Inorg. Chem. 1984, 23, 1713–1718 1713

Table I gives important bond distances and angles. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material. Figure 1 shows the structure and atom-numbering scheme.

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Registry No. 1 (R = Et, R′ = Me), 86502-52-5; 1 (R = Et, R′ = H), 86502-53-6; 1 (R = Et, R′ = Cl), 86502-54-7; 1 (R = Me, R′ = H), 89746-68-9; 2, 89746-63-4; 3, 89746-64-5; 4, 89746-65-6; 5, 89746-66-7; 6, 89746-67-8; HCl, 7647-01-0; HBr, 10035-10-6.

Supplementary Material Available: Details of the X-ray procedures and tables of general temperature expressions, bond angles, bond distances, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Contribution from the Anorganisch-Chemisches Institut,
Technische Universität München, 8046 Garching, FRG

Tridentate 1-Methyluracil in a Tetranuclear Pt_2,Ag_2 Complex. Crystal Structure and Solution Behavior of Bis(μ_3-1-methyluracilato)bis(*cis*-diammineplatinum(II))disilver Tetranitrate–2-Water (Head–Tail), *cis*-$[(NH_3)_2Pt(C_5H_5N_2O_2)Ag]_2(NO_3)_4 \cdot 2H_2O$

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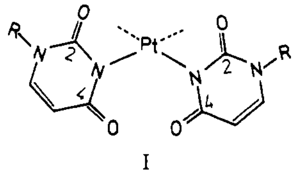
The interaction of a mono- and a dinuclear complex of *cis*-$(NH_3)_2Pt^{II}$ containing the 1-methyluracil anion ligand, 1-MeU, *cis*-$[(NH_3)_2Pt(1\text{-MeU})H_2O]^+$ (**1**) and *cis*-$[(NH_3)_2Pt(1\text{-MeU})]_2^{2+}$ (head–tail) (**2**), with $AgNO_3$ in aqueous solution has been studied by ^1H NMR spectroscopy, and two heteronuclear complexes containing Pt(II) and Ag(I) bound to 1-MeU have been isolated and characterized. The crystal structure of the head–tail Pt(II) dimer derivative has been determined. *cis*-$[(NH_3)_4Pt_2(C_5H_5N_2O_2)_2Ag_2](NO_3)_4 \cdot 2H_2O$ crystallizes in the monoclinic space group $C2/c$ with 4 formula units in a cell having dimensions $a = 13.810$ (2) Å, $b = 16.279$ (2) Å, $c = 11.871$ (2) Å, and $\beta = 95.58$ (1)°. The structure has been refined on 1797 reflections to $R = 0.051$ and $R_w = 0.056$. The two ligands are arranged in head–tail fashion. Each 1-MeU ligand bridges two *cis*-$(NH_3)_2Pt^{II}$ through N(3) and O(4) and at the same time is bound to Ag through O(2). Thus, the 1-MeU ligands are tridentate, binding two Pt(II) and one Ag(I). The four heavy atoms are lined up within the molecular cation, giving rise to intramolecular distances of 2.892 (1) Å for Pt–Pt and 2.853 (2) Å for Pt–Ag. Adjacent cations are related by a C_2 symmetry operation, leading to an intermolecular Ag–Ag separation of 3.954 (3) Å, with nitrate ions bridging neighboring Ag atoms. The Pt coordination spheres show some deviation from pure square-planar toward a distorted tetrahedral geometry. The second heteronuclear complex that has been isolated is *cis*-$[(NH_3)_2(ONO_2)Pt(C_5H_5N_2O_2)Ag]NO_3$. It contains Pt(II) bound to the 1-MeU ligand through N(3) and Ag(I) coordinated through O(4) and/or O(2). IR and Raman spectra are used to support this interpretation, and the usefulness of vibrational spectroscopy for the study of heteronuclear $Pt_xAg_yL_z$ complexes is critically examined. ^1H NMR spectroscopy has been used to study the effect of Ag(I) on the equilibrium $2cis\text{-}[(NH_3)_2Pt(1\text{-MeU})D_2O]^+ \rightleftharpoons [(NH_3)_2Pt(1\text{-MeU})]_2^{2+}$ (head–tail). The results indicate a competition between Ag(I) and Pt(II) for O(4) of 1-MeU, very much as in the system Ag(I)/*cis*-$[(NH_3)_2Pt(1\text{-MeU})]_2^{2+}$ (head–head).

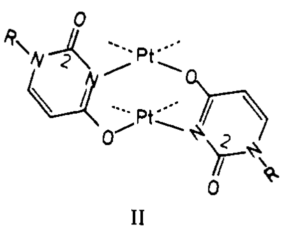
Introduction

In the course of our studies on the coordinating properties of the *cis*-diammineplatinum(II) residue toward the model nucleobases 1-methyluracil and 1-methylthymine and the interaction of the products formed with additional metal ions, we have thus far isolated and structurally characterized three types of heteronuclear complexes. These compounds are of Pt,M,L_2; Pt_2,M,L_4; and Pt_4,M,L_4 stoichiometries, with Pt representing *cis*-$(NH_3)_2Pt^{II}$, M the heterometal, and L the monoanion of 1-methyluracil, 1-MeU, and 1-methylthymine, 1-MeT, respectively (counterions omitted).[2-4] All three types of compounds (I) are derivatives of *cis*-$(NH_3)_2PtL_2$ and are obtained on subsequent reaction with a second *cis*-$(NH_3)_2Pt^{II}$ and/or other heterometal ions. Coordination of the second and third metal occurs stepwise, with occupation of the exocyclic oxygens of L taking place in pairs, e.g. O(4),O(4) and O(2),O(2). Formation of these heteronuclear complexes may be attributed to two factors: the favorable stereochemical arrangement of the four exocyclic oxygens for metal coordination and the increased basicities of these sites as a consequence of Pt(II) replacing the proton at N(3) of 1-methyluracil and 1-methylthymine.[3a,5]



I

The present study has been undertaken to separate these two factors by studying the ligating properties of the head–tail dimer *cis*-$[(NH_3)_2Pt(1\text{-MeU})]_2(NO_3)_2$ toward Ag(I). In this dimer (II), the structure of which has been reported by Faggiani et al.,[6] the only oxygens available for additional metal binding, O(2), are too far away to accommodate any joint intramolecular interaction for binding of a third metal ion. Consequently, any metal binding to these sites should be attributed essentially to the influence of the electron distribution in the N(3),O(4)-bridged 1-methyluracilato ligand.



II

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(1) On leave from the Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, 79 Ulm, FRG.

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Moreover, the present study provided an opportunity to investigate the effect of Ag(I) on the solution equilibrium of the head–tail dimer with its mononuclear precursor *cis*-$[(NH_3)_2Pt(1\text{-}MeU)H_2O]^+$, which has recently been reported by us in the absence of Ag(I).[7]

Experimental Section

Preparation. *cis*-$[(NH_3)_2Pt(1\text{-}MeU)H_2O]NO_3$ and both the head–head and the head–tail dimers *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2$ were prepared as previously described.[7]

cis-$[(NH_3)_4Pt_2(1\text{-}MeU)_2Ag_2](NO_3)_4{\cdot}2H_2O$ was obtained as follows: A 50-mg sample of the head–tail dimer (trihydrate) was dissolved in 1 mL of water, and 150 mg of $AgNO_3$ was added. The yellow sample (pH 5) was centrifuged and ketp at 3 °C. After 5 days, 60 mg of the Pt_2,Ag_2 product was collected on a filter as yellow, transparent columns; yield 88% based on Pt. Anal. Calcd for $Pt_2Ag_2C_{10}H_{26}N_{12}O_{17}$: C, 9.94; H, 2.17; N, 13.91; Ag, 17.85. Found: C, 10.31; H, 2.15; N, 14.10; Ag, 17.8.

If cocrystallization of the head–head dimer and $AgNO_3$ was performed in a more dilute solution (2-mL volume) and over a longer period of time (10 days), the yield of the Pt_2,Ag_2 product was lower and, after initial filtration of several crops of it, a colorless, crystalline material was obtained in low yield. This material has been identified by elemental analysis and by IR and Raman spectroscopy as *cis*-$[(NH_3)_2(ONO_2)Pt(1\text{-}MeU)Ag]NO_3{\cdot}H_2O$. It was isolated in high yield (85%) on cocrystallization of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)H_2O]NO_3$ with a (4–8)-fold excess of $AgNO_3$ at 3 °C as colorless microcubes. Anal. Calcd for $PtAgC_5H_{13}N_6O_9$: C, 9.94; H, 2.17; N, 13.91; Ag, 17.85. Found: C, 9.89; H, 2.06; N, 13.73; Ag, 19.4. Formulation as 1.1 Ag per Pt fits the Ag value better, which suggests that under the high-concentration conditions of crystallization the product may contain more than 1 Ag per Pt.

Spectra. ^1H NMR spectra were recorded on a JEOL JNM-FX 60 FT NMR spectrometer in D_2O as previously described.[5] IR spectra were recorded on a Perkin-Elmer 580 grating spectrometer as KBr pellets and Nujol mulls (CsI windows). Raman spectra were recorded on a Coderg PH 1 instrument with krypton laser excitation (647.1 nm; 20–200 mW depending on the sample stability). Raman intensities reported in Table V refer to signal heights. pD values were obtained by adding 0.4 to the pH meter reading unless Ag(I) was present. Then, approximate pD values were determined by means of pH indicator paper.

Crystallography. A crystal of dimensions 0.12 × 0.20 × 0.22 mm³ was mounted in a Lindemann glass capillary. X-ray measurements were carried out on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). The cell parameters of the monoclinic crystal were determined by a least-squares fit of the parameters of the orientation matrix for the setting angles of 15 reflections. They are (at −40 °C) $a = 13.810\ (2)$ Å, $b = 16.279\ (2)$ Å, $c = 11.871\ (2)$ Å, and $\beta = 95.58\ (1)°$. Corresponding to the systematic extinctions the space group is *Cc* or *C*2/*c* (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$). *C*2/*c* was verified by the solution and refinement of the structure in this space group. Densities: $\rho_{obsd} = 3.00$ and $\rho_{calcd} = 3.021$ g/cm³ for $Z = 4$ and mol wt 1208.30.

Intensity Data: $+h,+k,\pm l$ reflections measured out to $2\theta_{max} = 48°$; scan rate $1.2 \le \dot{\omega} \le 29.3°\ min^{-1}$, depending on the intensity of a preliminary scan; $\Delta\omega = 1°$; time spent for measuring background intensities at each end of the scan interval, half of the scan time; empirical absorption correction applied ($\mu = 115.6\ cm^{-1}$); intensity, $I = (S - B/\beta)\dot{\omega}$ and $\sigma(I) = (S + B/\beta^2)^{1/2}\dot{\omega}$ (scan count S, total background count B, time ratio of total background to scan β); 1797 reflections with $I > 0.7\sigma(I)$ used in calculations of $F_o = (I/Lp)^{1/2}$ and $\sigma(F_o) = \sigma(I)/(2F_oLp)$.

Structure Determination and Refinement. The positions of the Pt and Ag atoms were determined from a Patterson synthesis. Subsequent difference Fourier syntheses revealed the positions of O, N, and C atoms. Least-squares refinement with anisotropic temperature parameters for Pt and Ag and isotropic temperature factors for the other atoms led to $R = 0.051$ and $R_w = 0.056$ ($R_w = \sum(||F_o| - |F_c||)w^{1/2}(\sum|F_o|w^{1/2})$, with $w = 1.3/(\sigma^2(F_o) + 0.0024F_o^2)$. Hydrogen atoms were ignored at all stages. Scattering factors were taken from Cromer and Mann[8] for neutral atoms. Anomalous dispersion corrections, real and imaginary, were obtained from Cromer and Liberman.[9] Final atomic parameters are listed in Table I. The SHELX program package[10] and OTTO[11] (geometry program) were used.

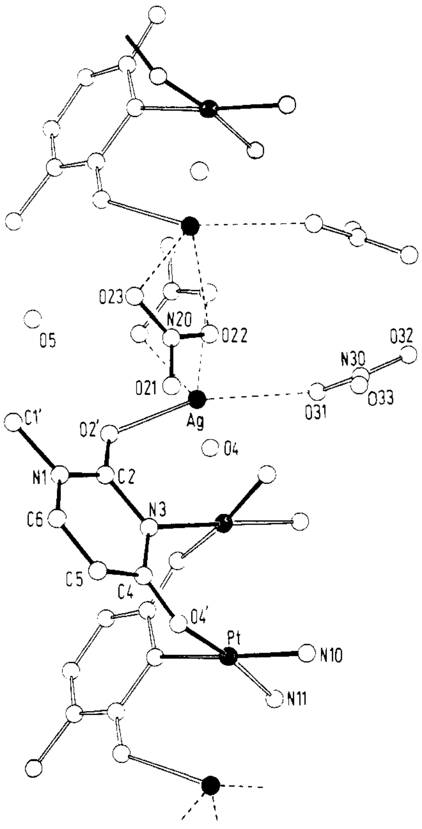

Figure 1. Section of the crystal structure of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)Ag]_2(NO_3)_4{\cdot}2H_2O$ projected along the *x* axis. Only the atoms of the asymmetric unit are labeled. The 2-fold rotation axes (parallel *y*) run from left to right.

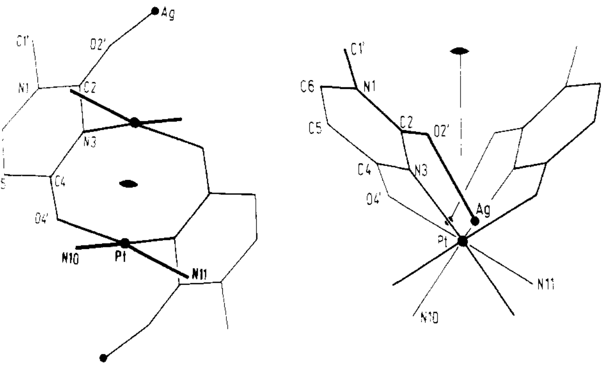

Figure 2. Projection of the tetranuclear cation along its 2-fold symmetry axis (left) and along the Pt–Pt vector (right).

Results and Discussion

Structure. A section of the crystal structure of the tetranuclear Pt_2,Ag_2,L_2 compound is displayed in Figure 1, and two views of the cation are shown in Figure 2. Selected interatomic distances and angles are listed in Table II, conformational parameters in Table III, and hydrogen-bonding contacts in Table IV.

The two 1-MeU ligands are arranged in a head–tail fashion with *cis*-$(NH_3)_2Pt^{II}$ binding through N(3) and O(4) each and Ag binding through the O(2) sites. Thus, 1-methyluracil acts

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[10] Sheldrick, G. M. SHELX program package, University of Göttingen, FRG.

[11] Thewalt, U. OTTO geometry program, University of Ulm, FRG.

Table I. Atomic Coordinates for *cis*-$[(NH_3)_2Pt(1\text{-}MeU)Ag]_2(NO_3)_4\cdot 2H_2O$

atom	*x*	*y*	*z*
Pt	0.48608 (4)	0.26398 (3)	0.86917 (4)
Ag	0.56366 (14)	0.23495 (12)	0.40654 (13)
N(1)	0.3489 (9)	0.0530 (7)	0.5277 (10)
C(2)	0.4200 (10)	0.1111 (8)	0.5338 (12)
N(3)	0.4232 (8)	0.1661 (7)	0.6285 (10)
C(4)	0.3592 (10)	0.1570 (8)	0.7093 (12)
C(5)	0.2786 (10)	0.0999 (9)	0.6927 (12)
C(6)	0.2804 (11)	0.0499 (9)	0.6007 (13)
C(1′)	0.3412 (11)	−0.0029 (10)	0.4300 (13)
O(2′)	0.4771 (8)	0.1172 (6)	0.4622 (9)
O(4′)	0.3677 (7)	0.2011 (6)	0.7990 (8)
N(10)	0.4015 (9)	0.3673 (7)	0.8642 (10)
N(11)	0.5962 (9)	0.3247 (7)	0.9566 (10)
N(20)	0.3288 (9)	0.2058 (8)	0.2921 (10)
O(21)	0.2853 (9)	0.2034 (8)	0.3783 (9)
O(22)	0.3970 (9)	0.2552 (7)	0.2859 (11)
O(23)	0.3039 (10)	0.1587 (9)	0.2162 (12)
N(30)	0.5609 (9)	0.4551 (8)	0.3751 (11)
O(31)	0.6176 (9)	0.3961 (7)	0.4001 (10)
O(32)	0.5961 (8)	0.5214 (7)	0.3406 (10)
O(33)	0.4723 (10)	0.4506 (8)	0.3894 (11)
O(4)[a]	0.75	0.25	0.50
O(5)[a]	0.50	0.0203 (15)	0.25

[a] The water oxygen atoms O(4) and O(5) are situated on "special positions" with occupancy factors of 0.5.

Table II. Interatomic Distances (Å) and Angles (deg) for *cis*-$[(NH_3)_2Pt(1\text{-}MeU)Ag]_2(NO_3)_4\cdot 2H_2O$[a]

Pt-Pt^{i}	2.892 (1)	N(1)-C(1′)	1.470 (19)
-Ag^{i}	2.853 (2)	-C(2)	1.360 (19)
-N(10)	2.046 (12)	-C(6)	1.345 (20)
-N(11)	2.015 (12)	C(2)-O(2′)	1.218 (18)
-O(4′)	2.037 (10)	-N(3)	1.434 (18)
-N(3)^{i}	2.026 (11)	N(3)-C(4)	1.375 (19)
Ag-Ag^{ii}	3.954 (3)	C(4)-O(4′)	1.280 (17)
-O(2′)	2.386 (11)	-C(5)	1.449 (20)
-O(22)	2.611 (13)	C(5)-C(6)	1.365 (20)
-O(22)^{ii}	2.421 (13)	N(20)-O(21)	1.237 (16)
-O(23)^{ii}	2.744 (12)	-O(22)	1.246 (17)
-O(31)	2.730 (12)	-O(23)	1.207 (17)
-O(4)	2.712 (2)	N(30)-O(31)	1.256 (17)
		-O(32)	1.269 (16)
		-O(33)	1.253 (18)
N(10)-Pt-N(3)^{i}	176.4 (5)	C(2)-N(1)-C(6)	122.8 (13)
-O(4′)	88.2 (4)	N(1)-C(2)-N(3)	116.3 (13)
-N(11)	90.7 (5)	O(2′)-C(2)-N(1)	122.1 (14)
N(11)-Pt-N(3)^{i}	86.8 (5)	-N(3)	121.6 (13)
-O(4′)	173.0 (4)	C(2)-N(3)-C(4)	120.5 (12)
O(4′)-Pt-N(3)^{i}	94.6 (5)	N(3)-C(4)-C(5)	120.7 (13)
O(2′)-Ag-O(22)^{ii}	120.6 (4)	O(4′)-C(4)-N(3)	120.5 (12)
C(2)-O(2′)-Ag	129.4 (8)	-C(5)	118.7 (13)
C(1′)-N(1)-C(2)	118.0 (12)	C(4)-C(5)-C(6)	114.7 (13)
-C(6)	118.9 (13)	C(5)-C(6)-N(1)	124.2 (14)

[a] Symmetry transformations: (i) $1-x, y, {}^3/_2-z$; (ii) $1-x, y, {}^1/_2-z$.

Table III. Conformational Parameters of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)Ag]_2(NO_3)_4\cdot 2H_2O$

(a) Least-Squares Planes and Deviations (Å) of Individual Atoms from Planes[a]

Pt Coordination Sphere (Plane I)

$$-5.2558x - 4.1845y + 10.9344z - 5.884 = 0$$

(Pt)	−0.04	O(4′)	0.08
(Pt^{i})	−2.79	N(10)	−0.08
N(3)^{i}	−0.08	N(11)	0.08

1-Methyluracil (Plane II)

$$7.3955x - 10.6006y + 5.7353z - 5.006 = 0$$

N(1)	0.04	(Pt)	0.78
C(2)	−0.02	(Pt^{i})	−0.38
N(3)	−0.03	(O(4′))	0.17
C(4)	0.05	(O(2′))	−0.07
C(5)	−0.03	(C(1′))	0.02
C(6)	−0.02	(Ag)	−1.00

(b) Dihedral Angles (deg)[b]

plane I/plane I′	29.8	plane II/plane II′	81.3
plane I/plane II′	96.1		

[a] In the equations for the planes, *x*, *y*, and *z* are coordinates referred to the (*a*, *b*, *c*) basis. The letter i indicates an atom related by the symmetry transformation $(1-x, y, {}^3/_2-z)$ to an atom of the fundamental unit. Atoms in parentheses were given zero weight in the calculations. The other atoms were given unit weight. [b] I′ represents the plane through the coordination atoms of the second Pt atom, Pt^{i}, of the dimer and II′ the plane of the second 1-MeU ring.

Table IV. Close Contacts (Å) in *cis*-$[(NH_3)_2Pt(1\text{-}MeU)Ag]_2(NO_3)_4\cdot 2H_2O$

Possible Hydrogen Bonds			
O(2′)-O(5)	3.02	N(11)-O(21)^{i}	3.13
O(4′)-O(4)^{i}	3.12	N(11)-O(33)^{i}	2.96
N(10)-O(31)^{i}	2.87	N(11)-O(21)^{iv}	2.89
N(10)-O(23)^{iii}	2.93	N(11)-O(32)^{v}	2.86
N(10)-O(32)^{v}	3.28	O(23)-O(4)^{ii}	3.00
N(10)-O(33)^{v}	3.13	O(31)-O(4)	3.16
Contacts between Nitrate Groups			
O(22)-O(22)^{ii}	3.05	O(22)-O(31)^{ii}	3.18

[a] Symmetry transformations: (i) $1-x, y, {}^3/_2-z$; (ii) $1-x, y, {}^1/_2-z$; (iii) ${}^1/_2-x, {}^1/_2-y, 1-z$; (iv) ${}^1/_2+x, {}^1/_2-y, {}^1/_2+z$; (v) $x, 1-y, {}^1/_2+z$.

as a tridentate ligand. Distances between the heavy metals within the tetranuclear cation are 2.892 (1) Å for Pt–Pt and 2.853 (2) Å for Pt–Ag. As depicted in Figure 2, the Pt_2,Ag_2,L_2 cation exhibits a crystallographic C_2 symmetry. The Pt atoms have slightly distorted-square-planar coordination spheres. While Pt–N and Pt–O bond lengths are normal, two of the four bond angles deviate from 90° and the four coordinating atoms are no longer coplanar but show a tendency for tetrahedral distortion. As with related dinuclear complexes of *cis*-$(NH_3)_2Pt^{II}$,[2-4,6,7,12-17] the Pt coordination planes in Pt_2,Ag_2,L_2 are slightly tilted toward each other, interestingly to a smaller extent (29.8°) than in the parent head–tail dimer with no Ag present (35.8°).[6] This decrease in the tilt angle is accompanied by a shortening of the Pt–Pt distance (2.892 (1) Å in Pt_2,Ag_2,L_2) as compared to Pt_2,L_2 (2.954 (2) Å) and a simultaneous increase in the torsion angle about the Pt–Pt′ vector (24.3° in Pt_2,Ag_2,L_2 but 20.5° (average) in Pt_2,L_2).

The Ag atoms do not exhibit a distinct coordination geometry. Only two of the six surrounding oxygens form reasonably strong bonds with each Ag: the exocyclic O(2) oxygen of the 1-MeU ligand (2.386 (11) Å) and O(22) (at $1-x, y, {}^1/_2-z$) of a nitrate (2.421 (13) Å). Distances to other nitrate oxygens and the water molecule are considerably longer (2.61–2.74 Å). Formally, O(22) of NO_3^- can be considered a bridge between two symmetry-related Ag atoms.

The 1-MeU ligands are essentially planar, with only the coordinating exocyclic oxygens deviating somewhat. In contrast, the N(3)-bonded Pt is substantially out of the ligand plane (0.38 Å) in the direction of the O-bonded 1-MeU ligand, as are the O(4)-bound Pt (0.78 Å) and the O(2)-bound Ag (1.00 Å). The geometry of the 1-methyluracil ligand[18] is not

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(18) Voet, D.; Rich, A. *Prog. Nucleic Acid Res. Mol. Biol.* **1970**, *10*, 183.

greatly affected by Pt and Ag coordination. Exceptions are the increase in C(2)–N(3) bond length (1.434 (18) Å) in Pt_2,Ag_2,L_2 compared to 1.38 Å in 1-MeUH and the decrease in the C(2)–N(3)–C(4) angle (120.5 (12)°) as compared to 126° in neutral 1-MeUH.

The packing within the crystal is such as to produce infinite chains of Pt_2,Ag_2,L_2 cations parallel to the crystallographic *z* direction, with intermolecular Ag–Ag separations of 3.954 (3) Å and nitrate anions bridging adjacent Ag atoms. These chains are separated by additional nitrate groups and water of crystallization, which are involved in extensive hydrogen bonding with NH_3 groups of the *cis*-$(NH_3)_2Pt^{II}$ residues (Table IV). Expectedly, O(2′) does not participate in hydrogen bonding to the same extent as in the head–tail parent compound: There is just one contact of 3.02 Å to O(5) in the Pt_2,Ag_2,L_2 compound, whereas in the Ag-free compound each of the two exocyclic O(2) oxygens is in contact with three hydrogen donors. Unusually short distances between the oxygens of adjacent nitrates are not observed (≥3.05 Å).

Solution Behavior. The interaction of Ag(I) with the 1-MeU ligands of the monomeric *cis*-$[(NH_3)_2Pt(1\text{-}MeU)H_2O]^+$ (**1**) and the head–tail dimer *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}$ (**2**) in aqueous solution occurs in two steps. In a fast initial reaction, coordination of Ag(I) to the available oxygens of 1-MeU takes place; in a slow secondary reaction, an equilibrium between Pt_1 and Pt_2 species is reached.

Coordination of Ag. Ag(I) binding to the exocyclic oxygens of **1** and **2** is evident from ^1H NMR shifts of the 1-MeU resonances. With increasing amounts of Ag(I) present, 1-MeU resonances are shifted downfield.[19] For example, with c_{Pt} = 0.1 M, c_{Ag} = 0.4 M, and pD 4–5, the following shifts to lower field are observed: for **1**, Δ(H5) = 0.06 ppm, Δ(H6) = 0.05 ppm, $\Delta(CH_3)$ = 0.02 ppm; for **2**, Δ(H5) = 0.04 ppm, Δ(H6) = 0.02 ppm. No distinct signals of heteronuclear Pt_x,Ag_y complexes are observed, consistent with fast exchange between free and bound Ag(I) on the NMR time scale. Interestingly, the H5 doublets, which exhibit ^{195}Pt satellites of $^4J_{^{195}Pt-^1H} \simeq$ 14–15 Hz, in both cases are shifted slightly more than the H6 doublets, even though the only available exocyclic oxygen of the dimer (O(2)) is closer to C(6) than to C(5). The same is also true for the interaction between the corresponding head–head dimer and Ag(I), which leads to formation of Pt_4,Ag,L_4, with Pt binding to N(3),O(4) and Ag binding to O(2).[4] There, respective shifts are somewhat larger, however, being 0.11 ppm for H5, 0.07 ppm for H6, and 0.03 ppm for CH_3 under identical experimental conditions. These findings clearly indicate the need to be careful in the interpretation of metal coordination sites at heterocyclic rings on the basis of chemical shifts.[20]

Equilibration of Pt_1 and Pt_2 Species. In the presence of Ag(I), the ^1H NMR spectra of **1** and **2** show further changes with time (Figure 3) that are qualitatively similar to those observed in the absence of Ag(I) and can be interpreted likewise.[7] As we have shown,[7] **1** undergoes condensation reactions in aqueous solution to give the head–tail dimer **2** in addition to a second dinuclear compound *cis*-$[(NH_3)_2(1\text{-}MeU)Pt(OH)Pt(1\text{-}MeU)(NH_3)_2]^+$ (**3**), which contains a bridging hydroxo group and two terminal 1-MeU ligands each bound to Pt through N(3). The distribution of **1**–**3** is pH dependent, with **1** and **2** being favored under acidic conditions and **3** formed around neutral pH. In the pD range 4–5, the distribution of **1**:**2**:**3** approaches 35:60:5 after several days at room temperature and a total Pt concentration of 0.1 M.

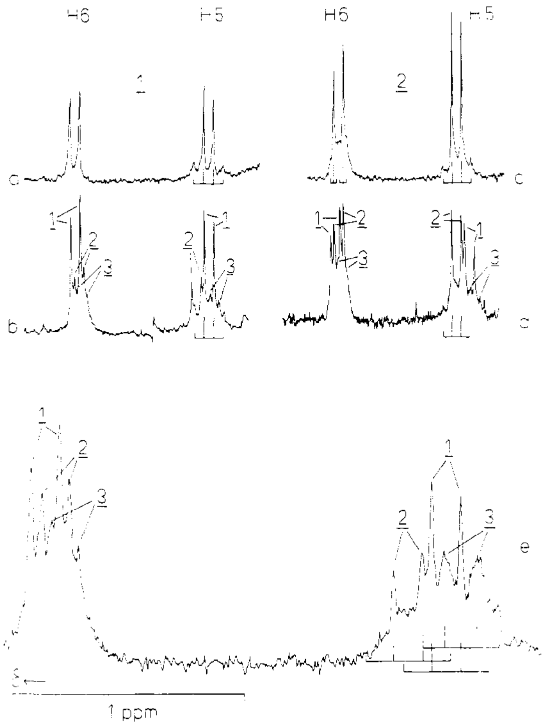

Figure 3. ^1H NMR spectra (H5 and H6 regions only) of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)H_2O]^+$ in D_2O (0.1 M Pt) in the presence of $AgNO_3$ (0.4 M), pD 4.2, (a) immediately after mixing and (b) after 15 min at 60 °C, 48 h at 22 °C, of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}$ (head–tail) in D_2O (0.1 M Pt) in the presence of $AgNO_3$ (0.4 M), pD 5.6, (c) immediately after mixing and (d) after 4 days at 22 °C, and of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)H_2O]^+$ with $AgNO_3$ (e) after 2 h at 60 °C, 11 days at 22 °C. The spectrum obtained from the head–tail dimer in the presence of $AgNO_3$ is almost identical under these conditions. Signals 1–3 are due to Ag adducts of the monomer *cis*-$[(NH_3)_2Pt(1\text{-}MeU)H_2O]^+$, the head–tail dimer *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}$, and the μ-OH dimer *cis*-$[(NH_3)_2(1\text{-}MeU)Pt(OH)Pt(1\text{-}MeU)(NH_3)_2]^+$, respectively.

Prompted by the results shown in Figure 3, which demonstrate than an equilibrium is reached regardless if one starts out with the monomer **1** or the head–tail dimer **2**, we examined the behavior of **1** and **2** in the absence of Ag and got analogous results. There are, however, a few differences between the spectra obtained with or without Ag(I). First, the resonances of **1**–**3** are shifted downfield when Ag(I) is present, indicating that all three species interact with Ag(I) to give heteronuclear Pt,Ag complexes. Second, the distribution of **1**–**3** is somewhat different with Ag(I) present (c_{Pt} = 0.1 M, c_{Ag} = 0.4 M, pD 4–5), reducing the amount of head–tail dimer slightly: **1**:**2**:**3** = 25:70:5. This result tends to suggest that Ag coordinates to O(4) of the 1-MeU ligand of the monomer **1**, thus competing with dimerization of **1**. Third, while both **1** and **2** form intensely blue-colored solutions with time, and especially on brief warming to 50–60 °C, no comparable coloration is observed in the presence of a 4-fold excess of Ag(I).

Interaction between the Head–Head Dimer and Ag(I). In contrast to the head–tail dimer **2**, the head–head dimer shows no tendency to equilibrate with its starting components

$$cis\text{-}[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+} + 2H_2O \rightleftharpoons cis\text{-}(NH_3)_2Pt(1\text{-}MeU)_2 + cis\text{-}[(NH_3)_2Pt(H_2O)_2]^{2+}$$

in solution as long as no Ag(I) is present. This also explains the considerably faster and virtually quantitative formation of the head–head dimer as compared with the head–tail dimer.[7] Addition of Ag(I) to an aqueous solution of the head–head dimer leads to the downfield shifts of the 1-MeU resonances mentioned above, indicating Ag(I) coordination to O(2) as

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[19] The observed downfield shifts are not due to protonation of the 1-MeU ligand, since this takes place at considerably lower pH only. Cf. ref 5 and 7.

[20] For this subject, see also: Marzilli, L. G. *Prog. Inorg. Chem.* **1977**, *23*, 255.

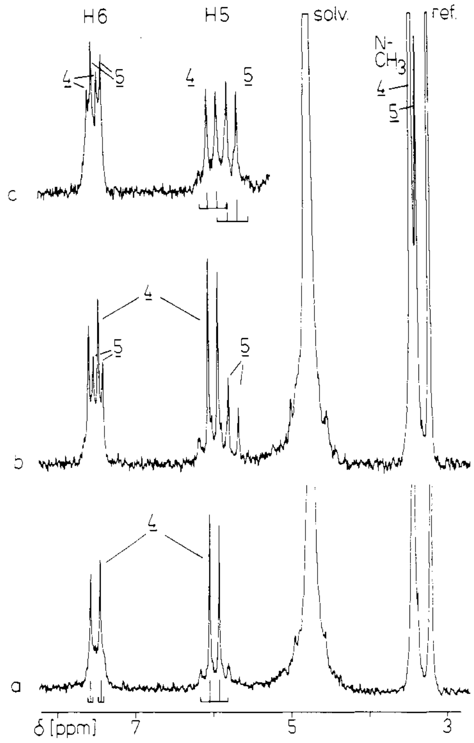

Figure 4. ^1H NMR spectra of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2$ (head–head) in D_2O (0.1 M Pt) in the presence of $AgNO_3$ (0.4 M), pD 5.5, (a) immediately after mixing, (b) after 2 min at 85 °C, and (c) after 2 days at 25 °C. Signals 4 correspond to *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}\cdot Ag_n^{n+}$ (with head–head arrangement of 1-MeU ligands) and are shifted downfield relative to the signals of the head–head dimer along (cf. text). Signals 5 are due to *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Ag_n]^{n+}$ and are shifted downfield relative to the signals of *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ as well. Reference is NMe_4^+.

confirmed by the crystal structure of Pt_4AgL_4.[4] In a slow secondary reaction, which is accelerated on slight warming (40 °C), a partial decomposition takes place

$$cis\text{-}[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}\cdot Ag_n^{n+} \rightarrow cis\text{-}(NH_3)_2Pt(1\text{-}MeU)_2\cdot Ag_n^{n+} + cis\text{-}[(NH_3)_2Pt(H_2O)_2]^{2+}$$

besides formation of a small amount of brown-blue, dichroic crystals.[4] This is depicted in Figure 4. Depending upon the Pt:Ag ratio applied, several distinct species of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Ag_n]^{n+}$ have been isolated in crystalline form (e.g., $n = 0.5, 1.0, 1.5$).[21] These results clearly demonstrate the fact that there is a competition between Ag(I) and cis Pt(II) for the O(4) site of the 1-MeU ligands and indirectly confirm the observations on the differing quantities of head–tail platinum dimers being formed in the absence or presence of Ag(I).

IR and Raman Spectra. The interpretation of the Pt,Ag,L compound as *cis*-$[(NH_3)_2(ONO_2)Pt(1\text{-}MeU)Ag]NO_3$ is based on IR and Raman spectroscopic arguments. N(3)–Pt binding is deduced from the positions of several characteristic 1-MeU modes (cm^{-1}) (e.g., 801 vs (Ra), vw (IR); 647 s (Ra), w (IR); 601 s (Ra), s (IR); 495 s (Ra), s (IR)), which are close to those previously reported by us for N(3)-platinated 1-MeU[7] and differ significantly from those found in the spectra of the head–head dimer, the head–tail dimer,[7] and the dinuclear Pt,Cu,L_2 complex[2] with simultaneous N(3),O(4) metal binding. There is no hard evidence from the vibrational spectra that Ag(I) actually is coordinated to one or both exocyclic oxygens of 1-MeU, yet several weak arguments are in favor of such an assumption and do not exclude it. First, the solution studies suggest this interaction. Second, the position of the intense Raman ring-breathing mode at 801 cm^{-1} shows a trend to somewhat higher energy as compared to the cases of *cis*-$[(NH_3)_2Pt(1\text{-}MeU)H_2O]^+$ (798 cm^{-1}), *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ (792 cm^{-1}), and the mixed nucleobase complexes *cis*-$[(NH_3)_2Pt(1\text{-}MeU)X]^+$ (X = 1-methylcytosine[22] (792 cm^{-1}), 9-ethylguanine[22] (799 cm^{-1})). Third, the vibrational spectra of Pt_2,Ag,L_2 (L = 1-MeT),[3a] Pt_4,Ag,L_4 (L = 1-MeU),[4] and Pt_2,Ag_2,L_2, all with crystallographically confirmed Ag coordination to an exocyclic oxygen of the pyrimidine ligand, do not reveal any significant shifts of bands as compared to the Pt starting compound. Fourth, the relative intensity of the ring-breathing mode (vide infra) seems to suggest Ag binding as well.

Table V. Positions and Relative Raman Intensities of Ring-Breathing and Ring-Stretching Modes of 1-MeU

compd	br mode, cm^{-1}	str mode, cm^{-1}	rel intens br/str	phase
$(NH_3)_2Pt(1\text{-}MeU)H_2O^+$	800	1248	1.2	solid
$(NH_3)_2Pt(1\text{-}MeU)_2$	792	1241	1.5	solid
	796	1244	1.4	H_2O
$(NH_3)_2Pt(1\text{-}MeU)(9\text{-}EtG)^+$	799	1247	1.3	solid
$(NH_3)_2Pt(1\text{-}MeU)(ONO_2)Ag^+$	801	1244	0.9	solid
$[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}$ (head-head)	809, 816	1240, 1236	0.6	solid
$[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}$ (head-tail)	819	1244	0.6	H_2O
$(NH_3)_4Pt_2(1\text{-}MeU)_2Ag_2^{4+}$	819	1241	0.3	solid

Two sets of nitrate absorptions are identified in the vibrational spectra of Pt,Ag,L, corresponding to free nitrate (essentially D_{3h} symmetry; 1041 vs, 709, 723 vw cm^{-1} (Ra); 1770 vw, 1380 vs, 1040 vw, 820 vs cm^{-1} (IR)) and coordinated nitrate (C_s or C_1 symmetry; 1498 m, 1487 m, 1286 w, 1270 m, 1000 s, 988 s cm^{-1} (Ra); 1485 s, 1280 s, 990 s cm^{-1} (IR)).[23] With Ag–ONO_2 interactions causing virtually no reduction of nitrate D_{3h} symmetry,[24] yet Pt–ONO_2 interactions causing perturbations of the nitrate absorptions of the magnitude observed in the present case,[25] it is concluded that the bands of the coordinated nitrate are due to *cis*-$(NH_3)_2Pt(1\text{-}MeU)ONO_2$.

The interaction between Ag(I) and NO_3^- ions in Pt_2,Ag_2,L_2, as it is observed in the crystal structure, is not evident from the vibrational spectra. This is not surprising with regard to the findings in $AgNO_3$, however. In the Raman spectrum only a single, very intense band due to the NO stretch (ν_1) is observed at 1043 cm^{-1}. On the other hand, the appearance of two ν_4 modes (711, 726 w cm^{-1} (Ra)) and two ($\nu_1 + \nu_2$) combinations (1750, 1765 w cm^{-1} (IR)) is indicative of the presence of at least two crystallographically different "ionic" nitrates.

As to the 1-MeU modes, preservation of the N(3),O(4)-bridged Pt_2 unit in the Pt_2,Ag_2,L_2 compound is confirmed by the close similarity in positions of respective bands in the spectra of the head–tail dimer and its derivative. Again, the presence of Ag(I) cannot be deduced on the basis of clear shifts of bands in the vibrational spectra. There is, however, one observation referring to the relative intensities of the two strongest Raman bands, the ring-stretching mode around 1240 cm^{-1} and the ring-breathing mode around 800 cm^{-1}, that appears to be of some diagnostic value. While in the Pt complexes with monodentate 1-MeU (N(3) bound), the ring-

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(21) Goodgame, D. M. L.; Rollins, R. W.; Lippert, B., submitted for publication in *Polyhedron*.

(22) Structural and preparative details will be reported elsewhere.

(23) Other Raman-active NO_3 modes, expected around 790 and 820 cm^{-1}, are superimposed with intense 1-MeU modes.

(24) Vratny, F. *Appl. Spectrosc.* **1959**, *13*, 59.

(25) (a) Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Inorg. Chem.* **1977**, *16*, 1525. (b) Britten, J.; Lippert, B.; Lock, C. J. L.; Pilon, P. *Inorg. Chem.* **1982**, *21*, 1936.

breathing mode always is more intense than the ring-stretching mode (ratio 1.2-1.5). In the complexes with a second or third metal coordinated through the exocyclic oxygen(s) of 1-MeU, the relative intensities of these two modes are inverted (Table V).

Conclusion

Three aspects of the results described here appear to be noteworthy.

(1) Binding of a heterometal to the exocyclic oxygens of a N(3)-platinated 1-methyluracilate ligand is not restricted to a cis arrangement of two 1-MeU ligands. Although an arrangement of this kind, as found for example in Pt_2,Ag,L_4 and Pt_4,Ag,L_4, may contribute to the formation of these complexes, the results presented here indicate that this favorable steric factor is not a prerequisite for the formation of heteronuclear complexes in general. Thus, the ligating properties of N(3)-platinated 1-MeU and 1-MeT should be attributed primarily to the favorable charge distribution in these ligands, similar to the situation with N(3)-mercurated 1-MeT as shown by Guay and Beauchamp.[26]

(2) Association of small building blocks of dinuclear or, as in the present case, tetranuclear units, which has previously been found to occur through intermolecular hydrogen bonding[7,12,13] or metal-metal interactions,[14] can also be accomplished through anion bridging. Though nitrate bridging in the compound described here certainly is restricted to the solid state, there is the possibility that anions with good coordinating properties could act in such a way in solution as well.

(3) The solution behavior of the head-head and the head-tail dimers *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2^{2+}$ in the presence of Ag(I) shows that the Pt-O bonds in these complexes are labile. The Pt-O bonds are cleaved not only by strongly coordinating anions such as Cl^-, which compete with oxygen for Pt(II),[12] but also by cations such as Ag(I), which then compete with Pt(II) for oxygen donors of the 2,4-pyrimidinedione ligands.

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Registry No. *cis*-**1**(NO_3), 85715-80-6; *cis*-**2**$(NO_3)_2$ (head-tail dimer), 75790-29-3; *cis*-**2**$(NO_3)_2$ (head-head dimer), 85886-74-4; *cis*-$[(NH_3)_4Pt_2(1\text{-}MeU)_2Ag_2](NO_3)_4 \cdot 2H_2O$, 89637-18-3; *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$, 83350-97-4; *cis*-$[(NH_3)_2Pt(1\text{-}MeU)(9\text{-}EtG)]^+$, 89637-19-4; *cis*-$[(NH_3)_2Pt(1\text{-}MeU)X]^+$ (X = 1-methylcytosine), 89637-20-7.

Supplementary Material Available: Tables of atomic and thermal parameters and observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(26) Guay, F.; Beauchamp, A. *Inorg. Chim. Acta* **1982**, *66*, 57.

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Paramagnetic Hydride Complexes of Niobium(IV) and Tantalum(IV)[1]

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The d^3 complexes $TaCl_2(PMe_3)_4$ and $NbCl_2(PMe_3)_4$ are prepared by reduction of MCl_5 with sodium amalgam in diethyl ether in the presence of excess PMe_3 and isolated as brown crystalline solids in 60 and 25% yields, respectively. Red-brown $NbCl_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] is obtained in 90% yield via reduction of $NbCl_4(dmpe)_2$ in THF. These MCl_2 adducts, as well as the previously reported $TaCl_2(dmpe)_2$, all react readily with dihydrogen at 25 °C. Paramagnetic, eight-coordinate M(IV) hydride complexes, $MCl_2H_2L_4$, are isolated from the $TaCl_2(PMe_3)_4$, $TaCl_2(dmpe)_2$, and $NbCl_2(dmpe)_2$ reactions. The yields of $TaCl_2H_2(PMe_3)_4$ (red), $TaCl_2H_2(dmpe)_2$ (red-orange), and $NbCl_2H_2(dmpe)_2$ (red-orange) range from 75 to 90%. These d^1 hydrides have been characterized by infrared and electron spin resonance spectroscopy, by magnetic susceptibility, and, in the case of the two tantalum complexes, by low-temperature X-ray crystallography. $TaCl_2H_2(PMe_3)_4$ adopts a distorted dodecahedral geometry in the solid state while $TaCl_2H_2(dmpe)_2$ is more appropriately described as a distorted square-antiprismatic complex. The hydride ligands in both complexes were located and refined. Crystal data (at -160 °C) are as follows: for $TaCl_2H_2(PMe_3)_4$, monoclinic space group Cc, $a = 15.127$ (3) Å, $b = 12.005$ (3) Å, $c = 12.410$ (2) Å, $\beta = 92.49$ (1)°, $V = 2251.6$ Å^3, $Z = 4$, $d_{calcd} = 1.647$ g cm^{-3}; for $TaCl_2H_2(dmpe)_2$, orthorhombic space group $P2_12_12_1$, $a = 9.781$ (4) Å, $b = 15.842$ (8) Å, $c = 13.832$ (6) Å, $V = 2143.3$ Å^3, $Z = 4$, $d_{calcd} = 1.717$ g cm^{-3}.

Introduction

The first paramagnetic hydride complexes of niobium and tantalum, viz., Cp_2MH_2 (M = Nb, Ta) and $TaH_4(dmpe)_2$, were reported in 1974 by Kochi, Parshall, and their coworkers.[3,4] They were prepared by reacting the corresponding M(V) hydrides with photogenerated *tert*-butoxy radicals (eq 1 and 2) and characterized low-temperature electron spin resonance (ESR) spectroscopy. None of these 17-electron, d^1 species was sufficiently stable at ambient temperature to permit isolation, a feature that necessarily frustrated any thorough investigation of their physicochemical properties, structural chemistry, and reactivity.[5]

$$2Cp_2MH_3 + t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2Cp_2MH_2 + 2\text{-}t\text{-BuOH} \quad (1)$$

$$2TaH_5(dmpe)_2 + t\text{-BuOO-}t\text{-Bu} \xrightarrow{h\nu} 2TaH_4(dmpe)_2 + 2\text{-}t\text{-BuOH} \quad (2)$$

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(2) (a) The University of Michigan. (b) Indiana University.

(3) Elson, I. H.; Kochi, J. K.; Klabunde, U.; Manzer, L. E.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 7374.

(4) dmpe is an acronym for 1,2-bis(dimethylphosphino)ethane or $Me_2PCH_2CH_2PMe_2$.

(5) The reactions of metastable Cp_2NbH_2 with several olefins have been studied by ESR. See: Elson, I. H.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1263.

0020-1669/84/1323-1718$01.50/0