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Novel Bis(triphenylphosphine)platinum(II) Complexes Containing a Thiourea or a 1,3-Diethylthiourea Dianion as an N,S-Chelating Ligand

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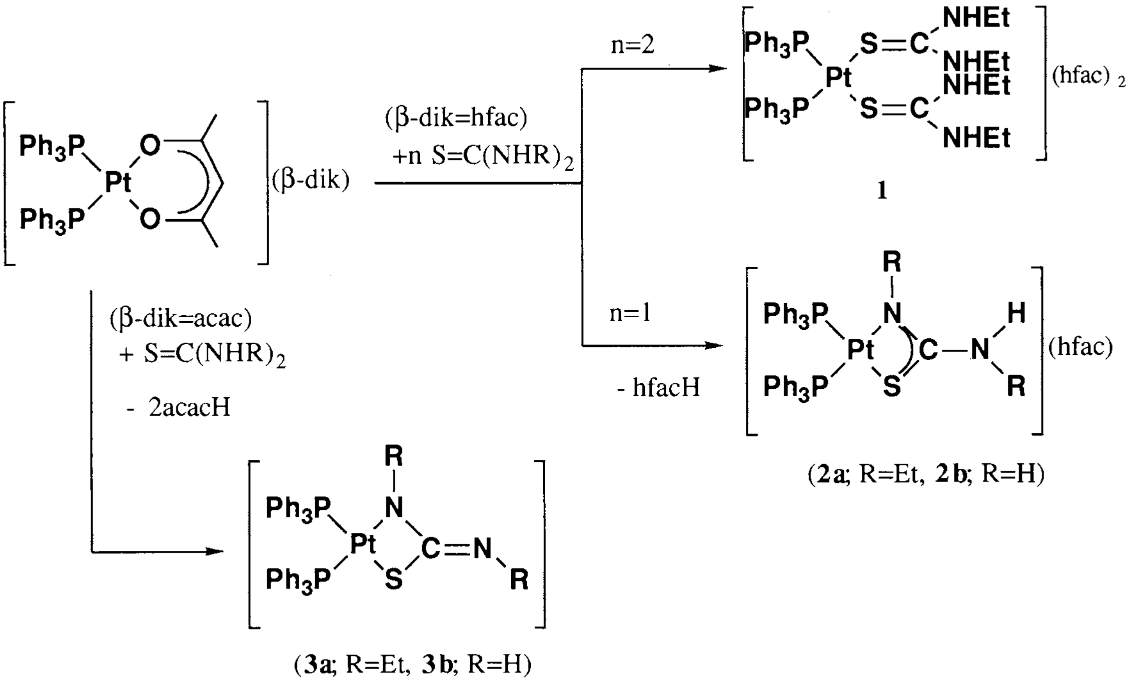
Three kinds of platinum(II) complexes, $[\mathrm{Pt}\{\mathrm{S{=}C(NHEt)_2}\}_2(\mathrm{PPh_3})_2](\mathrm{hfac})_2$, $[\overline{\mathrm{Pt}\{\mathrm{N(R)C(NHR)S}}\}(\mathrm{PPh_3})_2]\mathrm{X}$ (**2**; R=Et or H, X=hfac) and $[\overline{\mathrm{Pt}\{\mathrm{N(R)C(NR)S}}\}\text{-}(\mathrm{PPh_3})_2]$ (R=Et (**3a**) or H), containing thiourea derivatives as neutral, monoanionic, and dianionic ligands, respectively, have been prepared. Thioureido(1-) complex **2** (R=Et, X=OTs) was also prepared by protonation of **3a** with $\mathrm{TsOH{\bullet}H_2O}$. The structure of **3a** with an N,S-chelating thioureido(2-) ligand was determined by single-crystal X-Ray diffraction.

Thiourea and its derivatives are important in biochemistry and used widely as starting materials for preparation of the medicines like thiouracyl. Hence their coordination chemistry has been studied for a variety of metals.1) They usually act as a neutral unidentate or a bridging ligand, both through their sulfur atom and a few examples for preparations of the N,S-chelated thioureido(1-) complexes have appeared.2) However, to our knowledge we never saw complexes containing thiourea dianion as a ligand. We now report the preparations (Scheme 1) and the structures of the bis(triphenylphosphine)platinum(II) complexes with thiourea, thioureido(1), and thioureido(2-) ligands.

To a solution of $[\mathrm{Pt(hfac)(PPh_3)_2}](\mathrm{hfac})$,3) prepared in situ from $[\mathrm{Pt(hfac)_2}]$ (1 equiv.) and $\mathrm{PPh_3}$ (2 equiv.) in $\mathrm{CH_2Cl_2}$ (hfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedionate anion), was added 1,3-diethylthiourea ($\mathrm{Et_2TU}$) (2 equiv.). On addition of pentane, white crystals of $[\mathrm{Pt}\{\mathrm{S{=}C(NHEt)_2}\}_2(\mathrm{PPh_3})_2](\mathrm{hfac})_2$ **1** was deposited in an 84% yield.4) When equimolar $\mathrm{Et_2TU}$ or thiourea(TU) was added to the above solution of $[\mathrm{Pt(hfac)(PPh_3)_2}](\mathrm{hfac})$, $[\overline{\mathrm{Pt}\{\mathrm{N(R)C(NHR)S}}\}(\mathrm{PPh_3})_2](\mathrm{hfac})$ (**2a**; R=Et,5) **2b**; R=H) was obtained as white crystals (**2a**, 60% and **2b**, 70% yields). Both the ^{1}H and ^{13}C NMR signals of the hfac in **1** and **2** showed no coupling to ^{195}Pt and the values of chemical shifts and coupling constants (J(F-H), J(F-C)) are characteristic of the counter anion.6) The ν(C=O) and ν(C=C) IR bands characteristic of the hfac anion were observed in the region of 1500-1700 $\mathrm{cm^{-1}}$.6) The ^{13}C NMR signals of $\mathrm{Et_2TU}$ in **1** in acetone-d_6 are very broad compared with those of $\mathrm{PPh_3}$, suggesting that the free rotation around C-N bonds is appreciably restricted on the NMR time scale. The ^{31}P NMR spectrum of **1** was contaminated by a small amount of **2a**. This implies one of the hfac anions abstracted an amine proton from the coordinated thiourea ligand.

When an equimolar amount of Et_2TU or TU was added to a solution of $[Pt(acac)(PPh_3)_2](acac)$, prepared in situ from $[Pt(acac)_2]$ (1 equiv.) and PPh_3 (2 equiv.) in MeOH,7) $[\overline{Pt\{N(R)C(NR)S\}}(PPh_3)_2]$ (**3a**; R=Et,8) **3b**; R=H) was isolated as yellow cubic crystals in a 60% yield for **3a** and as pale yellow crystals in an 80% yield for **3b**, respectively. Thus, more basic acac anion could abstract two amine protons from the coordinated thiourea ligand. In contrast with **2a**, **3a** has no IR bands assignable to ν(NH) in the region of 3500-3100 cm^{-1} and has no NH signal in ^{1}H NMR.



Scheme 1.

Figure 1 shows an X-ray molecular structure for **3a** and selected bond distances and angles.9) In this complex, the nitrogen atom (N1) and the sulphur atom of the diethylthioureido(2-) are coordinated to the platinum, and form a four-membered ring. The coordination geometry around the platinum atom is distorted from an ideal square planar, apparently due to the small bite of the chelating ligand. In the diethylthioureido(2), the atoms are almost coplanar except for the terminal carbons in the both ethyl groups. The geometry of the thiourea moiety is quite different from that of the monodentate thiourea derivatives,10) and of the C,S-chelated tetramethylthiourea.11) Bond angles around C(TU), N1, and N2 indicate these atoms have a sp^2 hybridized character. The planarity of N1, C(TU), N2 and S suggests the conjugated π molecular orbital among these atoms. In the monodentate neutral thiourea derivatives, the two central carbon-nitrogen bond distances are almost equal.10) On cotrast, the C(TU)-N2 bond distance in **3a** is much shorter than that of C(TU)-N1, and this designates C(TU)-N2 double bond character. These difference in both C-N bond lengths are also observed in C,S chelated thiourea derivatives.11) The bond angle of the C(TU)-N1-C(ETA)1 shows rather normal value for sp^2. The decreased angle of the Pt-N1-C(TU) (101(2)) by the four- membered- ring formation, increases the angle of Pt-N1-C(ETA)1 (139(2)). These distortions in the four membered ring were also found in molybdenum complexes of the N,S chelated P,P-diphenyl-N-methyl-phosphinothioformamido and its analogues.2c, 12)

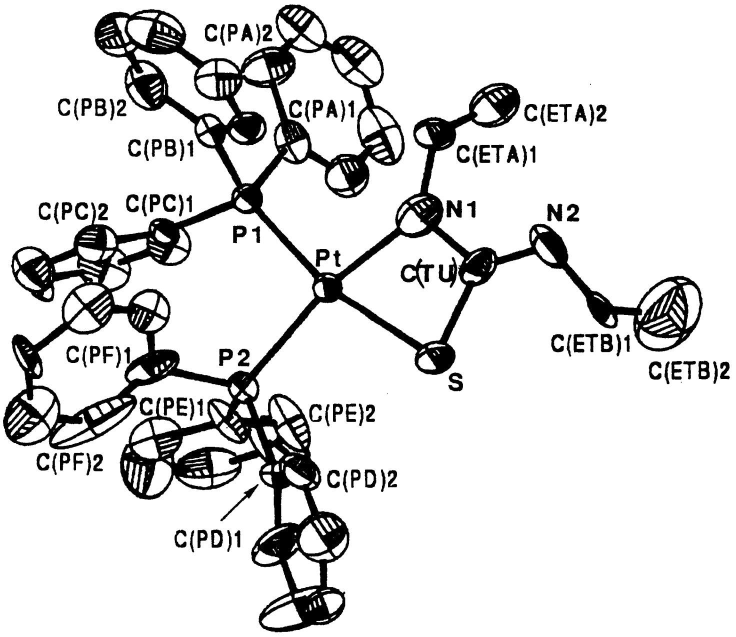


Fig. 1. A view of the structure of **3a**. Selected bond lengths (Å) and angles(°): Pt-P1 2.274(6), Pt-P2 2.269(6), Pt-S 2.332(8), Pt-N1 2.05(3), S-C(TU) 1.77(2), N1-C(TU) 1.42(4), N1-C(ETA)1 1.46(4), N2-C(TU) 1.31(3), N2-C(ETB)1 1.49(4), P1-Pt-P2 96.4(2), P1-Pt-S 166.0(2), P1-Pt-N1 95.5(8), P2-Pt-S 96.9(2), P2-Pt-N1 168.1(8), S-Pt-N1 71.3(8), Pt-S-C(TU) 81.3(8), Pt-N1-C(TU) 101(2), Pt-N1-C(ETA)1 139(2), C(TU)-N1-C(ETA)1 119(2), C(TU)-N2-C(ETB)1 116(2), S-C(TU)-N1 107(2), S-C(TU)-N2 129(2), N1-C(TU)-N2 124(2).

Since the dianionic ligand in **3a** still keeps basicity on its noncoordinating N2 atom, complex **3a** readily reacted with an equimolar amount of p-toluenesulfonic acid monohydrate($TsOH{\bullet}H_2O$) in CH_2Cl_2 to afford $[Pt\{N(Et)C(NHEt)S\}(PPh_3)_2](OTs)$ **2c** as white crystals in an 80% yield. The N,S-chelation of the monoanionic thioureido ligand in **2c** was confirmed by NMR spectral evidence.[13)]

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4) All new complexes were satisfactorily characterized by microanalytical and spectroscopic data.

1: IR(Nujol) 3280m, 3240s, 3150w (NH), 1677s, 1528vs (hfac) 1595 (Et_2TU) cm^{-1}. ^1H NMR (acetone-d_6) δ 0.79[≈6H, br, CH_3], 3.0[≈4H, br. CH], 5.61[1H, hfac-CH], 7.6-7.9[≈15H, Ph]. ^{13}C NMR (acetone-d_6) δ 14.3[br, CH_3], 40.1 [br, CH_2], 84.6[hfac-CH], 119.0[q, ^1J(F-C)=299 Hz, hfac-CF_3], 168.0[br, J(Pt-C)=28 Hz, CS], 173.3 [q, ^1J(F-C)=30 Hz, hfac-CO]. ^{31}P NMR (acetone-d_6) δ 16.6 [J(Pt-P)=2436 Hz] (contaminated by a small amount of **2a**).

5) **2a**: IR(nujol) 3210w, 3140w (NH), 1675s, 1542vs, 1530vs (hfac), 1600vs (Et_2TU) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 0.21 [3H, t, J(H-H)=7 Hz, Pt-N-$CH_2C\mathit{H}_3$], 1.12[3H, t, J(H-H)=7 Hz, CH_3], 2.75 [≈2H, m, ^3J(H-H)=7 Hz, ^4J(P-H)=6 Hz, ^3J(Pt-H)=42 Hz, Pt-N-$C\mathit{H}_2CH_3$], 3.21[≈2H, quintet, ^3J(H-H)=^3J(NH-H)=7 Hz, CH_2], 5.43[≈1H, br, hfac-CH], 7.24, 7.34 [≈30H, br. Ph]. ^{13}C NMR (CD_2Cl_2) δ 12.6 [d, J(P-C)=0.5 Hz, J(Pt-C)=4 Hz, Pt-N-CH_2-$\mathit{C}H_3$], 15.4[CH_3], 36.0 [d, J(P-C)=2 Hz, J(Pt-C)=4 Hz, CH_2], 43.4[t, J(P-C)=6 Hz, J(Pt-C)=19 Hz, Pt-N-$\mathit{C}H_2$-CH_3], 83.9 [hfac-CH], 118.7[q, J(F-C)=291 Hz, hfac-CF_3], 172.9 [q, J(F-C)=30 Hz, hfac-CO], 176.2 [t, J(P-C)=4 Hz, J(Pt-C)=95 Hz, CS]. ^{31}P NMR (CD_2Cl_2) δ 10.4 [d, J(P-P)=21 Hz, J(Pt-P)=3318 Hz], 15.7 [d, J(P-P)=21 Hz, J(Pt-P)=3226 Hz] Mol. wt (CH_2Cl_2) 1055 (calcd. 1058).

6) S. Okeya, H. Sazaki, M. Ogita, T. Takemoto, Y. Onuki, Y. Nakamura, B. K. Mohapatra, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1978 (1981) ; S. Okeya, Y. Nakamura, and S. Kawaguchi, *ibid.*, **54**, 3396 (1981).

7) The spectroscopic data for this ion pair is to be published.

8) **3a**: IR(nujol) 1585vs (Et_2TU) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 0.32 [3H, t, J(H-H)=7 Hz, Pt-N-CH_2-$C\mathit{H}_3$], 1.00 [3H, t, J(H-H)=7 Hz, CH_3], 2.78 [2H, dq, J(H-H)=7 Hz, J(P-H)=5 Hz, J(Pt-H)=40 Hz, Pt-N-$C\mathit{H}_2$-CH_3], 3.08 [2H, q, J(H-H)=7 Hz, CH_2], 7.2-7.4 [30H, m, Ph]. ^{13}C NMR (CD_2Cl_2) δ 14.7 [J(Pt-C)=6 Hz, Pt-N-$CH_2\mathit{C}H_3$], 17.6 [CH_3], 39.6[CH_2], 45.5 [t, J(P-C)=5 Hz, Pt-N-$\mathit{C}H_2$-CH_3], 167.6 [t, J(P-C)=3 Hz, J(Pt-C)≈80 Hz, CS]. ^{31}P NMR (CD_2Cl_2) δ 12.6 [d, J(P-P)=21 Hz, J(Pt-P)=3164 Hz], 17.5 [d, J(P-P)=21 Hz, J(Pt-P)=3152 Hz]. Mol. wt. (CH_2Cl_2) 840 (calcd. 850).

9) Crystal data of **3a** : F.W.=849.9, monoclinic, $P2_1/a$, a=20.378(6), b=11.932(6), c=14.970(5) Å, β=95.02(3)°, U=3626(2) $Å^3$, Z=4, Dc=1.56 g cm^{-3}, Dm=1.53 g cm^{-3}, μ(Mo $K\alpha$)=40.8 cm^{-1}. R=0.069, Rw=0.066. Total 3360 independent reflections with $|Fo|>3\sigma|(Fo)|$ (2θ max=60°) were used.

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13) **2c**: ^1H NMR (CD_2Cl_2) δ 0.06 [3H, t, J(H-H)=10 Hz, Pt-N-$CH_2C\mathit{H}_3$], 1.09 [3H, t, J(H-H)=7 Hz, CH_3], 2.31 [3H, Ts-CH_3], 2.71 [2H, m, Pt-N-$C\mathit{H}_2$-CH_3], 3.12 [2H, quintet, ^3J(H-H)=^3J(NH-H)=7 Hz, CH_2], 7.3-7.5 [≈34H, Ph]. ^{13}C NMR (CD_2Cl_2) δ 12.9 [br, Pt-N-CH_2CH_3], 15.7 [CH_3], 21.4 [Ts-CH_3], 35.9 [CH_2], 43.6 [br, Pt-N-$\mathit{C}H_2CH_3$]. ^{31}P NMR (CD_2Cl_2) δ 10.4 [d, J(P-P)=21 Hz, J(Pt-P)=3310 Hz], 15.7 [d, J(P-P)=21 Hz, J(Pt-P)=3222 Hz].

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