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Stereospecific Intramolecular S→Pt Transmethylation from 8-(Methylthio)quinoline to Coordinated $PtMe_2$: Formation of *syn*-[*fac*-$Pt^{IV}Me_3$(μ-8-quinolinethiolato)]$_2$ with Stacked Quinoline Rings

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Summary: Sulfur to platinum(II) transmethylation was observed on reacting [$PtMe_2$(μ-SMe_2)]$_2$ or [$PtMe_2$(μ-SEt_2)]$_2$ with 8-(methylthio)quinoline (mtq) for extended periods of time or on heating of the isolable intermediate $PtMe_2$(mtq). The final product, syn-[fac-$PtMe_3$(μ-qt)]$_2$ (qt^- = 8-quinolinethiolato), exhibits two quinoline rings in a nearly stacked arrangement. This internal redox reaction involving organometallic platinum constitutes a variant of the well-known platinum complex induced S-demethylation and proceeds in a stereospecific manner, as indicated by CD_3 labeling experiments.

S-Demethylation is a biochemically important reaction within methyl transfer metabolism.[1] However, there is also a well-established synthetic *S*-demethylation reactivity, found first with inorganic platinum(II) in 1883[2] and later with related halide compounds of palladium(II) and gold(III). Typically, these reactions involve a transfer of the methyl group to an external acceptor.[3] In a wider context, metal-induced S−C bond breaking is an essential step in the important technical process of hydrodesulfurization.[4]

In this report we describe (i) the ability of the organoplatinum(II) fragment $PtMe_2$ to engage in *S*-demethylation originating from the neutral chelate ligand 8-methylthioquinoline (mtq),[3−5] leading (ii) to an internal reduction/oxidative addition reaction to *fac*-trimethylplatinum(IV) moieties, which are (iii) bridged by π/π stacked 8-quinolinethiolato (qt^-) ligands as the demethylation products. Also, (iv) both the final product, [$PtMe_3$(μ-qt)]$_2$, and the intermediate, $PtMe_2$(mtq), were crystallographically characterized (Figures 1 and 2)[6] and (v) deuterium labeling of the *S*-methyl group allowed us to determine the stereoselectivity of the reaction.

The precursor complexes[7] [$PtMe_2$(μ-SMe_2)]$_2$ and [$PtMe_2$(μ-SEt_2)]$_2$ react with mtq to give $PtMe_2$(mtq),[8] as is evident from spectroscopy and crystal structure analysis (Figure 1).[6] The data show the typical[9] difference from the previously[5] characterized $PtMe_4$(mtq): viz., a slight shortening of Pt−N and Pt−S bonds.

$$2(\mathrm{N}{\wedge}\mathrm{SMe}) + [\mathrm{PtMe_2}(\mu\text{-}\mathrm{SR_2})]_2 \xrightarrow[25\ ^\circ\mathrm{C},\ 4\ \mathrm{h}]{\mathrm{THF}} 2\mathrm{PtMe_2}(\mathrm{N}{\wedge}\mathrm{SMe}) + 2\mathrm{SR_2} \quad (1)$$

$$\mathrm{N}{\wedge}\mathrm{SMe} = \mathrm{mtq}$$

Under prolonged heating the product from eq 1 is converted via eq 2[10] to a new compound, which was identified by ^1H NMR and crystal structure analysis (Figure 2)[6] as a rearranged dimer (eq 3).

This product could also obtained in small amounts by reacting mtq and [$PtMe_2$(μ-SMe_2)]$_2$[7a] at 293 K for several months.

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[6] Crystal data for $PtMe_2$(mtq): M = 400.40, monoclinic, $P2_1/n$, a = 8.0481(16) Å, b = 14.164(3) Å, c = 10.821(2) Å, β = 104.896(14)°, V = 1192.0(3) Å^3, Z = 4, D_c = 2.231 g/cm^3, μ(Mo Kα) = 11.912 mm^{-1}, T = 173 K, $2\theta_{max}$ = 56°, 3076 independent reflections collected on a Siemens P4 four-circle diffractometer. Refinement of 2883 reflections (138 parameters) with $I > 2\sigma(I)$ converged at final R1 = 0.0503 and wR2 = 0.1212. Crystal data for [$PtMe_3$(μ-qt)]$_2$: M = 800.80, monoclinic, $P2_1/n$, a = 9.7319(19) Å, b = 16.430(2) Å, c = 15.533(2) Å, β = 96.750(14)°, V = 2466.5(7) Å^3, Z = 4, D_c = 2.157 g/cm^3, μ(Mo Kα) = 11.514 mm^{-1}, T = 173 K, $2\theta_{max}$ = 56°, 6284 independent reflections collected on a Siemens P4 four-circle diffractometer. Refinement of 5948 reflections (289 parameters) with $I > 2\sigma(I)$ converged at final R1 = 0.0482 and wR2 = 0.1108.

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[8] $PtMe_2$(mtq): a solution of 320 mg (0.507 mmol) of [Pt_2Me_4(μ-SEt_2)$_2$] and 178 mg (1.015 mmol) of mtq in 25 mL of dry THF was stirred at ambient temperature for 4 h. After half of the solvent volume was evaporated, the resulting precipitate was collected by filtration and washed with cold diethyl ether to yield 365 mg (90%) of orange microcrystals. Single crystals were obtained from a THF solution at −10 °C. ^1H NMR (250 MHz, 300 K, acetone-d_6): δ 9.44 (d, 1H, H2, $^3J_{H-H}$ = 5.0 Hz), 8.77 (d, 1H, H4, $^3J_{H-H}$ = 8.3 Hz), 8.33 (d, 1H, H7, $^3J_{H-H}$ = 7.3 Hz), 8.09 (d, 1H, H5, $^3J_{H-H}$ = 7.9 Hz), 7.74 (t, 1H, H6, $^3J_{H-H}$ = 7.3 Hz, 7.9 Hz), 7.52 (dd, 1H, H3, $^3J_{H-H}$ = 8.3 Hz, 5.0 Hz), 2.83 (s, 3H, SCH_3, $^3J_{Pt-H}$ = 30.2 Hz), 0.79 (s, 3H, PtMe, $^2J_{Pt-H}$ = 83.6 Hz), 0.72 (3H, PtMe, $^2J_{Pt-H}$ = 87.8 Hz). ESI-MS: m/z 400.1 (M^+); calcd 400.0. Anal. Calcd for $C_{12}H_{15}NPtS$: C, 36.00; H, 3.78; N, 3.50. Found: C, 36.13; H, 4.04; N, 3.29.

[9] Hasenzahl, S.; Hausen, H.-D.; Kaim, W. *Chem. Eur. J.* **1995**, *1*, 95.

10.1021/om049247l CCC: $30.25

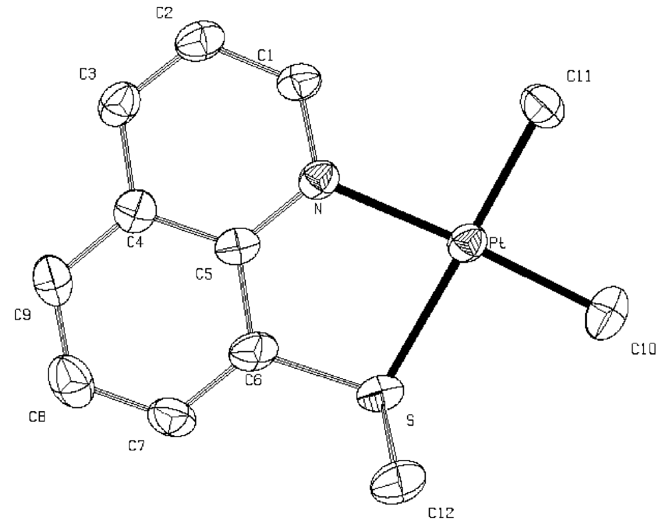
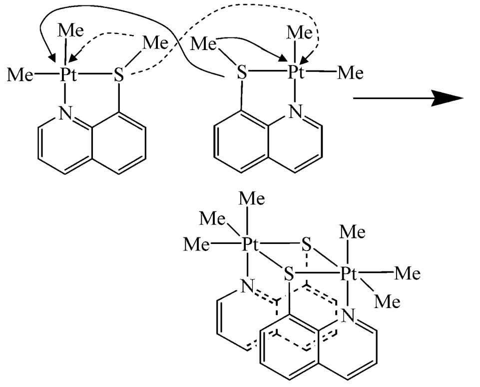


Figure 1. Molecular structure of PtMe$_2$(mtq) in the crystal state (thermal ellipsoid plot at the 30% level; H atoms are not shown for clarity). Selected bond distances (Å) and angles (deg): Pt−C10 = 2.055(9), Pt−C11 = 2.059(8), Pt−N = 2.126(7), Pt−S = 2.305(2); C10−Pt−C11 = 88.1(4), C10−Pt−N = 176.2(3), C11−Pt−N = 95.3(3), C10−Pt−S = 92.8(3), C11−Pt−S = 176.2(3), N−Pt−S = 83.92(19).

$$2\ \mathrm{PtMe_2(N{^\wedge}SMe)} \xrightarrow[66^\circ\mathrm{C},\ 1\ \mathrm{d}]{\mathrm{THF}} [\mathit{fac}\text{-}\mathrm{PtMe_3}(\mu\text{-}\mathrm{N{^\wedge}S})]_2 \qquad (2)$$

$\mathrm{N{^\wedge}S^-} = \mathrm{qt^-}$



(3)

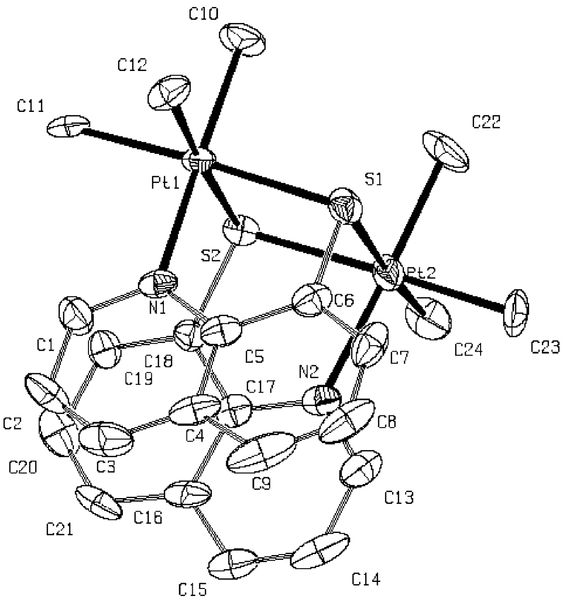


Figure 2. Molecular structure of *syn*-[*fac*-PtMe$_3$(μ-qt)]$_2$ in the crystal state (thermal ellipsoid plot at the 30% level, H atoms are not shown for clarity). Selected bond distances (Å) and angles (deg): Pt1−C10 = 2.056(10), Pt1−C11 = 2.138(10), Pt1−C12 = 2.109(10), Pt1−N1 = 2.149(8), Pt1−S1 = 2.410(3), Pt1−S2 = 2.490(2), Pt2−C22 = 2.057(11), Pt2−C23 = 2.104(10), Pt2−C24 = 2.091(11), Pt2−N2 = 2.180(8), Pt2−S2 = 2.401(3), Pt2−S1 = 2.483(3); C10−Pt1−C12 = 87.7(5), C10−Pt1−C11 = 87.4(4), C10−Pt1−N1 = 175.9(4), C10−Pt1−S1 = 94.9(4), C10−Pt1−S2 = 88.3(3), C11−Pt1−C12 = 89.6(4), C11−Pt1−N1 = 95.3(3), C11−Pt1−S1 = 176.7(2), C11−Pt1−S2 = 91.5(3), C12−Pt1−N1 = 89.3(4), C12−Pt1−S1 = 92.9(3), C12−Pt1−S2 = 175.8(3), N1−Pt1−S1 = 82.6(2), N1−Pt1−S2 = 94.7(2), S1−Pt1−S2 = 86.14(8), C22−Pt2−C23 = 87.2(6), C22−Pt2−C24 = 87.7(5), C22−Pt2−N2 = 176.1(5), C22−Pt2−S2 = 94.2(4), C22−Pt2−S1 = 87.8(4), C23−Pt2−C24 = 86.7(5), C23−Pt2−N2 = 96.0(4), C23−Pt2−S2 = 178.5(4), C23−Pt2−S1 = 93.6(4), C24−Pt2−N2 = 90.3(4), C24−Pt2−S2 = 93.4(4), C24−Pt2−S1 = 175.4(3), N2−Pt2−S2 = 82.6(2), N2−Pt2−S1 = 94.2(2), S2−Pt2−S1 = 86.49(8), Pt1−S1−Pt2 = 93.66(8), Pt1−S2−Pt2 = 93.67(8).

In the intramolecular redox reaction (2) the oxidation Pt$^{\mathrm{II}}$ → Pt$^{\mathrm{IV}}$ is offset by a reduction of the transferred methyl group from the +I state (bonded to S) to the −I state (bonded to platinum).

The product structure shows two *fac*-PtMe$_3$ fragments bridged by two thiolate sulfur atoms from the newly formed qt$^-$ ligand.[11,12] The virtually planar Pt$_2$S$_2$ core is slightly asymmetric with alternating short (2.41 Å) and long (2.49 Å) Pt−S bonds and nonbonded distances of 3.5684(7) Å (Pt1−Pt2) and 3.347(3) Å (S1−S2). The angles S−Pt−S and Pt−S−Pt are about 86.3 and 93.7°, respectively. In comparison to Pt$^{\mathrm{IV}}$Me$_4$(mtq),[5] [*fac*-Pt$^{\mathrm{IV}}$Me$_3$(μ-qt)]$_2$ shows comparable Pt−N but longer Pt−S distances, despite the negative charge on the thiolate sulfur atoms; the necessity of forming the Pt$_2$S$_2$ ring is held responsible for this (asymmetric) weakening of Pt−S bonds.

Of the two possible isomers with either syn- or anti-positioned N atoms of the N∧S chelate ligand qt$^-$ relative to the Pt$_2$S$_2$ plane, the syn alternative has been found. This situation implies close contact between the two quinoline rings in an almost stacking mode (Figure 2), with nonbonded atoms separated by only 3.134(12) Å (N2- - -C6) or 3.146(12) Å (N1- - -C18). Such small atom−atom distances between nonbonded aromatic rings are indicative of substantial π/π interaction;[13] they are significantly smaller than the interplanar distance of 3.35 Å in graphite. The dihedral angle between the two quinoline rings is 16.4°; the inter-ring distances

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(10) [*fac*-PtMe$_3$(μ-qt)]$_2$: a THF solution of 230 mg of PtMe$_2$(mtq) was heated to reflux for 1 day. After evaporation of the solvent and washing with diethyl ether, 185 mg (80%) of orange-red microcrystals was obtained. Single crystals were collected from a methyl *tert*-butyl ether solution layered with *n*-hexane. ^{1}H NMR (250 MHz, 300 K, DMSO-d_6): δ 8.86 (d, 1H, H2, $^3J_{\mathrm{H-H}} = 1.7$ Hz), 8.33 (d, 1H, H4, $^3J_{\mathrm{H-H}} = 8.3$ Hz), 7.69 (d, 1H, H7, $^3J_{\mathrm{H-H}} = 8.0$ Hz), 7.58−7.52 (m, 2H), 7.45 (d, 1H, H3, $^3J_{\mathrm{H-H}} = 8.3$ Hz), 1.30 (s, 3H, PtMe, $^2J_{\mathrm{Pt-H}} = 71.6$ Hz), 0.65 (s, 3H, PtMe, $^2J_{\mathrm{Pt-H}} = 61.5$ Hz), 0.11 (s, 3H, PtMe, $^2J_{\mathrm{Pt-H}} = 69.0$ Hz). Anal. Calcd for $C_{24}H_{30}N_2Pt_2S_2$: C, 36.00; H, 3.78; N, 3.50; Found: C, 36.19; H, 3.97; N, 3.25.

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(12) A qualitatively similar but more distorted related structure with bridging/chelating dimethyldithiocarbamato ligands was reported: Heard, P. J.; Kite, K.; Nielsen, J. S.; Tocher, D. A. *Dalton* **2000**, 1349.

(13) Janiak, C. *Dalton* **2000**, 3885.

become greater on moving away from the Pt_2S_2 scaffold. It can be speculated that the π/π attraction favors the formation of the syn isomer during reaction 2, whereas the fac configuration is the preferred arrangement for $Pt^{IV}Me_3L_3$ species.[14]

The strictly stereospecific nature of reactions 2 and 3 is evident from a deuteration experiment using SCD_3 instead of SCH_3 in mtq* (made from qt^- and CD_3I) and $PtMe_2(N\wedge SMe)^*$ under otherwise analogous conditions (eq 2).[10] The ^1H NMR signal at 0.11 ppm for [*fac*-$PtMe_3$-(μ-$N\wedge S$)$]_2$ is completely absent in the deuterated species (Figure S1; Supporting Information), in agreement with the selective migration of the sulfur-bonded methyl group (C12 in Figure 1) to the axial positions of the product, as C12 trans to S2 or as C24 trans to S1 (Figure 2).[15]

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Supporting Information Available: CIF files giving X-ray crystallographic data for $PtMe_2(mtq)$ and *syn*-[*fac*-$PtMe_3$-(μ-qt)$]_2$ and figures giving ^1H NMR spectra in the CH_3 region. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] (a) The assignment is based on established correlations between chemical shifts[15b] or $^{195}Pt-^1H$ coupling constants[15c,d] with the Pt−Me environment due to the trans influence.[15d] The groups Me10 and Me22 trans to neutral pyridine-type N are thus identified with the signal at 1.30 ppm.[15b] The methyl groups trans to thiolate S experience a high-field shift[15b] and reduction of $J(^{195}Pt-^1H)$.[15d] According to a general inverse linear correlation between $J(^{195}Pt-^1H)$ and the Pt−C distance[15c] the signal at 0.11 ppm with the higher J value at 69.0 Hz vs 61.5 Hz for the 0.65 ppm signal is thus associated with the methyl groups Me12 and Me24, which exhibit the smaller average Pt−C bond length of 2.100 vs 2.121 Å for Me11 and Me23. (b) Abel, E. W.; Orrell, K. G.; Stephenson, D. *J. Organomet. Chem.* **1989**, *373*, 401. (c) Fekl, U.; van Eldik, R.; Lovell, S.; Goldberg, K. I. *Organometallics* **2000**, *19*, 3535. (d) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.