NEW COMPLEXES OF MOLYBDENUM(II) AND TUNGSTEN(II) WITH A C,N-CHELATED STANNYLENE

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Received February 1, 2007
Accepted April 24, 2007

Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organometallic chemistry.

Two new complexes of $[Sn\{2-[(CH_3)_2NCH_2]C_6H_4\}_2]$ with $[Mo(\eta^5-C_5H_5)(CO)_3Cl]$ and $[W(\eta^5-C_5H_5)(CO)_3Cl]$, respectively, were prepared via insertion of stannylene into the Mo–Cl or W–Cl bond forming thus the transition metal–tin bond. These complexes were studied by IR, NMR and X-ray diffraction techniques. The tin atom in these complexes is five-coordinated with the carbon atoms of ligands and transition metal in equatorial plane and the chlorine and the nitrogen donor atoms in axial positions. The attempts to photolyse, reduce or fluorinate the prepared complexes and characterize the products of these reactions failed.

Keywords: Stannylene; C,N-ligand; Molybdenum; Tungsten; X-ray diffraction; Stannanes; Organotin compounds; Half-sandwich complexes.

One of the goals in the chemistry of organometallic compounds is to prepare and structurally characterize bi- or oligometallic species and clusters, which are of great interest due to their potential use in preparation of new materials. The majority of attempts to produce such a compound deal with the chemistry of Group 14, mainly with the chemistry of silicon and tin[1]. There are two basic synthetic aproaches possible; (i) the use of simple substitution reactions of Group 14 metals in a higher oxidation state (IV) (Fig. 1A–1C), (ii) the use of coordination of a lone electron pair or redox reactions of Group 14 metal complexes in a lower oxidation state (II), and

Collect. Czech. Chem. Commun. 2007, Vol. 72, Nos. 5–6, pp. 629–636

doi:10.1135/cccc20070629

thus the formation of carbene-like species or products of oxidative addition (Fig. 1D, 1E). The R_2Sn group can be used as bridging for two transition metals as well (Fig. 1F). This bridge is labile in coordinating solvents (THF, pyridine, acetone, acetonitrile) and used stannylene can be taken here both as Lewis base and acid[2].

Although many low-valent complexes of Group 6 metals with tin are known, there is no higher-valent metal of Group 6–Group 14 metal species known formed via oxidative addition.

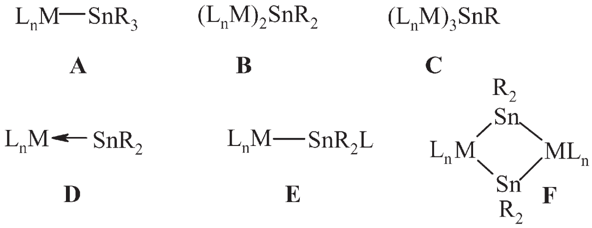


FIG. 1
Observed Sn–M bond fashion in heterooligometallic complexes

Tin(II) complexes or organotin(II) compounds of general formula R_2Sn or RSnX are known as stannylenes and can be divided into two different classes: (i) with π-bond Sn–ligand[3] or (ii) with σ-bond Sn–ligand[4]. As these compounds are kinetically unstable to oxidation or moisture but thermally robust they need to be stabilized by a bulky ligand, donor substituent or a low-valent transition metal fragment. The use of a C,N-chelating ligand for such a stabilization has been explored recently: two species were prepared and structurally characterized as $[Sn\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}_2]$[5] (**1**) and $[(CO)_5WSn\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}_2]$[6]. Based on our previous knowledge, we decided to study the reactivity of $[Sn\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}_2]$ with transition metal complexes. In this paper, we communicate on a reactivity of C,N-chelated stannylene with molybdenum(II) or tungsten(II) complexes.

EXPERIMENTAL

General

All experiments were carried out in an argon atmosphere using the standard Schlenk technique. [(Dimethylaminomethyl)]benzene, *n*-butyllithium, tin(II) chloride, cyclopentadienyltungsten tricarbonyl chloride (**3**) and cyclopentadienylmolybdenum tricarbonyl chloride (**2**) were obtained from commercial sources (Sigma–Aldrich). Toluene, benzene, *n*-hexane and *n*-pentane were dried over and distilled from sodium/potassium alloy, degassed and stored over potassium mirror. {[2-(Dimethylamino)methyl]phenyl}tin(II) (**1**) was prepared according to published procedure[6]. IR spectra (ν, cm^{-1}) were recorded on Perkin–Elmer 684 instrument as Nujol suspensions. Melting points were measured in vacuum sealed ampoules and are uncorrected. Elemental analyses were made on a Fisons Instruments apparatus at the Department of Organic Chemistry of University of Pardubice.

ESR Spectroscopy

The ESR spectra of solutions were measured at ambient temperature at X-band (ν ~ 9.5 GHz) using an ERS 221 spectrometer (Magnettech Berlin). A microwave power of 1 mW, sufficiently below the saturation power, was used.

NMR Spectroscopy

The solution ^{1}H (500.13 MHz), $^{119}Sn\{^{1}H\}$ (186.50 MHz) and $^{13}C\{^{1}H\}$ (125.76 MHz) NMR spectra (δ, ppm; *J*, Hz) of the studied compounds were measured on a Bruker Avance 500 spectrometer equipped with 5-mm probes with *z*-gradient in the temperature range of 200–310 K. The solutions were obtained by dissolving of 10 mg of each compound in 0.5 ml of deuterated solvents. The ^{1}H chemical shifts were calibrated relative to the signal of residual toluene (δ 2.09) and benzene (δ 7.16), respectively. The ^{119}Sn chemical shifts are referred to external neat tetramethylstannane (δ 0.0) and the ^{13}C chemical shifts are referred to residual signal of benzene (δ 128.30). Positive chemical shifts values denote shifts to the higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode.

Crystallography

Yellowish crystals of **5** were obtained from a Et_2O solution at –35 °C**.** The intensity data for **5** were collected on a KUMA KM-4 CCD kappa-axis diffractometer using a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) at 150(2) K. The structure was solved by direct methods (SIR92)[7]. All reflections were used in the structure refinement based on F^2 by the full-matrix least-squares technique (SHELXL97)[8]. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were inserted in calculated positions and isotropically refined assuming a “ride-on” model.

Crystallographic data for **5**: $C_{26}H_{29}ClN_2O_3SnW$, $M = 755.50$, orthorhombic, $Pna2_1$, $a = 19.615(2)$ Å, $b = 9.591(2)$ Å, $c = 14.288(2)$ Å, α, β, γ = 90.00°, $Z = 4$, $V = 2688.0(7)$ Å^3, $D_c = 1.867$ g cm^{-3}, $\mu = 5.334$ mm^{-1}, $T_{min} = 0.24366$, $T_{max} = 0.64976$; 25209 reflections measured ($\theta_{max} = 27.5°$), 6035 independent ($R_{int} = 0.0165$), 5343 with $I > 2\sigma(I)$, 311 parameters, $S = 0.975$, R_1(obs. data) = 0.0127, wR_2(all data) = 0.0230; max., min. residual electron density = 0.566, –0.423 e Å^{-3}.

CCDC 635197 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

$[\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}_2Sn(Cl)\text{-}Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ (**4**)

A solution of compound **1** (0.15 g, 0.39 mmol) in 20 ml of benzene was added dropwise during 30 min to 0.108 g of **2** (0.39 mmol) dissolved in 10 ml of benzene at room temperature. The red reaction mixture was stirred overnight and then evaporated to dryness in vacuo. The crude product was extracted with diethyl ether, the solution was filtered and left to crystallize in a freezer at –35 °C. Yellowish crystals appeared in several days, yield 0.209 g (81%). M.p. 147–148 °C. ^{1}H NMR (C_6D_6, 300 K): 8.45 (bd, $^3J_{HH}$ = 7.3, 2 H, H6); 7.33 (t, $^3J_{HH}$ = 6.9, 2 H, H4); 7.28 (t, $^3J_{HH}$ = 7.1, 2 H, H5); 7.04 (d, $^3J_{HH}$ = 7.0, 2 H, H3); 4.92 (s, 5 H, Cp); 4.09 (d, $^2J_{HAHB}$ = 13.2, 2 H, NCH_2); 3.04 (d, $^2J_{HAHB}$ = 13.1, 2 H, NCH_2); 1.72 (s, 12 H, NCH_3). ^{119}Sn{^{1}H} NMR (C_6D_6, 295 K): 60.02. IR (Nujol): 1998 (s, CO), 1929 (s, CO), 1916 (s, CO), 1892 (s, CO), 425 (w, SnCl). For $C_{26}H_{29}ClN_2O_3SnMo$ (667.6) calculated: 46.78% C, 4.38% H, 4.20% N; found: 46.9% C, 4.4% H, 4.3% N.

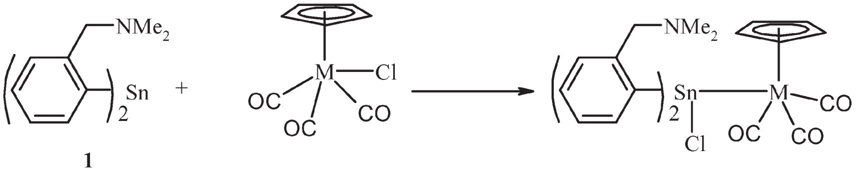
$[\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}_2Sn(Cl)\text{-}W(\eta^5\text{-}C_5H_5)(CO)_3]$ (**5**)

A solution of compound **1** (0.19 g, 0.49 mmol) in 20 ml of benzene was added dropwise during 30 min to 0.181 g of **3** (0.49 mmol) dissolved in 10 ml of benzene at room temperature. The original deep red color of reaction mixture turned to slight yellow in 5 min. The solution was stirred overnight then the solvent was evaporated in vacuum to dryness. The crude product was extracted with diethyl ether, greenish precipitate was filtered off and the solution was left to crystallize in a freezer at –35 °C. Yellowish crystals appeared in several days, yield 0.307 g (83%). M.p. 172–173 °C. ^{1}H NMR (C_6D_6, 300 K): 8.41 (d, $^3J_{HH}$ = 6.8, $^3J_{119Sn,1H}$ = 75, 2 H, H6); 7.34 (t, $^3J_{HH}$ = 7.0, 2 H, H4); 7.27 (d, $^3J_{HH}$ = 7.3, 2 H, H3); (t, $^3J_{HH}$ = 7.5, 2 H, H5); 4.95 (s, 5 H, Cp); 4.10 (d, $^2J_{HAHB}$ = 13.3, 2 H, NCH_2); 3.05 (d, $^2J_{HAHB}$ = 13.4, 2 H, NCH_2); 1.85 (s, 12 H, NCH_3); (200 K, toluene-d_8): 9.12 (1 H, H6); 8.01 (2 H, H1); 7.62, 7.53, 7.42, 7.32, 6.89 (br, H-Ar); 4.74 (5 H, Cp); 4.35 (br, 1 H); 4.10 (br, 1 H); 3.48 (br, 1 H); 2.52 (br, 1 H); 1.89 (br, 3 H); 1.76 (d-br, 3 H). ^{13}C{^{1}H} NMR (C_6D_6, 295 K): 216.99 (CO), 146.4 (Ar), 144.56 (Ar), 137.72 (Ar), 90.99 (Cp), 66.03 (NCH_2), 45.20 [$N(CH_3)_2$]. ^{119}Sn{^{1}H} NMR (C_6D_6, 295 K): –54.83; (200 K): –64.84. IR (Nujol): 2000 (s, CO), 1929 (s, CO), 1916 (s, CO), 1895 (s, CO), 423 (w, SnCl). For $C_{26}H_{29}ClN_2O_3SnW$ (755.5) calculated: 41.38% C, 3.87% H, 3.71% N; found: 41.5% C, 3.9% H, 3.8% N.

RESULTS AND DISCUSSION

Compounds **4** and **5** were prepared according to Fig. 2 via insertion of C,N-chelated stannylene into the molybdenum– or tungsten–chlorine bond producing yellow benzene solutions or yellowish powders of satisfactory EA and NMR spectra. The structure of such complexes can be compared with previously reported compounds of Lappert[9], Power[10] or Mobley[11] who prepared their species via substitution reactions. Based on similar values of three main absorptions in the carbonyl stretching region and of ^{1}H NMR shifts of hydrogen atoms of the Cp ring, we can conclude that the structures of **4** and **5** are approaching those of Lappert made from Sn(IV) compounds by substitution, more than those of Power who started from heteroleptic organotin(II) chloride. As deduced from ^{1}H NMR spectral pattern (AB pattern for NCH_2 groups), the structures **4** and **5** can be described as trigonal bipyramid on the tin atom with the electropositive atoms (C, C, and Mo or W) in equatorial, and the chlorine atom and one of the nitrogen donor atoms in axial positions. The other nitrogen is not bonded to tin and both chelating ligands are thus non-equivalent. This is also supported by a low-temperature ^{1}H NMR where the non-equivalency of the ligands is visible at 200 K in the case of **5** (**4** was not studied because of its limited solubility). There are two sets of signals for each group except for Cp at this temperature. Also the carbonyl signal in ^{13}C NMR of **5** is downfield-shifted (9 ppm) in comparison to compounds of Power $[(Cp(CO)_3M–Sn(C_6H_3\text{-}2,6\text{-}Ar)]$ [10] where tin(II) is present, which is in good agreement with greater electron density on the transition metal which could be a result of greater back-bonding into the π^* orbitals of the carbonyls. The ^{119}Sn chemical shift values are good indicators of Sn(II) to Sn(IV) oxidation, as there is a difference in the shift of the starting stannylene and complexes formed reaching ca. 100 ppm (for Mo (**4**)) or 200 ppm (for W (**5**)). These values are the highest ones with respect to earlier studied phenylstannanes with C,N-chelation[12].

The solid-state structure of **5** was determined by X-ray diffraction measurement of the single crystalline material. This experiment has confirmed previous suggestions about the structure obtained from analytical experiments in solution. Compound **5** has the trigonal bipyramidal geometry at the tin atom with nearly planar equatorial plane (C11, C21, W1) and medium-strong Sn–N1 coordination. The Sn–W bond length is somewhat shorter than was found for compounds of Power (Sn–W 2.8199(6) Å for **5**, and 2.9107(10) and 2.9030(8) Å for $[Cp(CO)_3M–Sn(C_6H_3\text{-}2,6\text{-}Ar)])$[10]. The rest of bonds and angles present is in good agreement with the values found in Cambridge Structural Database[13] for compounds containing Sn(IV)–W(II)Cp(CO) fragments.



1

2; M = Mo
3; M = W

4; M = Mo
5; M = W

FIG. 2
Preparation of complexes **4** and **5**

Compounds **4** and **5** are not stable in solution at room temperature and decompose to [Sn{2-[$(CH_3)_2NCH_2$]C_6H_4}$_2$$Cl_2$] and an unidentified insoluble yellowish powder. In order to explore reactivity of compounds **4** and **5** under the photolysis conditions, in substitution and with reducing agents, with the main intention to promote elimination of carbon monoxide and thus a formation of multiple bonds between the metals as described for some complexes of germanium[14] or trapping an unusual valence state, complexes **4** and **5** were photolyzed and reacted with potassium, sodium borohydride, and the known fluorination reagent {2-[$(CH_3)_2NCH_2$]C_6H_4}*n*-Bu_2SnF[15]. Photolyses of THF solutions of both **4** and **5** were performed in vacuum in sealed quartz tubes with a 40 W UV-lamp in ESR spectrometer. During and after this procedure, no signal was observed in ESR spectrum and only a small amount of insoluble material was formed. A similar result was ob-

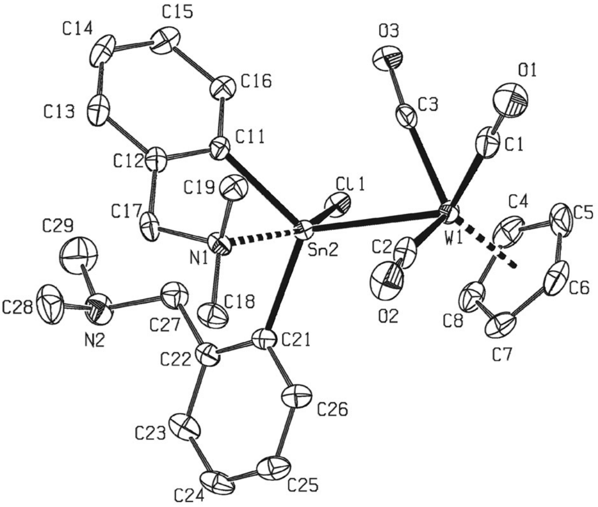


FIG. 3

The molecular structure (ORTEP 50% probability level) of **5**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (in Å) and angles (in °): Sn(2)–C(11) 2.153(2), Sn(2)–C(21) 2.164(2), Sn(2)–Cl(1) 2.5482(8), Sn(2)–W(1) 2.8203(3), W(1)–C(1) 1.979(3), W(1)–C(2) 1.981(3), W(1)–C(3) 1.982(3), W(1)–C(5) 2.304(3), W(1)–C(6) 2.313(2), W(1)–C(4) 2.338(3), W(1)–C(7) 2.339(3), W(1)–C(8) 2.360(2), C(1)–O(1) 1.146(3), C(2)–O(2) 1.158(3), C(3)–O(3) 1.161(3), W1–Cp(Cg) 2.001; C(11)–Sn(2)–C(21) 113.16(9), C(11)–Sn(2)–Cl(1) 90.94(6), C(21)–Sn(2)–Cl(1) 93.40(6), C(11)–Sn(2)–W(1) 127.27(6), C(21)–Sn(2)–W(1) 119.04(6), Cl(1)–Sn(2)–W(1) 92.919(15), C(1)–W(1)–Sn(2) 128.88(7), C(2)–W(1)–Sn(2) 80.82(7), C(3)–W(1)–Sn(2) 69.87(7), C(4)–W(1)–Sn(2) 98.55(7), C(5)–W(1)–Sn(2) 133.93(7), C(6)–W(1)–Sn(2) 136.67(6), C(7)–W(1)–Sn(2) 101.95(7), C(8)–W(1)–Sn(2) 82.06(6) tained when the equivalent amount of potassium was sublimed to the tube and the same procedure with **4** and **5** was performed. In the case of heterogeneous reactions of **4** and **5** with sodium borohydride in benzene, it should be mentioned that the color of reaction mixtures changed dramatically but no change in ^{1}H and ^{119}Sn NMR spectra was observed. Only partially successful was the methatetical exchange reaction of chlorine for fluorine in the case of **4**, where three fluorinated tin species with quite high couplings (71.1 ppm, 3619.9 Hz; –258.3 ppm, 3263.8 Hz; –307.9 ppm, 2655.8 Hz) were observed in ^{119}Sn NMR spectrum one hour after mixing **4** and $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}n\text{-}Bu_2SnF$ 1:1 in NMR tube in benzene. The conversion of $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}n\text{-}Bu_2SnF$ to $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}n\text{-}Bu_2SnCl$ was confirmed by the presence of the signal at –50.78 ppm in the ^{119}Sn NMR spectrum[16]. This reactivity topic will be further studied.

The financial support of the Science Foundation of the Czech Republic (grant No. 203/07/0468) and the Ministry of Education, Youth and Sports of the Czech Republic (project VZ0021627501) is acknowledged.

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