Preparation, Characterization, and Properties of Various Novel Ionic Derivatives of Pentacarbonyltungsten

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The complexes [Li(DIME)$_2$][W(CO)$_5$L] [L = OCN **2**, NCS **3a**, PPh$_2$ **4**, SiMe$_2$Ph **8**, N(SiMe$_3$)$_2$ **9**, CH$_2$Ph **10**, Si$_6$Me$_{11}$ **11**; DIME = diethylene glycol dimethyl ether] have been prepared by reaction of [Li(DIME)$_2$][W(CO)$_5$I] (**1**) with KOCN, KSCN, NaPPh$_2$, LiSiMe$_2$Ph, LiN(SiMe$_3$)$_2$, PhCH$_2$MgCl, and KSi$_6$Me$_{11}$, respectively. Photochemical ligand substitution in W(CO)$_6$ has been used as an alternative method for the preparation of pentacarbonyl tungstates; [K(DIME)$_2$][W(CO)$_5$NCS] (**3b**), [Na(DIME)$_2$][W(CO)$_5$N$_3$] (**5**), [Li(DIME)$_2$][W$_2$(CO)$_{10}$(μ-H)] (**6**), and [K(DIME)$_2$][W$_2$(CO)$_{10}$(μ-CN)] (**7**) were synthesized in this manner. The molecular structure of [Li(DIME)$_2$][W(CO)$_5$-Si$_6$Me$_{11}$] (**11**) has been determined by X-ray diffraction analysis. The spectral and chemical properties of **2–11** are discussed. Pyrolysis of **11** leads to tungsten silicide and tungsten carbide.

Introduction

For a long time, chemists have been interested in [M^0(CO)$_5$X]$^-$ anions of the Group VIA elements.[1] The fact that they could easily be prepared from M(CO)$_6$ and R$_4$N$^+$X$^-$[2] and their role as starting materials in the synthesis of derivatives of the relevant transition metals attracted considerable attention. In 1963, Abel and co-workers reported the synthesis of pentacarbonylhalometallate anions.[2] They were able to isolate R$_4$N$^+$[M(CO)$_5$X]$^-$ species from reactions of tetraalkylammonium halides with metal hexacarbonyls, but the products were characterized only by infrared spectroscopy. The authors indicated that the goal of isolating and purifying these compounds was frustrated by decomposition. In a recent communication, we described a cation design that should offer improved thermal stability.[3]

Because transition metal silicon compounds are useful precursors for metal silicides, the design of suitable compounds fulfilling this role is very important.[4] The chemistry of ionic transition metal silyl derivatives remains largely unexplored. Only a few compounds of this type derived from monosilanes have been reported.[5]

In our laboratory, compounds of the type [Li(DIME)$_2$][M(CO)$_5$I] [M = W (**1**), Mo] have been synthesized with a modification of the method described by Abel and co-workers. It is very easy to substitute the iodine while retaining the d^6-character of the tungsten, and hence the [W(CO)$_5$I]$^-$ anion represents an interesting and versatile building block. Silyllithium or Grignard reagents react with complexes such as the [W(CO)$_5$I]$^-$ anion. In the present work, we describe the preparation and properties of new compounds including pseudohalide derivatives in order to further development in this field.

Accordingly, we decided to introduce the Si$_6$Me$_{11}$ group into this anionic complex of tungsten. Some transition metal compounds of undecamethylcyclohexasilane have been described in the last few years,[6] but as far as we are aware, only one X-ray structure analysis of a cyclohexasilyl transition metal compound has hitherto been published.[7] We report herein on the synthesis and characterization of [Li(DIME)$_2$][W(CO)$_5$Si$_6$Me$_{11}$] (**11**), for which single-crystal structural data could be obtained.

Among the transition metal silicides, those of tungsten offer excellent oxidation resistance. Consequently, they are being considered as potential high-temperature structural materials, capable of operating well beyond the stable temperature limits possible with superalloys. WSi$_2$ has a high melting temperature of 2165 °C.[8] The fabrication and characterization of W−Si−C phases is a challenge in materials science. It would be very desirable if such high-temperature resistant materials could be prepared from potential precursors such as **11**.

Results and Discussion

The iodide complex **1** was chosen as the starting compound for the synthesis of further [W(CO)$_5$L]$^-$ anions. It was generated by the reaction of W(CO)$_6$ with anhydrous lithium iodide diethyl ether complex (LiI · OEt$_2$) in DIME (diethylene glycol dimethyl ether). Complex **1** reacts with a variety of reagents under substitution of the iodide by the incoming nucleophile (see Schemes 1 and 3). Reactions with potassium cyanate and potassium thiocyanate were performed in DME at room temperature. However, these reactions provide the pseudohalide pentacarbonyltungstates **2** and **3a** only as mixtures with the starting material **1**.

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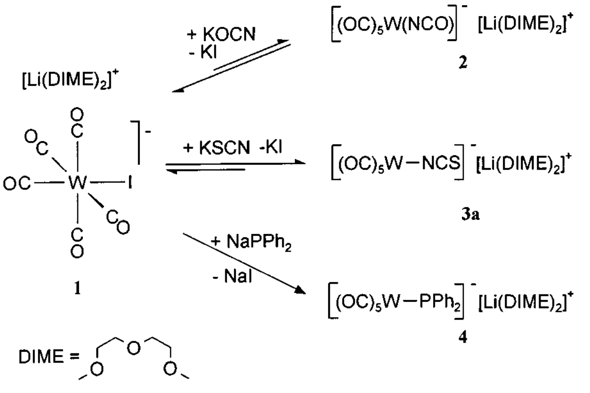


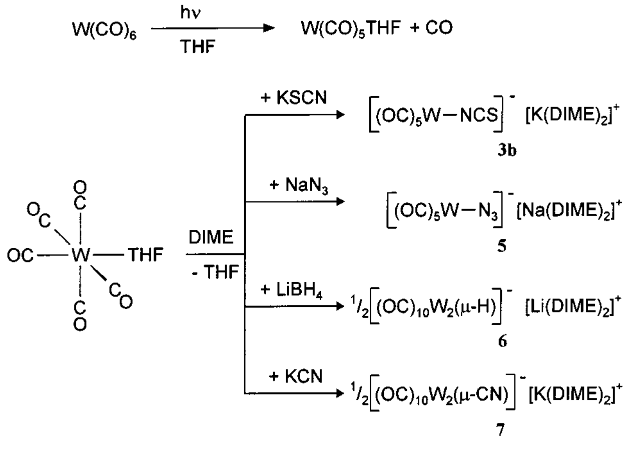
Scheme 1. Substitution of iodide by pseudohalide ions

The infrared spectra of **2** and **3a** feature four bands in the carbonyl stretching region.[9] While only three infrared bands are to be expected for rigorous C_{4v} symmetry, the rather weak band at 1960 cm^{-1} in **3a** can be assigned to the formally infrared inactive B_1 mode.[10] The characteristic modes of the pseudohalides are found at 2245 cm^{-1} (ν_{NCO} in **2**) and 2090 cm^{-1} (ν_{NCS} in **3a**). All attempts to separate **2** and **3a** from the starting compound **1** by recrystallization were unsuccessful. As the product mixture contained **1** as the major and **2** as the minor component, we were unable to obtain a full spectroscopic characterization of **2**. Specifically, it could not be established whether the cyanate ion is coordinated through nitrogen or oxygen at the tungsten atom.

Reaction of **1** with sodium diphenylphosphide in THF/dioxane yielded a red oil, the NMR and IR spectroscopic data of which were consistent with the formula $[Li(DIME)_2][W(CO)_5PPh_2]$. The infrared spectrum features four bands attributable to the $W(CO)_5$ fragment at 2045, 1964, 1936, and 1880 cm^{-1}. In the ^{13}C-NMR spectrum, the signals of the CO carbon atoms are split into doublets due to coupling with the phosphorus atom bound to the $W(CO)_5$ fragment.

The reaction of the tungsten pentacarbonyl THF adduct with pseudohalides represents an alternative route for preparing substitution products of the type $[(OC)_5W-X]^-$ (see Scheme 2). Donor adducts of $W(CO)_5$ have been used previously as reactive intermediates.[11] It is easy to prepare $W(CO)_5THF$ from $W(CO)_6$ by photochemical ligand substitution in THF solution.

Reaction of $W(CO)_5THF$ with KSCN in DIME yields **3b** as a yellow microcrystalline powder. The ^{13}C-NMR spectrum features one signal due to the thiocyanate carbon atom at $\delta = 135.1$ and three signals due to the DIME ligand coordinated at the potassium ion. The signals of the CO carbon atoms are found at $\delta = 197.6$ and 201.6, with an intensity ratio of 1:4. The $^1J(^{13}C,^{183}W)$ coupling constant, which is well resolved in the spectrum of this compound, has a value of 129.2 Hz. The spectroscopic data of compound **3b** correspond well with the data of $[NEt_4][W(CO)_5NCS]$, which was described by Buchner and Schenk.[12] The infrared spectrum of **3b** features four bands in the carbonyl stretching region and one characteristic band for the stretching mode of the NCS ligand as described above. Generally, the thiocyanate ion is able to coordinate to metals through either the nitrogen or the sulfur atom. The high frequency ν_{CN} band indicates that in this case the thiocyanate is coordinated to the tungsten through the nitrogen atom.[13] As mentioned above, the product **3a** formed by nucleophilic substitution of iodide by SCN^- was found to be contaminated with the starting compound **1**; however, the product of the photochemical reaction sequence was free from impurities.



Scheme 2. Anionic derivatives starting from $W(CO)_5THF$

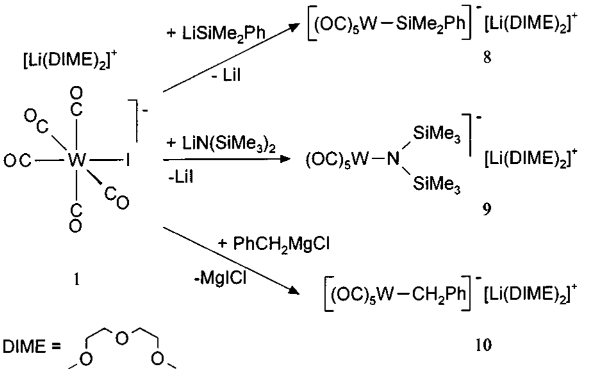
Reaction of potassium selenocyanate (KSeCN) with $W(CO)_5THF$ in DIME failed to give the desired product $[K(DIME)_2][W(CO)_5NCSe]$ in all cases, even at low temperatures. Instead, a finely divided black precipitate was formed, which was identified as elemental selenium by flame photometry and its melting point (215−217°C).

Sodium azide decomposes in solution if it is exposed to strong light. Therefore, the synthesis of $[Na(DIME)_2][W(CO)_5N_3]$ **5** was performed in a two-step sequence. The $W(CO)_5THF$ adduct was prepared photochemically as above. The solution of $W(CO)_5THF$ thus formed was then added dropwise to a solution of sodium azide protected from bright light. The product **5** was found to be air- and light-sensitive and was characterized by its ^{13}C-NMR and IR spectra. The ^{13}C-NMR spectrum features the characteristic 1:4 peak intensity ratio due to the CO carbon atoms at low field, as well as additional signals due to the DIME ligand (for details, see the Experimental Section). Four IR bands are seen in the carbonyl stretching region. One additional weak band at 2080 cm^{-1} can be assigned to the asymmetric stretching mode of the azide group. To assess the stability of compound **5** in solution, the NMR sample was stored for one week at room temperature. When an NMR spectrum was recorded after this period, the ^{13}C-NMR signals of the $[W(CO)_5N_3]^-$ ion could no longer be detected. New signals were seen, which corresponded to $W(CO)_6$ and $[W(CO)_5NCO]^-$. The mechanism of decomposition of $[W(CO)_5N_3]^-$ might be analogous to the Curtius rearrangement.[14] Reactions of metal carbonyls with N_3^- have been studied extensively.[15]

Because the tetrahydroborate ion is isoelectronic with the fluoride, hydroxide, amide, and methyl ions, we were also interested in carrying out reactions of $W(CO)_5THF$ with lithium tetrahydroborate. The ^{13}C-NMR data of **6** reveal the presence of a $W(CO)_5$ unit, since two signals for carbonyl carbon atoms are seen, with an intensity ratio of 1:4. One signal at $\delta = -12.55$ is seen in the ^{1}H-NMR spectrum of **6**. It is split into a triplet due to coupling with two tungsten atoms $[^{1}J(^{1}H,^{183}W) = 42.0\ Hz]$. The chemical shift and coupling constant of this proton are characteristic features of such μ-hydrogen-bridged ditungsten complexes. A few examples have been described previously, which showed very similar chemical shifts and coupling constants as those found for **6**.[16] In addition, we observed signals due to a BH_4-containing side-product in the NMR spectra of **6**, which are most probably attributable to a small amount of $[Li(DIME)_2][W(CO)_4(\mu^2\text{-}BH_4)]$. It was not possible to remove this impurity by recrystallization.

Reaction of $W(CO)_5THF$ with potassium cyanide in THF in the presence of DIME yielded a yellow microcrystalline powder. The ^{13}C-NMR spectrum of this substance reveals the presence of two different $W(CO)_5$ units, since two sets of carbonyl carbon atom signals with an intensity ratio of 1:4 are seen. This pattern is suggestive of the formation of a dimeric CN-bridged complex. The carbon atom signal of the CN group is found at $\delta = 152.5$. Five bands are seen in the carbonyl stretching region of the IR spectrum (see Experimental Section). There is probably a superposition of the absorptions of the two different $W(CO)_5$ fragments. The stretching mode of the cyanide group is observed at 2124 cm^{-1}. Comparable compounds, such as the bridged complex $[PPN][W_2(CO)_{10}(\mu\text{-}CN)]$ and $[NEt_4][W(CO)_5CN]$, show absorptions at 2121 cm^{-1} and 2104 cm^{-1}, respectively.[17] The high wavenumber shift of the ν_{CN} mode, together with the aforementioned NMR data, lead us to the conclusion that the bridged complex $[K(DIME)_2][(OC)_5W(\mu\text{-}CN)W(CO)_5]$ **7** was formed in this reaction.

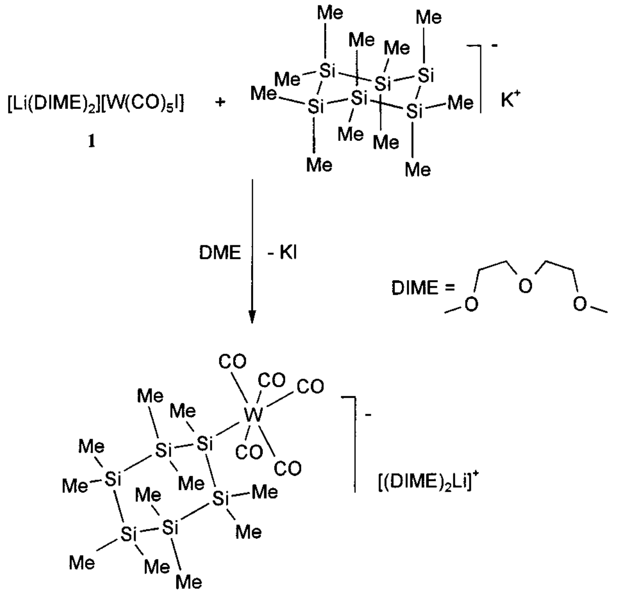
Reaction of $[Li(DIME)_2][W(CO)_5I]$ (**1**) with 1 molar equivalent of lithium bis(trimethylsilyl)amide $Li[N(SiMe_3)_2]$ in tetrahydrofuran gave $[Li(DIME)_2][W(CO)_5N(SiMe_3)_2]$ (**9**). Treatment of **1** with the Grignard reagent $PhCH_2MgCl$ in diethyl ether solution afforded complex **10** (Scheme 3). Complex **8** was prepared by adding a solution of $[Li(DIME)_2][W(CO)_5I]$ (**1**) in DME to an excess of $LiSiMe_2Ph$.



Scheme 3. Syntheses of compounds **8**−**10** by nucleophilic substitution

Complexes **8**, **9**, and **10** were isolated and purified by extraction with pentane. Subsequent recrystallization from dichloromethane gave yellowish solids. Compounds **8**−**11** can be safely dried in vacuo at room temperature without loss of the DIME ligands. Complex **9** proved to be more air-sensitive than compounds **8**, **10**, and **11**. The IR spectra of compounds **8**, **9**, and **10** exhibit three ν_{CO} bands ($2A_1$ and E). These stretching modes are in agreement with data found for the corresponding neutral $M(CO)_5X$ species.[18] The ^{1}H-NMR spectra are indicative of the presence of the DIME ligand (3 signals) and also feature characteristic signals for the substituents at the tungsten atom: $\delta = 7.54$ (m, SiPh), 0.58 ($SiMe_2$) for **8**; $\delta = 0.0$ ($SiMe_3$) for **9**; $\delta = 7.26$ (m, Ph), 1.25 (CH_2) for **10**. The ^{13}C-NMR data of **9** and **10** confirm the presence of the DIME ligand (3 signals) and of the substituents at the tungsten atom (see Experimental Section). The ^{29}Si-NMR peak of **8** at $\delta = -6.13$ gives evidence that one silicon atom is present.

Undecamethylcyclohexasilyl potassium (KSi_6Me_{11}) is well-established as a useful reagent for the synthesis of a variety of transition metal silyl complexes. $[Li(DIME)_2][W(CO)_5Si_6Me_{11}]$ (**11**) was prepared according to Scheme 4. The reaction of one equivalent of $[Li(DIME)_2][W(CO)_5I]$ with KSi_6Me_{11} in DME at ambient temperature resulted in the novel substance $[Li(DIME)_2][W(CO)_5Si_6Me_{11}]$ (**11**).



11

Scheme 4. Synthesis of compound **11**

The cyclohexasilyl derivative **11** was found to be more stable than complexes **8**−**10**. In the solid state, **11** is prone to very slow decomposition in air. It decomposes thermally between 160 and 250°C (TG). It is quite soluble in protic solvents, for example, wet methanol, with no evidence of decomposition in solution detectable in the NMR spectrum. Recrystallization from dichloromethane/pentane at −20°C gave analytically pure yellow crystals of **11** suitable for an X-ray crystallographic study. The structure was solved and refined in space group $P2_1/n$. **11** crystallizes in discrete ionic pairs; the structure of the cation is shown in

Figure 1. The lithium atom is coordinated by two DIME molecules in a distorted octahedral coordination geometry. The tridentate ether molecules chelate the lithium atom with meridional coordination. The Li−O bond lengths in **11** of 2.009 to 2.285 Å are in the same range as the Li−O distances reported for **1**.[3] The structures of these cations are isotypic.

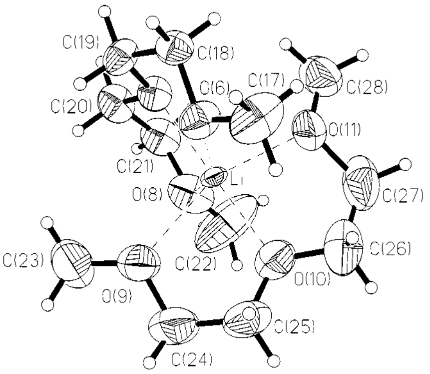


Figure 1. Structure of the $[Li(DIME)_2]^+$ cation in **11**

The structure of the undecamethylcyclohexasilylpentacarbonyltungsten anion is shown in Figure 2. The $[W(CO)_5Si_6Me_{11}]^-$ anion has approximately C_{4v} symmetry with a W−Si bond length of 2.670(2) Å, which is slightly longer than the corresponding distance of 2.614(2) Å in $[PPN][W(CO)_5SiMe_3]$.[19] The tungsten atom resides in an almost regular octahedron with $CO_{eq}-W-CO_{eq}$ angles very close to 90° and a $CO_{ax}-W-Si_{ax}$ angle of 175.3(2)°. The W−C distances for the four equatorial CO ligands range from 2.011 to 2.044 Å, while the W−C bond to the axial CO ligand measures only 1.966(6) Å. This is possibly a reflection of a greater π-back-bonding to the CO ligand situated *trans* to the silyl group. Two of the four equatorial CO′s are bent towards the Si_6Me_{11} ligand, resulting in Si(1)−W−C(4) and Si(1)−W−C(5) angles of 84.6(2) and 80.2(2)°, respectively. The cyclohexasilyl ligand adopts a chair conformation with the $W(CO)_5$ group in an equatorial position.

Crystallographic data and data collection parameters are listed in Table 3. Salient bond lengths and angles are listed in Table 1.

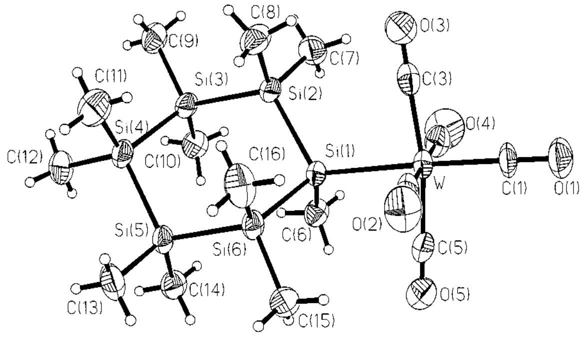


Figure 2. Structure of the $[W(CO)_5Si_6Me_{11}]^-$ anion in **11**

Table 1. Selected bond lengths [Å] and bond angles [°] in **11**

W−C(1)	1.966(6)	Li−O(6)	2.285(10)
W−C(2)	2.017(8)	Li−O(7)	2.046(9)
W−C(3)	2.011(7)	Li−O(8)	2.138(10)
W−C(4)	2.044(8)	Li−O(9)	2.274(11)
W−C(5)	2.016(8)	Li−O(10)	2.009(10)
W−Si(1)	2.670(2)	Li−O(11)	2.118(11)
C(1)−O(1)	1.176(8)	O(10)−Li−O(7)	177.9(6)
C(2)−O(2)	1.151(9)	O(7)−Li−O(8)	79.4(4)
C(3)−O(3)	1.163(9)	O(7)−Li−O(6)	75.5(3)
C(4)−O(4)	1.122(9)	O(7)−Li−O(11)	98.1(4)
C(5)−O(5)	1.162(9)	O(7)−Li−O(9)	105.2(4)
C(4)−W−C(3)	90.2(3)		
C(4)−W−C(5)	89.7(3)		
C(2)−W−C(3)	90.4(3)		
C(2)−W−C(5)	89.8(3)		
C(1)−W−Si(1)	175.3(2)		

In the infrared spectrum of **11**, four metal carbonyl bands at 2020 (w), 1915 (m), 1890 (s), and 1860 (m) cm^{-1} are observed, which are characteristic of a metal pentacarbonyl anion.[2] The IR bands can be assigned to the three IR-active fundamental vibrations ($2A_1 + E$) expected for a C_{4v} metal pentacarbonyl species and to the B_1 vibration, although this is IR inactive for rigorous C_{4v} geometry. This assessment is in agreement with those for the corresponding $M(CO)_5X$ species by Casey.[9a] The ^{1}H-NMR signals of the DIME ligands are observed at δ = 3.40 (s, CH_3) and δ = 3.56 and 3.65 (m, CH_2CH_2). The ^{1}H-NMR resonances for the methyl groups bonded to the silicon appear in the typical range with δ values near to zero (see Table 2).

Table 2. ^{1}H-, ^{13}C-, and ^{29}Si-NMR data of compound **11**[a]

δ^{1}H DIME	Me−Si	δ^{13}C DIME	CO	Si−Me	δ^{29}Si
3.65, 3.56 (CH_2), 3.40 (CH_3)	0.49, 0.22, 0.15, 0.14, 0.11, 0.10	70.75, 69.30 (CH_2), 59.31 (CH_3)	212.16, 207.67	−2.14, −3.18, −3.79, −4.19, −4.85, −5.95, −6.79	−75.7, −42.0, −40.7, −30.7

[a] Recorded in $CDCl_3$ at 25°C; data in ppm are relative to Me_4Si at δ = 0.0.

The fact that six signals are observed indicates that the silicon ring adopts a chair conformation. Single-crystal structure analysis confirms this assumption. The ^{29}Si-NMR spectrum of compound **11** features four resonances for the *cyclo*-silyl ligand bonded at the metal atom (Table 2). The ^{29}Si-NMR chemical shifts for the anion $[W(CO)_5Si_6Me_{11}]^-$ move progressively to higher field relative to the shifts for the analogous $[Mo(CO)_5Si_6Me_{11}]$,[7] which is the expected trend for complexes of this type.[20] The ^{13}C-NMR data of **11** are in agreement with the proposed structure (Table 2).

Pyrolysis of $[Li(DIME)_2][W(CO)_5Si_6Me_{11}]$ (11)

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed using a MOM Budapest Derivato-

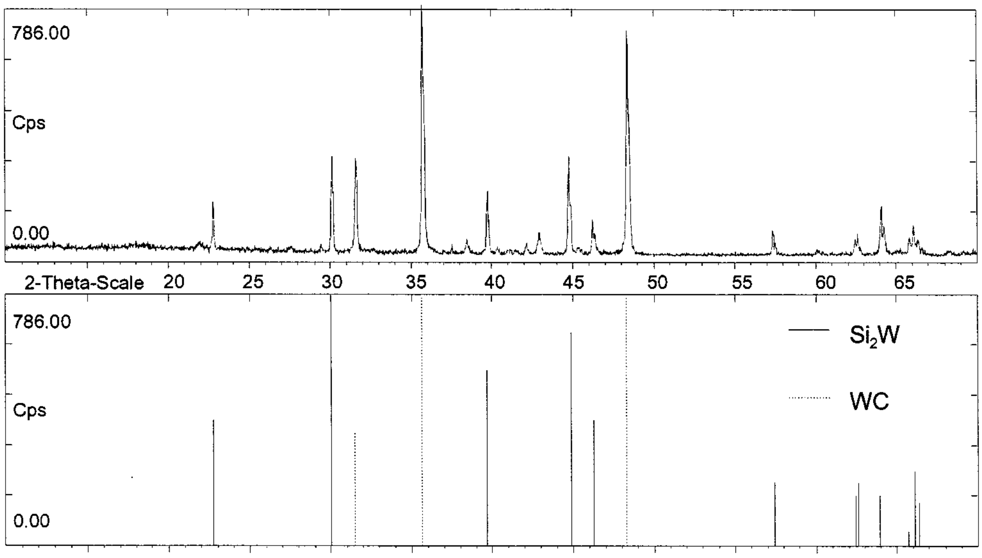


Figure 3. Comparison of the XRD pattern of the pyrolyzed sample of $[Li(DIME)_2][W(CO)_5Si_6Me_{11}]$ (**11**) (top) with powder diffraction files: 11−0195 WSi_2, 25−1047 WC (bottom)

graph. An atmosphere of Ar (at a flow rate of 200 mL/min^{-1}) and a corund open pan were used for the experiment. A sample of **11** was heated at a rate of 5 °C min^{-1} up to 1400°C. Decomposition started at 160°C and reached a maximum rate at 230°C. The mass lost amounted to 29% of the sample mass at 250°C, which corresponds to the loss of 2 DIME molecules per formula unit. The following substances could be detected by GC analysis: CO at 400−1000°C, CH_4 at 500−800°C, and H_2 < 1200°C. X-ray analysis after the pyrolysis indicated that the product was mainly a mixture of WSi_2 and WC (Figure 3).

Conclusions

In conclusion, $[Li(DIME)_2][W(CO)_5I]$ (**1**) reacts readily with nucleophilic reagents such as alkyls and organoamides, -phosphides, and -silyls. The preferred site of reactivity is the W−I bond. Thus, it is evident that **1** is a highly useful reagent for preparing a wide variety of $W(CO)_5$ derivatives. Reaction of **1** with pseudohalides leads to mixtures of starting material and product. This is probably due to the weak nucleophilicity of the pseudohalides. Therefore, the salt elimination route is not suitable for preparing pure pseudohalide−pentacarbonyltungstate derivatives. However, it is possible to obtain these derivatives by using the photochemical reaction sequence via $W(CO)_5THF$. The X-ray crystal structure of **11** confirms that the cyclohexasilyl ring is bound to the tungsten. The production of pure tungsten silicide is a challenging task with potential applications in materials science; thus it is noteworthy that thermolysis of **11** produces WSi_2 together with WC. Further investigations concerning the synthesis and thermal decomposition pathways of metal−silicon compounds are currently under way.

Experimental Section

All preparative work and sample handling was carried out under Ar with dry glassware and in dry solvents. Diethylene glycol dimethyl ether (DIME) was repeatedly distilled from freshly cut Na until effervescence was no longer observed. It was distilled once more and then stored in a sealed flask in a drybox prior to use. Starting materials $W(CO)_6$ and $Li[N(SiMe_3)_2]$ were purchased from Fluka Chemie AG. $W(CO)_6$ was vacuum-sublimed prior to use. All alkaline pseudohalides were dried in vacuo for 4 h prior to use. The syntheses of $PhCH_2MgCl$,[21] $LiSiMe_2Ph$,[22] and KSi_6Me_{11}[23] were carried out according to established procedures.

NMR spectra were recorded on a Bruker MSL 200 spectrometer. − Elemental analyses were performed on a CHN-O-Rapid (Heraeus). The carbon values recorded were systematically lower due to carbide formation. − Infrared spectra were recorded on a Specord 75 IR instrument in the range 4000 to 400 cm^{-1} for samples pressed into a KBr disc. − X-ray powder diffraction patterns were obtained using a Siemens D5000 diffractometer with Cu-K_α radiation.

Synthesis of $[Li(DIME)_2][W(CO)_5I]$ (1): A sample of $W(CO)_6$ (5.0 g, 0.014 mol) was added to a solution of $LiI{\cdot}Et_2O$ (3.0 g, ≈ 0.014 mol) in diethylene glycol dimethyl ether (20 mL). The mixture was heated at 80°C for 2 days, during which it became bright yellow. IR monitoring showed the formation of a species with a ν(CO) pattern typical for $[W(CO)_5L]$ species: $\tilde{\nu}$ = 1950, 1915, 1850 cm^{-1}. The solvent was removed in vacuo to leave a yellow residue. This was redissolved in dichloromethane and then treated with *n*-pentane to give yellow crystals of **1** (isolated yield 93.7%). − ^1H NMR ($CDCl_3$/TMS): δ = 3.75, 3.64, 3.45 (DIME). − ^{13}C NMR ($CDCl_3$/TMS): δ = 202.62, 197.18 (CO), 70.58, 69.37, 59.54 (DIME). − $C_{17}H_{28}ILiO_{11}W$ (697.8): calcd. C 21.88, H 3.02; found C 21.74, H 3.10.

Synthesis of $[Li(DIME)_2][W(CO)_5NCO]$ (2) and $[Li(DIME)_2][W(CO)_5NCS]$ (3a): $[Li(DIME)_2][W(CO)_5I]$ (**1**) (0.003 mol) and an equimolar amount of KOCN or KSCN, respectively, were suspended in DME and the mixture was stirred for 24 h at room temperature. The solvent was then evaporated in vacuo, and the remaining solid was washed with *n*-pentane and taken up in dichloromethane. The resulting suspension was filtered to remove insoluble alkaline halides. Addition of *n*-pentane to the clear solution and cooling to 5°C led to the deposition of **3a** as a yellow solid. − ^{1}H NMR ($CDCl_3$/TMS): δ = 3.74, 3.63, 3.46 (DIME). − ^{13}C NMR ($CDCl_3$/TMS): δ = 201.4 (CO_{ax}), 197.6 (CO_{eq}), 135.4 (NCS), 70.7, 69.3 (DIME). − IR (KBr): ν_{CO} = 2060 (w), 1960 (w, sh), 1910 (s), 1860 (m) cm^{-1}; ν_{NCS} = 2090 (w) cm^{-1}. The spectra of **3a** prepared by this method show additional signals attributable to **1**.

Synthesis of [K(DIME)$_2$][W(CO)$_5$NCS] (3b): W(CO)$_5$THF was prepared immediately prior to use by irradiating a solution of $W(CO)_6$ (2.5 g, 0.0071 mol) in dry THF (concentration about 0.1 mol/L) under Ar for 4 h with a high-pressure Hg lamp (160 W).[24] Meanwhile, a solution of potassium thiocyanate (0.69 g, 0.0071 mol) in DIME (15 mL) was prepared. The synthesized tungsten pentacarbonyl THF adduct was then added to this solution over a period of 10 min. The resulting mixture was stirred for 24 h at room temperature. The solvent and excess $W(CO)_6$ were then removed in vacuo. Pentane was added, the product was isolated by filtration, washed with *n*-pentane, and dried in vacuo to afford **3b** as a yellow microcrystalline powder. − ^{1}H NMR ($CDCl_3$/TMS): δ = 3.66, 3.59, 3.42 (DIME). − ^{13}C NMR ($CDCl_3$/TMS): δ = 201.6 (CO_{ax}), 197.6 [$^1J(^{13}C,^{183}W)$ = 129.2 Hz (CO_{eq})], 135.1 (NCS), 71.5, 69.9, 59.0 (DIME). − IR (KBr): ν_{CO} = 2066 (w), 1975 (w, sh), 1918 (s), 1864 (m) cm^{-1}; ν_{NCS} = 2093 (w) cm^{-1}.

Synthesis of [Li(DIME)$_2$][W(CO)$_5$PPh$_2$] (4): [Na(dioxane)$_n$][PPh$_2$] was prepared according to the method of Issleib.[25] [Li(DIME)$_2$][W(CO)$_5$I] (2.54 g, 0.0035 mol) was dissolved in THF (40 mL) and a solution of [Na(dioxane)$_n$][PPh$_2$] (ca. 0.01 mol) in THF/dioxane (23 mL) was added at −76°C. The resulting mixture was stirred for a period of 10 h, during which the colour changed from yellow/orange to red. DIME (20 mL) was then added to the reaction mixture. The resulting suspension was filtered and the solvents were evaporated in vacuo. All attempts at crystallization led only to a clear red oil **4**. − ^{1}H NMR ($CDCl_3$/TMS): δ = 7.73, 7.23, 7.04 (Ph), 3.75, 1.86 (THF), 3.72, 3.62, 3.44 (DIME). − ^{13}C NMR ($CDCl_3$/TMS): δ = 204.7 [$^2J(^{13}C,^{31}P)$ = 12.9 Hz (CO_{ax})], 201.2 [$^1J(^{13}C,^{183}W)$ = 123.9 Hz (CO_{eq})], 151.2 [$^1J(^{13}C,^{31}P)$ = 12.3 Hz (C_{ipso})], 133.4 [$^2J(^{13}C,^{31}P)$ = 10.9 Hz (C_{ortho})], 126.8 [$^3J(^{13}C,^{31}P)$ = 7.7 Hz (C_{meta})], 125.5 (C_{para}), 71.0, 69.7, 59.4 (DIME), 68.0, 25.6 (THF). − IR (THF): ν_{CO} = 2045 (w), 1964 (w, sh), 1936 (s), 1880 (m) cm^{-1}.

Synthesis of [Na(DIME)$_2$][W(CO)$_5$N$_3$] (5): W(CO)$_5$THF was prepared as described above. Sodium azide (0.46 g, 0.0071 mol) was dissolved in methanol (60 mL) and THF (80 mL) and then DIME (20 mL) was added to the solution. The tungsten pentacarbonyl THF adduct was added dropwise to this mixture with stirring. After stirring for 10 h, the solvents were evaporated in vacuo and excess *n*-pentane was added to the yellow residue. The resulting yellow solid was collected by filtration and washed with *n*-pentane. The solid residue was redissolved in THF, the resulting solution was filtered, and *n*-pentane was added to the filtrate to crystallize the product. The product was found to be sensitive to light and air. It decomposes in CH_2Cl_2 and $CHCl_3$. In solution, the product converts into $W(CO)_6$ and [Na(DIME)$_2$][W(CO)$_5$NCO]. − ^{1}H NMR (CD_3OD/TMS): δ = 3.62, 3.54, 3.36 (DIME). − ^{13}C NMR (CD_3OD/TMS): δ = 203.4 (CO_{ax} N_3), 199.8 [$^1J(^{13}C,^{183}W)$ = 129.3 Hz (CO_{eq} N_3)], 202.2 (CO_{ax} OCN), 199.4 (CO_{eq} OCN), 192.4 [$W(CO)_6$], 72.9, 71.3, 59.1 (DIME). − IR (THF): ν_{CO} = 2040 (w), 1965 (s), 1910 (s), 1865 (m) cm^{-1}, ν_{N3} = 2080 (w) cm^{-1}; ν_{OCN} = 2245 (w) cm^{-1}.

Synthesis of [Li(DIME)$_2$][W$_2$(CO)$_{10}$(μ-H)] (6): W(CO)$_5$THF was prepared as described above. $LiBH_4$ (0.185 g, 0.0085 mol) was dissolved in a mixture of THF (60 mL) and DIME (20 mL). The tungsten pentacarbonyl THF adduct was added dropwise to the $LiBH_4$ solution over a period of 15 min. at 0°C and the reaction mixture was stirred for 8 h. After evaporation of the solvent, the residue was redissolved in THF, the resulting solution was filtered, and *n*-pentane was added to the filtrate. The clear solution was cooled to −20°C to crystallize the product. − ^{1}H NMR (CD_3CN/TMS): δ = 3.61, 3.52, 3.35 (DIME), −12.55 [$^1J(^1H,^{183}W)$ = 42.0 Hz (WH)]. − ^{13}C NMR (CD_3CN/TMS): δ = 202.0 (CO_{ax}), 199.7 [$^1J(^{13}C,^{183}W)$ = 124.2 Hz (CO_{eq})], 71.7, 70.2, 59.1 (DIME); impurities: $LiBH_4$: ^{1}H NMR (CD_3CN/TMS): δ = −0.46 [quadruplet, $^1J(^1H,^{11}B)$ = 83.2 Hz]. − ^{11}B NMR (CD_3CN/$BF_3 \cdot Et_2O$): δ = −39.43; [Li(DIME)$_2$][W(CO)$_4$(μ^2-BH$_4$)]: ^{1}H NMR (CD_3CN/TMS): δ = −11.84 (weak). − ^{13}C NMR (CD_3CN/TMS): δ = 201.4, 200.8 (CO, weak). − IR (KBr): ν_{CO} = 2071 (w), 2041 (m), 2014 (w), 1966 (m, sh), 1936 (s), 1873 (s, br), 1839 (m), 1802 (w, sh) cm^{-1}; ν_{BH} = 2246 (s, br) cm^{-1}.

Synthesis of [K(DIME)$_2$][W$_2$(CO)$_{10}$(μ-CN)] (7): W(CO)$_5$THF was prepared as described above. Potassium cyanide (0.55 g, 0.0085 mol) was dissolved in a mixture of THF (40 mL) and DIME (20 mL). The tungsten pentacarbonyl THF adduct was then added dropwise to the potassium cyanide solution over a period of 15 min. at 0°C. The resulting mixture was stirred for 4 h and then the remaining traces of KCN were filtered off. The solvent was removed under reduced pressure, *n*-pentane was added to the residue, and the precipitate was collected by filtration. The green-yellow solid was taken up in THF and filtered, and the collected solid was washed with *n*-pentane and dried in vacuo to afford a yellow microcrystalline powder **7**. The product was found to be sensitive to light and air. − ^{1}H NMR ($CDCl_3$/TMS): δ = 3.65, 3.59, 3.42 (DIME). − ^{13}C NMR ($CDCl_3$/TMS): δ = 202.3 (CO_{ax} NC), 197.9 [$^1J(^{13}C,^{183}W)$ = 129.0 Hz (CO_{eq} NC)], 200.2 (CO_{ax} CN), 196.9 [$^1J(^{13}C,^{183}W)$ = 125.0 Hz (CO_{eq} CN)], 152.5 (CN), 71.5, 70.0, 59.0 (DIME). − IR (THF): ν_{CO} = 2057 (w), 1971 (sh), 1934 (s), 1900 (m), 1880 (m); ν_{CN} = 2124 (w). − UV/vis (EtOH): λ_{max} (ε/$l \cdot mol^{-1} \cdot cm^{-1}$) = 230 (80870), 248 (54515), 338 (3947), 362 (4021), 384 (2740) nm.

Synthesis of [Li(DIME)$_2$][W(CO)$_5$SiMe$_2$Ph] (8): A solution of **1** (0.005 mol, 3.49 g) in DME (20 mL) was added slowly, over a period of 4 h, to an excess of $LiSiMe_2Ph$ (0.006 mol) in THF. The mixture was stirred for further 3 h and then the solvents were removed in vacuo. The remaining orange solid was redissolved in dichloromethane (20 mL) and this solution was filtered. Pentane (50 mL) was added to the clear yellow filtrate and complex **8** crystallized on cooling. The mother liquor was removed by means of a cannula. The residue was washed with pentane, dried in a stream of argon, and then at oil-pump vacuum to afford 2.8 g (79%) of **8** as a yellow solid. − ^{1}H NMR ($CDCl_3$/TMS): δ = 7.54 (SiPh), 3.68, 3.59, 3.43 (DIME), 0.58 ($SiMe_2$). − ^{29}Si NMR (dichloromethane/D_2O): δ = −6.13. − IR ($CHCl_3$): ν_{CO} = 1925, 1887, 1815 cm^{-1}. − $C_{25}H_{39}LiO_{11}SiW$ (706.1): calcd. C 42.52, H 5.51; found C 41.86, H 5.53.

Synthesis of [Li(DIME)$_2$][W(CO)$_5$N(SiMe$_2$)$_2$] (9): A solution of **1** (0.005 mol, 3.49 g) in THF was cooled to −76°C, whereupon 5 mL (0.005 mol) of a 1 M solution of Li[N(SiMe$_3$)$_2$] in THF was added. The mixture was stirred for 2 h while being allowed to warm to room temperature. After evaporation of the solvent, the residue was redissolved in DME (20 mL) and the resulting solution was filtered. Pentane was added to the clear yellow solution to start the crystallization. After cooling, the yield of **9** was 1.4 g (38.3%). The product was recrystallized from dichloromethane/pentane to afford an orange solid. − ^{1}H NMR ($CDCl_3$): δ = 3.71, 3.60, 3.40 (DIME), 0.00 ($SiMe_3$). − ^{13}C NMR ($CDCl_3$): δ = 205.67, 197.04 (CO), 70.43, 69.19, 59.45 (DIME), 2.39 ($SiMe_3$). − IR ($CDCl_3$): ν_{CO} = 1928, 1874, 1855 cm^{-1}. − $C_{19}H_{46}LiO_{11}Si_2W$ (731.32): calcd. C 31.20, H 6.28; found C 30.76, H 6.22.

Synthesis of [Li(DIME)$_2$][W(CO)$_5$CH$_2$Ph] (10): $PhCH_2MgCl$ (0.005 mol, 12.8 mL of a 0.4 M Grignard solution) was treated with a solution of 0.005 mol (3.49 g) of **1** in DME (20 mL) and the resulting mixture was stirred for 2 h at room temperature. Subsequent evaporation of the solvents left a yellow solid, which was taken up in dichloromethane (30 mL) under cooling. This mixture was then filtered and the filtrate was concentrated to dryness to afford 1.7 g (51.4%) of **10**. − ^{1}H NMR ($CDCl_3$/TMS): δ = 7.26 (Ph), 3.74, 3.64, 3.44 (DIME), 1.25 (CH_2). − ^{13}C NMR ($CDCl_3$/TMS): δ = 138.78, 130.68, 128.73, 126.48 (Ph), 70.85, 69.58, 59.49 (DIME), 45.58 (CH_2). − IR ($CDCl_3$): ν_{CO} = 1934, 1916, 1885 cm^{-1}. − $C_{24}H_{35}LiO_{11}W$ (662.04): calcd. C 43.54, H 5.28; found C 43.45, H 5.24.

Synthesis of [Li(DIME)$_2$][W(CO)$_5$Si$_6$Me$_{11}$] (11): KSi_6Me_{11} was prepared from *cyclo*-Si_6Me_{12} (2.6 g, 0.007 mol) and $KOC(CH_3)_3$ (0.78 g, 0.007 mol) in DME (10 mL) and then added dropwise at room temperature over a period of 15 min. to a stirred solution of **1** (5.08 g, 0.007 mol) in DME (20 mL). After stirring the mixture at room temperature for 12 h, the solvent was removed under reduced pressure. Then, a mixture of *n*-pentane/dichloromethane (1:1, 20 mL) was added to the residue and the precipitate was filtered off. The filtrate was concentrated to dryness under reduced pressure and *n*-pentane (20 mL) was added to the residue to produce a slightly yellow suspension. An orange oil separated from the mixture after addition of approximately 10 drops of dichloromethane. Yellow crystals of **11** deposited from the oil after 1 d at −20°C. Yield: 4.82 g (74%). The NMR data are shown in Table 2. − IR (nujol): ν_{CO} = 2020 (w), 1915 (m), 1890 (s), 1860 (m). − $C_{28}H_{61}LiO_{11}Si_6W$: calcd. C 36.04, H 6.58; found C 35.91, H 6.74.

Experimental Procedure for X-ray Crystallography: A suitable single crystal of **11** was mounted on a glass fibre under paraffin oil and transferred to the diffractometer. Diffraction measurements were made on an Enraf−Nonius CAD-4 diffractometer at −83°C using graphite-monochromated Cu-K_α radiation (λ = 1.5418 Å) with ω−2θ scans. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and allowed to ride on their corresponding carbon atoms. An empirical absorption correction was performed on the basis of ψ scans. Crystallographic data and the results of the refinements are summarized in Table 3. Full crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100623. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 3. Crystal data and structure refinement for [Li(DIME)$_2$][W(CO)$_5$Si$_6$Me$_{11}$] (**11**)

	11
Empirical formula	$C_{28}H_{61}LiO_{11}Si_6W$
Formula weight	933.10
Temperature	190(2) K
Wavelength	1.54180 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 19.116(2) Å, α = 90° b = 14.308(2) Å, β = 96.810(10)° c = 20.264(3) Å, γ = 90°
Volume	4639.7(11) Å^3
Z	4
Density (calculated)	1.336 Mg/m^3
Absorption coefficient	6.468 mm^{-1}
F(000)	1912
Crystal size	0.4 × 0.3 × 0.15 mm
θ range for data collection	3.32−74.77°
Index ranges	$-20 \le h \le 20$, $0 \le k \le 17$, $-25 \le l \le 9$
Reflections collected	14335
Independent reflections	9517 [R(int) = 0.0944]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	9517/0/439
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0575, wR_2 = 0.1453
R indices (all data)	R_1 = 0.0787, wR_2 = 0.1609
min. transmission	0.6843
max transmission	0.9998
Largest diff. peak and hole	2.051 and −3.071 e·Å^{-3}

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