

The Influence of an Acetyl Group on the Cyclopentadienyl Ring in the Formation of Sn–Mo(W) Complexes by Nucleophilic Displacement Reactions, Crystal and Molecular Structure of $\text{CH}_3\text{COC}_5\text{H}_4(\text{CO})_3\text{MoSnPh}_2\text{Cl}$

Ji-Tao Wang,* Hai-Yang He,† and Yu-Ming Xu

Department of Chemistry, Nankai University, Tianjin 300071, P. R. China

Jie Sun and Xiang-Fu Kong

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China

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ABSTRACT

Sodium tricarboxylacetylcyclopentadienylmolybdenum (tungsten) reacted with Ph_2SnL_2 ($\text{L} = \text{Cl}, \text{Br}$) in a 1:1 ratio or even a 4:1 ratio only to afford bimetallic complexes $\text{CH}_3\text{CO}-\text{C}_5\text{H}_4(\text{CO})_3\text{MSnPh}_2\text{L}$ ($\text{M} = \text{Mo}, \text{W}$; $\text{L} = \text{Cl}$ or Br), which have been characterized by elemental analyses, IR and ^1H NMR spectroscopy. The acetyl group on the Cp ring exerts an electron-withdrawing effect that makes the organomolybdenum anion a less effective nucleophilic agent in displacing the remaining halogen from the $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnPh}_2\text{L}$. The bimetallic complex could be isolated, and the crystal structure of the titled complex is orthorhombic, $a = 16.271$, $b = 10.247(2)$, $c = 14.450(2)$ Å, $Z = 4$, space group $\text{Pna}2_1$, and the Mo atom has a 3:4 piano stool structure with an Sn–Mo bond length of 2.7683(6) Å. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:169–172, 1998

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

†Present address: Department of Chemistry, Shandong University, Jinan 250100, China.

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INTRODUCTION

Transition metal and main group metal bonded complexes have received extensive attention recently. There are several synthetic methods for obtaining such complexes [1]. Nucleophilic displacement reactions are some of the convenient and useful methods [12]. Cleland et al. [3] studied such reactions and found the type of leaving group on the main group metal to be of importance. When the transition metal complex anion reacted with Ph_2GeX_2 ($\text{X} = \text{Cl}, \text{Br}$), only Cl was displaced to yield the bimetallic complex, even with a fourfold excess of the anion, whereas for $\text{X} = \text{Br}$, two Br atoms were displaced to give the trimetallic complex. Considerable spectroscopic data of these complexes in solution have been

TABLE 1 Atomic Coordinates and $B_{\text{iso}}/B_{\text{eq}}$

Atom	X	Y	Z	B_{eq}
C(18)	0.0748(3)	−0.1810(5)	0.0219(5)	4.1(1)
C(19)	0.1360(4)	−0.2036(5)	−0.0516(5)	3.9(1)
C(20)	0.2222(3)	−0.2011(4)	−0.0114(4)	3.3(1)
C(21)	0.3069(4)	−0.2199(6)	−0.0603(5)	4.5(1)
C(22)	0.3065(6)	−0.2427(7)	−0.1615(6)	6.0(2)

TABLE 2 Selected Bond Lengths (Å)

Bond	Distance	Bond	Distance	Bond	Distance
Sn–Mo	2.7683(6)	Sn–Cl	2.398(2)	Sn–C(4)	2.152(6)
Sn–C(10)	2.143(5)	Mo–C(1)	2.000(6)	Mo–C(2)	1.991(6)
Mo–C(3)	2.003(6)	Mo–C(16)	2.335(5)	Mo–C(17)	2.376(6)
Mo–C(18)	2.353(5)	Mo–C(19)	2.315(5)	Mo–C(20)	2.312(4)
C(1)–O(1)	1.143(6)	C(2)–O(2)	1.139(7)	C(3)–O(3)	1.130(7)
C(21)–O(4)	1.211(8)	C(20)–C(21)	1.487(8)	C(21)–C(22)	1.481(10)

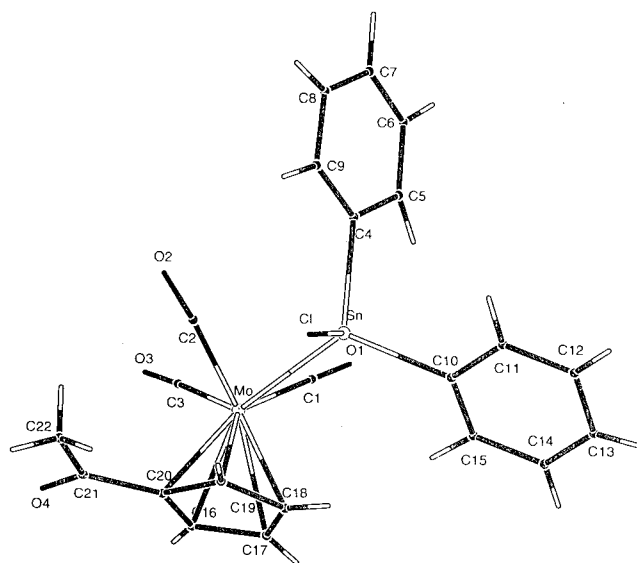
TABLE 3 Selected Bond Angles (°)

Atom				Angle			
Mo	Sn	Cl	105.36(4)	Mo	Sn	C(4)	120.1(1)
Mo	Sn	C(10)	118.7(1)	Cl	Sn	C(4)	100.6(2)
Cl	Sn	C(10)	100.9(1)	C(4)	Sn	C(10)	107.5(2)
Sn	Mo	C(1)	71.9(2)	Sn	Mo	C(2)	72.2(1)
Sn	Mo	C(3)	131.1(2)	C(1)	Mo	C(2)	105.5(2)
C(1)	Mo	C(3)	78.9(2)	C(2)	Mo	C(3)	79.3(3)
Mo	C(1)	O(1)	177.4(5)	Mo	C(2)	O(2)	175.4(5)
Mo	C(3)	O(3)	177.5(5)	O(4)	C(21)	C(20)	119.1(7)
O(4)	C(21)	C(22)	121.8(7)	C(20)	C(21)	C(22)	119.1(7)

obtained, yet single-crystal structures of Sn-VIB metal complexes are little revealed. In recent years, transition metal complexes containing the acetyl-cyclopentadienyl ligand have been used for study of the nucleophilicity of the metals. In the course of studying the reactivities of nucleophilic displacement of halogen on the tin moiety, we found that the electron-withdrawing effect of an acetyl group on the Cp ligand of the transition metal has a great influence on its nucleophilicity. When the $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3$ anion reacted with Ph_2SnX_2 , no matter whether $\text{X} = \text{Cl}$ or Br , only one halogen atom was displaced, and no trimetallic complexes were found. The bimetallic complexes $\text{Ph}_2\text{Sn}(\text{Cl})\text{M}(\text{CO})_3\text{C}_5\text{H}_4\text{COCH}_3$ and $\text{Ph}_2\text{Sn}(\text{Br})\text{M}(\text{CO})_3\text{C}_5\text{H}_4\text{COCH}_3$ ($\text{M} = \text{Mo}$, W) were obtained.

EXPERIMENTAL

All reactions were carried out under an argon atmosphere. Diglyme and THF were distilled from sodium benzophenone ketyl. Elemental analyses and melting-point determinations were performed with a Perkin-Elmer model 240C analyzer and a Yanako MP-5000 apparatus, respectively. IR spectra were recorded on a Nicolet FT-IR 5 DX spectrometer and the ^1H NMR spectra on a Jeol FX90Q NMR spectrometer. $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ were purchased from Strem Chemicals Inc. Ph_2SnCl_2 , Ph_2SnBr_2 , and

**FIGURE 1.** the molecular structure of $\text{CH}_3\text{COC}_5\text{H}_4(\text{CO})_3\text{MoSnPh}_2\text{Cl}$.

$\text{CH}_3\text{COC}_5\text{H}_4\text{Na}$ were prepared by the published methods [5,6].

Preparation of $\eta^5\text{-CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{Na}$ (I)

A 0.29 g (2.2 mmol) amount of $\text{CH}_3\text{COC}_5\text{H}_4\text{Na}$ was dissolved in 20 mL of THF and 0.53 g (2 mmol) of

$\text{Mo}(\text{CO})_6$ was added. The mixture was then refluxed for 20 hours. The mixture turned brown and was cooled for use in subsequent reactions.

Preparation of $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnPh}_2\text{Cl}$ (II)

A 0.52 g (1.5 mmol) amount of Ph_2SnCl was added to (I), and this mixture was stirred overnight at room temperature. Then the mixture was concentrated and chromatographed on silica gel with methylene chloride/hexane (3:7) as eluent. The yellow band solution was collected, the solvent pumped off, and the residue recrystallized from methylene chloride/hexane to afford 0.36 g (41%) of a yellow crystalline product. Only the same product was obtained even with a fourfold excess of (I) was used in the reaction. (II) has a mp 99–100°C; anal. calcd. for $\text{C}_{22}\text{H}_{17}\text{ClMoO}_4\text{Sn}$ (%): C, 44.63; H, 2.98. Found (%): C, 44.18; H, 2.82. IR (KBr disc) ν_{co} : 2020.9, 1953.5, 1919.1, 1682.1 cm^{-1} . ^1H NMR (CDCl_3 , δ): 7.66–7.32 (m, 10H), 5.88 (t, 2H), 5.54 (t, 2H), 2.28 (s, 3H).

Preparation of $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnPh}_2\text{Br}$ (III)

A 0.65 g (1.5 mmol) amount of Ph_2SnBr_2 was added to (I), and the mixture was stirred overnight at room temperature. Then, the workup was similar to that employed for the isolation of (II) to yield 0.38 g (38%) of a yellow, crystalline substance. The same product was obtained with use of a fourfold excess of (I). It melts at 98–99°C. Anal. calcd. for $\text{C}_{22}\text{H}_{17}\text{BrMoO}_4\text{Sn}$ (%): C, 41.13; H, 2.67. Found (%): C, 40.71, H, 2.69. IR (KBr disc) ν_{co} : 2024.2, 1958.6, 1909.4, 1696.1 cm^{-1} . ^1H NMR (CDCl_3 , δ): 7.80–7.4 (m, 10H), 5.96 (t, 2H), 5.52 (t, 2H), 2.30 (s, 3H).

Preparation of $\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{Na}$ (IV)

A 0.29 g (2.2 mmol) amount of $\text{CH}_3\text{COC}_5\text{H}_4\text{Na}$ was dissolved in 20 mL of diglyme, and 0.70 g (2 mmol) of $\text{W}(\text{CO})_6$ was added, the mixture then being refluxed for 12 hours. The mixture turned brown and was cooled for use in subsequent reactions.

Preparation of $\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{SnPh}_2\text{Cl}$ (V)

A 0.52 g (1.5 mmol) amount of Ph_2SnCl_2 was added to (IV), and the mixture was stirred overnight at room temperature. The mixture was poured into water, and the residue was dissolved in methylene chloride and chromatographed on silica gel with methylene chloride/hexane (3:7), being used as eluent. The yellow band solution was collected, the solvent

pumped off, and the residue recrystallized from methylene chloride/hexane to afford 0.5 g (50%) of a yellow crystalline substance. The same product was obtained when a fourfold excess of (IV) was used, mp 101–102°C. Anal. calcd for $\text{C}_{22}\text{H}_{17}\text{ClO}_4\text{SnW}$ (%): C, 38.61; H, 2.49. Found (%): C, 38.71; H, 2.61, IR (KBr disc) ν_{co} : 2016.0, 1942.2, 1909.4, 1679.7 cm^{-1} . ^1H NMR (CDCl_3 , δ): 7.66–7.28 (m, 10H), 5.98 (t, 2H), 5.56 (t, 2H), 2.30 (s, 3H).

Preparation of $\text{CH}_3\text{C}_5\text{H}_4\text{W}(\text{CO})_3\text{SnPh}_2\text{Br}$ (VI)

A 0.65 g (1.5 mmol) amount of Ph_2SnBr_2 was added to (IV), and the mixture was stirred overnight at room temperature. Then the mixture was treated similarly to the procedure used for isolation of (V) to yield 0.50 g (38%) of yellow crystalline substance. The same product was obtained when a fourfold excess of (IV) was used. Mp 97–99°C. Anal. calcd for $\text{C}_{22}\text{H}_{17}\text{BrO}_4\text{SnW}$ (%): C, 36.27; H, 2.24. Found (%): C, 36.14; H, 2.20. IR (KBr disc) ν_{co} : 2016.0, 1950.4, 1901.2, 1696.1 cm^{-1} . ^1H NMR (CDCl_3 , δ): 7.65–7.3 (m, 10H), 5.98 (t, 2H), 5.56 (t, 2H), 2.28 (s, 3H).

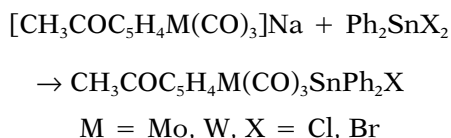
Single-Crystal Structural Determination of (II)

Crystals of (II) suitable for X-ray diffraction were obtained from methylene chloride/hexane in the refrigerator. A yellow prismatic crystal with dimensions of $0.20 \times 0.20 \times 0.30$ mm was mounted on a glass fiber and placed on a Rigaku AFC 7R diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71060$). A total of 2945 independent reflections was collected at a temperature of 20°C using the -20 scan technique to a maximum 2θ value of 55.0° . The final cycle of full-matrix least-squares refinement was based on 2405 observed reflections [$I > 3\sigma(I)$] and converged with unweighted and weighted agreement factors of 0.022 (R) and 0.026 (Rw), respectively. The structure was solved by the direct method and Fourier syntheses. The nonhydrogen atoms were refined anisotropically. The crystal belongs to the orthorhombic space group Pna21, with $a = 15.271(2)$, $b = 10.247(2)$, $c = 14.450(2)$ Å³, $V = 2261(1)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.747$ g cm⁻³, $\mu = 18.00$ cm⁻¹, $F(000) = 1160$.

RESULTS AND DISCUSSION

Bimetallic complexes $\text{CH}_3\text{COC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnPh}_2\text{X}$ (M = Mo, W; X = Cl, Br) were synthesized by the salt elimination reaction between the anion of tricarbonylacetyl-cyclopentadienyltungsten (or molybdenum) and the diphenyldihalostannane. All new complexes

were characterized by elemental analyses, and IR, ^1H NMR spectroscopy. In their IR spectra, there are three ν_{co} absorption bands, exhibiting the terminal metal carbonyls. ^1H NMR spectra are very similar and unusual.



Salt elimination reactions normally proceed readily at room temperature. The leaving group of a main group metal like Ge has great influence on the result of the preparation of transition metal–Ge bonded complexes, as mentioned above [3]. We have reported [7] that when a dialkyl or diaryl dichlorostannane was reacted with the complex anion of tungsten containing a cyclopentadienyl or a more electron-releasing group, methyl-cyclopentadienyl, it was easy to obtain W–Sn–W bonded trimetallic complexes and difficult to control the partial displacement of halogen to obtain the bimetallic complexes when the tungsten anion was in excess. However, the reaction of the anion of acetyl-cyclopentadienyl tungsten (or Mo) with Ph_2SnX_2 ($\text{X} = \text{Cl}$ or Br) either in a molar ratio of 1:1 or with an excess, 2:1, no trimetallic complexes were obtained. Edelmann and Behrens reported [8] that, when $\text{OHCC}_5\text{H}_4\text{M}(\text{CO})_3\text{Na}$ reacted with Me_2SnCl_2 , only $\text{OHCC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnMe}_2\text{Cl}$ ($\text{M} = \text{Cr, Mo}$) was obtained. This indicates that the presence of an electron-withdrawing group on the ligand of the M anion greatly diminishes its nucleophilicity. The crystal structure of (II) shows that the acetyl substituent occupies a coplanar position with the Cp ring, the steric “umbrella effect” enhancing the electron-withdrawing effect, thus retarding the displacement of a halogen atom on tin.

The X-ray structure of (II) shows that the terminal CO groups bonding with Mo deviate from linearity, forming bond angles of $177.4(5)^\circ$, $175.4(5)^\circ$, and $177.5(5)^\circ$ with each other, together with SnPh_2Cl forming another ligand to Mo. Thus, the complex (II) assumes a 3:4 piano stool structure with respect to the Mo atom. The bond length of Sn–Cl is $2.398(2) \text{ \AA}$, much shorter than that of Sn–Cl in trichlorostannane sodium (2.48 \AA) [1]. Also, the Mo–Sn bond distance in (II), $2.7683(6) \text{ \AA}$, is considerably shorter than the sum of covalent radii Mo and Sn ($1.61 + 1.39 \text{ \AA}$) [10].

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REFERENCES

- [1] M. S. Holt, W. L. Wilson, J. H. Nelson, *Chem. Rev.*, **89**, 1989, 11.
- [2] H. Sharma, K. H. Pannel, *Organometallics*, **3**, 1994, 4946.
- [3] A. J. Cleland, S. A. Fieldhouse, B. H. Freeland, R. J. O'Brien, *Chem. Comm.*, 1977, 155.
- [4] N. J. Coville, K. E. Plooy, W. Pickle, *Coord. Chem. Rev.*, **116**, 1992, 1.
- [5] W. F. Edgell, *J. Am. Chem. Soc.*, **76**, 1954, 1169.
- [6] W. Hart, *J. Am. Chem. Soc.*, **102**, 1980, 1196.
- [7] H.-Y. He, J.-T. Wang, Y.-M. Xu, *Chem. Res. in Chinese University*, in press.
- [8] F. Edelmann, U. Behrens, *J. Organomet. Chem.* **309**, 1986, 87.
- [9] P. Kubacek, R. Hoffmann, Z. Havlas, *Organometallics*, **1**, 1982, 180.
- [10] E. C. Onyriukam, S. J. Rettig, A. Storrm, *Can. J. Chem.*, **64**, 1986, 321.