Unusual Four-Membered Chelate Rings of Pt^{IV} with a Cytosine Nucleobase

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Abstract: Oxidation of *trans*-$[Pt(NH_3)_2(1\text{-MeC})_2](NO_3)_2$ (1-MeC = 1-methylcytosine, $C_5H_7N_3O$, bound to Pt through N3) with H_2O_2 gives *trans,trans,trans*-$[Pt(NH_3)_2(1\text{-MeC})_2(OH)_2](NO_3)_2\cdot 2H_2O$ (**1**). From strongly acidic HNO_3 solution **1** crystallizes in its monoprotonated form *trans,trans*-$[Pt(NH_3)_2(1\text{-MeC})_2(OH)(OH_2)](NO_3)_3\cdot 3H_2O$ (**2**). In weakly to moderately acidic medium (HNO_3) or on warming, **1** is converted into two other complexes, *trans*-$[Pt(NH_3)_2(1\text{-MeC})(1\text{-MeC}^-)(OH)](NO_3)_2\cdot H_2O$ (**3**) and *trans,trans*-$[Pt(NH_3)_2(1\text{-MeC}^-)_2](NO_3)_2\cdot 2H_2O$ (**4**), which contain one and two chelating, anionic 1-methylcytosinato ligands, 1-MeC^-, bound to the Pt through N3 and N4. **1** crystallizes in the space group $P2_1/n$ with a = 13.036 (2) Å, b = 9.011 (1) Å, c = 9.682 (1) Å, β = 111.20 (2)°, V = 1060.3 Å^3, Z = 2. **2** crystallizes in the space group $P\bar{1}$ with a = 10.630 (2) Å, b = 11.005 (3) Å, c = 12.336 (3) Å, α = 110.75 (3)°, β = 91.09 (3°), γ = 113.29 (3)°, V = 1218.1 Å^3, Z = 2. The crystal data for **3** are as follows: space group $P2_1/c$, a = 7.117 (2) Å, b = 23.864 (4) Å, c = 11.802 (2) Å, β = 91.82 (2)°, V = 2003.4 Å^3, Z = 4. The crystal data for **4** are as follows: space group also $P2_1/c$, a = 7.230 (3) Å, b = 10.576 (4) Å, c = 13.186 (2) Å, β = 100.92 (3)°, V = 990.0 Å^3, Z = 2. The structures were refined to R (R_w) = 0.049 (0.059) for **1**, 0.038 (0.038) for **2**, 0.075 (0.075) for **3**, and 0.048 (0.056) for **4** on the basis of 1647 (**1**), 5508 (**2**), 3433 (**3**), and 1419 (**4**) independent reflections with $F_o \geq 2\sigma F_o$ (**1**, **2**, **4**) and $F_o \geq 3\sigma F_o$ (**3**), respectively. The N3,N4 chelates in **3** and **4** represent novel metal binding patterns with a cytosine nucleobase and at the same time the first examples of nucleobase chelates involving platinum. In these chelates, Pt–N3 and Pt–N4 distances are short and of comparable lengths, namely 1.969 (13) and 2.032 (16) Å in **3** and 2.037 (9) and 2.038 (10) Å in **4**. The four-membered chelate rings in **3** and **4** are almost coplanar with the cytosine planes, dihedral angles being 7° (**3**) and 1° (**4**), respectively. Chelate formation causes enormous variations in bond angles about the platinum, e.g., 65–106° in **3** and 64–116° in **4**, and large changes in ring angles of the cytosine ligands, in particular about N3 and C4. The solution behavior of all four complexes has been studied with use of ^1H NMR spectroscopy and potentiometric titration. The pK_a for the equilibrium $2 \rightleftharpoons 1 + H^+$ has been estimated to be <1. Heating of **1** (**2**) in 3.5 N HNO_3 leads to displacement of 1-MeC. DCl (1 N) causes substitution of OH ligands by Cl^-, the substitution of the C5 proton of 1-MeC by Cl^-, and eventually displacement of the modified nucleobase. Conversion of **1** into **3** and **4** occurs in slight to moderate acidic solution (pH 5.5–1.5). Isolated **3** (**4**), when redissolved in H_2O, equilibrates with **1** and **4** (**3**). Two feasible ways of chelate formation are proposed, and the possible significance of four-membered chelate rings in metal ions–nucleobase interactions is briefly discussed.

Numerous studies on the interaction of anticancer Pt^{II} compounds with nucleic acids or their constituents, the nucleobases, have provided a reasonably good understanding of the coordination chemistry of Pt^{II} electrophiles with these ligands in recent years.[2] A similarly well developed chemistry of Pt^{IV} is lacking, although it originally was a Pt^{IV} compound, *cis*-$Pt(NH_3)_2Cl_4$, which caused filamentous growth of bacteria and subsequently led to the discovery of antitumor activity of Pt coordination compounds.[3] This deficiency is paralleled by the—compared to Pt^{II} compounds—relatively small number of Pt^{IV} complexes tested for antitumor activity and actually in clinical use, respectively.[4] Lately there have been attempts to rebalance this situation somewhat by (i) synthesizing *and* fully characterizing Pt^{IV} compounds that are porentially active,[5] and (ii) studying their interactions with nucleic acids.[6] However, virtually no systematic work on model studies, which might be of great help in understanding (ii), has been done as yet. The importance of (i) probably most convincingly has been demonstrated by Dabrowiak and co-workers,[6a] who showed that DNA cleavage, previously attributed to *cis,cis,trans*-$Pt(NH_3)_2Cl_2(OH)_2$,[6c] actually was due to hydrogen peroxide present in the crystal lattice of the Pt complex.

A particularly interesting aspect of the biorelevant chemistry of Pt^{IV} coordination compounds is the question of drug activation through a possible in vivo reduction to Pt^{II}. There is conflicting evidence on such a possibility. While no covalent binding of complexes of type *cis,cis,trans*-$Pt(A)_2Cl_2(OH)_2$ (A = NH_3 or $(CH_3)_2CHNH_2$) to closed-circular DNA within 18 h at 30 °C could be detected, the respective reduced species *cis*-$Pt(A)_2Cl_2$ readily react with DNA under identical conditions.[6b] Animal testing (Yoshida ascites) of a limited number of Pt^{IV} complexes showed that only those Pt^{IV} compounds are active that have active reduction products.[7] On the other hand, Pt^{IV} complexes of type *cis,cis,trans*-$Pt(A)_2Cl_2(OH)_2$ have been demonstrated to be more efficient inducers of bacteriphage λ than their Pt^{II} reduction products, and experiments with a DNA repair deficient strain point toward different lesions for Pt^{IV} and Pt^{II} complexes.[8]

Considering the fact that redox potentials of Pt^{IV}/Pt^{II} couples are modulated by the ligands attached to the metal, the following question—intracellular reduction or not?—may even be irrelevant in the sense that both possibilities, direct binding to nucleic acids

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(2) See, e.g., various articles in the following: (a) *Platinum Coordination Complexes in Cancer Chemotherapy*; Hacker, M. P., Douple, E. B., Krakoff, I. E., Eds.; Martinus Nijhoff Publishers: Boston, 1984. (b) *Platinum, Gold, and Other Metal Chemotherapeutic Agents*; Lippard, S. J., Ed.; American Chemical Society: Washington, DC, 1983; ACS Symp. Ser. 209. (c) *Nucleic Acid-Metal Interactions*; Spiro, T. G., Ed.; Wiley: New York, 1980.

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(covalently or via hydrogen bonding) or preceding reduction, might be possible for complexes containing different ligands. The work described below was performed under the assumption that covalent binding of Pt^{IV} to nucleobases in principle is possible, though formation of such complexes is expected to be considerably slower than for Pt^{II} complexes. Using a preformed Pt^{II} complex *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2]^{2+}$ and oxidizing it to the Pt^{IV} complex *trans,trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)_2]^{2+}$ (1-MeC = neutral 1-methylcytosine), we were interested in structural and in particular reaction properties of this compound. In the course of this study we observed a rather unexpected, facile interconversion of a monodentate 1-MeC ligand, bound to Pt via N(3), to a chelating deprotonated 1-MeC ligand (N(3),N(4) binding) and vice versa. To our knowledge this is the first example of an equilibrium between a η_1 and a η_2 binding pattern involving a nucleobase and at the same time the first example of a cytosine chelate involving the endocyclic N(3) position and the exocyclic N(4) atom.

A preliminary report on the crystal structure of the bis(chelate) *trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC^-)_2](NO_3)_2\cdot 2H_2O$ has appeared.[9]

Experimental Section

Preparation. *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2](NO_3)_2$ was prepared as previously described.[10]

trans-$[Pt(NH_3)_2(1\text{-}MeC)_2]Cl_2\cdot 2H_2O$ was obtained in a similar way from *trans*-$Pt(NH_3)_2Cl_2$[11] and 1-MeC[12] (molar ratio 1:2, H_2O, 5 h 80 °C, evaporation and recrystallization from hot water) in 65% yield. Colorless, thin columns. Anal. Calcd for $[Pt(NH_3)_2(C_5H_7N_3O)_2]Cl_2\cdot 2H_2O$: C, 20.5; H, 4.1; Pt, 33.3. Found: C, 20.2; H, 4.1; Pt, 33.2.

trans,trans,trans-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)_2](NO_3)_2\cdot 2H_2O$ (**1**). To a solution of *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2](NO_3)_2$ (300 mg in 10 mL of H_2O) 10 mL of an aqueous solution of H_2O_2 (10%) was added dropwise. The solution was then warmed to 70 °C for 25 min (evolution of O_2) and then concentrated in a stream of nitrogen to 8 mL volume and finally allowed to further evaporate for 2 days at 22 °C. Large, slightly yellow prims of **1** were collected and then briefly washed with water and dried in air. Yield 250 mg. Anal. Calcd for $[Pt(NH_3)_2(C_5H_7N_3O)_2(OH)_2](NO_3)_2\cdot 2H_2O$: C, 17.8; H, 3.9; N, 20.8; O, 28.5. Found: C, 17.9; H, 4.0; N, 21.1; O, 29.1.

trans,trans,trans-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)_2]Cl_2\cdot 2H_2O\cdot 2H_2O_2$ (**1a**) was prepared in a similar way by treating *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2]Cl_2\cdot 2H_2O$ (190 mg in 5 mL of H_2O) with H_2O_2 (6 mL of 10% H_2O_2, 15 min at 60 °C) and by slow evaporation of the resulting solution at 3 °C. The microcrystalline, colorless precipitate was collected and washed with water and finally acetone. Yield 170 mg. Anal. Calcd for $[Pt(NH_3)_2Pt(C_5H_7N_3O)_2(OH)_2]Cl_2\cdot 2H_2O\cdot 2H_2O_2$ or alternatively (cf. text) $[Pt(NH_3)_2(C_5H_7N_3O)_2(OOH)_2]Cl_2\cdot 4H_2O$: C, 17.5; H, 4.4; N, 16.3; O, 23.1; Pt, 29.2. Found: C, 17.5; H, 4.5; N, 16.1; O, 23.1; Pt, 28.3.

trans,trans-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)(OH_2)](NO_3)_3\cdot 3H_2O$ (**2**) was isolated from a solution of **1** (60 mg) in 4 N HNO_3 (2.5 mL) which had been warmed for 2 min to 50 °C and was then allowed to stand for 2–3 h at 22 °C. Pale yellow cubes, yield 50 mg. Anal. Calcd for $[Pt(NH_3)_2(C_5H_7N_3O)_2(OH)(OH_2)](NO_3)_3\cdot 3H_2O$: C, 15.9; H, 3.9; N, 20.4; O, 33.9; Pt, 25.9. Found: C, 15.9; H, 4.0; N, 20.5; O, 34.0; Pt, 26.0.

trans,trans-$[Pt(NH_3)_2(1\text{-}MeC^-)_2](NO_3)_2\cdot 2H_2O$ (**4**). An aqueous suspension of **1** (150 mg in 10 mL) was acidified with a drop of diluted HNO_3 (pH 2.6) and kept at 50–60 °C until it had evaporated to a volume of 3–5 mL. From the then yellow solution, 30 mg of **4** crystallized on cooling to room temperature. The precipitate was collected, washed with water, and dried in air. Addition of 5–10 mL of H_2O to the resulting solution, evaporation in a 50–60 °C water bath, and subsequent cooling gave a second crop of **4** (35 mg). Two more repetitions of this procedure gave an additional 25 mg of **4**. Alternatively, heating of an aqueous solution of **1** (50 mg in 1.5 mL, 5 min 90 °C) without addition of acid (pH 4.5) resulted in formation of a yellow solution from which 20 mg of **4** crystallized within 6 days at 22 °C after addition of a seed crystal. Deep yellow cubes. Anal. Calcd for $[Pt(NH_3)_2(C_5H_6N_3O)_2](NO_3)_2\cdot 2H_2O$: C, 18.8; H, 3.5; N, 22.0. Found: C, 19.2; H, 3.6; N, 22.2.

trans-$[Pt(NH_3)_2(1\text{-}MeC)(1\text{-}MeC^-)(OH)](NO_3)_2\cdot H_2O$ (**3**) was obtained together with **4** and possibly one or two minor side products on complete evaporation to dryness of a heated (acidified or not) solution of **1** as described for **4**. Typically, a solution of **1** (100 mg in 10 mL of H_2O, pH 4) was allowed to evaporate to 6 mL volume in a 50 °C water bath and the yellow solution was then transferred on a watch glass. The residue obtained after complete evaporation consisted of ca. 70 mg of **3** and 20 mg of **4**. Both products were separated by hand under a microscope and **3**, which in contrast to **4** is well soluble in water, was recrystallized from water at room temperature. The resulting product again contained small amounts of **4** and possibly also other components in small quantities. Slightly yellow, long columns. Anal. Calcd for $[Pt(NH_3)_2(C_5H_7N_3O)(C_5H_6N_3O)(OH)](NO_3)_2\cdot H_2O$: C, 18.8; H, 3.5; Pt, 30.6. Found: C, 18.4; H, 3.5; Pt, 30.4.

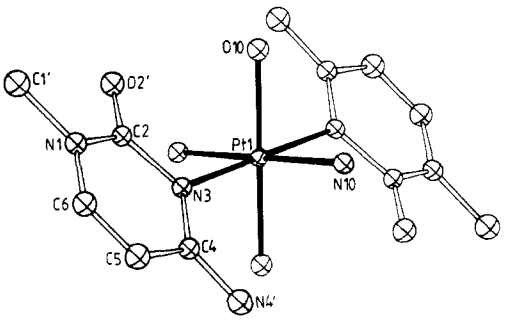

Figure 1. Cation of *trans,trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)_2](NO_3)_2\cdot 2H_2O$ (**1**) with the atoms labeled. Pt is on an inversion center.

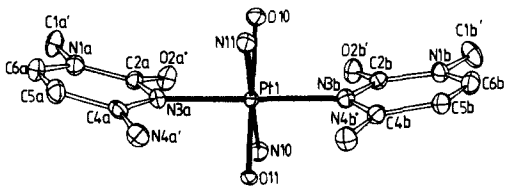

Figure 2. Cation of *trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)(OH_2)](NO_3)_3\cdot 3H_2O$ (**2**) with atom-numbering scheme. O(10) is the aqua and O(11) the hydroxo group.

Spectra. IR spectra were recorded on Perkin-Elmer 577 and 580 grating spectrometers as KBr pellets and Nujol mulls (CsI windows). Raman spectra were obtained on a Coderg PH 1 instrument with krypton laser excitation (647.1 nm). ^1H NMR spectra were recorded on a JEOL JNM-FX 60 FT-NMR spectrometer in D_2O or acidified (DNO_3, DCl, CF_3COOD) solutions. pD values were obtained by adding 0.4 unit to the pH meter reading. Shifts are quoted on the δ scale and are calculated relative to TSP (sodium 3-(trimethylsilyl)propanesulfonate). The internal standard used was $[N(CH_3)_4]BF_4$ (3.19 ppm downfield from TSP).

Potentiometric titrations were carried out on a Metrohm E 536 potentiograph.

Crystallography. The X-ray measurements of **1**, **2**, **3**, and **4** were carried out at room temperature on a PHILIPS-PW 1100 single-crystal diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The unit cell dimensions were calculated from reflections centered on the diffractometer as follows: **1**, 17 reflections, θ range 18–21°; **2**, 26 reflections, θ range 12–18°; **3**, 16 reflections, θ range 12–18°; **4**, 28 reflections, θ range 10–16°. Crystal data and other experimental details concerning the data collection are summarized in Table I. Intensity data for all compounds were collected with use of $\theta/2\theta$ scans. The reflection intensities were corrected for Lorentz and polarization effects and, in a later stage, for absorption by an empirical method using a program by Walker and Stuart.[13] The coordinates of the platinum atoms in all four compounds were obtained from three-dimensional Patterson synthese, and the other non-hydrogen atoms were located by subsequent ΔF syntheses. H atoms were ignored at all stages. In **2**, **3**, and **4**, all atoms were refined with anisotropic temperature factors, and in **1** only the Pt atom was refined anisotropically. The atomic coordinates and equivalent isotropic temperature factors (calculated from the U_{ij} values by $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*a_ia_j$ with U_{ij} in Å^2) are given in Tables II–V. Scattering factors for neutral atoms were taken from Cromer and Mann.[14] Anomalous dispersion corrections were applied.[15] For the

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Table I. Crystal Data and Experimental Details for **1**, **2**, **3** and **4**

compound	1	2	3	4
fw	673.47	754.49	637.44	637.44
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	13.036 (2)	10.630 (2)	7.117 (2)	7.230 (3)
b, Å	9.011 (1)	11.005 (3)	23.864 (4)	10.576 (4)
c, Å	9.682 (1)	12.336 (3)	11.802 (2)	13.186 (2)
α, deg	90	110.75 (3)	90	90
β, deg	111.20 (2)	91.09 (3)	91.82 (2)	100.92
γ, deg	90	113.29 (3)	90	90
V, Å^3	1060.3	1218.1	2003.4	990.0
Z	2	2	4	2
d_{calcd}, gcm^{-3}	2.109	2.057	2.113	2.138
d_{meas}, gcm^{-3}	2.11	2.06	2.11	2.13
crystal size, mm	0.5 × 0.5 × 0.3	0.1 × 0.3 × 0.5	0.1 × 0.2 × 0.4	0.1 × 0.1 × 0.1
μ, cm^{-1}	64.2	56.0	67.7	68.6
θ range	2–25	2–26	2–25	2–27
no. of unique refl.	1871	5530	3519	2165
no. of refl. used in the calculations	1647 $F_o > 2\sigma F_o$	5508 $F_o > 2\sigma F_o$	3433 $F_o > 3\sigma F_o$	1419 $F_o > 2\sigma F_o$
no. of parameters	71	343	280	142
R	0.049	0.038	0.075	0.048
$R_w(F)$	0.059	0.038	0.075	0.056
highest peak in the final diff map	2.0 e/Å^3 1.4 Å from Pt(1)	1.2 e/Å^3 1.2 Å from Pt(1)	2.1 e/Å^3 1.5 Å from Pt(1)	1.7 e/Å^3 1.1 Å from Pt(1)

Table II. Atomic Coordinates and Equivalent Isotropic Temperature Factors of *trans,trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)_2](NO_3)_2\cdot 2H_2O$ (**1**)

atom	x	y	z	U
cation				
Pt(1)	0.5000 (0)	0.5000 (0)	0.5000 (0)	0.018 (1)
O(10)	0.3942 (4)	0.3374 (5)	0.4972 (6)	0.027 (1)
N(10)	0.3750 (5)	0.5655 (7)	0.3092 (8)	0.024 (1)
N(1)	0.6047 (5)	0.1359 (7)	0.3047 (8)	0.026 (1)
C(1′)	0.6089 (9)	−0.0254 (10)	0.3334 (14)	0.037 (2)
C(2)	0.5817 (6)	0.2251 (8)	0.4005 (9)	0.022 (2)
O(2′)	0.5699 (4)	0.1727 (5)	0.5116 (6)	0.032 (1)
N(3)	0.5681 (5)	0.3798 (6)	0.3736 (7)	0.022 (1)
C(4)	0.5878 (7)	0.4361 (10)	0.2552 (10)	0.025 (2)
N(4′)	0.5860 (7)	0.5802 (9)	0.2310 (9)	0.035 (2)
C(5)	0.6134 (7)	0.3346 (9)	0.1520 (10)	0.034 (2)
C(6)	0.6185 (7)	0.1924 (8)	0.1805 (3)	0.0.32 (2)
nitrate anion				
N(20)	0.8463 (5)	0.2664 (7)	0.5673 (8)	0.032 (2)
O(20)	0.8416 (6)	0.3207 (8)	0.6738 (9)	0.055 (2)
O(21)	0.8482 (6)	0.3453 (8)	0.4597 (9)	0.065 (2)
O(22)	0.8515 (5)	0.1328 (6)	0.5494 (7)	0.041 (1)
Water				
O(30)	0.3357 (6)	0.8292 (8)	0.1226 (9)	0.044 (2)

calculations, the SHELX program package[16] was used.

Results and Discussion

Crystal Structures of 1 and 2 with Monodentate 1-MeC Ligands. The cations of *trans,trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)_2](NO_3)_2\cdot 2H_2O$ (**1**) and *trans,trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)(OH_2)](NO_3)_3\cdot 3H_2O$ (**2**) are shown in Figures 1 and 2. Interatomic distances and angles within the Pt coordination sphere in **1** and **2** are listed in Table VI. Geometries of the NO_3^- ions in all four structurally characterized complexes are normal and are given in the supplementary material.

The cation of **1** is centrosymmetrical, leading to an all-trans arrangement of the three different types of ligands. Although NH_3 and OH groups cannot be unambiguously differentiated by X-ray analysis, the assignment used in Figure 1 is based on the expected differences in hydrogen bonding properties of both groups observed in the crystal, with NH_3 acting as H donor and OH acting preferentially as H acceptor. Neither the Pt–NH_3 bond lengths observed in **1** (2.058 (6) Å) nor the Pt–N(1-MeC) bond length (2.061 (6) Å) differ significantly from those of the Pt^{II} precursor *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2](NO_3)_2$ with respective distances being 2.067 (10) and 2.023 (8) Å.[10] The geometries of the 1-MeC rings in **1** and the Pt^{II} precursor are rather similar as well (for **1** see below), but the dihedral angles between the 1-MeC plane and the PtN_4 plane are markedly different: 56.2° in **1** as compared to 78.2° in *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2]^{2+}$. This

Table III. Atomic Coordinates and Equivalent Isotropic Temperature Factors of *trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)(OH_2)](NO_3)_3\cdot 3H_2O$ (**2**)

atom	x	y	z	U
cation				
Pt(1)	0.1293 (1)	0.4242 (1)	0.2263 (1)	0.020 (1)
N(10)	0.0920 (5)	0.5749 (5)	0.3587 (4)	0.030 (3)
N(11)	0.1730 (5)	0.2731 (5)	0.0966 (4)	0.029 (3)
O(10)	0.1758 (4)	0.3291 (4)	0.3288 (3)	0.031 (3)
O(11)	0.0911 (4)	0.5095 (4)	0.1199 (3)	0.021 (3)
N(1a)	−0.2637 (5)	0.1289 (6)	0.2543 (5)	0.034 (4)
C(1a′)	−0.3195 (7)	0.0969 (7)	0.3545 (6)	0.044 (5)
C(2a)	−0.1389 (5)	0.2505 (6)	0.2813 (5)	0.028 (4)
O(2a′)	−0.0812 (4)	0.3280 (5)	0.3839 (3)	0.037 (3)
N(3a)	−0.0788 (4)	0.2791 (5)	0.1875 (4)	0.026 (3)
C(4a)	−0.1538 (6)	0.2012 (6)	0.0738 (5)	0.032 (4)
N(4a′)	−0.1087 (6)	0.2403 (6)	−0.0114 (5)	0.040 (4)
C(5a)	−0.2815 (7)	0.0753 (7)	0.0499 (6)	0.041 (5)
C(6a)	−0.3334 (6)	0.0429 (7)	0.1401 (6)	0.040 (5)
N(1b)	0.5500 (5)	0.7073 (5)	0.4020 (4)	0.033 (4)
C(1b′)	0.6203 (7)	0.7718 (9)	0.5284 (6)	0.049 (6)
C(2b)	0.4081 (6)	0.6258 (6)	0.3772 (5)	0.028 (4)
O(2b′)	0.3447 (4)	0.6048 (5)	0.4561 (4)	0.038 (3)
N(3b)	0.3393 (5)	0.5656 (5)	0.2603 (4)	0.028 (3)
C(4b)	0.4090 (6)	0.6004 (6)	0.1773 (5)	0.030 (4)
N(4b′)	0.3426 (6)	0.5558 (6)	0.0671 (4)	0.038 (4)
C(5b)	0.5582 (6)	0.6822 (7)	0.2049 (6)	0.035 (5)
C(6b)	0.6237 (6)	0.7332 (7)	0.3161 (6)	0.039 (5)
nitrate anions				
N(1)	0.7197 (6)	1.1293 (6)	0.7111 (5)	0.040 (4)
O(1)	0.6504 (6)	1.1040 (8)	0.7866 (5)	0.076 (7)
O(2)	0.8414 (6)	1.1474 (8)	0.7241 (5)	0.075 (6)
O(3)	0.6675 (6)	1.1361 (6)	0.6248 (5)	0.065 (6)
N(2)	0.0426 (5)	0.0302 (6)	−0.2010 (5)	0.034 (4)
O(4)	−0.0047 (6)	−0.0035 (5)	−0.1190 (4)	0.058 (5)
O(5)	0.1282 (5)	0.1550 (5)	−0.1802 (4)	0.047 (4)
O(6)	0.0027 (6)	−0.0650 (5)	−0.3043 (4)	0.051 (4)
N(3)	0.4720 (7)	0.6676 (8)	−0.1723 (6)	0.052 (6)
O(7)	0.5256 (6)	0.6789 (7)	−0.0791 (5)	0.067 (6)
O(8)	0.5533 (11)	0.7146 (18)	−0.2286 (9)	0.194 (24)
O(9)	0.3449 (6)	0.6167 (7)	−0.2042 (7)	0.080 (7)
water				
O(12)	0.1842 (5)	0.4210 (6)	0.5573 (4)	0.050 (4)
O(13)	0.0269 (6)	0.1571 (6)	0.5592 (5)	0.062 (5)
O(14)	0.1207 (6)	0.4154 (6)	−0.1706 (5)	0.059 (5)

(16) Sheldrick, G. M. *SHELX, Program for Crystal Structure Determination*; University of Göttingen, Göttingen, 1976.

Table IV. Atomic Coordinates and Equivalent Isotropic Temperature Factors of *trans*-$[Pt(NH_3)_2(1\text{-}MeC)(1\text{-}MeC^-)(OH)](NO_3)_2\cdot H_2O$ (3)

atom	*x*	*y*	*z*	*U*
cation				
Pt(1)	0.3325 (1)	0.0836 (1)	0.7104 (1)	0.033 (1)
N(1)	0.5953 (18)	0.0722 (5)	0.6424 (11)	0.042 (12)
N(2)	0.0679 (21)	0.0977 (6)	0.7812 (14)	0.061 (17)
O(1)	0.4781 (15)	0.1091 (5)	0.8522 (11)	0.054 (12)
N(1a)	0.2847 (18)	0.2464 (5)	0.5604 (13)	0.048 (14)
C(1a′)	0.3123 (31)	0.3074 (7)	0.5813 (21)	0.071 (24)
C(2a)	0.3371 (20)	0.2111 (6)	0.6532 (13)	0.038 (14)
O(2a′)	0.4054 (19)	0.2284 (5)	0.7392 (10)	0.058 (13)
N(3a)	0.3084 (15)	0.1555 (5)	0.6294 (10)	0.034 (11)
C(4a)	0.2179 (23)	0.1356 (6)	0.5347 (13)	0.042 (15)
N(4a′)	0.1908 (18)	0.0798 (6)	0.5584 (16)	0.064 (18)
C(5a)	0.1764 (22)	0.1717 (7)	0.4402 (15)	0.046 (16)
C(6a)	0.2107 (21)	0.2259 (7)	0.4619 (15)	0.048 (17)
N(1b)	0.3099 (17)	−0.0937 (5)	0.7232 (11)	0.040 (12)
C(1b′)	0.3239 (26)	−0.1397 (7)	0.6421 (15)	0.054 (18)
C(2b)	0.3427 (19)	−0.0398 (6)	0.6915 (12)	0.034 (13)
O(2b′)	0.3844 (17)	−0.0295 (4)	0.5952 (9)	0.048 (11)
N(3b)	0.3318 (15)	0.0033 (5)	0.7757 (10)	0.036 (11)
C(4b)	0.2903 (20)	−0.0107 (6)	0.8818 (12)	0.037 (14)
N(4b′)	0.2861 (18)	0.0299 (6)	0.9601 (12)	0.070 (16)
C(5b)	0.2554 (24)	−0.0672 (7)	0.9121 (13)	0.045 (16)
C(6b)	0.2564 (21)	−0.1067 (7)	0.8329 (13)	0.043 (15)
nitrate anions				
N(10)	0.8154 (20)	0.2790 (6)	0.1345 (14)	0.053 (16)
O(10)	0.8152 (19)	0.3294 (5)	0.1532 (13)	0.072 (16)
O(11)	0.7240 (22)	0.2616 (7)	0.0544 (13)	0.088 (20)
O(12)	0.9000 (24)	0.2457 (7)	0.1965 (16)	0.099 (22)
N(20)	0.1640 (19)	0.0362 (6)	0.2477 (12)	0.048 (14)
O(20)	0.1861 (18)	−0.0055 (5)	0.1858 (9)	0.052 (12)
O(21)	0.2235 (28)	0.0819 (6)	0.2259 (13)	0.091 (21)
O(22)	0.0789 (19)	0.0266 (7)	0.3386 (12)	0.078 (17)
water				
O(30)	0.8665 (27)	0.1761 (6)	0.9211 (14)	0.093 (21)

Table V. Atomic Coordinates and Equivalent Isotropic Temperature Factors of *trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC^-)_2](NO_3)_2\cdot 2H_2O$ (4)

atom	*x*	*y*	*z*	*U*
cation				
Pt(1)	0.5000 (0)	0.5000 (0)	0.5000 (0)	0.032 (1)
N(10)	0.5988 (14)	0.4599 (9)	0.3671 (8)	0.036 (6)
N(1)	0.9457 (13)	0.2658 (7)	0.6698 (6)	0.032 (6)
C(1′)	1.1411 (17)	0.2618 (13)	0.7297 (11)	0.055 (8)
C(2)	0.8805 (18)	0.3831 (10)	0.6256 (9)	0.040 (8)
O(2)	0.9850 (14)	0.4776 (7)	0.6315 (8)	0.047 (7)
N(3)	0.6987 (14)	0.3813 (7)	0.5786 (6)	0.033 (6)
C(4)	0.5863 (15)	0.2786 (10)	0.5688 (8)	0.032 (7)
N(4′)	0.4182 (15)	0.3173 (9)	0.5133 (8)	0.042 (7)
C(5)	0.6550 (17)	0.1570 (10)	0.6089 (9)	0.039 (7)
C(6)	0.8329 (18)	0.1596 (9)	0.6569 (9)	0.038 (7)
nitrate anion				
N(20)	0.6939 (14)	0.1279 (9)	0.3409 (7)	0.038 (7)
O(20)	0.7381 (19)	0.0186 (7)	0.3315 (11)	0.067 (8)
O(21)	0.7993 (12)	0.2062 (8)	0.3939 (6)	0.050 (7)
O(22)	0.5350 (13)	0.1688 (9)	0.2973 (8)	0.063 (8)
water				
O(30)	0.8422 (14)	0.6183 (9)	0.0207 (8)	0.061 (7)

difference appears to be primarily caused by the interference of NH_3 and OH ligands with the exocyclic groups (O(2′) and N(4′)) of the 1-MeC rings in the octahedral Pt^{IV} complex as opposed to the situation in the square-planar Pt^{II} complex. Similar small dihedral angles (41–53°) have been observed in Pt^{IV} complexes containing uracil ligands.[17]

Intramolecular distances $NH_3(10)$–O(2′), OH(10)–O(2′), and OH(10)–$NH_2(4)$ and the respective angles about the possible donor atoms for hydrogen bonding are not indicative of any hydrogen bonding within the cation of **1**. There are, however, several intermolecular distances (<3.4 Å) which presumably reflect hydrogen bonding interactions (cf. supplementary material). Important with respect to the differentiation of OH and NH_3 ligands mentioned above are the contacts between N(10) and the nitrate oxygens O(20), 3.06 Å, and O(22), 3.01 Å. Although hydrogen atoms were not located, we assume that these two contacts reflect two $NH_3\cdots O$ hydrogen bonds rather than a single, disordered hydrogen bond between OH and NO_3^-.[18] As a consequence, the O(10)–O(30) contact of 2.80 Å should be a hydrogen bonding interaction in which the OH ligand accepts a proton from a water molecule.

(17) Müller, G.; Riede, J.; Beyerle-Pfnür, R.; Lippert, B. *J. Am. Chem. Soc.* **1984**, *106*, 7999.

Table VI. Interatomic Distances (Å) and Angles (deg) about the Pt in **1** and **2**

		1	
Pt(1)–N(10)	2.058 (6)	O(10)–Pt(1)–N(10)	83.1 (2)
Pt(1)–O(10)	2.005 (5)	O(10)–Pt(1)–N3)	92.9 (2)
Pt(1)–N(3)	2.061 (6)	N(10)–Pt(1)–N(3)	89.3 (2)
		2	
Pt(1)–N(10)	2.050 (5)	N(10)–Pt(1)–N(11)	178.0 (2)
Pt(1)–N(11)	2.072 (5)	N(10)–Pt(1)–O(10)	96.8 (2)
Pt(1)–O(10)	2.065 (5)	N(10)–Pt(1)–O(11)	86.9 (2)
Pt(1)–O(11)	1.981 (4)	N(10)–Pt(1)–N(3a)	91.1 (2)
Pt(1)–N(3a)	2.073 (5)	N(10)–Pt(1)–N(3b)	90.7 (2)
Pt(1)–N(3b)	2.082 (5)	N(11)–Pt(1)–O(10)	81.7 (2)
		N(11)–Pt(1)–O(11)	94.6 (2)
		N(11)–Pt(1)–N(3a)	90.2 (2)
		N(11)–Pt(1)–N(3b)	88.0 (2)
		O(10)–Pt(1)–O(11)	176.1 (2)
		O(10)–Pt(1)–N(3a)	90.5 (2)
		O(10)–Pt(1)–N(3b)	89.6 (2)
		O(11)–Pt(1)–N(3a)	90.7 (2)
		O(11)–Pt(1)–N(3b)	89.1 (2)
		N(3a)–Pt(1)–N(3b)	178.2 (2)

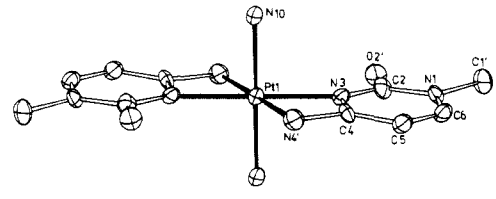


Figure 3. Cation of *trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC^-)_2](NO_3)_2\cdot 2H_2O$ (**4**).

The cation of **2**, *trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)(OH_2)]^{3+}$, possesses three ligands (OH, OH_2, NH_3) which cannot rigorously differentiated by X-ray methods. However, hydrogen bonding consideration and the significant differences between Pt–O(10), 2.064 (4) Å, and Pt–O(11), 1.981 (4) Å, are consistent with the atom assignment used in Figure 2, with O(10) being the aqua group and O(11) being the OH group (see below).

No major differences in bond lengths and bond angles about the Pt and in the 1-MeC ring exist between **1** and **2**. Dihedral angles between the PtN_4 plane and the two rings in **2** do not differ much (52° and 53.6°) and are close to the value found in **1**. Interestingly, in both compounds the Pt atoms are not copolanar with the heterocyclic rings, with deviations of 0.26 Å (ring b in **2**), 0.43 Å (**1**), and 0.54 Å (ring a in **2**), the latter corresponding to a 29° angle between the 1-MeC plane and the Pt–N(3) vector (cf. Figure 2).

Within the cation, short contacts are observed between N(10) and O(2a′), O(2b′), 2.75 and 2.77 Å, between O(10) and the two exocyclic oxygens, 2.67 and 2.83 Å, and between O(11) and N(4a′), N(4b′), 2.72 and 2.66 Å, but only in the latter case are the angles (99°, 96°) around the assumed H donors N(4a′) and N(4b′) reasonable to assume hydrogen bonding interactions, whereas in the former, angles about N(10) and O(10) are too small (<80°).

As to possible intermolecular hydrogen bonding interactions (cf. supplementary material), groups contacting nitrate oxygens

(18) (a) Lock, C. J. L. In *Inorganic Chemistry in Biology and Medicine*; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1980; ACS Symp. Ser. 140, pp 209–224. (b) Britten, J. F.; Lippert, B.; Lock, C. J. L.; Pilon, P. *Inorg. Chem.* **1982**, *21*, 1936.

Table VII. Interatomic Distances (Å) and Angles (deg) about the Pt Atom in **3** and **4** and Geometry of the Chelate Rings

(a) Pt Coordination Sphere			
		3	
Pt(1)–N(1)	2.076 (12)	N(1)–Pt(1)–N(2)	178.3 (6)
Pt(1)–N(2)	2.112 (14)	N(1)–Pt(1)–O(1)	85.2 (5)
Pt(1)–O(1)	2.033 (12)	N(1)–Pt(1)–N(3a)	89.6 (5)
Pt(1)–N(3a)	1.969 (13)	N(1)–Pt(1)–N(4a′)	94.6 (6)
Pt(1)–N(4a′)	2.032 (16)	N(1)–Pt(1)–N(3b)	92.0 (5)
Pt(1)–N(3b)	2.066 (13)	N(2)–Pt(1)–O(1)	93.7 (6)
		N(2)–Pt(1)–N(3a)	89.3 (6)
		N(2)–Pt(1)–N(4a′)	86.1 (7)
		N(2)–Pt(1)–N(3b)	89.2 (5)
		O(1)–Pt(1)–N(3a)	99.9 (5)
		O(1)–Pt(1)–N(4a′)	164.9 (6)
		O(1)–Pt(1)–N(3b)	88.7 (5)
		N(3a)–Pt(1)–N(4a′)	65.0 (6)
		N(3a)–Pt(1)–N(3b)	171.3 (5)
		N(4a′)–Pt(1)–N(3b)	106.4 (6)
		4	
Pt(1)–N(10)	2.059 (11)	N(10)–Pt(1)–N(3)	88.9 (4)
Pt(1)–N(3)	2.037 (9)	N(10)–Pt(1)–N(4′)	91.8 (4)
Pt(1)–N(4′)	2.038 (10)	N(3)–Pt(1)–N(4′)	63.9 (4)
(b) Chelate			
		3	
N(3a)–C(4a)	1.36 (2)	Pt(1)–N(4a′)–C(4a)	94 (1)
C(4a)–N(4a′)	1.38 (2)	N(4a′)–C(4a)–N(3a)	104 (2)
		C(4a)–N(3a)–Pt(1)	97 (1)
		4	
N(3)–C(4)	1.35 (1)	Pt(1)–N(4′)–C(4)	95 (1)
C(4)–N(4′)	1.36 (2)	N(4′)–C(4)–N(3)	106 (1)
		C(4)–N(3)–Pt(1)	95 (1)

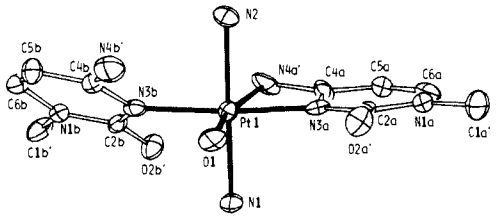


Figure 4. Cation of *trans*-$[Pt(NH_3)_2(1\text{-MeC})(1\text{-MeC}^-)(OH)](NO_3)_2 \cdot H_2O$ (**3**).

are considered H donors. A series of such contacts with reasonable angles about the donors exist for the groups assigned to O(10) and N(11), which suggests that they are aqua and ammine groups, respectively. Consistent with this interpretation, the group trans to O(10), O(11) acts as a H acceptor (see above) and has a shorter bond to the Pt, as might be expected for a hydroxo ligand as opposed to aqua and ammine ligands (see Table VI).

Crystal Structures of 3 and 4 Containing Chelating 1-MeC⁻ Ligands. The cation of *trans,trans*-$[Pt(NH_3)_2(1\text{-MeC}^-)_2](NO_3)_2 \cdot 2H_2O$ (**4**) is depicted in Figure 3, and details of the Pt coordination geometry and that of the chelate ring are given in Table VII. The cation possesses centrosymmetry, containing two 1-methylcytosinato ligands chelating the Pt^{IV} through N(3) and the exocyclic, deprotonated amino group N(4′), and in addition two NH_3 groups. Pt–N(3) and Pt–N(4′) distances are short and virtually identical (2.037 (9) and 2.038 (10) Å), unlike in most chelates of neutral cytosine ligands involving N(3) and O(2′). There, usually the M–O(2′) bond is considerably longer than the M–N(3) bond[19] or alternatively both bonds are quite long.[20] On the other hand, in a dinuclear complex of *cis*-$(NH_3)_2Pt^{II}$ containing bridging 1-methylcytosinato rings, Pt–N(3) and Pt–N(4′) bonds

Table VIII. Selected Dihedral Angles (deg) between Planes[a]

		1	
Pt(1), N(10), O(10) plane	/	1-MeC plane	100
Pt(1), N(10), N(3) plane	/	1-MeC plane	56
		2	
N(10), N(11), O(10), O(11) plane	/	1-MeC plane (a)	104
N(10), N(11), O(10), O(11) plane	/	1-MeC plane (b)	83
N(10), N(11), N(3a), N(3b) plane	/	1-MeC plane (a)	52
N(10), N(11), N(3a), N(3b) plane	/	1-MeC plane (b)	54
O(10), O(11), N(3a), N(3b) plane	/	1-MeC plane (a)	47
O(10), O(11), N(3a), N(3b) plane	/	1-MeC plane (b)	43
1-MeC plane (a)	/	1-MeC plane (b)	21
		3	
chelate plate	/	1-MeC⁻ plane (a)	7
N(3a), N(4a′), N(3b), O(1) plane	/	1-MeC plane (b)	41
1-MeC⁻ plane (a)	/	1-MeC plane (b)	35
		4	
Pt(1), N(3), N(10) plane	/	chelate plane	87
chelate plane	/	1-MeC plane	1

[a] Equations and deviations of atoms given in the supplementary material.

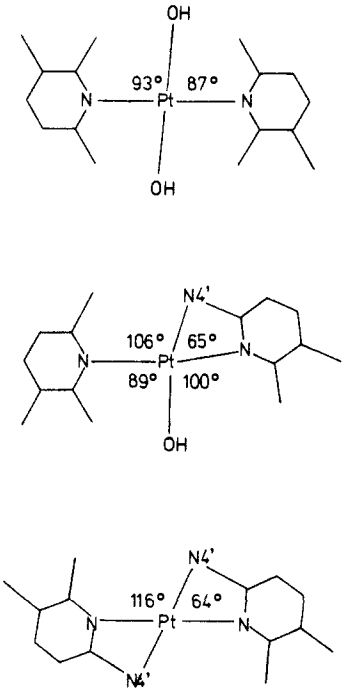


Figure 5. Comparison of planes perpendicular to the Pt–(NH_3)-vectors of **1** (top), **3** (middle), and **4** (bottom) with angles around the Pt atoms indicated.

are of comparable lengths as well (2.01 (2)–2.06 (3) Å).[21]

The chelate rings in **4** are roughly planar and at the same time almost coplanar with the cytosine ring (Table VIII). While the NH_3 groups are approximately at right angles to the chelate planes, the angles about the Pt in the chelate plane undergo large deviations from the normal 90°, alternating between 64° (internal chelate angle N(3)–Pt–N(4′)) and 116° (external angle N(3)–Pt–N(4′*)).

The cation of *trans*-$[Pt(NH_3)_2(1\text{-MeC})(1\text{-MeC}^-)(OH)](NO_3)_2 \cdot H_2O$ (**3**), which is shown in Figure 4, contains a neutral 1-MeC ring (b) coordinated to Pt through N(3) and an anionic 1-MeC⁻ ring (a) chelating Pt in the same way as in **4**. **3** thus represents the intermediate between **1** and **4**. The geometry of the four-membered chelate ring in **3** is rather similar to that in **4** (Table VII), but the angles about Pt are different. In Figure 5 angles are compared for the planes in **1**, **2**, and **4** that are roughly perpendicular to the Pt–NH_3 vectors. As can be seen, minor

(19) (a) Gagnon, C.; Beauchamp, A. L.; Tranqui, D. *Can. J. Chem.* **1979**, *57*, 1372. (b) Authier-Martin, M.; Beauchamp, A. L. *Ibid.* **1977**, *55*, 1213. (c) Szalda, D. J.; Marzilli, L. G.; Kistenmacher, T. J. *Inorg. Chem.* **1975**, *14*, 2076.

(20) Ogawa, K.; Kumihashi, M.; Tomita, K.-I.; Shirotake, *Acta Crystallogr., Sect. B* **1980**, *B36*, 1793.

(21) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111.

Table IX. Interatomic Distances (Å) and Angles (deg) of Monodentate 1-MeC Ligands and of Chelating 1-MeC$^-$ Ligands

		chelating	
	monodentate[a]	3 (ring a)	4
N(1)–C(1′)	1.48 (1)	1.49 (2)	1.48 (2)
N(1)–C(2)	1.36 (1)	1.42 (2)	1.41 (1)
C(2)–O(2′)	1.23 (1)	1.19 (2)	1.25 (2)
C(2)–N(3)	1.42 (1)	1.37 (2)	1.34 (2)
N(3)–C(4)	1.36 (1)	1.36 (2)	1.35 (1)
C(4)–N(4′)	1.33 (1)	1.38 (2)	1.36 (2)
C(4)–C(5)	1.46 (1)	1.43 (2)	1.44 (2)
C(5)–C(6)	1.33 (1)	1.34 (3)	1.32 (2)
C(6)–N(1)	1.38 (1)	1.35 (2)	1.38 (1)
C(1′)–N(1)–C(6)	120 (1)	123 (2)	122 (1)
C(1′)–N(1)–C(2)	118 (1)	115 (2)	117 (1)
C(6)–N(1)–C(2)	122 (1)	122 (2)	121 (1)
O(2′)–C(2)–N(1)	120 (1)	123 (2)	122 (1)
O(2′)–C(2)–N(3)	121 (1)	125 (2)	125 (1)
N(1)–C(2)–N(3)	119 (1)	112 (1)	114 (1)
C(2)–N(3)–C(4)	119 (1)	129 (1)	125 (1)
Pt–N(3)–C(2)	116 (1)	137 (1)	139 (1)
Pt–N(3)–C(4)	124 (1)	97 (1)	95 (1)
N(4′)–C(4)–N(3)	120 (1)	104 (1)	106 (1)
N(4′)–C(4)–C(5)	120 (1)	135 (2)	133 (1)
N(3)–C(4)–C(5)	120 (1)	121 (2)	122 (1)
Pt–N(4′)–C(4)		94 (1)	95 (1)
C(4)–C(5)–C(6)	119 (1)	114 (2)	113 (1)
C(5)–C(6)–N(1)	121 (1)	125 (2)	125 (1)

[a] Average value from **1**, **2** (rings a and b), and **3** (ring b). Individual data are given in the supplementary material.

deviations from the ideal 90° angles exist even for **1**, which most likely are due to interference of OH and exocyclic groups of the 1-MeC rings as also observed in related uracil complexes of Pt^{IV},[17] but the large deviations in **3** and **4** result from chelate formation. With **3**, only the angle between the two monodentate ligands (cytosine ring b and OH(1)) is close to the usual 90°, whereas the others are 65.0 (6), 99.9 (5), and 106.4 (6)°. As already mentioned, the variations in the bis(chelate) **4** are even larger.

Comparison of the four-membered chelates in **3** and **4** with five-membered, planar chelates of deprotonated 8-hydroxoquinoline, for example, reveals deviations from 90° about the metal as well (e.g., 75° with Pt^{IV},[22] 81° with Tc^{V} [23]),[24] but these are clearly smaller than in **3** and **4**. Expectedly, the internal chelate angle at the metal is again close to 90° if the chelate ring is saturated and therefore more flexible, e.g., 85° in 2-aminoethanolato chelates of Pt^{IV}.[5c]

Cytosine Geometry. Interatomic distances and angles of the cytosine rings in **1**–**4** are compiled in Table IX. Comparison with the geometry of the free 1-methylcytosine[25] shows that Pt^{IV} binding through N(3) has relatively little effect on the ligand (**1**, **2**, and ring b of **3**). Only some of the external ring angles are altered, e.g., decrease of O(2′)–C(2)–N(1) (118.6 (1)° in the free ligand, 120.5 (6)° av. in **1**, **2**) and increase of N(4′)–C(4)–N(3) (117.8 (1)° in the free ligand, 121.1 (6)° av. in **1**, **2**), and the C(2)–N(3) bond (1.358 (2) Å in free 1-MeC) is slightly lengthened in **1** and **2** (1.406 (8)–1.417 (9) Å). We suspect that the angle deformations are caused by steric interference of OH and NH_3 ligands with N(4′) and O(2′), rather than a genuine effect of the heavy metal.

Chelation of the 1-MeC$^-$ ring leads to only minor alterations in bond lengths (e.g., reversal of the above-mentioned increase in C(2)–N(3) distance, 1.343 (15) Å in **4**) but to considerable changes in angles. As compared to monodentate Pt binding via N(3), N(3), N(4) chelation affects the angles about N(3) the most: Pt–N(3)–C(4) is compressed by 25–29°, while Pt–N(3)–O(2) (by 20–22°) and the internal ring angle C(2)–N(3)–C(4) (by 5–8°) open up to compensate the angle deformation caused by Pt. At the C(4) position, the decrease in N(3)–C(4)–N(4′) (by ca. 15°) is accompanied by a similar increase in the C(5)–C(4)–N4′) angle. There are three more alterations in ring angles which, though smaller in magnitude than those at N(3) and C(4), are crystallographically significant: a decrease of the internal angle at C(5) by 3–5° and a simultaneous increase of the angle at C(6) by a similar value, and finally an increase in the N(3)–C(2)–O(2′) angle by 3–4°.

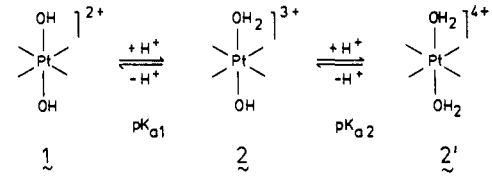
Table X. ^1H NMR Data of Pt^{II} Starting Complex and of Pt^{IV} Oxidation Products **1**–**4**[a,b]

	H(6)	H(5)	CH_3	pD
Pt^{II} complex[b]	7.65, d (7.3 Hz)	6.07, d, $^4J_{^{195}Pt-^1H}$ = 15.0 Hz	3.45, s	5.7
1	7.69, d (7.6 Hz)	5.98, d, $^4J_{^{195}Pt-^1H}$ = 11.7 Hz	3.44, s	2–5
2	7.71, d (7.4 Hz)	5.97, d, $^4J_{^{195}Pt-^1H}$ = 12 Hz	3.47, s	3.5 N DNO_3
3	7.61, d (7.6 Hz), $^5J_{^{195}Pt-^1H}$ = 3.9 Hz	5.67, d	3.42, s	5.5
	7.67, d (7.3 Hz)	5.88 d, $^4J_{^{195}Pt-^1H}$ = 10.2 Hz		
4	7.69, d (7.5 Hz)	5.65, d[c]	3.42, s	2.7

[a] In D_2O; shifts in ppm (δ scale) relative to TSP. [b] Pt^{II} starting compound *trans*-$[Pt(NH_3)_2(1\text{-MeC})_2](NO_3)_2$. [c] Coupling with ^{195}Pt not observed due to low concentration of **4**.

Solution Behavior of 1 and Chelate Formation. The ^1H NMR chemical shifts and coupling constants of **1** in D_2O are listed in Table X. As compared to the Pt^{II} starting compound *trans*-$[Pt(NH_3)_2(1\text{-MeC})_2](NO_3)_2$, CH_3 and H(5) resonances of the 1-MeC rings are shifted upfield in 1 (0.01 and 0.10 ppm), while H(6) is shifted downfield (0.04 ppm). The $^4J_{^{195}Pt-^1H(5)}$ value of **1** (11.7 Hz) is smaller than that of the Pt^{II} compound (15.5 Hz), an expected consequence of the differences in metal oxidation states.[26]

There are no changes in chemical shifts of resonances of **1** down to pD 0, which indicates that the 1-MeC ligands are not protonated. Even in 3.5 N DNO_3, H(6) and CH_3 resonances exhibit a slight downfield shift only, 0.02 and 0.03 ppm. However, heating of this solution (90 °C) results in displacement of cytosine ($\tau_{1/2} \simeq 7$ min) which then is present in solution in its monoprotonated form 1-MeCH$^+$. Potentiometric titration of **1** with HNO_3 down to pH 1 does not reveal protonation of the OH ligands either. We conclude that the protonation process below occurs only well below



1 **2** **2′**

pH 1, hence the protonated forms **2** and **2′** are strong acids, unlike $[Pt(NH_3)_5(OH_2)]^{4+}$, for example, which has a pK_a value of 4.[27] This finding is in agreement with the experimental result that isolation of **2** requires strongly acidic conditions. It is noted that in the related nucleobase complex of 9-methyladenine, *trans*-$[Pt(OH)_2(NH_3)_3(9\text{-MeA})]^{3+}$, the hydroxo ligands are protonated also only below pH 1.[28]

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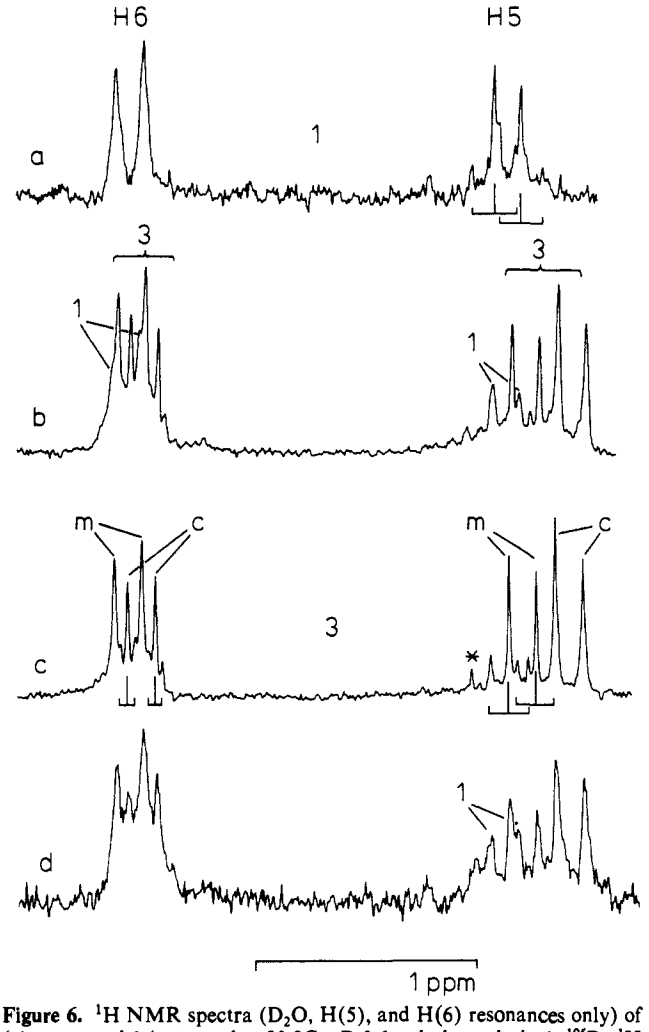

Figure 6. ^1H NMR spectra (D_2O, H(5), and H(6) resonances only) of (a) compound **1** (saturated at 22 °C, pD 3.6, colorless solution); ^{195}Pt–^1H coupling satellites are indicated; (b) spectrum a after 3 min at 90 °C (pD unchanged, slightly yellow solution); within 18 h after warming precipitation of **4** occurs; (c) isolated **3** (0.08 M, pD 5.5) immediately after dissolving; resonances due to chelating (c) and monodentate (m) cytosine rings and ^{195}Pt–^1H coupling satellites are indicated; the asterisk denotes an unidentified species; (d) spectrum c after 5 days at 22 °C; the sample contains precipitated **4**.

Potentiometric titration of **1** with NaOH (up to pH 10) does not indicate any deprotonation of NH_3 groups and/or cytosine amine groups. This behavior contrasts the sometimes considerable acidities of ammonia ligands coordinated to Pt^{IV}, e.g., ca. 7 for pK_{a1} of $[Pt(NH_3)_6]^{4+}$.[29] From our data it is not possible to estimate the degree of NH_2 acidification as a consequence of Pt^{IV} binding to N(3), though we suspect that it might be higher than in the case of Pt^{II} where it has been found not to excede 2–3 log units.[30]

Rapid ^1H NMR spectroscopic changes of aqueous solutions of **1** were observed under the following conditions: (i) Slight to moderate acidification with acids containing weakly coordinating anions (DNO_3, CF_3COOD, pD 3–0.5), (ii) heating (50–90 °C) without addition of acid, and (iii) addition of DCl.

(i) ^1H NMR spectra (H(5), H(6) region only) of freshly dissolved **1** and after heating are compared in Figure 6 (a and b). After heating at least three sets of resonances can be distinguished which are assigned to **1** (1 set) and **3** (two sets, corresponding to 1-MeC and 1-MeC$^-$ ligands). The poor solubility of **4** in water does not permit a decision concerning its presence in the mixture, but **4** is formed as evident from its precipitation with time. The

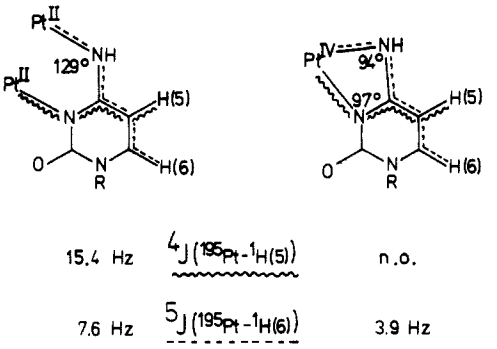

Figure 7. Coupling between the ^{195}Pt isotope and the aromatic ring protons in the head–tail (1-MeC$^-$) dimer of *cis*-$(NH_3)_2Pt^{II}$ (ref 21) and in the (1-MeC$^-$) chelate of Pt^{IV} in compound **3**.

^1H NMR spectrum of **3**, which is given in Figure 6c, reveals several interesting details: Shifts of both H(5) and H(6) resonances of the monodentate 1-MeC and the chelating 1-MeC$^-$ occur upfield from those of **1**. It was in particular the substantial upfield shift of one of the new H(5) doublets which suggested that deprotonation of the ligand must have occurred, since nucleobase stacking interactions as an alternative explanation seemed highly unlikely. The pH independence of the new resonances further ruled out any (fast) acid–base equilibrium.

The four-bond coupling constant ^4J between ^{195}Pt and H(5) in the termial, neutral cytosine ligand of **3** is 10.2 Hz and thus close to the value observed in **1**. However, no coupling is resolved for the H(5) signal of the chelating cytosinato ligand. With the H(6) resonances, things are reversed: While no coupling is observed for the terminal ligand, H(6) of the chelating ligand shows weak coupling ($^5J \simeq 3.9$ Hz) with the ^{195}Pt isotope. It is noted that in the dinuclear Pt^{II} complex containing deprotonated 1-methylcytosine ligands bridging through N(3) and N(4),[21] this value is almost twice as large ($^5J = 7.6$ Hz), which suggests that not only the differences in oxidation states but possibly also the small angle of 94° about N(4′) in **3** account for the weaker coupling in **3** (cf. Figure 7). Similarly, the small angle of 97° at N(3) may be the reason why the ^4J value becomes so small that the coupling satellites of H(5) of the 1-MeC$^-$ ligand are no longer resolved.

(ii) Qualitatively, the changes that occur if **1** is dissolved in diluted DNO_3 (e.g., pD 1.5) are similar to those described in (i). As early as 15–30 min after sample preparation (30 °C), signals of **3** grow at the expense of those of **1**. At the same time the originally colorless solution becomes slightly yellow. After 24 h at 30 °C, the spectrum is identical with that of a sample heated for a few minutes to 90 °C (cf. Figure 6b).

(iii) Treatment of **1** with hydrochloric acid leads to substitution of 1-MeC by Cl$^-$. For example, in 1 N DCl, within 5 days at 22 °C, approximately 95% of the originally bound 1-MeC has been replaced by Cl$^-$ as evident from ^1H NMR spectroscopy and the precipitation of the insoluble *trans*-$Pt(NH_3)_2Cl_4$.[31] Of these 95% released nucleobase and approximately one-third consist of 5-chloro-1-methylcytosine in its protonated form (^1H NMR, D_2O, pD 0:8.24 ppm, s (H(6)); 3.48 ppm, s (CH_3)). Since the amount of this modified nucleobase does not change once all cytosine has been displaced from the Pt complex, chlorination at the 5-position must have occurred while the cytosine ligand was still coordinated to Pt. It is consistent with this idea that in the NMR spectrum a second singlet at 8.02 ppm is observed which disappears with time and therefore is attributed to a 5-chloro-1-methylcytosine molecule still coordinated to Pt. We note, in this context, that we have isolated and characterized complexes of Pt^{IV} containing 5-chloro-1-methylcytosine ligands which were obtained through treatment of 1-methylcytosine complexes of Pt^{II} with Cl_2 gas,[32] in a way analogous to that described for related uracil complexes.[17]

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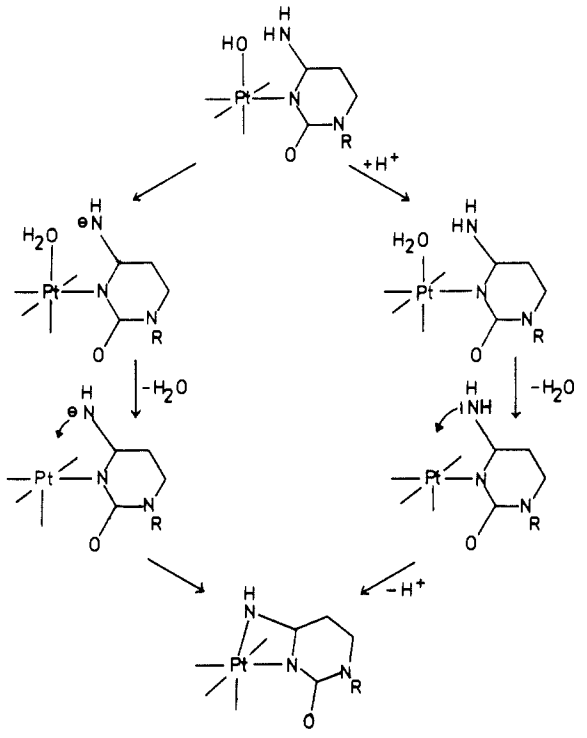

Figure 8. Feasible pathways for the formation of (1-MeC$^-$) chelates from complexes containing a monodentate (1-MeC) ligand and a OH group in the cis position.

Though substitution of the proton at C(5) by Cl^- may also be achieved in the absence of Pt by means of Cl_2,[33] the relatively mild conditions leading to chlorination of the complexed 1-MeC are noteworthy.

Displacement of 1-MeC or its 5-Cl derivative from **1** is markedly slowed down or even prevented at higher pH (1–2). Also, **3** appears to be converted in dilute HCl to a relatively stable complex that still contains the chelate ring. The composition of this compound is presently studied.

Solution Behavior of 3 and 4. The ^1H NMR spectrum of freshly dissolved **3**, which is shown in Figure 6c, changes within several days at room temperature (Figure 6d). The major new products are **1** (evident from NMR) and **4** (crystallization from solution). Formation of the equilibrium

$$\mathbf{1} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} \mathbf{3} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} \mathbf{4}$$

explains why recrystallization of **3** always yields a mixture of products, with reasonable yields of **3** obtainable only if the crystallization process of **3** is relatively fast. On the other hand, the isolation of **4** is facilitated by the fact that its solubility in water is so poor.

The bis(chelate) **4** requires heating to dissolve in water. Once dissolved, the spectrum again is qualitatively identical with those in b and d of Figure 6, with **3** being the major component, followed by **1** and possibly one or two additional minor products.

Chelate Formation. As to the possible mechanism of the interconversion **1** → **3** and **3** → **4**, two feasible ways are shown in Figure 8. The first one implies (i) proton abstraction from the exocyclic NH_2 group of 1-MeC by the OH ligand, (ii) loss of H_2O and formation of a five-coordinate intermediate, and (iii) intramolecular nucleophilic attack of the deprotonated N(4′) atom on Pt. An alternative route with (i) protonation of OH by added acid, (ii) loss of water, (iii) nucleophilic attack of NH_2 on Pt, and (iv) loss of H^+ seems to explain chelate formation in acidic medium better than the first way; however, it requires the postulate that N(4), despite its very low basicity, is quite nucleophilic. On the other hand, the low basicity of the OH group in **1** (cf. $pK_{a1} < 1$ for **2**) seems to rule against the first possibility and rather favor the second one.

In any case, it is important to recognize that chelate formation does not cause any change in pH and above all does not require alkaline conditions leading to a deprotonation of the exocyclic amino group of the cytosine ring. Previously reported substitution reactions of amino protons of cytosine and adenosine rings by CH_3Hg^+ occurred in alkaline medium if CH_3HgX (X = NO_3^-, ClO_4^-) was the starting material or directly from preformed CH_3HgOH.[34] Clearly, the lower acidity of $[CH_3Hg(OH_2)]^+$[35] as compared to $Pt^{IV}(OH_2)$ in **2** is responsible for this difference.

Raman Spectra of 1 and 1a. Observations[5d,6a] that H_2O_2 oxidation of Pt^{II} complexes may lead to perhydrate adducts have prompted us to study the vibrational spectra of compounds **1** and **1a** in more detail. While **1** does not exhibit any Raman band in the range expected for ν(O–O) of H_2O_2 (880 cm^{-1}),[36] which is consistent with the results of the crystal structure determination, compound **1a** has a moderately intense band in this range, at 867 cm^{-1}. In aqueous solution this band is shifted to 878 cm^{-1}. Because of superposition with other bands, the IR spectrum (solid state) is not very informative with regard to a differentiation between H_2O_2 in a skew or a trans-planar conformation. Moreover, at present we cannot fully rule out formulation of **1a** as a hydroperoxo complex of composition *trans,trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OOH)_2]Cl_2 \cdot 4H_2O$ rather than a hydrogen peroxide adduct, *trans,trans,trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2(OH)_2]Cl_2 \cdot 2H_2O_2 \cdot 2H_2O$, mainly because the differences in vibrational spectra between **1** and **1a** sem to be almost too big to be explained solely by differences in intermolecular hydrogen bonding due to the differing anions. However, substitution of Cl^- in **1a** by NO_3^- (via $AgNO_3$) results in formation of **1** containing no H_2O_2, and the ^1H NMR spectra of **1** and **1a** are identical.

Conclusion

The results reported in this paper appear to be significant for several reasons: (i) They represent a novel metal binding mode for a cytosine nucleobase previously not observed[9] and provide, for the first time, crystallographic evidence for chelate formation of a platinum electrophile with a nucleobase. On the basis of geometrical considerations, similar four-ring chelates of deprotonated nucleobases should in principle be possible for all naturally occurring bases, that is also for adenine (N(1),N(6)), guanine (N(1),N(2) or N(1),O(6)), and thymine or uracil (N(3),O(4) or N(3),O(2)). (ii) The crystal structure details of compounds **3** and **4** reveal an enormous angular flexibility about the Pt. Clearly, *sterical* arguments against certain metal binding patterns, e.g., N(7),O(6) chelate formation with guanine, need to be used carefully. (iii) Nucleobase deprotonation apparently is achieved in a condensation reaction between a hydroxo ligand and a very weakly acidic proton (here NH_2) of a nucleobase and takes place even in acidic solution. Reactions of this type certainly are not restricted to Pt^{IV}. (iii) Chelate formation of the type described may be an intermediate in a process leading to metal migration on the heterocyclic ring. It is feasible that under the influence of another nucleophile the N(3),N(4′) chelate of 1-MeC$^-$ opens in a way that only the metal–N(4′) bond is retained, hence the metal migrates from N(3) via N(3),N(4′) to N(4′).

Acknowledgment. We thank the Deutsche Forschungsge-

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meinschaft, the Fonds der Chemischen Industrie, the Technische Universität München, and Degussa for their support.

Registry No. 1, 102149-59-7; **1a**, 102210-45-7; **2**, 102149-62-2; **3**, 102149-65-5; **4**, 101181-55-9; *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2]Cl_2$, 102210-44-6; *trans*-$Pt(NH_3)_2Cl_2$, 14913-33-8; *trans*-$[Pt(NH_3)_2(1\text{-}MeC)_2](NO_3)_2$, 76068-67-2.

Supplementary Material Available: Listings of observed and calculated structure factors, atomic parameters, and structural details (64 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of the Bridging Thiocarbyne Radical, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^\bullet$

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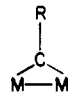
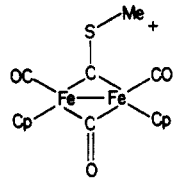
Abstract: The bridging thiocarbyne radical, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^\bullet$ (**2**), is prepared by a 1-electron reduction of the thiocarbyne cation, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^+$ (**1**), with sodium naphthalenide or electrochemically ($E^\circ = -0.78$ V vs. Ag/AgCl). The emerald green radical, **2**, which is sufficiently stable to be studied for an hour at 0 °C, has been characterized by its IR, UV-vis, and EPR spectra as well as its reactions with PhSSPh and PhSeSePh, which give $Cp_2Fe_2(EPh)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)$ and $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}C(SMe)EPh]$, where E = S or Se. Both the terminal and bridging CO groups of the radical, **2**, exchange rapidly with ^{13}CO at 0 °C; this contrasts with cation, **1**, which is inert under these conditions. The lability of the CO groups in **2** makes it a catalyst for the substitution of CO groups by PEt_3, PMe_2Ph, $PMePh_2$, and *t*-BuNC in **1** to form $Cp_2Fe_2(L)(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)^+$. Cyclic voltammetric studies of **1** in the presence of L suggest that **2** catalyzes these substitution reactions by a radical chain electron transfer mechanism.

Dinuclear transition-metal complexes containing a bridging carbyne ligand



are well-known,[1] and several reactions which occur at the carbyne carbon have been described.[1,2] Recently, we reported[3] the reaction of $Co(CO)_4^-$ with the bridging thiocarbyne complex



1

to give an unusual triply bridging thiocarbyne complex, $Cp_2Fe_2Co(CO)_3(\mu\text{-}CO)_2(\mu_3\text{-}CSMe)$. We noticed[3,4] that reactions with relatively strongly reducing metal carbonyl anions ($CpFe(CO)_2^-$, $Re(CO)_5^-$, and $Mn(CO)_5^-$) gave products which could be attributed to processes involving electron transfer from the anion to the thiocarbyne cation, **1**. In this paper, we report the 1-electron reduction of **1** to give the first example of a bridging dinuclear carbyne radical, $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)^\bullet$ (**2**), which has been characterized by its EPR, IR, and electrochemical properties. Radical **2** has also been identified as a key labile intermediate in the catalysis of CO substitution in **1** by chemical and electrochemical reducing agents.

Experimental Section

Unless stated otherwise, all manipulations were carried out under argon or deoxygenated nitrogen in Schlenkware at room temperature. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Acetonitrile, CH_2Cl_2, and hexane were stirred overnight with CaH_2 and then distilled under N_2. The complex $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSMe)]PF_6$ (**1**) was prepared by using a modification[4] of the method described by Quick and Angelici.[5] Solutions of sodium naphthalenide (NaNp) were prepared by stirring 1:1 molar ratios of sodium and naphthalene in THF.[6] The salt, NBu_4PF_6 (Bu = *n*-Bu), was prepared by a published procedure.[7] The phosphines, PEt_3, PMe_2Ph, and $PMePh_2$, were fractionally distilled and stored under N_2. A 1-L flask of 92 atom % ^{13}CO was obtained from U.S. Services, Inc., Summit, NJ. All other reagents were commercial products of the highest purity available and were used as received.

A Perkin-Elmer Model 320 or Beckman DU-8 spectrometer was used for measuring UV-visible spectra. Infrared spectra were recorded with a Perkin-Elmer 681 spectrometer. The IR spectra were referenced to the 1603.0-cm^{-1} band of polystyrene. The ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q or Nicolet NT-300 spectrometer and were taken in deuterated (>95.5%) solvents. Chemical shifts were reported in ppm downfield from the internal standard Me_4Si. Electron paramagnetic resonance (EPR) spectra were obtained on samples in CH_3CN (0.1 M NBu_4PF_6) or THF in a 60.0 × 17.0 × 0.25 mm flat quartz cell with a Bruker Model ER 2000-SRC spectrometer. Temperature control

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