Silyl-, Germyl-, and Stannyl-Substituted Group 6 Pentacarbonyl Metalates

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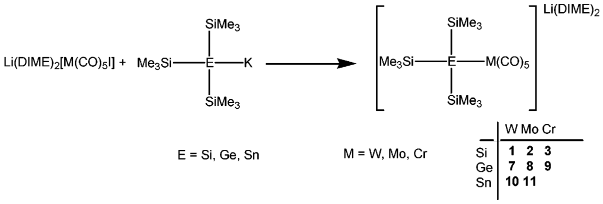
Reactions of silylated silyl-, germyl-, and stannyl anions with group 6 halogenpentacarbonyl metalates gave the respective pentacarbonyl metalate derivatives. With the exception of a stannylated chromate all compounds were obtained in good yields and selectivity. An alternative approach employing group 6 metal hexacarbonyls in the reaction with the group 14 anions worked equally well. All compounds were fully characterized spectroscopically, and four compounds were subjected to single-crystal structure analysis.

Our continuing program on the synthesis of transition metal silicon compounds[1] employing oligosilyl anions[2] has led us to study derivatives of group 6 pentacarbonyl metalates. For the preparation of the latter electrophilic metalates are required.[3,4,8c] Using tetraalkylammonium group 6 pentacarbonyl chlorometalates triphenylsilyl, -germyl, and -stannyl derivatives have been obtained[5] and reaction with tris(trimethylstannyl)silyllithium afforded the respective chromium, molybdenum, and tungsten adducts.[6] The introduction of the DIME (diethylene glycol dimethyl ether) coordinated lithium salts of the iodopentacarbonyl metalates of tungsten and molybdenum and the use of undecamethylcyclohexasilanylpotassium[7] allowed for the synthesis of undecamethylcyclohexasilanyl derivatives.[8] Besides salt elimination, also direct carbonyl substitution reactions of group 14 anions with group 6 metal hexacarbonyl compounds are known. In the reaction of group 6 metal hexacarbonyls with triphenylsilyllithium initial attack at a carbonyl carbon atom was shown to be followed by a substitution reaction.[9] Similar chemistry had also been observed for several germyllithium compounds.[10]

The facile conversion of pentacarbonyl metalates with tris(trimethylstannyl)silyllithium[6] and undecamethylcyclohexasilanylpotassium[8] encouraged us to study the reactions of the lithium salts of the iodopentacarbonyl metalates of tungsten, molybdenum, and chromium with tris(trimethylsilyl)silylpotassium[2a,11] (eq 1).



	W	Mo	Cr
Si	**1**	**2**	**3**
Ge	**7**	**8**	**9**
Sn	**10**	**11**	

(1)

The reactions of tris(trimethylsilyl)silylpotassium with the iodotungstenate proceeded smoothly in THF with a slight excess of the silylating agent and was found to be equally effective for the cases of the molybdenum and chromium metalates to give the respective oligosilylated compounds (**2**, **3**) in good yields (eq 1).

Reaction of bis(trimethylsilyl)methylsilyl- and 1,1,3,3,3-pentakis(trimethylsilyl)-2,2-dimethyltrisilanylpotassium[2] with the iodotungstenate could be accomplished in the same manner (**4**, **5**), whereas the use of pentakis(trimethylsilyl)disilanylpotassium required the use of diethyl ether as solvent and proceeded much slower (**6**) (eq 2).

To expand our study also to the heavier congeners of group 14, we investigated the reaction of the iodo metalates with tris(trimethylsilyl)germyl-[2g,12] and tris-

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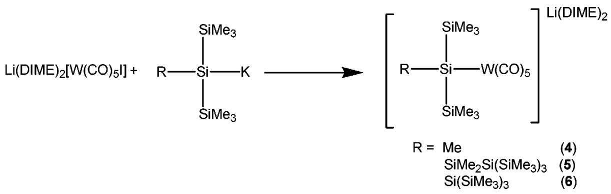
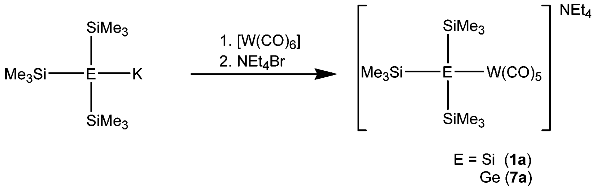


(2)

(trimethylsilyl)stannylpotassium.[13] Reactions of the germylanion under the same condition as described above for the silylanion with the metalates of all three group 6 metals gave the expected compounds in good yield (**7**, **8**, **9**) (eq 1). However, attempts to obtain also the respective metalated tin compounds proceeded cleanly only for the cases of tungsten and molybdenum (**10**, **11**). Efforts to achieve the formation of tris(trimethylsilyl)stannyl pentacarbonylchromate resulted in the formation of a substantial amount of tetrakis(trimethylsilyl)stannane, some hexakis(trimethylsilyl)distannane, and two compounds that are likely to contain a chromium tin bond.

The syntheses of all described compounds could be achieved in good yields, and isolation was straightforward. Characterization employing spectroscopic methods (UV, IR, and NMR) worked very well, but it turned out to be difficult to obtain single crystals suitable for X-ray diffraction analysis. Only the tin adducts (**10**, **11**) gave crystals, which could be used to carry out structure analyses. The fact that crystal structures of compounds with the tetraethylammonium counterion[6] could be obtained led us to investigate this cation. Therefore the direct reaction of tris(trimethylsilyl)silyl- and tris(trimethylsilyl)germylpotassium compounds with tungsten hexacarbonyl followed by exchange of the counterion was examined. This worked well, and single crystals of sufficient quality (**1a**, **7a**) (eq 3) were isolated.



(3)

The thermal stability of all investigated compounds was not very great. The stannylated compounds **10** and **11** started to decompose at 80 °C. Decomposition of the silyl and germyl chromates proceeded at 130 °C, and the respective molybdenum and tungsten compounds decomposed around 150 °C.

An attempt to convert **1** into a neutral species by reaction with $NO[BF_4]$[14] led to the cleavage of the tungsten−silicon bond and the formation of tris(trimethylsilyl)silyl fluoride. Initial efforts to carry out NMR spectroscopy in deuterochloroform resulted in a slow but steady conversion of **1** to tris(trimethylsilyl)silyl chloride. Subjecting **1** to a reaction with potassium *tert*-butoxide did not result in formation of a 1,2-dianionic compound.[2e] However, in the case of compound **5** the terminal tris(trimethylsilyl)silyl group was metalated. The resulting dianionic compound did not show back-biting to the metal and is currently investigated with respect to its potential as precursor for heterobimetallic complexes.

IR spectra of the carbonyl region of compounds **1**−**3** and **7**−**11** exhibit the expected three bands ($2A_1 + E$) for molecules with approximate C_{4v} symmetry. For compounds **5** and **6** with a more distorted C_{4v} symmetry an additional band (B_1) can be observed. These results are in accordance with the general infrared spectroscopic behavior of pentacarbonyl metalates $[M(CO)_5R]^-$.[15]

^{29}Si NMR spectroscopy of the compounds reveals some trends. The chemical shifts of the trimethylsilyl groups of the metalated tris(trimethylsilyl)silyl units are around −4.5 ppm. Compared to tetrakis(trimethylsilyl)silane (−9.6 ppm),[11] these values represent downfield shifts of 5.1. Comparison of the trimethylsilyl resonances of the analogous germyl-substituted metal complexes (∼−1.7 ppm) with the respective tetrasilylated compound (−5.5 ppm)[12] displays the same downfield shift picture. The situation is somewhat different for the metalated tin compounds, where the resonances of the metalated compounds (−10.9 ppm) are shifted upfield compared to tetrakis(trimethylsilyl)stannane (−9.3 ppm).[13]

For the tris(trimethylsilyl)silylated compounds the ^{29}Si NMR resonance of the silicon atom attached directly to the metal should be most significant. The respective values for the tungsten (**1**), molybdenum (**2**), and chromium (**3**) compounds are −149.8, −140.1, and −122.6 ppm, respectively. A very similar spectral behavior was observed for the analogous tris(trimethylstannyl)silylated compounds[6] and also the undecamethylcyclohexasilanyl derivatives.[8]

For the stannylated compounds **10** and **11** ^{119}Sn NMR shifts are of similar relevance. The spectral situation is similar to the picture of the ^{29}Si NMR spectra. Again a downfield shift can be observed moving from the tungsten complex (**10**: −667 ppm) to molybdenum (**11**: −618 ppm).

The ^{13}C NMR spectra of all compounds studied show two resonances in the carbonyl region. The more intense signal at lower field is attributed to the four carbonyl ligands in *cis*-position. While the signals for the respective silyl and germyl derivatives are very similar, the tris(trimethylsilyl)stannyl ligand causes a shift of 2−4 ppm to lower field. The nature of the metal is of course more influential on the carbonyl resonances. Moving from chromium to tungsten a decrease of some 25 ppm of the respective resonances was found.[16]

Compounds **10** and **11** were the only examples of the lithium metalates that gave crystals suitable for X-ray diffraction analysis. However, the quality of the crystals was not superior. Therefore, compounds with the tetraethylammonium counterions (**1a**, **7a**) were prepared, which could easily be crystallized and were used to obtain good crystallographic data.

Compounds **10** and **11** crystallize in the monoclinic space group *Pn* with very similar cell parameters. The structures are isomorphous (Figure 1, only **11** shown). Besides the metalate a lithium cation coordinated by two molecules of DIME is found in the asymmetric unit.

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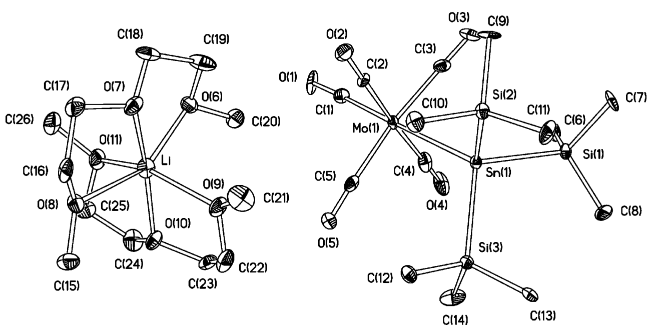

Figure 1. Molecular structure of **11** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity.

For both structures unusually high residual electron density was found in the proximity of the heavy atoms. This effect is most likely caused by the poor quality of the crystals (Table 1).

Compounds **1a** and **7a** both crystallize in the monoclinic space group *Cc*. Again the cell constants are almost identical and the structures are isomorphous (Figure 2, only **7a** shown). Due to the better quality of crystals, residual electron densities in these cases are as small as expected (Table 1).

Generally the bonds of group 14 groups to the negatively charged metalates are longer than usual, and this was also found for our cases. Observed W−Si distances range from 2.389 to 2.708 Å with typical values being around 2.56 Å.[17] Compared to related complexes ($[W(CO)_5SiMe_3]^-$, 2.614 Å;[18] $[W(CO)_5Si_6Me_{11}]^-$, 2.670 Å;[8a] $[W(CO)_5Si(SnMe_3)_3]^-$, 2.653 Å[6]), **1a** has the longest bond (2.685 Å). The W−Ge distance of **7a** (2.724 Å) is the longest found. W−Ge contacts so far were found to exhibit bond lengths between 2.486 and 2.681 Å.[17] For structurally characterized compounds containing Sn−W and Sn−Mo units a large variety of different bonding situations exists. The only reported example related to our molecules is $[PPN][W(CO)_5SnPh_3]$,[19] displaying a Sn−W distance of 2.813 Å. Compared to this, the Sn−W (2.873 Å) and Sn−Mo (2.876 Å) distances of **10** and **11** are both longer. All four structures display octahedrally coordinated pentacarbonyl fragments with an attached trimethylsilylated group 14 element. While all carbonyl ligands in *cis*-position to the bulky group show M−CO distances of about 2.02 Å, the carbonyls in *trans*-position experience a *trans*-effect and are therefore more closely bound to the metal (Table 2). While for compounds **10** and **11** an almost perfect *trans*-arrangement was found (Sn−M−CO: 179.3(5)° and 178.7(4)°), the compounds with the ammonium counterions (**1a**, **7a**) show a slight distortion (E−W−CO: 172.63(15)° and 172.96(17)°). For all compounds it was found that the two carbonyl groups, which are in an *eclipsed* conformation (Si−E−M−C: 10−20°) to the trimethylsilyl groups, occupy almost perfect octahedral positions (E−M−CO: 87−90°), whereas the carbonyls in *gauche* orientation (Si−Sn−M−C: 40−50°) slightly bend toward the bulky ligand (E−M−CO: 84−85°). A similar observation has been made previously for $Li[Me_{11}Si_6Mo(CO)_5]$.[8b]

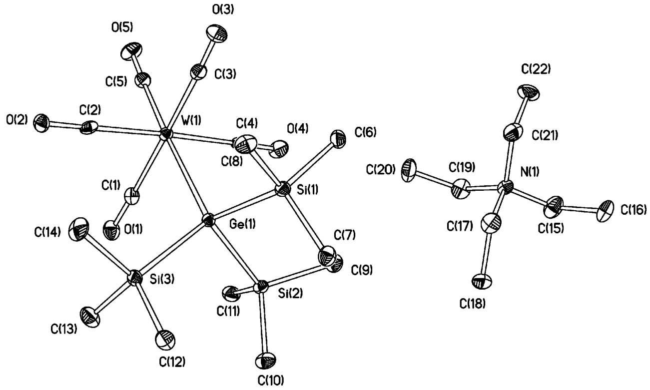

Figure 2. Molecular structure of **7a** with 30% probability thermal ellipsoids; all hydrogen atoms omitted for clarity.

Table 1. Crystallographic Data for Compounds 1a, 7a, 10, and 11

	1a	7a	10	11
empirical formula	$C_{22}H_{47}NO_5Si_4W$	$C_{22}H_{47}GeNO_5Si_3W$	$C_{26}H_{55}LiO_{11}Si_3SnW$	$C_{26}H_{55}LiMoO_{11}Si_3Sn$
M_w	701.82	746.32	937.45	849.54
temp [K]	100(2)	100(2)	100(2)	100(2)
size [mm]	0.42 × 0.28 × 0.22	0.40 × 0.32 × 0.22	0.33 × 0.25 × 0.22	0.33 × 0.30 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Cc*	*Cc*	*Pn*	*Pn*
a [Å]	12.196(2)	12.206(2)	13.136(3)	13.171(3)
b [Å]	13.590(3)	13.590(3)	11.189(2)	11.244(2)
c [Å]	19.382(4)	19.385(4)	13.592(3)	13.646(3)
α [deg]	90	90	90	90
β [deg]	97.42(3)	97.70(3)	91.61(3)	91.64(3)
γ [deg]	90	90	90	90
V [Å ^{3}]	3185.8(11)	3186.5(11)	1997.0(7)	2020.1(7)
Z	4	4	2	2
ρ_{calc} [g cm^{-3}]	1.463	1.556	1.559	1.397
abs coeff [mm^{-1}]	3.805	4.692	3.639	1.063
$F(000)$	1424	1496	936	872
θ range	2.12 to 25.00 deg.	2.12 to 24.50 deg.	1.82 to 25.00 deg.	1.81 to 24.50
no. of reflens collected/unique	11 022/5470 [R(int) = 0.0223]	10 647/5108 [R(int) = 0.0324]	19 709/6978 [R(int) = 0.1027]	13 223/6560 [R(int) = 0.0728]
completeness to θ [%]	25.00 [99.9]	24.50 [99.6]	25.00 [100.0]	24.50 [99.9]
no. of data/restraints/params	5470/2/312	5108/2/312	6978/50/399	6560/2/403
goodness of fit on F^2	0.906	0.926	1.074	1.056
final R indices [$I > 2\sigma(I)$]	R1 = 0.0213, wR2 = 0.0514	R1 = 0.0253, wR2 = 0.0615	R1 = 0.0810, wR2 = 0.1984	R1 = 0.0831, wR2 = 0.2061
R indices (all data)	R1 = 0.0218, wR2 = 0.0516	R1 = 0.0267, wR2 = 0.0621	R1 = 0.0868, wR2 = 0.2040	R1 = 0.0916, wR2 = 0.2149
largest diff peak/hole [e$^-$/Å^3]	0.988 and −0.320	0.879 and −0.440	10.534 and −2.324	6.307 and −1.371

Table 2. Selected Bond Lengths [Å] and Bond Angles [deg] with Estimated Standard Deviations of Compounds 1a, 7a, 10, and 11

	(**1a**) W−Si	(**7a**) W−Ge	(**10**) W−Sn	(**11**) Mo−Sn
M−CO *trans*	1.986(5)	1.985(6)	1.921(14)	1.973(13)
M−CO *cis*	2.027(9), 2.029(5), 2.033(8), 2.050(5)	2.025(8), 2.030(6), 2.031(6), 2.038(9)	2.00(2), 2.00(2), 2.02(2), 2.06(2)	2.009(19), 2.009(17), 2.028(16), 2.031(12)
M−E	2.6851(13)	2.7242(8)	2.8729(13)	2.8764(14)
E−$SiMe_3$	2.3379(18), 2.3525(17), 2.3643(17)	2.3740(17), 2.3813(16), 2.3947(16)	2.565(5), 2.570(5), 2.592(4)	2.579(4), 2.579(4), 2.597(4)
E−M−CO	172.63(15), 83.12(14), 85.1(2), 92.0(2), 94.69(14)	172.96(17), 82.94(17), 84.8(2), 91.0(2), 93.94(16),	179.3(5), 84.5(6), 85.1(5), 86.1(5), 92.1(6)	178.7(4), 84.4(4), 84.9(4), 87.1(4), 90.3(3)
Si−E−Si	101.31(6), 104.85(6), 105.48(7)	101.58(6), 105.21(6), 106.08(6)	104.63(15), 106.86(15), 107.20(15)	104.40(12), 106.46(12), 106.80(12)

Experimental Part

All reactions were carried out under an atmosphere of dry argon or nitrogen. ^1H (300 MHz), ^{13}C (75.4 MHz), ^{29}Si (59.3 MHz), and ^{119}Sn (111.8 MHz) NMR spectra were recorded in CH_2Cl_2 solution with a D_2O capillary. The INEPT pulse sequence was used for the amplification of the ^{29}Si NMR signal.[20] The completeness of reactions was usually controlled by NMR spectroscopy. IR and electronic spectra were measured from CH_2Cl_2 solutions.

For X-ray structure analysis crystals were mounted onto the tip of a glass fiber, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer (wavelength 0.71073 Å). The data were reduced to F^2_o and corrected for absorption effects with SAINT[21] and SADABS,[22] respectively. Structures were solved using direct methods and refined by full-matrix least-squares method (SHELXL97).[23] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data can be found in Table 1. More detailed information for all structures can be found in the Supporting Information. All data have been deposited at the Cambridge Crystallographic Deposition Centre: CCDC 260991 (**1a**), CCDC 260989 (**7a**), CCDC 262665 (**10**), CCDC 260990 (**11**). The data can be retrieved via www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered at the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB21Ez; fax: (+44) 1223-336-033.

General Procedure for the Synthesis of $[Li(DIME)_2][M(CO)_5E(SiMe_3)_3]$ (M = Cr, Mo, W; E = Si, Ge, Sn). Tris(trimethylsilyl)silylpotassium,[2a] tris(trimethylsilyl)germylpotassium,[2g] and tris(trimethylsilyl)stannylpotassium[13] were prepared in situ in THF. The respective pentacarbonyl metalate was added to the solution. All reactions were allowed to complete overnight, except for reactions with the pentacarbonylchromate, which required longer reaction times (3−5 days). The volatiles were removed in vacuo, and the residue was extracted with diethyl ether. Crystals were obtained from the concentrated solutions at −37 °C.

$[Li(DIME)_2][W(CO)_5Si(SiMe_3)_3]$ (**1**) was prepared from 300 mg of $Si(SiMe_3)_4$ (0.94 mmol, 1.4 equiv), 105 mg of KO^tBu (1.4 equiv), and 485 mg of $[Li(DIME)_2][W(CO)_5I]$ (0.67 mmol). Pale yellow crystals, yield: 415 mg (0.49 mmol, 73%). ^1H NMR: δ 3.54 (m, 8H), 3.46 (m, 8H), 3.27 (s, 12H), 0.04 (s, 27H). ^{13}C NMR: δ = 207.6, 206.2, 70.7, 69.4, 59.2, 4.5. ^{29}Si NMR (THF): δ −4.5, −149.8. IR: ν_{CO} 2028 (m), 1896 (vs), 1850 (s). UV: $\lambda_{max}(\epsilon)$ 289 nm (16900 cm^{-1} mol^{-1} L), 345 nm (2800 cm^{-1} mol^{-1} L). $C_{26}H_{55}LiO_{11}Si_4W$ (846.84) calcd C 36.88 H 6.55; found C 36.48 H 6.45.

$[NEt_4][W(CO)_5Si(SiMe_3)_3]$ (1a). Tris(trimethylsilyl)silylpotassium[2a] was prepared from 250 mg of $Si(SiMe_3)_4$ (0.78 mmol) and 87 mg of KO^tBu (1 equiv) in DME (2 mL). The solution was added to a suspension of 274 mg of tungsten hexacarbonyl (1 equiv) in DME. Gas evolution ceased after 30 min. After 12 h the solvent was removed and the residue extracted with dichloromethane. An equimolar amount of tetraethylammonium bromide (164 mg) was added, and the solution stirred overnight. After filtration the volatiles were removed and the residue was extracted with diethyl ether. Yellow crystals precipitated from the concentrated orange filtrate at −37 °C. Yield: 302 mg (0.43 mmol, 48%). ^1H NMR: δ 2.95 (q, J = 7.3 Hz, 8H), 1.08 (tt, J = 7.3 Hz, 1.8 Hz, 12H), −0.08 (s, 27H). ^{13}C NMR: δ 208.0, 206.4, 52.6, 7.4, 4.4. ^{29}Si NMR: δ −4.5, −148.7. IR: ν_{CO} 2048 (m), 1894 (vs), 1846 (s). $C_{22}H_{47}NO_5Si_4W$ (701.79) calcd C 37.65 H 6.75 N 2.00; found C 37.29 H 6.77 N 1.87.

$[Li(DIME)_2][Mo(CO)_5Si(SiMe_3)_3]$ (2) was prepared from 250 mg of $Si(SiMe_3)_4$ (0.78 mmol, 1.4 equiv), 87 mg of KO^tBu (1.4 equiv), and 355 mg of $[Li(DIME)_2][Mo(CO)_5I]$ (0.56 mmol). Pale yellow crystals, yield: 301 mg (0.40 mmol, 71%). ^1H NMR: δ 3.58 (m, 8H), 3.48 (m, 8H), 3.29 (s, 12H), 0.04 (s, 27H). ^{13}C NMR: δ 218.2, 216.4, 70.3, 69.1, 59.3, 4.5. ^{29}Si NMR: δ −4.6, −140.1. IR: ν_{CO} 2029 (m), 1901 (vs), 1854 (s). $C_{26}H_{55}LiMoO_{11}Si_4$ (758.94) calcd C 41.15 H 7.30; found C 40.91 H 7.23.

$[Li(DIME)_2][Cr(CO)_5Si(SiMe_3)_3]$ (3) was prepared from 300 mg of $Si(SiMe_3)_4$ (0.94 mmol, 1.5 equiv), 105 mg of KO^tBu (1.5 equiv), and 370 mg of $[Li(DIME)_2][Cr(CO)_5I]$ (0.62 mmol). Pale yellow crystals, yield: 365 mg (0.51 mmol, 82%). ^1H NMR: δ 3.61 (m, 8H), 3.52 (m, 8H), 3.33 (s, 12H), 0.11 (s, 27H). ^{13}C NMR (THF): δ 231.3, 227.8, 71.8, 70.3, 59.4, 4.6. ^{29}Si NMR: δ −4.7, −122.6. IR: ν_{CO} 2010 (m), 1888 (vs), 1851 (s). $C_{26}H_{55}CrLiO_{11}Si_4$ (715.00) calcd C 43.68 H 7.75; found C 43.39 H 7.81.

$[Li(DIME)_2][W(CO)_5Si_3Me_7]$ (4) was prepared from 143 mg of methyltris(trimethylsilyl)silane (0.54 mmol), 61 mg of KO^tBu (0.54 mmol), and 316 mg of $[Li(DIME)_2][W(CO)_5I]$ (0.44 mmol). Pale yellow crystals, yield: 192 mg (0.24 mmol, 56%). ^1H NMR: δ 3.46 (m, 8H), 3.38 (m, 8H), 3.20 (s, 12H), 0.13 (s, 3H), −0.12 (s, 18H). ^{13}C NMR: δ 211.1, 207.8, 70.6, 69.3, 59.1, 0.9, −6.5. ^{29}Si NMR: δ −7.6, −87.1. IR: ν_{CO} 2023 (m), 1888 (vs), 1851 (s). $C_{24}H_{49}LiO_{11}Si_3W$ (788.69) calcd C 36.55 H 6.26; found C 36.50 H 6.21.

$[Li(DIME)_2][W(CO)_5Si_8Me_{17}]$ (5) was prepared from 219 mg of hexakis(trimethylsilyl)-2,2-dimethyltrisilane (0.40 mmol), 44 mg of KO^tBu (0.40 mmol), and 259 mg of $[Li(DIME)_2][W(CO)_5I]$ (0.36 mmol). Pale yellow crystals, yield: 198 mg (0.18 mmol, 51%). ^1H NMR: δ 3.54 (m, 8H), 3.44 (m, 8H), 3.25

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(s, 12H), 0.34 (s, 6H), 0.09 (s, 27H), 0.06 (s, 18H). ^{13}C NMR: δ 206.7, 206.1, 70.3, 69.1, 59.4, 7.8, 5.7, 4.1. ^{29}Si NMR: δ −4.9, −9.7, −22.2, −117.0, −120.9. IR: ν_{CO} 2029 (m), 1938 (w), 1896 (vs), 1851 (s). $C_{34}H_{79}LiO_{11}Si_8W$ (1079.47) calcd C 37.83 H 7.38; found C 37.60 H 7.30.

$[Li(DIME)_2][W(CO)_5Si_7Me_{15}]$ (6) was prepared from 150 mg of hexakis(trimethylsilyl)disilan (0.30 mmol), 34 mg of KO^{t}Bu (0.30 mmol), and 198 mg of $[Li(DIME)_2][W(CO)_5I]$ (0.27 mmol). The silylanion was generated in THF, the solvent was evaporated, and the residue was taken up in diethyl ether. After addition of the metalate the suspension was stirred overnight. The formed precipitate was removed by filtration, the filtrate was concentrated, and a few drops of pentane were added. Pale yellow crystals formed at −37 °C, yield: 118 mg (0.12 mmol, 43%). ^{1}H NMR : δ 3.44 (m, 8H), 3.34 (m, 8H), 3.16 (s, 12H), 0.01 (s, 27H), −0.01 (s, 18H). ^{13}C NMR: δ 205.9, 205.6, 70.4, 69.2, 59.4, 6.3, 5.0. ^{29}Si NMR: δ −4.5, −9.6, −122.5, −143.7. IR: ν_{CO} 2031 (m), 1937 (w), 1895 (vs), 1857 (s). $C_{32}H_{73}LiO_{11}Si_7W$ (1021.31) calcd C 37.63 H 7.20; found C 37.36 H 7.13.

$[Li(DIME)_2][W(CO)_5Ge(SiMe_3)_3]$ (7) was prepared from 250 mg of $Ge(SiMe_3)_4$ (0.68 mmol, 1.4 equiv), 77 mg of KO^{t}Bu (1.4 equiv), and 355 mg of $[Li(DIME)_2][W(CO)_5I]$ (0.49 mmol). Pale yellow crystals, yield: 283 mg (0.32 mmol, 65%). ^{1}H NMR: δ 3.57 (m, 8H), 3.48 (m, 8H), 3.29 (s, 12H), 0.07 (s, 27H). ^{13}C NMR (THF): δ 207.3, 206.5, 71.8, 70.3, 58.5, 4.9. ^{29}Si NMR (THF): δ −1.7. IR: ν_{CO} 2027 (m), 1893 (vs), 1843 (s). UV: λ_{max} (ϵ) 298 nm (10 000 cm^{-1} mol^{-1} L), 349 nm (1900 cm^{-1} mol^{-1} L). $C_{26}H_{55}GeLiO_{11}Si_3W$ (891.36) calcd C 35.03 H 6.22; found C 35.15 H 6.37.

$[NEt_4][W(CO)_5Ge(SiMe_3)_3]$ (7a) was prepared analogously to **1a** from 155 mg of $Ge(SiMe_3)_4$ (0.42 mmol, 1 equiv), 48 mg of KO^{t}Bu (1 equiv), and 149 mg of tungsten hexacarbonyl (1 equiv). Yellow crystals, yield: 181 mg (0.24 mmol, 57%). ^{1}H NMR: δ 3.09 (q, J = 7.3 Hz, 8H), 1.20 (t, J = 7.3 Hz, 12H), −0.08 (s, 27H). ^{13}C NMR: δ 209.0, 207.0, 52.8, 7.5, 4.7. ^{29}Si NMR: δ −1.5. $C_{22}H_{47}GeNO_5Si_3$ (746.32) calcd C 35.41 H 6.35 N 1.88; found C 35.07 H 6.49 N 1.72.

$[Li(DIME)_2][Mo(CO)_5Ge(SiMe_3)_3]$ (8) was prepared from 250 mg of $Ge(SiMe_3)_4$ (0.68 mmol, 1.5 equiv), 77 mg of KO^{t}Bu (1.5 equiv), and 291 mg of $[Li(DIME)_2][Mo(CO)_5I]$ (0.46 mmol). Yellow crystals, yield: 234 mg (0.29 mmol, 64%). ^{1}H NMR: δ 3.57 (m, 8H), 3.47 (m, 8H), 3.28 (s, 12H), 0.06 (s, 27H). ^{13}C NMR: δ 219.2, 216.7, 70.4, 69.2, 59.4, 4.9. ^{29}Si NMR: δ −1.8. IR: ν_{CO} 2028 (m), 1900 (vs), 1848 (s). $C_{26}H_{55}GeLiMoO_{11}Si_3$ (803.46) calcd C 38.87 H 6.90; found C 38.41 H 6.88.

$[Li(DIME)_2][Cr(CO)_5Ge(SiMe_3)_3]$ (9) was prepared from 250 mg of $Ge(SiMe_3)_4$ (0.68 mmol, 1.4 equiv), 77 mg of KO^{t}Bu (1.4 equiv), and 291 mg of $[Li(DIME)_2][Cr(CO)_5I]$ (0.49 mmol). Yellow crystals, yield: 187 mg (0.25 mmol, 50%). ^{1}H NMR: δ 3.50 (m, 8H), 3.40 (m, 8H), 3.22 (s, 12H), 0.02 (s, 27H). ^{13}C NMR: δ 232.8, 228.5, 70.5, 69.2, 59.4, 4.7. ^{29}Si NMR: δ −1.5. IR: ν_{CO} 2008 (m), 1888 (vs), 1859 (s). $C_{26}H_{55}CrGeLiO_{11}Si_3$ (759.52) calcd C 41.12 H 7.30; found C 40.45 H 7.29.

$[Li(DIME)_2][W(CO)_5Sn(SiMe_3)_3]$ (10) was prepared from 275 mg of $Sn(SiMe_3)_4$ (0.67 mmol, 1.4 equiv), 75 mg of KO^{t}Bu (1.4 equiv), and 346 mg of $[Li(DIME)_2][W(CO)_5I]$ (0.48 mmol). Pale brownish crystals, yield: 347 mg (0.37 mmol, 78%). ^{1}H NMR: δ 3.55 (m, 8H), 3.45 (m, 8H), 3.26 (s, 12H), 0.11 (s, 27H). ^{13}C NMR: δ 211.1, 208.2, 70.3, 69.1, 59.3, 4.8. ^{29}Si NMR: δ −10.8. ^{119}Sn NMR: −667.0. IR: ν_{CO} 2020 (m), 1889 (vs), 1843 (s). UV: $\lambda_{max}(\epsilon)$ 298 nm (15 200 cm^{-1} mol^{-1} L), 331 nm (4100 cm^{-1} mol^{-1} L). $C_{26}H_{55}LiO_{11}Si_3SnW$ (937.46) calcd C 33.31 H 5.91; found C 33.02 H 5.70.

$[Li(DIME)_2][Mo(CO)_5Sn(SiMe_3)_3]$ (11) was prepared from 275 mg of $Sn(SiMe_3)_4$ (0.67 mmol, 1.5 equiv), 75 mg of KO^{t}Bu (1.5 equiv), and 284 mg of $[Li(DIME)_2][Mo(CO)_5I]$ (0.45 mmol). Pale brownish crystals, yield: 274 mg (0.32 mmol, 72%). ^{1}H NMR: δ 3.57 (m, 8H), 3.47 (m, 8H), 3.28 (s, 12H), 0.12 (s, 27H). ^{13}C NMR: δ 221.2, 218.5, 70.2, 69.0, 59.3, 4.8. ^{29}Si NMR: δ −10.9. ^{119}Sn NMR: −618.0. IR: ν_{CO} 2021 (m), 1896 (vs), 1850 (s). $C_{26}H_{55}LiMoO_{11}Si_3Sn$ (849.56) calcd C 36.76 H 6.53; found C 36.41 H 6.44.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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