ORGANOMETALLICS

Volume 12, Number 3, March 1993

Communications

Bioorganometallic Chemistry. 2. Synthesis and Structural Studies of the Reactions of a Nucleobase, 1-Methylcytosine, with a (η^5-Pentamethylcyclopentadienyl)rhodium Aqua Complex

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Received December 23, 1992

*Summary: The reactions of a nucleobase, 1-methylcytosine (MC), with a Cp*Rh aqua complex, [(η^5-Cp*)Rh(H_2O)$_2$(OTf)$_2$]$_x$ (2), provided two different complexes depending on the solvent media. Complex 3, [(η^5-Cp*)Rh(η^1(N3)-MC)(η^2(O2,N3)-MC)](OTf)$_2$, was formed when acetone was used as the solvent; however, when complex 3 was recrystallized from water (pH 5.1) or when water was used as the reaction solvent, complex 4, trans-[(η^5-Cp*)Rh(η^1(N3)-MC)(μ-OH)]$_2$(OTf)$_2$, was isolated as a crystalline solid. The structures of 3 and 4 were verified by ^{1}H NMR, FAB/MS, elemental analysis, and single-crystal X-ray analysis. The structure of complex 3 showed one MC ligand bound via N3 and the other chelated via N3 and C=O2 (Rh–O2 = 2.251(6) Å). Inspection of several bond lengths of complex 4 indicates extensive intramolecular hydrogen bonding of the μ-OH groups with the exocyclic NH_2 (HO---HNH = 1.93(1) Å) and the 2-C=O group (OH---O=C = 1.96(1) Å).*

The reactions of inorganic metal complexes with DNA/RNA nucleobases, nucleosides, nucleotides, and oligonucleotides have been extensively studied,[1] while few studies have been directed toward organometallic complexes with these biologically important ligands.[2] We have been investigating the coordination chemistry of the highly electrophilic (η^5-pentamethylcyclopentadienyl)rhodium dicationic complex [Cp*Rh(S)$_3$]$^{2+}$ (S = CH_3COCH_3, CH_3-

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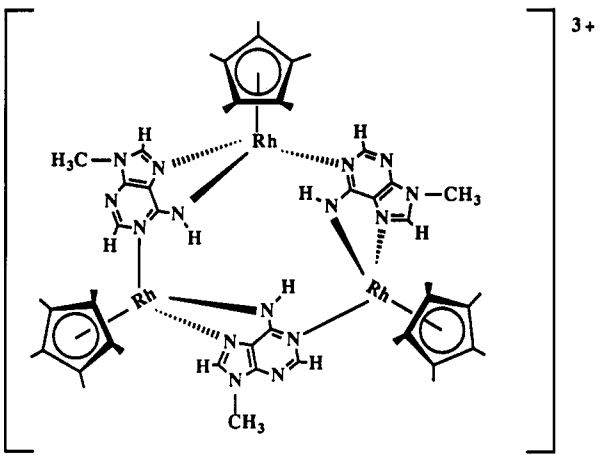
CN) with nitrogen heterocyclic compounds in organic solvents.[3] Similar studies in aqueous solution with biologically important nitrogen ligands as mentioned above are of interest in view of the utility of Cp*Rh aqua complexes as anchors for single DNA molecules, in conjunction with surface microscopy techniques, for application to the human genome involving mapping and sequencing DNA bases,[4] and as potential chemotherapeutics as well as reagents in biotechnology.[1b,c]

Recently, we reported that 9-methyladenine formed an unusual and unprecedented cyclic trimer, $[(\eta^5\text{-Cp*})\text{Rh}(\mu_2\text{-}\eta^1(N1)\text{:}\eta^2(N6,N7)\text{-9-methyladenyl})]_3(\text{OTf})_3$ (1) upon reaction in water with a (η^5-pentamethylcyclopentadienyl)rhodium aqua complex, 2, from pH 6 to 9.[5] In that study, it was evident that the formation of the η^2(N6,N7) five-



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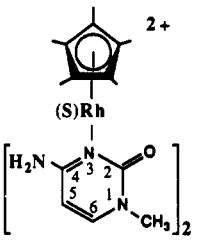
membered adenyl chelate occurred by a condensation reaction of the exocyclic NH_2 group with 2, a reactive Cp*Rh hydroxy species at pH 5–7.[5,6] Similar cyclic trimer structures were also observed for adenosine,[5] adenosine 3′-monophosphate, and the phosphate methyl ester of adenosine 5′-monophosphate in reactions with 2 in aqueous solution.[7]

In order to ascertain the scope of this condensation reaction with nucleobases that have exocyclic NH_2 groups, we studied the reaction of the aqua complex 2, having an empirical formula of $[\text{Cp*Rh}(H_2O)_2(\text{OTf})_2]_x$, with 1-methylcytosine (MC). We found that two different Cp*Rh 1-methylcytosine complexes could be isolated depending on the solvent media used in the reaction.

Reaction of 2 with 2 equiv of 1-methylcytosine in acetone for 36 h, followed by extraction with CH_2Cl_2, gave an orange precipitate (67%), complex 3, whose ^{1}H NMR spectrum in DMSO-d_6 revealed only one set of 1-methylcytosine and Cp* resonances and considerable downfield chemical shifts for H5 and H6 in comparison to free 1-methylcytosine ($\Delta\delta$(H5) = 0.25 ppm, $\Delta\delta$(H6) = 0.26 ppm). In



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addition, two broad N(4)H_2 resonances were also shifted downfield upon coordination (7.70, 8.50 ppm compared to free 1-methylcytosine at 6.91 ppm). The FAB/MS data were consistent with a monomeric species (*m*-nitrobenzyl alcohol; *m/z* 512, [Cp*Rh(MC)(OTf)]) and provided no evidence for a dimer. The ^{1}H NMR data (one set of 1-methylcytosine signals for 3 down to −90 °C in CD_3OD) supports the solution structure of 3 as $[(\eta^5\text{-Cp*})\text{Rh}(\eta^1(N^3)\text{-MC})_2(\text{S})](\text{OTf})_2$, where a solvent molecule (S = H_2O, DMSO, CH_3OH) appears to take up the third coordination site on (η^5-Cp*)Rh.[8]

An X-ray structural determination of compound 3 recrystallized from methanol, a weakly coordinating solvent, clearly shows, *in the solid state*, that one of the 1-methylcytosine ligands bonds via a four-membered-ring chelate, N3-Rh-O=C2 (Rh–N3a, 2.143(7) Å; Rh–O2a, 2.251(6) Å) with the other ligand bound through the expected N3 site (Rh–N3b, 2.126(8) Å) (Figure 1). Several structurally characterized examples of cytosine N3,O2 metal semichelates exist and exhibit longer M–O bond lengths (M = Cu, 2.76 Å; M = Cd, 2.64, 2.56, and 2.89 Å; M = Hg, 2.84 Å)[9] in comparison to those observed in compound 3. The structural consequences of N3,O2 chelation, versus N3 coordination alone, are manifested in complex 3 by a longer C–O bond length (C2a–O2a, 1.264(10) Å; C2b–O2b, 1.209(11) Å), a shorter C2–N3 bond length (C2a–N3a, 1.350(10) Å; C2b–N3b, 1.402(11) Å), a

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(8) Complex 3, $[(\eta^5\text{-Cp*})\text{Rh}(\eta^1(N3)\text{-MC})(\eta^2(O2,N3)\text{-MC})](O_3SCF_3)_2$: In a Vacuum Atmospheres drybox, 200 mg of $[\text{Cp*Rh}(H_2O)_2(\text{OTf})_2]_x$ (0.36 mmol) and 91 mg of 1-methylcytosine (MC, 0.73 mmol) were slurried for 36 h in 20 mL of acetone. The solvent of the orange solution was stripped in vacuo, and the remaining orange solid was slurried in 20 mL of CH_2Cl_2 for 2 h and then filtered and dried to give 195 mg (67%) of complex 3. Analytically pure 3 was obtained by recrystallization from minimal methanol. ^{1}H NMR (DMSO-d_6, ppm): 8.52 (b, 1H, NH), 7.82 (d, J_{HH} = 7.4 Hz, 1 H, H6), 7.72 (b, 1H, NH), 5.84 (d, J_{HH} = 7.4 Hz, 1 H, H5), 3.28 (s, 3 H, Me), 1.71 (s, 15H, Cp*). FAB/MS (*m*-nitrobenzyl alcohol; *m/z* (relative intensity) 512.1 (52), [Cp*Rh(MC)(OTf)]; 387.0 (18), [Cp*Rh(OTf)]; 362.1 (100), [Cp*Rh(MC)]; 237.0 (30), [Cp*Rh − H]; 126.1 (40), [MC + H]. Anal. Calcd for $RhO_8S_2F_6N_6C_{22}H_{29}$: C, 33.60; H, 3.72; N, 10.67. Found: C, 33.35; H, 3.75; N, 10.33. Orange needles of $[(\eta^5\text{-Cp*})\text{Rh}(\eta^1(N3)\text{-MC})(\eta^2(N3,O2)\text{-MC})](O_3SCF_3)_2\cdot 1.5\text{MeOH}$ were obtained from methanol/Et_2O solution at −30 °C under an inert atmosphere. Crystal data: Mo Kα(λ = 0.710 73 Å); T = 130 K; space group $P2_1/n$; Z = 4; a = 9.096(3) Å, b = 27.396(7) Å, c = 13.952(5) Å, β = 99.14(3)°; 0° > 2θ > 50°; 4160 observed reflections ($F > 4.0\sigma(F)$); R = 0.0717 and R_w = 0.0745. To satisfactorily refine the structure, one of the two methanol molecules present in the crystal was modeled at 100% site occupancy and the second at 50% occupancy. The structure was solved by the Patterson method using SHELXTL PLUS.

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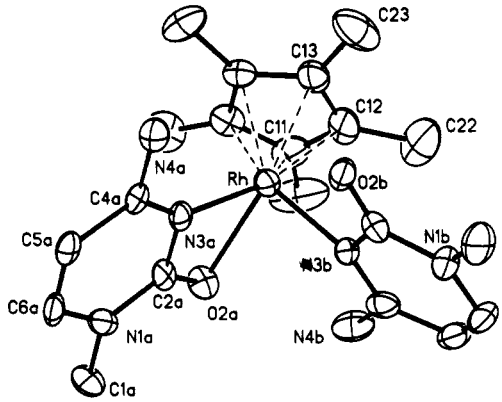

Figure 1. Molecular structure of **3**, $[(\eta^5\text{-Cp*})Rh(\eta^1(N3)\text{-MC})(\eta^2(O2,N3)\text{-MC})](OTf)_2 \cdot 1.5MeOH$, with atoms shown as 50% ellipsoids. Only the cation is shown for clarity. Selected bond lengths (Å) and angles (deg): Rh–N3a, 2.143 (7); Rh–N3b, 2.126 (8); Rh–O2a, 2.251 (6); N3a–Rh–N3b, 90.0 (3); N3a–Rh–O2a, 61.0 (2); O2a–Rh–N3b, 88.0 (2).

shorter C4–N4 bond length (N4a–C4a, 1.308 Å; N4b–C4b, 1.349(13) Å), and a smaller O2–C2–N3 bond angle (O2a–C2a–N3a, 117.1(7)°; O2b–C2b–N3b, 121.6(8)°). The N4a---O2b through-space distance (3.175 Å) precludes any intramolecular hydrogen bonding between these sites.

Upon recrystallization of complex **3** from H_2O (pH 5.1), a new complex, **4**, is formed. Complex **4** can also be isolated by the dropwise addition of a deoxygenated, aqueous solution of 1 equiv of 1-methylcytosine to an aqueous solution of **2** that was adjusted to pH 5–6 by addition of NaOH. The ^1H NMR spectrum of **4** in DMSO-d_6 showed upfield chemical shifts for H5 (5.27 ppm) and H6 (7.45 ppm) of 0.32 and 0.09 ppm, respectively, in comparison to free 1-methylcytosine, while one set of exocyclic NH_2 protons at 7.18 ppm was shifted downfield by 0.27 ppm. The other exocyclic NH_2 signal was not observed and is apparently broadened into the base line. FAB/MS verified the dimeric nature of **4** (*m*-nitrobenzyl alcohol; *m/z* 766, $[(Cp^*Rh)_2(MC)(\mu\text{-OH})](OTf)$; *m/z* 659, $[Cp^*Rh(\mu\text{-OH})]_2(OTf)$, while the single-crystal X-ray analysis confirmed the trans stereochemistry and the extensive intramolecular hydrogen bonding of the bridging hydroxyl groups with the C=O and the exocyclic NH_2 groups (Figure 2).[10] This hydrogen-bonding network creates a hydrophobic environment around the metal centers and appears to be the reason that **4** is insoluble in H_2O at pH 5.1.

The core structure of **4** is quite similar to *cis*-[3a] and *trans*-$[(\eta^5\text{-Cp*})Rh(\eta^1\text{-(N)})(\mu\text{-OH})]_2^{2+}$ [11] dimeric complexes with heteroaromatic nitrogen ligands (cis stereochemistry,

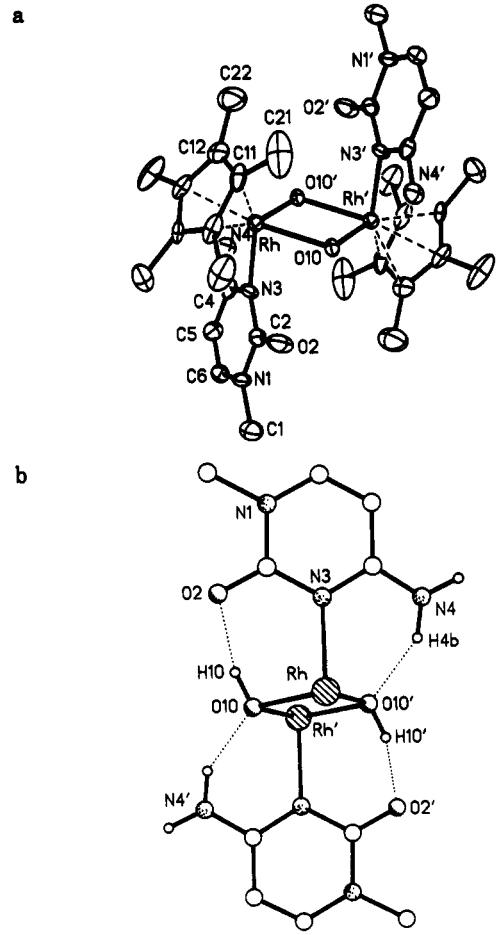

Figure 2. (a, upper view) Molecular structure of **4**, *trans*-$[(\eta^5\text{-Cp*})Rh(\eta^1(N3)\text{-MC})(\mu\text{-OH})]_2(O_3SCF_3)_2$, with atoms as 50% ellipsoids. Selected bond length (Å) and angles (deg): Rh–N3, 2.181(5); Rh–O10, 2.138(5); Rh–O10′, 2.118(5); C(2)–O(2), 1.232(10); C(4)–N(4), 1.32(9); H4b–O10′, 1.93(1); H10–O2, 1.96(1); N3–Rh–O10, 87.9(2); Rh–O10–Rh′, 101.2(2); N(4)–C(4)–N(3), 117.7(6); O(2)–C(2)–N(3), 123.1(6); N4–H4–O10′, 149(1); O10–H10–O2, 155(1). (b, lower view) Structure of the $[Rh(\mu\text{-OH})(MC)]_2$ core emphasizing the intramolecular hydrogen bonding.

N = quinoline, **5**; trans stereochemistry, N = pyridine, **6**); however, some slight differences are apparent. The planar $Rh_2(\mu\text{-OH})_2$ fragment of **4** shows a wider O–Rh–O angle of 78.8(2)° in comparison to **5** (75.1(1), 74.8(1)°) and **6** (76.8-(2)°). As well, a smaller Rh–O–Rh angle (101.2(2)°) for **4** was observed in comparison to 104.7(1) and 105.0(1)° for **5** and 103.1(2)° for **6**. This results in a closer Rh–Rh through-space distance of 3.290(2) Å for **4** in comparison to 3.322(1) Å for **5** and 3.308(1) Å for **6**.

This slight deformation is presumably caused by the unusual binding of the 1-methylcytosine in which the $(Rh\text{–}OH)_2$ core *acts as a covalent electrophile, a hydrogen bond donor, and a hydrogen bond acceptor*. This system is a rare example of a complex in which a μ-hydroxy ligand exhibits simultaneous hydrogen bond donor and acceptor capabilities.[11] Although other metal complexes of 1-methylcytosine have shown extensive *inter*molecular

(10) Complex **4**, $[(\eta^5\text{-Cp*Rh})(\eta^1(N3)\text{-MC})(\mu\text{-OH})]_2(O_3SCF_3)_2 \cdot 4H_2O$: Complex **3** (43 mg) was dissolved in 5 mL of deoxygenated water, and the solution was stirred for 36 h, resulting in precipitation of a yellow-orange solid. The volume of the reaction mixture was reduced to ca. 2 mL, and the orange precipitate (23 mg, 81%) was collected by filtration and dried for 18 h under vacuum. ^1H NMR (DMSO-d_6, ppm): 7.45 (H6, d, J_{HH} = 7.4 Hz, 1 H); 7.18 (NH, b, 1H), 5.27 (H5, d, J_{HH} = 7.4 Hz, 1 H); 3.18 (CH_3, s, 3 H); 1.78 (Cp*, s, 15H). FAB/MS (*m*-nitrobenzyl alcohol; *m/z* (relative intensity)): 766 (10), $[(Cp^*Rh(\mu\text{-OH}))_2(MC)(OTf) - H_2O]$; 659 (23), $[(Cp^*Rh(\mu\text{-OH}))_2(OTf)]$; 641 (13), $[(Cp^*Rh(\mu\text{-OH}))_2(OTf) - H_2O]$; 512 (20), $[Cp^*Rh(MC)(OTf)]$; 362 (82), $[Cp^*Rh(MC)]$; 237 (25), $[Cp^*Rh - H]$; 149 (100), [OTf]; 126 (30), [MC + H]. Anal. Calcd for $Rh_2O_{14}S_2F_6N_6C_{32}H_{54}$: C, 33.99; H, 4.81; N, 7.43. Found: C, 33.53; H, 4.40; N, 7.82. Orange parallelepipeds of **4** were obtained from water at room temperature. Crystal data: Mo Kα (λ = 0.710 73 Å); T = 130 K; space group $P2_1/n$; Z = 2; a = 8.077(2) Å, b = 19.541(4) Å, c = 13.508(3) Å, β = 106.50(3)°; 2484 observed reflections ($F > 4.0\sigma(F)$); R = 0.0486 and R_w = 0.0480. The structure was solved by direct methods using SHELXTL PLUS. Hydrogen atoms bonded to carbon were located from a difference map and subsequently refined using a riding model with C–H = 0.96 Å and isotropic U values equal to 1.2 times the equivalent isotropic U of the bonded carbon. The amino and hydroxy hydrogens were also located on the difference map and restrained to have N–H and O–H bond lengths of 0.94(2) and 0.92(2) Å, respectively, and fixed isotropic U's but were otherwise not constrained. A difference map was featureless.

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hydrogen bonding,[13] we are unaware of a system which recognizes the bonding capabilities of this ligand so readily in an *intra*molecular fashion. In addition, the formation of **4** provides some evidence for the structure of the reactive aqua complex **2** that corroborates the FAB/MS data, obtained previously, indicating a dimeric $[Cp^*Rh(\mu\text{-}OH)]_2$ cationic complex (pH dependent).[5]

Condensation reactions between the exocyclic NH_2 of 1-methylcytosine and M–OH centers to form either four-membered-ring chelates (η^2(N3,N4); Cp_2Mo^{2+}, Pt^{IV}) or μ-1-methylcytosyl complexes (Pt^{II}) are well documented.[2d,13a,13c] However, we were not able to induce a similar condensation reaction between the exocyclic NH_2 and the μ-OH group with **4**. Mild thermolysis (70 °C for 16 h) of **4** in DMSO-d_6 solutions results in overall decomposition with no evidence of a condensation reaction. The fact that we observe no apparent condensation reaction of the exocyclic NH_2 group with the bridging OH group could be indicative of the pronounced stability of the extensive intramolecular hydrogen-bonding regime shown in **4** or simply a manifestation of the instability of a four-membered-ring chelate. Thermolysis of **3** under the same conditions gave a similar result, while heating **3** in acetone-d_6 at 50 °C for 24 h showed no reaction.

In future publications, we will report on the reactivity of **2** with other nucleobases, nucleotides, and sequence-specific oligonucleotides as well as its utility as a tether, simultaneously bonding to both glass or electrode surfaces and sequence-specific oligonucleotide–single DNA molecules, for eventual application to sequence and map the human genome.[4c]

Acknowledgment. The studies at LBL were generously supported by Laboratory Directed Research and Development Funds and the Department of Energy under Contract No. DE-AC03-76SF00098. We thank Dr. Mina J. Bissell of LBL for her support of this project.

Supplementary Material Available: Tables of crystal data, atomic coordinates and isotropic displacement coefficients, bond lengths, bond angles, and anisotropic displacement coefficients for **3** and **4** (18 pages). Ordering information is given on any current masthead page.

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