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# 基于 1-(2-吡啶甲基)-1,2,4-三唑的金属有机化合物的合成及反应研究

陈丹峰　潘爱清　陆继廷　唐良富*

(南开大学化学系,元素有机化学国家重点实验室,天津　300071)

**摘要**：合成了 1-(2-吡啶甲基)-1,2,4-三唑(L)并研究了其与有机锡和羰基钼(钨)的配位反应,合成了通过三唑 4 位氮原子以单齿形式配位的有机锡衍生物 $L_2SnR_2Cl_2$(R=Me,*n*-Bu 或 Ph)和羰基金属配合物 $LM(CO)_5$(M=Mo 或 W),以及 N,N 螯合双齿配位的四羰基金属配合物 $LM(CO)_4$。当用氯化苄处理 L 时,制得了相应的三唑盐,该盐用氧化银处理后与 $M(CO)_5THF$ 或 $M(CO)_4(NHC_5H_{10})_2$($NHC_5H_{10}$ 为哌啶)反应,得到了基于三唑的氮杂环卡宾衍生物 $L'M(CO)_5$ 和 $L'M(CO)_4$(L′=1-(2-吡啶甲基)-4-苄基-1,2,4-三唑-5-碳烯)。X-射线单晶衍射分析表明,在 $L'M(CO)_5$ 中氮杂环卡宾配体 L′表现为通过卡宾碳配位的单齿配体;而在 $L'M(CO)_4$ 中,L′表现为通过卡宾碳和吡啶氮原子配位的螯合[C,N]双齿配体。

**关键词**：氮配体；卡宾；三唑；钼；钨；锡

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# Synthesis and Related Reactivity of Organometallic Complexes Based on 1-(2-Pyridylmethyl)-1,2,4-triazole

CHEN Dan-Feng　PAN Ai-Qing　LU Ji-Ting　TANG Liang-Fu*

(*Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin* 300071, *China*)

**Abstract:** 1-(2-Pyridylmethyl)-1,2,4-triazole (L) has been synthesized by the reaction of 1,2,4-triazole with 2-chloromethylpyridine. Reaction of L with $R_2SnCl_2$ gave 2:1 adducts of $L_2SnR_2Cl_2$ (R=Me, *n*-Bu or Ph). Treatment of L with $M(CO)_6$ yielded complexes $LM(CO)_5$ and $LM(CO)_4$ (M=Mo or W). X-ray structural analyses indicated that L acted as a monodentate ligand through the exodentate nitrogen atom of the triazole ring in complexes $L_2SnR_2Cl_2$ and $LM(CO)_5$, while a *N*,*N*-chelating bidentate ligand was observed in $LM(CO)_4$. 1-(2-Pyridylmethyl)-4-benzyl-1,2,4-triazolium chloride was obtained by the reaction of L with $PhCH_2Cl$. Treatment of this triazolium salt with $Ag_2O$, and succedent metal transfer reaction with $M(CO)_5THF$ or $M(CO)_4(NHC_5H_{10})_2$ ($NHC_5H_{10}$ represents piperidine) yielded N-heterocyclic carbene complexes $L'M(CO)_5$ and $L'M(CO)_4$ (L′=1-(2-pyridylmethyl)-4-benzyl-1,2,4-triazol-5-ylidene), respectively. In the former, L′ acted as a monodentate ligand by the carbene carbon, while L′ served as a chelating bidentate ligand by the pyridyl nitrogen and the carbene carbon atoms in the latter. CCDC: 973255, **1**; 973463, **5**; 973464, **8**; 973465, **10**.

**Key words:** N ligand; carbene; triazole; molybdenum; tungsten; tin

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*通讯联系人。E-mail:lftang@nankai.edu.cn;会员登记号:S060015703M。

Owing to the existence of more than one active coordinate nitrogen atom in triazole ring, the coordination chemistry of triazole has been widely explored in the documents[1-3]. A number of transition metal complexes containing triazole and its derivatives have been synthesized and characterized, which usually aggregate dinuclear, oligonuclear and polynuclear metal complexes, and exhibit fascinating structures and interesting properties[1-5]. In recent years, *N*-heterocyclic carbenes based on the 1,2,4-triazole ring have received more and more attention[6-16]. Triazolylidenes exhibit different steric and electronic environments compared to imidazolylidenes, owing to the presence of an additional nitrogen atom in the ring. Some triazolylidene complexes have been found to show significantly higher catalytic activity in comparison to their imidazolylidene analogues[12]. We have been interested in the chemistry of 1,2,4-triazole derivatives, which showed variable coordination modes depending on different metals[17-19]. For example, bis(1,2,4-triazol-1-yl)methanes coordinated to the tin atoms through exodentate nitrogen atoms on the 4-position of triazole rings to form linkage coordination polymers, which led to a bridging instead of a general chelating coordination mode[18]. While the chelating bidentate coordination mode using two endodentate nitrogen atoms was observed when coordinated to group 6 metal carbonyl complexes[19]. As an extension of our investigations on 1,2,4-triazole derivatives, we herein report the synthesis of 1-(2-pyridylmethyl)-1,2,4-triazole as well as its related reactivity.

## 1 Experimental

All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled prior to use according to standard procedures. NMR ($^1$H, $^{13}$C and $^{119}$Sn) were recorded on a Bruker 400 spectrometer, and the chemical shifts were reported in ppm with respect to the reference (internal $SiMe_4$ for $^1$H and $^{13}$C NMR, external $SnMe_4$ for $^{119}$Sn NMR). These assignments were confirmed by standard Bruker gradient enhanced HMBC and HMQC pulse sequences. IR spectra were recorded as KBr pellets on a Nicolet 380 spectrometer. Element analyses were carried out on an Elementar Vairo EL analyzer. $Mo(CO)_4(NHC_5H_{10})_2$ and $W(CO)_4(NHC_5H_{10})_2$ were prepared by the published methods[20].

### 1.1 Synthesis of 1-(2-pyridylmethyl)-1,2,4-triazole (L)

The mixture of 2-chloromethylpyridine-HCl (2.2 g, 13.4 mmol), 1,2,4-triazole (0.84 g, 12.2 mmol), tetrabutylammonium bromide (0.1 g, 0.31 mmol) and sodium hydroxide (5.0 g, 125 mmol) in a mixed solvent of toluene (40 mL) and water (10 mL) was stirred and heated at reflux for 6 h. After cooling to room temperature, the organic layer was separated and the aqueous phase was extracted with dichloromethane. The organic layers were combined and dried over $MgSO_4$. After evaporating the solvent, the residue was purified by column chromatography on silica using ethyl acetate/ethanol (4:1, *V*/*V*) as eluent. The yellow eluate was concentrated to dryness under reduced pressure to give yellow oils, which slowly solidified during storage. Yield: 1.5 g (77%). $^1$H NMR ($CDCl_3$): $\delta$ 5.49 (s, 2H, $CH_2$), 7.18 (d, *J*=7.8 Hz, 1H), 7.25~7.28 (m, 1H), 7.70 (dt, *J*=1.7 Hz, *J*=7.7 Hz, 1H), 8.60 (d, *J*=4.5 Hz, 1H) ($C_5H_4N$), 7.99, 8.27 (s, s, 1H, 1H, $C_2H_2N_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 54.8 ($CH_2$), 122.1, 123.2, 137.1, 143.8, 149.6, 152.1, 154.5 ($C_5H_4N$ and $C_2H_2N_3$). Anal. Calcd. for $C_8H_8N_4$ (%): C 59.99, H 5.03, N 34.98; found(%): C 60.04, H 5.03, N 34.61.

### 1.2 Reaction of L with $R_2SnCl_2$ (R=Me, *n*-Bu or Ph)

To a stirred solution of L (0.16 g, 1 mmol) in $CH_2Cl_2$ (5 mL) at room temperature, the solution of $R_2SnCl_2$ (1 mmol) in hexane (5 mL) was added. A white solid precipitated out immediately during the reaction of $Me_2SnCl_2$ as well as $Ph_2SnCl_2$ while no solid formed during the reaction of *n*-$Bu_2SnCl_2$. After the reaction mixture was stirred for 6 h at room temperature, the precipitate was filtered off in the case of $Me_2SnCl_2$ as well as $Ph_2SnCl_2$, and the solvent was removed under reduced pressure in the reaction of *n*-$Bu_2SnCl_2$ to give crude products, which were washed with cold hexane and recrystallized from $CH_2Cl_2$/hexane to give colorless crystals of complexes **1~3**.

Complex $L_2SnMe_2Cl_2$ (**1**) was obtained by the reaction of $Me_2SnCl_2$ with L in a yield of 89%. $^1$H NMR ($CDCl_3$): $\delta$ 1.25 (s, 6H, $CH_3$), 5.50 (s, 4H, $CH_2$), 7.23~7.31 (m, 4H), 7.72 (dt, $J$=1.6 Hz, $J$=7.7 Hz, 2H), 8.59 (d, $J$=4.5 Hz, 2H) ($C_5H_4N$), 8.06, 8.46 (s, s, 2H, 2H, $C_2H_2N_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 12.3 ($CH_3$), 55.3 ($CH_2$), 122.5, 123.7, 137.4, 143.8, 149.9, 153.9, 151.3 ($C_5H_4N$ and $C_2H_2N_3$). $^{119}$Sn NMR ($CDCl_3$): $\delta$ −5.73. Anal. Calcd. for $C_{18}H_{22}Cl_2N_8Sn$(%): C 40.03, H 4.11, N 20.75; Found (%): C 39.72, H 3.70, N 20.71.

Complex $L_2Sn(n\text{-}Bu)_2Cl_2$ (**2**) was obtained by the reaction of $n$-$Bu_2SnCl_2$ with L in a yield of 74%. $^1$H NMR ($CDCl_3$): $\delta$ 0.94 (t, $J$=7.3 Hz, 6H, $CH_3$), 1.37~1.44 (m, 4H), 1.76~1.85 (m, 8H) ($CH_2$), 5.51 (s, 4H, $CH_2N$), 7.21~7.31 (m, 4H), 7.73 (dt, $J$=1.7 Hz, $J$=7.7 Hz, 2H), 8.60 (d, $J$=4.4 Hz, 2H) ($C_5H_4N$), 8.01, 8.35 (s, s, 2H, 2H, $C_2H_2N_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 12.3, 26.3, 27.1, 28.4 (carbons of $n$-butyl), 55.0 ($CH_2$), 122.5, 123.5, 137.5, 144.0, 149.7, 152.0, 154.3 ($C_5H_4N$ and $C_2H_2N_3$). $^{119}$Sn NMR ($CDCl_3$): $\delta$ 45.5. Anal. Calcd. for $C_{24}H_{34}Cl_2N_8Sn$(%): C 46.18, H 5.49, N 17.95; Found(%): C 46.50, H 5.85, N 17.53.

Complex $L_2SnPh_2Cl_2$ (**3**) was obtained by the reaction of $Ph_2SnCl_2$ with L in a yield of 85%. $^1$H NMR (DMSO-$d_6$): $\delta$ 5.62 (s, 4H, $CH_2$), 7.23~7.49, 7.90~7.96 (m, m, 10H, 6H) ($C_6H_5$ and $C_5H_4N$), 8.09, 8.61 (s, s, 2H, 2H, $C_2H_2N_3$), 8.77~8.82 (m, 2H, $C_5H_4N$). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 53.0 ($CH_2$), 123.0, 123.7, 127.0, 127.5, 134.8, 138.9, 144.8, 148.0, 151.2, 154.1, 155.8 ($C_6H_5$, $C_5H_4N$ and $C_2H_2N_3$). $^{119}$Sn NMR (DMSO-$d_6$): $\delta$ −279.4. Anal. Calcd. for $C_{28}H_{26}Cl_2N_8Sn.CH_2Cl_2$(%): C 46.50, H 3.77, N 14.96; Found(%): C 46.30, H 3.42, N 14.46.

### 1.3 Reaction of L with $M(CO)_6$ (M=Mo or W)

A solution of $M(CO)_6$ (1 mmol) and L (0.16 g, 1 mmol) dissolved in THF (40 mL) was irradiated with a 300 W high-pressure Hg lamp for 20 h at room temperature. After the reaction complete, the solvent was removed in vacuo, and the residual solid was purified by column chromatography on silica using ethyl acetate as eluent to yield two products. The first green-yellow band was identified as complexes $LMo(CO)_5$ (**4**) or $LW(CO)_5$ (**5**), and the second green-yellow band was identified as complexes $LMo(CO)_4$ (**6**) or $LW(CO)_4$ (**7**), by their spectroscopic data as well as X-ray crystal diffraction of **5**.

Data for **4**, yield: 5%. $^1$H NMR ($CDCl_3$): $\delta$ 5.45 (s, 2H, $CH_2$), 7.31~7.36 (m, 2H), 7.77 (dt, $J$=1.7 Hz, $J$=7.7 Hz, 1H), 8.63 (d, $J$=4.6 Hz, 1H) ($C_5H_4N$), 7.87, 8.40 (s, s, 1H, 1H, $C_2H_2N_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 55.8 ($CH_2$), 122.9, 123.9, 137.5, 146.4, 150.2, 152.3, 154.4 ($C_5H_4N$ and $C_2H_2N_3$), 204.2 (4C), 213.1 (1C) (CO). IR $\nu$(C≡O): 2 072 (m), 1 943 (sh), 1 909 (vs), 1 881 (sh), 1 841 (s) cm$^{-1}$. Anal. Calcd. for $C_{13}H_8MoN_4O_5$(%): C 39.41, H 2.04, N 14.14; Found(%): C 39.12, H 2.42, N 14.03.

Data for **5**, yield: 67%. $^1$H NMR ($CDCl_3$): $\delta$ 5.46 (s, 2H, $CH_2$), 7.32~7.38 (m, 2H), 7.78 (dt, $J$=1.7 Hz, $J$=7.7 Hz, 1H), 8.64 (d, $J$=4.7 Hz, 1H) ($C_5H_4N$), 7.98, 8.54 (s, s, 1H, 1H, $C_2H_2N_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 55.9 ($CH_2$), 123.0, 124.1, 137.6, 147.8, 150.3, 152.3, 155.4 ($C_5H_4N$ and $C_2H_2N_3$), 197.9 (4C), 201.6 (1C) (CO). IR $\nu$(C≡O): 2 070 (m), 1 971 (sh), 1 934 (s), 1 901 (vs), 1 872 (sh) cm$^{-1}$. Anal. Calcd. for $C_{13}H_8N_4O_5W$(%): C 32.26, H 1.67, N 11.57; Found (%): C 32.48, H 1.60, N 11.69.

Data for **6**, yield: 43%. $^1$H NMR ($CD_3COCD_3$): $\delta$ 5.85 (s, 2H, $CH_2$), 7.51~7.56 (m, 1H), 7.87 (d, $J$=7.7 Hz, 1H), 8.09 (dt, $J$=1.6 Hz, $J$=7.7 Hz, 1H), 9.11 (dd, $J$=0.8 Hz, $J$=5.4 Hz, 1H) ($C_5H_4N$), 8.44, 8.82 (s, s, 1H, 1H, $C_2H_2N_3$). $^{13}$C NMR ($CD_3COCD_3$): $\delta$ 54.4 ($CH_2$), 125.2, 127.5, 140.4, 146.8, 155.5, 156.4, 156.6 ($C_5H_4N$ and $C_2H_2N_3$), 206.9 (2C), 221.0 (1C), 221.8 (1C) (CO). IR $\nu$(C≡O): 2 015 (s), 1 896 (vs), 1 867 (s), 1 816 (vs) cm$^{-1}$. Anal. Calcd. for $C_{12}H_8MoN_4O_4$(%): C 39.15, H 2.19, N 15.22; Found(%): C 39.43, H 2.03, N 15.68.

Data for **7**, yield: 18%. $^1$H NMR ($CD_3COCD_3$): $\delta$ 5.89 (s, 2H, $CH_2$), 7.52~7.56 (m, 1H), 7.92 (d, $J$=7.7 Hz, 1H), 8.13 (t, $J$=7.3 Hz, 1H), 9.23 (d, $J$=5.3 Hz, 1H) ($C_5H_4N$), 8.54, 8.85 (s, s, 1H, 1H, $C_2H_2N_3$). $^{13}$C NMR ($CD_3COCD_3$): $\delta$ 55.6 ($CH_2$), 125.9, 127.8, 140.5, 146.7, 155.4, 156.8, 157.6 ($C_5H_4N$ and $C_2H_2N_3$), 204.2 (2C), 212.6 (1C), 213.2 (1C) (CO). IR $\nu$(C≡O): 2 009 (s), 1 879 (vs), 1 852 (sh), 1 808 (vs) cm$^{-1}$. Anal. Calcd. for $C_{12}H_8N_4O_4W$(%): C 31.60, H 1.77, N 12.29; Found (%): C 31.52, H 1.86, N 11.84.

### 1.4 Heating of 5 in dioxane

The solution of **5** (20 mg, 0.04 mmol) in dioxane (20 mL) was stirred and heated at reflux for 6 h. After removing the solvent, the residue was purified by column chromatography on silica using ethyl acetate as eluent to give **7**. Yield: 11 mg (61%).

### 1.5 Synthesis of L′HCl (L′=1-(2-pyridylmethyl)-4-benzyl-1,2,4-triazol-5-ylidene)

$PhCH_2Cl$ (1.97 mL, 17 mmol) was added to the solution of L (2.75 g, 17.2 mmol) in $CH_3CN$ (10 mL), then the reaction mixture was stirred and heated at reflux for 24 h. After cooling to room temperature, the solvent was concentrated to 5 mL, and toluene (30 mL) was slowly added. Oil was separated, which slowly solidified to give a slightly yellow solid. This solid was filter off, and washed with toluene and ether to afford L′HCl. Yield: 4.51 g (92%). $^1$H NMR ($CDCl_3$): $\delta$ 5.83 (s, 2H, $CH_2C_5H_4N$), 5.86 (s, 2H, $CH_2C_6H_5$), 7.41~7.57 (m, 5H, $C_6H_5$), 7.26~7.27 (m, 1H, 5-$C_5H_4N$), 7.59 (m, 1H, 3-$C_5H_4N$), 7.84 (t, $J$=7.7 Hz, 1H, 4-$C_5H_4N$), 8.50 (d, $J$=8.5 Hz, 1H, 6-$C_5H_4N$), 8.70 (s, 1H, 3-$C_2H_2N_3$), 12.09 (s, 1H, triazolium). $^{13}$C NMR ($CDCl_3$): $\delta$ 52.0 ($CH_2C_6H_5$), 57.1 ($CH_2C_5H_4N$), 129.4, 129.7, 129.9, 132.0 ($C_6H_5$), 123.4 (2-$C_5H_4N$), 124.1 (3-$C_5H_4N$), 137.5 (4-$C_5H_4N$), 143.2 (6-$C_5H_4N$), 144.5 (2-$C_5H_4N$), 150.0 (3-$C_2H_2N_3$), 151.2 (5-$C_2H_2N_3$). HRMS (ESI, *m/z*): 251.1291 (Calcd. for $C_{15}H_{15}N_4$: 251.1297, $[M-Cl]^+$, 100%).

### 1.6 Synthesis of L′W(CO)$_5$ (8)

$Ag_2O$ (0.12 g, 0.52 mmol) was added to the solution of L′HCl (0.14 g, 0.49 mmol) in $CH_3CN$ (10 mL). The reaction mixture was stirred for 24 h in dark place at room temperature, and filtered off. The filtrate was concentrated to dryness and the solution of $W(CO)_5THF$ in THF, prepared in situ by irradiation of a solution of $W(CO)_6$ (0.18 g, 0.5 mmol) in THF (40 mL) for 8 h, was added. The mixture was stirred and heated at 30 ℃ for 24 h, and filtered off. The solvent was removed under a reduced pressure. The residue was purified by column chromatography on silica using ethyl acetate as eluent to give **8** as a slightly yellow solid. Yield: 0.10 g (36%). $^1$H NMR ($CDCl_3$): $\delta$ 5.50 (s, 2H, $CH_2C_6H_5$), 5.84 (s, 2H, $CH_2C_5H_4N$), 7.01 (d, $J$=7.9 Hz, 1H, 3-$C_5H_4N$), 7.22~7.25 (m, 1H, 5-$C_5H_4N$), 7.69 (td, $J$=7.7 Hz, $J$=1.4 Hz, 1H, 4-$C_5H_4N$), 8.60 (d, $J$=4.7 Hz, 1H, 6-$C_5H_4N$), 7.25~7.29 (m, 2H), 7.42~7.48 (m, 3H) ($C_6H_5$), 7.77 (s, 1H, $C_2HN_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 54.6 ($CH_2C_6H_5$), 59.1 ($CH_2C_5H_4N$), 128.4, 129.2, 129.6, 134.0 ($C_6H_5$), 121.4 (3-$C_5H_4N$), 123.0 (5-$C_5H_4N$), 136.9 (4-$C_5H_4N$), 149.8 (6-$C_5H_4N$), 155.0 (2-$C_5H_4N$), 143.0 ($C_2HN_3$), 185.0 (W-$C_{carbene}$), 196.9 (4C), 200.0 (1C) (CO). IR $\nu$(C≡O): 2 064 (s), 1 962 (sh), 1 913 (vs), 1 890 (vs) cm$^{-1}$. Anal. Calcd. for $C_{20}H_{14}N_4O_5W$ (%): C 41.84, H 2.46, N 9.76; Found (%): C 41.86, H 2.86, N 9.94.

### 1.7 Synthesis of L′Mo(CO)$_4$ (9)

This complex was obtained similarly as above-mentioned for **8** as a yellow solid, while $W(CO)_5THF$ was replaced by $Mo(CO)_4(NHC_5H_{10})_2$. The eluent was $CH_2Cl_2$. Yield: 84%. $^1$H NMR ($CDCl_3$): $\delta$ 5.42 (s, 2H, $CH_2C_5H_5N$), 5.49 (s, 2H, $CH_2C_6H_5$), 7.20 (td, $J$=7.1 Hz, J=1.0 Hz, 1H, 5-$C_5H_4N$), 7.47 (d, $J$=7.7 Hz, 1H, 3-$C_5H_4N$), 7.78 (td, $J$=7.7 Hz, $J$=1.6 Hz, 1H, 4-$C_5H_4N$), 9.09 (dd, $J$=5.4 Hz, $J$=0.7 Hz, 1H, 6-$C_5H_4N$), 7.33~7.43 (m, 5H, $C_6H_5$), 7.71 (s, 1H, $C_2HN_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 52.7 ($CH_2C_6H_5$), 58.0 ($CH_2C_5H_4N$), 128.7, 128.9, 129.3, 134.5 ($C_6H_5$), 123.4 (2-$C_5H_4N$), 125.2 (3-$C_5H_4N$), 138.3 (4-$C_5H_4N$), 155.5 (2-$C_5H_4N$), 157.1 (6-$C_5H_4N$), 141.3 ($C_2HN_3$), 199.4 (Mo-$C_{carbene}$), 208.0 (2C), 218.0 (1C), 223.6 (1C) (CO). IR $\nu$(C≡O): 2 006 (s), 1 896 (s), 1 861 (s), 1 813 (vs) cm$^{-1}$. Anal. Calcd. for $C_{19}H_{14}MoN_4O_4$ (%): C 49.79, H 3.08, N 12.22; Found (%) C 49.88, H 3.56, N 12.37.

### 1.8 Synthesis of L′W(CO)$_4$ (10)

This complex was obtained similarly as above-mentioned for **8** as a yellow solid, while $W(CO)_5THF$ was replaced by $W(CO)_4(NHC_5H_{10})_2$. The eluent was $CH_2Cl_2$. Yield: 78%. $^1$H NMR ($CDCl_3$): $\delta$ 5.45 (s, 2H, $CH_2C_5H_5N$), 5.48 (s, 2H, $CH_2C_6H_5$), 7.21 (td, $J$=7.1 Hz, $J$=1.0 Hz, 1H, 5-$C_5H_4N$), 7.53 (d, $J$=7.7 Hz, 1H, 3-$C_5H_4N$), 7.84 (td, $J$=7.7 Hz, $J$=1.6 Hz, 1H, 4-$C_5H_4N$), 9.26 (dd, $J$=5.4 Hz, $J$=0.7 Hz, 1H, 6-$C_5H_4N$), 7.36~7.43 (m, 5H, $C_6H_5$), 7.74 (s, 1H, $C_2HN_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 53.2 ($CH_2C_6H_5$), 58.9 ($CH_2C_5H_4N$), 128.9, 129.0, 129.4, 134.3 ($C_6H_5$), 124.1 (2-$C_5H_4N$), 125.2 (3-$C_5H_4N$), 138.4 (4-$C_5H_4N$), 155.6 (2-$C_5H_4N$), 158.6 (6-$C_5H_4N$), 141.5 ($C_2HN_3$), 195.4 (W-$C_{carbene}$), 203.1 (2C),

212.8 (1C), 213.8 (1C) (CO). IR $\nu$(C≡O): 2 002 (s), 1 888 (s), 1 859 (s), 1 809 (vs) cm$^{-1}$. Anal. Calcd. for $C_{19}H_{14}N_4O_4W$ (%): C 41.78, H 2.58, N 10.26; Found (%): C 41.71, H 2.61, N 10.41.

### 1.9 Heating of 8 in dioxane

The solution of **8** (32 mg, 0.06 mmol) in dioxane (20 mL) was stirred and heated at reflux for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica using $CH_2Cl_2$ as eluent to give **10** (24 mg, 80%).

### 1.10 X-ray crystallography

Colorless crystals of **1** and green-yellow crystals of **5**, **8** and **10** suitable for X-ray analysis were grown by slow diffusion of hexane into their $CH_2Cl_2$ solutions at −18 ℃. All intensity data were collected with a Rigaku Saturn CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda$=0.071 073 nm). Semi-empirical absorption corrections were applied using the Crystalclear program[21]. The C(10) and C(14) atoms of the phenyl group and the N(4) and C(17) atoms of the pyridyl group in **8** were disorder, and their occupancy factors were refined to 0.75. In addition, the N(3) and C(7) atoms of the triazole ring in this complex were also disorder, their occupancy factors were refined to 0.5. The structures were solved by direct methods and difference Fourier map using SHELXS of the SHELXTL package and refined with SHELXL[22] by full-matrix least-squares on $F^2$. All nonhydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for these complexes is listed in Table 1.

CCDC: 973255, **1**; 973463, **5**; 973464, **8**; 973465, **10**.

## 2 Results and discussion

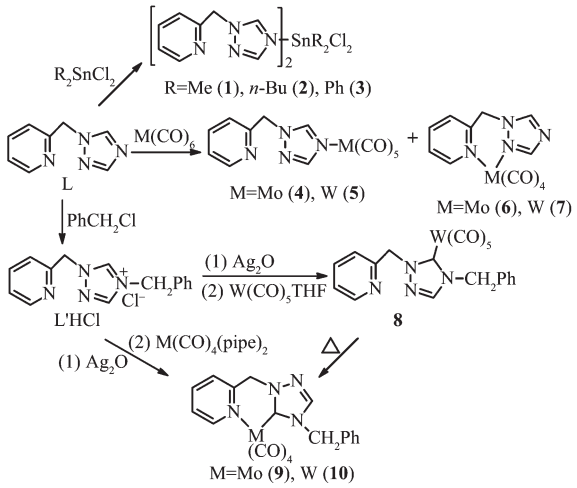
### 2.1 Synthesis and reaction of 1-(2-pyridylmethyl)-1,2,4-triazole

1-(2-Pyridylmethyl)-1,2,4-triazole (L) was readily obtained by the reaction of 2-chloromethylpyridine

**Table 1　Crystallographic data and refinement parameters for complexes 1, 5, 8 and 10**

| Complex | **1** | **5** | **8** | **10** |
|---|---|---|---|---|
| Formula | $C_{18}H_{22}Cl_2N_8Sn$ | $C_{13}H_8N_4O_5W$ | $C_{20}H_{14}N_4O_5W$ | $C_{19}H_{14}N_4O_4W$ |
| Formula weight | 540.03 | 484.08 | 574.20 | 546.19 |
| Crystal size / mm | 0.24×0.22×0.18 | 0.20×0.14×0.12 | 0.20×0.18×0.12 | 0.32×0.20×0.15 |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Orthorhombic |
| Space group | *Pbca* | *C*2/*c* | $P2_1/c$ | *Pbca* |
| *a* / nm | 0.978 51(15) | 1.109 2(2) | 2.767 9(5) | 0.851 18(4) |
| *b* / nm | 1.010 67(16) | 1.981 5(4) | 0.654 11(14) | 1.506 97(6) |
| *c* / nm | 2.320 9(4) | 1.414 9(3) | 2.220 8(5) | 2.888 26(13) |
| $\beta$ / (°) | | 98.694(3) | 90.119(4) | |
| *V* / nm$^3$ | 2.295 3(6) | 3.074 1(11) | 4.020 8(15) | 3.704 8(3) |
| *Z* | 4 | 8 | 8 | 8 |
| *T* / K | 296(2) | 293(2) | 113(2) | 293(2) |
| $D_c$ / (g·cm$^{-3}$) | 1.563 | 2.092 | 1.897 | 1.958 |
| 2$\theta$ range / (°) | 3.50~50.06 | 4.12~50.04 | 2.94~55.86 | 5.40~50.02 |
| *F*(000) | 1 080 | 1 824 | 2 208 | 2 096 |
| $\mu$ / mm$^{-1}$ | 1.367 | 7.546 | 5.786 | 6.270 |
| Number of reflections measured | 10 696 | 8 090 | 37 958 | 9 017 |
| Number of reflections observed ($R_{int}$) | 2 019 (0.026 8) | 2 723 (0.061 8) | 9 605 (0.0438) | 3 253 (0.044 0) |
| Number of reflections observed with ($I \geqslant 2\sigma(I)$) | 1 681 | 2 108 | 7 885 | 2 496 |
| Number of parameters | 133 | 208 | 541 | 253 |
| Residuals $R_1$, $wR_2$ ($I \geqslant 2\sigma(I)$) | 0.029 8, 0.072 3 | 0.030 5, 0.069 7 | 0.028 7, 0.059 1 | 0.044 5, 0.104 9 |
| Goodness-of-fit | 1.110 | 1.008 | 1.106 | 1.065 |

with 1,2,4-triazole. This ligand is potentially a chelating bidentate ligand by the pyridyl nitrogen atom and the endodentate nitrogen of the triazole ring, or a bridging bidentate ligand by the pyridyl nitrogen atom and the exodentate nitrogen of the triazole ring. Reaction of L with $R_2SnCl_2$ (R=Me, *n*-Bu or Ph) in a 1∶1 or 2∶1 molar ratio gave the same 2∶1 adducts of **1**~**3** (Scheme 1), according to the results of their elemental analyses and $^1$H NMR data.




Scheme 1 Reactions of 1-(2-pyridylmethyl)-1,2,4-triazole

The structure of **1** has been confirmed by X-ray structural analyses, and is presented in Fig.1, which clearly demonstrates that 1-(2-pyridylmethyl)-1,2,4-triazole coordinates to the tin atom only through the exodentate nitrogen atom of the triazole ring. The pyridyl nitrogen atom does not take part in the coordination. The pyridyltriazole only acts as a monodentate ligand toward the tin atom, which is six-coordinate with a slightly distorted octahedral geometry, containing two nitrogen atoms of triazolyl groups, two methyl carbons as well as two chlorine atoms in an all-trans configuration. The Sn(1)-N(3) bond distance is 0.236 3(2) nm, comparable to those in other diorganotin derivatives with monodentate N-donor ligands, such as 0.245 4(7) nm in $(CH_2Tz_2)SnPh_2Br_2$ (Tz=1,2,4-triazol-1-yl)[18]. The two triazolyl groups are parallel to each other.

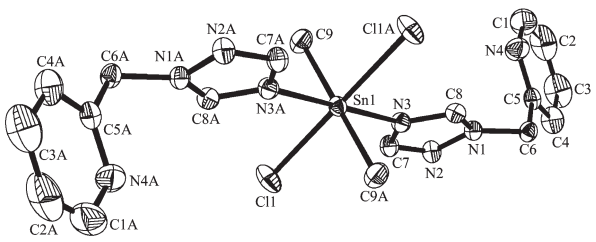



Fig.1 Molecular structure of **1** with the thermal ellipsoids drawn at the 30% probability level

Reaction of L and $M(CO)_6$ (M=Mo or W) under the irradiation of 300 W high-pressure Hg lamp gave complexes **4**~**7**. In addition, upon heating of 5 in refluxing dioxane, complex **7** was obtained in reasonable yield. These four complexes have characterized by IR and NMR spectra. The IR spectra of **4** and **5** are significantly different from those of **6** and **7**. The former two complexes display a $\nu$(C≡O) band at 2 072 cm$^{-1}$ (**4**) as well as 2 070 cm$^{-1}$ (**5**), corresponding to the $A_{1eq}$ mode for the pseudo $C_{4v}$ metal center in the $M(CO)_5$ fragment[23], while the latter two complexes show four bands in the carbonyl stretching region, consistent with a typical *cis*-tetracarbonyl arrangement[24]. The $^{13}$C NMR spectra of these four complexes also support the suggested structures. For example, two signals of the metal carbonyl carbon atoms with *ca.* a 1∶4 intensity ratio were observed in **4** and **5**, consistent with their monosubstituted pentacarbonyl structure.

These results have been further confirmed by the X-ray crystal analysis of **5**. Selected bond distances and angles are listed in Table 2, and the structure of **5** is presented in Fig.2. 1-(2-Pyridylmethyl)-1,2,4-triazole acts as a monodentate ligand to the tungsten atom only through the exodentate nitrogen atom of the

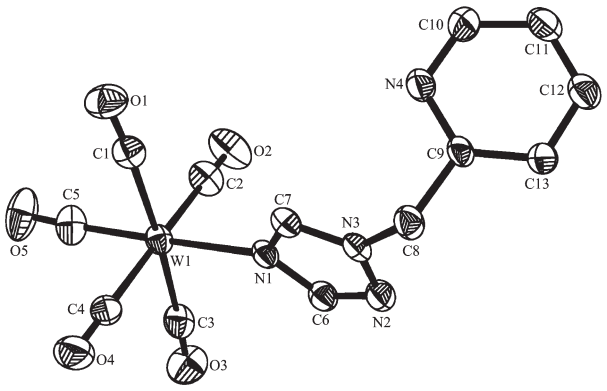


Fig.2 Molecular structure of **5** with the thermal ellipsoids drawn at the 30% probability level

**Table 2　Selected bond distances (nm) and angles (°) for complexes 1, 5, 8 and 10**

| | | | | | |
|---|---|---|---|---|---|
| Complex **1** | | | | | |
| Sn(1)-C(9) | 0.211 9(3) | Sn(1)-N(3) | 0.236 3(2) | Sn(1)-Cl(1) | 0.255 51(9) |
| N(3)-Sn(1)-N(3A) | 180.0(1) | N(3)-Sn(1)-Cl(1A) | 90.25(8) | Cl(1)-Sn(1)-Cl(1A) | 180.00(6) |
| C(9)-Sn(1)-N(3) | 87.5(1) | C(5)-C(6)-N(1) | 112.4(3) | | |
| Complex **5** | | | | | |
| W(1)-C(1) | 0.202 9(8) | W(1)-C(2) | 0.204 1(8) | C(1)-O(1) | 0.113 3(7) |
| W(1)-C(5) | 0.195 1(8) | W(1)-N(1) | 0.225 6(4) | C(5)-O(5) | 0.116 5(8) |
| W(1)-C(1)-O(1) | 175.6(6) | W(1)-C(2)-O(2) | 177.5(7) | W(1)-C(3)-O(3) | 177.5(7) |
| W(1)-C(4)-O(4) | 179.5(7) | W(1)-C(5)-O(5) | 177.4(8) | C(1)-W(1)-C(3) | 175.7(3) |
| C(1)-W(1)-C(5) | 86.3(3) | C(2)-W(1)-C(4) | 177.2(3) | C(3)-W(1)-C(4) | 88.3(3) |
| C(1)-W(1)-N(1) | 91.3(2) | C(5)-W(1)-N(1) | 177.4(2) | N(3)-C(8)-C(9) | 112.5(5) |
| Complex **8** | | | | | |
| W(1)-C(1) | 0.203 5(3) | W(1)-C(2) | 0.204 6(3) | C(2)-O(2) | 0.113 8(3) |
| W(1)-C(3) | 0.200 1(3) | W(1)-C(6) | 0.223 5(3) | C(3)-O(3) | 0.114 9(3) |
| W(1)-C(1)-O(1) | 176.1(3) | W(1)-C(2)-O(2) | 176.8(2) | W(1)-C(3)-O(3) | 179.2(3) |
| W(1)-C(4)-O(4) | 177.9(2) | W(1)-C(5)-O(5) | 175.4(2) | C(1)-W(1)-C(3) | 87.20(12) |
| C(1)-W(1)-C(4) | 177.39(11) | C(1)-W(1)-C(6) | 93.42(10) | N(1)-C(8)-C(9) | 110.6(2) |
| C(3)-W(1)-C(6) | 177.53(10) | C(2)-W(1)-C(5) | 175.41(11) | N(2)-C(15)-C(16) | 110.8(2) |
| Complex **10** | | | | | |
| W-C(7) | 0.222 0(8) | W-C(18) | 0.193 4(9) | C(19)-O(4) | 0.112 9(10) |
| W-N(1) | 0.229 2(6) | W-C(19) | 0.204 6(10) | C(18)-O(3) | 0.118 0(10) |
| W(1)-C(16)-O(1) | 174.3(7) | C(7)-W-C(17) | 172.4(3) | C(7)-W-N(1) | 79.4(3) |
| W(1)-C(17)-O(2) | 178.7(8) | C(7)-W-C(19) | 95.5(3) | C(18)-W-N(1) | 174.9(3) |
| W(1)-C(18)-O(3) | 176.4(7) | C(16)-W-C(19) | 170.9(3) | N(2)-C(6)-C(5) | 112.0(7) |
| W(1)-C(19)-O(4) | 174.0(8) | C(18)-W-C(19) | 84.3(4) | N(3)-C(9)-C(10) | 113.5(7) |

Symmetric code: **1**: A $-x+2, -y+1, -z$.

triazole ring, like that in **1**. The tungsten atom adopts a slightly distorted octahedral structure. The W-N distance is 0.225 6(4) nm, similar to those reported in other octahedral tungsten (0) complexes with triazole ligands, such as 0.224 8(3) nm in $PhCOCH(CH_2SPh)TzW(CO)_5$[17] and 0.226(1) nm in $CH_2(3,5\text{-}Me_2Tz)_2W(CO)_4$[19].

## 2.2　Synthesis of NHC-complexes based on 1-(2-pyridylmethyl)-1,2,4-triazole

Treatment of L with $PhCH_2Cl$ gave 1-(2-pyridylmethyl)-4-benzyl-1,2,4-triazolium chloride in good yield. Reaction of this triazolium salt with $Ag_2O$, and succedent treatment with $W(CO)_5THF$ or $M(CO)_4(NHC_5H_{10})_2$ yielded N-heterocyclic carbene (NHC) complexes **8~10** (see Scheme 1). Complex **8** can also be converted to **10** upon heating in refluxing dioxane. Compared with the spectrum of the triazolium salt precursor, a notable change in the $^1H$ NMR spectra of **8 ~10** was the disappearance of the characteristic proton signal of triazolium, indicating the formation of NHC complexes. Moreover, an obvious carbene carbon signal was observed in the range of 185~200 ppm in their $^{13}C$ NMR spectra, which is comparable to those of reported NHC-Mo or W complexes[25]. In addition, the characteristic carbonyl signals in the IR and $^{13}C$ NMR spectra of **8** were similar to those of **4** and **5**. For example, a $\nu(C\equiv O)$ band corresponding to the $A_{1eq}$ mode for the pseudo $C_{4v}$ metal center in the

$M(CO)_5$ fragmen was also observed in the IR spectrum of **8**. On the other hand, the carbonyl signals in the IR and $^{13}C$ NMR spectra of **9** and **10** were similar to those of **6** and **7**. Four bands in the carbonyl stretching region, matched along with a typical *cis*-tetracarbonyl arrangement, were observed in these four complexes. These results suggest that the structure of **8** is similar to those of **4** and **5**, while the structures of **9** and **10** are similar to those of **6** and **7**.

The molecular structure of **8** was confirmed by X-ray structural analyses, which was consisted of two crystallographically independent molecules with similar structural parameters. One of them is presented in Fig.3. As shown in the figure, 1-(2-pyridylmethyl)-4-benzyl-1,2,4-triazol-5-ylidene acts as a monodentate ligand by the carbene carbon to the tungsten atom, and the pyridyl nitrogen atom does not take part in the coordination to the metal center, consistent with the spectroscopic analyses of IR and NMR. The W-$C_{NHC}$ bond distance is 0.223 5(3) nm (see Table 2), comparable to those observed in NHC-supported $W(CO)_5$ complexes[25-26]. Four carbonyls cis to the NHC ligand deviate from linearity, indicating that the presence of the steric repulsion between the ligand and these carbonyls. To decrease the steric repulsion, the phenyl group and pyridyl ring are driven away from the metal center.

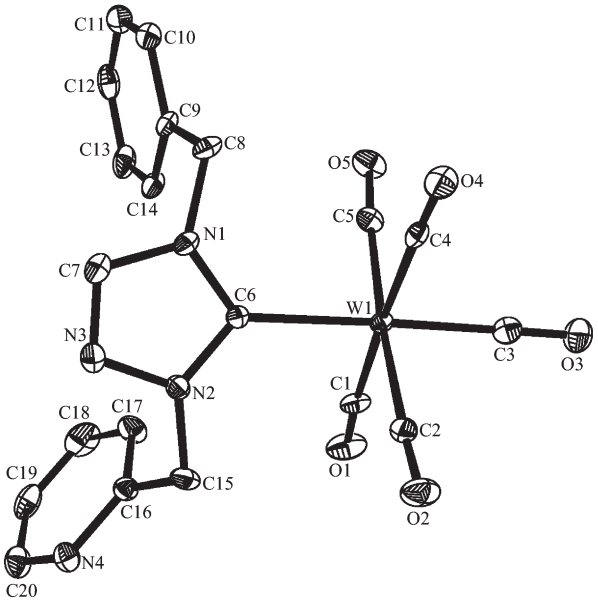



Fig.3 Molecular structure of **8** with the thermal ellipsoids drawn at the 30% probability level

The molecular structure of **10** is shown in Fig.4, and selected bond distances and angles are listed in Table 2. The functionalized NHC-based on triazole acts as a chelating $\kappa^2$-[N,C] bidentate ligand by the pyridyl nitrogen and the carbene carbon atoms, giving a six-membered metallacycle with a boat conformation. The W-$C_{NHC}$ bond distance is 0.222 0(8) nm, slightly shorter than that in **8**, possibly owing to the chelation effect of the ligand. At the same time, the chelation effect augments the steric repulsion between the ligand and two *cis*-carbonyls, which results in the W(1)-C(16)-O(1) angle of 174.3(7)°, W(1)-C(19)-O(4) angle of 174.0 (8)° and C (16)-W (1)-C (19) angle of 170.9(3)° deviating from linearity, and the N(2)-C(6)-C(5) angle of 112.0(7)° and N(3)-C(9)-C(10) angle of 113.5(7)° deviating from the tetrahedral geometry of the $sp^3$ hybridized carbon atom. The W-N bond distance is 0.229 2 (6) nm, longer than that in **5**, but very close to those reported for other octahedral tungsten (0) complexes with pyridyl groups, such as 0.228 3(3) nm in $CH_2(Py)(3\text{-}Bu^tPz)W(CO)_4$ (Py=pyridyl, Pz=pyrazol-1-yl)[27].

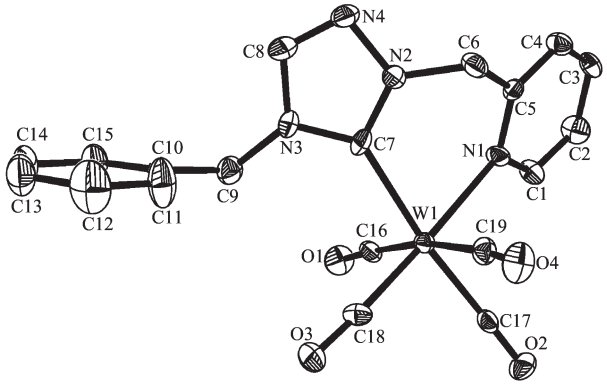



Fig.4 Molecular structure of **10** with the thermal ellipsoids drawn at the 30% probability level

In summary, 1-(2-pyridylmethyl)-1,2,4-triazole has been synthesized, which can act as a monodentate ligand through the exodentate nitrogen atom of the triazole ring in complexes $L_2SnR_2Cl_2$ and $LM(CO)_5$. A N,N-chelating bidentate coordination mode is also observed in LM $(CO)_4$. The NHC-complexes $L'M(CO)_5$ and $L'M(CO)_4$ based on L have been obtained by the carbene transfer reaction of the corresponding NHC-

Ag complex, in which the monodentate coordination mode through the carbene carbon and the chelating [N,C] bidentate coordination mode by the pyridyl nitrogen and the carbene carbon atoms are observed.

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