

Reversible radical complex formation of an organometallic diplatinum(IV) compound

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Abstract

Crystallographically characterized *anti*-[(μ -bmptz){*fac*-PtBrMe₃]₂], bmptz = 3,6-bis(2-(4-methylpyridyl))-1,2,4,5-tetrazine, could be reversibly reduced at -0.36 V vs. [FeCp₂]^{+/-} in CH₂Cl₂/0.1 M Bu₄NPF₆ to a persistent anion. Despite the presence of two conjugatively coupled platinum(IV) centers and the bromide ligands as potential leaving groups it is the bridging bmptz ligand which accepts the added electron within the tetrazine ring as evident from EPR and UV–Vis spectroelectrochemistry of that diplatinum(IV) radical complex. The function of the methyl groups in the [*fac*-PtMe₃]⁺ ions is discussed in contrast with the related entity [*fac*-Re(CO)₃]⁺.

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Keywords: EPR spectroscopy; Platinum compound; Spectroelectrochemistry; Trimethylplatinum group

1. Introduction

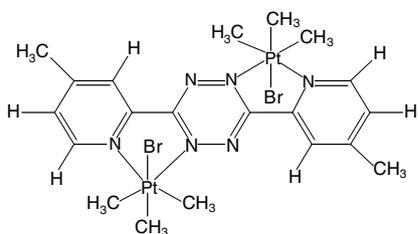
Methylplatinum compounds have long played a prominent role in organometallic chemistry due to their stability in both +II and +IV oxidation states of the metal [1]. While methylplatinum(II) complexes have been studied with respect to Shilov-type C–H bond activation, the multiply methylated Pt^{IV} systems were often obtained as stable products of methylation or oxidative addition reactions and, vice versa, as starting materials for reductive elimination processes [2]. Both PtMe₄ [3] and PtMe₃X (X = halide [4]) compounds of α -diimines and related unsaturated chelate ligands were investigated to elucidate their electronic structures, focussing especially on the kind of possible charge transfer from the methylplatinum moiety to the low-lying π^* orbital of the acceptor ligand. The concept of ligand-to-ligand charge transfer (LLCT) or,

more precisely, sigma bond-to-ligand charge transfer (SBLCT) was put forward to explain excited state properties such as absorption spectra and photoreactivity [3,4]. This process is expected to weaken σ bonds in axial positions, allowing selective activation of metal–halide or metal–carbon bonds [5]. While Pt–C(alkyl) bonds are considered quite stable and their formation or activation is typically associated with classical two-electron reactivity, the electron transfer induced labilization of metal–alkyl functions [5,6] should also be applicable to this inert system [7].

Herein we describe the synthesis, structure and characterization of a first dinuclear model compound, *anti*-[(μ -bmptz){*fac*-PtBrMe₃]₂, using the bis-chelating π acceptor ligand 3,6-bis(2-(4-methylpyridyl))-1,2,4,5-tetrazine (bmptz) [8]. The effect of double Pt^{IV} coordination to a π conjugated acceptor bridge was expected to be quite pronounced, and the site of electron addition was probed using EPR and spectroelectrochemistry. The formal analogy also invited a comparison of [*fac*-PtMe₃]⁺ with the related [*fac*-Re(CO)₃]⁺ [5].

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2. Results and discussion

The orange complex $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2]$ was obtained by reacting the bridging ligand and $[\text{PtBrMe}_3]_4$ [9] in the appropriate molar ratio. The product from recrystallization was only one isomer as verified by ^1H NMR spectroscopy, its identity as the *anti* isomer was confirmed by X-ray crystallography (Table 1, Fig. 1). The bond parameters are in the normal range [10] and will not be discussed further, a more detailed structural study of azo-containing complexes with the PtMe_3X group will be presented at a later stage.

The neutral *anti*- $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2]$ is reduced reversibly at -0.36 V vs. $[\text{FcCp}_2]^{+/0}$ in $\text{CH}_2\text{Cl}_2/0.1\text{ M}$ Bu_4NPF_6 to a persistent anion (Fig. 2). Neither oxidation (at $+1.02\text{ V}$ anodic peak potential) nor the second reduction at -1.8 V cathodic peak potential were found reversible. Previous studies of tetrazine complexes [11] showed

Table 1
Selected bond distances and angles for *anti*- $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2]$ (for numbering see Fig. 1)

distances (Å)		angles (deg)	
Pt(1)–C(9)	2.041(17)	C(9)–Pt(1)–C(8)	87.8(7)
Pt(1)–C(8)	2.073(16)	C(9)–Pt(1)–C(7)	91.0(8)
Pt(1)–C(7)	2.084(19)	C(8)–Pt(1)–C(7)	85.5(8)
Pt(1)–N(2)	2.137(11)	C(9)–Pt(1)–N(2)	97.0(6)
Pt(1)–N(1)	2.195(14)	C(8)–Pt(1)–N(2)	175.1(6)
Pt(1)–Br(1)	2.606(17)	C(7)–Pt(1)–N(2)	94.6(6)
N(1)–C(1)	1.308(19)	C(9)–Pt(1)–N(1)	174.5(6)
N(1)–C(5)	1.388(19)	C(8)–Pt(1)–N(1)	97.5(6)
N(2)–N(3)	1.300(16)	C(7)–Pt(1)–N(1)	88.1(6)

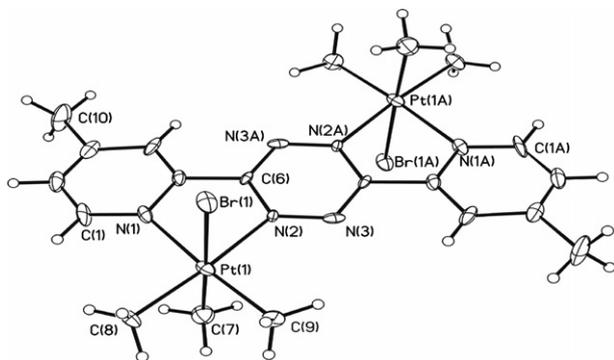


Fig. 1. Molecular structure of *anti*- $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2]$ in the crystal.

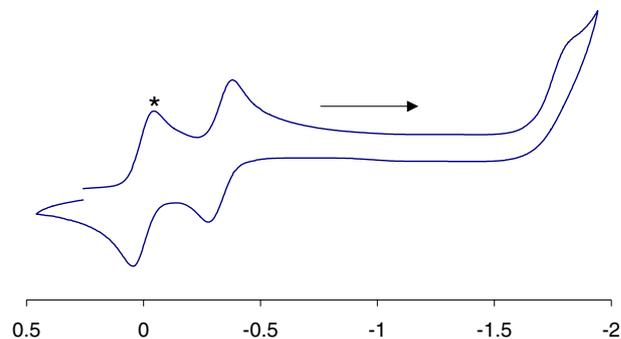


Fig. 2. Cyclic voltammogram (first and second reduction) of *anti*- $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2]$ in $\text{CH}_2\text{Cl}_2/0.1\text{ M}$ Bu_4NPF_6 (* = ferrocene wave).

generally very large differences of $>1.0\text{ V}$ between the first and second reduction while the (irreversible) oxidation of the PtMe_3X group must involve the halide or carbanionic ligands. The reduction potential compares with about -0.15 V vs. $[\text{FcCp}_2]^{+/0}$ for the related, similarly neutral $[(\mu\text{-bptz})\{\text{fac-ReBr}(\text{CO})_3\}_2]$, *bptz* = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, believed to be studied as the *anti* isomer [12]. In both cases it is remarkable that the first reduction step does not appreciably labilize the bromide ligands which would constitute excellent leaving groups. Reductively caused metal–halide bond dissociation has been observed for several platinum metal complexes [13].

The site of electron addition to a transition metal complex can often be conveniently determined by EPR spectroscopy. While odd electron platinum species like Pt^{III} are typically characterized by extremely shifted *g* factors [14] or even by EPR silence [15] the tetrazines exhibit the distinct localization of an added electron on the four nitrogen atoms, leading to typically resolved spectra [11,12]. For symmetrically dinuclear bis-chelate complexes of *bptz* or *bmptz* radical anions two EPR hyperfine coupling constants from two pairs of ^{14}N (tetrazine) nuclei ($I = 1$) are thus expected, additional coupling with the ^{195}Pt nuclei ($I = 1/2$, 33.8% natural abundance) is usually detectable [16,17] because of the large isotropic hyperfine constant $a_o = 1227.84\text{ mT}$ [18]. The *g* factors of tetrazine radical anions and of their metal complexes are mostly near the free ligand value of about 2.004 [11], and the spin delocalization to the pyridyl rings is negligible.

The results obtained for electrologically generated *anti*- $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2]^-$ as shown in Fig. 3 are in agreement with a nearly complete spin localization at the tetrazine ring. The *g* factor at 2.0053, i.e. close to 2.004, suggests that the heavy Pt and Br atoms with their very large spin–orbit constants do not appreciably contribute to the singly occupied molecular orbital. However, the hyperfine interaction does not only involve two pairs of ^{14}N (tetrazine) nuclei with typical [11,12] coupling constants of 0.37 and 0.74 mT, it also requires the inclusion of ^{195}Pt coupling (2.35 mT, 2 Pt nuclei) and interaction with the $^{79,81}\text{Br}$ isotopes (0.55 mT, 2 Br) with their nuclear spin of $I = 3/2$ [18]. The chelate situation with the binding to two equivalent spin bearing tetrazine nitrogen atoms

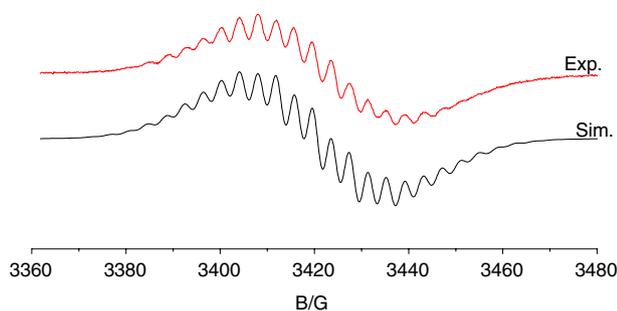


Fig. 3. EPR spectrum of *anti*-[(μ -bmptz){*fac*-PtBrMe₃]₂]⁻ generated by in situ electrolysis in CH₂Cl₂/0.1 M Bu₄NPF₆ (top) with computer simulation (bottom; 0.35 mT line width, for parameters see text).

seems to promote hyperfine interaction of both PtBr units via spin polarization.

The neutral *anti*-[(μ -bmptz){*fac*-PtBrMe₃]₂] exhibits a broad band in the UV region with an absorption maximum at 325 nm ($\epsilon = 27000 \text{ M}^{-1} \text{ cm}^{-1}$) and an absorption tail in the visible reaching almost till 700 nm (Fig. 4).

The tetrazines have weak $n \rightarrow \pi^*$ transitions around 550 nm ($\epsilon \approx 500 \text{ M}^{-1} \text{ cm}^{-1}$) and intense $\pi \rightarrow \pi^*$ transitions at about 300 nm [11]. For instance, free bmptz in dichloromethane has $\lambda_{\text{max}} = 542$ and 295 nm ($\epsilon = 430$ and $22800 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. However, in addition to intra-ligand (IL) transitions of this kind we must consider intense singlet metal-to-ligand charge transfer (¹MLCT) bands in the UV region, possibly overlapping with the IL band as well as sigma bond-to-ligand charge transfer (SBLCT) transitions and perhaps triplet features (³MLCT) as further weak absorptions in the visible. Unlike other alkylmetal complexes with unsaturated chelate ligands [3,6,7] the complex is not light-sensitive.

On reversible reduction as monitored by spectroelectrochemistry (Fig. 4) there is a high-energy shift and partial splitting of the UV band (IL and MLCT transitions) to 270(sh) and 296 nm ($\epsilon = 24200 \text{ M}^{-1} \text{ cm}^{-1}$) whereas the bands in the visible are diminished and partially structured: 380(sh), 495 nm ($\epsilon = 1700 \text{ M}^{-1} \text{ cm}^{-1}$), 532 nm ($\epsilon = 1400 \text{ M}^{-1} \text{ cm}^{-1}$). Unlike many radical anions the one-electron reduced tetrazines do not exhibit conspicuous IL

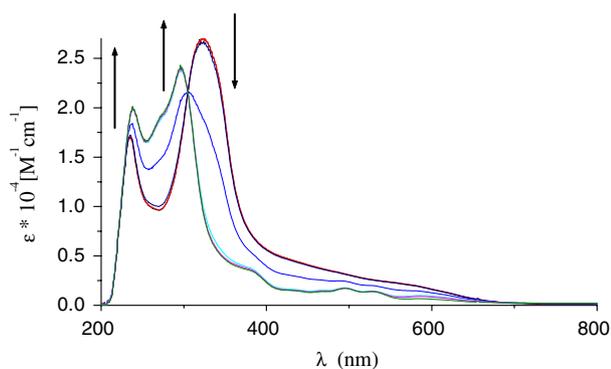


Fig. 4. UV-Vis spectroelectrochemistry in CH₂Cl₂/0.1 M Bu₄NPF₆ of the transition *anti*-[(μ -bmptz){*fac*-PtBrMe₃]₂]^{(e)-(-)}.

absorption in the visible or infrared region [11]. We therefore assign these discernible bands to the above mentioned MLCT and SBLCT transitions involving the singly occupied MO (SOMO).

There is a formal correspondence between [*fac*-PtMe₃]⁺ and [*fac*-Re(CO)₃]⁺, both being structurally inert entities with 5d⁶ configuration on the metal. Whereas the [*fac*-Re(CO)₃]⁺ group exhibits low-energy metal-to-ligand charge transfer (MLCT) absorptions and metal-based oxidation which is often accompanied by CO dissociation [5,12,19], the oxidation of the [*fac*-PtMe₃]⁺-containing complex may primarily involve the formally carbanionic organic ligands [7]. The potential for electrochemical and/or photochemical activation will therefore be studied further. Similar to the rhenium(I) system the *fac*-trimethylplatinum(IV) cation may possibly engage in the formation of electroactive supramolecular structures, e.g. molecular rectangles [20] with suitable combinations of bridging ligands.

Summarizing, we have shown that even with two reductively sensitive Pt^{IV} and metal-halide bonds present, the tetrazine ligands can accommodate at least one added electron reversibly to form a persistent radical complex intermediate, characterized by EPR and UV-Vis spectroelectrochemistry. In this context the concepts of intermediate electron storage (“electron reservoir function” [21,22]) and “18 + δ electron configuration” [22c] come to mind which serve to accumulate charge until the right number for a low-activation chemical process has been gathered. The second electron uptake of tetrazine occurs at a very negative potential which leaves this system less suitable for studying the actual bond cleavage, however, other such ligands with closer spaced electrochemical waves promise to be more suitable for research aimed at successive one-electron reactivity of organometallic reaction centers [23].

3. Experimental

3.1. Instrumentation

EPR spectra in the X band were recorded with a Bruker System ESP300 equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter. ¹H NMR spectra were taken on a Bruker AC 400 spectrometer. UV-Vis-NIR absorption spectra were recorded on J&M TIDAS (200–2350 nm) and on Shimadzu UV-3101 (200–1100 nm) spectrophotometers. Cyclic voltammetry was carried out at room temperature (293 K) in CH₂Cl₂/0.1 M Bu₄NPF₆ solution using a three-electrode configuration (Pt working electrode, Pt counter electrode, Ag wire pseudo-reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc⁺) couple served as internal reference. Spectroelectrochemistry was performed at ambient temperature using an optically transparent thin-layer electrode (OTTLE) cell [24]. A two-electrode capillary served to generate intermediates for X band EPR studies [25].

3.2. Synthesis

Bmptz and $[\text{Pt}(\text{CH}_3)_3\text{Cl}]_4$ were synthesized in accordance with the literature [8,9].

3.2.1. $[\text{Pt}(\text{CH}_3)_3\text{Br}]_4$

This compound was synthesized by a halogen exchange reaction. An amount of 0.1 g (0.09 mmol) of $[\text{Pt}(\text{CH}_3)_3\text{Cl}]_4$ was dissolved in 20 ml of CH_2Cl_2 . In a separate flask, 0.38 g (3.6 mmol) NaBr were dissolved in 20 ml methanol and these two solutions were mixed and stirred for 3 days. The colorless residue after removing the solvents was treated with 20 ml of CH_2Cl_2 and stirred. The mixture was filtered and 20 ml of CH_2Cl_2 were again added to the solid. After stirring and filtering, the filtrates were combined and the solvent removed. The colorless residue was washed with methanol. Yield: 90 mg, 77%. ^1H NMR (CDCl_3) δ = 1.51 (s, 36H, CH_3 , $J_{\text{Pt}-\text{CH}_3}$: 79.2 Hz).

3.2.2. *anti*- $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2]$

Amounts of 0.150 g of $[\text{Pt}(\text{CH}_3)_3\text{Br}]_4$ (0.12 mmol) and 0.062 g of bmptz (0.23 mmol) were dissolved in 35 ml of benzene and stirred 2 days at room temperature to yield a brown precipitate. The mixture was filtered and the solid washed twice with 10 ml portions of benzene and dried under vacuum. Recrystallization from dichloromethane and hexane yielded 120 mg (57%) of the dichloromethane solvate. Anal. Calcd. for $\text{C}_{21}\text{H}_{32}\text{Br}_2\text{Cl}_2\text{N}_6\text{Pt}_2$ (989.38 g/mol): C, 25.50; H, 3.26; N, 8.49. Found: C, 25.65; H, 3.33; N, 8.45%. ^1H NMR (CDCl_3 , numbering according to heterocyclic nomenclature) 8.84 (d, 2H, $\text{H}^{3,3'}$, $^4J_{\text{H}_3-\text{H}_5}$: 1.05 Hz), 7.81 (dd, 2H, $\text{H}^{5,5'}$, $^3J_{\text{H}_5-\text{H}_6}$: 5.43 Hz, $^4J_{\text{H}_5-\text{H}_3}$: 0.91 Hz), 8.90 (d, 2H, $\text{H}^{6,6'}$, $^3J_{\text{H}_6-\text{H}_5}$: 5.64 Hz $J_{\text{H}_6-\text{Pt}}$: 17.82 Hz), 0.80 (s, 6H, CH_3 , $^2J_{\text{Pt}-\text{H}}$: 74.06 Hz), 1.78 (s, 6H, CH_3 , $^2J_{\text{Pt}-\text{H}}$: 72.78 Hz), 1.79 (s, 6H, CH_3 , $^2J_{\text{Pt}-\text{H}}$: 72.11 Hz), 2.74 (s, 6H, CH_3 on pyridyl).

3.2.3. X-ray crystallography

Crystal data of *anti*- $[(\mu\text{-bmptz})\{\text{fac-PtBrMe}_3\}_2] \times \text{H}_2\text{O}$: orange red plate (0.20 × 0.20 × 0.04 mm) from wet CH_3NO_2 , $\text{C}_{20}\text{H}_{32}\text{Br}_2\text{N}_6\text{OPt}_2$, $M = 921.51$, space group *Fddd*, orthorhombic, $a = 11.434(2)$, $b = 26.180(4)$, $c = 15.929(2)$ Å, $\beta = 106.687(17)^\circ$, $V = 4567.6(14)$ Å³, $Z = 16$, $\rho_{\text{calc}} = 1.171$ g cm⁻³, μ (Mo K α) = 0.71073 mm⁻¹, diffractometer Siemens P4, $T = 173$ K, 2θ range $3 \leq 2\theta \leq 50^\circ$, 3837 collected and 3253 unique reflections, programs SHELXTL 5.03 [26] and SHELXL-97 [27], refinement with all data on F^2 , hydrogen atoms on calculated positions, 139 parameters, 2 restraints, absorption correction by Ψ -scans, $R_1 = 0.075$ for 3253 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1743$ (all data). For the water molecule the O–H distances were restrained to meaningful values.

4. Supplementary material

CCDC 628343 contains the supplementary crystallographic data for this paper. 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.

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