$$\begin{tikzcd} CO_2\cdot + Ru(III)\text{-cyt } c(III) \arrow[r, "k'"] & Ru(II)\text{-cyt } c(III) + CO_2 \arrow[dd, "k_u"] \\ \text{or} & \\ CO_2\cdot + Ru(III)\text{-cyt } c(III) \arrow[r, "k''"] & Ru(III)\text{-cyt } c(II) + CO_2 \end{tikzcd} \qquad (2)$$

unmodified cyt *c*(III) (eq 1). After that, a slow increase in absorbance occurs with time (Figure 2b). The absorbance vs. time for this part of the trace fits first-order kinetics with a rate constant $k_u = 82 \pm 20$ s^{-1}. This reaction corresponds to the intramolecular electron-transfer reaction shown in eq 3. The rate constant k_u

$$\text{Ru(II)–cyt } c\text{(III)} \xrightarrow{k_u} \text{Ru(III)–cyt } c\text{(II)} \qquad (3)$$

was found to be independent of dosage (at low dosage). At high dosage the proportion of the signal due to the slow reaction decreases,[14] as expected, if both the iron and ruthenium centers on the same molecule are reduced. The intermolecular electron-transfer reaction[11] involving two different cytochrome molecules is expected to be negligible at the concentrations used (ca. 2×10^{-5} M).

For a reducing agent such as $CO_2\cdot$, one would not expect significant discrimination between the two electronic isomers Ru(II)–cyt *c*(III) and Ru(III)–cyt *c*(II). However, we observed only 30–40% of the Ru(II)–cyt *c*(III) intermediate in this reduction. We are currently using different alcohol radicals such as pentaerythritol ($C(CH_2OH)_4$) in an effort to increase the concentration of the Ru(II)–cyt *c*(III) intermediate. Simic et al.[10] have shown that the pentaerythritol radical reduces cyt *c* with a rate constant $<10^6$ M^{-1} s^{-1}. By use of different alcohols the amount of Ru(II)–cyt *c*(III) could be increased since such a bulky radical may show selectivity toward the surface-bound $[(NH_3)_5Ru^{III}]$ moiety over the less exposed heme group.

The results in this communication have extended our intramolecular electron-transfer measurements from model peptides[2,3] to proteins. The distance between the His-33 moiety and the heme can be estimated from the crystal structures[12] of the oxidized and reduced tuna cytochrome *c* to be 12–16 Å, depending on which imidazole nitrogen the ruthenium is bound to and the conformation of the His-33 side chain. This long-range electron transfer across polypeptides, although in itself not biologically relevant, demonstrates that given a driving force of ~0.1 eV, electron transfer within proteins can take place rapidly at long distances.

We are currently attempting the synthesis of a variety of ruthenium–cytochrome *c* derivatives with different substituted ruthenium complexes of the type $[L(NH_3)_4Ru^{III}]$[13] in order to observe intramolecular electrons transfer from the ruthenium to the iron (heme), as well as from the iron (heme) to the ruthenium in the protein. Experiments with such derivatives should help us to understand the effect of driving force on the rate of intramolecular electron transfer between a donor and acceptor held at long distances. Other experiments of this nature with redox reagents covalently bound to proteins at different distances will help us to understand the dependence of rate of electron transfer on distance for different intervening peptide residues.

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Registry No. $[(NH_3)_5Ru(OH)_2)]^{2+}$, 21393-88-4; Ru, 7440-18-8; Fe, 7439-89-6; histidine, 71-00-1; cytochrome *c*, 9007-43-6.

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(14) The fate of Ru(II)–cyt *c*(II) could not be determined under the experimental conditions used since slow changes (ca. <500 ms) could not be monitored because of the large S/N ratio of the xenon detector.

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Reaction between Cyanate Ion and Ethylene Coordinated to Platinum: A New Route to Carbamoyl Complexes

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Nucleophilic attack to coordinated olefins[1] and oxidative addition to central metal[2] are known to occur readily in platinum(II) complexes. We now show that an appropriate combination of these two processes leads to the formation of a chelating *N*-ethylenecarbamoyl group from ethylene and cyanate ion.

We recently isolated a stable olefin complex of platinum(II), $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine),[3] the reactivity of which toward nucleophiles was greatly enhanced and resembled that of other cationic complexes of platinum-group metals such as iron,[4] ruthenium, and rhodium.[5]

The reaction of a suspension of $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)](ClO_4)$, in water at room temperature, with twice the stoichiometric amount of sodium cyanate afforded a white precipitate in 40% yield based on platinum, and neutralization of the resulting basic solution produced a further 30% yield of product. This compound dissolved in dichloromethane and could be isolated as colorless needles upon cooling.

The elemental analysis $[C_{10}H_{23}ClN_4O_3Pt$ (C, H, Cl, N)] and ^{1}H NMR [(CD_2Cl_2, $Si(CH_3)_4$) δ 2.99, 2.81, 2.79, and 2.75 (4 s, 4 × 3 H, CH_3N); 5.60 (br, $^3J_{Pt-H} = 66$ Hz, HN)[6] and other unresolved resonances in the range 2.2–3.7 (m, 8 H, CH_2)] and IR spectra [(KBr pellets, cm^{-1}) 3540 and 3410 (ν_{OH}, water of crystallization), 3270 and 1630 (ν_{NH} and $\nu_{C=O}$, carbamoyl group),[7] 2210 and 1330 (ν_{asym} and ν_{sym}, isocyanate group), 350 (ν_{PtCl})] were in accord with the formula $[\overline{Pt(CH_2CH_2NHC}{=}O)Cl(NCO)$-

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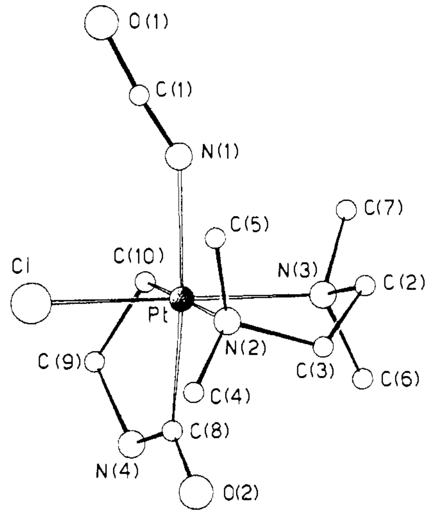


Figure 1. Molecular structure of the complex $[\overline{\mathrm{Pt(CH_2CH_2NHC}}{=}\mathrm{O)}\text{-}\mathrm{Cl(NCO)(tmen)}]$.

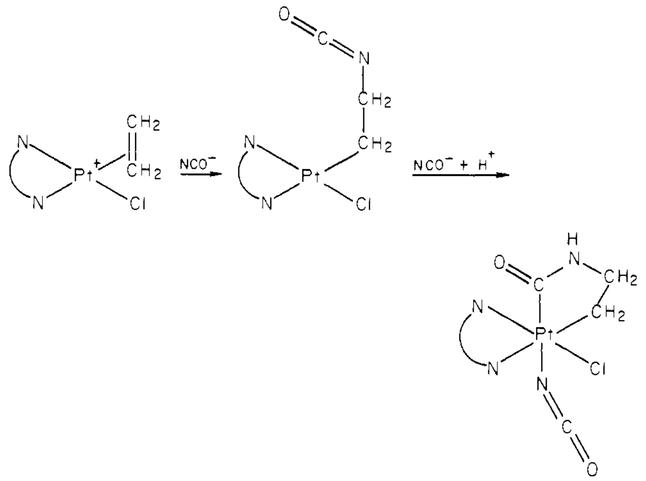
$(\mathrm{tmen})]\cdot H_2O$.

An X-ray crystallographic analysis of this complex definitively established its structure (Figure 1).[8] The octahedral coordination around platinum[9] involves a nitrogen atom from an isocyanate ion, a chloride ion, two nitrogen atoms from a chelating tmen unit, and two carbon atoms from a novel chelating *N*-ethylenecarbamoyl group.

The arrangement of the equatorial ligands strictly resembles that of the starting $[\mathrm{Pt}(\eta^2\text{-}C_2H_4)\mathrm{Cl}(\mathrm{tmen})]^+$ complex.[10] The pentaatomic platinum-*N*-ethylenecarbamoyl ring is puckered with Pt, C(10), C(9), N(4), and C(8) atoms deviating from the mean plane passing through them by 0.001 (1), 0.18 (3), −0.28 (4), −0.02 (3), and 0.11 (4) Å, respectively; the Pt atom and the C(8), N(4), and O(2) atoms of the carbamoyl group are instead strictly coplanar. The isocyanate ligand is quite regular but surprisingly inclined with respect to the Pt–N(1) bond. Carbamoyl groups have been shown to coordinate as C-bonded monodentate ligands,[11] or as C,O-bonded bidentate ligands in other complexes.[12]

A plausible reaction sequence leading to the formation of this compound is shown in Scheme I. Initially the ethylene of $[\mathrm{Pt}(\eta^2\text{-}C_2H_4)\mathrm{Cl}(\mathrm{tmen})]^+$ undergoes nucleophilic attack by a cyanate ion to form a *N*-ethyleneisocyanate ligand; this, in turn, adds electrophilically to the metal, which behaves as a Lewis base in a reaction analogous to oxidative addition. This second step is assisted by a second cyanate ion, which enters the coordination sphere of platinum, and by a proton, abstracted from the solvent, which neutralizes the negative charge on nitrogen. Protonation of a coordinated isocyanate to give a carbamoyl complex has been reported previously.[13]

Scheme I



The cyanate ion is generally thought of as being a nucleophilic reagent due to the high electron density localized on the terminal nitrogen atom.[14] However, the potential electrophilic character of the central carbon, which has been recently recognized for the isoelectronic and isostructural carbon dioxide molecule,[15] has not been established. In principle, this reagent should be able to give "bifunctional reactions" with complexes containing an electron-rich transition metal and an acidic center close together in the same molecule. These conditions appear to be met by $[\mathrm{Pt}(\eta^2\text{-}C_2H_4)\text{-}\mathrm{Cl}(\mathrm{tmen})]^+$ and NCO^- which react to yield the formation of a metallaazacyclopentane.

The net incorporation of a H(NCO) into a metal–olefin moiety to form a carbamoyl complex represents a new, and hitherto unexplored, route to this class of complexes, the importance of which in synthetic and speculative chemistry is rapidly increasing.[16] In addition we feel that this reaction could have some relevance to studies on the catalytic activity of platinum metals and the activation of biphilic, donor–acceptor molecules including carbon dioxide.[17]

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Registry No. $[\mathrm{Pt}(\eta^2\text{-}C_2H_4)\mathrm{Cl}(\mathrm{tmen})](\mathrm{ClO_4})$, 71639-56-0; $[\overline{\mathrm{Pt}\text{-}(\mathrm{CH_2CH_2NHC}}{=}\mathrm{O})\mathrm{Cl}(\mathrm{NCO})(\mathrm{tmen})]\cdot H_2O$, 83802-03-3; sodium cyanate, 917-61-3.

Supplementary Material Available: Final atomic coordinates, atomic thermal parameters, table of bond distances and angles, and listing of structure factor amplitudes (12 pages) are available. Ordering information is given on any current masthead page.

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(8) The colorless crystals of the complex were always of poor quality and mostly twinned. Several crystals were examined; three were used for the structure determination. The best results were obtained from a roughly prismatic crystal (of approximate dimensions 0.10 × 0.15 × 0.20 mm³). Crystal data: $C_{10}H_{21}ClN_4O_2Pt\cdot H_2O$, $F_w = 477.86$, monoclinic, space group $P2_1/n$, $a = 9.706$ (5), $b = 14.021$ (6), $c = 11.556$ (5) Å, $\beta = 91.77$ (3)°, $V = 1572$ (1) Å³, $Z = 4$; $\rho_{calcd} = 2.02$ g cm^{-3}, $\mu(\mathrm{Mo}K\alpha) = 92.0$ cm^{-1}, $\bar{\lambda} = 0.710688$ Å. Number of measured reflections 2781 ($3 \leq \theta \leq 25°$); number of observed reflections 1531 [$I \geq 2\sigma(I)$]. The cell dimensions and intensity data were collected on a Siemens single-crystal diffractometer. The structure was solved by the heavy-atom method and refined by full-matrix least-squares analysis with anisotropic thermal parameters for the Pt and Cl atoms only. Final *R* value 0.094 (observed reflections only).

(9) Relevant bond distances (Å): Pt–Cl, 2.309 (5); Pt–N(1), 2.13 (1); Pt–N(2), 2.21 (1); Pt–N(3), 2.14 (1); Pt–C(8), 2.04 (2); Pt–C(10), 2.12 (2); N(1)–C(1), 1.11 (2); C(1)–O(1), 1.19 (2); N(3)–C(2), 1.48 (2); C(2)–C(3), 1.51 (3); C(3)–N(2), 1.55 (3); C(8)–N(4), 1.35 (2); C(8)–O(2), 1.18 (2); N(4)–C(9), 1.43 (2); C(9)–C(10), 1.55 (2). Relevant bond angles (deg): N(1)–C(1)–O(1), 174 (2); C(1)–N(1)–Pt, 147(1); Pt–C(10)–C(9), 104 (1); C(10)–C(9)–N(4), 111 (2); C(9)–N(4)–C(8), 122(2); N(4)–C(8)–O(2), 125 (2); N(4)–C(8)–Pt, 111(1); O(2)–C(8)–Pt, 124 (1).

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