from I has taken place in preference to CO loss.[10] Note that II itself reacts with 1 equiv of $PhMe_2P$ in a straightforward CO substitution reaction that yields $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$ as the only product. Thus the presence of the *endo*-hydrogens appears to provide I with a special mode of reactivity.

In the presence of $\geq$10-fold excess of $PhMe_2P$, I undergoes complete fragmentation. A first-order rate dependence on each of [I] and [$PhMe_2P$] was determined.[11] Thus, we suggest that the initial reaction of the ligand with the cluster substrate is an associative process leading to an adduct intermediate. Although we have no direct spectroscopic evidence for the latter, the formation of the final products can be rationalized in terms of the open-cluster intermediates shown in Scheme I. The addition of a pair of electrons supplied by the phosphorus donor should cause I to open from a tetrahedral to a "butterfly" geometry.[7,12] Further attack by $PhMe_2P$ causes fragmentation by cleavage of a butterfly "wing-tip". Thus, one pathway is defined by the formation of $PhMe_2P{\cdot}BH_3$ and $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]^-$[13] and provides a route to a specifically disubstituted derivative of $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$. This in itself is unusual since direct reaction of the latter with phosphine ligand is reported to lead to cluster fragmentation rather than to a substituted product,[14] although our own studies indicate that fragmentation is accompanied by a reaction yielding a mixture of substituted multimetal derivatives.[15] The second pathway generates $Fe(CO)_3(PhMe_2P)_2$ and an unstable phosphine-substituted ferraborane anion that we have not been able to isolate. Attempts to force the reaction specifically along a single fragmentation path have not been successful.

In conclusion, the reactions of I with Lewis bases not only emphasize the delicate balance between cluster substitution and degradation, but also show that, under mild conditions, I is subject to substitution via H_2 rather than CO elimination. In the latter pathway, ligand association is presumed to occur at the metal. Before cleavage of additional base can take place, the Fe_3B cluster extrudes two skeletal hydrogens and closes to the original tetrahedral form. In addition, we note that even under conditions of high ligand concentration where cluster degradation leads to the formation of $L{\cdot}BH_3$, the reaction is slower than when base L reacts with free BH_3 or even when L displaces a weaker base L′ from $L'{\cdot}BH_3$.[16] This, too, evidences the special nature of the cluster-bound BH_3 in I.

Acknowledgment. The support of the National Science Foundation (Grant CHE-84-08251) is gratefully acknowledged.

Registry No. I, 92055-45-3; PMe_2Ph, 672-66-2; NEt_3, 121-44-8; CO, 630-08-0; H_2O, 7732-18-5.

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(9) $[Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)BH_2]^-$: IR ν_{CO} (toluene, cm^{-1}) 2052 w, 1990 vs, 1963 s, 1934 m, 1872 m; ^{31}P NMR ($CD_3C(O)CD_3$, 20 °C) δ 30.2 (m, 1 P); ^{11}B NMR ($CD_3C(O)CD_3$, −20 °C) δ 56.8 (br, dd, $\{^1H\}J_{BH} \approx 140$ Hz (terminal), $J_{BH} \approx 40$ Hz (bridge)); ^1H NMR ($CD_3C(O)CD_3$, −20 °C) δ 7.49–7.37 (m, 5 H, *Ph*Me_2P), 1.25 (m, 6 H, Ph*Me*$_2$P), 6.0 (br, 1 H, terminal BH), −11.6 (br, 1 H, Fe–H–B).

(10) We have noted that H_2 elimination is a prominent feature of another reaction of I: Housecroft, C. E.; Fehlner, T. P. *Organometallics* **1986**, *5*, 379.

(11) [I]PPN (0.192 mmol) in acetone (6.0 mL) was divided into four equal aliquots and each was reacted with $PhMe_2P$: 0.48, 0.96, 1.44 and 1.44 mmol respectively. Each reaction was followed by ^{11}B NMR for a period of 2–3 half-lives; ^{11}B NMR integrals were used as measures of [I]. The overall second-order rate constant was determined as 0.074 $M^{-1}\,min^{-1}$ at 30 °C.

(12) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(13) $[(\mu\text{-}H)Fe_3(CO)_8(\mu\text{-}CO)(PhMe_2P)_2]^-$ exhibits a characteristic resonance at δ −14.3 in the ^1H NMR spectrum close to that of the unsubstituted $[(\mu\text{-}H)Fe_3(CO)_{10}(\mu\text{-}CO)]^-$ (δ −14.75).

(14) Lourdichi, M.; Pince, R.; Dahan, F.; Mathieu, R. *Organometallics* **1983**, *2*, 1417.

(15) Housecroft, C. E., unpublished observations.

(16) Fehlner, T. P. In "Boron Hydride Chemistry"; Muetterties, E. L., Ed., Academic Press: New York, 1975; p 175.

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Structural Characterization of Two Isomeric Hydrazido(2–) Intermediates in the Conversion of Molybdenum-Bound Dinitrogen to Ammonia and Hydrazine[1]

Sir:

The hydrazido(2–) (NNH_2) ligand is the only nitrogen–hydride intermediate to be detected or isolated from the reactions of bis(dinitrogen) complexes of molybdenum that form ammonia and hydrazine.[2,3] The reactions of *trans*-$[Mo(N_2)_2(triphos)(PPh_3)]$ (**1**), where triphos = $Ph_2P(CH_2CH_2PPh_2)_2$, with anhydrous HCl and HBr in a variety of organic solvents lead to ammonia and hydrazine in varying yields.[4-6] In all of these latter reactions two isomeric hydrazido(2–) complexes ($[MoX(NNH_2)(triphos)(PPh_3)]X$ where X = Br or Cl) are formed during the reaction. Examples of these isomers have been separated and shown to behave differently in reactions with acid. On the basis of these differences in chemistry, we originally assigned one isomer (**A** isomer) as having coordinated X trans to [NNH_2] and the other isomer (**B** isomer) as having PPh_3 trans to [NNH_2].[5] A recent crystal structure of an **A** isomer and a **B** isomer revealed a much more subtle difference that results from the configuration at the center phosphorus atom of the triphos ligand and not an interchange of ligands.

The reaction of anhydrous HCl with solid **1** gave $[MoCl(NNH_2)(triphos)(PPh_3)]Cl$, as a mixture of **2A** and **2B**, as reported previously.[5] $PPhMe_2$ (4-fold excess) was added dropwise with swirling to a brown-green toluene solution of the mixture of **2A** and **2B**. This solution was allowed to stand under N_2 for 15 h, at which time solvent was decanted from the amber, coffin-shaped crystals.[7] The crystals were washed in the flask with toluene (3 × 15 mL) and pentane (15 mL) and suction-filtered with use of a water aspirator. The yield of crystals of $[MoCl(NNH_2)(triphos)(PPh_3)]Cl$ (**2A**)[8] suitable for X-ray diffraction studies was 9.6%. (Usual yields of **2A** as a powder were 20%.)

In a similar experiment, PPh_2Me was added to a solution of **2A** and **2B** in toluene. After isolation of **2A** as a powder, the filtrate volume was reduced by 50%. After the mixture was allowed to sit under N_2 for 18 h, the solvent was decanted from the olive green, layered-looking rectangular prisms of $[MoCl(NNH_2)(triphos)(PPh_2Me)]Cl$ (**2B′**),[9] which were washed with toluene (3 × 15 mL) and pentane (15 mL) and suction-dried; yield 14%. This same complex together with the **A** isomer analogue was observed in the $^{31}P\{^1H\}$NMR spectrum of a solution of $Mo(N_2)_2(triphos)(PPh_2Me)$ in THF solution after treatment with

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(1) (a) Reactions of Coordinated Dinitrogen. 17. (b) Part 15: George, T. A.; Howell, D. B. *Inorg. Chem.* **1984**, *23*, 1502–1503.

(2) (a) Anderson, S. N.; Fakley, M. E.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1981**, 1973–1980. (b) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197–292.

(3) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461–7467.

(4) Baumann, J. A.; George, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 6153–6154.

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(7) In the absence of $PPhMe_2$ and acid, **2A** precipitates and **2B** slowly decomposes in solution. $PPhMe_2$ reacts with **2B** to form $[MoCl(NNH_2)(triphos)(PPhMe_2)]Cl$, which remains in solution and does not react further to give ammonia under these conditions. There is no evidence that **2A** and **2B** are interconvertible.

(8) For elemental analysis and $^{31}P\{^1H\}$ and ^1H NMR data, see ref 5.

(9) Anal. Calcd for $C_{47}H_{48}Cl_2MoN_2P_4{\cdot}0.5C_7H_8$: C, 62.04; H, 5.36; N, 2.87. Found: C, 62.23; H, 5.54; N, 2.11. $^{31}P\{^1H\}$NMR [80.984 MHz, CD_2Cl_2, 23 °C, $PhP_a(CH_2CH_2P_bPh_2)_2$, Ph_3P_x, $^2J_{P_aP_b} = 0.0$ Hz]: 68.97 (d, $^2J_{P_aP_x} = 169.1$ Hz, P_a), 35.52 (d, $^2J_{P_bP_x} = 18.4$ Hz, P_b), 7.32 ppm (dt, P_x). Chemical shifts (ppm) are referenced to 85% H_3PO_4, and positive values are downfield.

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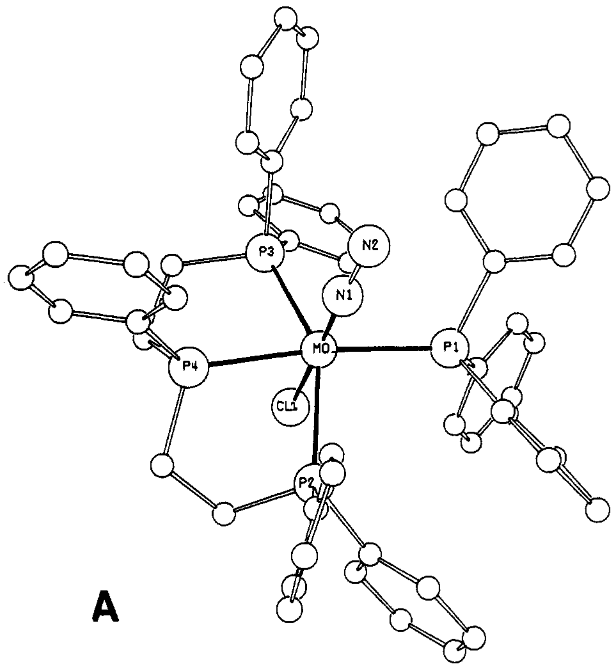

Figure 1. Perspective view of the structure of the cation [MoCl(NNH$_2$)(triphos)(PPh$_3$)]$^+$ of **2A**. Selected bond lengths (Å) and angles (deg) are as follows: Mo–N1 = 1.694 (12), Mo–P1 = 2.556 (4), Mo–P2 = 2.564 (4), Mo–P3 = 2.506 (4), Mo–P4 = 2.475 (4), Mo–Cl = 2.503 (4), N1–N2 = 1.34 (2); P1–Mo–P2 = 95.9 (1), P1–Mo–P3 = 106.3 (1), P1–Mo–P4 = 172.9 (1), P1–Mo–N1 = 85.8 (4), P1–Mo–Cl = 91.4 (1), P1–Mo–P3 = 148.2 (1), P2–Mo–P4 = 77.7 (1), P2–Mo–N1 = 108.7 (4), P2–Mo–Cl = 79.1 (1), P3–Mo–P4 = 78.5 (1), P3–Mo–N1 = 95.6 (4), P3–Mo–N1 = 99.1 (4), P4–Mo–Cl = 84.4 (1), N1–Mo–Cl = 171.9 (4), Mo–N1–N2 = 172.2 (11).

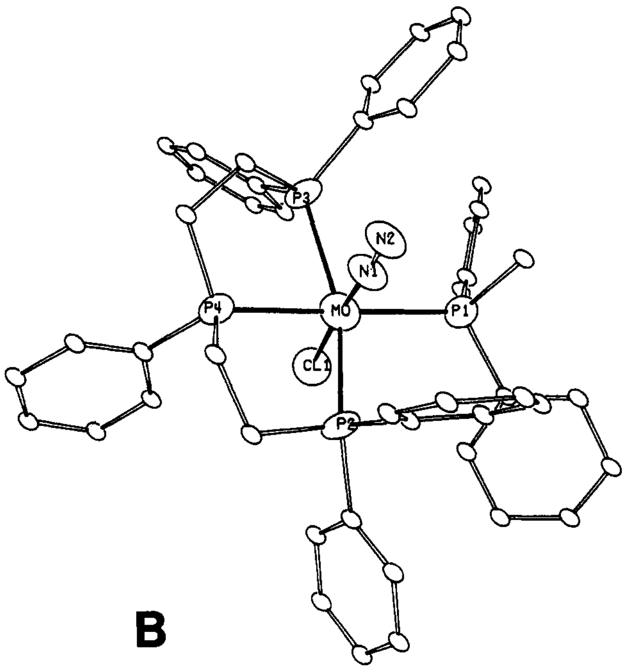

Figure 2. Perspective view of the structure of the cation [MoCl(NNH$_2$)(triphos)(PPh$_2$Me)]$^+$ of **2B′**. Selected bond lengths (Å) and angles (deg) are as follows: Mo–N1 = 1.778 (18), Mo–P1 = 2.552 (7), Mo–P2 = 2.513 (7), Mo–P3 = 2.475 (4), Mo–P4 = 2.475 (4), Mo–Cl = 2.479 (7), N1–N2 = 1.31 (2), P1–Mo–P2 = 101.7 (2), P1–Mo–P3 = 99.1 (2), P1–Mo–P4 = 176.7 (3), P1–Mo–N1 = 94.0 (6), P1–Mo–Cl = 83.3 (2), P1–Mo–P3 = 157.0 (2), P2–Mo–P4 = 80.6 (2), P2–Mo–N1 = 82.2 (6), P2–Mo–Cl = 96.8 (2), P2–Mo–P4 = 79.1 (2), P3–Mo–N1 = 86.7 (6), P3–Mo–Cl = 95.3 (2) P4–Mo–N1 = 88.7 (6), P4–Mo–N1 = 88.7 (6), P4–Mo–Cl = 94.1 (2), N1–Mo–Cl = 176.9 (6), Mo–N1–N2 = 178.1 (15).

HCl. The only noticeable difference between the $^{31}P\{^1H\}$ NMR spectra of **2B** and **2B′** was the chemical shifts of the monodentate phosphines; those for the triphos phosphorus atoms and the coupling constants showed very little change and significantly less than the differences between **2A** and **2B**, for example.

Extensive studies of **2B′** with HBr and HCl in various solvents have revealed no major differences in the relative yields of ammonia and hydrazine when compared with similar reactions of a mixture of **2A** and **2B** although the absolute yields are generally less.[10] The absolute yields of products further decreased for the analogous complex containing PMe$_2$Ph. In solution, $^{31}P\{^1H\}$ NMR studies of **2B**, **2B′**, and the PMe$_2$Ph analogue (also prepared by phosphine exchange) have shown that the relative rate of PR$_3$ dissociation in the absence of acid is PPh$_3$ >> PPh$_2$Me >> PMe$_2$Ph; generally the amount of nitrogen reduction follows the same order.

The structures[11] of the molecular cations [MoCl(NNH$_2$)(triphos)(PPh$_3$)]$^+$ of **2A** and [MoCl(NNH$_2$)(triphos)(PPh$_2$Me)]$^+$ of **2B′** are shown in Figures 1 and 2. Crystals of **2B′** contain two molecules of solvation: one each of toluene and pentane per molecule of **2B′**. Both complexes display similar pseudooctahedral coordination environments about the Mo atom, with the four phosphorus donors of the triphos and the monodentate phosphine defining the equatorial plane about the molybdenum, while the chloride donor and N1 of the end-on hydrazido(2−) ligand occupy axial positions. In either case, the Mo–N1 distance is short and the N1–N2 distance is intermediate between calculated single and double bond distances, indicating a high degree of delocalization and significant multiple-bond character throughout the Mo–N1–N2 moiety. A notable structural difference between **2A** and **2B′** is the relative configuration at the central phosphorus donor of the triphos ligand, P4. In **2A**, the phenyl ring attached to P4 is syn to the N1–N2 group relative to the P1P2P3P4 plane, whereas in **2B′** the configuration at P4 is inverted to produce the anti orientation. The most apparent geometrical variation is the difference of ca. 0.36 Å in the position of Mo relative to the phosphorous planes of **2A** and **2B′**. While the Mo atom is displaced 0.28 Å from the phosphorus plane toward N1 in **2A**, the Mo atom has moved 0.08 Å below the phosphorous plane in **2B′** in the direction of the coordinated chloride. The angles involving the triphos P donors with Mo and N1 also reflect the orientation of the central phenyl group; thus, in **2A** the triphos P–Mo–N1 angles are obtuse, presumably to minimize steric interaction between the phenyl group and the hydrazido(2−) ligand, while in **2B′** the angles are acute. An intriguing structural feature of **2A** is the orientation of a phenyl group on each of P2, P3, and P4 so as to provide a pocket for the hydrazido(2−) group. In contrast, the hydrazido group in **2B′** occupies a much less sterically congested site.

The chloride counterion in **2B′** is located above P1 and is hydrogen-bonded to a hydrazido(2−) hydrogen atom whereas in **2A** no such hydrogen-bonding is observed.

To our knowledge, only one other example has been reported of isomers resulting from the orientation of this phenyl group in a six-coordinate triphos-containing complex. This involved the complex *cis*-[RuH(P(OMe)$_3$)$_2$(triphos)][BF$_4$].[12]

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(10) Until very recently we were unable to separate **2A** and **2B**. Therefore, the ammonia- and hydrazine-forming reactions were carried out with a mixture of **2A** and **2B** and compared to similar studies with pure **2B′**.

(11) Crystal data are as follows. MoC$_{52}$H$_{50}$N$_2$P$_4$Cl$_2$ (**2A**): monoclinic space group $P2_1$ with a = 13.714 (2) Å, b = 13.924 (2) Å, c = 14.279 (3) Å, β = 102.44 (1)°, V = 2662.6 (11) Å^3 to give D_{calcd} = 1.24 g·cm^{-3} for Z = 2. The structure solution and refinement are based on 2457 independent reflections with $I_o \geq 3\sigma(I_o)$ (Mo Kα, λ = 0.71069 Å; μ = 4.92 cm^{-1}). The current discrepancy factor is 0.0689. MoC$_{59}$H$_{66}$N$_2$P$_4$Cl$_2$ (**2B′**): triclinic space group $P\bar{1}$ with a = 12.922 (2) Å, b = 13.552 (3) Å, c = 18.067 (4) Å, α = 106.04 (1)°, β = 107.65 (1)°, γ = 97.22 (1)°, V = 2820.7 (14) Å^3 to give D_{calcd} = 1.29 g·cm^{-3} for Z = 2. Structure solution and refinement, based on 2672 reflections with $I_o \geq 3\sigma(I_o)$ (Mo Kα, μ = 4.70 cm^{-1}), converged at a conventional residual factor of 0.0833.

(12) Letts, J. B.; Mazanec, T. J.; Meek, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 3898–3905.

One consequence of the configuration at P4 is the nonequivalence of the two N_2 ligands in **1**. This is manifested in the preferential protonation of the less hindered N_2 ligand, as previously noted.[5]

There are significant differences in the reactivity of the **A** and **B** isomers as illustrated by (i) their reactions with acid to produce ammonia and hydrazine,[5] (ii) addition of NEt_3 (2 mol) to a **B**[13] isomer in CH_2Cl_2 solution at room temperature resulting in the immediate loss of all nitrogen as N_2 but a similar result not occurring with **2A**, and (iii) the lability of PPh_3 to exchange in **2B** but not **2A**. Presently, it is not obvious how these differences arise. One notable feature about the solid-state structure of **2B′** is the open volume above P4 in the coordination sphere.

Work is in progress to delineate this problem and understand why the **B** isomers favor hydrazine formation whereas the **A** isomers favor ammonia formation in solvents of low dielectric constant.[14]

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE83-05478.

Supplementary Material Available: For **2A** and **2B′**, fully numbered molecular structure projections and listings of final atomic coordinates and isotropic thermal parameters (15 pages). Ordering information is given on any current masthead page.

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(13) Carried out by using $[MoCl(NNH_2)(triphos)(PPhMe_2)]Cl$.[5]

(14) A full report of the structural data and allied chemistry will be submitted for publication in *Inorg. Chem.*

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Received December 17, 1985

Facile Substitution of NH_3 Ligands in a Diplatinum(III) Complex of 1-Methyluracil

Sir:

The degree of inertness of amine ligands in *cis*-diamineplatinum complexes and its possible relevance in biological systems, specifically with regard to the mode of action of Pt antitumor agents, still are a matter of debate. While there has been a report on the release of amine from dichloro(ethylenediamine)platinum(II) under in vivo conditions,[1] similar in vitro studies have provided no evidence for an amine labilization on binding of *cis*-diamineplatinum(II) complexes to DNA.[2,3] On the other hand, in model systems the replacement of NH_3 or other amine ligands from platinum complexes has been shown to occur occasionally, e.g. on reaction with poly(A),[4] during the reaction of *cis*-$(NH_3)_2Pt(H_2O)_2^{2+}$ with pyrimidine nucleobases leading to "platinum blues",[5] or in the presence of S-containing ligands such as methionine.[6] Recently, we could demonstrate by X-ray analysis the conversion of *cis*-$[(NH_3)_2Pt(MeC)Cl]Cl$ (MeC = 1-methylcytosine) into *trans*-$(NH_3)Pt(MeC)Cl_2$[7] and further that via this route formation of tris(nucleobase) complexes of Pt(II) is possible.[8]

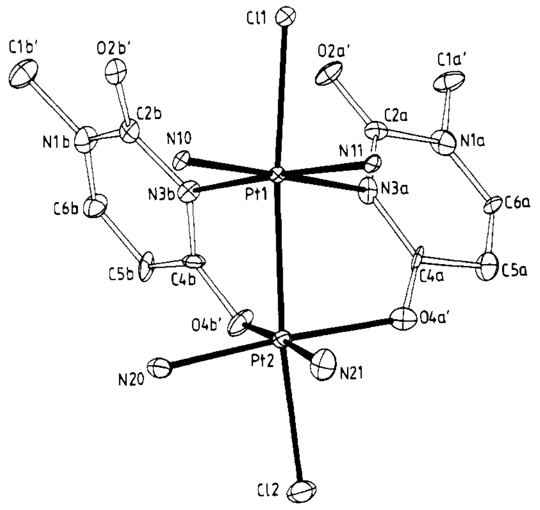

Figure 1. Molecular structure of the cation of $[Cl(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2Cl]Cl_2\cdot3.5H_2O$ (**2**).

We herewith wish to report yet another example of NH_3 replacement from a platinum coordination compound, the facile substitution of two cis-arranged ammonia ligands in a diplatinum(III) complex containing bridging 1-methyluracil ligands in a head–head orientation. Reaction occurs in 1 N HCl solution at room temperature or at 3 °C. Interestingly, only the two NH_3 groups trans to the two coordinating O4 oxygens of the two 1-MeU ligands are replaced by chloride, yet the NH_3 ligands trans to the N3 sites are not.

The two diplatinum(III) complexes described here were prepared via another diplatinum(III) precursor, *cis*-$[(NO_2)(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2](NO_3)_3\cdot H_2O$ (head–head) (**1**),[9] which was obtained from the diplatinum(II) complex *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2](NO_3)_2$ (head–head)[10] through oxidation with concentrated HNO_3. The identity of **1** has been established by elemental analysis and X-ray crystallography.[11] **1** is unusual in the sense that it is the first structurally characterized diplatinum(III) complex with unequal coordination numbers (6 and 5) of the two Pt atoms.

cis-$[Cl(NH_3)_2Pt(1\text{-}MeU)_2Pt(NH_3)_2Cl]Cl_2\cdot3.5H_2O$ (**2**) was prepared as follows: 100 mg of **1** was dissolved in 1.5 mL of 1 N HCl; the resulting yellow solution was centrifuged from any undissolved material and then allowed to evaporate in air at 22 °C. After 24 h, 65 mg of orange cubes of **2** was collected.[12,13] Slow evaporation (several days) of the filtrate gave other products as well, two of which (*cis*-$(NH_3)_2PtCl_4$ and neutral 1-MeUH) were identified by IR spectroscopy.

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(9) 1-MeU is the monoanion of 1-methyluracil, 1-MeUH.

(10) Lippert, B.; Neugebauer, D.; Raudaschl, G. *Inorg. Chim. Acta* **1983**, *78*, 161.

(11) Lippert, B.; Schöllhorn, H.; Thewalt, U., *J. Am. Chem. Soc.*, in press.

(12) Crystal data for **2** at −120 °C: a = 20.813 (5) Å, b = 14.266 (3) Å, c = 17.704 (4) Å, β = 97.13 (2)°, V = 5216.0 Å^3, monoclinic system, space group $I2/c$, Z = 8, ρ_{calcd} = 2.303 g cm^{-3}. Of the 6493 independent reflections (Phillips PW-1100 diffractometer, −120 °C, λ = 0.71069 Å, $\theta/2\theta$ technique with θ_{max} = 28°, Lp and empirical absorption corrections), 4700 reflections with $F_o > 2\sigma_{F_o}$ were used and gave a final R = 0.056. The SHELX program package was used for the calculations. The coordinates of the Pt atoms were taken from Patterson maps; the other non-hydrogen atoms were located by subsequent ΔF syntheses. All atoms, except the water oxygens, were refined anisotropically. Elemental analysis[13] and density measurements (ρ_{obsd} = 2.35 in CH_3I/CH_2I_2) favor formulation of **2** as a 4.5-hydrate. Crystallographically, only 3.5 water molecules were found, but we cannot exclude the possibility of an additional, disordered water molecule present, e.g. at x = 0.1885, y = 0.0632, z = 0.7324. Although we also considered the possibility that two different modifications of **2** might be present, determinations of cell constants of several samples originating from different preparations did not confirm such an assumption.

(13) Anal. Calcd for $[Cl(NH_3)_2Pt(C_5H_5N_2O_2)]_2Cl_2\cdot4.5H_2O$: C, 12.89; H, 3.36; N, 12.03; O, 14.60; Cl, 15.22; Pt, 41.89. Found: C, 12.89; H, 3.27; N, 12.25; O, 14.55; Cl, 15.40; Pt, 41.9.

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