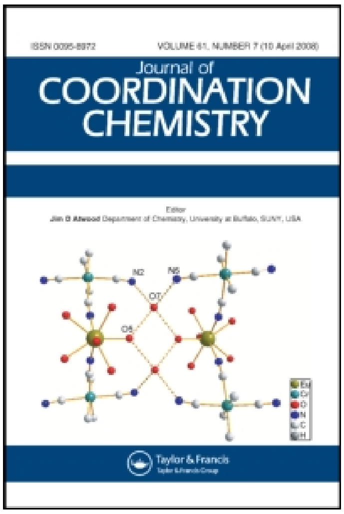

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# Synthesis of (4-methoxycarbonyl-1-naphthoyl)cyclopentadienyl M–Sn(IV) heterobimetallic complexes

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Reaction of cyclopentadienyl sodium with dimethyl 1,4-naphthalenedicarboxylate in a 1 : 1 or 2 : 1 ratio in THF yielded functionalized cyclopentadienyl anions $CH_3O_2CC_{10}H_6C(O)Cp^-$, which reacted with $M(CO)_6$ to give carbonyl metal anions $CH_3O_2CC_{10}H_6C(O)CpM(CO)_3^-$ (M = Mo or W). Treatment of these carbonyl metal anions with $R_nSnX_{4-n}$ (R = Ph or Me; X = Cl or Br; $n = 2$ or 3) yielded heterobimetallic complexes $CH_3O_2CC_{10}H_6C(O)CpM(CO)_3SnR_nX_{3-n}$, which have been characterized by elemental analysis, NMR and IR spectroscopy. In addition, treatment of complexes $CH_3O_2CC_{10}H_6C(O)CpM(CO)_3SnPh_3$ with HCl resulted in cleavage of Sn–C bonds to give $CH_3O_2CC_{10}H_6C(O)CpM(CO)_3SnCl_3$ in good yield. The crystal structure of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3SnCl_3$ was determined by X-ray diffraction, showing that Mo adopts a 3 : 4 piano stool structure; this complex is linked into a two-dimensional network through weak intermolecular C–H···O and Cl···Cl interactions.

*Keywords*: Cyclopentadienyl; Heterobimetallic complex; Group 6 carbonyl complex; Organotin; Crystal structure

## 1. Introduction

Heterobimetallic complexes have been the subject of extensive investigations due to their unusual structures, reactions and potential catalytic activities [1–7]. They often display higher activity and selectivity than mononuclear complexes, possibly from cooperation effect of two metals. Among these complexes, M–Sn bonded complexes have also drawn extensive attention and been used in many catalytic processes [8–15]. We recently became interested in studying transition metal-tin bonded heterobimetallic complexes owing to their unusual structures and reactivity. Our investigation suggested that these transition metal-tin bonded heterobimetallic complexes can be used in construction of heteronuclear organometallic macrocycles [16, 17]. We also found that functionalized acetylcyclopentadienyl M–Sn bonded heterobimetallic complexes reacted with benzoylhydrazine or arylthiocarboxyhydrazide to yield new heteronuclear organometallic hetrocycles [18–20]. As part of our ongoing interest in functionalized

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cyclopentadienyl heterobimetallic complexes, we report herein the synthesis and characterization of (4-methoxycarbonyl-1-naphthoyl)cyclopentadienyl M–Sn bonded heterobimetallic complexes.

## 2. Experimental

All reactions were carried out under an argon atmosphere using standard Schlenk and cannula techniques. Solvents were dried by standard methods prior to use [21]. NMR spectra were obtained on a Bruker AV300 spectrometer using $CDCl_3$ as solvent unless otherwise noted, and the chemical shifts are reported in ppm with respect to the reference. IR spectra were obtained from a Brucker Equinox 55 spectrometer using KBr discs. Element analyses were carried out on a Corder M73 EL analyzer. Melting points were reported with an X-4 digital melting-point apparatus and were uncorrected.

### 2.1. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpNa$ (1)*

Solution of cyclopentadienyl sodium in 40 $cm^3$ of THF, prepared from the reaction of cyclopentadiene (13 $cm^3$, 157.6 mmol) with Na (2.4 g, 104 mmol), was added dropwise to a refluxing solution of dimethyl 1,4-naphthalenedicarboxylate (24.42 g, 100 mmol) in 100 $cm^3$ of THF. After addition, the reaction mixture was stirred and refluxed for 25 h. During this period, yellow solid precipitated. Cooling to room temperature, the precipitate was filtered off, washed with absolute ether, and dried in vacuum to yield yellow solid of **1** (24.6 g, 82%). The same product was also obtained when a twofold excess of cyclopentadienyl sodium was used to react with dimethyl 1,4-naphthalenedicarboxylate in THF.

### 2.2. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3Na$*

Complex **1** (0.66 g, 2.2 mmol) was added to a solution of $Mo(CO)_6$ (0.53 g, 2 mmol) in 30 $cm^3$ of THF. The mixture was stirred and refluxed for 20 h to obtain a purple-red solution of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3Na$. After cooling to room temperature, the solution was ready for subsequent use.

### 2.3. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3SnPh_3$ (2)*

To the above solution of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3Na$ in THF, $Ph_3SnCl$ (0.77 g, 2 mmol) was added and stirred overnight at room temperature. The solvent was removed *in vacuo*, and the residue was extracted with $CH_2Cl_2$. After removing the $CH_2Cl_2$ under vacuum, the residue was purified by column chromatography on silica using $CH_2Cl_2$/hexane ($V:V=2:1$) as eluent. The yellow eluent was concentrated to dryness, and the residue was recrystallized from $CH_2Cl_2$/hexane to give yellow crystals of **2** (1.06 g). Yield: 66%. M.p.: 185–187°C. Anal. Calcd for $C_{39}H_{28}MoO_6Sn$ (%): C, 58.02; H, 3.50. Found: C, 58.51; H, 3.71. $^1H$ NMR: $\delta$ 8.80, 8.02, 7.91, 7.59–7.45 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 7.39–7.36, 7.23–7.15 (m, m, 6H, 9H, $C_6H_5$); 5.62, 5.23

(t, t, 2H, 2H, $C_5H_4$); 3.96 (s, 3H, $CH_3$). $^{13}$C NMR: $\delta$ 192.09 (C=O, ketone), 167.45 (C=O, ester), 141.79, 139.69, 136.49, 131.54, 130.43, 130.29, 128.86, 128.56, 128.24, 128.10, 127.75, 126.21, 125.23, 124.01, ($C_{10}H_6$ and $C_6H_5$), 102.71, 93.48, 92.27 ($C_5H_4$), 52.54 ($OCH_3$). The signals of the carbons of the C≡O groups were not observed possibly owing to low solubility and low sensitivity of these carbonyl carbons. IR (cm$^{-1}$): $\nu$(C≡O) = 2006.7 (vs), 1946.3 (s), 1911.8 (vs); $\nu$(C=O, ester) = 1718.0 (s); $\nu$(C=O, ketone) = 1667.8 (s).

### 2.4. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3SnPh_2Cl$ (3)*

Complex **3** was obtained similarly using $Ph_2SnCl_2$ instead of $Ph_3SnCl$ as described above for **2**. After the similar workup, yellow crystals of **3** were obtained. Yield: 58%. M.p.: 136–138°C. Anal. Calcd for $C_{33}H_{23}ClMoO_6Sn$ (%): C, 51.77; H, 3.03. Found: C, 51.24; H, 2.92. $^1$H NMR: $\delta$ 8.82, 8.06, 7.92, 7.64–7.54 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 7.49–7.36, 7.30–7.25 (m, m, 4H, 6H, $C_6H_5$); 5.79, 5.47 (t, t, 2H, 2H, $C_5H_4$); 3.99 (s, 3H, $CH_3$). IR (cm$^{-1}$): $\nu$(C≡O) = 2016.4 (vs), 1952.6 (s), 1916.2 (vs); $\nu$(C=O, ester) = 1719.4 (s); $\nu$(C=O, ketone) = 1647.2 (s).

### 2.5. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3SnPh_2Br$ (4)*

Complex **4** was obtained similarly using $Ph_2SnBr_2$ instead of $Ph_3SnCl$ as described above for **2**. After similar workup, yellow crystals of **4** were obtained. Yield: 56%. M.p.: 152–154°C. Anal. Calcd for $C_{33}H_{23}BrMoO_6Sn$ (%): C, 48.93; H, 2.86. Found: C, 49.11; H, 2.49. $^1$H NMR: $\delta$ 8.86, 8.10, 7.96, 7.67–7.57 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 7.51–7.45, 7.32–7.27 (m, m, 4H, 6H, $C_6H_5$); 5.90, 5.58 (t, t, 2H, 2H, $C_5H_4$); 4.03 (s, 3H, $CH_3$). IR (cm$^{-1}$): $\nu$(C≡O) = 2030.2 (vs), 1956.1 (s), 1906.1 (vs); $\nu$(C=O, ester) = 1713.1 (s); $\nu$(C=O, ketone) = 1672.1 (s).

### 2.6. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3SnMe_2Cl$ (5)*

Complex **5** was obtained similarly using $Me_2SnCl_2$ instead of $Ph_3SnCl$ as described above for **2**. After similar workup, yellow crystals of **5** were obtained. Yield: 64%. M.p.: 125–127°C. Anal. Calcd for $C_{23}H_{19}ClMoO_6Sn$ (%): C, 43.06; H, 2.99. Found: C, 43.03; H, 3.11. $^1$H NMR: $\delta$ 8.76, 8.07, 7.88, 7.56–7.33 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 5.81, 5.53 (t, t, 2H, 2H, $C_5H_4$); 4.00 (s, 3H, $OCH_3$); 0.83 (s, 6H, $SnCH_3$). IR (cm$^{-1}$): $\nu$(C≡O) = 2034.2 (vs), 1966.9 (s), 1915.0 (vs); $\nu$(C=O, ester) = 1712.6 (s); $\nu$(C=O, ketone) = 1670.1 (s).

### 2.7. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpW(CO)_3Na$*

Complex **1** (0.66 g, 2.2 mmol) was added to a solution of $W(CO)_6$ (0.70 g, 2 mmol) in 30 cm$^3$ of diglyme. The mixture was stirred and slightly refluxed for 8 h to obtain a purple-red solution of $CH_3O_2CC_{10}H_6C(O)CpW(CO)_3Na$. After cooling to room temperature, the solution was ready for subsequent use.

### 2.8. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpW(CO)_3SnPh_3$ (6)*

To the above solution of $CH_3O_2CC_{10}H_6C(O)CpW(CO)_3Na$ in diglyme, $Ph_3SnCl$ (0.77 g, 2 mmol) was added and stirred overnight at room temperature. The solvent was removed *in vacuo* at less than 60°C, and the residue was extracted with $CH_2Cl_2$. After removing the $CH_2Cl_2$ solvent, the residue was purified by column chromatography on silica using $CH_2Cl_2$/hexane ($V:V=2:1$) as eluent. The yellow eluent was concentrated to dryness, and the residue was recrystallized from $CH_2Cl_2$/hexane to give yellow crystals of **6** (1.01 g). Yield: 59%. M.p.: 183–185°C. Anal. Calcd for $C_{39}H_{28}O_6SnW$ (%): C, 52.33; H, 3.15. Found: C, 51.90; H, 3.41. $^1H$ NMR: $\delta$ 8.80, 8.11, 7.99, 7.69–7.59 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 7.45–7.41, 7.31–7.25 (m, m, 6H, 9H, $C_6H_5$); 5.73, 5.43 (t, t, 2H, 2H, $C_5H_4$); 4.05 (s, 3H, $CH_3$). IR ($cm^{-1}$): $\nu(C{\equiv}O) = 2014.3$ (vs), 1939.3 (s), 1904.0 (vs); $\nu$(C=O, ester) = 1717.2 (s); $\nu$(C=O, ketone) = 1671.1 (s).

### 2.9. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpW(CO)_3SnPh_2Cl$ (7)*

Complex **7** was obtained similarly using $Ph_2SnCl_2$ instead of $Ph_3SnCl$ as described above for **6**. After similar workup, yellow crystals of **7** were obtained. Yield: 53%. M.p.: 140–142°C. Anal. Calcd for $C_{33}H_{23}ClO_6SnW$ (%): C, 46.44; H, 2.72. Found: C, 46.30; H, 3.17. $^1H$ NMR: $\delta$ 8.82, 8.06, 7.92, 7.62–7.55 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 7.49–7.45, 7.30–7.26 (m, m, 4H, 6H, $C_6H_5$); 5.82, 5.58 (t, t, 2H, 2H, $C_5H_4$); 3.99 (s, 3H, $CH_3$). IR ($cm^{-1}$): $\nu(C{\equiv}O) = 2012.0$ (vs), 1942.9 (s), 1904.1 (vs); $\nu$(C=O, ester) = 1719.7 (s); $\nu$(C=O, ketone) = 1648.4 (s).

### 2.10. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpW(CO)_3SnPh_2Br$ (8)*

Complex **8** was obtained similarly using $Ph_2SnBr_2$ instead of $Ph_3SnCl$ as described above for **6**. After similar workup, yellow crystals of **8** were obtained. Yield: 54%. M.p.: 155–157°C. Anal. Calcd for $C_{33}H_{23}BrO_6SnW$ (%): C, 44.14; H, 2.58. Found: C, 43.79; H, 2.35. $^1H$ NMR: $\delta$ 8.89, 8.12, 7.99, 7.71–7.62 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 7.56–7.53, 7.35–7.33 (m, m, 4H, 6H, $C_6H_5$); 5.90, 5.64 (t, t, 2H, 2H, $C_5H_4$); 4.05 (s, 3H, $CH_3$). IR ($cm^{-1}$): $\nu(C{\equiv}O) = 2029.2$ (vs), 1957.2 (s), 1905.5 (vs); $\nu$(C=O, ester) = 1712.4 (s); $\nu$(C=O, ketone) = 1672.3 (s).

### 2.11. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpW(CO)_3SnMe_2Cl$ (9)*

Complex **9** was obtained similarly using $Me_2SnCl_2$ instead of $Ph_3SnCl$ as described above for **6**. After similar workup, yellow crystals of **9** were obtained. Yield: 56%. M.p.: 127–129°C. Anal. Calcd for $C_{23}H_{19}ClO_6SnW$ (%): C, 37.87; H, 2.63. Found: C, 38.10; H, 2.70. $^1H$ NMR: $\delta$ 8.89, 8.15, 7.99, 7.70–7.60 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 5.92, 5.64 (t, t, 2H, 2H, $C_5H_4$); 4.04 (s, 3H, $OCH_3$); 0.90 (s, 6H, $SnCH_3$). $^{13}C$ NMR: $\delta$ 210.66, 204.43 (C≡O), 191.38 (C=O, ketone), 167.30 (C=O, ester), 139.01, 131.51, 130.71, 130.32, 128.52, 128.12, 127.91, 126.33, 125.24, 124.33 ($C_{10}H_6$), 102.20, 93.70, 90.12 ($C_5H_4$), 52.37 ($OCH_3$), 3.44 ($SnCH_3$); IR ($cm^{-1}$): $\nu(C{\equiv}O) = 2011.9$ (vs), 1938.8 (s), 1902.4 (vs); $\nu$(C=O, ester) = 1710.9 (s); $\nu$(C=O, ketone) = 1663.2 (s).

### 2.12. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpMo(CO)_3SnCl_3$ (10)*

Complex **2** (0.40 g, 0.5 mmol) was dissolved in 20 $cm^3$ of $CH_2Cl_2$, and the solution was cooled to −15°C. Dry HCl gas was continuously bubbled into the solution; the color of the solution slowly turned orange from yellow. After 1 h, the solvent was removed, and the residue was recrystallized from $CH_2Cl_2$/hexane to afford yellow crystals of **10** (0.28 g). Yield: 82%. M.p.: 160–162°C. Anal. Calcd for $C_{21}H_{13}Cl_3MoO_6Sn$ (%): C, 36.97; H, 1.92. Found: C, 36.89; H, 2.28. $^1H$ NMR: $\delta$ 8.84, 8.11, 7.97, 7.66–7.59 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 6.05, 5.78 (m, m, 2H, 2H, $C_5H_4$); 4.00 (s, 3H, $CH_3$). $^{13}C$ NMR: $\delta$ 222.18, 218.87 (C≡O), 191.12 (C=O, ketone), 167.29 (C=O, ester), 137.82, 131.98, 131.72, 130.39, 128.93, 128.56, 128.06, 126.77, 125.47, 124.99 ($C_{10}H_6$), 105.51, 95.65, 92.92 ($C_5H_4$), 52.91 ($OCH_3$); IR ($cm^{-1}$): $\nu$(C≡O) = 2049.9 (vs), 1977.3 (br, vs); $\nu$(C=O, ester) = 1719.8 (s); $\nu$(C=O, ketone) = 1672.1 (s).

### 2.13. *Preparation of $CH_3O_2CC_{10}H_6C(O)CpW(CO)_3SnCl_3$ (11)*

Complex **11** was obtained similarly using **6** instead of **2** as described above for **10**. After similar workup, yellow crystals of **11** were obtained. Yield: 85%. M.p.: 169–171°C. Anal. Calcd for $C_{21}H_{13}Cl_3O_6SnW$ (%): C, 32.75; H, 1.70. Found: C, 32.88; H, 2.04. $^1H$ NMR: $\delta$ 8.89, 8.16, 8.00, 7.73–7.64 (d, d, d, m, 1H, 1H, 1H, 3H, $C_{10}H_6$); 6.14, 5.93 (t, t, 2H, 2H, $C_5H_4$); 4.05 (s, 3H, $CH_3$). $^{13}C$ NMR: $\delta$ 209.34, 207.25 (C≡O), 190.58 (C=O, ketone), 167.27 (C=O, ester), 137.66, 132.10, 131.76, 130.38, 129.02, 128.65, 128.11, 126.85, 125.42, 124.96 ($C_{10}H_6$), 103.73, 94.89, 90.62 ($C_5H_4$), 52.95 ($OCH_3$); IR ($cm^{-1}$): $\nu$(C≡O) = 2046.0 (vs), 1984.9 (s), 1941.8 (vs); $\nu$(C=O, ester) = 1719.4 (s); $\nu$(C=O, ketone) = 1670.6 (s).

### 2.14. *Crystal structure determination of 10*

Crystals of **10** suitable for X-ray analysis were obtained by slow diffusion of hexane into the $CH_2Cl_2$ solution of this complex at −18°C. Intensity data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) using the $\omega/2\theta$ scan technique, and a semi-empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data is listed in table 1.

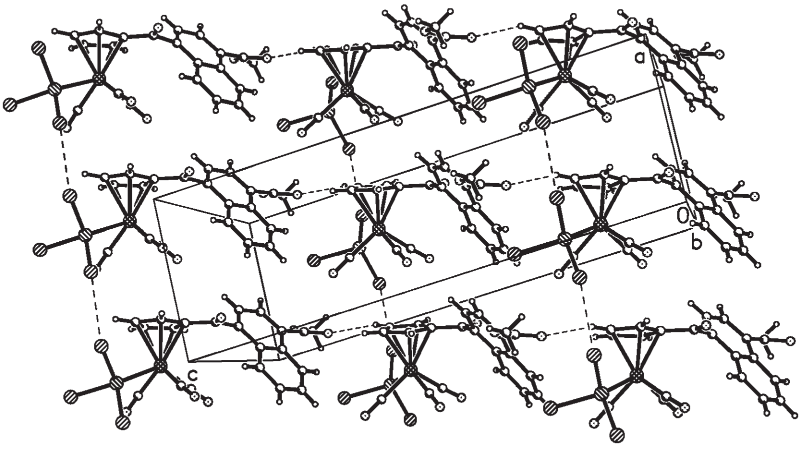
## 3. Results and discussion

### 3.1. *Synthesis and characterization of complexes*

The reaction of cyclopentadienyl sodium with dimethyl 1,4-naphthalenedicarboxylate in a 1 : 1 or 2 : 1 ratio in THF only yielded functionalized cyclopentadienyl sodium $CH_3O_2CC_{10}H_6C(O)CpNa$ (**1**) (scheme 1). This compound is stable under oxygen- and water-free conditions, and can be stored for several months at −10°C without notable decomposition. Treatment of this compound with $M(CO)_6$ (M = Mo or W), and subsequently with organotin halide yielded heterobimetallic complexes

Table 1. Crystallographic data for **10**.

| | |
|---|---|
| Formula | $C_{21}H_{13}Cl_3MoO_6Sn$ |
| Formula weight | 682.29 |
| Crystal size ($mm^3$) | $0.16 \times 0.22 \times 0.28$ |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 6.940(3) |
| $b$ (Å) | 15.859(6) |
| $c$ (Å) | 21.444(8) |
| $\beta$ (°) | 94.270(5) |
| $V$ (Å$^3$) | 2353.7(15) |
| $2\theta$ range (°) | 3.80–50.04 |
| $Z$ | 4 |
| $T$ (K) | 293(2) |
| $F(000)$ | 1320 |
| $\lambda$ (Mo-K$\alpha$) (Å) | 0.71073 |
| Absorption coefficient ($mm^{-1}$) | 1.969 |
| Calcd density ($g\,cm^{-3}$) | 1.925 |
| Reflections collected | 12589 |
| Independent reflections ($R_{int}$) | 4158 (0.0241) |
| No. of parameters | 290 |
| Residuals $R$, $R_w$ [$I \geq 2\sigma(I)$] | 0.0357, 0.0840 |
| Goodness-of-fit | 1.031 |



Scheme 1. Synthesis of the complexes: $n = 3$, R = Ph, M = Mo **2**, W **6**; $n = 2$, R = Ph, X = Cl, M = Mo **3**, W **7**; $n = 2$, R = Ph, X = Br, M = Mo **4**, W **8**; $n = 2$, R = Me, X = Cl, M = Mo **5**, W **9**; M = Mo **10**, W **11**.

$CH_3O_2CC_{10}H_6C(O)CpM(CO)_3SnR_nX_{3-n}$ (**2**–**9**). In addition, reactions of **2** and **6** with dry HCl in cooled $CH_2Cl_2$ resulted in cleavage of the Sn–C bonds to give $CH_3O_2CC_{10}H_6C(O)CpM(CO)_3SnCl_3$ **(10** and **11)** in good yield, indicating that the metal–metal bonds in these two complexes are reasonably stable. Complexes **2**–**11** are moderately soluble in polar solvents such as acetone, chlorinated solvents, and their solutions can be manipulated transitorily in air.

All above-described complexes have been characterized by elemental and spectroscopic analyses. Their IR spectra show three typical metal carbonyl stretching bands in

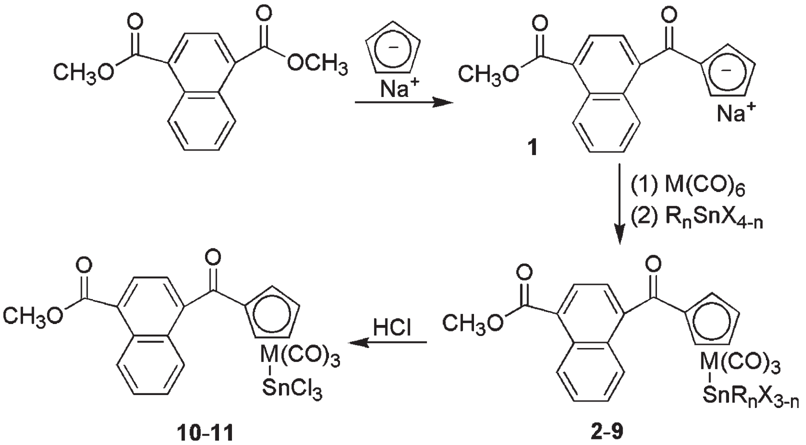


Figure 1. The molecular structure of **10**. The thermal ellipsoids are drawn at the 30% probability level.

the range 1900–2050 cm$^{-1}$. In addition, a characteristic absorption of the ester carbonyl is observed between 1710 and 1720 cm$^{-1}$, while the corresponding characteristic absorption of the ketone carbonyl appears in the range of 1640–1680 cm$^{-1}$. These results are consistent with suggested structures of **2**–**11**. The $^{1}$H NMR spectra also exhibit the expected proton signals, such as two sets of cyclopentadienyl ring resonances, corresponding to the monosubstituted cyclopentadienyl group, as well as a single peak at ca 4 ppm for the methyl group. The $^{13}$C NMR spectra of complexes **2** and **9**–**11** also support the proposed structures, which clearly show two sets of carbonyl (C=O) signals. Their ketone carbonyl and ester carbonyl signals are observed at ca 190 and 167 ppm, respectively. Furthermore, in **9**–**11** two metal carbonyl (C≡O) carbon signals with ca a 1 : 2 intensity ratio have also been observed in the range 204–223 ppm.

### 3.2. *Crystal structure of 10*

The molecular structure of **10** has also been confirmed by X-ray diffraction analysis as shown in figure 1. Selected bond distances and angles are listed in table 2. As seen in figure 1, the molybdenum atom adopts a 3 : 4 piano four-legged square pyramid structure, as calculated by Kubacek for $CpML_4$ complexes [22], and the tin atom is situated in a distorted tetrahedral environment. The Sn–Mo bond distance is 2.7152(8) Å, similar to those reported in related complexes, such as 2,4-$(NO_2)_2C_6H_3NHN=C(CH_3)CpMo(CO)_3SnCl_3$ (2.7040(7) Å) [18] and $CH_3COCpMo(CO)_3SnCl_3$ (2.7307(8) Å) [23]. The average Sn–Cl bond distance is 2.339 Å, also similar with that in $CH_3COCpMo(CO)_3SnCl_3$ (2.353 Å). In addition, to reduce the repulsion of the $SnCl_3$ unit and naphthoyl group, these two groups are situated in *trans*-positions of the cyclopentadienyl group.

The dihedral angle between cyclopentadienyl plane and naphthyl plane is 122.9°. There is a good conjugate relationship between the ketone carbonyl group with the cyclopentadienyl ring, instead of the naphthyl plane. The O(4) and C(9) atoms are slightly out of the cyclopentadienyl plane (only −0.0129 Å for O(4) and 0.0076 Å for

Table 2. Selected bond distances (Å) and angles (°) for **10**.

| | | | |
|---|---|---|---|
| Sn(1)–Cl(1) | 2.323(1) | O(1)–C(1) | 1.134(6) |
| Sn(1)–Cl(2) | 2.354(2) | O(2)–C(2) | 1.137(6) |
| Sn(1)–Cl(3) | 2.340(1) | O(3)–C(3) | 1.135(6) |
| Sn(1)–Mo(1) | 2.7152(8) | O(4)–C(9) | 1.211(6) |
| Mo(1)–C(1) | 2.017(6) | O(5)–C(20) | 1.195(6) |
| Mo(1)–C(2) | 2.000(6) | O(6)–C(20) | 1.325(7) |
| Mo(1)–C(3) | 2.007(6) | O(6)–C(21) | 1.445(6) |
| Cl(1)–Sn(1)–Cl(2) | 99.11(8) | O(1)–C(1)–Mo(1) | 176.6(5) |
| Cl(3)–Sn(1)–Cl(2) | 100.53(8) | O(2)–C(2)–Mo(1) | 175.7(5) |
| Cl(1)–Sn(1)–Mo(1) | 120.48(5) | O(3)–C(3)–Mo(1) | 179.4(5) |
| Cl(3)–Sn(1)–Mo(1) | 113.96(5) | C(20)–O(6)–C(21) | 116.0(4) |
| C(2)–Mo(1)–C(1) | 109.4(2) | C(8)–C(7)–C(9) | 129.4(4) |
| C(2)–Mo(1)–Sn(1) | 75.1(1) | O(4)–C(9)–C(7) | 119.3(4) |
| C(3)–Mo(1)–Sn(1) | 130.9(1) | O(4)–C(9)–C(10) | 121.6(4) |
| O(5)–C(20)–C(13) | 124.2(5) | C(7)–C(9)–C(10) | 119.0(4) |
| O(6)–C(20)–C(13) | 110.9(4) | O(5)–C(20)–O(6) | 124.8(5) |
| O(4)–C(9)–C(10)–C(11) | 125.6(6) | C(12)–C(13)–C(20)–O(5) | −135.8(6) |
| O(4)–C(9)–C(10)–C(15) | −51.8(8) | C(14)–C(13)–C(20)–O(5) | 44.0(8) |
| C(6)–C(7)–C(9)–O(4) | −0.4(8) | C(21)–O(6)–C(20)–O(5) | −2.0(9) |
| C(8)–C(7)–C(9)–O(4) | 177.8(5) | C(21)–O(6)–C(20)–C(13) | 179.6(5) |

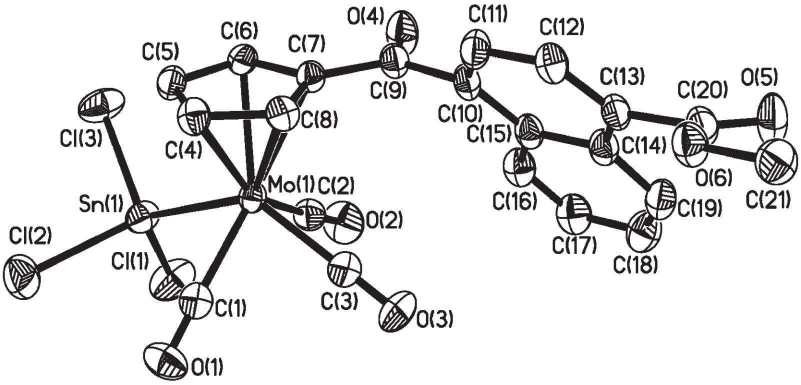


Figure 2. The crystal packing diagram of **10** emphasizing the weak intermolecular interactions (O(5)···C(5)$^{\mathrm{i}}$ = 3.095(3) Å, O(5)···H(5)$^{\mathrm{i}}$ = 2.356(2) Å, Cl(1)···Cl(3)$^{\mathrm{ii}}$ = 3.418(1) Å; symmetry code: $^{\mathrm{i}}x-0.5$, $-y+1.5$, $z-0.5$, $^{\mathrm{ii}}x-1$, $y$, $z$) and the two-dimensional network.

C(9), respectively), but markedly deviate from the naphthyl plane (−0.5562 Å for O(4) and 0.2576 Å for C(9), respectively). The torsion angles of ∠C(6)–C(7)–C(9)–O(4) (−0.4(8)°) and ∠O(4)–C(9)–C(10)–C(11) (125.6(6)°) also indicate that this carbonyl group $\pi$-system is coplanar with the adjacent cyclopentadienyl ring system, instead of the naphthyl phane. The ester carbonyl group also has poor coplanarity with the naphthyl plane with O(5) and C(20) atoms markedly deviating from the naphthyl plane (−0.4180 Å for O(5) and 0.2326 Å for C(20), respectively).

Some weak intermolecular Cl···Cl interactions and C–H···O hydrogen bonds are observed in the crystal packing (figure 2). The noncovalent Cl(1)···Cl(3) distance is 3.418(1) Å (van der Waals radii of two Cl atoms is 3.6 Å), and the O(5)···H(5) distance is 2.356(2) Å. This complex is linked into a two-dimensional network through these weak intermolecular Cl···Cl and C–H···O interactions.

## Supplementary information

Crystallographic data (CIF files) for the structure **10** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 634265. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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