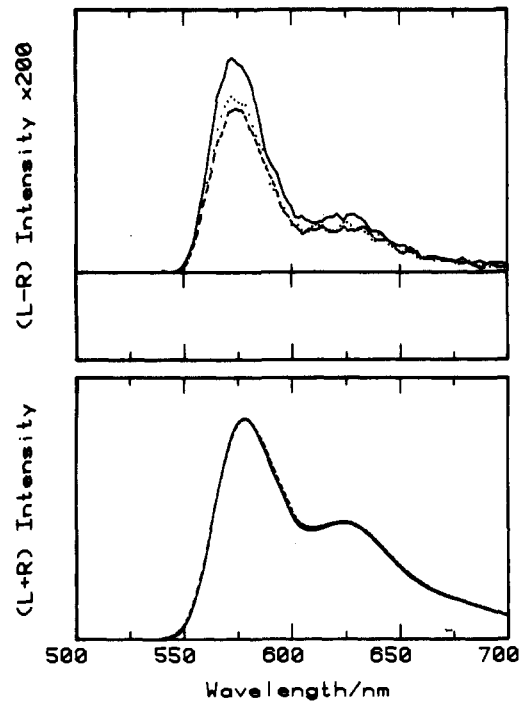

Figure 3. MCPL (top) and total luminescence (bottom) of $Ru(bpy)_3^{2+}$ in poly(vinyl alcohol) film. The concentration was 5×10^{-4} M, dissolved as the chloride salt. The temperatures are 120 K (—), 130 K (···), and 137 K (– –). Other details are as in Figure 1.

the 4:5 propionitrile/butyronitrile system occurring about 10 K lower in temperature. Figure 3 shows the MCPL of $Ru(bpy)_3^{2+}$ in PVA over the same temperature range as in Figure 1. A small decrease in intensity of the MCPL is seen, and measurements taken over a wider temperature range reveal basically $1/T$ (C term) behavior.[14]

The interpretation of the MCPL data in Figures 1 and 2 is straightforward. The marked drop in the MCPL signal, from that observed in the glass phase to that observed in the liquid phase, is exactly the behavior we expect for a transition from a delocalized to a localized species. Measurements taken at higher temperatures reveal little further reduction in the MCPL, consistent with a residual B term. Figure 4 shows a comparison of the shift of the luminescence maximum and the MCPL strength derived from the data in Figure 1 for the 4:1 ethanol/methanol solvent system. This clearly shows that the localization process occurs more quickly than the solvent dipole relaxation process. The relative rates of shift and localization, both distinct as revealed by the MCPL, occur at *different* rates in the two solvent systems studies. The details of the spectra depend slightly on the thermal history of the sample and the concentration of the cation used, but the basic phenomenon as revealed in Figures 1, 2, and 4 is repeated in each case. In the 4:5 propionitrile/butyronitrile system, the MCPL drops even more quickly compared to the shift of the luminescence maximum.

We have considered the possibility that part of the reduction of the MCPL is due to the photoselection process[15] but conclude that only a small fraction of the reduction can arise from this mechanism.

The dependence of the MCPL reduction phenomenon on the temperature range of the glass–fluid transition and its absence in PVA and single crystal[15] establishes that the localization is not intrinsic at 100 K and must involve either solvent reorientation or counterion reorientation. The fact that the localization does not follow the solvent dipole reorientation behavior suggests that the driving force may be counterion reorientation, but this matter needs further detailed investigation.

We are currently analyzing these data quantitatively, along with lifetime and time-resolved luminescence measurements, which along with MCPL measurements completely substantiate our viewpoint. The interpretation of the MCPL reduction can be put

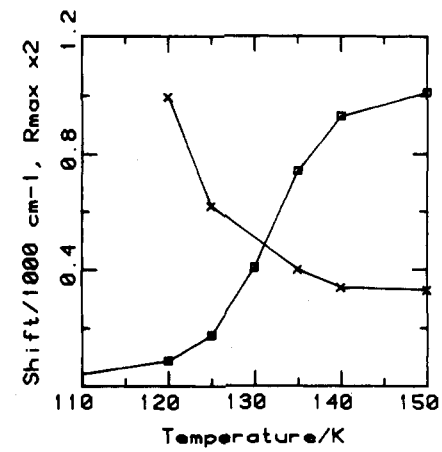

Figure 4. Shift of the luminescence maximum (obtained from corrected spectra) of $Ru(bpy)_3^{2+}$ in 4:1 ethanol/methanol (Figure 1) (□) from its position at 100 K and R_{max} and ratio of the peak MCPL to the peak luminescence (×).

independently by using the simple qualitative arguments given.

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Research School of Chemistry
Australian National University
Canberra, ACT 2601, Australia

James Ferguson
Elmars Krausz*

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A Bimetallic Ruthenium Hydride Borohydride Complex with Unusually Short Ruthenium–Boron Distances. X-ray Crystal Structure of [(tripod)HRu(μ,η^2-BH_4)RuH(tripod)]BPh_4 (tripod = $MeC(CH_2PPh_2)_3$)

Sir:

The coordination modes of the tetrahydroborate ligand BH_4^- in transition-metal complexes have been shown to be quite versatile, adopting unidentate,[1] bidentate,[2] and tridentate[2] coordination. Although numerous examples exist in the extant literature of BH_4^- bound to a single metal, cases in which BH_4^- bonds to more than one metal are rare.[3] The first example of a bimetallic group 8 tetrahydroborate complex with a μ,η^2-BH_4^- ligand is now reported.[4]

Treatment of a yellow CH_2Cl_2 solution of $RuH(BH_4)$(tripod) (**1**)[5] with MeOH at room temperature results in a darkening in color with concomitant evolution of gas. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicates quantitative conversion to a single cation, **2**, showing a singlet at δ +39.33. Salts containing cation **2** can be isolated from MeOH solution with BF_4^-,

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(4) Recently, Fehlner and co-workers reported a trinuclear iron compound in which BH_4^- bonds in a μ,η^3-manner: Vites, J. C.; Eigenbrot, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4633.
(5) Compound **1** was prepared by reaction of $NaBH_4$ and $[Ru(tripod)(MeCN)_3](CF_3SO_3)_2$ in MeOH, which in turn was synthesized by treatment of $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]Cl$ with 4 molar equiv of $AgCF_3SO_3$ in acetonitrile. (See also: Crabtree, R. H.; Pearman, A. J. *J. Organomet. Chem.* **1978**, *157*, 335.)

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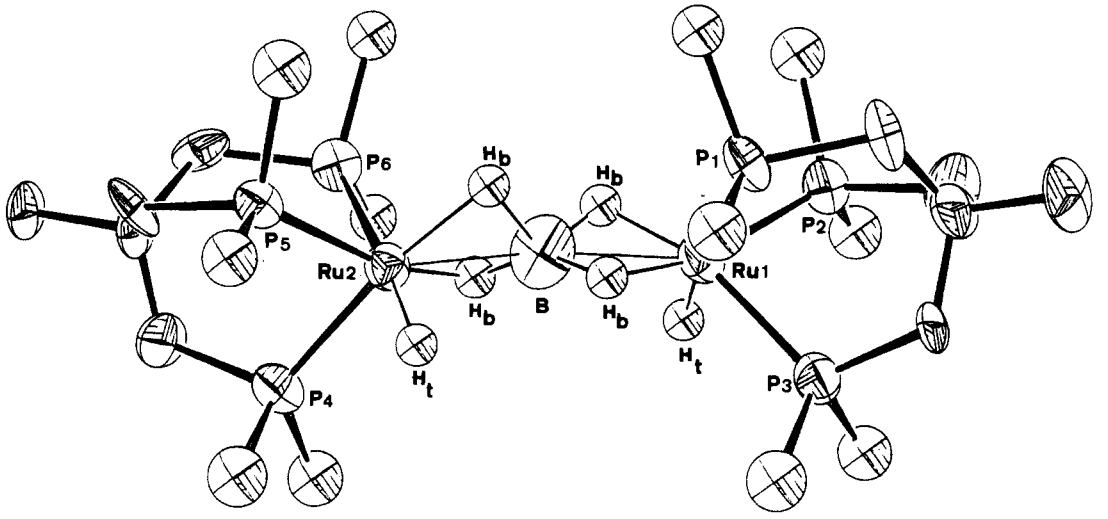

Figure 1. ORTEP view of cation **2**. Relevant bond lengths (Å) and angles (deg): Ru1–B, 2.08 (3); Ru2–B, 2.12 (3); Ru1–P1, 2.341 (5); Ru1–P2, 2.276 (5); Ru1–P3, 2.288 (5); Ru2–P4, 2.260 (5); Ru2–P6, 2.336 (5); Ru2–P5, 2.281 (5); Ru–H_b (av), 1.62 (11); Ru–H_t (av), 1.52 (9); Ru1–B–Ru2, 172.2 (1.2); P1–Ru1–P2, 90.3 (2); P1–Ru1–P3, 90.6 (2); P2–Ru1–P3, 86.3 (2); P4–Ru2–P5, 89.4 (2); P4–Ru2–P6, 85.8 (2); P5–Ru2–P6, 91.3 (2).

PF_6^-, and BPh_4^- as counterions.[6] Detailed studies were carried out on [**2**]PF_6. Its ^1H NMR spectrum was temperature-invariant over the range −115 to +80 °C and showed, besides the signals due to aromatic and aliphatic protons of the tripod ligand,[7] a broad doublet at δ −4.90. A band at 1885 cm^{-1} (br, s) in the infrared spectrum (KBr, CH_2Cl_2) was assigned to a hydride stretch by deuterium substitution. Since the spectral data were not conclusive, a crystal structure determination of [**2**]BPh_4 was undertaken.[8] The geometry of cation **2** is shown in Figure 1.

Cation **2**, [(tripod)HRu(μ,η^2-BH_4)RuH(tripod)]$^+$, consists of two {RuH(tripod)}$^+$ fragments bridged by a distorted tetrahedral BH_4^- unit. The six donor atoms around ruthenium define a distorted octahedron with each phosphorus trans to a hydride, either bridging or terminal. Two of the Ru–P distances (average 2.338 (3) Å) are longer than the others (average 2.276 (11) Å), as expected from the difference in trans influence of the terminal vs. bridging hydrides.[9]

It is noteworthy that Ru–B distances, 2.08 (3) and 2.12 (3) Å, are comparable with the sum of the covalent radii of Ru and B (2.13 Å).[10] This contrasts with the case of $(PPh_3)_2Cu(\mu,\eta^2\text{-}BH_4)Cu(PPh_3)_2^+$,[3b] where the Cu–B distances (average 2.22 (1) Å) are longer than the sum of the covalent radii for Cu and B (2.15 Å).[10] This may be an indication of a direct Ru–B interaction in **2**.

The structural and solution data for **2** can be reconciled by invoking a dynamic process equilibrating the phosphorus nuclei and the hydrides. Such a process could involve facile fluxionality around the B center;[11] scrambling of the terminal and bridging hydride could be expected as a result.[12,13]

Compound **2** does not react (1) with BH_4^- in MeCN or CH_2Cl_2/THF, (2) with $LiBEt_3H$ in CH_2Cl_2/THF, or (3) with nucleophiles such as NEt_3 or NaOMe in refluxing MeOH. The stabilty of **2** is noteworthy since in cases 1 and 2 compound **1** could have been regenerated and, in case 3, removal of BH_3 would have yielded [(tripod)Ru(μ-H)$_3$Ru(tripod)]$^+$. This is expected to be stable as the analogous Fe compound is known[14] as are the related compounds $[(PR_3)_3M(\mu\text{-}H)_3M(PR_3)_3]^+$ (M = Ru,[15] Os[16]). However, when **2** (in 1,2-$C_2H_4Cl_2$) is treated with the Lewis acid BH_3 (as its THF adduct) and then with H^- (as $LiBEt_3H$), **1** is regenerated.[17]

Acknowledgment. We thank Dr. P. S. Pregosin for the ^{11}B NMR spectra and much stimulating discussion. This work was supported by the Forschungskommission der ETH (L.F.R.), the Exchange Programme Swiss National Science Foundation/Consiglio Nazionale delle Ricerche (C.S.), and NATO Research Grant 85-0068 (A.A.).

Registry No. **1**, 103500-11-4; [**2**]PF_6, 103500-13-6; [**2**]BPh_4, 103500-14-7; [Ru(tripod)(MeCN)$_3$]$(CF_3SO_3)_2$, 103500-16-9; [$Ru_2(\mu$-Cl)$_3$(tripod)$_2$]Cl, 103500-17-0.

Supplementary Material Available: Tables of final coordinates and thermal parameters (S1) and bond distances and angles (S2) and atom-

(6) Although the original anion X was not identified, we believe that it is a boron-containing anion formed from the reaction of the "missing" BH_4^- with MeOH: Kadlec, V.; Hanzlik, J. *Collect. Czech. Chem. Commun.* **1974**, *39*, 3200.

(7) The measurements over the range −115 °C to room temperature were carried out in $CD_2Cl_2/CDCl_3$, the others in 1,2-$C_2H_4Cl_2$. ^1H NMR (CD_2Cl_2, 22 °C, 250 MHz): δ 7.50 (t, 24 H), 7.14 (t, 12 H), 6.99 (t, 24 H), 2.39 (d, J_{PH} = 7 Hz, 12 H), 1.68 (br q, J_{PH} = 2 Hz, 6 H), −4.90 (br d, J_{PH} = 20 Hz, 6 H).

(8) Pale yellow crystals of [**2**]BPh_4 were obtained by layering a CH_2Cl_2 solution with MeOH and allowing the solvents to slowly evaporate. A crystal of prismatic habit and of approximate dimensions 0.1 × 0.08 × 0.06 mm was used for the data collection. Compound [**2**]BPh_4 is monoclinic, space group $P2_1/c$, with the following unit cell constants: a = 19.266 (8) Å, b = 25.209 (12) Å, c = 18.856 (16) Å, β = 94.77 (5)° (least-squares-refined values), Z = 4, V = 9126 (1) Å^3, ρ_{calcd} = 1.213 g cm^{-3}. Data were collected on a CAD4 diffractometer up to a $2\theta_{max}$ = 36° at room temperature (Mo K$\bar{\alpha}$ graphite-monochromated radiation) using a $\theta/2\theta$ scan and a variable scan speed to insure constant statistical precision of the collected intensities (maximum scan speed 10.5° min^{-1}, maximum counting time 55 s, scan widths calculated from the formula θ = 1.00 + 0.35 tan θ). A total of 5283 independent reflections $\pm h,+k,+l$) were collected of which 3714 were considered observed having $|F_o| \geq 2.5\dagger(F_o)$) and subsequently used for the solution and refinement of the structure. Data were collected for Lorentz and polarization and for absorption by using an empirical correction (ψ-scans); transmission factors were in the range 0.82–0.98. The structure was solved by standard Patterson and Fourier methods and refined by block diagonal least squares to the present R = 0.070, with anisotropic temperature factors for the Ru, B, P, and aliphatic C atoms and isotropic temperature factors for the others. The positions of the hydride atoms, both bridging and terminal, were located in the final Fourier maps and refined with fixed isotropic thermal factors (B_{iso} = 5.5 Å^2). Upon convergence the last Fourier difference map showed no unusual features or evidence of disorder.

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numbering scheme for **2** (14 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Laboratorium für anorganische Chemie
ETH-Zentrum
CH-8092 Zürich, Switzerland

Larry F. Rhodes
Luigi M. Venanzi*

Istituto di Chimica Farmaceutica
Università di Milano
I-20131 Milano, Italy

Carla Sorato
Alberto Albinati

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Spectroscopic Evidence for Stacking and Electrostatic Interactions between Nucleoside 5′-Monophosphates and a Platinum DNA Intercalator, (2,2′-Bipyridine)(ethylenediamine)platinum(II), in Dilute Aqueous Solution

Sir:

Intercalative DNA binding by metal complexes involving planar aromatic rings is now well recognized and receives considerable attention in view of its relevance to the antitumor activity of drugs and usefulness for probing nucleic acid structures.[1] Lippard et al.[1-3] found that the platinum(II) complexes of aromatic amines such as $[Pt(terpy)Cl]^+$, $[Pt(phen)(en)]^{2+}$, and $[Pt(bpy)(en)]^{2+}$ bind to DNA by intercalation, whereas the complex of an aliphatic amine $[Pt(en)_2]^{2+}$ and the nonplanar complex $[Pt(py)_2(en)]^{2+}$ do not.[4] The X-ray diffraction patterns of intercalator–DNA complexes[3,5] and the crystal structure analyses of model intercalative complexes of AMP with $[Pt(terpy)Cl]^+$[6] and double-helical deoxycytidylyl-(3′–5′)-deoxyguanosine with $[Pt(terpy)(SCH_2CH_2OH)]^+$[7] revealed the existence and modes of the intercalative interactions. Intercalative binding is a crucial step for the sequence-specific DNA binding, and a number of investigations have been reported for various metal complex–DNA interactions, such as stereoselective intercalations by chiral complexes,[8] sequence-specific binding and cleavage by Fe(II)–bleomycin,[9] Fe(II)–EDTA linked to DNA-binding distamycin[10] or methidium[11] or *cis*-$[Pt(en)Cl_2]$ linked to acridine orange,[12] and cleavage by the Cu(I)–phenanthroline complex.[13]

Although these investigations reasonably indicate the importance of the stacking between the planar aromatic rings of DNA and the intercalators, information on the interaction with mononucleotides as DNA constituents would offer a further insight into the intercalator–DNA bond, where the base specificity, if

Chart I

$$Pt(bpy)(en) + L \underset{}{\overset{K}{\rightleftharpoons}} Pt(bpy)(en)\cdots L$$

L	AMP	GMP	CMP	UMP
Base	adenine	guanine	cytosine	uracil

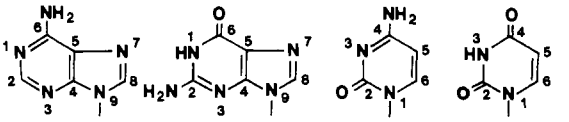

Table I. CD Spectral Data for Pt(bpy)(en)–L Systems in Water at ≥300 nm ([Pt(bpy)(en)] = 0.5 mM)

L	[L]/mM	pH	λ_{max}/nm ($\Delta\epsilon$/M(Pt)$^{-1}$ cm^{-1})
AMP	0.5	7.0	314 (+0.31)
	2.5	7.0	319 (+0.92)
	5.0	2.0	
	5.0	7.0	319 (+1.14)
GMP	0.5	7.0	320 (+0.26)
	2.5	7.0	319 (+0.50)
	5.0	2.0	319 (+0.12)
	5.0	7.0	319 (+0.69)
adenosine	0.5	7.0	
	5.0	7.0	326 (+0.15)
	5.0	10.0	326 (+0.12)

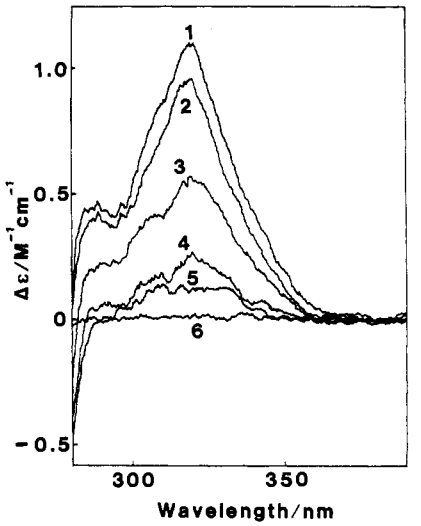

Figure 1. Ionic strength dependence of the CD spectrum due to the Pt(bpy)(en)–AMP interaction. The spectra were measured at room temperature with a JASCO J-500C spectropolarimeter for aqueous solutions (pH 6.8–7.7) containing 0.5 mM Pt(bpy)(en) and 5.0 mM AMP (disodium salt) at the following concentrations (M) of added $NaClO_4$: curve 1, 0; curve 2, 0.01; curve 3, 0.1; curve 4, 0.5; curve 5, 1.0; curve 6, baseline. The $\Delta\epsilon$ values are based on the concentration of Pt(bpy)(en).

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