Notiz / Note

Synthesis and Structural Characterization of the Bent Nitrosyl Organometallic Complex $[NBu_4][Pt(C_6Cl_5)_2Cl_2(NO)]$[+]

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The title complex has been prepared in 36% yield by reaction of $[NBu_4]_2[\textit{trans}\text{-}Pt(C_6Cl_5)_2Cl_2]$ with $NOClO_4$ (1:1) in CH_2Cl_2. The anion exhibits an almost tetragonal-pyramidal geometry (X-ray analysis), the platinum atom being virtually located in the basal plane and the NO ligand occupying the apical position. The Pt–N–O unit is bent [119.5(8)°].

Nitrosyl-metal complexes constitute a well-defined area in inorganic chemistry, which has been extensively studied and reviewed[1]. The early bonding model based on the NO^+/NO^- dichotomy[2a] has been largely superseded by calculation techniques relying on the MO correlation method[2b]. This approach has proven remarkably successful in comprehensively rationalizing both the structure and the reactivity of the known nitrosyl-metal complexes. The surprisingly few reports on mononuclear nitrosyl complexes of platinum[3] and our previous findings[4] about the anomalous geometry of the complex $[NBu_4][Pt(C_6Cl_5)_4(NO)]$ have prompted us to extend our studies to other related anionic platinum substrates.

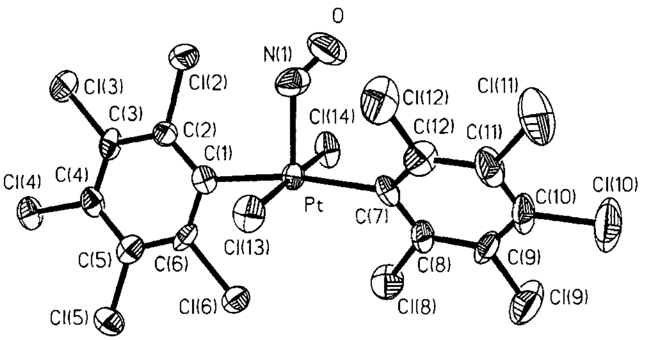

Figure 1. Thermal ellipsoid plot of the (*SPY*-5-21)-dichloronitrosylbis(pentachlorophenyl)platinate(1–) ($\mathbf{2b}^-$) anion. Selected distances [Å] and angles [°]: Pt–N1 2.054(9), Pt–C1 2.107(9), Pt–C7 2.124(9), Pt–Cl13 2.312(2), Pt–Cl14 2.313(2), N1–O 1.141(14); Pt–N1–O 119.5(8)

Complexes $[NBu_4]_2[\textit{trans}\text{-}Pt(C_6X_5)_2Cl_2]$ [X = F (**1a**)[5a], Cl (**1b**)[5b]] react with $NOClO_4$ in CH_2Cl_2 at room temperature according to eq. (1). Once isolated as solids, the salts $[N(PPh_3)_2]$**2a** and $[NBu_4]$**2b** are reasonably stable and can be handled and weighed in the air. However, over long periods of time, they are best kept below 4°C. In solution, their stability is much more limited.

$$[NBu_4]_2[\textit{trans}\text{-}Pt(C_6X_5)_2Cl_2] + NOClO_4 \rightarrow [Pt(C_6X_5)_2Cl_2(NO)]^- \qquad (1)$$

1a: X = F $\qquad$ $\mathbf{2}^-$
b: X = Cl

The crystal structure of $[NBu_4]$**2b** has been determined by X-ray diffraction methods (Figure 1). The anion $\mathbf{2b}^-$ has been found to exhibit an almost tetragonal-pyramidal geometry: the platinum atom is virtually located in the basal plane[6a], and the NO ligand occupies the apical position of the pyramid[6b]. The Pt–N–O unit is clearly bent [119.5(8)°] towards one of the chlorine atoms (torsion angle Cl14–Pt–N1–O 27.6°).

Nitrosyl derivatives of $\{M-N-O\}^8$ configuration in a five-coordinate environment have been predicted to exhibit a linear arrangement if they adopt a trigonal-bipyramidal geometry or a bent disposition in tetragonal-pyramidal structures[2b]. To our knowledge, however, none of these possible geometries have been materialized as yet in the platinum chemistry. In fact, the only mononuclear nitrosyl complex of platinum structurally characterized, $[NBu_4][Pt(C_6Cl_5)_4(NO)]$, is in contradiction to these theoretical expectations, as it has been shown to contain a linear Pt–N–O unit in a tetragonal-pyramidal global environment[4]. Complex $[NBu_4]$**2b** is therefore, the first mononuclear nitrosyl complex of platinum whose structure agrees with that theoretically predicted[7]. According to the classical point of view, which relates the coordination geometry of the M–N–O unit (either linear or angular) with the charge of the nitrosyl ligand (+ or –, respectively), a linear arrangement should be expected to exhibit a shorter M–N distance[1b] as observed for instance in the model complex $[RuCl(NO)_2(PPh_3)_2][PF_6]$[8]. On the contrary, a comparison of the structural features concerning the Pt–N–O unit in complexes $[NBu_4][Pt(C_6Cl_5)_4(NO)]$ and $[NBu_4][Pt(C_6Cl_5)_2Cl_2(NO)]$ reveals that the Pt–N distance is longer in the former [2.22(6) Å, linear] than in the latter complex [2.054(9) Å, angular].

The synthetic method applied to the preparation of these simple five-coordinate platinum compounds (eq. 1) can be considered as an evidence of the marked basic character exhibited by the platinum center in the starting products **1a** and **1b**. This seems to be a

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[+] Throughout this paper, the convention of Enermark and Feltham to classify metal-nitrosyl complexes $\{M-N-O\}^n$ according to the number of electrons (n) with an important d character has been used (see ref.[2b]).

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general feature of anionic square-planar complexes of platinum(II)[9].

Further work aimed to extend the synthetic method reported here to other platinum substrates is being carried out.

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Experimental

The starting compounds **1a**[5a], **1b**[5b], $NOClO_4$[10a], and $[N(PPh_3)_2]Cl$[11] were prepared according to literature methods.

Caution: it is advisible not to attempt the following reactions in organic solvents other than CH_2Cl_2 or $CHCl_3$, as $NOClO_4$ is known to react violently with, for instance, acetone, diethyl ether, and ethanol[10b].

Tetra-n-butylammonium Dichloronitrosylbis(pentachlorophenyl)-platinate ($[NBu_4]$**2b**): During the reaction of a CH_2Cl_2 (20 ml) solution of **1b** (0.30 g, 0.24 mmol) with $NOClO_4$ (31 mg, 0.24 mmol), the initially yellow solution gradually turned red. After 30 min of stirring, the solvent was evaporated in vacuo, the residue was extracted with Et_2O (60 ml) and the extract filtered off. Concentration of the filtrate afforded a residue which upon treatment with MeOH (10 ml) gave a brown solid. Yield 87 mg (36%). – IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1776 (N–O)[12], 846 (X-sensitive)[13], 602 [$\nu_{as}(PtC_2)$], 335 [$\nu_{as}(PtCl_2)$]. – ^{13}C NMR ([^2H]chloroform, −60°C): δ = 142.92 (C_{ipso}), 139.95 (*p*-C), 138.08 (*o*-C), 129.86 (*m*-C), 129.80 (*m*-C), 129.47 (*o*-C), 57.54 (α-CH_2), 23.35 (β-CH_2), 19.41 (γ-CH_2), 13.75 (CH_3). – MS (FAB), *m/z*: 759 [$C_{12}Cl_{12}Pt^-$]. – $C_{28}H_{36}Cl_{12}N_2OPt$ (1037.1): calcd. C 32.43, H 3.50, N 2.70; found C 31.83, H 3.48, N 2.47.

Crystal Data for $[NBu_4]$**2b**[14]: Suitable single crystals were obtained by low-temperature (−30°C) diffusion of an *n*-hexane layer into a CH_2Cl_2 solution of the complex. Crystal size: 0.25 × 0.25 × 0.15 mm; Siemens/STOE AED2; graphite-monochromated Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å). $C_{28}H_{36}Cl_{12}N_2OPt$: M_r = 1034.1; space group *C2/c*, a = 43.861(7), b = 8.557(2), c = 20.830(5) Å, β = 95.03(2)°, V = 7788(3) Å^3, d_{calc} = 1.764 g/cm^3, Z = 8, μ(Mo-K_α) = 44.53 cm^{-1}; absorption correction: ψ-scan method (8 reflections); transmission factors: 0.3593/0.1806; T = −50°C; $2\Theta_{max}$ = 47° ($+h$, $+k$, $\pm l$); scan = $\omega/2\Theta$. 5746 independent reflections were measured, 4141 were used for calculations [$I \geqslant 3\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares methods[15]. R = 0.046, R_w = 0.060, 401 parameters, GOF = 0.91.

Bis(triphenylphosphoranylidene)ammonium Dichloronitrosylbis-(pentafluorophenyl)platinate ($[N(PPh_3)_2]$**2a**): A MeOH solution (10 ml) of $[NBu_4]$**2a** was prepared as described above by starting from **1a** (0.30 g, 0.28 mmol) and $NOClO_4$ (35.8 mg, 0.28 mmol). Subsequent addition of $[N(PPh_3)_2]Cl$ (0.23 g, 0.40 mmol) caused the precipitation of $[N(PPh_3)_2]$**2a** (0.11 g, 33% yield). – IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1812 (N–O)[12], 961 (C–F), 782, 761 (X-sensitive)[13], 341 [$\nu_{as}(PtCl_2)$]. – ^{19}F NMR ([^2H]chloroform, 23°C): δ = −117.3 (2 F, *o*-F), −126.2 (2 F, *o*-F), −161.3 (2 F, *p*-F), −162.7 (2 F, *m*-F), −164.2 (2 F, *m*-F). – MS (FAB), *m/z*: 629 [$C_{12}Cl_2F_{10}NOPt^-$]. – $C_{48}H_{30}Cl_2N_2OP_2Pt$ (1168.7): calcd. C 49.33, H 2.59, N 2.40; found C 48.88, H 2.33, N 2.11.

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[6] [6a] The metal center deviates about −0.11 Å from the best least-squares plane defined by Pt–C1–C7–Cl13–Cl14, which is the largest deviation shown by any other of the defined atoms. – [6b] The Pt–N vector forms an angle of only 3.1° with the normal to the referred basal plane.

[7] It seems sensible to asume for the related pentafluorophenyl derivative $[Pt(C_6F_5)_2Cl_2(NO)]^-$ (**2a**$^-$) a structure close to that established for **2b**$^-$, considering their obvious relationship and their analogous spectroscopic properties.

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