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Inorganic Chemistry Communications 10 (2007) 1222–1225

INORGANIC CHEMISTRY COMMUNICATIONS

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Synthesis and characterization of half-sandwich Ir and Ru complexes containing Mnt ligand (Mnt = maleonitriledithiolate)

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Received 8 June 2007; accepted 26 July 2007
Available online 3 August 2007

Abstract

The reaction of $[Cp^*IrCl_2]_2$ and $[(p\text{-Cymene})RuCl_2]_2$ with disodium maleonitriledithiolate (Na_2Mnt) yield the 16-electron complexes $Cp^*Ir(Mnt)$ (**1**) and $[(p\text{-Cymene})Ru(Mnt)]$ (**2**). Complexes **1** and **2** can further react with PPh_3 to form the corresponding 18-electron complexes $Cp^*Ir(Mnt)PPh_3$ (**3**) and $[(p\text{-Cymene})Ru(Mnt)PPh_3]$ (**4**). All complexes have been fully characterized by IR and NMR spectroscopy, as well as elemental analysis. The molecular structures of **1** and **4** have been confirmed by X-ray crystallography.

Keywords: Iridium; Ruthenium; Half-sandwich complexes; Maleonitriledithiolate ligand; Structure

Dithiolene compounds as ligands have been extensively studied over the past 40 years due to their non-innocent bonding with transition metals [1,2]. In particular, a series of transition metal complexes with Mnt lignand (Mnt = maleonitriledithiolate) have been under considerable debate owing to their novel properties such as redox, magnetism, conducting and non-linear optics [3]. Compared with Ni and Cu complexes containing the Mnt ligand which have been extensively studied [4], the half-sandwich transition metal complexes containing Mnt ligand have relatively rarely been investigated [5]. In previous work, we have already reported the synthesis of the 16-electron "pseudo-aromatic" half-sandwich complexes $[Cp^*M\{E_2C_2(B_{10}H_{10})\}]$ (M = Co, Rh, Ir; E = S, Se), $[(p\text{-Cymene})Ru\{E_2C_2(B_{10}H_{10})\}]$ (E = S, Se) [6], and suggests that this species may be promising for further transformations owing to its electron deficiency at the metal center. These complexes have been used as models to study the Lewis base adduct containing *N* or *N*-heterocyclic carbene ligands to form stable 18-electron complexes which have mono-, bi-, tri- and tetra- nuclear molecular structures [7].

Aiming at the development of versatile and rational methods for the synthesis of 16-electron half-sandwich $Cp^*Ir(III)$ and $(p\text{-Cymene})Ru(II)$ complexes, Na_2Mnt has been chosen as dithiolene ligand. The red complex $Cp^*Ir(Mnt)$ (**1**) and dark-red $[(p\text{-Cymene})Ru(Mnt)]$ (**2**) were synthesized by the reaction of the half-sandwich iridium dichloride complex $[\{Cp^*IrCl(\mu\text{-Cl})\}_2]$ [8] and ruthenium dichloride complex $[\{(p\text{-Cymene})RuCl(\mu\text{-Cl})\}_2]$ [9] with disodium maleonitriledithiolate (Na_2Mnt) [10] in ethanol solution. The complexes **1** and **2** can further react with PPh_3 to give the complexes $Cp^*Ir(Mnt)PPh_3$ (**3**) [11] and $[(p\text{-Cymene})Ru(Mnt)PPh_3]$ (**4**), respectively (Scheme 1). The complex **3** is known, but the synthetic method for **3** in this paper is different from the literature reported [5b]. The new complexes **1**, **2** and **4** are neutral and air-stable in solid state. They can be soluble in polar organic solvents, such as THF, DMF and CH_2Cl_2. The IR spectra of these complexes in the solid state all exhibit intense C≡N stretching at about 2200 cm^{-1}. The molecular structures of **1** and **4** have been determined by X-ray single crystal diffraction method. The single crystals of **1** and **4** were obtained by slow diffusion of hexane into a concentrated solution of the corresponding complex in dichloromethane at room temperature, respectively [12].

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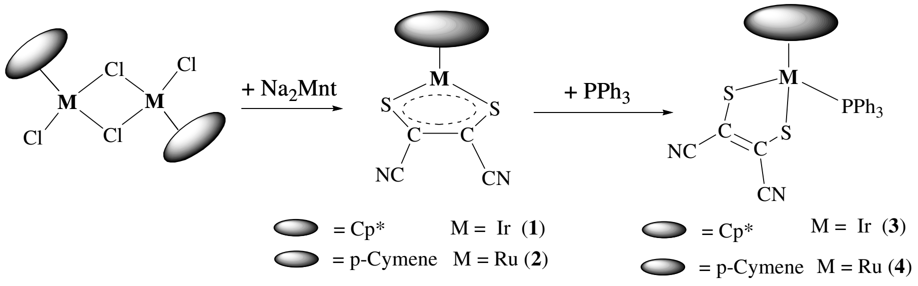
doi:10.1016/j.inoche.2007.07.023



Scheme 1. Synthesis of complexes **1**, **2**, **3** and **4**.

The iridium(III) center in complex **1** adopts a two-legged piano-stool conformation with five-coordinate geometry, assuming the Cp* ligand functions as three coordinate ligand (Fig. 1). The mononuclear 16-electron dithiolene complex **1** corresponds to point group symmetry C_{2v} with two perpendicular mirror planes, in which the two essentially planar five-membered rings Cp* and IrS_2C_2 are arranged perpendicular to each other with the dihedral angle being 88.449(181)°. It is interesting that the complex **1** contains an almost planar metallacycle IrC_2S_2. The five-membered ring is bent with a dihedral angle along S···S vector of 178.73(16)°, which can be also found in the complex $Cp^*Ir[C_2S_2(B_{10}H_{10})]$ (178.07°) [13]. The Ir–S bond lengths (av. 2.2284(19) Å) are significantly shorter than in the 18-electron oligosulfide precursor complex $Cp^*IrPMe_3(SH)_2$ (av. 2.375 Å) [14], but comparable with the corresponding Ir–S bond distances in the 16-electron complexes $Cp^*Ir[S_2C_2(COOMe)_2]$ (av. 2.233 Å) [15], $Cp^*Ir[C_2S_2(B_{10}H_{10})]$ (av. 2.263 Å) [13] and $Cp^*Ir(S_2C_6H_4)$ (av. 2.248 Å) [16].

There are two pairs of independent molecules in the unit cell of **1** (Fig. 2). The structure is similar to $Cp^*Ir[C_2S_2(B_{10}H_{10})]$. The two molecules adopt the different tropism and form rectangular hole along the *b*-axis in the packing structure, the distances between the two N atoms of Mnt ligand and the least-square plane of Cp* (plane C) are 3.3300 and 3.3745 Å, respectively, and the average lengths of four C atoms of Mnt ligand are 3.6224 Å (3.5196 Å, 3.5447 Å, 3.6991 Å, 3.7264 Å). The two planes C_4N_2 and Cp* dihedral angle is 8.637(345)°, which shows the π–π stacking interaction. The neighboring molecules of **1** are paired and staggered in face to face fashion along the C–C edge of Mnt ligand forming the two parallel planes (planes A and B) with an average separation of 3.7450 Å, which indicates the presence of weak π–π stacking interaction (Fig. 2). The two different kinds of intracyclic π–π interaction decide the special packing shape.

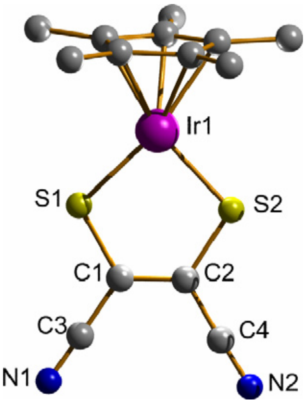


Fig. 1. Molecular structure of the Cp*Ir(mnt) (**1**); all hydrogen atoms are omitted for clarity. Selected distances (Å) and angels (°): Ir(1)–S(1) 2.2254(19), Ir(1)–S(2) 2.2314(19), C(1)–C(2) 1.337(10); S(1)–Ir(1)–S(2) 88.58(7).

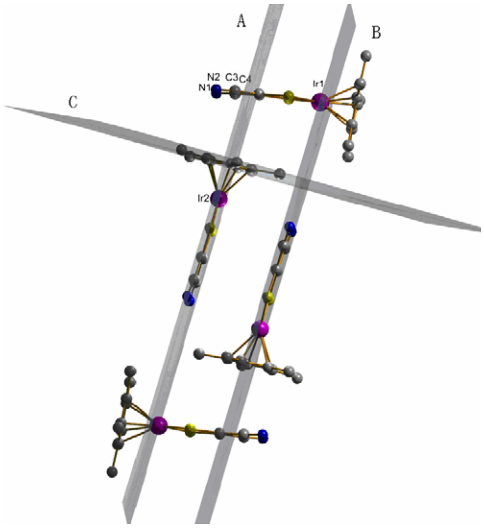


Fig. 2. Four units in stacking of the complex **1**. All hydrogen atoms are omitted for clarity. Ir, C, N and S atoms are represented by pink, gray, blue, and yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In Fig. 3, the ruthenium(III) center adopts a three-legged piano-stool conformation in complex **4** that possess a *p*-Cymene ruthenium half-sandwich tripod structure in which two legs are sulfur atoms from the Mnt chelate ligand and the third leg is phosphorous from the PPh_3 ligand.

The complex **2** takes up PPh_3 to give coordinative saturated 18-electron products, in which the dihedral angle RuS_2/S_2C_2 along the S···S vector is 178.659(99)°, and the dihedral angle between the *p*-Cymene fragment and the five-membered ring of RuS_2C_2 is 54.595(231)°, which is deviated from the vertical plane because of the repulsion from the PPh_3 ligand. The Ru–S bond lengths (av. 2.3531(13) Å) are

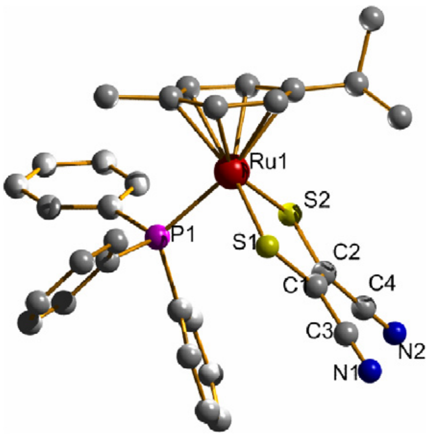


Fig. 3. Molecular structure of the *p*-CymeneRu(mnt)PPh$_3$ (**4**); All hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Ru(1)–S(1) 2.3566(16), Ru(1)–S(2) 2.3496(16), Ru(1)–P(1) 2.3211(14), C(1)–C(2) 1.360(7); S(1)–Ru(1)–S(2) 87.49(5).

slightly shorter than the corresponding complex (*p*-Cymene) Ru[$S_2C_2(B_{10}H_{10})$](PMe$_3$) (av. 2.392(1) Å) [17].

In summary, half-sandwich Ir and Ru complexes with Mnt ligands have been synthesized and characterized. The 16-electron complexes Cp*Ir(mnt) (**1**) and [(*p*-Cymene)Ru(mnt)] (**2**) react with PPh$_3$ to form the corresponding 18-electron complexes Cp*Ir(Mnt)PPh$_3$ (**3**) and [(*p*-Cymene)Ru(Mnt)PPh$_3$] (**4**). The preparation of another 18-electron Mnt complexes of Ir and Ru with the Lewis base containing N of poly-pyridine or C of N-heterocyclic carbene ligands are now in progress.

Acknowledgements

Financial support by the National Science Foundation of China for Distinguished Young Scholars (20531020, 20421303), by the National Basic Research Program of China (2005CB623800) and by Shanghai Science and Technology Committee (05JC14003, 06XD14002) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 649877 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: (+44) 1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.07.023.

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[11] *Synthesis of* **1**: [Cp*IrCl$_2$]$_2$(398 mg, 0.5 mmol) was added to a solution of Na$_2$Mnt (186 mg, 1 mmol) in degassed ethanol (50 mL) in a Schlenk tube and kept at room temperature to stir for 16 h. The color of the solution changed slowly from orange-yellow to red. After removal of the solvent, the residue was redissolved in 3 mL of dichloromethane and chromatographed on silica gel. Elution with dichloromethane gave a red zone. Evaporation under reduced pressure and crystallization from CH$_2$Cl$_2$/hexane afford **1**(384 mg 82%). Anal. Calcd. for $C_{14}H_{15}IrN_2S_2$(%): C 35.96, H 3.23, N 5.99. Found: C 35.62, H 3.46, N 5.88, ^{1}H NMR (500 M CDCl$_3$, ppm): $\delta = 2.19$ (s, η^5-C$_5$H$_5$, 10H). IR (KBr disk): $v = 2205\ \mathrm{cm}^{-1}$ (–CN). Synthesis of **2**: [(*p*-Cymene)RuCl$_2$]$_2$(306 mg, 0.5 mmol) was added to a solution of Na$_2$Mnt (186 mg, 1 mmol) in degassed ethanol (50 mL) in a Schlenk tube and kept at room temperature to stir for 16 h. The color of the solution changed slowly from red to dark-red. After removal of the solvent, the residue was redissolved in 3 mL of dichloromethane and chromatographed on silica gel. Elution with dichloromethane gave a dark-red zone. Evaporation under reduced

pressure and crystallization from CH_2Cl_2/hexane afford **2**(285 mg 76%). Anal. Calcd. for $C_{14}H_{14}RuN_2S_2$(%): C 44.78, H 3.75, N 7.46 Found: C 44.62, H 3.79, N 7.39 . ^{1}H NMR (500 M $CDCl_3$, ppm): $\delta = 1.14$ (m, $(CH_3)_2$, 6H), 1.70 (s, CH_3, 3H), 2.71 (br, CH, 1H), 5.04 (d, aromatic, 2H), 5.45 (d, aromatic, 2H), IR (KBr disk): $v = 2196$ (–CN) cm^{-1}. Synthesis of **4**: [*p*-CymeneRu(Mnt)] (38 mg, 0.1 mmol) was added to a solution of PPh_3 (26.2 mg, 0.1 mmol) in dichloromethane (20 mL) and kept at room temperature to stir for 4 h. After removal of the solvent. The residue was crystallization from CH_2Cl_2/hexane afford **4** (57.3 mg 90%). Anal. Calcd. for $C_{32}H_{29}RuN_2S_2P$ (%): C 60.17, H 4.73, N 4.38. Found: C 60.22, H 4.80, N 4.30. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): $\delta = 1.12$ (m, $(CH_3)_2$, 6H), 1.69 (s, CH_3, 3H), 2.71 (br, CH, 1H), 5.00 (d, aromatic, 2H), 5.44 (d, aromatic, 2H), 7.46 (br, $(C_6H_5)_3$, 15H). IR (KBr disk): $v = 2193\ cm^{-1}$ (–CN).

[12] Diffraction data of **1** and **4** were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL), SADABS absorption corrections were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. Crystallography data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center, CCDC 649877(**1**) and 649878 (**4**) for complexes **1** and **4**. Data for the crystal structure analysis of complex **1** ($C_{14}H_{15}IrN_2S_2$, $M_r = 467.60$) crystallized in the triclinic space group $P\bar{1}$ with $a = 8.835(3)$ Å, $b = 12.992(4)$ Å, $c = 14.453(5)$ Å , $\alpha = 98.399(4)°$, $\beta = 97.728(4)°$, $\gamma = 106.045\ (4)°$, $V = 1550.4(9)$ Å^3, $Z = 4$, $D_c = 2.003\ g\ cm^{-3}$, $R_1 = 0.0367$, $wR_2 = 0.0868$ for final data and $R_1 = 0.0480$, $wR_2 = 0.0899$ for final all data, GOF = 0.983; data for the crystal structure analysis of complex **4** ($C_{33}H_{31}Cl_2N_2PRuS_2$, $M_r = 722.66$) crystallized in the monoclinic space group P2(1)/*n* with $a = 12.060(7)$ Å, $b = 17.698(10)$ Å, $c = 15.478(9)$ Å, $\beta = 96.227(9)°$, $V = 3284(3)$ Å^3, $Z = 4$, $D_c = 1.462\ g\ cm^{-3}$, $R_1 = 0.0514$, $wR_2 = 0.1055$ for final data and $R_1 = 0.0896$; $wR_2 = 0.1164$ for final all data, GOF = 0.913.

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