_6$): δ = 7.59-7.53 (m, 4H), 7.26-7.17 (m, 6H) (aromatic protons), 5.03 (dd, $^3J_{H-H}$= 6.6 Hz, $^4J_{H-H}$= 1.0 Hz, 2H, o-C$_6$H$_5$*Cr(CO)$_3$), 4.56 (tt, $^3J_{H-H}$= 6.3 Hz, $^4J_{H-H}$= 1.0 Hz, 1H, p-C$_6$H$_5$*Cr(CO)$_3$), 4.23 (t, $^3J_{H-H}$= 6.3 Hz, 2H, m-C$_6$H$_5$*Cr(CO)$_3$), 0.49 (s, 9H, GeMe$_3$) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): δ = 233.52 (Cr(CO)$_3$), 136.94 (ipso-C$_6$H$_5$), 135.61 and 128.84 (o- and m-C$_6$H$_5$), 129.43 (p-C$_6$H$_5$), 100.25 (ipso-C$_6$H$_5$*Cr(CO)$_3$), 100.11 and 90.79 (o- and m-C$_6$H$_5$*Cr(CO)$_3$), 94.80 (p-C$_6$H$_5$*Cr(CO)$_3$), -0.49 (GeMe$_3$) ppm. MS (EI) m/z (%): 558 ([M]$^+$, 2), 474 ([M – 3CO]$^+$, 100), 422 ([M – Cr(CO)$_3$]$^+$, 42), 412 ([M – CO - GeMe$_3$]$^+$, 22), 356 ([M – 3CO - GeMe$_3$]$^+$, 4), 304 ([Ph$_3$Ge]$^+$, 34), 227 ([Ph$_2$Ge]$^+$, 24), 52 ([Cr]$^+$, 3). UV/vis (CH$_2$Cl$_2$), λ_{max}, nm (ε, M^{-1} cm^{-1}): 232 (sh) (2.47x10^4), 263 (sh) (0.53x10^4), 320 (0.67x10^4). IR (KBr) v, cm^{-1}: 1971 (s) (A$_1$, CO), 1910/1894 (s) (E, CO). IR (nujol) v, cm^{-1}: 1974 (s) (A$_1$, CO), 1897 (s) (E, CO). HRMS (ESI), m/z [M-H]$^+$, calcd. 556.7121, found 556.7107. C$_{24}$H$_{24}$CrGe$_2$O$_3$ (557.7200): Calcd. C 51.68, H 4.34; Found: C 51.26, H 4.12 %.

Me$_3$GeGePh$_2$(Ph-η^6)Mo(CO)$_3$ (3b). Analogously to **3a** using Mo(CO)$_3$(NCMe)$_3$ (**2b**) (0.70 g, 2.30 mmol) and Me$_3$GeGePh$_3$ (**3**) (0.89 g, 2.11 mmol). The reaction was accompanied by a noticeable decomposition (precipitation of a black precipitate). After evaporation, dissolving in ether and passing through a pad of SiO$_2$, ^{1}H NMR analysis of the mixture obtained indicates the presence of initial compound **3** (major) and complex **3b** (trace amounts). For complex **3b**: ^{1}H NMR (400.130 MHz, C$_6$D$_6$): δ = 5.22 (dd, $^3J_{H-H}$= 6.5 Hz, $^4J_{H-H}$= 0.8 Hz, 2H, o-C$_6$H$_5$*Mo(CO)$_3$), 4.75 (tt, $^3J_{H-H}$= 6.5 Hz, $^4J_{H-H}$= 0.8 Hz, 1H, p-C$_6$H$_5$*Mo(CO)$_3$), 4.44 (t, $^3J_{H-H}$= 6.5 Hz, 2H, m-C$_6$H$_5$*Mo(CO)$_3$) ppm. Other signals are overlapped with the signals of Me$_3$GeGePh$_3$ (**3**). IR (nujol) v, cm^{-1}: 1978 (s) (A$_1$, CO), 1900 (s) (E, CO). HRMS (ESI), m/z [M-H]$^+$, calcd. 600.6565, found 600.6548.

Me$_3$GeGePh$_2$(Ph-η^6)W(CO)$_3$ (3c). *Method 1.* Analogously to **3a** using W(CO)$_3$(NCMe)$_3$ (**2c**) (0.78 g, 1.99 mmol) and Me$_3$GeGePh$_3$ (**3**) (0.59 g, 1.40 mmol). After chromatography (SiO$_2$) initial **3** (0.27 g, R_f 0.6, ether/petroleum ether 1:4) and target complex **3c** (0.14 g, 27 %, conversion 54 %, R_f 0.3, ether/petroleum ether 1:3, orange powder) were isolated.

Method 2. Solid W(CO)$_6$ (**1c**) (0.42 g, 1.19 mmol) was added to the solution of Me$_3$GeGePh$_3$ (**3**) (0.50 g, 1.19 mmol) in a mixture of (nBu)$_2$O/THF (10:1) (30 mL). The mixture obtained was frozen in liquid nitrogen, evacuated in high pressure and warmed to room temperature (procedure was repeated three times). Then it was refluxed on oil bath (150 ºC) for 5 h, whereas significant decomposition (black precipitate) was observed. Then all volatile materials were removed under reduced pressure, the residue was dissolved in ether and the residue was passed through a pad of SiO$_2$ indicating the decomposition. ^{1}H NMR (400.130 MHz, C$_6$D$_6$): δ = 7.57-7.53 (m, 6H), 7.24-7.17 (m, 4H) (aromatic protons), 4.98 (dd, $^3J_{H-H}$= 6.3 Hz, $^4J_{H-H}$= 1.2 Hz, 2H, o-C$_6$H$_5$*W(CO)$_3$), 4.50 (tt, $^3J_{H-H}$= 6.3 Hz, $^4J_{H-H}$= 1.2 Hz, 1H, p-C$_6$H$_5$*W(CO)$_3$), 4.17 (tt, $^3J_{H-H}$= 1.2 Hz, 2H, m-C$_6$H$_5$*W(CO)$_3$), 0.45 (s, 9H, GeMe$_3$) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): δ = 209.95 (W(CO)$_3$), 136.98 (ipso-C$_6$H$_5$), 135.50 and 128.91 (o- and m-C$_6$H$_5$), 129.54 (p-C$_6$H$_5$), 97.63 (ipso-C$_6$H$_5$*W(CO)$_3$), 97.23 and 89.19 (o- and m-C$_6$H$_5$*W(CO)$_3$), 91.86 (p-C$_6$H$_5$*W(CO)$_3$), -0.57 (GeMe$_3$) ppm. MS (EI) m/z (%): 690 ([M]$^+$, 4), 606 ([M – 3CO]$^+$, 22), 544 ([M – CO - GeMe$_3$]$^+$, 16), 488 ([M – 3CO - GeMe$_3$]$^+$, 2), 422 ([M – W(CO)$_3$]$^+$, 46), 304 ([Ph$_3$Ge]$^+$, 100), 227 ([Ph$_2$Ge]$^+$, 27), 52 ([Cr]$^+$, 2). UV/vis (CH$_2$Cl$_2$), λ_{max}, nm (ε, M^{-1} cm^{-1}): 233 (sh) (1.96x10^4), 291 (0.38x10^4), 322 (0.46x10^4). IR (nujol) v, cm^{-1}: 2924 (s), 2862 (m), 1980 (s) (A$_1$, CO), 1904 (s) (E, CO), 1460 (m). HRMS (ESI), m/z [M-H]$^+$, calcd. 688.5565, found 688.5567. C$_{24}$H$_{24}$Ge$_2$O$_3$W (689.5634): Calcd. C 41.80, H 3.51; Found: C 39.68, H 2.87 %.

Me$_3$GeGe(pTol)$_2$(pTol-η^6)Cr(CO)$_3$ (4a). Analogously to **3a** using Cr(CO)$_3$(NCMe)$_3$ (**2a**) (0.27 g, 1.04 mmol) and Me$_3$GeGe(pTol)$_3$ (**4**) (0.48 g, 1.04 mmol). After chromatography (SiO$_2$) initial **4** (0.15 g, R_f 0.8, toluene/petroleum ether 1:3) and target complex **4a** (0.24 g, 56 %, R_f 0.3, toluene/petroleum ether 1:3, conversion 68 %) were isolated as yellowish crystals. ^{1}H NMR (400.130 MHz, C$_6$D$_6$): δ = 7.58, 7.11 (2d, J_{H-H} = 6.7 Hz, each 4H, 2p-C$_6$H$_4$), 5.23, 4.23 (2d, J_{H-H} = 5.1 Hz, each 2H, p-C$_6$H$_4$*Cr(CO)$_3$), 2.10 (s, 6H, 2C$_6$H$_4$Me), 1.58 (s, 3H, C$_6$H$_4$Me*Cr(CO)$_3$), 0.58 (s, 9H, GeMe$_3$) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): δ = 234.06 (Cr(CO)$_3$), 139.17, 133.52 (2 ipso-C$_6$H$_4$Me-p), 135.64, 129.72 (2 o-C$_6$H$_4$Me-p), 110.60, 98.21 (2 ipso-C$_6$H$_4$Me-p*Cr(CO)$_3$), 101.05, 91.98 (2 o-C$_6$H$_4$Me-p*Cr(CO)$_3$), 21.31 (C$_6$H$_4$Me-p), 20.26 (C$_6$H$_4$Me-p*Cr(CO)$_3$), -0.46 (GeMe$_3$) ppm. MS (EI) m/z (%): 600 ([M]$^+$, 2), 516 ([M – 3CO]$^+$, 100), 464 ([M – Cr(CO)$_3$]$^+$, 454 ([M – CO - GeMe$_3$]$^+$, 18), 398 ([M – 3CO - GeMe$_3$]$^+$, 1), 38), 346 ([(pTol)$_3$Ge]$^+$, 14), 255 ([(pTol)$_2$Ge]$^+$, 32), 52 ([Cr]$^+$, 4). IR (THF) v, cm^{-1}: 1961 (s) (A$_1$, CO), 1887 (s) (E, CO). IR (nujol) v, cm^{-1}: 1970 (s) (A$_1$, CO), 1894 (s) (E, CO). UV/vis (CH$_2$Cl$_2$), λ_{max}, nm (ε, M^{-1} cm^{-1}): 233 (sh) (4.55x10^4), 267 (sh) (0.80x10^4), 321 (0.87x10^4). HRMS

(ESI), *m/z* [M-H]$^+$, calcd. 598.7924, found 598.7911. C$_{27}$H$_{30}$CrGe$_2$O$_3$ (599.7998): Calcd. C 54.07, H 5.04; Found: C 52.78, H 4.22 %.

Ph$_3$GeGePh$_2$(Ph-η^6)Cr(CO)$_3$ (5a). *Method 1.* Dimethyl succinate (0.46 g, 3.10 mmol) and Cr(CO)$_6$ (**1a**) (0.76 g, 3.44 mmol) were added to the suspension of Ph$_3$GeGePh$_3$ (**5**) (1.90 g, 3.10 mmol) in decalin (20 mL). Reaction mixture was frozen in liquid nitrogen, evacuated in vacuum and warmed to room temperature (three times); then it was heated at 190 ºC for 2 h. Then all volatile materials were removed under high vacuum, residue was purified by chromatography (SiO$_2$, petroleum ether, then petroleum ether/benzene 3:2), giving target compound **5a** (*R$_f$* 0.4, 0.18 g, 28 %, conversion 29 %) as a yellow powder and unreacted Ph$_3$GeGePh$_3$ (**5a**) (*R$_f$* 0.7 in benzene, 1.37 g).

Method 2. Analogously to **3c** (Method 2) using Cr(CO)$_6$ (**1a**) (0.31 g, 1.40 mmol) and Ph$_3$GeGePh$_3$ (**5**) (0.80 g, 1.32 mmol) in (*n*Bu)$_2$O/THF (10:1) mixture (20 mL), heating for 26 h. The residue was purified by chromatography (SiO$_2$, *R$_f$* 0.3, benzene/petroleum ether 1:3) giving **5a** (0.31 g, 32 %) as a yellow powder. ^{1}H NMR (400.130 MHz, C$_6$D$_6$): *δ* = 7.75-7.70 (m, 4H), 7.61-7.54 (m, 6H), 7.14-7.06 (m, 15H) (aromatic protons), 5.05 (d, *J*$_{H-H}$ = 6.3 Hz, 2H, *o*-C$_6$H$_5$*Cr(CO)$_3$), 4.48 (t, *J*$_{H-H}$ = 6.3 Hz, 1H, *p*-C$_6$H$_5$*Cr(CO)$_3$), 4.14 (t, *J*$_{H-H}$ = 6.3 Hz, 2H, *m*-C$_6$H$_5$*Cr(CO)$_3$) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): *δ* = 233.10 (Cr(*CO*)$_3$), 136.84 (Ge(*p*-C$_6$H$_5$)$_2$(Ph*Cr(CO)$_3$)), 136.14 (Ge(*p*-C$_6$H$_5$)$_3$), 135.94 and 128.90 (Ge(*o*- and *m*-C$_6$H$_5$)$_3$), 135.79 (Ge(*ipso*-C$_6$H$_5$)$_3$), 129.89 and 129.52 (Ge(*o*- and *m*-C$_6$H$_5$)$_2$(Ph*Cr(CO)$_3$)), 128.53 (Ge(*ipso*-C$_6$H$_5$)$_2$(Ph*Cr(CO)$_3$)), 100.60 (Ge(*ipso*-C$_6$H$_5$)*Cr(CO)$_3$)), 99.82 and 90.74 (Ge(*o*- and *m*-C$_6$H$_5$*Cr(CO)$_3$)), 94.27 (Ge(*p*-C$_6$H$_5$*Cr(CO)$_3$)) ppm. MS (EI) *m/z* (%): 744 ([M]$^+$, 2), 660 ([M – 3CO]$^+$, 43), 608 ([M – Cr(CO)$_3$]$^+$, 38), 412 ([M – CO - GePh$_3$]$^+$, 2), 357 ([M – 3CO - GePh$_3$]$^+$, 2), 304 ([Ph$_3$Ge]$^+$, 100), 227 ([Ph$_2$Ge]$^+$, 21), 151 ([PhGe + H]$^+$, 18), 52 ([Cr]$^+$, 2). UV/vis (CH$_2$Cl$_2$), *λ$_{max}$*, nm (*ε*, M^{-1} cm^{-1}): 238 (sh) (3.57x10^4), 267 (sh) (1.04x10^4), 322 (0.64x10^4). IR (nujol) *v*, cm^{-1}: 2932 (s), 1975 (s) (A$_1$, CO), 1900 (s) (E, CO), 1454 (s), 1370 (m). HRMS (ESI), *m/z* [M-H]$^+$, calcd. 742.9208, found 742.9211. C$_{39}$H$_{30}$CrGe$_2$O$_3$ (743.9282): Calcd. C 62.97, H 4.06; Found: C 60.72, H 3.66 %.

(C$_6$F$_5$)$_3$GeGePh$_2$(Ph-η^6)Cr(CO)$_3$ (6a). Analogously to **3c** (Method 2) using Cr(CO)$_6$ (**1a**) (0.15 g, 0.69 mmol) and (C$_6$F$_5$)$_3$GeGePh$_3$ (**6**) (0.58 g, 0.66 mmol) in (*n*Bu)$_2$O/THF (10:1) mixture (20 mL), heating for 30 h. The residue was purified by chromatography (SiO$_2$, *R$_f$* 0.3, ether/petroleum ether 1:3), giving **6a** (0.11 g, 16 %) as an orange powder. ^{1}H NMR (400.130 MHz, C$_6$D$_6$): *δ* = 7.58-7.54 (m, 4H), 7.04-7.00 (m, 6H) (aromatic rotons), 4.91 (d, ^{3}*J*$_{H-H}$ = 6.3 Hz, 2H, *o*-C$_6$H$_5$*Cr(CO)$_3$), 4.35 (t, ^{3}*J*$_{H-H}$ = 6.3 Hz, 1H, *p*-C$_6$H$_5$*Cr(CO)$_3$), 4.06 (t, ^{3}*J*$_{H-H}$ = 6.3 Hz, 2H, *m*-C$_6$H$_5$*Cr(CO)$_3$) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): *δ* = 232.17 (Cr(*CO*)$_3$), 149.85-149.66, 147.42-147.24, 144.88-144.78, 142.39-142.13, 139.16-138.85, 136.63-136.27 (6m, Ge(*C$_6$F$_5$*)$_3$), 135.19 and 129.04 (*o*- and *m*-C$_6$H$_5$), 131.25 (*ipso*-C$_6$H$_5$), 130.86 (*p*-C$_6$H$_5$), 97.79 and 90.94 (*o*- and *m*-C$_6$H$_5$*Cr(CO)$_3$), 95.16 (*ipso*-C$_6$H$_5$*Cr(CO)$_3$), 93.51 (*p*-C$_6$H$_5$*Cr(CO)$_3$) ppm. ^{19}F NMR (376.498 MHz, C$_6$D$_6$): *δ* = -124.29 – (-124.34) (2F), 148.61 – (-148.72) (1F), -159.46 – (-159.56) (2F) ppm. MS (EI) *m/z* (%): 1014 ([M]$^+$, 1), 930 ([M – 3CO]$^+$, 32), 878 ([M – Cr(CO)$_3$]$^+$, 22), 575 ([(C$_6$F$_5$)$_3$Ge]$^+$, 8), 304 ([Ph$_3$Ge]$^+$, 100), 167 ([C$_6$F$_5$]$^+$, 16), 52 ([Cr]$^+$, 2). UV/vis (CH$_2$Cl$_2$), *λ$_{max}$*, nm (*ε*, M^{-1} cm^{-1}): 234 (sh) (2.15x10^4), 261 (0.78x10^4), 322 (0.41x10^4). IR (nujol) *v*, cm^{-1}: 2852 (s), 1976 (s) (A$_1$, CO), 1901 (s) (E, CO), 1650 (m), 1462 (s), 1372 (m), 1082 (s). HRMS (ESI), *m/z* [M-H]$^+$, calcd. 1012.7777, found 1012.7782. C$_{39}$H$_{15}$CrF$_{15}$Ge$_2$O$_3$ (1013.7851): Calcd. C 46.20, H 1.49; Found: C 44.64, H 1.07 %.

Ph$_3$GeGeMe$_2$GePh$_2$(Ph-η^6)Cr(CO)$_3$ (7a). *Method 1.* Dimethyl succinate (0.30 g, 2.02 mmol, 2.0 eq.) and Cr(CO)$_6$ (**1a**) (0.49 g, 2.22 mmol, 2.2 eq.) were added to the suspension of [Ph$_3$Ge]$_2$GeMe$_2$ (**7**) (0.72 g, 1.01 mmol, 1.0 eq.) in decalin (20 mL). Reaction mixture was frozen in liquid

nitrogen, evacuated in vacuum and warmed to room temperature (three times); then it was heated at 190 ºC for 2 h. Then all volatile materials were removed under high vacuum, residue was purified by chromatography (SiO$_2$), giving unreacted [Ph$_3$Ge]$_2$GeMe$_2$ (**7**) (0.48 g, *R$_f$* 0.6, ether/petroleum ether 1:3) and target compound **7a** (0.10 g, 34%, *R$_f$* 0.3, ether/petroleum ether 1:2, conversion 33 %) as a yellow powder.

Method 2. Trigermane [Ph$_3$Ge]$_2$GeMe$_2$ (**7**) (0.24 g, 0.33 mmol) was added to the solution of Cr(CO)$_3$(NCMe)$_3$ (**2a**) (0.19 g, 0.73, 2.2 eq.) in THF (20 mL), the solution was refluxed for 2 h, then all volatile materials were removed under reduced pressure. The residue was purified by chromatography (SiO$_2$, ether/petroleum ether 1:2) giving initial compound **7** (*R$_f$* 0.7, 0.09 g) and target complex **7a** as a yellow powder (*R$_f$* 0.2, 0.08 g, 44 %, conversion 63 %). ^{1}H NMR (400.130 MHz, C$_6$D$_6$): *δ* = 7.44-7.34 (m, 10H), 7.15-7.07 (m, 15H) (aromatic protons), 4.80 (d, *J*$_{H-H}$ = 5.9 Hz, 2H, *o*-C$_6$H$_5$*Cr(CO)$_3$), 4.53 (br t, *J*$_{H-H}$ = 5.9 Hz, 1H, *p*-C$_6$H$_5$*Cr(CO)$_3$), 4.17 (br t, *J* = 5.9 Hz, 2H, *m*-C$_6$H$_5$*Cr(CO)$_3$), 0.81 (s, 6H, GeMe$_2$) ppm. ^{13}C NMR (100.613 MHz, C$_6$D$_6$): *δ* = 233.36 (Cr(*CO*)$_3$), 137.62 (Ge(*ipso*-C$_6$H$_5$)$_3$), 136.52 (Ge(*ipso*-C$_6$H$_5$)$_2$Ph*Cr(CO)$_3$), 135.91 and 128.81 (Ge(*o*- and *m*-C$_6$H$_5$)$_2$Ph*Cr(CO)$_3$), 135.78 and 128.71 (Ge(*o*- and *m*-C$_6$H$_5$)$_3$), 129.53 (Ge(*p*-C$_6$H$_5$)$_2$Ph*Cr(CO)$_3$), 129.01 (Ge(*p*-C$_6$H$_5$)$_3$), 100.54 (Ge(*ipso*-C$_6$H$_5$)*Cr(CO)$_3$), 99.95 and 90.80 (Ge(*o*- and *m*-C$_6$H$_5$)*Cr(CO)$_3$), 94.52 (Ge(*p*-C$_6$H$_5$)*Cr(CO)$_3$), -1.68 (GeMe$_2$) ppm. UV/vis (CH$_2$Cl$_2$), *λ$_{max}$*, nm (*ε*, M^{-1} cm^{-1}): 244 (sh) (3.60x10^4), 261 (sh) (2.10x10^4), 321 (0.38x10^4). IR (nujol) *v*, cm^{-1}: 2942 (s), 1972 (s) (A$_1$, CO), 1896 (s) (E, CO), 1452 (m). MS (EI) *m/z* (%): 847 ([M]$^+$, 1), 763 ([M – 3CO]$^+$, 22), 711 ([M – Cr(CO)$_3$]$^+$, 100), 407 ([Ph$_3$GeGeMe$_2$]$^+$, 12), 304 ([Ph$_3$Ge]$^+$, 22), 52 ([Cr]$^+$, 2). HRMS (ESI), *m/z* [M-H]$^+$, calcd. 845.6298, found 845.6281. C$_{41}$H$_{36}$CrGe$_3$O$_3$ (846.6372): Calcd. C 58.16, H 4.29; Found: C 60.12, H 4.52 %.

Keywords: Germanium • Oligogermanes • X-ray Diffraction Analysis • Carbonyl Complex • Chromium

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Entry for the Table of Contents

FULL PAPER

A series of transition metal carbonyl complexes bearing aryloligogermanes ligand was obtained and thoroughly investigated through NMR, IR, UV/vis spectroscopy, electrochemistry, DFT, and XRD. Oligogermanyl substituents have been found to have an electron donor behaviour, whereas the $M(CO)_3$ group is behaving as an electron withdrawing group. The dependences of the physical properties on the nature of M, R, Ar and on the number of Ge atoms were studied.
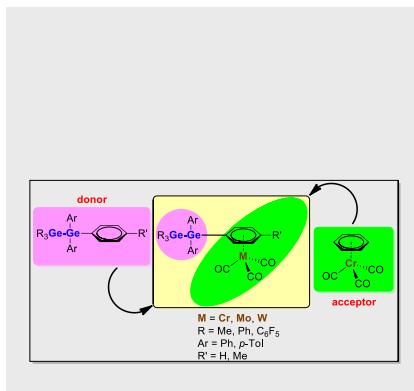
Oligogermanium Complexes

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