



Communication

Synthesis and structure of mixed-metal thiolate complex $\text{Cp}'\text{Cr}(\text{CO})_2(\mu\text{-SBu})\text{Pt}(\text{PPh}_3)_2$: Side-on-coordination of Cr–S double bond with platinum

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ABSTRACT

The reaction of $[\text{Cp}'\text{Cr}(\text{CO})_2(\mu\text{-SBu})]_2$ ($\text{Cp}' = \text{MeC}_5\text{H}_4$) with $(\text{PPh}_3)_2\text{Pt}(\text{PhC}\equiv\text{CPh})$ gives $\text{Cp}'\text{Cr}(\text{CO})_2(\mu\text{-SBu})\text{Pt}(\text{PPh}_3)_2$ (**2**) which could be regarded as a product of the substitution of acetylene ligand at platinum by a monomeric chromium–thiolate fragment. According to the X-ray diffraction analysis **2** contains single Cr–Pt (2.7538(15)) and Pt–S (2.294(2) Å) bonds while Cr–S bond (2.274(3) Å) is shortened in comparison with ordinary Cr–S bonds (2.4107(4)–2.4311(4) Å) in **1**. The bonding between Cr–S fragment and platinum atom is similar to the olefine coordination in their platinum complexes.

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1. Introduction

Mixed-metal clusters of platinum draw considerable attention as precursors for the catalysts for fuel cells [1]. Usually they could be prepared by insertion of Pt(0) complexes into the metal–metal [2], metal–hydrogen [3] and chalcogen–chalcogen [4,5] bonds. Stepwise assembling of the Pt-containing mixed-metal clusters is also possible with using of the complexes containing terminal thiolate ligands as the building blocks: $\text{Cp}_2\text{Ti}(\text{SR})_2$ (R = Me, Ph) [6], $[\text{Ni}(\text{SCH}_2\text{C}(\text{O})\text{NCH}_2\text{CH}_2\text{NC}(\text{O})\text{CH}_2\text{S})]^{2-}$ [7].

Recently we reported the preparation and structure of the monomeric thiolate complex $\text{CpCr}(\text{CO})_2(\text{SR})$ (R = ferrocenyl) which contains strongly shortened (2.136(1) Å) double Cr=SR bond [8]. Keeping in mind the unsaturated nature of this bond it was interesting to study the reaction of thiolate-bridged complex $[\text{CpCr}(\text{CO})_2(\text{SBu})]_2$ with Pt(0) complexes by analogy with Pt olefin complexes preparation.

2. Results and discussion

The reaction of $[\text{Cp}'\text{Cr}(\text{CO})_3]_2$ with dibutyl disulfide under mild conditions results in dimeric complex **1** which contains two bridging thiolate ligands with ordinary Cr–S bonds (2.4107(4)–2.4311(4) Å). Nonbonding Cr...Cr distance is 3.7105(4) Å. These parameters are

similar to found in the analogous structures at R = $\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ [8], Ph [9] or CH_2Ph [10]. Methylcyclopentadienyl groups adopt *cis*-position in respect to the Cr_2S_2 core and *n*-butyl groups are in *syn* conformation in respect to the S...S vector (Scheme 1).

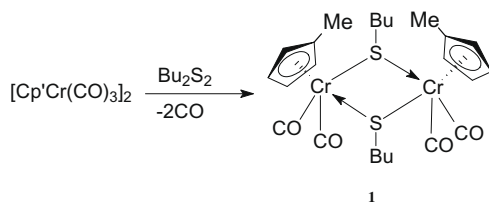
Complex **1** readily interacts with Pt(0) compound, $(\text{PPh}_3)_2\text{Pt}(\text{PhC}\equiv\text{CPh})$ giving dark-green prisms of $\text{Cp}'\text{Cr}(\text{CO})_2(\mu\text{-SBu})\text{Pt}(\text{PPh}_3)_2$ (**2**) – a product of the substitution of diphenylacetylene ligand at platinum by a monomeric chromium–thiolate fragment $\text{Cp}'\text{Cr}(\text{CO})_2\text{SBu}$. Due to elimination of Ph_2C_2 ligand it is probably possible to use another Pt(0) complexes like $(\text{PR}_3)\text{Pt}(\text{alkene})$ or $(\text{PR}_3)_3\text{Pt}$ as platinum source in this reaction. Such experiments are in progress (Scheme 2).

According to the X-ray diffraction data, chromium–thiolate fragment is coordinated via ordinary Cr–Pt (2.7538(15) Å) and Pt–S (2.294(2) Å) bonds. One of CO groups is a semi-bridging ligand (Cr(1)–C(1) 1.809(13) Å, Pt(1)–C(1) 2.633(10) Å, O(1)–C(1)–Cr(1) 170.9(9)°, ν_{CO} 1770 cm^{-1}) and one is terminal (Cr(1)–C(2) 1.804(8) Å, ν_{CO} 1840 cm^{-1}).

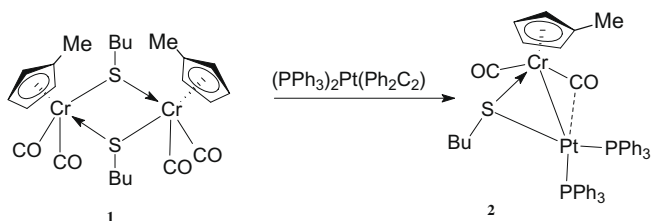
It is noteworthy that Cr–S distance in **2** (2.274(3) Å) is in between the ordinary Cr–S bond lengths in **1** (2.4 Å av.) and the double Cr=SR bond length (2.136(1) Å) in the abovementioned monomeric complex $\text{Cp}'\text{Cr}(\text{CO})_2\text{SC}_5\text{H}_4\text{FeCp}$ (**A**). Probably, the bonding in complex **2** could be considered as a side-on-coordination of the double Cr=SR bond to Pt atom. Charge decomposition analysis (CDA) [11] was used earlier as a tool to distinguish π -complex and metallacycle types of bonding for complexes of tungsten with side-on-coordinated π -ligands [12]. It was shown that $\text{W}(\text{CO})_5$ complexes were close to the first type but WCl_4 containing complexes

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Scheme 1.

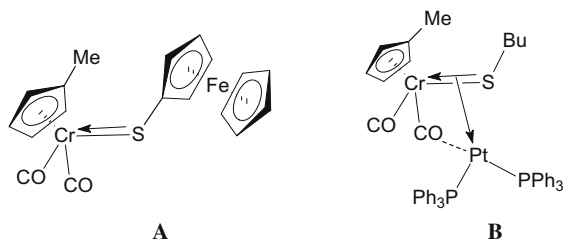


Scheme 2.

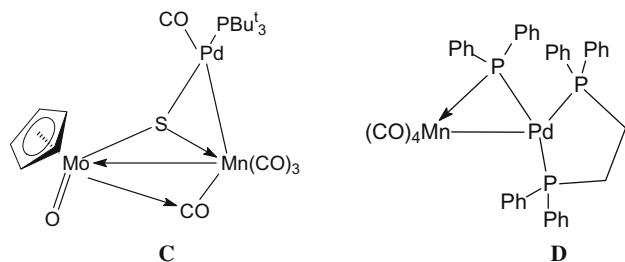
should be assigned to second type. It is difficult now to choose the definite type of bonding in the case of complex **2**. Probably the situation could be viewed as resonance between metallacycle structure **2** and π -complex. But the formal analogy between olefin coordination with Pt(0) and Cr=SR bonding with Pt in **2** unclosed the interesting way to new mixed-metal clusters based on well-known $M_2(\mu-SR)_2$ containing complexes as initial compounds (Scheme 3).

A few structurally characterized examples of complexes with such a bonding pattern are known. Thus in $CpMo(O)(\mu-CO)Mn(CO)_3Pd(CO)(PBu^t_3)(\mu^3-S)$ [4] the palladium atom forms ordinary Pd–S (2.3187(11) Å) and Pd–Mn (2.6387(7) Å) bonds, while the Mn–S (2.2476(12) Å) bond is shortened in respect to the normal ordinary Mn–S bonds (2.370(3)–2.380(3) Å) in $Cp^*MoMn(CO)_5-Pt(PPh_3)_2(\mu^3-S)_2$ [4] (Scheme 4).

The same type of coordination is observed in the manganese diphenylphosphide complex $(dppe)Pd(\mu-PPh_2)Mn(CO)_4$ which is isoelectronic with **2** [13]. It contains Pd– μ -P bond (2.2820(6) Å),



Scheme 3.



Scheme 4.

which is nearly as long as Pd–P_{dppe} bonds (2.3121(6), 2.2945(6) Å) but Mn–P bond (2.2465(7) Å) is considerably shorter than ordinary Mn–P bonds (2.38 Å av.) in dimeric $Mn_2(CO)_8(\mu-PPh_2)_2$ [14].

3. Conclusion

We can conclude that coordination of Pt atom with double metal-thiolate bond is similar to the other side-on- π -ligand coordination. Apparently the dissociation of dimeric transition metal complexes with chalcogenate or phosphide bridge ligands under action of Pt(0) or Pd(0) complexes could be a general synthetic approach to their mixed-metal clusters.

4. Experimental

4.1. General methods

All reactions were performed using standard Schlenk techniques under an atmosphere of dry argon. The solvents were purified, dried and distilled in argon atmosphere. $[Cp^*Cr(CO)_3]_2$ [15] and $Pt(PPh_3)_2(PhC\equiv CPh)$ [16] were prepared according to the published procedures. Infrared spectra were recorded on a Specord 75 IR spectrometer in KBr pellets. Elemental analyses were performed on a Carlo-Erba CHNS analyzer. 1H (400.1 MHz), NMR spectra were recorded using Bruker AV 400 spectrometer, being referenced to residual protons present in the deuterated solvents ($CDCl_3$) with respect to TMS at δ 0.

4.2. Synthesis of compound **1**

A solution of $[Cp^*Cr(CO)_3]_2$ (1.26 g, 2.94 mmol) and Bu_2S_2 (0.6 ml, 0.5 g, 2.82 mmol) in CH_2Cl_2 (50 ml) was stirred for 2 h at room temperature, refluxed for 1 h and then the solvent was removed at reduced pressure. Resulting yellowish-brown oil was extracted with heptane (2×30 ml) and filtered. The extract was reduced in volume to ca. 20 ml and kept at $-10^\circ C$ for 48 h to give dark-brown crystals which were decanted, rinsed with cooled hexane and dried *in vacuo*. Yield 0.82 g (37.5%).

Anal. Calc. for $C_{24}H_{32}S_2Cr_2O_4$: C, 52.16; H, 5.83; S, 11.60. Found: C, 51.79; H, 5.29; S, 10.92%.

IR-data (KBr, ν cm^{-1}): 2950 w., 2915 w., 2855 w., br., 1945 s., 1930 v.s., 1900 m., 1855 v.s., 1460 w., 1020 w., 830 m., 620 w., 540 m., 470 w.

4.3. Synthesis of compound **2**

A solution of $Pt(PPh_3)_2(PhC\equiv CPh)$ (0.27 g, 0.3 mmol) and $[Cp^*Cr(CO)_2]_2(\mu-SBu)_2$ (0.092 g, 0.17 mmol) in benzene (20 ml) was stirred for 2 h. All volatiles were removed at reduced pressure and the resulting green oil was triturated with hexane (10 ml) to yield dark-green powder. It was washed with hexane and extracted with diethyl ether (3×15 ml). After filtering the extract was concentrated to the half of initial volume at reduced pressure and stored at $-10^\circ C$ to provide dark-green crystals which were washed with hexane (5 ml) and dried *in vacuo*. Yield 176 mg (59%).

Anal. Calc. for $C_{48}H_{46}SCrPtP_2O_2$: C, 57.89; H, 4.66; S, 3.21. Found: C, 58.31; H, 4.49; S, 3.76%.

IR-data (KBr, ν cm^{-1}): 3035 w., 2940 w., 2910 w., 1840 v.s., 1770 s., 1465 m., 1430 m., 1170 w., 1080 m., 1020 w., 990 w., 810 w., 790 w., 780 w., 735 m., 685 s., 635 w., 580 w., 525 m., 510 s., 500 m., 490 w.

1H NMR [$CDCl_3$]: δ 0.6 (t, 3H, $J=7.4$, $S(CH_2)_3Me$), 0.95 (m, 2H, $S(CH_2)_3Me$), 1.1 (m, 1H, $S(CH_2)_3Me$), 1.4 (m, 1H, $S(CH_2)_3Me$), 1.8 (m, 1H, $S(CH_2)_3Me$), 2.0 (m, 1H, $S(CH_2)_3Me$), 1.8 (s, 3H, C_5H_4Me),

Table 1
Crystallographic data for compounds **1** and **2**.

	1	2
Formula	C ₂₄ H ₃₂ Cr ₂ O ₄ S ₂	C ₄₈ H ₄₆ CrO ₂ P ₂ PtS
Formula weight	552.62	995.94
Temperature, K	296(2)	296(2)
Space system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a (Å)	9.7620(3)	15.1301(15)
b (Å)	15.1484(5)	13.8476(13)
c (Å)	17.4425(6)	21.572(2)
α (°)	90	90
β (°)	99.294(8)	104.009(3)
γ (°)	90	90
Volume (Å ³)	2521.61(14)	4385.2(7)
Z	4	4
D _{calc} (g/cm ³)	1.456	1.509
Absorption coefficient (mm ⁻¹)	1.055	3.592
F(0 0 0)	1152	1992
θ Range for data collection	1.8–29.00	1.95–27.03
Number of reflections collected	22558	34886
Number of independent reflections, (R _{int})	6692 (0.0239)	9581 (0.1060)
Number of reflections I > 2σ(I) (N ₂)	5627	5041
Parameters	289	463
Goodness-of-fit (GOF) on F ²	0.998	0.937
R ₁ , wR ₂ (I > 2σ(I))	0.0277, 0.0754	0.0524, 0.1087
R ₁ , wR ₂ (all data)	0.0371, 0.0815	0.1335, 0.1524
Largest difference in peak and hole (e Å ⁻³)	0.380 and -0.293	2.000 and -0.587

3.4 (m, 1H, C₅H₄Me), 3.9 (m, 1H, C₅H₄Me), 4.3 (m, 1H, C₅H₄Me), 4.4 (m, 1H, C₅H₄Me), 7.0–7.7 (m, 30H, Ph).

4.4. X-ray crystallographic studies

Dark-brown crystals of **1** were grown from heptane solution at room temperature. Dark-green crystals of **2** were obtained by crystallization from diethyl ether/hexane solution at -10 °C. Crystallographic data and structure refinement details for structures **1** and **2** are listed in Table 1. Structures **1** and **2** were solved by direct

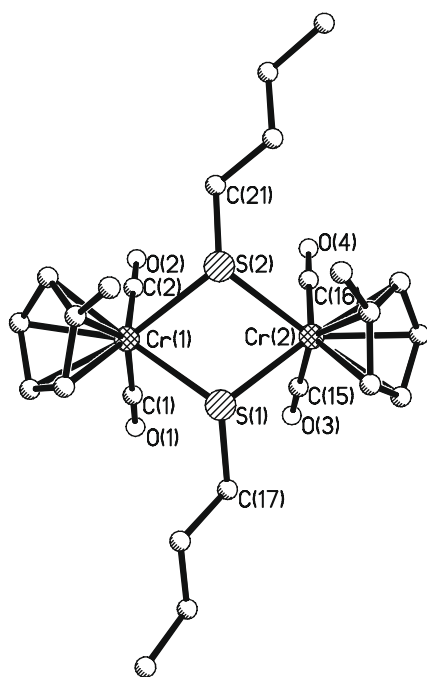


Fig. 1. Molecular structure of **1**. Selected bond distances (Å) and angles (°): Cr(1)–S(1) 2.4107(4), Cr(1)–S(2) 2.4311(4), Cr(2)–S(1) 2.4175(4), Cr(2)–S(2) 2.4183(4), Cr(1)–C(1) 1.8318(17), Cr(1)–C(2) 1.8278(18), Cr(2)–C(16) 1.8333(17), Cr(2)–C(15) 1.8309(16), S(2)–C(21) 1.8312(15), S(1)–C(17) 1.8271(15), Cr(2)–S(2)–Cr(1) 99.845(14), Cr(1)–S(1)–Cr(2) 100.44(14).

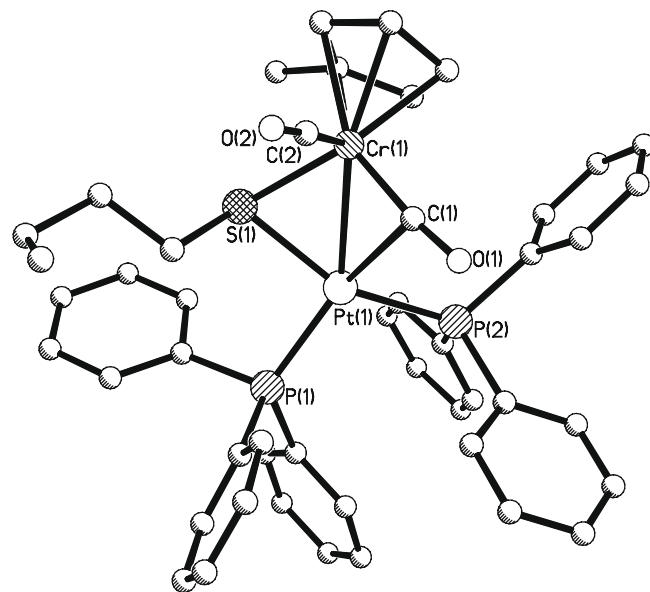


Fig. 2. Molecular structure of **2**. Selected bond distances (Å) and angles (°): Pt(1)–P(1) 2.308(2), Pt(1)–P(2) 2.285(2), Pt(1)–S(1) 2.294(2), Pt(1)–Cr(1) 2.7538(15), Cr(1)–S(1) 2.274(3), Cr(1)–C(1) 1.809(13), Pt(1)–C(1) 2.633(10), Cr(1)–C(2) 1.804(8), Cr(1)–S(1)–Pt(1) 74.13(9), O(1)–C(1)–Cr(1) 170.9(9).

methods and refined by means of least squares method for F² in anisotropic (isotropic for H atoms) approximation in SHELXTL package [17]. Positions of H atoms were calculated geometrically (Figs. 1 and 2).

5. Supplementary material

CCDC 712247 and 719178 contains the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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