The First Observation and Structural Characterization of (Formamide)platinum(IV) Complexes

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The reaction of *trans*-[$PtCl_4(EtCN)_2$] and two equivalents of the formamides RR′NCHO (R/R′ = Me/Me, Me/H, *t*Bu/H) in CH_2Cl_2 led to the formation of the compounds *cis*-[$PtCl_4${(O=)-CHNRR′}$_2$], two of which (R/R′ = Me/H, *t*Bu/H) were characterized by X-ray single-crystal diffractometry, as well as by elemental analysis, FAB^+-MS, and IR, ^1H, ^{13}C and ^{195}Pt NMR spectroscopy (including NOE, HMQC and INEPT experiments). The X-ray structures and IR spectroscopic data indicate the coordination of the formamides through the O atom and significant contribution of the bipolar structure $^-O–C(H)=^+NHR$ in the resonance hybrid of the ligands. The complexes *cis*-[$PtCl_4${(O=)CHNRR′}$_2$] represent the first example of (formamide)Pt^{IV} species and also a rare case of platinum(IV) complexes with neutral O-donor ligands.

Introduction

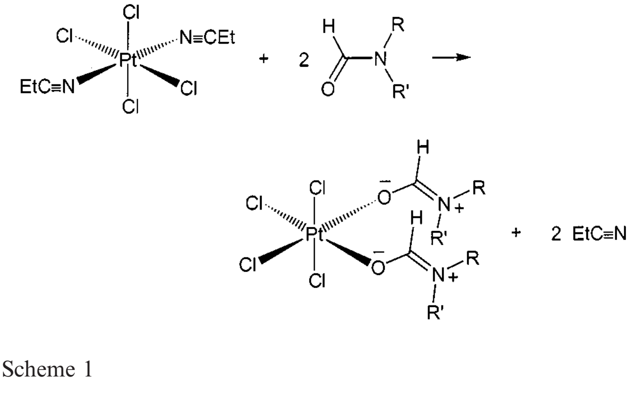
Complexes containing weak donor ligands are essential as synthons for synthetic studies and as efficient homogeneous catalysts.[1] In recent years they have become a subject of paramount importance for the construction of multi homo- and heterometallic systems[2] with application in materials science.[3,4] Ideally, the complexes with weak donor ligands utilized in these branches of chemistry must be soluble, readily available and contain ligands which are easily replaced.[1]

As far as platinum complexes are concerned, an approach for developing compounds with weak donors includes the generation of complexes with antisymbiotic soft platinum centers and hard donor ligands, which interact only poorly and thus the weakly bound donors can be replaced by better ligands.[1,5−7] Complexes of both Pt^{II} and Pt^{IV} with *anionic* monodentate hard O-donors, for example $MeCO_2^-$, NO_2^-, NO_3^-, OH^-, SO_4^{2-}, or bidentate *anionic* hard O,O- or O,N-donors, for example carboxamidates and acetylacetonates, are common.[5] In contrast, platinum species with *neutral* O-donors are quite scarce due to the soft character of the metal centers. Moreover, if platinum(II) complexes with ligated H_2O,[5] ROH,[8] $R_2S=O$,[9,10] THF[11] or O-bonded formamides and amides[12] are rare, to the best of our knowledge compounds of platinum(IV) containing *neutral* O-donors are even more scarce. Indeed, apart from (aqua)Pt^{IV} [13] species only acetone[14] and (2-pyridyldiphenylphosphane oxide)platinum(IV) complexes[15] with a Pt−O interaction are known. We report herein the first representatives of O-bonded formamide-based platinum(IV) complexes and their X-ray structural characterization.

Results and Discussion

Our interest in the preparation of (formamide)Pt^{IV} complexes was twofold. First, this work was performed within the framework of an on-going project devoted to the search for new starting materials for platinum chemistry,[10,16] and second, we hoped to prepare new materials for the extension of our previous work on nucleophilic additions to ligands bearing double[17] and triple bonds.[2,18−20]

The reaction between *trans*-[$PtCl_4(EtCN)_2$] and the formamides RR′NCHO in dichloromethane led to the formation of isomerically and analytically pure *cis*-[$PtCl_4${(O=)-CHNRR′}$_2$] (R/R′ = Me/Me, Me/H, *t*Bu/H) isolated from the reaction mixture in moderate yields (ca. 40%; Scheme 1).



Scheme 1

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More *cis*-[PtCl$_4${(O=)CHNRR′}$_2$] can be obtained by the addition of diethyl ether to the filtrate, although in all three cases the solids isolated in this way were contaminated with other products which are formed, in particular, by a facile platinum(IV)-mediated hydrolysis, in the presence of traces of water to give amide[21] and ammonia species,[20,22] of the highly reactive starting nitrile complex. We also anticipate that some admixtures may be derived from the coupling of nitriles and the amines HNRR′, the latter being formed from the uncontrolled degradation of formamides, which is a well-known reaction. It is also worthwhile to mention that an attempt to perform a similar reaction between *trans*-[PtCl$_4$(EtCN)$_2$] and the unsubstituted formamide H$_2$NCHO failed due to the formation of a mixture of highly soluble products.

The structures of *cis*-[PtCl$_4${(O=)CHNHR}$_2$] (R = Me, *t*Bu) were determined by X-ray single-crystal diffraction. The coordination polyhedra of the complexes are slightly distorted octahedra (Figure 1 and 2) and the two formamide species are mutually *cis.*

An inspection of the bond lengths in the formamide ligands shows that coordination results in an increased contribution of the bipolar structure $^{-}$O−C(H)=$^{+}$NHR in the resonance hybrid of the ligand, as previously observed for (dimethylformamide)Pt^{II} complexes.[11] Indeed, the C−O bond lengths [1.258(5) Å for R = Me and av. 1.271 Å for R = *t*Bu, Table 1 and 2] are longer than the C=O bond in amides (1.234 Å[24]) or in aldehydes (1.192 Å[24]), while the C−N bond [1.309(6) Å for R = Me and av. 1.305 Å for R = *t*Bu, Table 1 and 2] is shorter than that in the free amides (1.334 Å[24]).

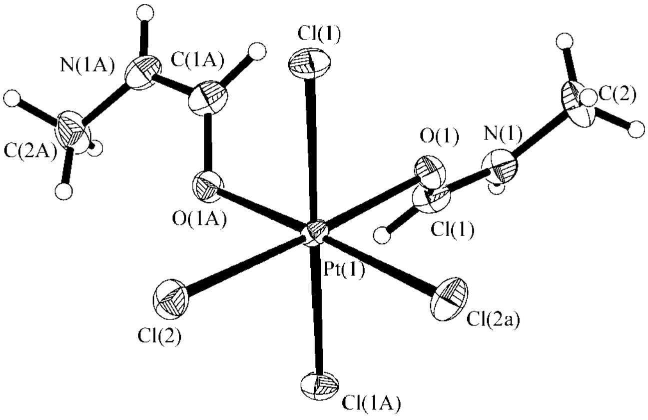

Figure 1. PLATON[23] drawing of *cis*-[PtCl$_4${(O=)CHNHMe}$_2$] with atomic numbering scheme

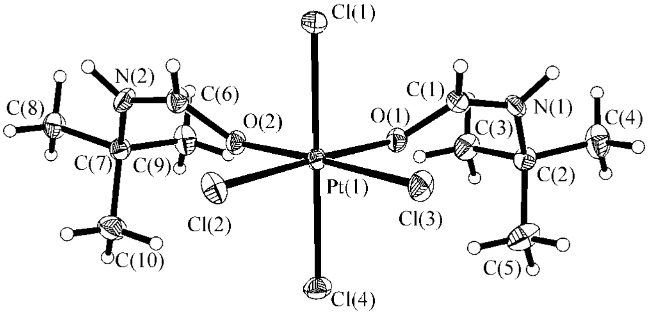

Figure 2. PLATON[23] drawing of *cis*-[PtCl$_4${(O=)CHNH*t*Bu}$_2$] with atomic numbering scheme

Table 1. Bond lengths [Å] and angles [°] for *cis*-[PtCl$_4${(O=)-CHNHMe}$_2$]

Pt−O(1)	2.057(3)	O(1)−C(1)	1.258(5)
Pt−Cl(2)	2.2788(10)	N(1)−C(1)	1.309(6)
Pt−Cl(1)	2.3106(11)	N(1)−C(2)	1.434(7)
O(1)#1−Pt−O(1)[a]	91.53(16)	Cl(2)−Pt−Cl(1)#1	90.60(4)
O(1)−Pt−Cl(2)	177.23(8)	Cl(1)−Pt−Cl(1)#1	178.81(5)
O(1)−Pt−Cl(2)#1	88.24(9)	Cl(2)−Pt−Cl(2)#1	92.11(5)
O(1)−Pt−Cl(1)	87.02(9)	C(1)−O(1)−Pt	120.2(3)
Cl(2)−Pt−Cl(1)	90.23(4)	C(1)−N(1)−C(2)	126.2(4)
O(1)−Pt−Cl(1)#1	92.15(9)	O(1)−C(1)−N(1)	120.5(5)

[a] Symmetry transformations used to generate equivalent atoms #1: $-x + 3/2$, $-y + 1$, z.

Table 2. Bond lengths [Å] and angles [°] for *cis*-[PtCl$_4${(O=)-CHNH*t*Bu}$_2$].

C(1)−O(1)	1.274(3)	C(1)−N(1)	1.300(3)
C(2)−N(1)	1.496(3)	C(2)−C(5)	1.515(3)
C(2)−C(4)	1.517(3)	C(2)−C(3)	1.526(3)
C(6)−O(2)	1.267(3)	C(6)−N(2)	1.309(3)
C(7)−N(2)	1.490(3)	C(7)−C(9)	1.517(3)
C(7)−C(10)	1.522(3)	C(7)−C(8)	1.524(3)
O(1)−Pt	2.045(2)	O(2)−Pt	2.0406(13)
Cl(1)−Pt	2.3123(5)	Cl(2)−Pt	2.2781(5)
Cl(3)−Pt	2.2783(5)	Cl(4)−Pt	2.3134(5)
O(1)−C(1)−N(1)	122.4(2)	N(1)−C(2)−C(5)	108.3(3)
N(1)−C(2)−C(4)	105.6(2)	C(5)−C(2)−C(4)	111.1(2)
N(1)−C(2)−C(3)	109.9(2)	C(5)−C(2)−C(3)	111.5(2)
C(4)−C(2)−C(3)	110.3(2)	O(2)−C(6)−N(2)	121.6(2)
N(2)−C(7)−C(9)	110.3(2)	N(2)−C(7)−C(10)	108.3(3)
C(9)−C(7)−C(10)	111.3(2)	N(2)−C(7)−C(8)	106.2(3)
C(9)−C(7)−C(8)	110.00(2)	C(10)−C(7)−C(8)	110.5(2)
C(1)−N(1)−C(2)	127.5(2)	C(6)−N(2)−C(7)	127.2(2)
C(1)−O(1)−Pt	119.55(13)	C(6)−O(2)−Pt	121.06(14)
O(2)−Pt−O(1)	87.67(6)	O(2)−Pt−Cl(2)	90.69(4)
O(1)−Pt−Cl(2)	177.03(5)	O(2)−Pt−Cl(3)	175.73(4)
O(1)−Pt−Cl(3)	89.47(4)	Cl(2)−Pt−Cl(3)	92.02(2)
O(2)−Pt−Cl(1)	91.92(5)	O(1)−Pt−Cl(1)	91.85(5)
Cl(2)−Pt−Cl(1)	90.69(2)	Cl(3)−Pt−Cl(1)	91.34(2)
O(2)−Pt−Cl(4)	85.84(5)	O(1)−Pt−Cl(4)	86.35(5)
Cl(2)−Pt−Cl(4)	91.06(2)	Cl(3)−Pt−Cl(4)	90.82(2)
Cl(1)−Pt−Cl(4)	177.18(2)		

In the IR spectra, the decrease of ν(C=O) by ca. 30−50 cm^{-1} with respect to the free ligands (see Exp. Sect.) also indicates[25] a coordination through the O atom and the contribution of the bipolar structure. It should be noted that the *cis*-geometry of the formamide compounds seems to be unusual for platinum(IV) chemistry, where in the vast majority of cases the substitution of the ligands in starting materials with a *trans* configuration gives rise to the appropriate *trans* products. Moreover, it has been reported that octahedral complexes of metals in a high oxidation state trend to isomerize from *cis* to *trans* irrespective of the nature of the ligated species.[26] In *cis*-[PtCl$_4${(O=)CHNHR}$_2$] (R = Me, *t*Bu), however, the formamides shorten the Pt−Cl (*trans* to O) bonds [av. 2.28 Å] substantially relative to those *trans* to Cl [av. 2.31 Å]. Perhaps the *trans* Pt−O bonds do not stabilize each other to the same extent and this might be a reason for the formation of the complexes in the *cis* configuration.

The ^{1}H NMR spectra of the monoalkyl complexes *cis*-$[PtCl_4\{(O{=})CHNHR\}_2]$ (R = Me, *t*Bu) display a =CH proton doublet resonance due to indirect coupling with the NH protons (proved by a double resonance ^{1}H{NH} experiment) with typical ^{195}Pt satellites. In both cases, NOE difference experiments showed a strong through-space interaction between the CH and NH protons of the ligated species, thus indicating the dominance of their *E*-conformation in solution. The positions of the signals in the ^{195}Pt NMR spectra of these complexes are in the normal range for other platinum(IV) compounds.

The complexes *cis*-$[PtCl_4\{(O{=})CHNRR'\}_2]$ represent the first example of (formamide)Pt^{IV} species and also a rare case of platinum(IV) complexes with neutral O-donor ligands. Useful properties of these complexes are their good solubilities (*cis*-$[PtCl_4\{(O{=})CHNMe_2\}_2]$, however, has a low solubility) in a number of organic solvents and also the solubility of *cis*-$[PtCl_4\{(O{=})CHNHMe\}_2]$ in water, and these features indicate that the formamide complexes can be used for synthesis in a homogeneous liquid phase. In conclusion, it is worthwhile to mention that the (formamide)platinum(IV) complexes may be important as precursors for further synthetic work by substitution, or by addition of nucleophiles to the O=C double bond activated by the quadruply charged platinum(IV) ion; these studies are underway in our group. We hope that the useful properties of these (formamide)platinum(IV) complexes, combined with their facile synthesis, will extend the range of reactions possible in synthetic platinum(IV) chemistry.

Experimental Section

Materials and Instrumentation: The formamides were obtained from Aldrich and used as received. *trans*-$[PtCl_4(EtCN)_2]$ was prepared according to a published method.[2,18] C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. All NMR spectra were recorded at ambient temperature on a Varian UNITY 300 [299.95, 75.42 and 64.48 MHz for ^{1}H, ^{13}C and ^{195}Pt NMR, respectively] and/or Bruker DPX−300 [300.13 and 75.47 MHz for ^{1}H and ^{13}C NMR, respectively]. An irradiating field power of 30 Hz for selective decoupling from the NH proton in double resonance experiment and a presaturation time of 1.0 s were used in the NOE-difference experiments. ^{1}H and ^{13}C chemical shifts are given relative to DMSO (δ = 2.50 and 39.5, respectively). ^{195}Pt chemical shifts are given relative to $Na_2[PtCl_6]$ ($K_2[PtCl_4]$, δ = −1630, as a standard) and the half-height line width is given in parentheses. No other sets of signals, besides those indicated below, were observed in the NMR spectra measured in [D$_6$]DMSO; in addition, the complexes were recovered intact from [D$_6$]DMSO solutions after the measurements by addition of diethyl ether, thus indicating the absence of any substitution reaction in [D$_6$]DMSO. This is consistent with the weak donor properties of Me_2SO towards a platinum(IV) center,[27] even though it is a good ligand for the platinum(II) ion.[28]

The inverse detection HMQC method with the BIRD sequence during the preparation period[29] was used to determine the heteronuclear spin-spin coupling constants $J^{195}{}_{Pt}\text{-}^{13}{}_{C}$. HMQC spectra were measured with a 128 × 1024 data matrix size with 256 scans per t_1 value (the delay for the creation of anti-phase magnetization was 3.5 ms and the relaxation delay was 1.0 s) and broadband ^{13}C decoupling with GARP-1[30] was applied during the acquisition (^{13}C: 90° pulse of 60 ms). The data were zero-filled in the t_1 dimension and a sine-bell filter was applied in both dimensions before the Fourier transformation. The $J^1{}_{H}\text{-}^{13}{}_{C}$ coupling constants and ^{13}C chemical shifts were obtained from the INEPT and DEPT-135 spectra.

Synthesis and Characterization. General Procedure: A solution of the formamide (0.14 mmol) in CH_2Cl_2 (0.5 mL) was added to solid *trans*-$[PtCl_4(EtCN)_2]$ (0.03 g, 0.07 mmol) and the reaction mixture was heated at 35 °C for 1−2 h, whereupon crystals started to form. At this point the mixture was cooled to 15−17 °C and left to stand at this temperature for 2 days. The dark-orange crystals were filtered off, washed with three 2-mL portions of CH_2Cl_2 and dried in air at room temperature. Yields were ca. 40%.

***cis*-[PtCl$_4${(O=)CHNHMe}$_2$]:** $C_4H_{10}Cl_4N_2O_2Pt$ (455.04): calcd. C 10.58, H 2.22, N 6.16; found C 10.92, H 2.14, N 5.90. − FAB$^+$-MS: *m*/*z* = 451 [M − 3H]$^+$. − TLC on Merck 60 F$_{254}$ SiO$_2$ plates: R_f = 0.64 (eluent Me_2CO/CH_2Cl_2, 1:1). − IR (KBr; selected bands): ṽ = 3347 m ν(N−H), 1638 s ν(C=O) cm^{-1} [in the free ligand ν(C=O) is found at 1668 cm^{-1}]. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.90 (s, 3 H, Me), 8.10 (d, with ^{195}Pt-satellites on each line, J_{PtH} = 22.1 Hz, J_{HH} = 5.3 Hz, 1 H, =CH), 10.20 (br. s, 1 H, NH). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 32.0 (CH$_3$) and 173.0 ($^1J_{CH}$ = 204 Hz, $^2J_{PtC}$ = 2 Hz, =CH). − ^{195}Pt NMR ([D$_6$]DMSO): δ = −381 (150 Hz).

***cis*-[PtCl$_4${(O=)CHNH*t*Bu}$_2$]:** $C_{10}H_{22}Cl_4N_2O_2Pt$ (539.20): calcd. C 22.28, H 4.11, N 5.20; found C 22.38, H 4.11, N 5.07. − FAB$^+$-MS: *m*/*z* = 561 [M + Na]$^+$, 539 [M]$^+$, 503 [M − Cl]$^+$, 468 [M − 2Cl]$^+$. − TLC on Merck 60 F$_{254}$ SiO$_2$ plates: R_f = 0.73 (eluent Me_2CO/CH_2Cl_2, 1:1). − IR (KBr; selected bands): ṽ = 3291 m ν(N−H), 1616 s ν(C=O) cm^{-1} [in the free ligand ν(C=O) is found at 1663 cm^{-1}]. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.34 (d, $^3J_{HH}$ = 4.8 Hz, 9 H, Me), 7.82 (d, with ^{195}Pt-satellites on each line, J_{PtH} = 23.9 Hz, J_{HH} = 4.6 Hz, 1 H, =CH), 10.26 (br. s, 1 H, NH). − ^{13}C{^{1}H} NMR ([D$_6$]DMSO): δ = 27.7 (CH$_3$), 53.7 (*t*-C), 166.9 ($^2J_{PtH}$ = 2 Hz, $^1J_{CH}$ = 204 Hz, =CH). − ^{195}Pt NMR ([D$_6$]DMSO): δ = −372 (150 Hz).

[PtCl$_4${(O=)CHNMe$_2$}$_2$]: $C_6H_{14}Cl_4N_2O_2Pt$ (483.09): calcd. C 15.03, H 2.92, N 5.85; found C 15.07, H 3.16, N 5.66. − FAB$^+$-MS: *m*/*z* = 482 [M − H]$^+$. − TLC on Merck 60 F$_{254}$ SiO$_2$ plates: R_f = 0.51 (eluent Me_2CO/CH_2Cl_2, 1:1). − IR (KBr; selected bands): ṽ = 3065 w, 3005 w, and 2960 mw ν(C−H), 1638 s ν(C=O) cm^{-1} [in the free ligand *ν*(C=O) is found at 1687 cm^{-1} in CCl$_4$ [25]]. − ^{1}H NMR ([D$_6$]DMSO): δ = 3.07 and 3.31 (s, 3 H each, Me), 8.12 (s + d, J_{PtH} = 21.2 Hz, 1 H, =CH). The solubility of the compound is insufficient to measure ^{13}C{^{1}H} and ^{195}Pt NMR spectra even at high accumulation times.

X-ray Structure Determination: X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). The Denzo and Scalepack[31] programs were used for cell refinements and data reduction. The structures of *cis*-[$PtCl_4\{(O=)CHNHMe\}_2$] (**1**) and *cis*-[$PtCl_4\{(O=)CHNH$*t*$Bu\}_2$] (**2**) were solved by direct methods using SIR97[32] and SHELXS-97[33] programs, respectively, with the WinGX[34] graphical user interface. The structure refinements were carried out with SHELXL-97.[35] A multi-scan absorption correction, based on equivalent reflections (XPERP in SHELXTL v5.1),[36] was applied to the data of both structure **1** (T_{max}/T_{min} 0.3812/0.2199) and structure **2** (T_{max}/T_{min} 0.2921/0.2100). In both structures the hydrogen atoms were constrained to ride on their parent atom. Selected bond lengths and angles are given in Table 1 and 2 and crystallographic data is summarized in Table 3. The crystal structures are shown in Figure 1 and 2.

Table 3. Crystallographic data for *cis*-[$PtCl_4\{(O=)CHNHMe\}_2$] (**1**) and *cis*-[$PtCl_4\{(O=)CHNH$*t*$Bu\}_2$] (**2**)

	1	**2**
Empirical formula	$C_4H_{10}Cl_4N_2O_2Pt$	$C_{10}H_{22}Cl_4N_2O_2Pt$
Fw	455.03	539.19
Temp, *K*	120	120
λ, Å	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pcca* (No. 54)	$P2_12_12_1$ (No. 19)
a, Å	12.1606(4)	10.0686(1)
b, Å	7.1754(2)	11.7214(2)
c, Å	13.3051(4)	15.2529(2)
V, Å^3	1160.97(6)	1800.12(4)
Z	4	4
ρ_{calcd}, g/cm^3	2.603	1.990
μ(Mo-K_α), mm^{-1}	12.978	8.387
R_1 [a]	0.0241	0.0114
wR_2 [b]	0.0601	0.0268

[a] $[I > 2\sigma(I)]$; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. – [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-159079 and -159080. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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