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Note

Mutual transformation between mono- and binuclear ruthenium complexes and their reactions with iminobis(diisopropylphosphinesulfide) ligand

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ABSTRACT

Treatment of $RuCl_3{\cdot}xH_2O$, PPh_3 and HCHO in boiling 2-methoxyethanol led to isolation of complex $[(PPh_3)(CO)ClRu(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2]$ (**1**) and $[RuCl_2(CO)(CH_3OH)(PPh_3)_2]$ (**2**), which could convert to each other under special conditions. **1** could turn to **2** in MeOH/Et_2O solvent in the presence of excess PPh_3, while **2** could transform to **1** in CH_2Cl_2/*n*-hexane solvent. Reactions of complex **1** or **2** with $KN[^iPr_2P(S)]_2$ afforded complex $[\{RuCl(CO)(PPh_3)\}_2(\mu\text{-}Cl)(\mu\text{-}\eta^2(S),\eta^2(S')\text{-}N(^iPr_2PS)_2)]$ (**3**), in which the $N[P(S)^iPr_2]_2^-$ ligand acts as a dinucleating tetraconnective unit through both sulfur atoms between two Ru(II) atoms. Complexes **1**, **2**, and **3** have been characterized spectroscopically and by X-ray crystallography.

1. Introduction

The coordination chemistry of iminobis(diisopropylphosphinechalcogenide) ligands has attracted great attention during the past decades since they can form stable complexes with a range of main group and transition metal ions [1,2]. Unlike the various binding modes of its analogous $[N(Ph_2PS)_2]^-$ ligand, the already known coordination modes of $[N(^iPr_2PS)_2]^-$ are listed in Chart 1 as fashion a–c according to CCDC searching results [3–9]. Usually, the $[N(^iPr_2PS)_2]^-$ ligand adopts fashion a when interacted with metal centre except for limited cases [3–6]. Iminobis(diisopropylphosphinechalcogenide) ligand $[^iPr_2P(X)NP(Y)^iPr_2]^-$ (X/Y = Se, Te) normally adopt fashion a, b, and e according to literature [6–9]. Recently, we are interested in Ru–S compounds with dithioimidodiphosphinate ligands, some of these complexes exhibited interesting reactivities, such as activating H_2, SO_2 and hydrazine [10]. We here describe the syntheses, reactions, and crystal structures of Ru disulfuroimidodiphosphinate compound.

2. Results and discussion

Red crystals of $[(PPh_3)(CO)ClRu(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2]$ (**1**) and yellow crystals of $[RuCl_2(CO)(CH_3OH)(PPh_3)_2]$ (**2**) were synthesized accidentally during preparation of $[RuHCl(CO)(PPh_3)_3]$ [11] by treatment of $RuCl_3{\cdot}xH_2O$ (0.52 g, 2.0 mmol), aqueous formaldehyde (40 mL, 40% w/v solution), and PPh_3 (3.16 g, 12 mmol) in 200 mL boiling 2-methoxyethanol. Clear orange solution was obtained instead of getting white precipitate of the above reaction even if the reaction time was extended to 24 h. It is found that the difference between the above reaction and the literature method [11] lies in the reaction scale, i.e., double amount chemicals and solvents were taken compared to the reported procedure. It is supposed that the addition of much larger amount of $RuCl_3{\cdot}xH_2O$ in 40 mL 2-methoxyethanol and 40 mL aqueous formaldehyde led to much more decrease of the reaction temperature. The lower temperature might not meet the demand for the formation of $[RuHCl(CO)(PPh_3)_3]$.

Interestingly, when chloride bridged dinuclear complex **1** recrystallized from MeOH/Et_2O solution in the presence of excess PPh_3, complex **2** should be isolated. And the similar is for the vice versa situation: when complex **2** recrystallized from CH_2Cl_2/*n*-hexane solution the complex **1** should be isolated. This phenomenon was proved by single crystal X-ray analysis. Treatment of **1** or **2** with $KN[^iPr_2P(S)]_2$ in THF at room temperature led to isolation of binuclear ruthenium complex $[\{RuCl(CO)(PPh_3)\}_2(\mu\text{-}Cl)(\mu\text{-}\eta^2(S),\eta^2(S')\text{-}N(^iPr_2PS)_2)]$ (**3**) as orange crystals in 70% yield (Scheme 1). The three PPh_3 ligands in **1** exhibited at 53.1, 41.8, 38.7 ppm in the ^{31}P NMR spectrum, while only one ^{31}P signal (42.6 ppm) was observed for **2** due to their *trans* position. Two ^{31}P signals (68.2, 41.8 ppm) showed in the ^{31}P NMR spectrum of **3**, ascribed to $N[P(S)^iPr_2]_2^-$ and PPh_3 ligand, respectively. A singlet at around 3.46 ppm could be assigned to the coordinated methanol molecule (*Me*OH) in ^1H NMR spectrum of **2**. The ^1H NMR spectra of **3** in $CDCl_3$ indicate the existence of both

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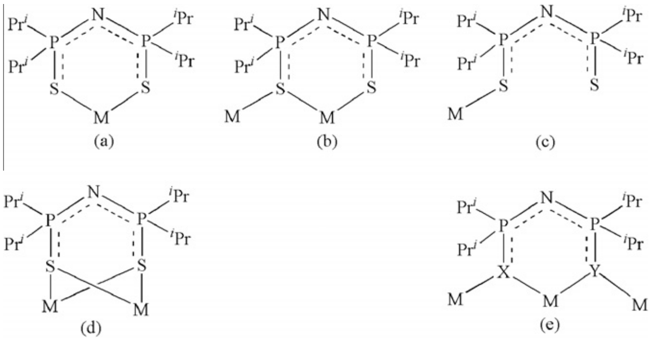


Chart 1. Bonding modes and coordination patterns of $[N(^iPr_2PS)_2]^-$.

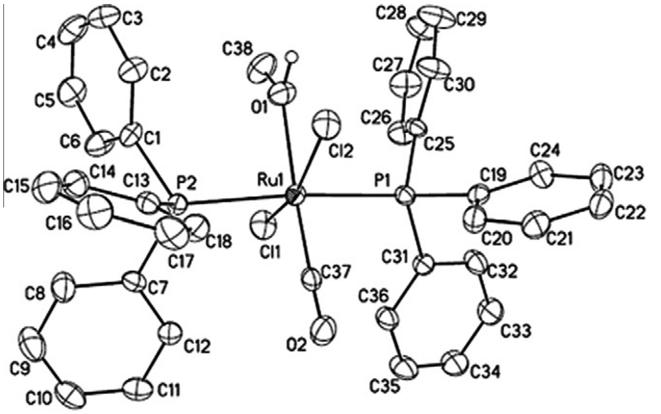
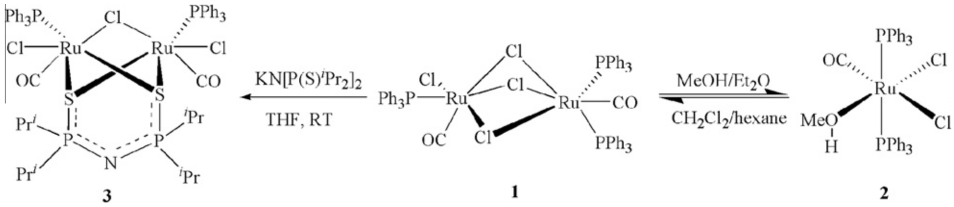


Fig. 2. Molecular structure of $[RuCl_2(CO)(CH_3OH)(PPh_3)_2]$ (**2**). Hydrogen atoms are omitted for clarity except for methanol molecule. Selected bonds (Å) and angles (°): Ru(1)–C(37) 1.829(6), Ru(1)–P(1) 2.402(1), Ru(1)–P(2) 2.401(1), Ru(1)–Cl(1) 2.362(2), Ru(1)–Cl(2) 2.415(2), Ru(1)–O(1) 2.196(4), P(1)–Ru(1)–P(2) 172.70(4), Cl(1)–Ru(1)–Cl(2) 162.64(5), C(37)–Ru(1)–O(1) 173.53(18).

PPh$_3$ and ^{i}Pr fragments. For example, two resonances around 0.61 and 1.29 ppm can be ascribed to the methyl groups of the ^{i}Pr clips. Two signals of C*H*(CH$_3$)$_2$ protons are around 2.08 and 2.78 ppm. The integral values clearly suggest the ratio of PPh$_3$ and $N[P(S)^iPr_2]_2^-$ ligand is 2:1, suggesting that imidodiphosphinate can serve as versatile bridging ligands to stabilize dinuclear metal complexes in solution. Two resonances of CO group (201.5, 199.5 ppm) were shown in the ^{13}C NMR spectrum of **1**, while one signal of 204.5 ppm exhibited in the ^{13}C NMR spectrum of **3** because of their symmetrical geometry. Furthermore, as has been observed in related systems there is a marked increase in the frequency of the (PNP) vibration of **3** (1261 cm^{-1}) compared to the free ligand $^iPr_2P(S)NHP(S)^iPr_2$ (936 cm^{-1}) [1].

The molecular structure of **1**, **2**, and **3** together with selected bond lengths and angles, are shown in Fig. 1–3. For **1**, the terminal Ru(2)–Cl(4) bond distance of 2.368(1) Å is slightly shorter than bridged Ru–Cl distance (2.42–2.52 Å). The Ru(1)···Ru(2) distance is 3.292(1) Å, slightly shorter than that in complex **3** (3.328(2) Å). In **2**, two triphenylphosphines are *trans* to each other, the Ru–O(MeOH) distance (2.196 Å) lies within the range found in other methanol coordinated ruthenium complexes (2.14–2.43 Å) [12]. For **3**, the bond length Ru(1)–S(1) (2.490(1) Å) is near to that of Ru(2)–S(2) (2.506(1) Å). The terminal Ru(1)–Cl(2) bond distance of 2.402(1) Å is almost the same to Ru(2)–Cl(1) (2.399(1) Å) bond



Scheme 1. Transformations of complexes **1**, **2**, and **3**.

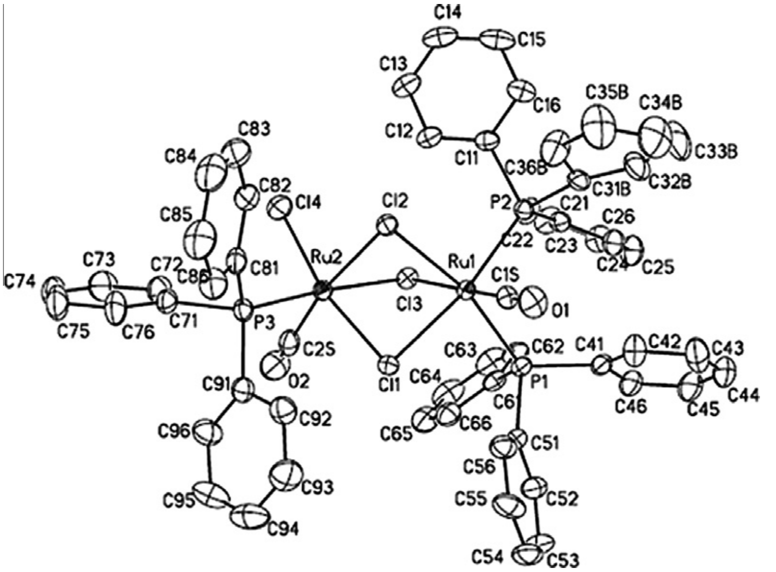


Fig. 1. Molecular structure of $[(PPh_3)(CO)ClRu(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2]$ (**1**). Hydrogen atoms are omitted for clarity. Selected bonds (Å) and angles (°): Ru(1)–Cl(1) 2.465(1), Ru(1)–Cl(2) 2.486(1), Ru(1)–Cl(3) 2.452(1), Ru(2)–Cl(1) 2.416(1), Ru(2)–Cl(2) 2.520(1), Ru(2)–Cl(3) 2.522(1), Ru(2)–Cl(4) 2.368(1), Ru(1)–C(1S) 1.829(4), Ru(2)–C(2S) 1.944(5), Ru(1)–P(1) 2.347(1), Ru(1)–P(2) 2.351(1), P(1)–Ru(1)–P(2) 100.3(3), Ru(1)–Cl(1)–Ru(2) 84.81(4), Ru(1)–Cl(2)–Ru(2) 82.22(4), Ru(1)–Cl(3)–Ru(2) 82.85(4).