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An amino acid bioconjugate of an organoplatinum tris(pyrazolyl)borate complex: Synthesis and structure of [*p*-(^tBuO–Phe–CO)C_6H_4Tp]$PtMe_3$

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Abstract

The platinum trimethyl complex of a benzoic acid-functionalized hydrido-tris(pyrazolyl)borate (Tp) ligand [*p*-$(HO_2C)C_6H_4$Tp]$PtMe_3$ **4** has been synthesized from the corresponding *p*-bromo complex [*p*-BrC_6H_4Tp]$PtMe_3$ **3**. Compound **4** may be readily coupled to biomolecules such as amino acids as exemplified by coupling to L-phenylalanine-*tert*-butylester to provide [*p*-(^tBuO–Phe–CO)C_6H_4Tp]$PtMe_3$ **5**. Compound **5** has been structurally characterized in the solid state by X-ray diffraction. It constitutes the first example of a tris(pyrazolyl)borate bioconjugate.

Keywords: Bioorganometallic chemistry; Bioconjugates; Amino acid; Platinum compounds; Tris(pyrazolyl)borate ligands

1. Introduction

Bioconjugates of organometallic compounds have become a topic of great interest in recent years since they offer opportunities in medicinal chemistry as lead structures for novel drugs and diagnostics [1,2]. As one example, complexes of the third row transition elements have been employed as heavy atom probes for protein crystallography or as probes for transmission electron microscopy [3]. Accordingly, there is a constant quest for ligands that will furnish novel air- and water-stable organometallic bioconjugate complexes. Such ligands must be readily functionalized appropriately for covalent linkage to a variety of biomolecules. Our group has been actively studying bioconjugates of both organometallic and inorganic complexes [4]. Herein, we report our initial results using the tris(pyrazolylborate) ligand system (Tp) [5] which include the first example of an organometallic tris(pyrazolylborate) bioconjugate. A reliable method for the formation of organometallic-bioconjugates is to employ a ligand or metal complex derivatized with a carboxylic acid group in a peptide-type coupling protocol in which the carboxylate group is transformed into an amide moiety [6]. Accordingly, we sought carboxylic acid derivatives of Tp complexes suitable for use in peptide-type coupling reactions. At the time of starting this work, we were aware of only one carboxylic acid-substituted Tp complex, [(*p*-$HO_2C)C_6H_4$Tp]$_2$Co, [7] which contains two chemically equivalent acid groups thus predisposing it to be conjugated to two identical biomolecules thereby limiting the scope of its applications. We now report that a benzoic acid derivative of a TpPt(IV) σ-organometallic complex, [8] *p*-$(HO_2C)C_6H_4$TpPtMe$_3$, may be synthesized as outlined in Scheme 1.

p-$BrC_6H_4BBr_2$ (**1**) is obtained from *p*-$Me_3SiC_6H_4Br$ and BBr_3 in a solvent-less reaction according to the method of Haubold et al. [9]. The preparation of the bromophenyl-substituted Tp derivatives *p*-BrC_6H_4TpM (M = Et_3NH, Li) by the reaction of *p*-$BrC_6H_4BBr_2$ with pyrazole and a base follows the precedent set by Wagner [10] and Reger [11] who recently made the [FcTp] (Fc = $C_5H_4FeC_5H_5$) and [*p*-IC_6H_4Tp] ligands in a similar fashion from $FcBBr_2$

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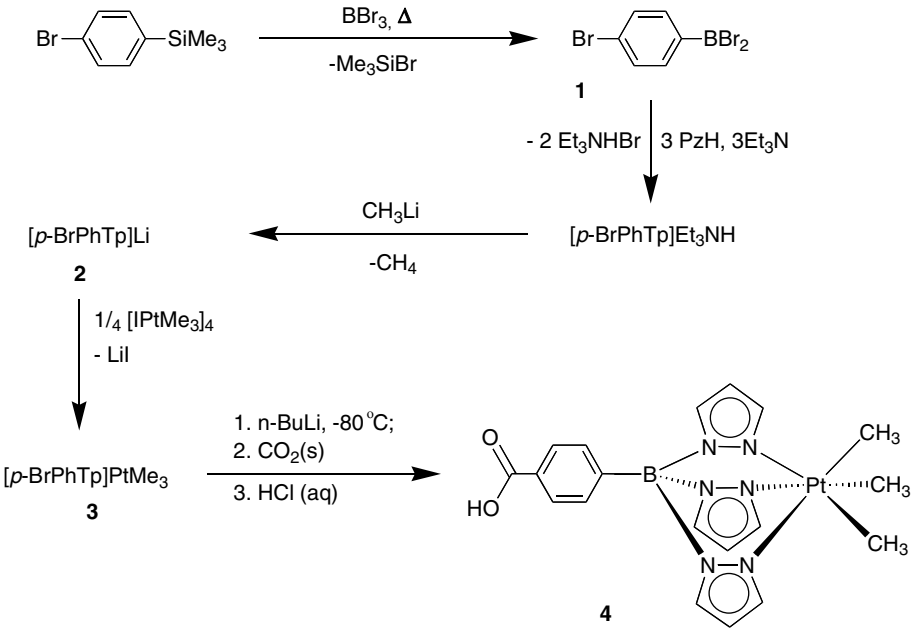


Scheme 1. Synthesis of the carboxy-substituted $TpPtMe_3$ precursor **4**.

and *p*-$IC_6H_4BBr_2$, respectively. A related method was used by Trofimenko and coworkers to make the transition metal sandwich complexes $(PhTp)_2M$ (M = Mn, Fe, Co, Ni, Cu, Zn) from $PhBCl_2$, excess pyrazole and a divalent metal salt [12]. Also, [*p*-BrC_6H_4Tp]Na was made by reacting *p*-$BrC_6H_4B(OH)_2$ with pyrazole and sodiumpyrazolide [7].

Similar to literature methods [13], the tetravalent organoplatinum complex *p*-$BrTpPtMe_3$ **3** is isolated from the reaction of [*p*-BrC_6H_4Tp]Li with $[IPtMe_3]_4$. A notable feature of the ^1H NMR spectrum of **3** is the signal for the [$PtMe_3$] moiety, the key parameters of which, δ 0.98 and $J_{Pt-H} = 69$ Hz, are identical to those reported for $TpPtMe_3$ [13a]. Conversion of **3** into the benzoic acid derivative [*p*-$(HO_2C)C_6H_4Tp$]$PtMe_3$ **4** is accomplished as outlined in Scheme 1 [7]. The presence of the carbonyl moiety of complex **4** is confirmed by a stretch at 1689 cm^{-1} in the infrared spectrum [14] and a signal at δ 172 in the ^{13}C NMR spectrum [15].

In order to test the suitability of **4** for use in coupling reactions to biomolecules, in particular in solid phase peptide synthesis, **4** was reacted with amino acid esters in a standard peptide synthesis protocol in solution [4a,4i]. For example, in dichloromethane **4** reacts with the phenylalanine-*tert*-butylester H-Phe-O^{t}Bu in the presence of TBTU and DiPEA to produce the amide [*p*-(Bu^tO–Phe–CO)C_6H_4Tp]$PtMe_3$ (**5**) (Scheme 2). The presence of the amide group of **5** is supported by the appearance of the [NHCO] moiety as a doublet ($\delta = 6.75$, $J = 7.5$ Hz) in the ^1H NMR spectrum, a peak in the ^{13}C NMR spectrum at δ 167 and a stretch in the IR spectrum at 1637 cm^{-1} which cumulatively provide evidence for the formation of the amide **5** [15].

Unequivocal identification of **5** has been made in the solid state by a single crystal X-ray diffraction experiment from which the structure shown in Fig. 1 was obtained.

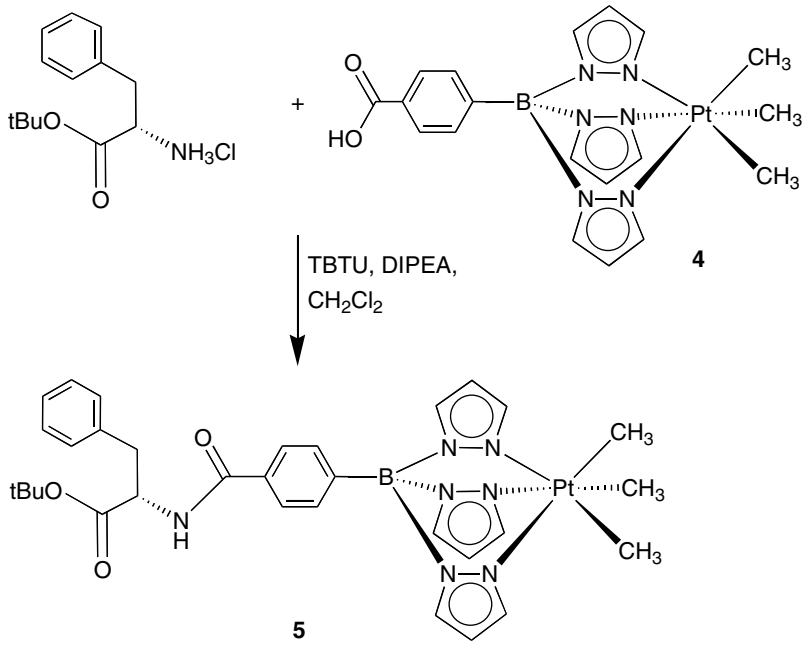
Most notably, **5** is the first example of a Tp-bioconjugate and the structure in Fig. 1 confirms the presence of the L-phenylalanine ester covalently attached to the Tp ligand framework. The metrical parameters of the distorted-octahedral geometry at platinum, including the Pt–N and Pt–C distances, are within the ranges observed in other $Tp^{R,R'}PtMe_3$ complexes [13c].

In summary, we have reported the synthesis of the novel benzoic acid-derivatized Tp-organoplatinum complex [*p*-$(HO_2C)C_6H_4Tp$]$PtMe_3$ (**4**). **4** has been shown to undergo coupling to phenylalanine-*tert*-butylester, using TBTU as the carboxylic acid activator, to give

[*p*-(^{t}BuO–Phe–CO)C_6H_4Tp]$PtMe_3$ (**5**), the first bioconjugate of a Tp-metal complex. **5** was structurally characterized in the solid state by X-ray diffraction thereby demonstrating the covalent linkage of the amino acid monomer derivative to the Tp ligand. Next to the cyclopentadienyl ligand, tris(pyrazolyl)borate (Tp) is one of the most frequently used ligands in inorganic and organometallic chemistry. This work introduces the Tp ligand to organometallic bioconjugate chemistry.

2. Experimental

Unless otherwise stated, all experimental techniques were carried out under an inert atmosphere of argon or dinitrogen employing standard high-vacuum and Schlenk techniques and an M-Braun glovebox. All reagents were purchased from commercial sources and used as received. Compound **1** was prepared according to the literature [9]. Anhydrous solvents obtained from commercial sources were used in all syntheses. NMR spectra were recorded at ambient temperature on a 300 MHz spectrometer with chemical shifts (δ) reported in parts-per-million (ppm) relative to the residual proton chemical shifts of the deuter-



Scheme 2. Synthesis of the $TpPtMe_3$ bioconjugate **5**.

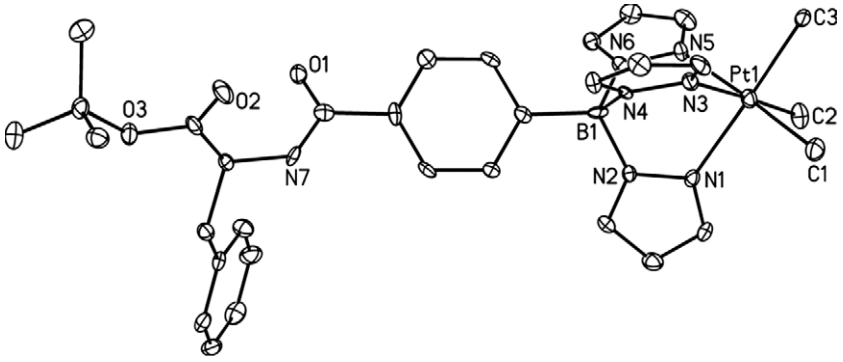


Fig. 1. ORTEP plot of the structure of *p*-[Bu′O–Phe–CO]$C_6H_4TpPtMe_3$ (**5**). Selected bond lengths (Å): Pt1–C2: 2.045(4); Pt1–C3: 2.047(3); Pt1–C1: 2.044(4); Pt1–N3: 2.111(3); Pt1–N5: 2.136(3); Pt1–N1 2.133(3). C–Pt–C angles are 88.6–88.8°, N–Pt–N angles are 84.8–86.4°.

ated solvent set relative to external TMS. Coupling constants (*J*) are quoted in Hertz. $^{13}C\{^1H\}$ assignments of the carbon-type (i.e. C, CH, CH_2, CH_3) were made from a standard Attached Proton Test (APT) experiment protocol. IR spectra were recorded on a Perkin–Elmer 1600 FTIR Series instrument as pressed KBr pellets. Elemental analyses were carried out at the University of Heidelberg IPMB analytical service laboratory. Mass spectra were run in the mass spectrometry service lab of the University of Bochum on a VG Instruments Autospec in FAB mode, positive ion detection.

1 (*p*-$BrC_6H_4BBr_2$): A mixture of boron tribromide (5.39 g, 21.5 mmol) and 1-bromo-4-trimethylsilyl-benzene (4.93 g, 21.5 mmol) were heated at 70 °C overnight in an ampoule sealed with a teflon stopcock. The volatile components of the reaction mixture were removed under reduced pressure leaving a purple-white solid residue which was sublimed under vacuum (ca. 60 °C, 10^{-2} mbar) to give *p*-$BrPhBBr_2$ as a white solid (5.9 g, 84%). Anal. Calc. for $C_6H_4BBr_3$: C, 22.06; H, 1.23. Found: C, 22.22; H, 1.31%. ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (2H, d, $J = 8.2$), 8.07 (2H, d, $J = 8.2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.6 (CH), 138.9 (CH).

2 (*p*-BrC_6H_4TpLi): A solution of *p*-$BrC_6H_4BBr_2$ (5.0 g, 15.31 mmol) in dichloromethane (ca. 5 mL) was added dropwise over ca. 90 min to a cooled (ice bath, ca. 0 °C) and rapidly stirred solution of pyrazole (3.18 g, 46.7 mmol) in dichloromethane (ca. 10 mL). At the end of dropwise addition, the mixture was stirred for 10 more minutes on the ice bath then triethylamine (4.73 g, 46.7 mmol) was added and the mixture was stirred overnight at room temperature. The solvents were removed from the mixture under reduced pressure leaving a white solid which was extracted with THF (60 mL) and filtered. The THF filtrate was cooled on an ice bath, treated with methyl lithium (10 mL of 1.6 M in Et_2O, 16 mmol) and stirred cold for

30 min. After warming to room temperature and stirring for 30 min, the solvents were removed from the reaction mixture under reduced pressure to give a yellow sticky solid which was washed with Et_2O (1×20 mL, 3×10 mL) and hexane (1×20 mL) and dried under reduced pressure leaving *p*-BrC_6H_4TpLi as a white solid (2.83 g, 49%). Anal. Calc. for $C_{15}H_{13}BBrLiN_6$: C, 48.05; H, 3.49; N, 22.41. Found: C, 47.82; H, 3.66; N, 22.28%. ^{1}H NMR (300 MHz, d_6-DMSO) δ 6.02 (3H, dt, $J = 0.5$, 1.8), 6.82 (3H, dd, $J = 0.5$, 1.8), 7.20–7.30 (4H, mult.), 7.42 (3H, dd, $J = 0.5$, 1.8); ^{13}C NMR (75 MHz, $CDCl_3$) δ 102.7 (CH), 119.2 (*C*Br or *C*B), 128.7 (CH), 133.7 (CH), 135.9 (CH), 139.0 (CH).

3 (*p*-$BrC_6H_4TpPtMe_3$): THF (ca. 5 mL) was added to a rapidly stirred mixture of *p*-BrC_6H_4TpLi (0.86 g, 2.29 mmol) and $IPtMe_3$ (0.84, 2.29 mmol) and the reaction was stirred overnight at room temperature. The solvent was removed from the homogeneous yellow reaction solution leaving a pale yellow solid which was extracted into refluxing hexane (2×45 mL) on the bench-top open to air, filtered and the solvent was removed under reduced pressure to give *p*-$BrTpPtMe_3$ as a mixture of colorless crystals and white powder (1.13 g, 81%). Anal. Calc. for $C_{18}H_{22}BBrN_6Pt$ (608.21 g mol^{-1}): C, 35.55; H, 3.65; N, 13.82. Found: C, 35.53; H, 3.82; N, 13.67%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (9H, s, $J_{Pt-H} = 69$), 6.22 (3H, d, $J = 2.2$), 7.54 (3H, d, $J = 2.2$), 7.63 (2H, d, $J = 8.4$), 7.69 (2H, d, $J = 8.4$), 7.87 (2H, d, $J = 8.4$); ^{13}C NMR (75 MHz, $CDCl_3$) δ −9.3 ($J_{Pt-C} = 673$, Pt*C*H_3), 105.7 (CH), 123.4 (CB or CBr), 131.6 (CH), 135.6 (CH), 136.8 (CH), 138.2 (CH). FAB-MS (pos.) 609.2 (45, $[M+H]^+$), 541.2 (70), 460.2 (100).

4 (*p*-$(HO_2C)C_6H_4TpPtMe_3$): ^{n}BuLi (0.40 mL, 2.5 M solution in hexane, 1 mmol) was added dropwise over 2 min to a cold (ca. −80 °C) solution of *p*-$BrTpPtMe_3$(**3**, 0.58 g, 0.95 mmol) in THF (ca. 20 mL) and the mixture was stirred for ca. 90 min cold. Excess solid dry ice (ca. 10 g) was added, the mixture was removed from the cold bath and stirred for ca. 90 min and then the volatile components were removed under reduced pressure leaving a white solid. On the bench-top open to air, the white solid was slurried in water (ca. 15 mL), treated with aqueous hydrochloric acid (2.5 mL, 2 N), stirred for 30 min then filtered, washed with water (2×30 mL) and dried to give *p*-$(HO_2C)PhTpPtMe_3$ as a white solid (0.38 g, 66%). Anal. Calc. for $C_{19}H_{23}BN_6O_2Pt$ (573.16 g mol^{-1}): C, 39.80; H, 4.04; N, 14.66. Found: C, 39.22; H, 4.22; N, 14.35%. ν (KBr) 1689; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (9H, s, $J_{Pt-H} = 70$), 6.24 (3H, t, $J = 2.2$), 7.55 (3H, d, $J = 2.2$), 7.65 (3H, d, $J = 2.2$), 8.15 (2H, d, $J = 8.4$), 8.28 (2H, d, $J = 8.4$); ^{13}C NMR (75 MHz, $CDCl_3$) δ −9.3 ($J_{Pt-C} = 673$, PtCH_3), 105.7 (CH), 129.8 (CH), 135.3 (CH), 135.6 (CH), 138.3 (CH), 172.2 (CO_2H). FAB-MS (pos.) 574.3 (70, $[M+H]^+$), 459.1 (100).

5 (*p*-[Bu^{t}O–Phe–CO]$C_6H_4TpPtMe_3$): To a room temperature slurry of *p*-$(HO_2C)PhTpPtMe_3$ (**4**, 0.20 g, 0.35 mmol) in dichloromethane (ca. 5 mL) was added *N*,*N*′-diisopropylethylamine (0.30 g, 2.38 mmol), *O*-(1H-benzotriazo-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium tetrafluoroborate (TBTU) (0.11 g, 0.35 mmol) and L-phenylalanine-*tert*-butyl ester hydrochloride (0.09 g, 0.35 mmol) and the mixture was stirred overnight. The solvent was removed under reduced pressure and, on the bench-top open to air, the residue was extracted into refluxing hexane (2×30 mL), filtered and the solvent was removed under reduced pressure leaving a sticky white solid which was washed with hexane (1×5 mL) giving *p*-[Bu^{t}O–Phe–CO]$C_6H_4TpPtMe_3$ as a white solid (0.075 g, 28%). Anal. Calc. for $C_{32}H_{40}BN_7O_3Pt$ (776.61 g mol^{-1}): C, 49.49; H, 5.19; N, 12.63. Found: C, 49.38; H, 5.30; N, 12.64%. ν (KBr) 1637, 1735; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (9H, s, $J_{Pt-H} = 70$), 3.29 (2H, d, $J = 6$), 5.03 (1H, vq, $J = 7.5$), 6.22 (3H, t, $J = 2.2$), 6.75 (1H, d, $J = 7.5$, N*H*), 7.20–7.30 (5H, m, C_6H_5), 7.53 (3H, d, $J = 2.2$), 7.63 (3H, d, $J = 2.2$), 7.90 (2H, d, $J = 8.4$), 8.07 (2H, d, $J = 8.4$); ^{13}C NMR (75 MHz, $CDCl_3$) δ −9.3 ($J_{Pt-C} = 673$, PtCH_3), 28.2 ($3 \times CH_3$, $C(CH_3)_3$), 38.0 (CH2), 54.1 (CH), 82.9 (COBu^t), 105.7 (CH), 126.7 (CH), 127.3 (CH), 128.6 (CH), 129.8 (CH), 134.3 (C), 135.4 (CH), 135.6 (CH), 136.4 (C), 138.1 (CH), 166.9 (NHCO), 171.0 (CO_2Bu^t). FAB-MS (pos.) 798.5 ($[M+Na-H]^+$), 777.5 ($[M+H]^+$), 721.4 ($[M-C_4H_8]^+$).

X-ray structure determination of **5**: Crystal structure analysis: A crystal of 5 (colorless needle, 0.25 mm × 0.07 mm × 0.07 mm) was placed on a glass capillary in perflourinated oil and measured in a cold gas flow. The intensity data were measured with a Bruker axs area detector (Mo K_α radiation, $\lambda = 0.71073$ Å, ω scan) at −60° C. $C_{32}H_{40}BN_7O_3Pt \cdot 2C_6H_6$, $M = 932.83$, monoclinic, $a = 9.6827(18)$ Å, $b = 9.5122(16)$ Å, $c = 22.670(3)$ Å, $\beta = 92.777(13)°$, $U = 2068.8(6)$ Å^3, $T = 105$ K, space group $P2_1$ (no. 4), $Z = 2$, 31 789 reflections collected, 9475 unique ($R_{int} = 0.0272$), $wR(F_2) = 0.0400$ (all data).

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Appendix A. Supplementary material

CCDC 607271 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via htpp://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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.10.028.

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