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New half-sandwich heterobimetallic CpMPt (M = Rh, Ir) dithiolato bridged complexes. X-ray structure of $[(PPh_3)_2Pt(\mu\text{-}S(CH_2)_2S)RhCl(\eta^5\text{-}C_5H_5)]BF_4$

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Abstract

Cationic heterobimetallic complexes **5**–**7** $[(PPh_3)_2Pt(\mu\text{-edt})MClCp']BF_4$ (edt = $^-S(CH_2)_2S^-$; **5**: M = Rh and Cp′ = η^5-C_5H_5; **6**: M = Rh and Cp′ = η^5-C_5Me_5 and **7**: M = Ir and Cp′ = η^5-C_5Me_5) were prepared by reaction of $[Pt(edt)(PPh_3)_2]$ with $[Cp'ClM(\mu\text{-}Cl)_2MClCp']$ in THF in the presence of two equivalents of $AgBF_4$. The crystalline structure of **5** was determined by X-ray diffraction methods.

Keywords: Heterobimetallic complexes; Platinum; Rhodium; Iridium; Dithiolato metalloligands

1. Introduction

Thiolates and sulfides have been extensively used to synthesize cyclopentadienyl heterobimetallic complexes because they are strong bridging ligands [1]. Although Groups 8–10 sulfide clusters have shown unique reactivities [2], there are few examples of heterobimetallic complexes with S-donor sulfide bridging ligands containing Groups 8–10 noble metals [1f,3]. Dithiolate bridging ligands are expected to provide more robust structures than thiolates, so *syn–anti* isomers in dinuclear complexes can be avoided. However, examples of heterometallic complexes with dithiolate bridging ligands ($^-SRS^-$) are scarce [4] and polymeric materials are often formed. Most of these examples contain early and late transition metals (ELHB).

In previous papers, we proved that if the appropriate dithiolate-containing metalloligand is selected, the desired heterobimetallic complexes can be prepared in high yields without the formation of polymeric species. We therefore used Pt(II) and Pd(II) dithiolato complexes stabilized with phosphine ligands to prepare a series of heterobimetallic MM′ (M = Pt(II) and Pd(II); M′ = Rh(I) and Ir(I)) complexes with alkyl dithiolate bridging ligands of general formula $[(phosphine)M(\mu\text{-dithiolate})M'L_2]^+$ (L_2 = 1,5-cyclooctadiene, $(CO)_2$, $(CO)(PR_3)$), and determined their structures by X-ray diffraction methods [5]. Here we present the first examples of d^8–d^6 cyclopentadienyl heterobimetallic complexes containing a dithiolate bridging ligand.

2. Results and discussion

Our initial strategy was to prepare CpRh(I)Pt complexes by reacting the cyclooctadiene species [CpRh(cod)] with the metalloligand $[Pt(edt)(PPh_3)_2]$ (edt = $^-S(CH_2)_2S^-$) (**1**). Diene complexes such as [RuClCp*(cod)] (Cp* = $C_5Me_5^-$) containing cyclopentadienyl ligands have been used in the synthesis of Ti–Ru heterobimetallic complexes [6]. In our study, we could not substitute the cod ligand in the rhodium complex even by bubbling H_2 through the solution.

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The second attempt at preparing heterobimetallic cyclopentadienyl complexes involved the direct reaction of the metalolligand **1** with dimer [CpClRh(μ-Cl)$_2$RhClCp] (**2**), but no reaction was observed. Finally, we prepared the cationic heterobimetallic complex **5** [(PPh$_3$)$_2$Pt(μ-edt)RhClCp)]BF$_4$ by initially treating dimer **2** with two equivalents of AgBF$_4$ in THF and then adding the platinum metalloligand **1** (Scheme 1). Complexes [(PPh$_3$)$_2$Pt(μ-edt)RhClCp*)]BF$_4$ (**6**) and [(PPh$_3$)$_2$Pt(μ-edt)IrClCp*)]BF$_4$ (**7**) were prepared following the same procedure. The reaction was very selective since no byproducts were detected. Complexes **5**–**7** were isolated as a air stable solids in good yields (75–86%) and in pure form (see analytical data in Section 3).

We obtained crystals of **5**, which were suitable for single crystal X-ray diffraction analysis, by recrystallization from hexane. Fig. 1 shows the ORTEP plot of the cation complex of **5**. The complex has a hinged structure in which the dithiolate acts as a bridging ligand between the two metals. The rhodium center has distorted tetrahedral geometry with the centroid of the Cp, the chloro and the dithiolato ligands occupying the coordination sites. The platinum center has a distorted square-planar environment. The *cis* angles S(1)–Pt(1)–S(2) and P(1)–Pt(1)–P(2) are 75.10(7) and 96.86(8)°, respectively, and the *trans* angles P(1)–Pt(1)–S(2) and P(2)–Pt(1)–S(1) are deviated from 180° (168.81(8) and 165.68(8)°, respectively). A similar distortion, attributed to repulsion between the PPh$_3$ terminal ligands, was observed in the structure of parent complex [Pt(edt)(PPh$_3$)$_2$] [7]. The intermetallic distance (3.354(8) Å) was longer than the one for metal–metal single bond (2.6 Å) [8].

The Pt–P distances (2.282(2) and 2.302(2) Å) in complex **5** were in the range reported for complex **1** (2.296(3) and 2.281(4) Å) and similar to those for [(PPh$_3$)$_2$Pt(μ-edt)Rh(cod)]ClO$_4$ (2.285(2) and 2.267(2) Å). The Pt–S distances (2.376(3) and 2.387(3) Å) in complex **5** were slightly longer that the Pt–S distances in **1** (2.328(4) and 2.313(4) Å) [7]. This was as expected for the bridging coordination to the two metals.

The torsion angle PtS$_2$Rh θ (124.6°) was greater than that of the related heterobimetallic complex [(PPh$_3$)$_2$Pt(μ-edt)Rh(cod)]ClO$_4$ (111.27°) [5a] and the homodinuclear complex [Rh(μ-edt)(cod)]$_2$ (104°) [9]. This was probably due to the steric requirements of the geometry of the Rh center.

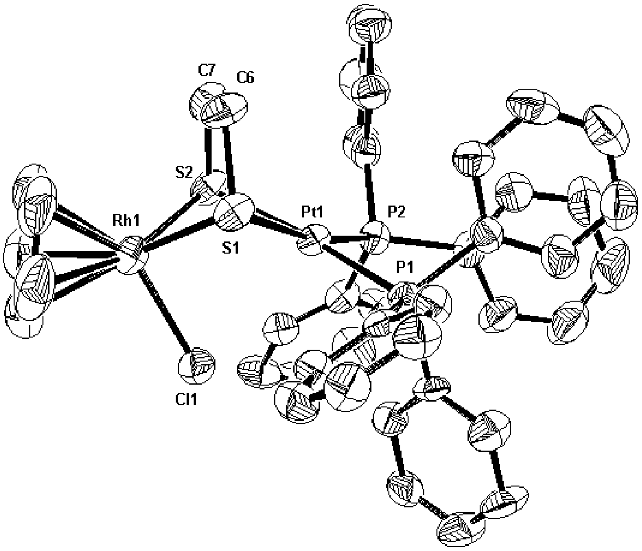
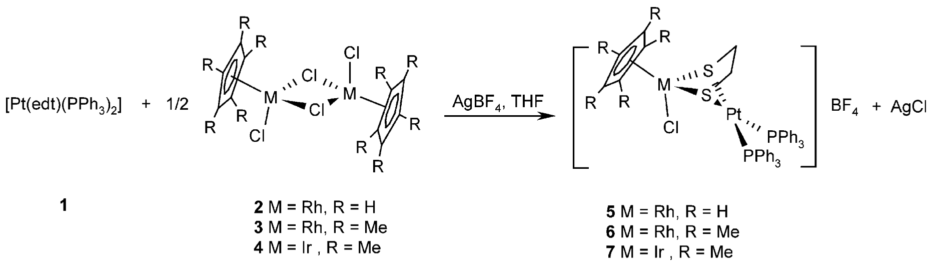


Fig. 1. ORTEP plot of **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, CH$_2$Cl$_2$ and BF$_4^-$ are omitted for clarity. Selected bond distances (Å) and angles (°): Pt–P(1) 2.282(2), Pt–P(2) 2.302(2), Pt–S(1) 2.376(3), Pt–S(2) 2.387(3), Pt–Rh 3.354(8), Rh–S(1) 2.376(2), Rh–S(2) 2.406(2), Rh–Cl 2.382(2), P(1)–Pt–P(2) 96.86(8), S(1)–Pt–S(2) 75.10(7), P(1)–Pt(1)–S(1) 94.29(8), P(2)–Pt(1)–S(2) 94.18(8), S(1)–Rh–S(2) 74.73(8), S(1)–Rh(1)–Cl(1) 89.95(8), Cl(1)–Rh(1)–S(2) 92.15(8), PtS$_2$Rh θ 124.6°.

Spectroscopic data showed that complexes **5**–**7** were stable in solution. The ^{1}H- and ^{13}C-NMR spectra showed one singlet for Cp and Cp* in all cases. The methylenic groups of the dithiolate bridging edt ligand appeared as two multiplet resonances in the ^{1}H-NMR ($\approx\delta$ 2.5–2.9 ppm), which were attributed to the protons oriented to the platinum and the rhodium or iridium centers, and as one singlet (ca. δ 40 ppm) in the ^{13}C-NMR spectra.

The ^{31}P-NMR spectra showed one signal in the δ 12–14 ppm, with the corresponding satellites attributed to the ^{31}P–^{195}Pt coupling, which was as expected for the equivalent phosphorus atoms. The coupling constants were higher in **5**–**7** (ca. 3240–3270 Hz) than in the mononuclear complex **1** (2884 Hz) [10]. This was also observed for related heterobimetallic complexes, which indicates that the M–P bond became stronger as a result



Scheme 1.

of the weakening of the M–S bond due to bridge coordination [5].

In conclusion, the successful synthesis of these complexes shows that the M-dithiolate species act efficiently as metalloligands for heterobimetallics synthesis.

3. Experimental

3.1. General methods

All complexes were synthesized using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. Complexes $[RhCpCl_2]_2$, $[RhCp^*Cl_2]_2$ and $[IrCp^*Cl_2]_2$ [11] and $[Pt(edt)(PPh_3)_2]$ [10] were prepared using methods described in the literature. All other reagents were used as commercially supplied. Elemental analyses were performed on a Carlo–Erba microanalyser. NMR spectra were recorded on a Varian Gemini 300 MHz spectrophotometer and chemical shifts were quoted in ppm downfield from internal $SiMe_4$ (^1H) or external 85% H_3PO_4 (^{31}P). FAB mass spectrometry was performed on a VG Autospect in a nitrobenzyl alcohol matrix.

3.2. Preparation of complex $[(PPh_3)_2Pt(\mu\text{-}S(CH_2)_2S)RhCl(\eta^5\text{-}C_5H_5)]BF_4$ (**5**)

$AgBF_4$ (35.5 mg, 0.1826 mmol) was added to a suspension of complex **2** (50.0 mg, 0.0913 mmol) in 5 ml of anhydrous and deoxigenated THF. The mixture was stirred for 5 min at room temperature (r.t.) and complex $[Pt(edt)(PPh_3)_2]$ (148.3 mg, 0.1826 mmol) was then added. The color of the solution changed to dark red. The silver chloride salts formed were removed by filtration through Celite. The filtrate was concentrated to ca. 2 ml and the precipitate was obtained by C_6H_{14} addition. The red solid was filtrated, washed with C_6H_{14} and vacuum dried. Complex **5** was obtained as a red solid. Yield: 161.0 mg, 80%. ^1H-NMR (300 MHz, $CDCl_3$, 20 °C): δ 2.95 (m, 2H, $-CHH-CHH-$, edt), 2.82 (m, 2H, $-CHH-CHH-$, edt), 5.52 (s, 5H, Cp), 7.2–7.5 (m, 30H, Ph, PPh_3). ^{13}C-NMR (75.4 MHz, $CDCl_3$, 20 °C): δ 40.6 (s, CH_2, edt), 87.3 (s, CH, Cp). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 20 °C): δ 13.5 (s with satellites, $^1J_{PPt} = 3243.9$ Hz). Anal. Calc. for $C_{43}H_{39}BF_4ClP_2PtRhS_2$: C, 46.84; H, 3.54; S, 5.81. Found: C, 46.82; H, 3.46; S, 5.78%. FAB: m/z 1115 $[MH-BF_4]^+$, 753 $[MH-PPh_3-Cp-Cl-BF_4]^+$.

3.3. Preparation of complex $[(PPh_3)_2Pt(\mu\text{-}S(CH_2)_2S)RhCl(\eta^5\text{-}C_5Me_5)]BF_4$ (**6**)

$AgBF_4$ (31.5 mg, 0.1618 mmol) was added to a solution of complex **3** (50.0 mg, 0.0809 mmol) in 5 ml of anhydrous and deoxigenated THF. The mixture was stirred for 5 min at r.t. and complex $[Pt(edt)(PPh_3)_2]$ (131.4 mg, 0.1618 mmol) was then added. The color of the solution changed to orange. The silver chloride salts formed were removed by filtration through Celite. The filtrate was concentrated to ca. 2 ml and the precipitate was obtained by C_6H_{14} addition. The red solid was filtrated, washed with C_6H_{14} and vacuum dried. Complex **5** was obtained as a red solid. Yield: 142.2 mg, 75%. ^1H-NMR (300 MHz, $CDCl_3$, 20 °C): δ 1.60 (s, 15H, Cp*), 2.61 (m, 2H, $-CHH-CHH-$, edt), 2.55 (m, 2 H, $-CHH-CHH-$, edt), 7.2–7.4 (m, 30 H, Ph, PPh_3). ^{13}C-NMR (75.4 MHz, $CDCl_3$, 20 °C): δ 8.8 (s, CH_3, Cp*) 42.4 (s, CH_2, edt), 97.1 (s, C, Cp*). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 20 °C): δ 12.5 (s with satellites, $^1J_{PPt} = 3272.9$ Hz). Anal. Calc. for $C_{48}H_{49}BF_4ClP_2PtRhS_2$: C, 49.13; H, 4.18; S, 5.46. Found: C, 49.08; H, 4.16; S, 5.37%. FAB: m/z 1085 $[MH-BF_4]^+$, 823 $[MH-PPh_3-Cp^*-Cl-BF_4]^+$.

3.4. Preparation of complex $[(PPh_3)_2Pt(\mu\text{-}S(CH_2)_2S)IrCl(\eta^5\text{-}C_5Me_5)]BF_4$ (**7**)

$AgBF_4$ (24.4 mg, 0.1256 mmol) was added to a solution of complex **4** (50.0 mg, 0.0628 mmol) in 5 ml of anhydrous and deoxigenated THF. The mixture was stirred for 5 min at r.t. and complex $[Pt(edt)(PPh_3)_2]$ (102.0 mg, 0.1256 mmol) was then added. The color of the solution changed to orange. The silver chloride salts formed were removed by filtration through Celite. The filtrate was concentrated to ca. 2 ml and the precipitate was obtained by C_6H_{14} addition. The red solid was filtrated, washed with C_6H_{14} and vacuum dried. Complex **7** was obtained as a red solid. Yield: 136.2 mg, 86%. ^1H-NMR (300 MHz, $CDCl_3$, 20 °C): δ 1.60 (s, 15H, Cp*), 2.70 (m, 2H, $-CHH-CHH-$, edt), 2.61 (m, 2 H, $-CHH-CHH-$, edt), 7.2–7.4 (m, 30 H, Ph, PPh_3). ^{13}C-NMR (75.4 MHz, $CDCl_3$, 20 °C): δ 8.5 (s, CH_3, Cp*) 43.5 (s, CH_2, edt), 90.1 (s, C, Cp*). $^{31}P\{^1H\}$-NMR (121.4 MHz, $CDCl_3$, 20 °C): δ 14.4 (s with satellites, $^1J_{PPt} = 3240.7$ Hz). Anal. Calc. for $C_{48}H_{49}BF_4ClIrP_2PtS_2$: C, 45.66; H, 3.88; S, 5.07. Found: C, 45.58; H, 3.89; S, 5.07%. FAB: m/z 1175 $[MH-BF_4]^+$, 911 $[MH-PPh_3-Cp^*-Cl-BF_4]^+$.

3.5. Crystal data for complex $[(PPh_3)_2Pt(\mu\text{-}S(CH_2)_2S)RhCl(\eta^5\text{-}C_5H_5)]BF_4\cdot CH_2Cl_2$ (**5**)

Suitable crystals of complex **5** were grown by diffusing *n*-hexane into a solution of the complex in dichloromethane and mounted on a glass fiber. The data were collected and processed at room temperature on a Mar Research image plate scanner. Graphite-monochromated Mo–K_α radiation was used to measure 95/2 frames, 180 s per frame.

Compound **5**: $C_{43}H_{39}BF_4ClP_2PtRhS_2\cdot 1CH_2Cl_2$, $M = 1184.97$, triclinic, $a = 11.050(57)$ Å, $\alpha = 87.29(6)^\circ$, $b = 14.471(57)$ Å, $\beta = 93.74(6)^\circ$, $c = 14.930$ Å, $\gamma = 71.58(6)^\circ$, $V = 2254.5$ Å^3, space group $P\bar{1}$ (2), $Z = 2$, $D_c = 1.746$ mg m^{-3}, $F(000) = 1160$. Dark red, crystal dimensions $0.1 \times 0.1 \times 0.3$ mm, $\mu(\text{Mo–K}_\alpha) = 38.55$ cm^{-1}.

The XDS [12] package was used to give the following: 5778 unique reflections [merging $R = 0.0276$]. The heavy atoms were found from the Patterson map using the SHELX-86 [13] program and refined subsequently from successive difference Fourier maps using SHELXL-93 [14] by full-matrix least-squares of 569 variables, to a final R-factor of 0.0418 for 5772 reflections with $[F_o] > 4_\sigma(F_o)$. All atoms were revealed by the difference Fourier map. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically and then refined with fixed isotropic atomic displacement parameters. The weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = \max((F_o^2, 0) + 2F_c^2)/3$, $a = 0.0359$ and $b = 18.11$ with $\sigma(F_o)$ from counting statistics, provided satisfactory agreement analyses. The final parameters R_1 ($[F_o] > 4_s(F_o)$) were 0.0418 and wR_2 (all data) were 0.0579 for $R_1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$ and $wR_2 = [\Sigma\, w(F_o^2 - F_c^2)/\Sigma\, w(F_o^2)^2)]^{1/2}$. The ORTEP diagram for **5** was generated using ORTEP-3 [15].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 183660 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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