

The synthesis of novel bridging cyclopentadienyl W–Sn(IV) bonded bimetallic complexes. Crystal structure of $\text{Cl}_3\text{SnMo}(\text{CO})_3\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{NHC}_6\text{H}_3(\text{NO}_2)_2$ and $\mu\text{-}[\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{N}(\text{CO})\text{Ph}]\text{W}(\text{CO})_3\text{SnCl}_2 \cdot (\text{EtOH})_2$

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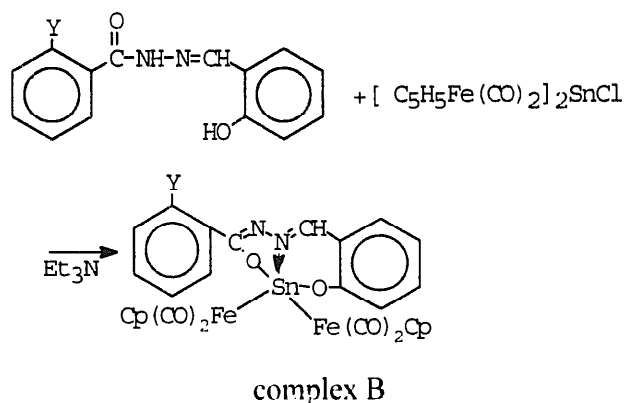
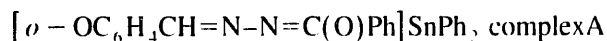
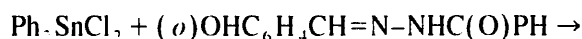
Abstract

The reaction of $\text{CH}_3\text{COC}_5\text{H}_4(\text{CO})_3\text{MoSnCl}_3$ with 2,4-dinitrophenyl-hydrazine yielded the corresponding hydrazone, $\text{Cl}_3\text{SnMo}(\text{CO})_3\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{NHC}_6\text{H}_3(\text{NO}_2)_2$ (**1**). Crystals of **1** are monoclinic: $a = 8.6724(9)$, $b = 21.549(2)$, $c = 12.378(1)$ Å, $\beta = 102.099(8)^\circ$, space group, $P2_1/n$, $Z = 4$, Mo–Sn distance 2.7040(7) Å. The reaction of $\text{CH}_3\text{COC}_5\text{H}_4(\text{CO})_3\text{WSnCl}_3$ with benzoyl-hydrazine in refluxing ethanol gave $\mu\text{-}[\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{N}(\text{CO})\text{Ph}]\text{W}-\text{SnCl}_2(\text{C}_2\text{H}_5\text{OH})_2$ (**2**). Crystals of **2** are monoclinic, $a = 16.897(2)$, $b = 13.780(1)$, $c = 12.429(2)$ Å, $\beta = 116.80(1)^\circ$, space group Cc , $Z = 4$, W–Sn distance 2.7767(9) Å. © 1997 Elsevier Science S.A.

Keywords: Cyclopentadienyl; Crystals; Hydrazone

1. Introduction

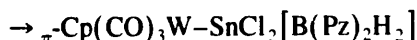
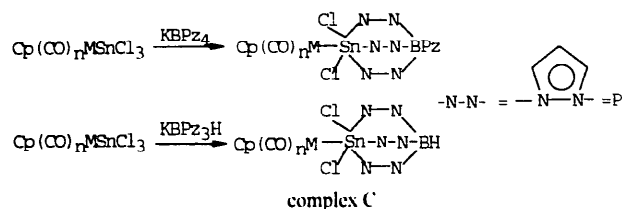
The synthesis and reactivity of cyclic metallic complexes are an active area in organometallic chemistry [1]. Metal with different coordination numbers in the complexes depends much on the ligand pattern. In our previous papers [2], we reported the Schiff base of salicylic aldehyde with benzoyl-hydrazine forming tridentate complexes with tin:



We also reported the reaction of trihalostannungsten(or Mo) complexes with potassium poly(1-pyrazolyl)borate. The tetrakis(1-pyrazolyl) borate anion and tris(1-pyrazolyl) borate anion reacts respectively with the trihalotin complexes to form the hexacoordinate tin complexes, while the bis(1-pyrazolyl)borate

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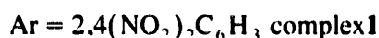
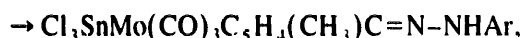
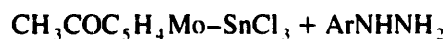
anion reacts with the same tin complex only to form the tetracoordinate tin complex:



where Cp = C₅H₅, Pz = 1-pyrazolyl.

Instead of trimetallic complex [Cp(CO)₃W]₂SnCl₂ and a tetracoordinate complex Cl₂Sn[B(Pz)₂H₂] was obtained [3].

In further investigation, we found that acetylcyclopentadienyl Mo(W) tin trihalide reacted with phenyl-hydrazine to form a normal hydrazone (1), in which tin is tetracoordinate, while the same trihalide reacted with benzoyl-hydrazine to form a novel bridging complex (2) with hexacoordinate tin:



It shows that a benzoyl-hydrazone of the functionalized acetyl cyclopentadienyl M-Sn complex behaves like a tridentate ligand *o*-OHC₆H₄CH=N-N=C(OH)Ph: salicylic aldehyde benzoyl-hydrazone. The product is a distorted dinuclear bicyclodiazastannoxide.

2. Experimental

All reactions were carried out in Argon atmosphere. Elemental analyses were done on a Perkin-Elmer model 240 analyser, melting point on a Yanako MP-5000 apparatus, IR on a Nicolet FT-IR 5DX spectrometer, and NMR on a Bruker AC2000 spectrometer.

Acetylcyclopentadienyl sodium was prepared according to the published report [4], and triphenyl-tin halide prepared by the known method [5].

2.1. Preparation of CH₃COC₅H₄Mo(CO)₃Na

Acetylcyclopentadienyl sodium (0.29 g, 2.2 mmol) was added into 10 ml of THF containing Mo(CO)₆ (0.53 g, 2 mmol). The mixture was heated and refluxed for 24 h, and a blue black solution was ready for the following use.

2.2. Preparation of CH₃COC₅H₄Mo(CO)₃Sn(Ph)₃

Into the 1.5 mmol of the above CH₃COC₅H₄Mo(CO)₃Na in THF, Ph₃SnCl (0.49 g, 1.5 mmol) was added and stirred overnight at room temperature. The solvent was removed under vacuum below 30°C. The residue was extracted with CH₂Cl₂. The solution was passed through an alumina column, which was then leached with 50:50 CH₂Cl₂/hexane to obtain a yellow solution, then the solvent was removed. The residue was dissolved again in CH₂Cl₂/hexane and crystallized to yield the titled complex, m.p. 150–158°C, yield 41% analyzed as C₂₈H₂₂MoO₄Sn: C: 52.48% (calc. 52.97%), H: 3.58% (calc. 3.49%) ν_{CO} in cm⁻¹ 2002.3, 1929.8, 1897.9; ν_{carbonyl} : 1690.2 cm⁻¹; ¹H NMR δ ppm, 7.36–7.58 (m, 15H), 5.74 (t, 2H), 5.33 (t, 2H), 2.25 (s, 3H).

2.3. Preparation of CH₃COC₅H₄W(CO)₃Na

A total of 0.29 g (2.2 mmol) CH₃COC₅H₄Na was added into 15 ml diglyme under argon, together with 0.7 g (2 mmol) W(CO)₆. The mixture was refluxed gently for 8 h to obtain a dark blue solution of CH₃COC₅H₄W(CO)₃Na, ready for the following use.

2.4. Preparation of CH₃COC₅H₄W(CO)₃SnPh₃

A total of 1.5 mmol of CH₃COC₅H₄W(CO)₃Na in solution was reacted with 1.49 g (1.5 mmol) of Ph₃SnCl and refluxed at room temperature overnight. Water was added to precipitate out the product. After filtering and drying, the solid was dissolved in CH₂Cl₂/hexane (30:70) mixed solvent, and the solution was passed through an alumina column. The eluate was dried in vacuum, and the residue was recrystallized from CH₂Cl₂ to obtain the product, analyzed as CH₃COC₅H₄W(CO)₃SnPh₃, yield 40%, m.p. 144–146°C, containing C: 46.51% (calc. 46.49%), H: 3.10% (calc. 3.04%), IR cm⁻¹: ν_{CO} 1999.6, 1983.0, 1922.2, (ν_{carbonyl}) 1693; ¹H NMR δ ppm: 7.40–7.67 (m, 15H), 5.80 (t, 2H), 5.32 (t, 2H), 2.28 (s, 3H).

2.5. Preparation of CH₃COC₅H₄Mo(CO)₃SnCl₃

1.0 mmol of CH₃COC₅H₄Mo(CO)₃SnPh₃ was dissolved in 15 ml of CH₂Cl₂, cooled to -15°C, HCl gas

was passed in, the solution become orange from light yellow. After half an hour, the reaction subsided. The solvent was removed and the residue dissolved in EtOH, and recrystallized to yield orange crystals, which was analyzed as the titled complex, yield 90%, m.p. 127–128°C, $C_{10}H_7Cl_3MoO_4Sn$: gave C, 23.62% (calc. 23.45%), H, 1.17% (calc. 1.38%), IR (in cm^{-1}): ν_{CO} : 2059.2, 1987.0, 1965.6; (ν_{carbonyl}): 1688.7, 1H NMR (δ ppm) 6.15 (t, 2H), 5.78 (t, 2H), 2.41 (s, 3H).

2.6. Preparation of $Cl_3SnMo(CO)_3C_5H_4(CH_3)C=N-NHC_6H_3(NO_2)_2 \cdot 2,4$ (complex 1)

0.34 g (0.5 mmol) of $Cl_3SnMo(CO)_3C_5H_4COCH_3$ was reacted with 0.2 g (1 mmol) of 2,4-dinitrophenylhydrazine, 1 ml of sulfuric acid, 5 ml of water in 20 ml of EtOH. The solution was refluxed for 1 h. Orange precipitate came out. The solid was taken out and crystallized from acetone. It was found to be the titled complex, 1 m.p. 194–195°C, yield 84%. Analyzed for $C_{16}H_{11}Cl_3MoN_4O_7Sn$: C, 24.63% (calc. 24.60%), H, 1.377% (calc. 1.42%), N, 7.44% (calc. 7.18%), IR (cm^{-1}) ν_{NH} 3195.7 ν_{CO} : 2044.6, 1975.0 1930.0, ν_{CN} , 1614.1, 1H NMR (δ ppm) 8.24–9.01 (m, 3H), 6.30–6.68 (m, 4H), 2.40 (s, 3H), 11.20 (s, 1H)

2.7. Preparation of $[C_5H_4(CH_3)C=N-N=C(O)Ph]Mo(CO)_3SnCl_2 \cdot (EtOH)_2$

0.34 g (0.5 mmol) of $Cl_3SnMo(CO)_3C_5H_4COCH_3$ was refluxed with 0.1 g (0.73 mmol) of benzoyl hydrazine in 20 ml of ethanol for 4 h. A clear solution was obtained. After cooling, an orange crystalline product came out, filtered and recrystallized from acetone to obtain a product, analyzed as $Cl_2SnMo(CO)_3C_5H_4(CH_3)-C=N-N=C(O)Ph \cdot (EtOH)_2$; yield 86%, decomposed upon melting. Elemental analysis: C, 36.88% (calc. 36.78%), H, 3.37% (calc. 3.50%), N, 3.94% (calc. 4.09%). IR (cm^{-1}) ν_{OH} 3450.5; ν_{CO} : 2016.0, 1948.8, 1925.8; ν_{CN} , 1623.3, 1H NMR: 7.42–6.10 (m, 5H), 5.48–5.76 (m, 4H), 2.40 (s, 3H), 2.55 (s, 6H), 3.60 (m, 4H).

2.8. Preparation of $CH_3COC_5H_4(CO)_3W-SnCl_3$

1 mmol of $CH_3COC_5H_4(CO)_3W-SnPh_3$ was dissolved in 15 ml of CH_2Cl_2 cooled to $-15^\circ C$. HCl gas was passed in and the solution turned to orange. After the reaction, the solvent was removed, the residue dried in vacuum and recrystallized from ethanol, and analyzed for $C_{10}H_7Cl_3O_4SnW$, yield 90%, m.p. 135–137°C. C: 20.00 (calc. 19.98%) H: 1.12% (calc. 1.17%).

2.9. Preparation of $Cl_2SnW(CO)_3C_5H_4(CH_3)C=N-N=C(O)Ph \cdot (EtOH)_2$

0.3 g (0.5 mmol) of $Cl_3SnW(CO)_3C_5H_4COCH_3$ and 0.1 g (0.73 mmol) of benzoyl hydrazine were refluxed

Table 1
Crystal data of complex 1 and 2

Complex	1	2
Empirical formula	$C_{16}H_{11}Cl_3MoN_4O_7Sn$	$C_{21}H_{22}Cl_2O_6N_2SnW$
Formula weight	692.27	773.88
Crystal habit	Prismatic	Prismatic
Crystal dimensions (mm)	0.20 × 0.30 × 0.40	0.20 × 0.20 × 0.30
Crystal system	Monoclinic	Monoclinic
Lattice type	Primitive	C-centered
<i>a</i> (Å)	8.6724(9)	16.897(2)
<i>b</i> (Å)	21.549(2)	13.780(1)
<i>c</i> (Å)	12.378(1)	12.459(2)
<i>V</i> (Å ³)	2261.7(4)	2605.6(6)
β (°)	102.099(8)	116.080(10)
Space group	$P2_1/n$	<i>Cc</i>
<i>Z</i>	4	4
D_{calc} (g cm ⁻³)	2.033	1.973
F_{000}	1336.00	1480.00
μ (cm ⁻¹)	20.57	56.17
Scan width	(1.73 + tan θ)°	(1.73 + 0.30 tan θ)°
$2\theta_{\text{max}}$	45.0°	55.0°
No. of unique reflections	3069	3061
No. of observations ($I < 3.00\sigma(I)$)	2554	2820
No. of variables	289	297
<i>R</i>	0.029	0.036
R_w	0.049	0.051

together in 20 ml of ethanol for 4 h. A clear solution was obtained; after cooling, a brown precipitate came out, which was filtered, washed with ethanol, dried in vacuum, and recrystallized from ethanol. Analyzed as $C_{21}H_{22}Cl_2O_6N_2SnW$, yield 80%, decomposed upon melting, C, 32.32% (calc. 32.56%), H, 3.9% (calc. 3.10%), N, 3.65% (calc. 3.85%). IR (cm^{-1}): ν_{OH} , 3459.8, ν_{CO} , 2024.2, 1958.6, 1934.0, ν_{CN} 1623.3; 1H NMR (δ ppm): 7.54–8.20 (m, 5H), 6.10–6.32 (m, 4H), 2.55 (s, 3H), $\delta_{(EtOH)}$: 2.60 (m, 6H), 3.60 (m, 4H).

2.10. X-ray crystallographic measurement

Single crystals of complex 1, and complex 2 were put on a Rigaku AFC7R diffractometer and subjected to graphite monochromated MoK radiation and 12 kW rotating anode generator with an $\omega-2\theta$ scan technique. The data were corrected for Lorentz and polarizing effects. Structures were resolved by direct method and expanded using Fourier technique. Non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for both complexes is listed in Table 1.

3. Results and discussion

3.1. Syntheses and spectral properties

The reaction between $CH_3COC_5H_4Mo(CO)_3SnCl_3$ and 2,4-dinitrophenyl hydrazine yielded a nonbridged

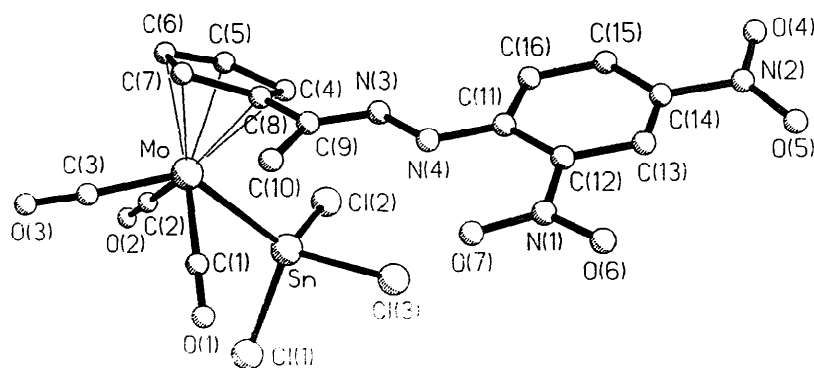


Fig. 1. Molecular structure of complex 1: $\text{Cl}_3\text{SnMo}(\text{CO})_3\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{NHC}_6\text{H}_3(\text{NO}_2)_2-2,4$.

complex 1, in which the imino nitrogen did not coordinate with Sn, so was $\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{SnCl}_3$ with phenyl hydrazine or semicarbazide. They gave the normal hydrazone or semicarbazone. It is known that a bidentate ligand does not expand the coordination number of tin from four to five or six. The benzoyl hydrazone provides one more dentate ligand by enolizing the $-\text{NH}-\text{CO}-$ to $-\text{N}=\text{C}(\text{OH})-$, but the semicarbazone $-\text{NH}-\text{C}(\text{O})-\text{NH}_2$ does not likewise enolize, so the latter remains to be a bidentate complexing ligand. The condensed product found was $\text{Cl}_3\text{SnW}(\text{CO})_3\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{NH}-\text{C}(\text{O})-\text{NH}_2$, in which Sn did not combine with the imino N. The IR spectra confirm the tetracoordinate tin complex having a $-\text{NH}-\text{N}=\text{C}-$ moiety in the complex. The $\nu_{\text{C}=\text{N}}$ in complex 1 (1614 cm^{-1}) is lower than that in complex 2 (1623 cm^{-1}). The $\nu_{\text{C}=\text{O}}$ values on the transition metals are also different, that of complex 1 are higher (2048.8, 1991.4, 1950.40) than that of

complex 2 (2024.2, 1958.6, 1934.0), in spite of the former triplets belong to Mo with smaller atomic weight than W.

The ^1H NMR spectra of the non-bridged complex 1 for Cp ring protons are of two sets, i.e., 6.83 and 6.38, and those of complex 2 are 6.32 and 6.00; the low field resonance of complex 1 maybe attributed to the influence of the electron withdrawing substituent on Cp and different coordination number of tin. The chemical shift of Cp ring protons of complex 2 is comparable to that of the reactant before its condensation with hydrazine, for $\text{CH}_3\text{COC}_5\text{H}_4(\text{CO})_3\text{MoSnCl}_3$, δ :6.15 and 5.78, and for $\text{CH}_3\text{COC}_5\text{H}_4-(\text{CO})_3\text{WSnCl}_3$, they are 6.19 and 5.89. A significant shift toward higher field for the Cp ring protons and lower wave number of the CO groups in the bridged complexes maybe due to the increment of coordination number of tin, in that $d-p$ interaction of N and O around Sn brings about the weakening of $d-d$

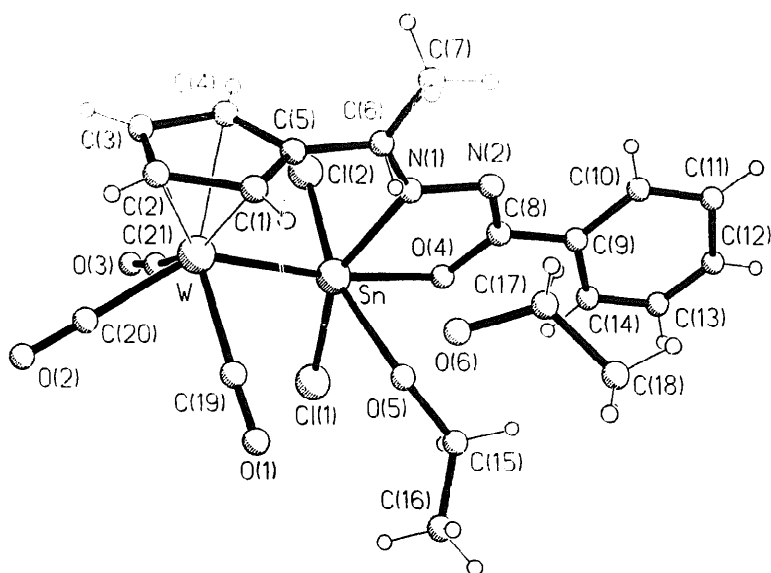


Fig. 2. Molecular structure of complex 2: $\mu[\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{N}=\text{C}(\text{O})\text{Ph}]\text{W}-\text{SnCl}_2(\text{EtOH})_2$.

interaction between Sn–W bond, in turn enhancing tungsten–carbonyl back bonding.

3.2. Crystal structure description of complex 1 and 2

The principle crystal data of complex 1 and 2 are shown in Table 1 and the structures in Figs. 1 and 2. They both show that the transition metal atom adopts a 3:4 (piano stool) square pyramid configuration. The Cp–Mo bond distances contain two long C–Mo bond 2.365 Å, one medium 2.330 Å and two short 2.304 Å, so the Cp ring sits slightly tilting in respect to the square pyramid, whose three CO ligands are bending, $\angle\text{Mo–C–O} = 178.0(6)$, 178.6 and 179.3° . The bond distance of C=O are 1.133(8), 1.136(8) and 1.139(8) Å, respectively, and Mo–C are 2.002(6), 2.003(7) and 2.007(7) Å, respectively. The above parameters show that three metal carbonyls are very similar and consistent with the terminal CO bonding arrangement. Unlike complex 2, the nitrogen atom of C=N bond does not coordinate with Sn. The coordination number of Sn is four and the coordination geometry around Sn is nearly tetrahedral with bond lengths of 2.325(2), 2.348(2) and 2.352(2) Å for Sn–Cl bond. The Cl–Sn–Cl bond angles range from $99.66(9)$ to $102.17(9)^\circ$, and $\angle\text{Mo–Sn–Cl}$ from $115.44(5)$ to $119.78(6)^\circ$. The $\angle\text{Mo–Sn–Cl}$ is larger than $\angle\text{Cl–Sn–Cl}$. The Mo–Sn bond distance is 2.7040(7) Å, and is considerably shorter than the sum of covalent radii (1.39 + 1.61 Å), which indicates the interaction of Sn–Mo. The dihedral angles between Cp plane and the Ph is 34.67° .

The crystal structure of complex 2 shows that there are two EtOH molecules, one of which is coordinated to Sn through O atom and another is in the crystal grating. The Sn–W bond and the molecular configuration are influenced by the ring structure, which resembles the bicyclic diazastannoxide, complex A and B in that there is a five-membered ring made up of Sn–N(1)–N(2)–C(8) and O(4) and a pseudo six-membered ring made up with Sn–W–C(1)–C(5)–C(6)–N(1) fused to form a hetero-bicyclo[4.3.0]nonane. The coordination geometry around tin atom is octahedral with Sn–Cl(1), Sn–Cl(2), Sn–W, Sn–N(1), Sn–O(4) and Sn–O(5) (the OH of EtOH). The *cis*-angles range from $71.7(4)$ to $96.6(1)^\circ$ and the *trans*-angles range from $153.7(3)$ to $163.4(3)^\circ$. There are severe distortions caused by the intramolecular coordination, in which Sn–N(1) is 2.237(9) Å and within the normal range for such bond. For comparison, Sn–N bond distance in complex A is 2.344(6) Å and that in complex B 2.247 Å [6]. The Sn–Cl in complex 2 is longer [2.445(3) to 2.454(4) Å] than Sn–Cl in complex 1 [2.325(2), 2.348(2) and 2.352(2) Å]. The

increment arises from the coordination of tin expanding from four to six, weakens the bonding between the Sn–Cl in complex 2. For Cp–W, the distances between C–W ranges from 2.23(1) to 2.36(1) Å comparable to Cp–Mo. The CO bond lengths of metal carbonyls are 1.16(2), 1.15(2) and 1.12(2) Å, and the W–C are 2.05(2), 2.04(2) and 1.92(2) Å. The W–C–O bond angles are $172(1)$, $174(1)$ and $177(1)^\circ$. All data show that one of the carbonyl group differs significantly than the other two. The W–Sn bond distance [2.7767(9) Å] is longer than Mo–Sn in complex 1 due to the hexacoordination of Sn, since W and Mo have a similar covalent radii. The Ph and Cp planes in complex 2 are closely perpendicular to each other with a dihedral angle of 98.13° .

4. Conclusion

The phenylhydrazone of the π -acetylated cyclopentadienyl–tungsten–stannic trichloride gave a normal tetra-coordinated tin(IV) derivative. The benzoylhydrazone of the similar π -acetylated cyclopentadienyl–tungsten–stannic dichloride gave a novel bridging ligand between the functionalized cyclopentadienyl ring and tin, making a hexacoordinated tin(IV), by coordination with EtOH besides two Cl atoms. The novel bridging ligand can be looked upon as a spatial chain between $\pi\text{-Cp-C(Me)=N=N=C(Ph)-O-Sn(OEt,EtOH,Cl}_2\text{)-W(CO)}_3^-$. The X-ray crystal structure diagram confirms the proposed novel bridging ligand.

Acknowledgements

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