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Reaction of Ferrocenyl Triselenide with Tris(triphenylphosphine)platinum

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Abstract—The reaction of ferrocenyl triselenide, $Fe(C_5H_4)_2Se_3$, with $Pt(PPh_3)_3$ is accompanied by elimination of one mole of $SePPh_3$ and gives a dimeric platinum(II) chelate complex with bridging selenium atoms, $[Fe(\mu\text{-}C_5H_4Se)_2Pt(PPh_3)]_2$, which was characterized by X-ray diffraction (CIF file CCDC no. 1055075).

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Chelating ferrocene diselenolate ligands attract considerable attention due to both the presence of easily and reversibly oxidized iron atom in the ferrocene nucleus [1] and the ability to bind various transition metals [2], including silver in the tetrahedral $[Ag_4(FcSe_2)_3]_2^-$ dianion [3], platinum in the $[Fe(\mu\text{-}C_5H_4Se)_2Pt(PBu_3)_2]$ monomer and the $[Fe(\mu\text{-}C_5H_4Se)_2Pt(PBu_3)]_2$ dimer [4], vanadium in $[Fe(\mu\text{-}C_5H_4Se)_2V(O)Cp^*]$ [5], rhenium in $[Fe(\mu\text{-}C_5H_4Se)_2Re(O)Tb]$ (Tb is hydrido-tris(1-pyrazolyl)borate) [6], and ruthenium and osmium in the $FcSe_2[M(NO)Cp^*]$ and $FcSe_2[Ru(CO)(C_6Me_6)]$ monomers [7]. These complexes were synthesized using the reactions of lithium or trimethylsilyl derivatives of ferrocene diselenolates with $Cl_2Pt(PPh_3)_2$ [8] and the reaction of $Fe(C_5H_4SeH)_2$ with $Pt(PPh_3)_4$ [9]. In all of these complexes, the metal atoms are bound only via cyclopentadienyl selenate bridges without forming direct metal–metal bonds (the M···M distances are longer than 4 Å).

It appeared of interest to use 1,2,3-triselena[3]ferrocenophane, $Fe(C_5H_4)_2Se_3$ (**I**), as the source of the chelating diselenate dianion $Fe(C_5H_4Se^-)_2$ capable of strong binding of transition metals M [10, 11]. According to X-ray diffraction data of **I**, no Fe···Se bonds (3.545, 3.823, 3.569 Å) are present and the Se–Se bond lengths are almost equal (2.332 Å) [12]. The ferrocene nucleus present in **I** can undergo reversible single-electron oxidation with, for example, tetracyanoquinodimethane (TCNQ) and halogens (X_2) to give (in the case of octamethylferrocenyl analog), the salts $[Fe(C_5Me_4)_2Se_3]^+X_3^-$ [13]. Furthermore, **I** is oxidized with phenyltellurium tribromide to give $[Fe(C_5H_4)_2Se_3]^+[PhTeBr_4]^-$, whereas oxidation with excess bromine is accompanied by partial destruction of the ferrocene nucleus giving the salt $[Fe(C_5H_4)_2Se_3]^+[FeBr_4]^-$ [14].

EXPERIMENTAL

All operations associated with the synthesis and isolation of compounds were carried out under argon in anhydrous solvents. Commercial ferrocene, *tert*-butyllithium, TMEDA, and selenium were used as received. Complex **I** was prepared by the procedure reported in [11] and $(PPh_3)_3Pt$ was synthesized by the procedure reported in [15]. Chemical analysis was performed using a Carlo Erba CHNS analyzer; the IR spectra were recorded on a Bruker Alpha FT IR spectrometer.

Synthesis of $Fe(C_5H_4Se)_2Pt(PPh_3)]_2$ (II · CH_2Cl_2). $FcSe_3$ (49 mg) was added to a solution of $Pt(PPh_3)_3$ (113 mg, 0.115 mmol) in toluene (10 mL). The resulting dark red solution was stirred for 30 min at 20°C. The light orange reaction mixture was evaporated to dryness and the residue was dissolved in 5 mL of CH_2Cl_2, filtered through a 2 cm silica gel layer, and washed with 10 mL of CH_2Cl_2. The orange solution was concentrated to one-third of the volume and 10 mL of hexane was added. The orange crystals of **II**, which formed upon keeping the solution for 24 h at –20°C, were separated by decanting, washed with hexane (2 × 3 mL), and dried in vacuum. The yield of solvate **II** · CH_2Cl_2 was 42 mg (43%).

For $C_{56}H_{46}P_2Se_4Fe_2Pt_2 \cdot CH_2Cl_2$ ($M = 1683.5$),

anal calcd. (%):	C, 40.66;	H, 2.87.
Found (%):	C, 40.17;	H, 2.43.

IR (ATR; ν, cm^{-1}): 3052 w, 3001 vw, 2918 vw, 1479 m, 1432 vs, 1403 w, 1377 w, 1354 w, 1310 vw, 1184 w, 1141 m, 1093 s, 1047 w, 1016 m, 997 w, 949 w, 877 m, 841 w, 810 m, 738 s, 701 w, 689 vs, 617 w, 601 w, 531 m, 497 s, 462 w.

X-Ray diffraction study of II · CH_2Cl_2 was performed on a Bruker APEX II CCD diffractometer. The crystal data and structure refinement details for **II** · CH_2Cl_2 are summarized in the table. The absorption corrections were applied by multiple measurement of equivalent reflections by the SADABS program [16]. The structure of **II** · CH_2Cl_2 was solved by the direct method and refined by the least-squares method on F^2 in the anisotropic approximation for non-hydrogen atoms (SHELX-2014) [17]. The coordinates of disordered atoms of the phenyl groups in **II** · CH_2Cl_2 were refined in the anisotropic approximation with equal distance restraint (SAME). The positions of H atoms were calculated geometrically. The structural contribution of the disordered CH_2Cl_2 solvate molecules to the crystal of **II** · $(CH_2Cl_2)_n$ was eliminated by the SQUEEZE protocol implemented in the PLATON program [18]. Selected bond lengths and angles for **II** · $(CH_2Cl_2)_n$ are given in the figure caption.

Atom coordinates and other parameters of the structure of **II** are deposited with the Cambridge Crystallographic Data Centre (no. 1055075; http://www.ccdc.cam.ac.uk/data_request/cif).

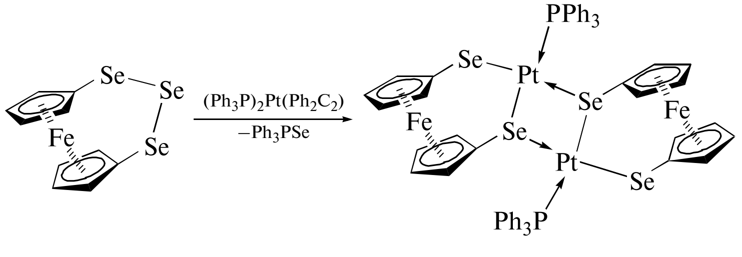
RESULTS AND DISCUSSION

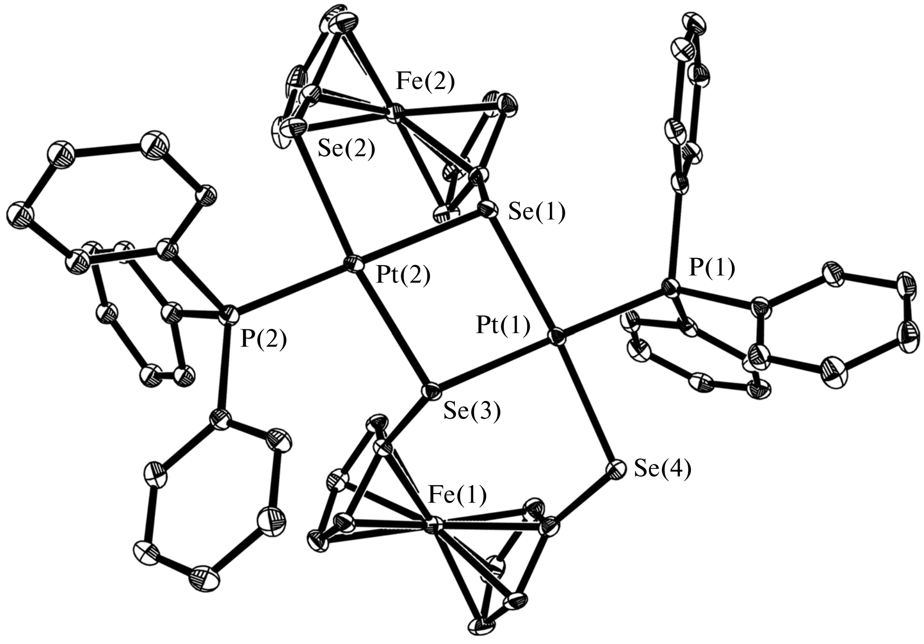
Previously, only few example of the use of ferrocenophane trichalcogenides as sources of ferrocenyl dichalcogenide ligands were known. In particular, in the reactions of $Fe(C_5H_4)_2S_3$ with trinuclear ruthenium and osmium carbonyls, trisulfide forms binuclear complexes with the $M_2(CO)_6$ core containing a ferrocenyl disulfide bridging ligand and the Ru—Ru bond or the Os—S—Os group, respectively. Note that in the former case, one sulfur atom of the trisulfide is split off, while in the latter case, it is incorporated in the complex [19]. As regards triselenide **I**, its reaction with $Pt(PPh_3)_4$ at 0°C gave only the red monomeric complex $[Fe(\mu\text{-}C_5H_4Se)_2Pt(PPh_3)_2]$ [9].

In our case, in the reaction of **I** with $Pt(PPh_3)_3$ at room temperature, the triselenide functions as the supplier of ferrocenyl diselenide chelating ligand uppon elimination of $SePPh_3$ to give first a red solution (apparently, as a result of formation of the abovementioned red monomer $[Fe(\mu\text{-}C_5H_4Se)_2Pt(PPh_3)_2]$ [9]), which rapidly turns into orange color with the formation of the dimeric Pt(II) chelate, $[Fe(\mu\text{-}C_5H_4Se)_2Pt(PPh_3)]_2$ (**II**), as orange crystals, which were characterized by X-ray diffraction (figure):

Crystallographic data and structure refinement details for **II** · CH_2Cl_2

Paramete	Value
M	1598.58
Radiation (λ, Å)	MoK_α (0.71073)
Measurement temperature, K	150(2)
Space group	$P\bar{1}$
a, Å	14.1338(5)
b, Å	15.0682(6)
c, Å	16.6038(6)
α, deg	113.287(1)
β, deg	97.065(1)
γ, deg	102.003(1)
V, Å^3	3093.1(2)
Z	2
ρ_{calcd}, g/cm^{-3}	1.716
μ, mm^{-1}	7.404
F(000)	1512
Scan range of θ, deg	1.37–26.41
Scan mode	ω
Number of independent reflections (N_1)	12528 (R_{int} = 0.0197)
Number of reflections with $I > 2\sigma(I)$ (N_2)	10642
Number of refinement parameters	583
GOOF (F^2)	1.057
R_1 for N_2	0.0288
wR_2 for N_1	0.0816
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.208/–1.168





Molecular structure of **II** · CH_2Cl_2. Selected bond lengths (Å): Pt(1)–Se(1), 2.4489(5); Pt(1)–Se(4), 2.4586(5); Pt(1)–Se(3), 2.4675(5); Pt(2)–Se(2), 2.4474(5); Pt(2)–Se(3), 2.4514(5); Pt(2)–Se(1), 2.4759(5); Pt(1)–P(1), 2.259(1); Pt(2)–P(2), 2.255(1).

Note that complex **II**, which is analogous in the composition to the thiolate complex $[Fe(C_5H_4S)_2Pt(PPh_3)]$ containing the short Fe →Pt bond (2.935(2) Å), which was previously obtained from ferrocenyl trisulfide and $Pt(PPh_3)_4$ [10]. Also, the dimeric structure of **II** is similar to the structure of the complex $[Fe(\mu\text{-}C_5H_4Se)_2Pt(PBu_3)]_2$, which was synthesized together with the monomer $[Fe(\mu\text{-}C_5H_4Se)_2Pt(PBu_3)_2]$ from the trimethylsilyl derivatives of the corresponding ferrocene diselenolates [4]. Probably, the replacement of the sulfur atom by a larger selenium atom prevents the formation of the $[Fe(C_5H_4Se)_2Pt(PPh_3)]$ monomer with the Fe →Pt bond, while the ease of elimination of the tertiary phosphine from the intermediate is, apparently, determined by the lower electron-donating ability of PPh_3 compared to PBu_3. However, the key characteristic features of the dimeric structures containing no Fe–Pt or Pt–Pt bonds but having Pt–Se and Pt–P bonds markedly shortened with respect with the sum of the covalent radii (2.56 and 2.43 Å, respectively [20]) coincide due to the additional dative interactions of platinum *d* electrons with the vacant *d*-orbitals of heavy non-transition elements [21].

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