of equimolar solutions of adamantanone and Eu(fod)$_3$ in $CDCl_3$ and used the Bouquant–Chuche equation to calculate both.[8] Reasonable agreement with known atmosphere pressure data was obtained;[9] our results are shown in Figure 1. Assuming a linear relation between ln $K$ and $P$, we have calculated the reaction volume $\Delta V^{\circ}_{\text{ass.}} = -RT\,\partial \ln K/\partial p$ to be $+8 \pm 2$ cm$^3$/mol at 21 °C. At the same time, the bound shift of $H_\alpha$ is reduced by 100 MPa from 13.1 to 11.6 and that of $H_{\beta/\text{syn}}$ from 6.6 to 5.5. In the free ligand, the resonances appear at $\delta_\alpha = 2.50$ and $\delta_\beta = 2.00$ ppm;[10] hence these reductions amount to 15–20%. Evidently, *both* the equilibrium concentration and the bound shift of the complex decline as the pressure is raised. Both of these effects are almost unique.

One possible explanation is that the metal–fod bonds may be lengthened somewhat as room is made for the additional ligand (Figure 2). The volume increase resulting from such lengthening by $\Delta r$ would to a first approximation equal the volume of a spherical shell of radius $r_{\text{av}}$ $(= \frac{1}{2}(r_0 + r_i))$ and thickness $\Delta r$; i.e., $4\pi\Delta r r_{\text{av}}^2$. In other words, it is proportional to the square of the radius. With small ligands and first-series transition-metal ions, this contribution to the volume change should therefore be modest; there is no reason to suppose that it compromises the many solvent exchange studies under pressure that have been reported, for example. But in the present case, even if half of the adamantanone molecule is buried in the coordination sphere, an increase of just 0.1 Å in the Eu–O distances would be enough to negate the hoped-for contraction.[11] X-ray data show that ionic radii do indeed increase by small amounts upon expansion of the number of ligands in the coordination sphere of virtually all monatomic cations.[12]

Alternatively, it is conceivable that these reactions have some feature unsuspected heretofore, in spite of the highly refined analyses that have been made of the shifts observed. Thus, if a substantial fraction of the uncomplexed shift reagent were in an oligomeric form, this could in principle also account for our observations.[13] Still another possibility is that Eu(fod)$_3$ in the absence of any other base in chloroform is strongly bound to the solvent, though evidence for such binding has been vainly sought by Raber.[14] Finally, pressure-induced geometric changes in the shift reagent itself[15] or in the solvent surrounding it[16] can also not be ruled out.

**Acknowledgment.** We gratefully acknowledge support by the Japanese Ministry of Education (travel grant to H.Y.) and the Swiss and U.S. National Science Foundations for support of this study (A.E.M. and W.J.leN.)

**Registry No.** Eu(fod)$_3$, 17631-68-4; Yb(fod)$_3$, 18323-96-1; Pr(fod)$_3$, 17978-77-7; adamantanone, 700-58-3; 5-phenyladamantan-2-one, 38584-33-7; 5-*tert*-butyladamantan-2-one, 84454-67-1; piperidine, 110-89-4; tetrahydrofuran, 109-99-9; pentanol, 96-41-3.

**Supplementary Material Available:** Graphs showing the effect of pressure on the chemical shifts of several substrates in the presence of shift reagents in several solvents and tabular summaries (14 pages). Ordering information is given on any current masthead page.

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[8] Bouquant, J.; Chuche, J. *Tetrahedron Lett.* **1973**, 493. Alternative approaches have been evaluated: Raber, D. J.; Hardee, L. E. *Org. Magn. Reson.* **1982**, *20*, 125. Our approach is dictated by experimental constraints.

[9] A recent report gives $K = 63$ or 51 dm$^3$ mol$^{-1}$ at 30 °C (two methods): Horskâ, A.; Hajek, M.; Trška, P. *P. Chem. Soc., Perkin Trans. 2* **1985**, 1523. An earlier value of 316 (Raber, D. J.; Johnston, M. D.; Janks, C. M.; Perry, J. W.; Jackson, G. F., III *Org. Magn. Reson.* **1980**, *14*, 32) has been revised to 94 (Raber, D. J.; Peters, J. A. *Magn. Reson. Chem.* **1985**, *23*, 621). Our value cannot be put on a par with the reported ones as our resolution is not as good, our signals are broader, and we cannot take small concentrations of other complexes such as $LS_2$ or $L_2S$ into account. However, the main sources of error should cancel in our treatment of the pressure induced *changes* in $K$.

[10] Literature values (ref 9): 13.1 or 14.0 and 6.9 or 7.2 (two methods) and 15.4 and 7.5, revised to 15.2 and 7.5, respectively. The other protons change too little and/or overlap too much to be useful in the calculations.

[11] We assumed a molar volume of 135 cm$^3$ for the adamantanone, and 8 Å for $r_{\text{av}}$.

[12] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. Huheey, J. E., Ed. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper and Row: New York, NY, 1983; Chapter 3. We thank Prof. J. Drenth (University of Groningen) for acquainting us with this literature.

[13] Such oligomerization appears to be substantial in $CCl_4$ (Bruder, A. H.; Tanny, S. R.; Rockefeller, H. A.; Springer, C. S. *Inorg. Chem.* **1974**, *13*, 880) but not in chloroform (Desreux, J. F.; Fox, L. E.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 2217).

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[15] Inagaki, F.; Miyazawa, T. *Prog. Nucl. Magn. Reson.* **1981**, *14*, 67.

[16] Electrostriction changes in reactions involving neutral species alone are usually considered to be negligible; however, see: Kelm, H.; Palmer, D. A. ref 4a, p 302. Whalley, E. *J. Chem. Phys.* **1963**, *38*, 1400.

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## Metallocene Antitumor Agents. Unusual $Mo(\eta^5\text{-}C_5H_5)_2Cl_2$ Nucleotide/Nucleobase Aqueous Coordination Chemistry

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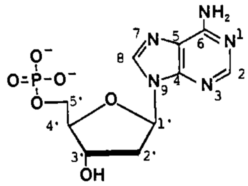
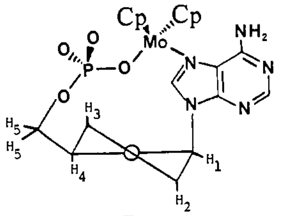
The complexes $Cp_2MX_2$ (M = Ti, V, Mo; X = halide or pseudohalide) exhibit antineoplastic activity against a wide spectrum of murine and human tumors,[1,2] with the key cellular target proposed to be DNA.[1,3] We have previously shown[4] that in aqueous solution near physiological pH, $Cp_2TiCl_2$ and $Cp_2VCl_2$ suffer more rapid and extensive chloride aquation than does *cis*-$Pt(NH_3)_2Cl_2$ (cisplatin)[5] and that the Ti-$C_5H_5$ ligation is hydrolytically unstable. In contrast to cisplatin, the binding of $Cp_2VCl_{2(aq)}$ to nucleotides is labile on the NMR time scale and predominantly phosphate-centered,[6] with minimal disruption of Watson–Crick base pairing.[6] We now report that $Cp_2MoCl_{2(aq)}$ exhibits an unusual nucleotide/nucleobase coordination chemistry which differs significantly from that of the aforementioned titanium and vanadium complexes.

As indicated by techniques described elsewhere,[4] $Cp_2MoCl_2$ (**1**) suffers more rapid ($t_{1/2} < 30$ min) and extensive (>98%) chloride aquation than does $Cp_2TiCl_2$ and $Cp_2VCl_2$. There is no detectable Mo–$C_5H_5$ protonolysis over a period of several weeks at pD 7.6. Titration of $Na_2$(5′-dAMP) (A) with **1** in $D_2O$ at pD



A



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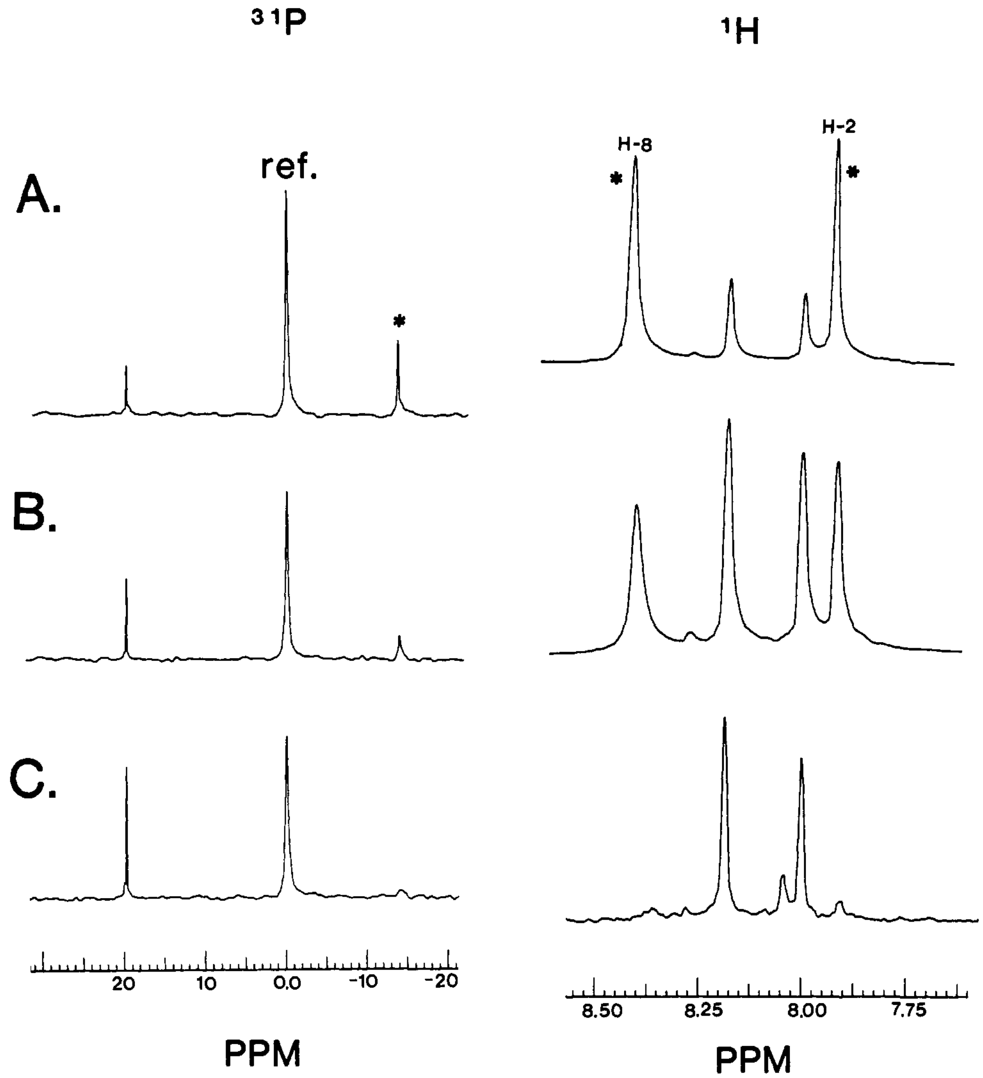

**Figure 1.** Titration of 5′-dAMP with Cp$_2$MoCl$_2$ in D$_2$O as monitored by 270 MHz $^1$H and 109 MHz $^{31}$P NMR spectroscopy. Asterisks (*) represent signals of free d(AMP) and ref. = external $^{31}$P reference signal. Phosphoric acid is at −18.45 ppm relative to the $^{31}$P reference. (A) 0.25 equiv of Cp$_2$MoCl$_2$, (B) 0.50 equiv of Cp$_2$MoCl$_2$, and (C) 1.0 equiv H of Cp$_2$MoCl$_2$.

7.6–7.8 reveals (Figure 1) an interaction which is *nonlabile* on the NMR time scale and ultimate formation of a 1:1 Cp$_2$Mo–nucleotide complex **2**. Structurally diagnostic NMR spectral features of **2** in D$_2$O and in DMSO-$d_6$ (allowing observation of the N(6)H$_2$ signal) (Table I) include magnetically nonequivalent Cp ligands, an upfield shift of H8 implicating N7 coordination,[5,8a–d] the pD dependence of the H2 and H8 chemical shifts[8e] as well as the ribose $^1$H coupling constants (verified by decoupling experiments) indicative of a major increase (~20% → ~50%) in the N(2′-exo-3′-endo) conformational population ($^3J_{1'2'} = 4.6$, $^3J_{1'2''} = 6.6$, $^3J_{2''3'} = 6.1$, $^3J_{2'3'} = 6.3$, $J_{2'2''} = 14.1$ Hz).[9,10] The 34-ppm downfield shift of the $^{31}$P signal indicates concurrent phosphate coordination.[11] Along with the monomeric character of **2**[12] and results on model compounds (vide infra), these data indicate an N7,PO chelation mode (e.g., B), the only other known mononuclear example of which is the recent reformulation of *cis*-Pt(NH$_2$CH$_3$)$_2$(5′-IMP) on the basis of NMR data.[10,13]

The reaction of **1** with 9-methyladenine (9-MeAd) at pH 7.5 followed by evaporation and addition of NH$_4^+$PF$_6^-$ yields two Cp$_2$Mo(9-MeAd$^-$)$^+$PF$_6^-$ isomers (**3**, ~90%; **4**, ~10%) which can

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(12) Pure samples of **2** can be prepared by reaction of 5′-dAMP and **1** in aqueous Et$_3$N, followed by evaporation, washing with CH$_2$Cl$_2$, and extraction with MeOH: mw calcd 556 g mol$^{-1}$, found 590 ± 60 g mol$^{-1}$ (cryoscopic in H$_2$O); 558 (FAB MS). Anal. Calcd for C$_{20}$H$_{22}$N$_5$O$_6$MoP: C, 43.17; H, 3.96; N, 12.59; P, 5.58. Found: C, 43.14; H, 4.00; N, 12.64; P, 5.60.

(13) Previously characterized (diffractometric) examples of N(7),PO coordination all involve polynuclear structures in which metal ions coordinate N(7) and PO units of different nucleotide molecules. (a) Aoki, K.; Clark, G. R.; Orbell, J. D. *Biochim. Biophys. Acta* **1976**, *425*, 369–371 ([Cu$_3$(5′-GMP)$_3$(8H$_2$O)·4H$_2$O]$_n$). (b) De Meester, P.; Goodgame, D. M. L.; Jones, T. J.; Skapski, A. C. *Biochim. Biophys. Acta* **1974**, *353*, 392–394 ([Zn(5′-IMP)]$_n$). (c) Goodgame, D. M. L.; Jeeves, L.; Reynolds, C. D.; Skapski, A. C. *Nucleic Acids Res.* **1975**, *2*, 1375–1379 ([Cd$_2$(5′-IMP)$_3$(H$_2$O)$_5$]$_3$). **Note Added in Proof**: The crystal structure of [Cp$_2$Mo(5′-dGMP)]$_2$ provides a further example of binuclear N7,PO coordination (Kuo, L. Y.; Sabat, M.; Marks, T. J., manuscript in preparation).

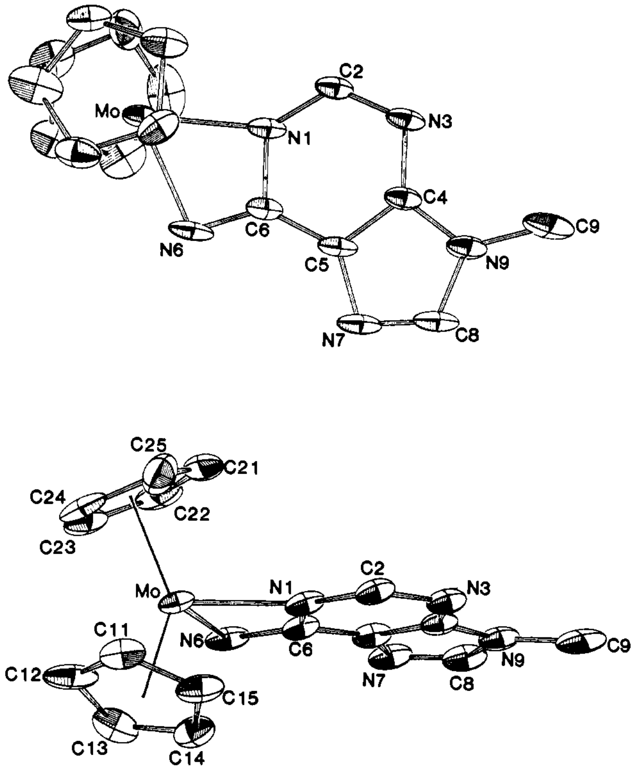

**Figure 2.** Two perspective views of the molecular structure of $Cp_2Mo$-(9-methyladenyl)$^+PF_6^-$ (**3**) showing the cationic portion. Important bond distances (Å) and angles (deg) are as follows: Mo–N(1) = 2.173 (3), Mo–N(6) = 2.145 (3), C(6)–N(1) = 1.382 (5), C(6)–N(6) = 1.314 (5), Mo–ring centroid = 2.005 (5) (av), N(1)–Mo–N(6) = 60.9, N(6)–C-(6)–N(1) = 108.5 (3), ring centroid–Mo–ring centroid = 128.9 (2), Mo–N(6)–C(6) = 97.0 (2), Mo–N(1)–C(6) = 93.5 (2).

be separated by fractional crystallization.[14] Complex **3** can be quantitatively converted to **4** by heating at 80 °C, suggesting that **3** is the kinetic product. $^1H$ NMR spectral parameters (Table I)[15] indicate $N(6)H_2$ deprotonation and $HN6^-$,N1 and $HN6^-$,N7 chelation in **3** and **4**, respectively. Diffraction results on **3**[16] confirm this unusual chelation mode (Figure 2). While the $Cp_2Mo$ portion of **3** is unexceptional,[17] the four-membered chelate ring contains a highly acute (60.9 (1)°) N(1)–Mo–N(6) angle and short (vide infra) Mo–N(6) (2.145 (3) Å) and Mo–N(1) (2.173 (3) Å) distances. The N(6)–C(6)–N(1) angle has contracted 11° (toward Mo) from that in free 9-MeAd.[18] These results can be compared with ∠O–Mo–N values of 74.1 (5)° and 73.4 (6)° in $(Cp_2\overline{MoNH_2\text{-}CH_2COO})^+Cl^-$ and $(Cp_2\overline{MoNH\text{-}(CH_3)CH_2COO})^+Cl^-$, respectively.[16a] The corresponding Mo–N distances in these latter complexes are 2.26 (1) and 2.23 (2) Å, respectively, and that in $[Cp_2\overline{MoNH_2CH(CH_2S})CO_2H]^+Cl^-$, 2.256 (7) Å.[16a] The recent elucidation of 1-methylcytosine $HN4^-$,N3–Pt(IV) coordination[19] constitutes the only other diffractometric report of such a four-membered nucleobase chelate ring.

**Table I.** NMR Spectroscopic Data for Free Ligands and Molybdenum Complexes[a]

| compound | H2[d] | H8[d] | $C_5H_5$[d] | N(6)H[d] | P |
|---|---|---|---|---|---|
| 5′-dAMP[b] | 7.92 (1) | 8.32 (1) | | | 4.8 |
| $Cp_2Mo$(5′-dAMP) (**2**)[b] | 7.97 (1) | 8.11 (1) | 5.31 (5) | | 38.0 |
| | | | 5.68 (5) | | |
| 5′-dAMP[c] | 8.12 (1) | 8.44 (1) | | 7.30 (2) | 4.8 |
| $Cp_2Mo$(5′-dAMP) (**2**)[c] | 8.13 (1) | 8.30 (1) | 5.76 (5) | 7.26 (2) | 42.0 |
| | | | 5.71 (5) | | |
| 9-methyladenine[c] | 8.14 (1) | 8.08 (1) | | 7.17 (2) | |
| $Cp_2Mo(9\text{-}MeAd^-)^+PF_6^-$ (**3**)[c] | 7.64 (1) | 8.00 (1) | 5.84 (10) | 6.90 (1) | |
| $Cp_2Mo(9\text{-}MeAd^-)^+PF_6^-$ (**4**)[c] | 8.16 (1) | 8.32 (1) | 5.88 (10) | 6.46 (1) | |

[a] $^1H$ data vs TMS; $^{31}P$ data vs 85% $H_3PO_4$. [b] In $D_2O$ at pD ~ 7.4. [c] In DMSO-$d_6$. [d] Number in parentheses denotes number of protons by integration.

These results illustrate the considerable kinetic and architectural fine structure of $Cp_2MX_2$–nucleobase/nucleotide complexation. Complementary studies with oligo- and polynucleotides are now in progress.

**Acknowledgment.** This research was supported by NSF (Grant CHE8306255). L.Y.K. is a Dee and Moody Fellow.

**Supplementary Material Available:** X-ray experimental details including positional and anisotropic displacement parameters and bond lengths and angles (8 pages); listings of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(14) (a) **3**: Anal. Calcd for $C_{16}H_{16}N_5MoPF_6$: C, 37.01; H, 3.11; N, 13.49; P, 5.97. Found: C, 35.80; H, 3.00; N, 13.32; P, 5.94. **4**: Found: C, 36.89; H, 3.07; N, 13.38; P, 5.89.

(15) H2,H8 assignments were verified with use of 9-MeAd deuteriated at C8: Charland, J. P.; Beauchamp, A. L. *Croat. Chem. Acta* **1984**, *57*, 693–701.

(16) Crystals of **3** from ether diffusion into an acetone solution are triclinic ($P\bar{1}$) with cell dimensions as follows: $a$ = 10.682 (3) Å, $b$ = 11.619 (5) Å, $c$ = 7.701 (5) Å, $\alpha$ = 106.93 (4)°, $\beta$ = 96.32 (3)°, and $\gamma$ = 86.98 (3)°; $V$ = 908.64 Å$^3$, $Z$ = 2, $d_{calcd}$ = 1.73 g cm$^{-3}$. With use of a crystal of dimensions 0.30 × 0.20 × 0.15 mm, 4212 reflections were measured at values of $h,\pm k,\pm l$ in the range $3.0° \le 2\theta \le 55°$, using Mo K$\alpha$ radiation. Of these, 3614 had $F_o > 3\sigma(F_o)$. The structure was solved by direct methods and Fourier techniques. Full-matrix least-squares refinement on 280 variables, using the SHELX76 package of programs with the Mo, and all C and N atoms anisotropic, converged with residuals $R$ = 0.045 and $R_w$ = 0.05. The $PF_6^-$ anion is threefold disordered around the nondisordered phosphorus atom.

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## Synthesis and X-ray Crystal Structure of a Heterobimetallic Ethyl-Bridged Organoaluminum Complex: $(C_5Me_5)_2Sm(\mu\text{-}C_2H_5)_2Al(C_2H_5)_2$[1]

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*Received June 29, 1987*

Since the discovery of Ziegler–Natta catalytic polymerization of alkenes,[2] the chemistry of organoaluminum complexes in association with other metallic species has been of great interest. Numerous heterobimetallic organoaluminum containing molecules have been synthesized, structurally characterized,[3-6] and studied

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(1) Presented in part at the 2nd International Conference on the Chemistry and Technology of the Lanthanides and Actinides, Libson, Portugal, April 1987; L(II)I and at the 193rd National Meeting of the American Chemical Society, Denver, Co, April 1987; Paper INOR 227.

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