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Reactivity of the $[CpM(PPh_3)_2]^+$ (M = Ru, Os) fragment with diethyldithiocarbamate

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Abstract

This paper reports on the reaction of $[CpM(PPh_3)_2(L)]^{+/0}$($Cp = \eta^5$–C_5H_5; M = Os, L = CH_3CN, DMSO Br; M = Ru, X = Cl, CH_3CN) with diethyldithiocarbamate ($S_2CNEt_2^-$). The exceptional kinetic stability of [Os–PPh_3] compared to [Ru–PPh_3] is reflected from the isolation of the monodentate diethyldithiocarbamate complex $[CpOs(PPh_3)_2(\kappa^1\text{-}S_2CNEt_2)]$ (**3**) and the bidentate diethyldithiocarbamate complex $[CpRu(PPh_3)(\kappa^2\text{-}S_2CNEt_2)]$ (**5**) as the only products. The structure of $[CpOs(PPh_3)_2(CH_3CN)]BF_4$ ($\mathbf{2 \cdot BF_4}$) and **5** were determined by X-ray diffraction.

Keywords: Osmium; Ruthenium; Dithiocarbamates; Cyclopentadienyl; X-ray diffraction

1. Introduction

Dithiocarbamates are versatile ligands, capable of forming complexes with all the transition elements and able to stabilize most in a range of oxidation states [1]. The CS_2^- group in dithiocarbamates (dtc) is usually a chelate but a few cases of monodentate dithiocarbamates are known [2]. Recently, Baird et al. have reported the unique chemistry of amino acid dithiocarbamates with the Ru(III) system where a very interesting CS_2^- elimination phenomenon was observed [3]. As far as the $[CpM(PPh_3)_2X]$ (M = Ru, X = Cl; M = Os, X = Br) systems are concerned, these compounds serve as excellent precursors for various organometallic complexes [4] and show very similar reactivity patterns except that the [Os]–PPh_3 bond is kinetically much more stable. Some dithiocarbamate as well as xanthate complexes have been known in both cases [5]. We have reported earlier, the preparation and reactivity of the acetonitrile complex $[CpOs(PPh_3)_2(CH_3CN)]BF_4$ ($\mathbf{2 \cdot BF_4}$) and have demonstrated that this compound is a much more desirable precursor for the preparation of chelate complexes of the type $[CpOs(PPh_3)(LL')]BF_4$(LL′ = bipy, phen) [6]. In pursuance of our interest in the synthesis of new complexes essentially bearing a cyclopentadienyl ligand, we wish to report here the contrasting reactivity behavior of the $[CpM(PPh_3)_2]^+$ (M = Os, Ru) fragment towards diethyldithiocarbamate.

2. Results and discussion

The reaction of $[CpOs(PPh_3)_2Br]$ with the sodium salt of diethyldithiocarbamate, $Na \cdot S_2CNEt_2$ in acetonitrile solvent in the presence of NH_4BF_4 under refluxing conditions lead to the formation of the monodentate $[S_2CNEt_2]$ complex $[CpOs(PPh_3)_2(\kappa^1\text{-}S_2CNEt_2)]$ (**3**) and a cationic complex, $[CpOs(PPh_3)_2(CH_3CN)]BF_4$ ($\mathbf{2 \cdot BF_4}$). Our earlier attempts to isolate pure **3** from $[CpOs(PPh_3)_2Br]$ and $Na \cdot S_2CNEt_2$ using methanol as a solvent were unsuccessful. The ^1H NMR spectrum showed the presence of a 1:1 ratio of complexes **3** and $\mathbf{2 \cdot BF_4}$ in the crude product, apart from the resonances corresponding to $\mathbf{2 \cdot BF_4}$, the

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resonances of the methylene protons of the [S_2CNEt_2] ligand of complex **3** appear as two sets of quartets at 4.03 and 3.72 ppm. A triplet at 1.27 ppm, assignable to the methyl protons of the [S_2CNEt_2] ligand, was also observed. Protons corresponding to the cyclopentadienyl ligand also appear at 4.74 ppm while the PPh_3 peaks are observed as a bunch in the aromatic region. The IR spectrum taken in KBr showed a strong peak at 1491 cm^{-1}, unambiguously assignable to the ν_{CN} vibration of [S_2CNEt_2] [7]. We also observed bands at 2277 cm^{-1} and 1084 cm^{-1} assignable to ν_{CN} of coordinated CH_3CN and ν_{BF} of BF_4^-. We have employed this synthetic strategy hoping that the *in situ* generated complex [$CpOs(PPh_3)_2(CH_3CN)$]BF_4 (**2 · BF$_4$**) would easily give **3** or the chelate complex [$CpOs(PPh_3)_2(\kappa^2\text{-}S_2CNEt_2)$]. Unfortunately, we never obtain the latter compound, and to our surprise attempts to separate **2 · BF$_4$** and **3** proved to be futile owing to the similar solubility of these two complexes.

Then, we attempted to synthesize **3** from [$CpOs(PPh_3)_2(CH_3CN)$]BF_4 (**2 · BF$_4$**) and $Na \cdot S_2CNEt_2$ in refluxing methanol (Scheme 1). The formation of **3** may be gauged by the appearance of white precipitate after about one hour of refluxing. But to our surprise, a ^1H NMR spectrum taken in $CDCl_3$ of this crude product still showed the presence of **2 · BF$_4$**. Fortunately, after many attempts, we were able to get single crystals from this crude product by slow diffusion of hexane into an acetone solution of this mixture; very pale yellow crystals were obtained after one week leaving an oily blackish-yellow residue on the wall of the crystallization tube and the ^1H NMR spectrum revealed that this is a decomposed material. The ^1H NMR, $^{13}P\{^1H\}$ NMR, IR, elemental analysis as well as the X-ray crystallographic analysis of these crystals has revealed that this compound is the starting [$CpOs(PPh_3)_2(CH_3CN)$]BF_4 (**2 · BF$_4$**). However, as no report of the structural data of this compound is available in the literature, we have reported this structure here. The ORTEP diagram is shown in Fig. 1. For the final attempt, we tried the reaction starting from a new complex [$CpOs(PPh_3)_2(DMSO)$]BF_4 (**4 · BF$_4$**), however this compound does not seem to undergo the anticipated substitution reaction in the present experimental conditions. The complex [$CpOs(PPh_3)_2(DMSO)$]BF_4 (**4 · BF$_4$**) was prepared by the reaction of [$CpOs(PPh_3)_2Br$] with an excess of DMSO in methanol. The compound is isolated as a very pale yellow hydroscopic powder. It was characterized with the help of IR, ^1H and $^{13}P\{^1H\}$ spectroscopy. The IR spectrum showed a band at 1023 cm^{-1}, assignable to S-bound DMSO [8].

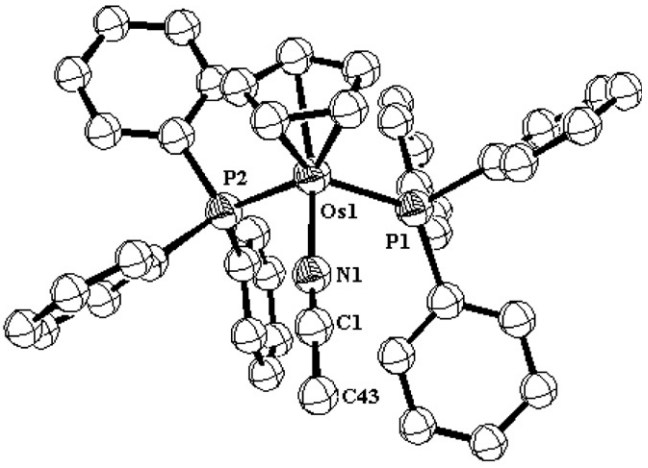
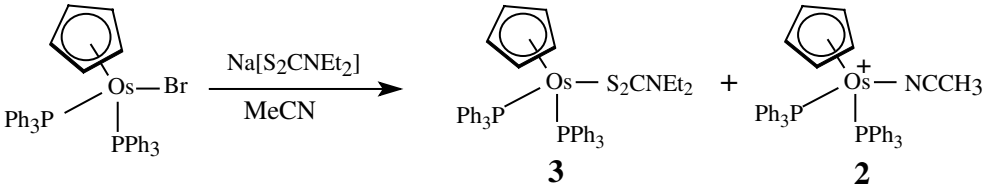


Fig. 1. Molecular structure of [$CpOs(PPh_3)_2(MeCN)$]BF_4 (**2 · BF$_4$**) with BF_4^- and all the hydrogens atoms omitted for clarity.

The ^1H NMR spectrum showed a resonance of the methyl group of the coordinated DMSO at 3.53 and 3.43 ppm. The $^{13}P\{^1H\}$ NMR showed a singlet at −2.67 ppm, suggesting a similar environment of both P atoms of the PPh_3 ligands. Thus, all our attempts to isolate the pure [$CpOs(PPh_3)_2(\kappa^1\text{-}S_2CNEt_2)$] (**3**) were unsuccessful.

In the complex [$CpOs(PPh_3)_2(CH_3CN)$]BF_4 (**2 · BF$_4$**), the osmium(II) centre adopts a pseudo-octahedral coordination geometry with an almost linear Os1–N1–C1 (171.16°) moiety occupying one site. The bond lengths N1–C1 (1.132(6) Å) and C1–C43 (1.455(8) Å) are in very close agreement with those reported for [$CpRu(CH_3CN)_3$]BF_4 where $N\text{–}C_{av} = 1.131$ Å and $C\text{–}C_{av} = 1.445$ Å [9]. The other coordination sites are occupied by a pentahapto-bound cyclopentadienyl ligand and two triphenylphosphines. The Os–P1 and Os–P2 bond lengths [2.328 Å and 2.343 Å respectively] are comparable with those found in [$CpOs(=C=C=CPh_2)(PPh_3)_2$][$PF_6$] [10] and [$CpOs(PPh_3)_2(OSO_2CF_3)$] [11].

We have extended our work to a closely related system, the reaction of [$CpRu(PPh_3)_2Cl$] or [$CpRu(PPh_3)_2(CH_3CN)$]BF_4 with $Na.S_2CNEt_2$ leads to the formation of an orange colored complex that is soluble in almost all common solvents, even in hexane. The IR spectrum showed a strong ν_{CN} peak at 1483 cm^{-1}. The ^1H NMR spectrum showed the resonance of the cyclopentadienyl ligand at 6.22 ppm, a bunch of peaks corresponding to methylene proton in the range of 3.76–4.42 ppm and a triplet at 1.28 ppm. Thus, IR and ^1H NMR data clearly suggested the formation of the expected well-known bidentate



Scheme 1.

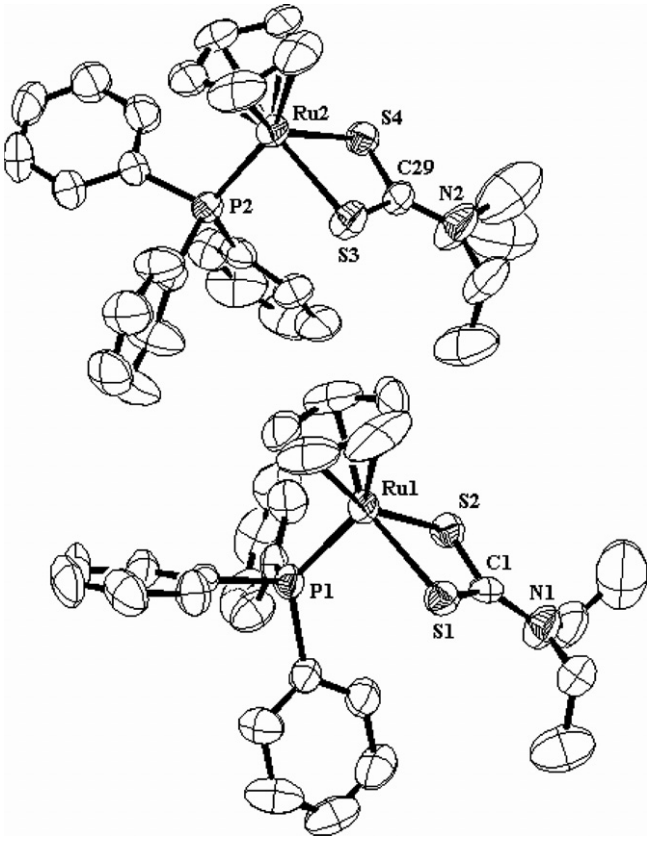


Fig. 2. Molecular structure of $[CpRu(PPh_3)_2(\kappa^2\text{-}S_2CNEt_2)]$ (**5**) with all the hydrogen omitted for clarity.

diethylthiocarbamato complex $[CpRu(PPh_3)(\kappa^2\text{-}S_2CNEt_2)]$ (**5**), the X-ray crystal structure determination also confirmed these spectroscopic evidences and has revealed that the compound contain two independent, discrete molecules (Fig. 2). The molecules are structurally identical except in the orientation of the ethyl group of the $[S_2CNEt_2]$ ligand. The metrical bonding parameters are comparable to those found in the analogous complexes $[CpRu(PPh_3)(S_2CNMe_2)]$ [12] and $[CpRu(PPh_3)(S_2CNPr_2)]$ [13].

3. Experimental

All solvents were dried and purified by standard procedures. ^1H and $^{13}P\{^1H\}$ NMR spectra were recorded on a Bruker 300 MHz spectrometer using Me_4Si and H_2PO_4 (85%) respectively as internal standards. IR spectra were recorded using a Nicolet Impact Spectrophotometer. $Na \cdot S_2CNEt_2 \cdot 3H_2O$ was obtained from a commercial source and was used as received. $[CpOs(PPh_3)_2Br]$ [14], $[CpOs(PPh_3)_2(MeCN)]BF_4$ (**2 · BF$_4$**) [6], $[CpRu(PPh_3)_2X]$, (X = Cl, MeCN) [15] were prepared according to literature procedures.

3.1. Synthesis of $[CpOs(PPh_3)_2(\kappa^1\text{-}S_2CNEt_2)]$ (3)

A mixture of $[CpOs(PPh_3)_2(MeCN)]BF_4$ (**2 · BF$_4$**) (0.05 g, 0.055 mmol) and $Na \cdot S_2CNEt_2 \cdot 3H_2O$ (0.013 g, 0.055 mmol) in 10 mL methanol was refluxed for 10 h, whereby the color of the solution changed to bright yellow with some whitish materials settling down at the bottom of the flask. The solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2 and filtered through a short silica gel column. Subsequent concentration and addition of excess hexane yielded a pale yellow powder containing a mixture of **3** and **2 · BF$_4$**. Yield: 0.038 g. ^1H NMR ($CDCl_3$, δ): 7.67–7.20 (m, 30H, Ph), 4.74 (s, 5H, Cp), 4.03 (qr, 2H, 7 Hz, CH_2), 3.72 (qr, 2H, 7 Hz, CH_2), 1.27 (t, 6H, CH_3). $^{13}P\{^1H\}$ NMR}: −1.53 (s). IR (KBr, cm^{-1}): 1491 (w), 1433 (ms), 1084 (ν_{BF}, s), 1055 (s), 750 (m), 697 (s).

3.2. Synthesis of $[CpOs(PPh_3)_2(DMSO)]BF_4$ (4 · BF$_4$)

A mixture of $[CpOs(PPh_3)_2Br]$ (0.1 g, 0.117 mmol) and dimethylsulfoxide (1 mL, 0.055 mmol) in methanol (30 mL) was refluxed for 3 h, whereby the color of the solution changed to very pale transparent yellow. The solvent was removed in vacuo and the residue was extracted with CH_2Cl_2 and loaded onto a short alumina column. The compound was eluted with methanol. Concentration of this methanol solution and addition of diethylether with vigorous shaking gave the very pale yellow solid of **4 · BF$_4$**. ^1H NMR ($CDCl_3$, δ): 7.49–7.14 (m, 30H, Ph), 5.47 (s, 5H, Cp), 3.53 (s, 3H, CH_3), 3.43 (s, 3H, CH_3). $^{13}P\{^1H\}$ NMR}: −2.67 (s). IR (KBr, cm^{-1}):1023 (ν_{SO}), 1089 (ν_{BF}).

3.3. Synthesis of $[CpRu(PPh_3)_2(\kappa^2\text{-}S_2CNEt_2)]$ (5)

A mixture of $[CpRu(PPh_3)_2(MeCN)]BF_4$ (0.05 g, 0.061 mmol) or $[CpRu(PPh_3)_2Cl]$ (0.044 g, 0.061 mmol) and $Na \cdot S_2CNEt_2 \cdot 3H_2O$ (0.014 g, 0.061 mmol) in methanol (10 mL) was refluxed for 8 h, then the solvent was removed *in vacuo* and the residue was extracted with CH_2Cl_2 and filtered through a short silica gel column. CH_2Cl_2 was removed *in vacuo* and the residue was extracted with hexane, which on standing overnight yielded orange crystals of **5**. Yield: 0.040 g, 59%. ^1H NMR ($CDCl_3$, δ): 7.67–7.31 (m, 30H, Ph), 6.22 (s, 5H, Cp), 4.53–3.42 (m, 12H, CH_2), 1.24 (t, 3H, 7.3 Hz, CH_3).$^{13}P\{^1H\}$ NMR}: 19.6 (s). IR (KBr, cm^{-1}): 1483 (ν_{CN}, s), 1457 (w), 1429(s), 1271 (s), 1214(w), 1141(m), 1089 (s), 748 (m), 696(s).

4. X-ray data collection and solution

Suitable single crystals for X-ray analysis of complex **2 · BF$_4$** were grown by slow diffusion of hexane into a concentrated acetone solution and **5** were grown by slow evaporation of a hexane/dichloromethane solution (1:2 v/v). A summary of the single-crystal X-ray structure analyses are shown in Table 1, and selected bond lengths and bond angles are presented in Tables 2 and 3 respectively. The X-ray intensity data were measured on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube

Table 1
Crystal data summary and structure refinement for complexes **2 · BF$_4$** and **5**

Empirical formula	$C_{43}H_{38}BF_4NOsP_2$	$C_{56}H_{60}N_2P_2Ru_2S_4$
Formula weight	907.69	1153.38
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71069
Crystal system	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*
Unit cell dimensions		
a (Å)	10.2948(13)	27.226(5)
b (Å)	17.080(2)	10.4000(18)
c (Å)	21.840(3)	19.566(3)
β (°)	90.310(2)	101.174(3)
Volume (Å^3)	3840.1(9)	5435.0(16)
Z,	4	4
D_{calc} (Mg/m^3)	1.565	1.410
F(000)	1788	2368
Absorption coefficient (mm^{-1})	3.455	0.806
Crystal size (mm)	0.45 × 0.20 × 0.10	0.13 × 0.20 × 0.44
θ Range for data collection (°)	1.51–28.29	0.76–28.41
Limiting indices	$-13 \leqslant h \leqslant 10$, $-22 \leqslant k \leqslant 17$, $-29 \leqslant l \leqslant 28$	$-29 \leqslant h \leqslant 36$, $-13 \leqslant k \leqslant 13$, $-26 \leqslant l \leqslant 17$
Reflections collected	25027	33187
Independent reflections (R_{int})	9272(0.0364)	12842(0.0737)
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	9272/0/469	7619/0/406
Goodness-of-fit on F^2	1.050	1.014
Final R_1	0.0370	0.0813
Final wR_2	0.0837	0.1905
Largest difference in peak and hole (e$^-$/Å^3)	0.886 and −0.644	0.99 and −0.815

Table 2
Selected bond lengths and angles for the compound [CpOs(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$ (**2 · BF$_4$**)

Bond lengths (Å)		Bond angle (°)	
C1–N1	1.132(6)	Os1–N1–C1	171.1(4)
C1–C43	1.455(8)	N1–C1–C43	179.4(9)
Os1–N1	2.026(3)	N1–Os1–P1	98.76(10)
Os1–P1	2.328(10)	N1–Os1–P2	91.76(11)
Os1–P2	2.348(10)	P1–Os1–P2	100.87(3)

Table 3
Selected bond lengths and angles for the compound [CpRu(PPh$_3$)$_2$-(κ^2- S$_2$CNEt$_2$)] (**5**)

Bond lengths (Å)		Bond angle (°)	
C1–N1	1.344(8)	N1–C1–S1	125.2(5)
C1–S1	1.702(7)	N1–C1–S2	123.7(5)
C1–S2	1.717(7)	S1–C1–S2	110.9(4)
Ru1–S1	2.4007(18)	S1–Ru1–S2	71.61(6)
Ru1–S2	2.4133(18)	P1–Ru1–S2	90.11(6)
P1–Ru1	2.2818(19)	P1–Ru1–S1	94.88(6)
C29–N2	1.320(9)	C1–S1–Ru1	89.1(2)
C29–S4	1.699(7)	S4–Ru2–S3	72.07(7)
C29–S3	1.718(7)	C29–S4–Ru2	88.6(2)
Ru2–S3	2.3982(19)	C29–S3–Ru2	87.9(2)
Ru2–S4	2.3921(19)	P2–Ru2–S4	95.44(7)
P2–Ru2	2.2892(19)	N2–C29–S4	125.5(6)
		S4–C29–S3	111.1(4)
		N2–C29–S3	123.4(6)

($\lambda = 0.71073$ Å) operated at 1600 W power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal. A total of 1850 frames were collected with a scan width of 0.3° in ω and the frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. Data were corrected for absorption effects using the multiscan technique (SADABS) [16]. The structures were solved and refined using the Bruker SHELXTL (Version 6.1) software package [17].

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Appendix A. Supplementary material

CCDC numbers 281619 and 604139 contain the supplementary crystallographic data for **2 · BF$_4$** and **5**. 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.poly.2006.09.042.

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