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Letters to the Editor

New tungsten carbyne complexes containing the triphenylgermyl and triphenylstannyl groups at the carbyne carbon atom $(Bu^tO)_3W\equiv C—EPh_3$ (E = Ge, Sn)

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Transition metal carbene complexes are widely used as catalysts in various metathesis reactions of olefins.[1] Metathesis of acetylenic hydrocarbons with the use of transition metal carbyne complexes has been much less studied.[2] The effect of the structure of carbyne complexes, in particular, the influence of the heteroatom at the carbyne carbon atom, on their catalytic activity in metathesis of acetylenes remains virtually unknown.

It is known[3,4] that the reactions of dimolybdenum and ditungsten hexaalkoxides with some acetylenic hydrocarbons and functionally substituted acetylenes afford alkylidyne complexes of the corresponding transition metals. We used this procedure for the preparation of new tungsten carbyne complexes $(Bu^tO)_3W\equiv C—GePh_3$ (**1**) and $(Bu^tO)_3W\equiv C—SnPh_3$ (**2**).

$$(Bu^tO)_6W_2 + Ph_3GeC\equiv CPr \xrightarrow{i} \mathbf{1} + \underset{\mathbf{3}}{(Bu^tO)_3W\equiv CPr}$$

$$(Bu^tO)_6W_2 + Ph_3SnC\equiv CEt \xrightarrow{ii} \mathbf{2} + \underset{\mathbf{4}}{(Bu^tO)_3W\equiv CEt}$$

i. C_5H_{12}, 20 °C, 0.5 h. *ii.* C_5H_{12}, 20 °C, 1 h.

The course of the reactions was monitored by ^1H NMR spectroscopy and the reactions were demonstrated to afford complexes **1** and **2** and known[3] alkylidyne derivatives **3** and **4**, respectively, in virtually quantitative yields. After separation of compounds **3** or **4** by vacuum sublimation, complexes **1** and **2** were isolated in 65.5% and 55.0% yields, respectively, as air-unstable colorless crystalline compounds, which are readily soluble in THF, benzene, and toluene and are moderately soluble in pentane. It should be noted that disubstituted acetylene $Ph_3GeC\equiv CGePh_3$ virtually did not react with $(Bu^tO)_6W_2$ under analogous conditions. According to the published data,[3] symmetrical heteroatom-containing acetylenes $Me_3EC\equiv CEMe_3$ (E = Si or Sn) are also inert with respect to the above-mentioned tungsten alkoxide.

It was demonstrated by ^1H NMR spectroscopy that metathesis of $EtC\equiv CPh$ at ~20 °C was induced by catalytic amounts of compound **2** in a toluene solution. The equilibrium was established in 2—3 min and the equilibrium mixture contained 20 mol.% of $EtC\equiv CEt$, 20 mol.% of $PhC\equiv CPh$, and 60 mol.% of $EtC\equiv CPh$. It is known[3,5] that metathesis of $EtC\equiv CPh$ under analogous conditions

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in the presence of the carbyne complex $(\mathrm{Bu^tO})_3\mathrm{W{\equiv}CBu^t}$ proceeded much more slowly and the equilibrium was reached in 4 h.

All experiments were carried out in evacuated sealed tubes with the use of the standard Schlenk techniques. The solvents were thoroughly dried and degassed. The reagents, *viz.*, $(\mathrm{Bu^tO})_6\mathrm{W_2}$,[6] $\mathrm{Ph_3GeC{\equiv}CPr}$,[7] $\mathrm{Ph_3SnC{\equiv}CEt}$,[8] and $\mathrm{EtC{\equiv}CPh}$,[9] were synthesized according to known procedures. The IR spectra were measured on a Perkin—Elmer-577 spectrometer. The samples were prepared under argon as Nujol mulls. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded on a Bruker DPX-200 spectrometer.

Triphenylgermylmethylidynetris(*tert*-butoxy)tungsten (1). A colorless solution of $\mathrm{Ph_3GeC{\equiv}CPr}$ (0.41 g, 1.1 mmol) in pentane (5 mL) was added to a dark-red solution of $(\mathrm{Bu^tO})_6\mathrm{W_2}$ (0.87 g, 1.08 mmol) in pentane (15 mL). The reaction mixture was kept at ~20 °C for 1 h after which the solution turned pale-brown. According to the ^{1}H NMR spectroscopic data, the reaction mixture contained only equivalent amounts of complexes **1** and **3**. Pentane was removed by evaporation *in vacuo*. Compound **3** was isolated from the solid residue by vacuum sublimation (40—50 °C, 10^{-2}—10^{-3} Torr, 4 h) in a yield of 0.40 g (80.5%) as colorless crystals. The data from ^{1}H and ^{13}C NMR spectroscopy are in agreement with the published data.[3] The solid residue obtained after sublimation was recrystallized from pentane to obtain complex **1** in a yield of 0.51 g (65.5%) as colorless crystals, which decomposed in an evacuated tube at 103—105 °C. Found (%): C, 51.56, H, 5.80. $\mathrm{C_{31}H_{42}GeO_3W}$. Calculated (%): C, 51.78, H, 5.89. IR, ν/cm^{-1}: 3060, 1430, 1085, 730, 700, 460 ($\mathrm{Ph_3Ge}$), 1160, 940 (W—O—C), 1350, 1240 ($\mathrm{Bu^t}$). ^{1}H NMR ($\mathrm{C_6D_6}$), δ: 1.38 (s, 27 H, $\mathrm{Bu^t}$); 7.14—7.31 (m, 9 H, H(3), H(4)); 7.83—7.89 (m, 6 H, H(2)). ^{13}C NMR ($\mathrm{C_6D_6}$), δ: 31.9 (Me); 80.2 ($\mathrm{WO\underline{C}Me_3}$, $^2J_{\mathrm{C},^{183}\mathrm{W}} = 5.0$ Hz); 128.4 (C(3)H); 129.0 (C(4)H); 135.7 (C(2)H); 140.8 (C(1)); 274.1 (W≡C, $^1J_{\mathrm{C},^{183}\mathrm{W}} = 274.2$ Hz).

Triphenylstannylmethylidynetris(*tert*-butoxy)tungsten (2). Complex **2** was synthesized and isolated as described above. The reaction of $(\mathrm{Bu^tO})_6\mathrm{W_2}$ (1.76 g, 2.18 mmol) with $\mathrm{Ph_3SnC{\equiv}CEt}$ (0.81 g, 2.01 mmol) afforded compound **4** in a yield of 0.44 g (49.5%) as a colorless viscous liquid (the data from ^{1}H and ^{13}C NMR spectroscopy are in agreement with the published data[3]) and complex **2** in a yield of 0.83 g (55.0%) as colorless crystals, which decomposed in an evacuated tube at 110—115 °C. Found (%): C, 48.61; H, 5.51. $\mathrm{C_{31}H_{42}SnO_3W}$. Calculated (%): C, 48.66, H, 5.53. IR, ν/cm^{-1}: 3060, 1430, 1070, 740, 695, 450 ($\mathrm{Ph_3Sn}$), 1165, 940 (W—O—C), 1360, 1240 ($\mathrm{Bu^t}$). ^{1}H NMR ($\mathrm{C_6D_6}$), δ: 1.42 (s, 27 H, $\mathrm{Bu^t}$); 7.11—7.32 (m, 9 H, H(3), H(4)); 7.82—7.89 (m, 6 H, H(2)). ^{13}C NMR ($\mathrm{C_6D_6}$), δ: 31.8 ($\mathrm{CH_3}$), 79.5 ($\mathrm{WOCMe_3}$, $^2J_{\mathrm{C},^{183}\mathrm{W}} = 4.4$ Hz); 128.9 (C(3)H); 129.2 (C(4)H); 137.5 (C(2)H, $^3J_{\mathrm{C,Sn}} = 39.1$ Hz); 142.4 (C(1), $^1J_{\mathrm{C},^{117/119}\mathrm{Sn}} = 521.4/545.5$ Hz); 272.2 (W≡CSn, $^1J_{\mathrm{C},^{183}\mathrm{W}} = 272.8$ Hz, $^1J_{\mathrm{C},^{117/119}\mathrm{Sn}} = 248.3/259.9$ Hz). ^{119}Sn NMR ($\mathrm{C_6D_6}$), δ: −192 ($^2J_{^{119}\mathrm{Sn},^{183}\mathrm{W}} = 707.9$ Hz).

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