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Synthesis of diorganoplatinum(IV) complexes by the S–S bond cleavage with platinum(II) complexes

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ABSTRACT

Reaction of $[PtR_2(NN)]$ (R = Me, *p*-MeC_6H_4 or *p*-$MeOC_6H_4$; NN = 2,2′–bipyridine, 4,4′–dimethyl–2,2′–bipyridine, 1,10–phenanthroline or 2,9–dimethyl–1,10–phenanthroline) with MeSSMe gives the platinum(IV) complexes *cis,trans*–$[PtR_2(SMe)_2(NN)]$. They are characterized by NMR spectroscopy and elemental analysis. The geometries and the nature of the frontier molecular orbitals of Pt(IV) complexes containing Pt–S bonds are studied by means of the density functional theory.

1. Introduction

Disulfides play an important role in transition metal based organic sulfur chemistry and biochemistry which can be activated by transition metal complexes [1–3]. These reagents constitute a large family of RS^- ligands that have been used for synthesis of transition metal complexes. Transition metal complexes including ligands of the type RS^-, where R is an organic group, are significant in catalysis [4,5], and in medicinal chemistry [6–8].

Due to reducing nature of the RS group, the related complexes in high oxidation states are rare. Thus, the few known stable platinum(IV) thiolates complexes have been reported [9–11]. Surprisingly, studies on the platinum complexes incorporating MeSSMe ligand have been relatively rare [12,13] and there are no reports on the molecular orbital analysis of thiolate complexes in organoplatinum(IV) chemistry.

Since the first report of the anticancer properties of cisplatin and the subsequent introduction of this compound into the clinic, a large number of Pt(II) and Pt(IV) complexes have been synthesized and examined for their antitumor activities [14–19]. In this connection, carboxylation of kinetically inert dihydroxoplatinum(IV) compounds with different reagents such as acid anhydrides and acyl chlorides to form bis(carboxylato)platinum(IV) complexes, which are useful antitumor agents, has been of increasing interest [20].

One way to synthesize the organoplatinum(IV) complexes is the oxidative addition reaction of organic substrates to electron rich Pt(II) complexes [21–23]. Furthermore, there has been a great interest in recent decades to investigate oxidative addition reactions as of the most popular types of organometallic reactions. We have also experimentally and theoretically studied the oxidative addition of different reagents to platinum(II) complexes resulting in the octahedral platinum(IV) complexes [24–34]. Continuing our interest in the use of oxidative addition reactions in the synthesis of new organometallic complexes, we have explored the formation of such complexes via oxidation of platinum(II) reagents by dimethyl disulfide. In fact, we report here the synthesis and characterization of Pt(IV) complexes $[PtR_2(SMe)_2(NN)]$ (R = Me, *p*-MeC_6H_4 or *p*-$MeOC_6H_4$; NN = 2,2′–bipyridine (bpy), 4,4′–dimethyl–2,2′–bipyridine (dmbpy), 1,10–phenanthroline (phen) or 2,9–dimethyl–1,10–phenanthroline (dmphen)), and the nature of the frontier orbitals of organoplatinum(IV) complexes in the presence of SMe group has been studied with the density functional calculations.

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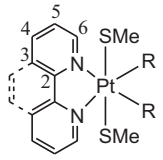
2. Experimental

2.1. General remarks

The ^{1}H NMR spectra were recorded as $CDCl_3$ solutions on a Bruker Avance DPX 250 MHz spectrometer and TMS was used as external reference. All the chemical shift and coupling constants are in ppm and Hz, respectively. Melting points were recorded on a Buchi 530 apparatus and are uncorrected. The microanalyses were performed using a Thermofinigan Flash EA-1112 CHNO rapid elemental analyzer. The known complexes, [Pt(*p*-$MeC_6H_4)_2$(phen)], **1a** [35], [Pt(*p*-$MeC_6H_4)_2$(bpy)], **1b** [36], [Pt(*p*-$MeC_6H_4)_2$(dmbpy)], **1c** [28], [$PtMe_2$(dmbpy)], **1e** [37], and [$PtMe_2$(dmphen)], **1f** [38], were prepared by literature methods. The complex [Pt(*p*-$MeOC_6H_4)_2$(dmbpy)], **1d**, was prepared similarly using *cis*-[Pt(*p*-$MeOC_6H_4)_2(SMe_2)_2$] precursor [39] and 4,4′−dimethyl−2,2′−bipyridine; yield 88%, mp 278 °C (decomp.); Anal. Calcd for $C_{26}H_{26}N_2O_2Pt$: C, 52.6; H, 4.4; N, 4.7. Found: C, 52.5; H, 4.5; N, 4.9. ^{1}H NMR data: δ 3.77 (s, 6H, Me groups on *p*-$MeOC_6H_4$ ligands), 2.42 (s, 6H, Me groups on dmbpy); aromatic protons of dmbpy ligand 8.48 [d, $^3J(H^5H^6) = 5.60$ Hz, $^3J(PtH) = 19.4$ Hz, 2H, H^6], 6.82 [d, $^3J(H^6H^5) = 5.60$ Hz, 2H, H^5], 7.85 (s, 2H, H^3); aromatic protons of $MeOC_6H_4$ ligands 7.39 [d, $^3J(PtH) = 64.18$ Hz, $^3J(H^mH^o) = 6.82$ Hz, 4H, H^o], 6.90 [d, $^3J(H^oH^m) = 6.82$ Hz, 4H, H^m].

2.2. Synthesis of platinum(IV) complexes containing SMe groups

The NMR labeling for Pt(IV) complexes is as follow:



2.2.1. [Pt(*p*-$MeC_6H_4)_2$(phen)(SMe)$_2$], **2a**

Excess of MeSSMe (0.5 mL, 11.25 M) was added to a solution of [Pt(*p*-$MeC_6H_4)_2$(phen)] (20 mg) in acetone (15 mL). The reaction mixture was stirred at room temperature for 2 h. The yellow solution turned colorless after this period. The solvent was evaporated, and residue was washed with acetone and dried in a vacuum. Yield 93%, mp 290 °C (decomp.). Anal. Calcd for $C_{28}H_{28}N_2PtS_2$: C, 51.6; H, 4.3; N, 4.3. Found: C, 51.7; H, 4.4; N, 4.3. ^{1}H NMR data: δ 1.02 (s, $^3J(PtH) = 36.31$, 6H, SMe), 2.32 (s, 6H, Me groups on *p*-MeC_6H_4 ligands), 6.92 [d, $^3J(H^oH^m)$ 7.90 Hz, 4H, H^m of *p*-MeC_6H_4 ligand], 7.44 [d, $^3J(H^mH^o) = 7.90$, $^3J(PtH^o) = 45.33$ Hz, 4H, H^o of *p*-MeC_6H_4 ligand], 9.18 [d, $^3J(H^2H^3) = 5.13$ Hz, $^3J(PtH^2) = 9.93$ Hz, 2H, H^2 of phen], 7.89 [dd, $^3J(H^3H^2) = 5.13$ Hz, $^3J(H^4H^3) = 8.17$ Hz, 2H, H^3 of phen], 8.55 [d, $^3J(H^4H^3) = 8.17$ Hz, 2H, H^4 of phen], 8.08 (s, 2H, H^5 of phen).

The following complexes were made similarly by using the appropriate Pt(II) complex and MeSSMe.

2.2.2. [Pt(*p*-$MeC_6H_4)_2$(bpy)(SMe)$_2$], **2b**

Yield 95% mp 295 °C (decomp.). Anal. Calcd for $C_{26}H_{28}N_2PtS_2$: C, 49.7; H, 4.5; N, 4.5. Found: C, 49.9; H, 4.5; N, 4.6. ^{1}H NMR data: δ 1.18 (s, $^3J(PtH) = 35.74$, 6H, SMe), 2.30 (s, 6H, Me groups on *p*-MeC_6H_4 ligands), 6.88 [d, $^3J(H^oH^m) = 8.06$ Hz, 4H, H^m of *p*-MeC_6H_4], 7.38 [d, $^3J(H^mH^o) = 8.06$, $^3J(PtH^o) = 44.84$ Hz, 4H, H^o of *p*-MeC_6H_4], 8.93 [d, $^3J(H^6H^5) = 5.61$ Hz, $^3J(PtH^6) = 11.11$ Hz, 2H, H^6 of bpy], 7.57 [m, $^3J(H^5H^6) = 5.61$ Hz, 2H, H^5 of bpy], 8.32 [m, $^3J(H^4H^3) = 7.98$ Hz, 2H, H^4 of bpy], 8.10 [d, $^3J(H^3H^4) = 7.98$ Hz, 2H, H^3 of bpy]. ^{13}C NMR data: δ 13.1 (s, Me groups on *p*-MeC_6H_4 ligands) 21.2 (s, C atoms of SMe groups); aromatic C atoms of bpy ligand 123.7 (s, C5), 126.6 (s, C5), 139.3 (s, C4), 150.0 (s, C6), 155.0 (s, C2); aromatic C atoms of *p*-MeC_6H_4 ligands 145.5 (s, $^1J(PtC)$ = 670.9 Hz, C atoms directly attached to Pt), 128.5 (s, C^o atoms), 133.7 (C^p atoms), 136.9 (C^m atoms).

2.2.3. [Pt(*p*-$MeC_6H_4)_2$(dmbpy)(SMe)$_2$], **2c**

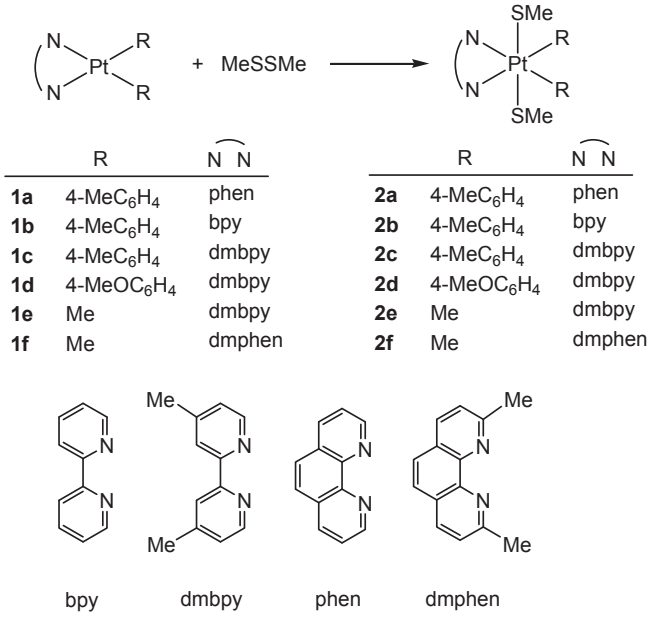
Yield 92%, mp 234 °C (decomp.). The reaction mixture was stirred for 5 days. Anal. Calcd for $C_{28}H_{32}N_2PtS_2$: C, 51.3; H, 4.9; N, 4.3. Found: C, 51.5; H, 4.6; N, 4.5. ^{1}H NMR data: δ 1.19 (s, $^3J(PtH) = 35.79$, 6H, SMe), 2.31 (s, 6H, Me groups on *p*-MeC_6H_4 ligands), 2.63 (s, 6H, Me groups on dmbpy), 6.87 [d, $^3J(H^oH^m) = 7.78$ Hz, 4H, H^m of *p*-MeC_6H_4], 7.38 [d, $^3J(H^mH^o) = 7.78$, $^3J(PtH^o) = 44.94$ Hz, 4H, H^o of *p*-MeC_6H_4], 8.73 [d, $^3J(H^6H^5) = 5.70$ Hz, $^3J(PtH^6) = 11.47$ Hz, 2H, H^6 of dmbpy], 7.32 [d, $^3J(H^5H^6) = 5.70$ Hz, 2H, H^5 of dmbpy], 8.11 [s, 2H, H^3 of dmbpy].

2.2.4. [Pt(*p*-$MeOC_6H_4)_2$(dmbpy)(SMe)$_2$], **2d**

Yield 95%, mp 240 °C (decomp.). The reaction mixture was stirred for 6 days. Anal. Calcd for $C_{28}H_{32}N_2O_2PtS_2$: C, 48.9; H, 4.7; N, 4.1. Found: C, 49.0; H, 4.4; N, 4.3. ^{1}H NMR data: δ 1.18 (s, $^3J(PtH) = 35.85$, 6H, SMe), 2.63 (s, 6H, Me groups on dmbpy), 3.80 (s, 6H, Me groups on *p*-$MeOC_6H_4$ ligands), 6.69 [d, $^3J(H^oH^m) = 7.18$ Hz, 4H, H^m of *p*-$MeOC_6H_4$], 7.43 [d, $^3J(H^mH^o) = 7.18$, $^3J(PtH^o) = 42.82$ Hz, 4H, H^o of *p*-$MeOC_6H_4$], 8.73 [d, $^3J(H^6H^5) = 5.74$ Hz, $^3J(PtH^6) = 11.52$ Hz, 2H, H^6 of dmbpy], 7.38 [d, $^3J(H^5H^6) = 5.74$ Hz, 2H, H^5 of dmbpy], 8.12 [s, 2H, H^3 of dmbpy].

2.2.5. [Pt(Me)$_2$(dmbpy)(SMe)$_2$], **2e**

Yield 89%, mp 175 °C (decomp.). Anal. Calcd for $C_{16}H_{24}N_2PtS_2$: C, 38.2; H, 4.8; N, 5.6. Found: C, 38.4; H, 4.7; N, 5.4. ^{1}H NMR data: δ 1.43 (s, $^2J(PtH) = 68.43$, 6H, MePt), 1.45 (s, $^3J(PtH) = 37.54$, 6H, SMe), 2.59 (s, 6H, Me groups on dmbpy), 8.72 [d, $^3J(H^6H^5) = 4.58$ Hz, $^3J(PtH^6) = 12.78$ Hz, 2H, H^6 of dmbpy], 7.45 [d, $^3J(H^5H^6) = 4.58$ Hz, 2H, H^5 of dmbpy], 8.01 [s, 2H, H^3 of dmbpy]. ^{13}C NMR data: δ −5.0 (s, $^1J(PtC) = 627.7$ Hz, MePt), 8.5 (s, $^2J(PtC) = 14.1$ Hz, SMe groups), 20.7 (s, C atoms of Me of dmbpy); aromatic C atoms of dmbpy ligand 123.1 (s, $^3J(PtC) = 8.7$ Hz, C3), 126.6 (s, $^3J(PtC) = 14.1$ Hz, C5), 145.7 (s, $^2J(PtC) = 14.1$, C6), 149.8 (s, C4), 153.3 (s, C2).



	R	N N
1a	4-MeC_6H_4	phen
1b	4-MeC_6H_4	bpy
1c	4-MeC_6H_4	dmbpy
1d	4-$MeOC_6H_4$	dmbpy
1e	Me	dmbpy
1f	Me	dmphen

	R	N N
2a	4-MeC_6H_4	phen
2b	4-MeC_6H_4	bpy
2c	4-MeC_6H_4	dmbpy
2d	4-$MeOC_6H_4$	dmbpy
2e	Me	dmbpy
2f	Me	dmphen

Scheme 1. Preparation of platinum(IV) complexes.