

# [Li(dime)<sub>2</sub>][W(CO)<sub>5</sub>I] as a novel synthon for the preparation of silyl, amino and organyl derivatives of pentacarbonyl tungsten (dime = diethylene glycol dimethyl ether)

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**The one-pot reactions of M(CO)<sub>6</sub> with dime in the presence of LiI·Et<sub>2</sub>O give [Li(dime)<sub>2</sub>][M(CO)<sub>5</sub>I] (M = W 1, Mo 2); the reaction of 1 with LiSiMe<sub>2</sub>Ph, LiN(SiMe<sub>3</sub>)<sub>2</sub> and PhCH<sub>2</sub>MgCl affords the novel complexes [Li(dime)<sub>2</sub>][W(CO)<sub>5</sub>R] [R = SiMe<sub>2</sub>Ph 3a, N(SiMe<sub>3</sub>)<sub>2</sub> 3b, CH<sub>2</sub>Ph 3c].**

Pentacarbonyl (alkyl- and aryl-alkoxycarbene) group 6 metal complexes have attracted much interest as useful reagents for organic synthesis.<sup>1,2</sup> The production of water-soluble catalysts is an area of considerable current interest.<sup>3</sup> The role of ionic metal complexes as active species in homogeneous catalysed reactions is well documented.<sup>4,5</sup> A simple chemical procedure for the synthesis of anionic monosubstituted derivatives of transition-metal carbonyls should be highly interesting, especially to generate coordinatively unsaturated species with potential applications in catalysis. The design of simple synthetic routes for these compounds is therefore very important.

Compounds containing the [M(CO)<sub>5</sub>X]<sup>-</sup> ion (M = Mo, W; X = Br) have been synthesized *via* difficult routes.<sup>6</sup> We found a very simple way to generate such complexes. The one-pot

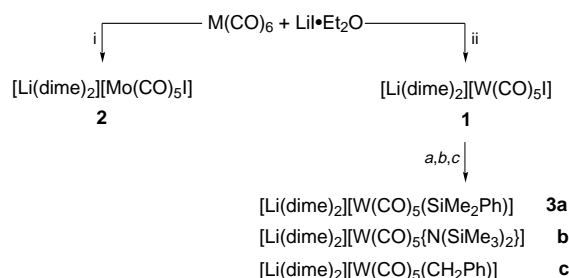
reaction of W(CO)<sub>6</sub> with dime in presence of LiI·Et<sub>2</sub>O leads to the hitherto unknown [Li(dime)<sub>2</sub>][W(CO)<sub>5</sub>I] **1** (Scheme 1).

The X-ray crystal structure analysis of **1** reveals the molecular structure shown in Fig. 1.† The structure was solved and refined in space group *P*2<sub>1</sub>/*c*. The lithium atom is coordinated by two molecules of dime with a distorted octahedral coordination geometry. The [W(CO)<sub>5</sub>I]<sup>-</sup> anion has nearly C<sub>4v</sub> symmetry with a W–I bond length of 2.871 Å.

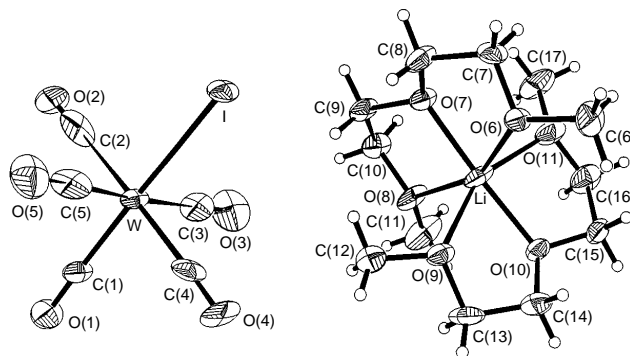
First experimental studies showed a surprising stability of **1** during dissolving tests in protic solvents. We could observe only very slow decomposition in the air. The same synthetic route was applied to the synthesis of [Li(dime)<sub>2</sub>][Mo(CO)<sub>5</sub>I] **2**.‡

The [W(CO)<sub>5</sub>I]<sup>-</sup> anion represents an interesting building block. It is very easy to substitute the iodine retaining the d<sup>6</sup> character of tungsten. We used the [W(CO)<sub>5</sub>I]<sup>-</sup> anion as a starting tungsten complex for reactions with different nucleophilic reagents to substitute the iodine. For example, complex **1** reacts with LiSiMe<sub>2</sub>Ph to give compound **3a**, and with a lithium amide (*b*) to give compound **3b**.§ Treatment of **1** with a Grignard reagent (*c*) produces complex **3c** (Scheme 1).§ All new compounds were isolated and purified by extraction with pentane and subsequent recrystallization with dichloromethane.

Further studies to extend the scope of these reactions to molybdenum carbonylates and to other nucleophilic reagents, as well as studies on the reactivity of the obtained products are under way.



**Scheme 1** Reagents and conditions: i, M = Mo, dime, 80 °C, –CO, –Et<sub>2</sub>O, 70%; ii, M = W, dime, 80 °C, –CO, –Et<sub>2</sub>O, 80%; a, LiSiMe<sub>2</sub>Ph, dime, 0 °C, –LiI, 64%; b, LiN(SiMe<sub>3</sub>)<sub>2</sub>, THF, 0 °C, –LiI, 84%; c, CH<sub>2</sub>PhMgCl, Et<sub>2</sub>O, 0 °C, –MgClI, 77%



**Fig. 1** Crystal structure of **1**. Selected bond distances (Å) and angles (°): W–I 2.871(2), W–C(1) 1.97(2), W–C(2), C(3), C(4), C(5) 2.04(2)–2.10(2); I–W–C(1) 178.7(3), I–W–C(2), C(3), C(4), C(5) 86.7(4)–91.2(4); Li–O 2.00(2)–2.22(2).

## Footnotes

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† All new compounds gave satisfactory analytical data.

‡ Crystal data for [Li(dime)<sub>2</sub>][W(CO)<sub>5</sub>I] **1** (yellow crystal from CH<sub>2</sub>Cl<sub>2</sub>–pentane): C<sub>17</sub>H<sub>28</sub>LiO<sub>11</sub>W, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 14.610(3), *b* = 13.232(1), *c* = 14.658(2) Å, β = 113.01(2)°, *U* = 2608.3(6) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.849 g cm<sup>-3</sup>, μ = 17.927 mm<sup>-1</sup>, *F*(000) = 1392. A single crystal of approximate dimensions 0.15 × 0.2 × 0.2 mm was mounted on a glass fibre under paraffin oil and transferred to the diffractometer. Data were collected at –83 °C on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu–Kα 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*<sup>2</sup> with anisotropic thermal parameters. Hydrogen atoms were calculated and allowed to ride on their corresponding carbon atoms. *R* = 0.0772 for 4111 reflections (*F*<sub>o</sub> > 2σ*F*<sub>o</sub>) and 0.0970 for all 5352 reflections, GOF = 1.005. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/411.

§ Experimental details and selected spectroscopic data: **1**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, SiMe<sub>4</sub>) δ 3.68, 3.57, 3.37 (dime); <sup>13</sup>C NMR (CDCl<sub>3</sub>, SiMe<sub>4</sub>) δ 202.4, 196.97 (CO), 70.20, 68.99, 59.40 (dime); IR (CDCl<sub>3</sub>, ν<sub>CO</sub>/cm<sup>-1</sup>) 1975, 1915, 1850. **2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, SiMe<sub>4</sub>) δ 3.71, 3.59, 3.41 (dime); <sup>13</sup>C NMR (CDCl<sub>3</sub>, SiMe<sub>4</sub>) δ 219.59, 204.56 (CO); 70.49, 69.25, 59.44 (dime); IR (CDCl<sub>3</sub>, ν<sub>CO</sub>/cm<sup>-1</sup>) 1982, 1933, 1859. **3a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, SiMe<sub>4</sub>) δ 7.54 (SiPh); 3.68, 3.59, 3.43 (dime); 0.58 (SiMe<sub>2</sub>); <sup>29</sup>Si NMR (CH<sub>2</sub>Cl<sub>2</sub>-D<sub>2</sub>O) δ –6.13; IR (CHCl<sub>3</sub>, ν<sub>CO</sub>/cm<sup>-1</sup>) 1925, 1887, 1815. **3b**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.71, 3.60, 3.40 (dime); 0.00 (SiMe<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)

$\delta$  205.67, 197.04 (CO); 70.43, 69.19, 59.45 (dime); 2.39 (SiMe<sub>3</sub>); IR (CDCl<sub>3</sub>,  $\nu_{\text{CO}}$ /cm<sup>-1</sup>) 1928, 1874, 1855. **3c**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, SiMe<sub>4</sub>)  $\delta$  7.26 (Ph); 3.74, 3.64, 3.44 (dime); 1.25 (CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, SiMe<sub>4</sub>)  $\delta$  138.78, 130.68, 128.73, 126.48 (Ph); 70.85, 69.58, 59.49 (dime); 45.58 (CH<sub>2</sub>); IR (CDCl<sub>3</sub>,  $\nu_{\text{CO}}$ /cm<sup>-1</sup>) 1934, 1916, 1885.

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