Ammonia and Carbon Dioxide from Urea. A Multinuclear NMR Study of the Activation of Urea by Platinum(II)

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Isotopically enriched (98% ^{15}N, 99% ^{13}C) urea, $^{15}NH_2{}^{13}CO^{15}NH_2$, reacts with $[dienPtOH_2]^{2+}$ in acetone to form principally $^{13}CO_2$, $^{15}NH_4{}^+$ and $[dienPt^{15}NH_3]^{2+}$. The reaction was monitored by combined one- and two-dimensional multinuclear (^1H, ^{13}C, ^{15}N) NMR spectroscopy. The initial product was $[dienPtOC(NH_2)_2]^{2+}$, in addition to a fluxional species detected spectroscopically at low temperature, which undergoes O- to N-linkage isomerization to $[dienPtNH_2CONH_2]^{2+}$. The latter complex, unlike the crystallographically characterized $[dienPtNH_2CONMe_2]^{2+}$, decomposes to CO_2, $NH_4{}^+$, and $[dienPtNH_3]^{2+}$. $[dienPtNCO]^{2+}$ was detected as an intermediate by ^{13}C NMR spectra and may be formed directly from $[dienPtNH_2CONH_2]^{2+}$ or its tautomer $[dienPtNH{=}C(OH)\,NH_2]^{2+}$ by elimination of ammonia or indirectly after hydrolysis to $[dienPtNH_2CO_2]^+$ through elimination of water. Addition of acid and water to acetone solutions of $[dienPtNCO]^{2+}$ rapidly produces $[dienPtNH_3]^{2+}$ and CO_2. The mechanism of the reaction is discussed.

Introduction

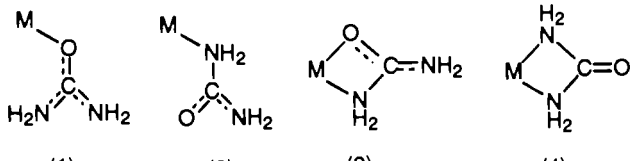
From a biological perspective, the interaction of urea with metals has relevance to the metalloenzymes, ureases, which are believed to contain two catalytic Ni(II) ions per protein subunit.[1] One or both nickel ions may bind directly to urea, thus activating it toward hydrolytic degradation to ammonia and carbon dioxide.

$$NH_2CONH_2 + H_2O = 2NH_3 + CO_2 \qquad K \sim 10^{-14}$$

Uncatalyzed hydrolysis of urea is not known in water but there is very slow ($k = 6 \times 10^{-10}$ s^{-1}, 25 °C, pH 2) elimination to ammonium and cyanate ions[1]

$$NH_2CONH_2 = NH_4{}^+ + NCO^-$$

Urea could potentially be a neutral ligand for transition metals acting as a monodentate (e.g. **1**, **2**) or bidentate (e.g. **3**, **4**) ligand



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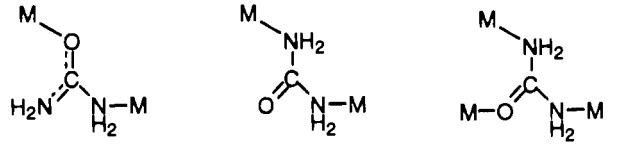

(5) (6) (7)

for one metal or as a bridging ligand (e.g. **5**−**7**) to two or three metals; only monodentate coordination (**1**, **2**) has been reported. Coordination via the more basic (to H^+) oxygen atom of urea (e.g. **1**) to a range of metals (e.g. Cr(III),[2] Mn(II),[3] Mn(III),[4] Co(II),[5] Co(III),[6,7] Ni(II),[8] Cu(II),[9] Zn(II),[10] Ru(III),[11] Rh(III)[12]) does not activate urea toward hydrolysis. Reports of ureas[7,10−14] bonded via nitrogen (e.g. **2**) to a metal (e.g. Co(III),[7,13] Ni(II),[10] Cu(II),[10] Ru(III),[11] Rh(III)[12,14a]) are less common. Only on Rh(III) have CO_2 and NH_3 been produced from urea.[12]

We recently found[14b] that the urea derivative NH_2CONMe_2 reacts with $[Pt(dien)OH_2]^{2+}$ to give both O- and N-bound dimethylurea complexes, but neither ammonia nor CO_2 was detected in solutions of these complexes. In contrast, we now show that urea reacts with $[Pt(dien)OH_2]^{2+}$ to form CO_2, ammonia, and $[dienPtNH_3]^{2+}$.

Experimental Section

Isotopically enriched (99% ^{13}C, 98% ^{15}N) samples of urea ($^{15}NH_2{}^{13}CO^{15}NH_2$, $^{15}NH_2CO^{15}NH_2$) were obtained from Cambridge Isotope Laboratories, Cambridge, MA. $[Pt(dien)OH_2](CF_3SO_3)_2$ was prepared

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Table 1. ^{13}C and ^{15}N NMR Data[a] for Ureas and Their Platinum(II) Complexes in Acetone-d_6

complex	label	^{13}C: δ ppm (J, Hz)	^{15}N: δ, ppm (J, Hz)
$O^{13}C(^{15}NH_2)_2$	**B**	162.0, t ($^1J_{C,N}$ 19.1) (*C*=O)	57.6, d ($^1J_{N,C}$ 19.1) (*N*H_2)
$OC(NH_2)NMe_2$		160.8 (*C*=O); 35.7 (N*Me*$_2$)	
$[dienPtO^{13}C(^{15}NH_2)_2]^{2+}$	**C**	51.2, 56.0 (dien); 166.4, t ($^1J_{C,N}$ 21.9) (*C*=O)	61.3, d ($^1J_{N,C}$ 21.9) (*N*H_2)
$[dienPtOC(NH_2)NMe_2]^{2+}$		51.1, 56.1 (dien); 164.1 (*C*=O); 36.8 (N*Me*$_2$)	
$[dienPt^{15}NH_2{}^{13}CO^{15}NH_2]^{2+}$	**E**	51.78, 55.06 (dien); 158.9, dd ($^1J_{C,N}$ 8, 22) (*C*=O)	74.4, dd ($^1J_{N,C}$ 22.7, $^2J_{N,C}$ 3.5) (−CO*N*H_2); −20 (Pt−*N*H_2−)[b]
$[dienPtNH_2CONMe_2]^{2+}$		51.4, 55.0 (dien); 157.7 (*C*=O); 37.7, 37.1 (N*Me*$_2$)	
$[dienPtOH_2]^{2+}$	**A**	50.9, 51.2, 56.4 (dien)[c]	
$[dienPt^{15}NH_3]^{2+}$	**I**	54.8, 52.0 (dien)	−65.5, s ($J_{N,Pt}$ 275) (Pt−*N*H_3)
$[dienPt(^{15}N^{13}CO)]^{2+}$	**G**	51.9, 55.4 (dien); 124.2, d ($^1J_{C,N}$ 38) (Pt−N*C*O)	nd[d]
$^{13}CO_2$	**F**	125.4 (*C*O_2)	
$^{15}NH_4^+$	**H**		0.0, s (*N*H_4^+)
	D	51.8, 55.3 (dien); 158.2, vbr s (*C*=O)	67.3, vbr s (CO*N*H_2); −1.5, vbr (Pt−*N*H_2CO)
	D[e]	51.5, 55.0 (dien); 158.0, dd ($^1J_{C,N}$ 22.9, 9.0) (*C*=O)	71.0, dd ($^1J_{N,C}$ 22.6, $^2J_{N,N}$ 4) (CO*N*H_2); −2.9, dd ($^1J_{N,C}$ 8.8, $^2J_{N,N}$ 4) (Pt−*N*H_2CO)

[a] 300 K, trifluoromethanesulfonate salts. [b] Only observed through $^{15}N-^{13}C$ HETCOR spectra (Figure 3c). [c] Three resonances due to acetone partial substitution (see ref 14c,b). [d] Resonance not detected. [e] 233 K.

as described.[14d] In a typical NMR experiment, $[Pt(dien)OH_2](CF_3SO_3)_2$ (0.15 mmol) and $^{15}NH_2{}^{13}CO^{15}NH_2$ (0.15 mmol) were dissolved in acetone-d_6 (0.5 mL) in a 5 mm NMR tube at initially 300 or 253 K. Subsequent reaction, which could be effectively halted by lowering the temperature to 253 K, was monitored by a combination of 1D and 2D NMR spectroscopy.

NMR experiments were conducted using a Bruker ARX 500 NMR spectrometer equipped with broad-band and triple-nucleus (H, C, N) 5 mm probes and variable-temperature control. Spectra were measured at 500.13 MHz (^1H), 125.76 MHz (^{13}C), or 50.68 MHz (^{15}N), and chemical shifts are reported relative to TMS or $^{15}NH_4^+$ (δ 0.00 ppm). Some ^1H and ^{13}C NMR spectra were also measured on a Varian Gemini spectrometer at 300 and 75 MHz respectively. $^{15}N-^1H$ coupling was detected using a standard gated Bruker pulse program (zggd). Two-dimensional heteronuclear ($^1H-^{15}N$, $^{13}C-^{15}N$) shift correlation spectroscopy (HETCOR) was performed using a slightly modified Bruker pulse program[15] (hxco). $^1H-^{15}N$ HETCOR spectra were obtained using a broad-band probe and the following parameters: 90° pulses, P1 = 17.5 μs (^{15}N) and P3 = 11.4 μs (^1H); delays, D1 = 4s, D2 (1/2J) and D3 (1/3J) based on $^1J_{H,N}$ = 100 Hz. $^{13}C-^{15}N$ HETCOR spectra were measured using a triple-nucleus probe with D1 = 2s, P1 = 18 μs (^{13}C), P3 = 54 μs (^{15}N), and D2 and D3 based on $^1J_{C,N}$ varied from 8 to 22 Hz in separate experiments.

Results

^{13}C NMR Spectral Data (Table 1). Figure 1a shows an initial $^{13}C\{^1H\}$ NMR spectrum for $[dienPt(OH_2)](CF_3SO_3)_2$ (species **A**) after mixing at 300 K for 1 min with urea $^{15}NH_2{}^{13}CO^{15}NH_2$ (species **B**) in the poor coordinating solvent acetone and cooling quickly to 233 K. The inset to Figure 1a shows the carbonyl region at 300 K. Three main species were evident (Figure 1a; **B**, **C**, **D**) along with some residual **A**, identified by its characteristic dien-^{13}C resonances at 50−60 ppm (Table 1), and a trace of species **E**. The triplet resonance at ~162 ppm was established as free urea (**B**) by a separate experiment in which more urea was added to the mixture. Its chemical shift was particularly concentration and temperature dependent. The most prominent resonance (**C**, δ_C ~166 ppm) is a triplet, indicating a carbon attached to two magnetically equivalent urea nitrogens. Two related ^{13}C resonances at δ_C ~51.2, 56.0 signify a symmetrical dien complex. Species **C** is thus assigned to the O-bonded urea complex $[dienPtO{=}^{13}C(^{15}NH_2)_2]^{2+}$, an assignment supported ahead by other spectra. Also chemical shifts (^{13}C, ^1H) assigned to **C** are almost identical (Table I) to those reported[14b] for $[dienPtOC(NH_2)NMe_2]^{2+}$.

At 300 K the third species **D** gave a broad singlet (δ_C ~158.2 ppm, Figure 1a inset) which resolved into a sharp doublet of doublets at 233 K (Figure 1a). This is consistent with **D** being fluxional, perhaps an exchanging species at 300 K, and possessing a carbonyl carbon attached to two inequivalent ^{15}N nitrogens. After 30 min at 300 K (Figure 1a inset), another species **E** had formed and is characterized by a similar ^{13}C resonance (δ_C ~158.9 ppm) which is a doublet of doublets (sharply resolved even at 300 K) and again is attributed to a carbonyl carbon attached to two inequivalent nitrogens. In the spectrum recorded at 30 min (Figure 1a inset) a trace resonance (not shown), identified ahead as CO_2, was present at 125.4 ppm (singlet, not $CF_3SO_3^-$).

After 1 h of reaction at 300 K (Figure 1b), the same species were present but in different ratios. Using the ^{13}C resonances of the concentration-invariant triflate counterion (119.5, 122.1,

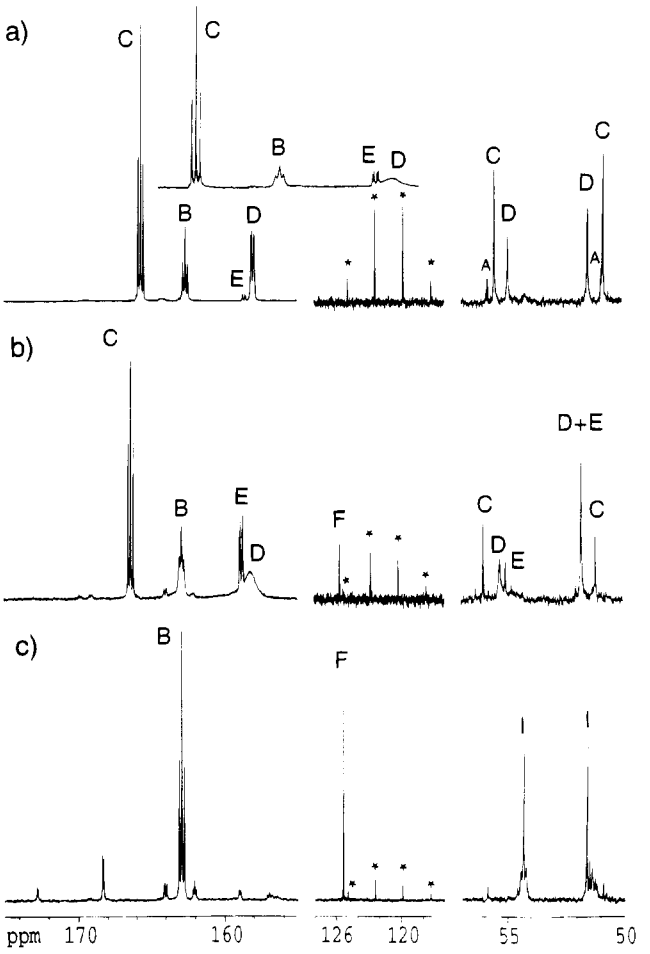

Figure 1. ^{13}C NMR spectra for $[dienPtOH_2](CF_3SO_3)_2$ reacted with $^{15}NH_2{}^{13}CO^{15}NH_2$ (1:1 mole ratio) in acetone-d_6 at 300 K: (a) after 10−30 min at 233 K (inset: 10−30 min at 300 K); (b) after 1 h at 300 K; (c) after 6 days at 300 K.

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123.4, 124.6 ppm) as internal standard, we were able to compare spectra over several hours and establish that, compared to Figure 1a (30 min), species **C** ($[dienPtOC(NH_2)_2]^{2+}$) diminished to about half its concentration after 5 h, while species **B** (urea) and **D** had not altered in concentration. On the other hand, species **E** had almost doubled in concentration and was associated with only two dien signals, consistent with a symmetrical ligand environment. **E** is assigned to the nitrogen-bonded linkage isomer $[dienPt^{15}NH_2{}^{13}CO^{15}NH_2]^{2+}$ which has almost the same NMR (^{13}C, ^1H) chemical shifts as the crystallographically[14a] characterized $[dienPtNH_2CONMe_2]^{2+}$. Its formation from **C**, $[dienPtO{=}^{13}C(^{15}NH_2)_2]^{2+}$, is consistent with O- to N-linkage isomerization previously identified for amides on $dienPt^{II}$ and on a similar time scale.[16]

Other minor doublet species at 164, 168, and 173 ppm formed and grew during the reaction. As these chemical shifts are typical of carbonyl carbons and must be attached to only one ^{15}N each, they are almost certainly carbamate species. The ^{13}C giving rise to the singlet resonance at 125.6 ppm (species **F**) cannot be attached to any ^{15}N and was separately established as $^{13}CO_2$ by adding dry ice.

After 6 days (Figure 1c), ^{13}C resonances for **A**, **C**, **D**, and **E** had virtually disappeared, leaving mainly urea (**B**), CO_2 (**F**), and $[dienPtNH_3]^{2+}$ (**I**). Using triflate signals for comparison, ~25% of the urea originally added to $[dienPtOH_2]^{2+}$ in acetone is estimated to be present in solution after 6 days; the remainder was converted to CO_2. Clearly some initially platinum-bound urea was subsequently released into solution. Ahead we deduce that this residual urea is not hydrolyzed because of competition for the metal by ammonia, 2 equiv liberated from each molecule of urea, producing the chemically inert $[dienPtNH_3]^{2+}$.

^{15}N NMR Spectral Data (Table 1). Figure 2a shows that, after 5 min of reaction between $[dienPtOH_2]^{2+}$ (**A**) and $^{15}NH_2{}^{13}CO^{15}NH_2$ (**B**), four resonances dominate the ^{15}N NMR spectrum at 233 K. These four signals belong to three species (**B**, **C**, **D**). The prominent doublet at δ_N ~61 ppm, consistent with two equivalent ^{15}N nitrogens bound to the ^{13}C-carbonyl of urea, was correlated by two-dimensional $^{13}C-^{15}N$ HETCOR (Figure 3b, supplementary material) to the ^{13}C resonance at δ_C ~166 ppm (species **C**) assigned to the oxygen-bonded urea complex, $[dienPtO{=}^{13}C(^{15}NH_2)_2]^{2+}$. The high-intensity doublet at 61 ppm is consistent with two equivalent nitrogens, and a gated (proton-coupled) ^{15}N spectrum (not shown) revealed ^{15}N attached to two protons. The doublet at δ_N ~57.6 ppm was established as urea (species **B**) by correlation (Figure 3b) to the ^{13}C resonance at δ_C ~162 ppm and after separate doping experiments with added $^{15}NH_2{}^{13}CO^{15}NH_2$.

The other two ^{15}N resonances (δ_N ~+67 ppm, −1.5 ppm) were broad at 300 K (Figure 2a inset), but each sharpened and resolved into doublets at lower temperature (Figure 2a), indicating one attached ^{13}C. In very well resolved spectra each doublet appeared as doublets of doublets indicative of inequivalent nitrogens ($^2J_{N,N}$ 3.5 Hz). Both these ^{15}N resonances correlated to the same ^{13}C-carbonyl resonance (δ_C 158.2 ppm; Figure 3a,b; supplementary material) establishing that they belong to **D**. At lower field (200 MHz, 243 K; spectrum not shown) the signal at −1.5 ppm also exhibited broad ^{195}Pt satellites ($^1J_{N,Pt}$ 220 Hz), indicating platinum coupling to this nitrogen; the other signal had a chemical shift (δ_N ~67.3 ppm) more typical of a free or O-bonded urea nitrogen.

(16) On the basis of the halving of the concentration of **C** and the almost doubling of the concentration of **E**, we estimate $k_{O\rightarrow N} = 4 \times 10^{-5}$ s^{-1}, 293 K. The rate of isomerization of $[dienPtOC(NH_2)NMe_2]^{2+}$ to $[dienPtNH_2CONMe_2]^{2+}$ in acetone-d_6 was determined[14b] as $k_{O\rightarrow N} = 6.4 \times 10^{-4}$ s^{-1}, 295 K. The identity of $[dienPtNH_2CONMe_2]^{2+}$ was established by X-ray crystallography and NMR spectrsocopy.[14a]

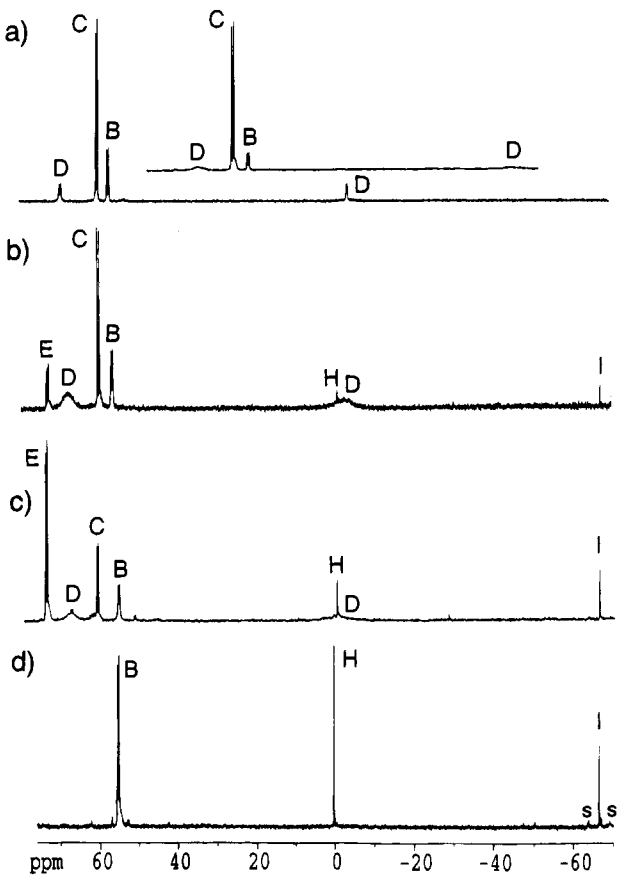

Figure 2. ^{15}N NMR spectra of the reaction at 300 K of $[dienPtOH_2](CF_3SO_3)_2$ and $^{15}NH_2{}^{13}CO^{15}NH_2$ in acetone-d_6: (a) after 5−15 min at 233 K (inset: 300 K); (b) after 60−75 min at 300 K; (c) after 6 h at 300 K; (d) after 6 days at 300 K.

After 1 h (Figure 2b) these same ^{15}N resonances were detected in addition to three new ones (species **E**, **H**, and **I**). The new doublet (**E**, δ_N ~74.4 ppm, 300 K) correlated to δ_C ~158.9 ppm and is assigned to $[dienPt^{15}NH_2{}^{13}CO^{15}\mathit{N}H_2]^{2+}$. Although the second nitrogen ($Pt-^{15}\mathit{N}H_2-$) was not detected for species **E**, it must be present since an expansion of the resolved spectrum for this species clearly showed a doublet of doublets at δ_N ~74.4 ($^2J_{N,N}$ 3.5 Hz, $^1J_{N,C}$ 22.7 Hz). The second nitrogen ($Pt\mathit{N}H_2-$) was eventually detected in the $^{13}C-^{15}N$ HETCOR spectrum (Figure 3c,d) at δ_N ~−20 ppm but is broadened into the baseline in Figure 2b. After 6 h (Figure 2c) species **C** had decreased while species **E** had increased, confirming the above observations from ^{13}C NMR spectroscopy.

Species **H** (δ_N ~0 ppm) was established as $^{15}NH_4{}^+$ by (i) its appearance as an ^{15}N singlet, indicating no attached carbon, (ii) chemical shift identical to that of a reference (5 M $^{15}NH_4NO_3$ in 2 M HNO_3) in a coaxial capillary, and (iii) a quintet in the gated (proton-coupled) ^{15}N spectrum indicating four attached protons. These protons gradually exchange with deuterium from acetone-d_6, a process that may be facilitated by water released from $[dienPtOH_2]^{2+}$ and/or protons from the acidic[14b] N-bonded urea. Species **I** (δ_N ~−65 ppm) was $[dienPt^{15}NH_3]^{2+}$, established by (i) a singlet resonance (no attached carbon), (ii) high-field chemical shift, analogous to that[17] for $[Pt(^{15}NH_3)_4]^{2+}$, (iii) gated (proton-coupled) ^{15}N NMR experiment splitting this signal into a quartet (three attached protons), and (iv) $^{195}Pt-^{15}N$ satellite signals (Figure 2d, labeled S). Other gated (proton-coupled) ^{15}N experiments showed triplets of doublets for **C**, **D**, and **E** confirming NH_2 groups.

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Table 2. ^{1}H NMR Spectral Data for Uncomplexed Ureas and for Those in (Diethylenetriamine)platinum(II) Complexes[a] in Acetone-d_6

complex	label	δ_H, ppm (^1J, Hz)[b] NMe$_2$	NH$_n$
$O^{13}C(^{15}NH_2)_2$	**B**		5.27[c] (5.42, DMSO-d_6, ($^1J_{H,N}$ 88.5)
$OC(NH_2)NMe_2$		2.79	5.60
$[dienPtO^{13}C(^{15}NH_2)_2]^{2+}$	C		−6.71[c] ($J_{H,N}$ 91.6) ($^{15}NH_2$)
$[dienPtOC(NH_2)NMe_2]^{2+}$		3.02	6.81
$[dienPt^{15}NH_2{}^{13}CO^{15}NH_2]^{2+}$	E		7.35[c,d] (Pt−NH_2); 7.28, 7.29[e] (CONH_2)
$[dienPtNH_2CONMe_2]^{2+}$		3.00	7.07
$[dienPtOH_2]^{2+}$	A		(7.35)[f]
$[dienPt^{15}NH_3]^{2+}$	I		4.12[c] ($J_{H,N}$ 72.3, $J_{H,Pt}$ 46.0) (Pt−NH_3)
$^{15}NH_4^+$	H		7.31[e] ($J_{H,N}$ 73.5)

[a] Trifluoromethanesulfonate salts at 300 K. [b] Dien resonances (not shown) were typically 2.8−3.4 (CH), 5.3−5.6 (NH_2), and 6.7−7.0 ppm (NH). [c] Doublet. [d] Broad signal. [e] Doublet of doublets. [f] Water ligand.

After 6 days (Figure 2d), resonances for urea (**B**), NH_4^+ (**H**), and $[dienPtNH_3]^{2+}$ (**I**) dominated the ^{15}N NMR spectrum. All results were reproduced with $^{15}NH_2{}^{12}CO^{15}NH_2$, which gave ^{15}N singlets only, except for **E** where a doublet ($^2J_{N,N}$ = 3.5 Hz) was observed.

^{1}H NMR Spectral Data (Table 2). After 10 min of reacting $[dienPtOH_2]^{2+}$ (**A**) with $^{15}NH_2{}^{13}CO^{15}NH_2$ (**B**) in acetone-d_6 (Figure 4a, supplementary material), there was only one prominent species (δ_H 6.71 ppm, doublet, $J_{H,N}$ 92 Hz). This correlated by $^1H-^{15}N$ HETCOR (Figure 5a, supplementary material) to δ_N ~+61.3 ppm identifying it as $[dienPtOC(NH_2)_2]^{2+}$ (**C**). At 300 K, protons for **D** are unresolved and have a chemical shift similar to that of **C**. In $^1H-^{15}N$ HETCOR spectra at 253 K, both nitrogens of unsymmetrical **D** (71 ppm, 3 ppm) correlate into a similar ^1H NMR region (7.1−7.3 ppm), near δ_H 6.9−7.1 of **C**. ^1H NMR resonances for $^{15}NH_2{}^{13}CO^{15}NH_2$ indicated that free urea (**B**) overlaps with the dien NH_2 resonance (~5.25−5.6 ppm). A $^1H-^{15}N$ HETCOR (Figure 5a, supplementary material) correlated the ^{15}N resonance seen after 10 min at ~57.6 ppm (species **B**) to a ^1H resonance of free urea (6.3 ppm, 253 K), the latter being extremely temperature and concentration dependent.

After 2.5 h (Figure 4b), other species were detected at δ_H ~4.1 ppm (doublet) and two around ~7.2 ppm (multiplet). A ^1H-^{15}N HETCOR (Figure 5b) correlated the ^1H signal (4.1 ppm) with a ^{15}N resonance (δ_N ~−65 ppm) characteristic of $[dienPt^{15}NH_3]^{2+}$ (**I**). Figure 5b shows nitrogens of **E** (74.4 ppm) and **H** (0 ppm) correlating into the same proton region (~7.3 ppm). Figure 4b inset shows a 300 MHz expansion of this region. A doublet for NH_4^+ (**H**) overlaps the six-line signal for protons of **E**. The Pt-$^{15}NH_2$− protons are a doublet (7.33 ppm), while the −$CONH_2$ protons each give doublets at 7.27 ppm ($J_{N,H}$ 89 Hz), 7.26 ppm ($^1J_{N,H}$ 91 Hz), their inequivalence resulting from restricted rotation about the partial CO=N bond.

After 6 days, mainly $[dienPt^{15}NH_3]^{2+}$ (**I**) was left (Figure 4c). Other products implicated in Figures 1 and 2 ($^{15}NH_4^+$, $^{15}NH_2{}^{13}CO^{15}NH_2$) exchange (H−D) with acetone-d_6 over this time, reducing ^1H signal intensities.

Intermediates in Urea Decomposition. Figure 6 shows the progressive decomposition of species **E**, ascribed to $[dienPtNH_2CONH_2]^{2+}$, as monitored by successive ^{13}C NMR spectra. After 6 h, Figure 6a indicates that most of **C**, $[dienPtO{=}^{13}C(^{15}NH_2)_2]^{2+}$, had rearranged to the thermodynamically more stable **E**, $[dienPt^{15}NH_2{}^{13}CO^{15}NH_2]^{2+}$. There had already been some decomposition of **E** to CO_2 (**F**) and $[dienPtNH_3]^{2+}$ (**I**) as well as some release of urea (**B**). Figure 6b was obtained after

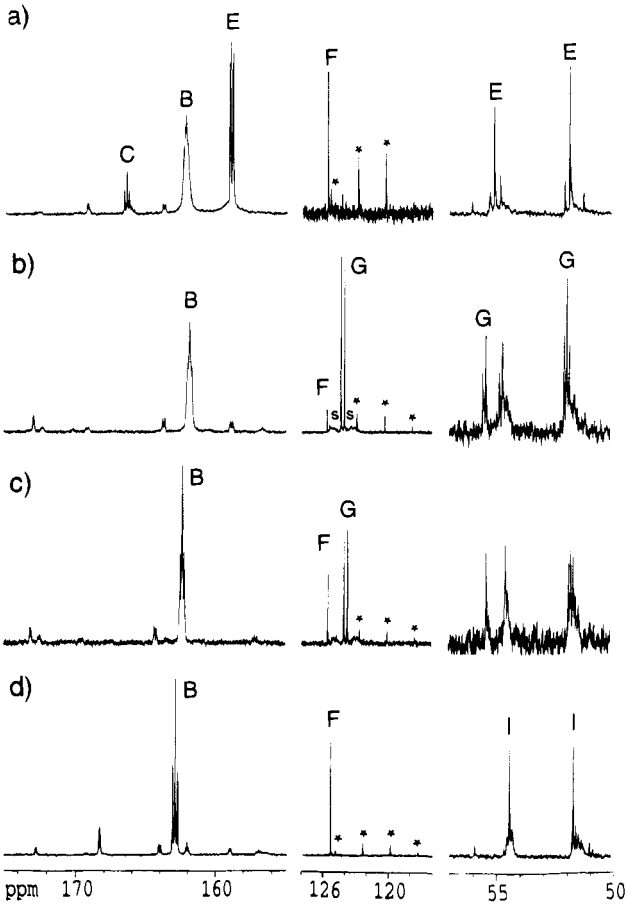


Figure 6. ^{13}C NMR spectra at 300 K for reaction of $[dienPtOH_2](CF_3SO_3)_2$ with $^{15}NH_2{}^{13}CO^{15}NH_2$ in acetone-d_6 after sequentially (a) 6 h, (b) cooling to 253 K for 10 days and recording at 300 K, (c) adding water, and (d) adding CF_3SO_3H.

cooling (253 K, 10 days) and then warming to 300 K (5 min). There is only one spectral change from Figure 6a; clearly species **C** and **E** have transformed into **G**, assigned to $[dienPt\{^{15}N^{13}CO\}]^+$ by (i) measuring the spectrum obtained (δ_c ~124.2, singlet) after separately adding $Na\{^{14}N^{12}CO^-\}$ to $[dienPtOH_2]^{2+}$ in acetone-d_6 and (ii) finding Pt satellites $^2J_{C,Pt}$ = 230 Hz (s, Figure 6b).

Adding trace water (Figure 6c) causes partial decomposition of **G**, $[dienPt^{15}N^{13}CO]^+$, to CO_2 (**F**) and $[dienPt^{15}NH_3]^{2+}$ (**I**). Some carbamate species are implicated in Figure 6 at δ_c >166 by doublet resonances, indicating carbonyls attached to one ^{15}N each. Adding CF_3SO_3H rapidly decomposes $[dienPt^{15}N^{13}CO]^+$ to $^{13}CO_2$ and $[dienPt^{15}NH_3]^{2+}$ (Figure 6d).

Discussion

Urea-Containing Reaction Products. We conclude that the main product (**C**) after 10 min of reaction of $[dienPtOH_2]^{2+}$ with urea in acetone is the O-bonded urea complex:

$$[dienPt(OH_2)]^{2+} + NH_2CONH_2 = [dienPtOC(NH_2)_2]^{2+} + H_2O$$

From ^{13}C NMR spectra we estimate that less than 10% urea is uncomplexed after 10 min, so the above equilibrium lies well to the right. Detection of an O-bonded urea complex is surprising, since Pt(II) is regarded as a soft metal and might be expected to prefer to coordinate the softer urea nitrogen. The result is consistent however with the detection of $[dienPtOC(NH_2)R]^{2+}$ (R = H, Me, NMe_2) as the initial (kinetic) product of the reaction of $[dienPtOH_2]^{2+}$ with other amides.[14]

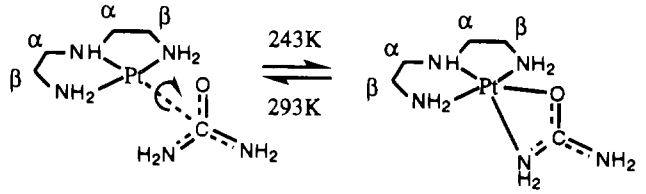
A second initial product (**D**) was detected, but its identity is unknown. Its NMR spectra are consistent with assignment as $[dienPtNH_2CONH_2]^{2+}$; however, we discounted this possibility. Species **D** shows dynamic NMR behavior consistent with fluxionality, broad signals at 300 K being resolved at lower temperatures. N−N scrambling is not the cause of this phenomenom:

$$[dienPt^*NH_2CONH_2]^{2+} = [dienPtNH_2CO^*NH_2]^{2+}$$

It would have to be fast on the NMR time scale for the nitrogens to broaden into the baseline on coalescence. Such urea scrambling could not be intermolecular, since resonances for the isomeric $[dienPtOC(NH_2)_2]^{2+}$ were well resolved (rather than broadened) at 300 K. Alternative intramolecular N−N (without N−O) scrambling is unlikely.

Although **E** has NMR (^{13}C, ^{15}N) parameters similar to those of **D** (Table 1), it does not show dynamic behavior at 300 K. Instead there is a six-line ^1H NMR signal for the urea protons of **E** (Figure 4b, inset) which we assign to the N-bonded urea complex $[dienPtNH_2CONH_2]^{2+}$ for the following reasons. First, the six-line resonance indicates three separate urea proton environments, expected for $Pt-{}^{15}NH_2{}^{13}C(=O){}^{15}NH_2$ where the $Pt-NH_2-C$ protons are equivalent and there is no $(PtNH_2{=}C)$ bond character because the nitrogen octet is filled. The other $(-CO{=}NH_2)$ protons should be inequivalent due to restricted rotation at 300 K about the partial C=N bond, which is expected to have greater π character than in free urea. This is observed in the X-ray structure[14a] of $[dienPtNH_2CONMe_2]^{2+}$, and three inequivalent urea proton resonances were also detected[7,12] in the ^1H NMR spectra of $[(NH_3)_5CoNH_2CONH_2]^{3+}$ and $[(NH_3)_5RhNH_2CONH_2]^{3+}$. On the other hand, **D** did not show this restricted rotation at 300 K. Second, other $[dienPtOC(NH_2)R]^{2+}$ species (R = H, Me, NMe_2) are formed exclusively from reactions of $[dienPtOH_2]^{2+}$ with $RCONH_2$ in acetone, and rearrangement to the N-isomer occurs on a time scale of minutes to hours.[14b,c] The assigned $[dienPtOC(NH_2)_2]^{2+}$ (**C**) transforms to $[dienPt-NH_2CONH_2]^{2+}$ (**E**) on a similar time scale ($t_{1/2} \sim 5$ h, 300 K), whereas **D** forms in ≤10 min at 300 K at a concentration that remains invariant for >5 h (although it eventually disappears). Third, formation of $[dienPtNCO]^{2+}$ and NH_4^+ is consistent with their precursor (**E**) being the addition product of these components, namely $[dienPtNH_2CONH_2]^{2+}$.

The observation of symmetric dien ligands in the 50−60 ppm ^{13}C NMR spectral region (two signals only) for both species **D** and **E** rules out their formulation as an N,O-urea-bridged dimer such as **5**, $[dienPt-NH_2C(NH_2){=}O-Pt(dien)]^{4+}$, and since both **D** and **E** contain inequivalent urea nitrogens, the symmetrical dimer **4**, $[dienPtNH_2CONH_2Pt(dien)]^{4+}$, can also be dismissed. One hypothetical possibility for the monomeric urea-containing species **D** is the unusual 5-coordinate species.



This might be fluxional at 300 K due to rotation about the Pt−C or C−O axes inverting positions of O and N or the two nitrogens, respectively. Such a π-bonded intermediate needs two inequivalent nitrogens with one coordinated to platinum at 230 K, where rotation might be slowed down. Finally, hydrogen bonding between the oxygen and dien NH_2 can be dismissed as we failed to detect any NOE. We are thus unable to establish the identity of intermediate **D** from the spectra reported.

Nevertheless a key feature of the chemistry is O- to N-linkage isomerization of urea, leading to an equilibrium mixture of **C** and **E**. The complication of ensuing reactions permits only a rough estimate of $K_{eq} \sim 10$ based on spectral resonances (e.g. Figure 6a, **C** vs **E**), favoring the N-bound linkage isomeric complex.

$$[dienPtOC(NH_2)R]^{2+} = [dienPtNH_2COR]^{2+} \qquad K_{eq}$$

Decomposition of Urea. Following establishment of the linkage isomer preequilibrium, a slow subsequent reaction proceeds to $[dienPtNH_3]^{2+}$, NH_4^+, CO_2, and urea. These ultimate products were unequivocably established by a *singlet* ^{13}C resonance for $^{13}CO_2$; a singlet ^{15}N resonance (−65.6 ppm), with ^{195}Pt satellites and three attached protons, displaced well upfield of both free urea and NH_4^+, for $[dienPt^{15}NH_3]^{2+}$; a singlet ^{15}N resonance (0 ppm) with four attached protons for $^{15}NH_4^+$; and ^{15}N, ^1H, and ^{13}C resonances for urea which grow in intensity upon adding $^{15}NH_2{}^{13}CO{}^{15}NH_2$. It is clear therefore that, notwithstanding the uncertain identity of intermediate **D**, the overall reaction stoichiometry is

$$[dienPtOH_2]^{2+} + \text{urea} = [dienPtO{=}C(NH_2)_2]^{2+} + H_2O$$

$$[dienPtO{=}C(NH_2)_2]^{2+} = [dienPtNH_2CONH_2]^{2+}$$

$$[dienPtNH_2CONH_2]^{2+} = [dienPtNHCONH_2]^{+} + H^+$$

$$[dienPtNH_2CONH_2]^{2+} + H_2O + H^+ = [dienPtNH_3]^{2+} + NH_4^+ + CO_2$$

$$\text{net: } [dienPtOH_2]^{2+} + \text{urea} + H^+ = [dienPtNH_3]^{2+} + NH_4^+ + CO_2$$

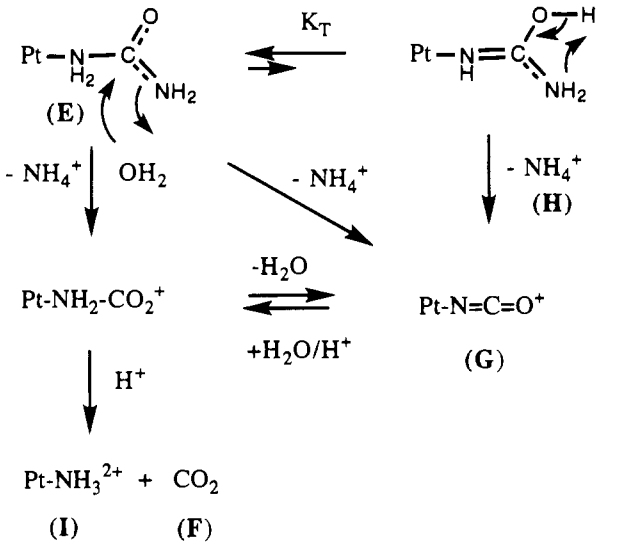
Mechanism of Urea Decomposition. $[dienPtOH_2]^{2+}$ reacts with NH_2CONMe_2 to form an isomer preequilibrium[14b] between $[dienPtNH_2CONMe_2]^{2+}$ and $[dienPtOC(NH_2)NMe_2]^{2+}$ in the first few hours. The major isomer $[dienPtNH_2CONMe_2]^{2+}$ was stable enough to be isolated and characterized by X-ray crystallography and NMR spectroscopy.[14a] However the isomer mixture eventually transforms to a more stable dimeric platinum complex and 1 equiv of displaced dimethylurea.[18] The dimer is characterized by four dien ^{13}C NMR resonances consistent with its inequivalent platinum environments and is likely $[dienPt-NH_2C(NMe_2){=}O-Pt(dien)]^{4+}$.[18]

The detection of ammonia and carbon dioxide in acetone solutions of urea, but not NH_2CONMe_2, mixed with $[dienPtOH_2]^{2+}$ suggested the possibility that the second nitrogen in urea might be important in coordinating to platinum; the NMe_2 nitrogen of dimethylureas does not appear to bind to metals[7] probably because the nitrogen lone pair is prefentially delocalized into the partial $C{=}NMe_2$ bond. Formation of a dimer would be consistent with the detected urea being liberated from platinum commensurate with formation of ammonia and carbon dioxide. There is however no evidence in this work for a platinum complex containing a bridging N,N-bonded (**4**) or N,O-bonded (**5**) urea ligand. What then is the mechanism of metal-mediated decomposition of urea?

The N-bonded urea complex (**E**) is less stable than the previously characterized[14a,b] $[dienPtNH_2CONMe_2]^{2+}$. The dif-

(18) Wickramasinghe, W. A.; unpublished results.

Scheme 1. Possible Mechanisms for Decomposition of Urea



ference in reactivity between the $[dienPtNH_2COR]^{2+}$ ($R = NH_2$, NMe_2) complexes may simply reflect the better leaving ability of NH_4^+ versus $NH_2Me_2^+$, their difference in acidity (K_a) being $\sim 10^2$. Detection of intermediate $[dienPtNCO]^{2+}$ and NH_4^+ is consistent with an elimination reaction (Scheme 1). The cyanate product could arise from elimination of NH_4^+ from $[dienPt\ NH_2CONH_2]^{2+}$ or its iminol tautomer $[dienPtNH{=}C(OH)NH_2]^{2+}$ or through elimination of water from $[dienPtNH_2CO_2]^+$. The iminol tautomer has not been detected for urea complexes before[7,14] although this does not rule it out as the putative intermediate for formation of the cyanate complex. Certainly it seems more disposed toward expulsion of NH_4^+ than does $[dienPtNH_2CONH_2]^{2+}$. Expulsion of water from $[dienPtNH_2CO_2]^+$ seems unlikely, since this requires hydrolysis of $[dienPtNH_2CONH_2]^{2+}$ to $[dienPtNH_2CO_2]^+$ followed by the reverse, dehydration to $[dienPtNCO]^{2+}$ and then rehydration (plus acid) to produce ammonia and carbon dioxide.

The decomposition of N-bonded cyanate to ammonia and carbon dioxide is however well-known for other metal systems[19] and requires acid and water to form intermediate carbamate complexes which very rapidly lose CO_2, leaving a metal–ammine complex. A similar process is likely for $[dienPt-NCO]^{2+}$, for which we have established that in acetone-d_6 both water and H^+ are required to produce $[dienPtNH_3]^{2+}$ and CO_2.

The release of uncomplexed urea during the formation of ammonia and carbon dioxide could be explained by its displacement from platinum by some of this ammonia, leading to $[dienPtNH_3]^{2+}$. This would also account for why the decomposition of urea is not catalytic, the liberated ammonia producing inert $[dienPtNH_3]^{2+}$. No other platinum-containing products were observed at the end of the reaction, so this seems a reasonable interpretation. Also addition of excess water to the reaction mixture when mainly species **E** is present (e.g. Figure 6a) leads to rapid release of some urea and formation of some $[dienPtOH_2]^{2+}$ (spectra not shown). Some ammonia reacts with acetone-d_6, as we observed signals at $\delta_H \sim 11.6$ ($^1J_{N,H}$ 90 Hz, doublet) and $\delta_N \sim 170.1$ (singlet) for $^{15}NH_2{=}^{12}C(CD_3)_2$. These resonances were correlated by $^1H-^{15}N$ HETCOR, and a gated (proton coupled) ^{15}N spectrum indicated an $^{15}NH_2$.

With respect to urease-mediated decomposition of urea, it has been proposed that hydrolysis of O-coordinated urea on Ni(II) leads to NH_3 and CO_2 via carbamate.[1] This is supported by observations[20] of substrates like formamide being processed, albeit orders of magnitude more slowly than urea. The heavier metal, platinum, from the same group as nickel and in the same oxidation state has been found to decompose urea via carbamates to ammonia and carbon dioxide. In this case cyanate was clearly an intermediate product.

$$NH_2CONH_2 + H_2O \rightarrow NH_2CO_2^- + NH_4^+ \quad \text{(hydrolysis)}$$

$$NH_2CO_2^- + 2H^+ \rightarrow NH_4^+ + CO_2$$

$$NH_2CONH_2 + H_2O \rightarrow NCO^- + NH_4^+ \quad \text{(elimination)}$$

$$NCO^- + 2H^+ \rightarrow NH_2CO_2^- \rightarrow NH_4^+ + CO_2$$

Metal-mediated degradation of ureas to ammonia and carbon dioxide is only known thus far[12,13] to occur if it involves both N-metalation of urea and a metal-bound cyanate intermediate *en route* to metal-bound carbamates. Spontaneous hydrolysis of urea via carbamate, without involving cyanate, to ammonia and carbon dioxide is unknown.

We were unable to quantitatively determine kinetic parameters by NMR for this complex system in acetone solutions. The complexes were also far too unstable to examine in water. However we can roughly estimate rates for consecutive reaction steps from NMR spectra. The rate constant for O- to N-isomerization in acetone is estimated[16] at $k_{O\rightarrow N} = 4 \times 10^{-5}\ s^{-1}$ (293 K) compared to that for the $(NH_5)_3Rh^{3+}$ system of $k_{O\rightarrow N} = 6.7 \times 10^{-5}\ s^{-1}$ (298 K) in water. It is difficult to obtain a good estimate of the rate of elimination of NH_4^+ from $[dienPtNH_2CONH_2]^{2+}$ in acetone. The lack of acid may retard this step, which appears to be rate-determining for CO_2 production, but we estimate $\sim 10^{-5}\ s^{-1}$ in acetone, which is again comparable to that for the Rh(III) system[12] in water. Cyanate decomposition to NH_4^+ and CO_2 in acetone containing excess acid is faster ($\sim 10^{-3}\ s^{-1}$) but comparable to that in aqueous acid for other metals (e.g. $(NH_5)_3M^{3+}$, M = Co, Rh, Ru). The approximate rate enhancement over known[1] elimination of NH_4^+ from urea to cyanate ($k = 6 \times 10^{-10}\ s^{-1}$, 25 °C, pH 2) is thus $\geq 10^5$. While this degree of activation of urea by $dienPt^{II}$ does not match enzymic activation ($k_{cat} \sim 10^3\ s^{-1}$),[1b] it is important model chemistry. To our knowledge $dienPt^{II}$ and $(NH_3)_5Rh^{III}$ are the only known activators of urea toward hydrolysis.

Acknowledgment. We thank Lynette Lambert, Dr. Appleton, and Prof. Craik (University of Queensland) for assistance with some ^{15}N NMR spectra.

Supplementary Material Available: Figures 3–5, showing $^{13}C-^{15}N$ HETCOR NMR and ^1H NMR spectra for the reaction of $[dienPtOH_2](CF_3SO_3)_2$ with $^{15}NH_2{}^{13}CO^{15}NH_2$ (4 pages). Ordering information is given on any current masthead page.

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