Binding of Amino-Dialkylated Adenines to Rhenium(III) and Rhenium(IV) Centers

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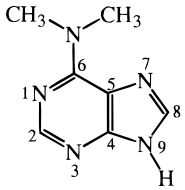
Amino-dialkylated adenines R_2AdH (R = Me, Et) react with $ReCl_3(MeCN)(PPh_3)_2$ to form *mer*,*cis*-$ReCl_3(R_2AdH)_2(PPh_3)$ complexes. Attempts to protonate the coordinated adenine with HCl led to the oxidized *trans*-$ReCl_4(R_2AdH)(PPh_3)$ compounds. In both types of complexes, the purine binds via the N3 site of the six-membered ring and makes an intramolecular N9−H···Cl hydrogen bond with a chloride ligand. A material of composition $ReCl_4(R_2AdH)(MeCN)$ was obtained by reacting R_2AdH with *cis*-$ReCl_4(MeCN)_2$. It turned out to be a $ReCl_4[R_2AdC(Me)═NH]$ complex containing a cyclic amidine ligand resulting from the insertion of the acetonitrile C≡N group in the N9−H bond of the N3-coordinated adenine unit. Crystal structures were determined for one compound of each type: $ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$, triclinic, $P\bar{1}$, a = 14.181(2) Å, b = 17.591(3) Å, c = 19.015(5) Å, α = 76.66(2)°, β = 86.80(2)°, γ = 87.02(1)°, Z = 4, R = 0.0606; $ReCl_4(Me_2AdH)(PPh_3)$, triclinic, $P\bar{1}$, a = 10.391(4) Å, b = 10.801(5) Å, c = 13.651(6) Å, α = 89.64(4)°, β = 83.49(3)°, γ = 65.14(4)°, Z = 2, R = 0.0432; $ReCl_4[Me_2AdC(Me)═NH]\cdot C_6H_6\cdot CH_2Cl_2$, monoclinic, $P2_1/c$, a = 13.941(3) Å, b = 13.656(3) Å, c = 12.874(2) Å, β = 105.47(2)°, Z = 4, R = 0.0406. Most of the signals in the ^{1}H NMR spectra of these paramagnetic species could be assigned.

Introduction

Purine nucleobases contain various pairs of donors suitably oriented to bridge adjacent metal atoms.[1] For instance, the N3/N9 region of the deprotonated form has the same topology as a carboxylate and compounds are known in which it plays a similar bridging role.[2] *N*6,*N*6-dialkyladenine (or 6-(dialkylamino)purine, R_2AdH, Chart 1) attracted our attention as a binuclear agent to support metal−metal bonded units such as Re_2^{6+}, because the alkyl groups hide the reactive N1 and N7 sites and prevent the formation of extended polymeric materials. Since our work with CH_3Hg^+ has shown that these sites remain accessible for protons,[3,4] dinuclear species containing several of these ligands should exhibit spectroscopic and other physical properties sensitive to H^+ over a broad pH range.

In a previous paper,[5] we reported on $Re_2Cl_2(R_2Ad)_4$ compounds whose properties were consistent with a "paddle-wheel" structure. However, their preparation via substitution on $[Re_2Cl_8]^{2-}$ and $Re_2Cl_2(acetate)_4$ generated mixtures of isomers corresponding to various relative orientations of the purines about the metal−metal axis. Considering that these ligands sometimes promote the formation of dimers from monomeric species,[2] we considered the possibility of preparing pure isomers by coupling monomeric rhenium complexes containing the purine specifically coordinated in a monodentate manner. This goal has not been reached yet, but the monomeric precursors have been found to contain adenine bonded via the unusual N3 site.

Chart 1



We are describing here the preparation and structure of these compounds, together with our efforts to interpret the ^{1}H NMR data of these paramagnetic Re(III) and Re(IV) monomers.

Experimental Section

Reactants and Methods. $ReCl_5$ (Aldrich) was kept in the glovebox under argon and used without further purification. The dialkyladenines were prepared from 6-chloropurine (Aldrich) and dialkylamines as described in the literature.[6] Dimethyladenine was C8,N9-deuterated by refluxing in D_2O for 2.5 h and evaporating to dryness. $ReCl_3(MeCN)(PPh_3)_2$ was prepared by the method of Rouschias and Wilkinson[7] and checked by ^{1}H NMR.[8]

The procedure described by the same authors was used to prepare *cis*-$ReCl_4(MeCN)_2$.[7] ^{1}H NMR ($(CD_3)_2CO$) (δ, ppm): −63.9. The structure was checked by X-ray diffraction.[9]

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^{1}H NMR spectra were recorded between 160 and −160 ppm on a Bruker AMX-300 spectrometer. The residual solvent signal (C_6D_6, 7.15 ppm; CD_2Cl_2, 5.32 ppm; $(CD_3)_2CO$, 2.04 ppm) was used as internal reference. Infrared spectra were obtained from CsI pellets with a Perkin-Elmer 1600 FT-IR instrument. FAB^+ mass spectra were recorded on a VG-Autospec Q apparatus in nitrobenzylic alcohol. Magnetic moments were determined on an Evans balance (Johnson-Matthey) calibrated with $HgCo(SCN)_4$ ($\chi = 16.44 \times 10^{-6}$ cgsemu). Corrections for diamagnetism were calculated from Pascal's constants.[10] Elemental analyses were performed by the Guelph Chemical Laboratories (Guelph, Canada).

Preparation of $ReCl_3(R_2AdH)_2(PPh_3)$. A mixture of $ReCl_3(MeCN)(PPh_3)_2$ (0.20 g, 0.23 mmol) and the dialkyladenine (0.92 mmol) is heated in toluene (40 mL). The initially insoluble solids have dissolved to a dark orange solution when the boiling temperature is reached, at which point heating is immediately stopped. The cooled solution is filtered to remove unreacted material, and the solvent is evaporated to $\sim^1/_4$ volume. Addition of a small amount of hexane may be needed to induce precipitation, especially for the diethyladenine complex. The orange solids are soluble in most common organic solvents including ether. Yields: ∼65%.

R = Me. Anal. Calcd for $ReCl_3PN_{10}C_{32}H_{33}$: C, 43.62; H, 3.77; N, 15.89; Cl, 12.07. Found: C, 44.05; H, 3.94; N, 15.56; Cl, 12.36. ^{1}H NMR (C_6D_6) (δ, ppm): 14.3 (*ortho* PPh_3), 12.2 (H2), 10.7, 9.1, 8.9 (CH_3), 8.6 (*meta* PPh_3), 8.1 (H2), 8.0 (*para* PPh_3), 5.3, 3.4 (H8), −3.4, −6.3 (NH). μ: 1.48 μ_B. FAB^+ (exact mass, *m*/*e*): calcd, 880.12506; found, 880.12800.

R = Et. ^{1}H NMR (C_6D_6) (δ, ppm): 14.3 (*ortho* PPh_3), 12.3 (H2), 8.6 (*meta* PPh_3), 8.0 (H2 and *para* PPh_3), 6.8, 6.4, 5.9, 5.7 (CH_2), 5.3, 3.1 (H8), 2.7, 2.6, 0.7, 0.6 (CH_3), −3.1, −7.1 (NH). μ: 1.72 μ_B. FAB^+ (exact mass, *m*/*e*): calcd for $ReCl_3PN_{10}C_{36}H_{41}$, 936.18768; found, 936.19120.

Preparation of $ReCl_4[R_2AdC(Me)=NH]$. A stoichiometric amount of *cis*-$ReCl_4(MeCN)_2$ (0.05 g) and the purine (0.02 g) is stirred in acetonitrile (10 mL) at room temperature for 1 d. The initially green solution turns orange-brown slowly. The solution is pumped to near dryness leaving a black crude product. Recrystallization in CH_2Cl_2−benzene yields very dark crystals giving an orange solution in CH_2Cl_2. The composition of the dimethyladenine compound was determined by X-ray diffraction work on a specimen from the crystallographically homogeneous sample. Yields: 45−55%. ^{1}H NMR (CD_2Cl_2) (δ, ppm): R = Me, 136.0 (H2), 48.1, 43.3 ((N)-CH_3), 3.5 (H8), 1.3 (amidine CH_3); R = Et, 137.3 (H2), 28.4, 27.5 (CH_2), 3.2 (H8), 1.4 (amidine CH_3), 0.3 broad (CH_2CH_3).

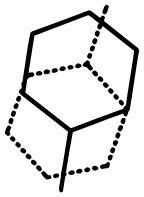
X-ray Diffraction Work. Crystallographic data for the three structures were collected with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Cu Kα radiation. The unit cells were determined from 25 centered reflections. The Niggli parameters unambiguously indicated that no higher symmetry was present. Crystal data are presented in Table 1. The intensity data collected (octants $h,\pm k,\pm l$ for $ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$, whole sphere for the other two compounds) were corrected for the effects of Lorentz, polarization, and absorption (NRCVAX package,[11] Gaussian integration). Reflections with intensity $I \geq 2\sigma(I)$ were retained for structure determination and refinement. Resolution was done by the direct methods of SHELXS-86.[12] Refinement was carried out on F^2 with the SHELXL-93 package.[13] Except when otherwise stated, the non-hydrogen atoms were refined anisotropically. Hydrogens were fixed at idealized positions with isotropic temperature factors related to those of the supporting atom by $U_H = 1.5\,U_C$ (CH_3) or $1.2U_{C,N}$ (other cases). The highest residuals in the final ΔF maps were near the metal.

Table 1. Crystal Data for $ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$ (**1**), $ReCl_4(Me_2AdH)(PPh_3)$ (**2**), and $ReCl_4[Me_2AdC(Me)=NH]\cdot C_6H_6\cdot CH_2Cl_2$ (**3**)

	1	**2**	**3**
formula	$C_{46}H_{49}Cl_3N_{10}PRe$	$C_{25}H_{24}Cl_4N_5PRe$	$C_{16}H_{20}Cl_6N_6Re$
fw	1065.50	753.47	695.29
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
T, K	268	215	298
a, Å	14.181(2)	10.391(4)	13.941(3)
b, Å	17.591(3)	10.801(5)	13.656(3)
c, Å	19.015(5)	13.651(6)	12.874(2)
α, deg	76.66(2)	89.64(4)	90
β, deg	86.80(2)	83.49(3)	105.47(2)
γ, deg	87.02(1)	65.14(4)	90
V, Å^3	4605(2)	1380(1)	2362.1(8)
Z	4	2	4
ρ_{calc}, g cm^{-3}	1.537	1.814	1.955
μ, mm^{-1}	7.29	12.72	16.27
R1[a]	0.0606	0.0432	0.0406
wR2[a]	0.1324	0.1119	0.1040

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Chart 2



$ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$. The compound crystallized from toluene as thin orange plates. A specimen of dimensions (mm) 0.18 × 0.12 × 0.03 was used, and the data were collected at −5 °C due to a phase transition occurring a lower temperature. The structure was solved and refined in the centric $P\bar{1}$ space group. The asymmetric unit consists of two independent complexes and four lattice toluene molecules, three of which are involved in a 2-fold orientational disorder of the type depicted in Chart 2. All (whole or fractional) toluene molecules were constrained to be hexagonal planar with C−C distances of 1.39 Å. The methyl group was also restricted to occupy this plane with a C-ring distance of 1.46 Å. Occupancy factors were refined, but the sum for each pair was normalized to unity. These atoms were refined isotropically, whereas the refinement for the remaining non-hydrogen atoms was anisotropic. Hydrogen positions were idealized at distances of 0.93 Å (C−H), 0.86 Å (N−H), or 0.96 Å (CH_3).

$ReCl_4(Me_2AdH)(PPh_3)$. Red-orange plates were obtained from CH_2Cl_2. The specimen used had the following dimensions (mm): 0.30 × 0.18 × 0.09. The intensity data were collected at −58 °C. Space group $P\bar{1}$ was used for refinement. The hydrogens were fixed at 0.94 Å (C−H), 0.87 Å (N−H), or 0.97 Å (CH_3).

$ReCl_4[Me_2AdC(Me)=NH]\cdot C_6H_6\cdot CH_2Cl_2$. Thin orange plates crystallized in a CH_2Cl_2−benzene mixture. The crystal used had the following dimensions (mm): 0.16 × 0.16 × 0.02. The $P2_1/c$ space group was unambiguously determined from the monoclinic Laue symmetry and the systematic absences (*h*0*l*, *l* odd; 0*k*0, *k* odd). The intensity data were collected at room temperature. There was no evidence of disorder for the lattice CH_2Cl_2 and benzene molecules. Hydrogen atoms were fixed at distances of 0.93 Å (C−H), 0.86 Å (N−H), or 0.96 Å (CH_3).

Results and Discussion

Synthesis and Reactivity of the $ReCl_3L_2(PPh_3)$ Compounds. The acetonitrile and one phosphine are cleanly displaced from $ReCl_3(MeCN)(PPh_3)_2$ by the dialkyladenines in toluene. In a series of exploratory runs to optimize reaction

(9) The compound belongs to the orthorhombic space group P*nma* with $a = 10.334(6)$ Å, $b = 13.482(4)$ Å, and $c = 9.692(7)$ Å. A full data set was collected and the structure was solved, but poor crystal quality precluded refinement below 0.15. Nevertheless, the connectivity and cis configuration were unambiguously established.

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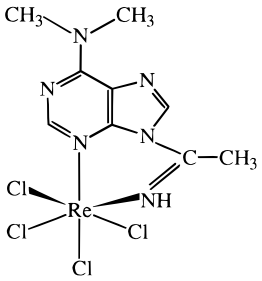
Chart 3



conditions, changes in reactant ratios and heating time showed no effect on the composition of the product. However, temperature had to be high enough for ligand substitution to take place: low-boiling solvents such as benzene and CH_2Cl_2 were inefficient. The complexes have the *mer*−*cis* configuration (refer to X-ray structure below) also exhibited by pyridine and imidazole complexes.[14,15] In these compounds, the adenines retain their acidic N9−H proton and coordinate as neutral ligands via the N3 site of the six-membered ring.

Coordinated adenine should show basic properties via the free lone pairs at N1 and N7. It has been shown that N7 can be accessed by H^+ despite the presence of interfering NR_2 groups in dialkyladenines.[4,5] Thus, protonation was attempted by adding a few drops (10-fold excess) of concentrated aqueous HCl to a toluene solution of $ReCl_3(R_2AdH)_2(PPh_3)$. Immediate reaction yielded a red-orange solid, which was not a simple protonated species. The new complex was first identified as a Re(IV) compound from the well-defined pattern of ^{1}H NMR signals of PPh_3, which have been found to be differently downfield-shifted by the paramagnetic Re(III) and Re(IV) centers.[8] This conclusion was confirmed by an X-ray study (see below) showing the compound to be *cis*-$ReCl_4(Me_2AdH)(PPh_3)$. Thus, the purine trans to PPh_3 in $ReCl_3(Me_2AdH)_2(PPh_3)$ had been replaced by a Cl^- ligand probably provided by HCl. Since the reduction product has not been identified, it is not sure H^+ is the oxidizing agent, but the reaction is certainly promoted by H^+, which removes the purine as the $Me_2AdH_2^+$ ion ($pk_a = 3.9$).[16] The diethyladenine complex reacts in the same manner.

Reacting the dialkyladenines with *cis*-$ReCl_4(MeCN)_2$ in acetonitrile always yielded the same major product, no matter the heating time or stoichiometric ratio. The ^{1}H NMR spectra appeared to be consistent with a $ReCl_4(MeCN)(R_2AdH)$ species, since they showed two equal peaks for H2 and H8 and three signals three times as intense initially assigned to $-NR_2$ and MeCN. The absence of a ν(C≡N) vibration at ∼2000 cm^{-1} provided no useful information, since this band is often extremely weak and undetected.[8] X-ray work on the Me_2AdH product (see below) showed that the two ligands were not independently coordinated: the N3-bonded adenine was connected via N9 to the quaternary carbon of acetonitrile, thereby producing a six-membred chelate including an amidine group (Chart 3). A related reaction has been reported between primary aromatic amines and $ReCl_4(MeCN)_2$[7] or a few other transition metal complexes.[17] This reaction probably proceeds via a *cis*-$ReCl_4(MeCN)(R_2AdH)$ intermediate, in which the purine is already N3-bonded as in the previous compounds. The electron-withdrawing effect of the metal at N3 increases the acidity of the N9−H proton, making the $N9^-$ lone pair available for nucleophilic attack on the nitrile carbon, whose nucleophilicity is simultaneously increased by coordination. Nevertheless, the alternate mechanism, whereby acetonitrile would be attacked by the purine before coordination, cannot be ruled out, since out attempts to isolate an intermediate failed.

These amidine chelates are stable in the solid state and in chlorinated hydrocarbon solution, as were those obtained by Rouschias and Wilkinson with anilines.[7]

Infrared Spectroscopy. At low frequency, a single broad band is observed at 316 cm^{-1} for the ν(Re−Cl) vibration in $ReCl_4(R_2AdH)(PPh_3)$, whereas two vibrations (∼298 and ∼309 cm^{-1}) are found for $ReCl_3(R_2AdH)_2(PPh_3)$. The amidine complexes exhibit a single band at ∼321 cm^{-1} with a low-frequency shoulder.

Individual assignment of the numerous bands to either PPh_3 or the purine was not attempted. Among the spectral features of dialkyladenines analyzed previously,[5] the band at 1137 cm^{-1} (Me_2AdH) or 1140 cm^{-1} (Et_2AdH), located in the N7−C8−N9 region, confirms that the N9−H bond is retained, since it is not affected by coordination in all our compounds: when the ligand binds via N9, this band loses intensity and a strong band at ∼1180 cm^{-1} appears. For the amidine complex, no bands due to C═N stretching could be identified, since the purine already possesses strong bands at ∼1600 cm^{-1}, where this vibration should occur for the amidine group.[7]

^{1}H NMR Spectroscopy. As shown in Figure 1, the spectrum of $ReCl_3(Me_2AdH)_2(PPh_3)$ is complex, consisting of signals for one PPh_3 and two nonequivalent adenines spread between −7 and +15 ppm by the paramagnetic Re(III) center. The PPh_3 protons were first identified from the typical pattern of chemical shifts noted in our earlier work on Re(III) complexes.[8] ^{1}H−^{1}H coupling is observed for the *meta* and *para* protons at 8.6 and 8.0 ppm, respectively, but not for the *ortho* proton, whose signal is broadened by the proximity to the paramagnetic center. The resonances of the adenine ligands were identified from a combination of variable-temperature, exchange, and deuteration experiments. Three signals are found for $-N(CH_3)_2$ protons, at 10.7, 9.1, and 8.9 ppm, respectively. An extra peak at ∼7.2 ppm is masked by C_6D_6 at room temperature, but its presence is readily revealed by changing the temperature. Thus, each $-N(CH_3)_2$ group in the nonequivalent adenines gives two distinct signals due to slow rotation about the C6−N6 bond. In the free ligand, faster rotation leads to averaging, but ring protonation or metal coordination induce π-electron transfer from the amino group into the ring, thereby increasing the double-bond character in the C6−NR_2 unit.[18] As the temperature is raised, these methyl signals gradually broaden and get closer. At the highest temperature studied (365 K), coalescence was close, but not yet reached at 400 MHz, which places $\Delta G^{\ddagger}$ slightly above 17.8 kcal mol^{-1}. A similar barrier of 16.6 kcal mol^{-1} has been found for $Re_2Cl_2(Me_2Ad)_4$.[5] The N−H signals were located (−3.4, −6.3 ppm) by exchange with CD_3OD. Finally, the H8 protons were identified (5.3, 3.4 ppm) by comparison with the compound prepared from C8-deuterated dimethyladenine. The diethyladenine complex gives a very similar spectrum for the ring protons. In this case, the ethyl groups show CH_2 signals between 5.7 and 6.8 ppm and CH_3 signals between 0.6 and 2.7 ppm.

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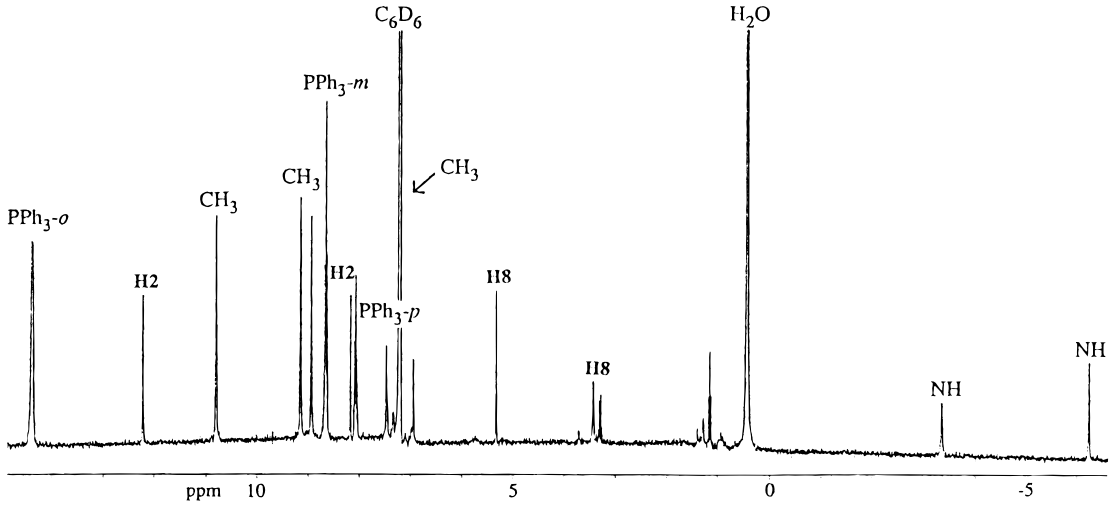

Figure 1. ^{1}H NMR spectrum of $ReCl_3(Me_2AdH)_2(PPh_3)$ in C_6D_6. Unassigned multiplets (~3 and ~1 ppm) are due to traces of ether.

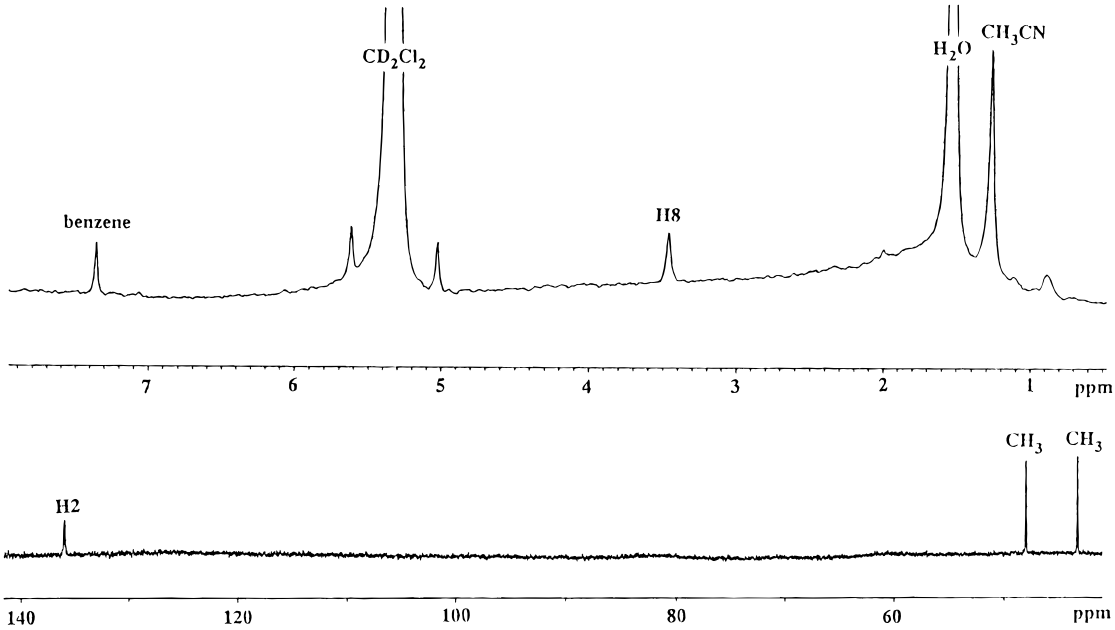

Figure 2. ^{1}H NMR spectrum of crystals of $ReCl_4[Me_2AdC(Me)=NH]\cdot C_6H_6\cdot CH_2Cl_2$ in CD_2Cl_2.

The remaining complexes discussed here contain the Re(IV) center. NMR results are scarce for compounds of this d^3 system. To our knowledge, data are available for only two Re(IV) complexes, namely $ReCl_4(PMePh_2)_2$ and $ReCl_4$(tri-*m*-tolylphosphine)$_2$.[8,19]

$ReCl_4(R_2AdH)(PPh_3)$, the reaction product of HCl with $ReCl_3(R_2AdH)_2(PPh_3)$, was identified as a Re(IV) species from the three sharp PPh_3 signals at ~19 (*ortho*), 10.7 (*para*), and 8.5 ppm (*meta*). These chemical shifts are typical of Re(IV) and different from those found for related Re(III) compounds.[8] Because of poor solubility, only the PPh_3 peaks were clearly defined.

The spectrum of $ReCl_4[Me_2AdC(Me)=NH]$ shown in Figure 2 contains relatively sharp signals covering a wide range of chemical shifts. No signal is observed near −64 ppm, where the starting material *cis*-$ReCl_4(MeCN)_2$ gives a singlet. Signal intensities and comparisons between the ethyl and methyl complexes allowed us to propose assignments for all except the N−H protons. The signal at 135 ppm is believed to originate from H2, on the basis of its relative intensity and proximity to the paramagnetic center. A signal of the same intensity at ~3 ppm is assigned to the remote H8 proton. Two methyl signals for the $-NMe_2$ group in slow rotation are observed near 40 ppm. These signals are absent from the spectra of the diethyl analogue, where the CH_2 protons appear at ~30 ppm and those of the ethyl CH_3 groups give a broad signal at 0.3 ppm. The amidine CH_3 protons (1.3 ppm) are observed close to the signal water for the Me_2AdH complex and masked by this signal for the Et_2AdH complex.

Crystal Structure of $ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$. The asymmetric unit contains two molecules of the complex and four lattice toluenes. The octahedral complex adopts the *mer*−*cis* configuration (Figure 3) found for $ReCl_3L_2(PPh_3)$ compounds with pyridines and 1-methylimidazole.[14] Departure from octahedral geometry is relatively large and similar in both molecules, as evidenced from the distances and angles given in Table 2. The Re−P distances are 2.443(2) Å, and the Re−N bonds trans to Cl are ~0.03 Å shorter than those trans to P, as observed for the above complexes. However, the pattern of Re−Cl bond lengths is different. In the above complexes, the mutually trans Re−Cl bonds (2.369 Å) were appreciably shorter than those trans to a Re−N bond (mean 2.390 Å). Therefore, our Re−Cl3 distances (2.385(2), 2.403(2) Å), trans to N, are normal, as are the Re−Cl2 distances (2.362(2), 2.365(2) Å) trans

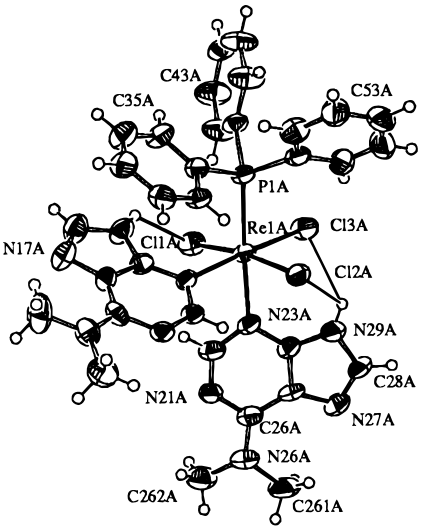

Figure 3. ORTEP drawing of $ReCl_3(Me_2AdH)_2(PPh_3)$ (molecule A). The structure of molecule B is very similar. Ellipsoids are drawn at the 50% probability level.

Table 2. Selected Distances (Å) and Angles (deg) for $ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$ (**1A**,**1B**), $ReCl_4(Me_2AdH)(PPh_3)$ (**2**), and $ReCl_4[Me_2AdC(Me)=NH]\cdot C_6H_6\cdot CH_2Cl_2$ (**3**)

	1A	1B	2	3
Re−Cl1	2.391(2)	2.392(2)	2.339(2)	2.351(2)
Re−Cl2	2.362(2)	2.365(2)	2.323(2)	2.343(2)
Re−Cl3	2.385(2)	2.403(2)	2.307(2)	2.327(1)
Re−Cl4			2.367(2)	2.330(2)
Re−P	2.445(2)	2.441(2)	2.545(2)	
Re−N10				2.094(4)
Re−N13	2.170(6)	2.151(6)	2.143(5)	2.100(5)
Re−N23	2.193(7)	2.188(6)		
N13−Re−N23	85.1(2)	86.2(2)		
N13−Re−Cl1	88.5(2)	90.1(4)	91.5(1)	85.9(1)
N23−Re−Cl1	83.7(2)	85.8(2)		
Cl2−Re−Cl1	171.47(7)	172.60(7)	177.55(5)	173.38(5)
Cl3−Re−Cl1	88.90(9)	87.91(8)	91.47(7)	91.38(5)
N13−Re−Cl2	89.6(2)	90.6(2)	87.4(1)	88.5(1)
N23−Re−Cl2	87.9(2)	86.9(2)		
N13−Re−Cl3	175.8(2)	176.7(2)	176.2(1)	93.9(1)
N23−Re−Cl3	91.3(2)	91.0(2)		
Cl2−Re−Cl3	92.50(8)	91.02(8)	89.79(7)	92.45(6)
N13−Re−Cl4			88.7(1)	173.4(1)
Cl3−Re−Cl4			93.74(6)	92.64(6)
Cl2−Re−Cl4			88.78(7)	91.48(6)
Cl1−Re−Cl4			89.04(7)	93.74(6)
N13−Re−P	94.3(2)	91.4(2)	91.1(1)	
N23−Re−P	174.1(2)	172.9(2)		
Cl1−Re−P	102.15(8)	100.96(7)	83.11(6)	
Cl2−Re−P	86.28(7)	86.39(7)	99.06(6)	
Cl3−Re−P	89.55(7)	91.62(7)	86.83(6)	
Cl4−Re−P			172.15(5)	
N10−Re−N13				86.1(2)
N10−Re−Cl1				86.7(1)
N10−Re−Cl2				89.5(1)
N10−Re−Cl3				178.1(1)
N10−Re−Cl4				87.3(1)

to Cl. The anomaly lies in the Re−Cl1 bonds (2.391(2) Å), which are longer than the expected 2.36 Å value. It is noteworthy that these Re−Cl1 bonds are also those involved in large distortions around the metal: the greatest deviations from 90° are observed for the Cl1−Re−P (102.15(8), 100.96(7)°) and N23−Re−Cl1 angles (83.7(2), 85.8(2)°), and they likely reflect constraints imposed by the clustering of many aromatic units around the metal.

Torsion angles in Table 3 show that the two independent molecules actually have very similar conformations. Coordination of the adenine ligand via N3 allows the N9−H proton to form an intramolecular N9−H···Cl bond (Table 4). Hydrogen bonding would be more efficient if the Cl1 (or Cl3) acceptor were in the plane of the purine, but coplanarity would introduce extremely short C2−H···Cl contacts (<2.5 Å) on the opposite side. N−H···Cl hydrogen bonding is retained and steric strain is relieved by the ligands being rotated ∼38° about the Re−N3 bond. The resulting hydrogen bonds are far from linearity and not very strong, although within the normal range of N···Cl separation.[20] Rotation of the adenine cis to the phosphine about the Re−N bond brings the five-membered ring on the side of the phosphine. In both molecules, the P−C31 bond is eclipsed with the Re−N13 bond (C−P−Re−N < 3°) and phenyl ring no. 3 is roughly parallel to the plane of the purine (dihedral angles ∼13°) at a distance of ∼3.2 Å. The Re−P−C31 angle, on this side, is also smaller than the other Re−P−C angles. This arrangement minimizes steric interaction and provides some van der Waals stabilization via π-stacking. The orientation of ring no. 3 imposes constraints on the remaining phosphine rings. Ring no. 4, which is above the Re−Cl1 bond (Cl1−Re−P−C41 = −31°), is almost parallel to the Re−P bond (Re−P−C41−C42 = 15.9° for A, −5.6° for B). As a result, an ortho proton H42 lies close (∼2.65 Å) to Cl1 and is likely responsible

Table 3. Selected Torsion Angles (deg) in $ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$ (**1A**,**1B**) and $ReCl_4(Me_2AdH)(PPh_3)$ (**2**)

	1A	1B	2
Cl1−Re−P1−C31	89.0(3)	93.7(3)	81.0(2)
Cl1−Re−P1−C41	−33.4(3)	−29.4(3)	−36.7(2)
Cl1−Re−P1−C51	−154.3(3)	−149.8(3)	−157.4(2)
Cl2−Re−P1−C31	−89.7(3)	−87.2(3)	−97.8(2)
Cl2−Re−P1−C41	147.9(3)	149.7(3)	144.5(2)
Cl2−Re−P1−C51	27.0(3)	29.3(3)	23.7(2)
Cl3−Re−P1−C31	177.8(3)	−178.1(3)	172.9(2)
Cl3−Re−P1−C41	55.4(3)	58.8(3)	55.2(2)
Cl3−Re−P1−C51	−65.5(3)	−61.6(3)	−65.6(2)
N13−Re−P1−C31	−0.3(4)	3.3(3)	−10.3(2)
Re−P1−C31−C32	60.1(7)	63.4(7)	−50.6(5)
Re−P1−C41−C42	15.9(7)	−5.6(8)	−72.6(6)
Re−P1−C51−C56	48.9(7)	43.0(7)	−32.4(6)[a]
Cl1−Re−N13−C14	−39.9(7)	−37.6(7)	32.2(5)
Cl2−Re−N13−C14	148.4(7)	149.8(7)	−145.7(5)
Cl1−Re−N23−C24	130.4(7)	128.5(7)	
Cl2−Re−N23−C24	−50.8(6)	−50.3(6)	
Cl3−Re−N23−C24	41.7(6)	40.6(2)	

[a] Re−P1−C51−C52.

Table 4. Distances (Å) and Angles (deg) in the Hydrogen Bonds

	N···Cl	H···Cl	N−H−Cl
$ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$			
N19A−H19A···Cl1A	3.036(8)	2.44	127
N29A−H29A···Cl2A	3.344(8)	2.96	110
N29A−H29A···Cl3A	3.119(7)	2.52	128
N19B−H19B···Cl1B	3.005(8)	2.37	131
N29B−H29B···Cl2B	3.278(8)	2.88	110
N29B−H29B···Cl3B	3.123(7)	2.51	129
$ReCl_4(Me_2AdH)(PPh_3)$			
N19−H19···Cl1	3.129(6)	2.67	114
N19−H19···Cl4	3.308(6)	2.76	122
$ReCl_4[Me_2AdC(Me)=NH]\cdot C_6H_6\cdot CH_2Cl_2$			
N10−H10···Cl2[a]	3.451(5)	2.60	169

[a] $-x, -y, 2 - z$.

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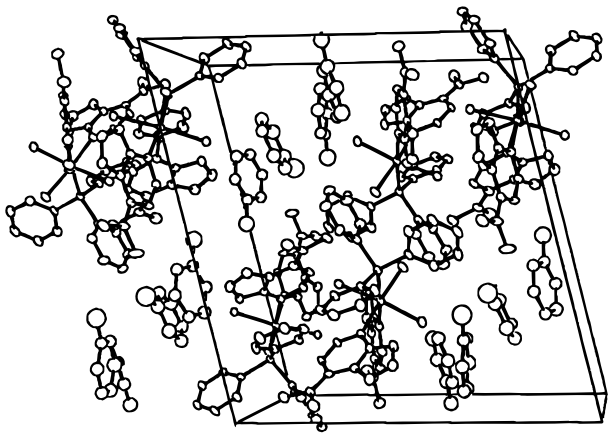

Figure 4. View of the unit cell for $ReCl_3(Me_2AdH)_2(PPh_3)\cdot 2C_6H_5CH_3$ down the *a* axis. The origin is in the upper left corner, and the *b* and *c* axes are in the plane of the figure, oriented to the right and vertically, respectively.

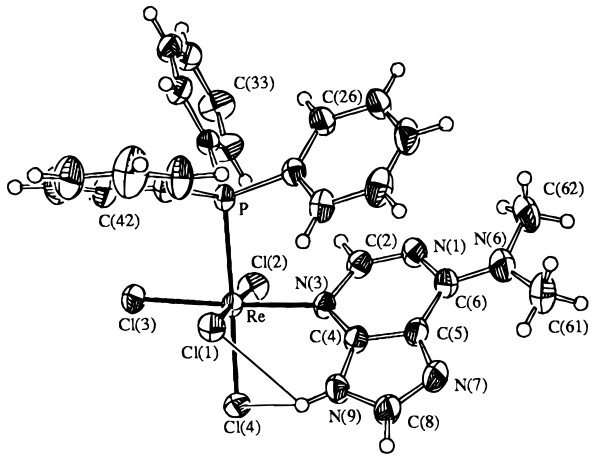

Figure 5. ORTEP drawing of *cis*-$ReCl_4(Me_2AdH)(PPh_3)$. Ellipsoids are drawn at the 50% probability level.

for the Cl1−Re−P angle being 10° greater than normal. It is not clear that such a distortion should lengthen the Re−Cl1, but it is probably not fortuitous that the abnormally long Re−Cl bond is also the one involved in the largest angular distortion.

A view of the unit cell is provided in Figure 4. Layers parallel to *a* along the *bc* diagonal contain the complex molecules interacting by normal van der Waals contacts. The asymmetric unit contains the unusually large number of four toluene solvent molecules, whose organization is also quite unusual: they define layers alternating with the layers of the complex. Most of the toluene molecules are involved in a 2-fold disorder, in which however they remain in the same plane and retain π-stacking interactions with their neighbors.

Crystal Structure of $ReCl_4(Me_2AdH)(PPh_3)$. This Re(IV) complex is the cis isomer (Figure 5). The Re−P bond (2.545(2) Å) is much longer than in the above and other Re(III) compounds,[14,21] but similar to those observed for the Re(IV) compound *trans*-$ReCl_4[P(m\text{-tolyl})_3]_2$.[8] In contrast, the Re−Cl and Re−N distances are shorter than in these other Re(III) complexes. The mutually trans Re−Cl1 (2.339(2) Å) and Re−Cl2 (2.323(2) Å) distances are similar to those of $ReCl_4[P(m\text{-tolyl})_3]_2$,[8] whereas the Re−Cl3 bond (2.307(2) Å), trans to N, is shorter and Re−Cl4 (2.367(2) Å), trans to P, is longer.

As above, the adenine ligand forms an intramolecular hydrogen bond with Cl1 (Table 4) and it is rotated by ∼32° about Re−N13 with respect to the Re−Cl1 bond (Table 3). This

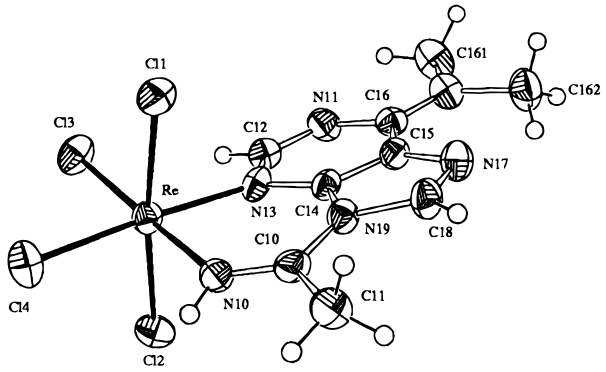

Figure 6. ORTEP drawing of $ReCl_4[Me_2AdC(Me)=NH]$. Ellipsoids are drawn at the 50% probability level.

time, the rotation takes the five-membered ring away from the phosphine, whose P−C bonds nevertheless adopt the same orientation as above with respect to the bonds in the $ReCl_3N$ plane (Table 3). Phenyl ring no. 3 is above the adenine unit (N13−Re−P1−C31 = −10°), roughly parallel to it (dihedral angle = 12°), and also participates in π-stacking contacts. Lesser crowding near the phosphine allows greater freedom for the orientation of the other phenyl rings. Ring no. 4 is roughly parallel to the $ReCl_3N$ plane (Re−P1−C41−C42 = −73°), which leaves space for Cl1 to move away from the adenine unit, decreasing the Cl1−Re−P angle to 83.11(6)°. On the other hand, ring no. 5 is more parallel to the Re−P bond (Re−P1−C51−C52 = −32°) and an ortho hydrogen H52 is close to Cl2 (2.53 Å). This is probably correlated with the large Cl2−Re−P angle of 99.06(6)°.

The Adenine Unit. In these two structures, the distances and angles in the adenine unit do not differ appreciably from those found in the free ligand[22] and from the typical values reported by Taylor and Kennard.[23] The only small differences in angles near C6 are related to the steric effect of the $-NMe_2$ group. Coordination to N3 has no detectable effect on the geometry in the C2−N3−C4 region. Our data confirm the presence of adenine as the N9−H tautomer, since changes in the state of protonation of the N atoms are known to introduce large differences on the C−N−C angles. The absence of protonation on N1 or N7 further confirms that $ReCl_4(Me_2AdH)(PPh_3)$ is a Re(IV) complex as opposed to a possible Re(III) species $ReCl_4(Me_2AdH_2)(PPh_3)$ containing a cationic adenine ligand.

Least-squares planes (see Supporting Information) show that the five- and the six-membered rings are individually planar, but the adenine unit is bent by 2−5° about the common C4−C5 bond. The $-NMe_2$ groups are roughly coplanar with the ring, but the CH_3 groups are often appreciably displaced from it by packing forces. Coordination does not take place exactly along the expected lone pair direction, the C4−N3−Re angle being ∼6° greater than C2−N3−Re. This effect contributes to improving N−H···Cl hydrogen-bonding efficiency. Also, the Re atoms is considerably distant from the planes (0.12−0.40 Å).

Crystal Structure of $ReCl_4[Me_2AdC(Me)=NH]\cdot C_6H_6\cdot CH_2Cl_2$. This Re(IV) complex is of the $ReCl_4(L\text{-}L')$ type and contains a six-membered chelate ring resulting from the coupling of the adenine unit with acetonitrile (Figure 6). The distances and angles in the chelate ring are given in Table 5. The

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Table 5. Distances (Å) and Angles (deg) in the Chelate Ring of $ReCl_4[Me_2AdC(Me)=NH]\cdot C_6H_6\cdot CH_2Cl_2$

N13−C14	1.359(7)	C14−N19	1.371(7)
N19−C10	1.392(7)	N10−C10	1.284(7)
C10−C11	1.480(7)		
Re−N13−C14	122.2(4)	N13−C14−N19	127.3(5)
C14−N19−C10	129.2(5)	N19−C10−N10	118.6(5)
N10−C10−C11	123.4(5)	N19−C10−C11	118.0(5)
Re−N10−C10	132.4(4)		

octahedron shows a significant, but relatively small, distortion keeping the cis angles, including the one in the chelate ring, in the 86−94° range (Table 2). The Re−N10 distance to the amidine nitrogen (2.094(4) Å) is longer than expected for a Re(IV)−nitrile bond, since a Re(III)−nitrile distance of 2.068(5) Å has been observed in $ReCl_3(MeCN)(PPh_3)_2$[21] and the bond to a Re(IV) center should be slightly shorter. The Re−N13 distance (2.100(5) Å) is shorter than those of $ReCl_4(Me_2AdH)(PPh_3)$ (2.143(5) Å) and $ReCl_4$(bipy) (2.133(5) Å).[24] The mutually trans Re−Cl distances (2.343(2), 2.351(2) Å) are longer than those trans to N donors (2.327(1), 2.330(2) Å). A similar pattern is noted for the Re−Cl bonds of $ReCl_4$(bipy), which possesses the same configuration of donor atoms, but the distances are systematically ∼0.02 Å shorter in the latter case.

The purine unit shows a small departure from planarity, as usual: slight puckering of the six-membered ring (maximum deviation of 0.020(4) Å for N13), almost perfectly planar five-membered ring, and slight bend of 1.4(2)° about the common C4−C5 bond. In the chelate ring, small displacements (maximum of 0.037(4) Å for N19) alternatively above and below the mean plane through the N13−C14−N19−C10−N10 part are noted, whereas the ring as a whole adopts an envelope arrangement, the Re atom lying 0.443(7) Å from this plane.

Binding Mode of Dialkyladenines. Complexation with monoanionic adenine consistently takes place at the deprotonated N9 site.[25] Neutral adenine (LH) shows greater variability, and three complexation/protonation patterns have been found. In $(LH_2)[Co(LH)_2(H_2O)_4]$, the ligands adopts the N9−M/N7−H pattern.[26] Coordination to N9 inevitably requires that N3 be close to other ligands in the sphere, and in this case it acts as a hydrogen-bond acceptor from an aqua ligand. The N3−M/N7−H pattern is found for $[NiCl(LH)\{N(CH_2CH_2NH_2)_3\}]Cl$,[27] where N9 accepts a hydrogen bond from the amine ligand. The only example for the N3−M/N9−H pattern is [(cod)Rh(Me_2-AdH)Cl],[28] in which an intramolecular N9−H···Cl hydrogen bond is formed. This has also been observed for purine itself and two other C6-substituted derivatives, and in all cases the coordination sphere includes a ligand able to accept a hydrogen bond.[29] Thus, the pattern actually adopted seems to depend on a delicate balance between intrinsic basicity of the donor atom and interligand interactions. Our compounds $ReCl_3(Me_2AdH)_2(PPh_3)$ and $ReCl_4(Me_2AdH)(PPh_3)$ belong to the latest class: like the Rh complex, they contain N3-bonded ligands forming intramolecular N9−H···Cl hydrogen bonds.[30]

Acknowledgment. We thank M. Simard and F. Bélanger-Gariépy for their assistance in solving the crystal structures. The financial support of the Natural Sciences and Engineering Research Council of Canada and the Fonds FCAR du Ministère de l'Éducation du Québec is also acknowledged.

Supporting Information Available: Tables of complete crystal data, final coordinates, temperature factors, distances and angles, torsion angles, and distances from the least-squares planes for the crystallographic study (41 pages). Ordering information is given on any masthead page.

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(30) Note added in proof: N3-coordination has been reported very recently (Meiser, C.; Song, B.; Freisinger, E.; Peilert, M.; Sigel, H.; Lippert, B. *Chem. Eur. J.* **1997**, *3*, 388.) for the square-planar complex [Pd(dien)(*N*6,*N*6,*N*9-trimethyladenine)]$^{2+}$. N3 is the only site accessible in this trimethylated ligand and steric hindrance is avoided by ligand rotation about the Pd−N3 bond to bring the 9-methyl group above the square plane.