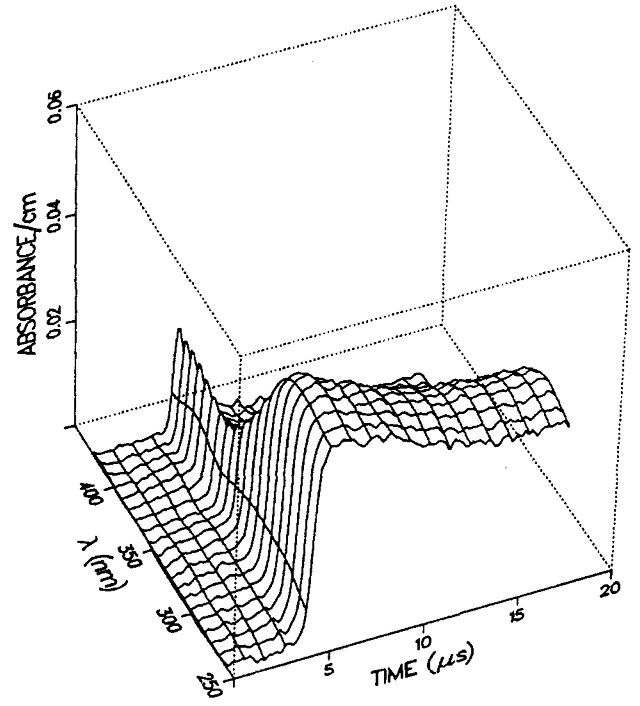


Figure 1. Time-resolved absorption spectrum obtained by pulse-irradiating an argon-saturated 2 mM solution of Bk(III) of pH 5, containing 0.1 M ethanol. Note: The rapidly decaying absorption at the long-wavelength end is due to the hydrated electron.

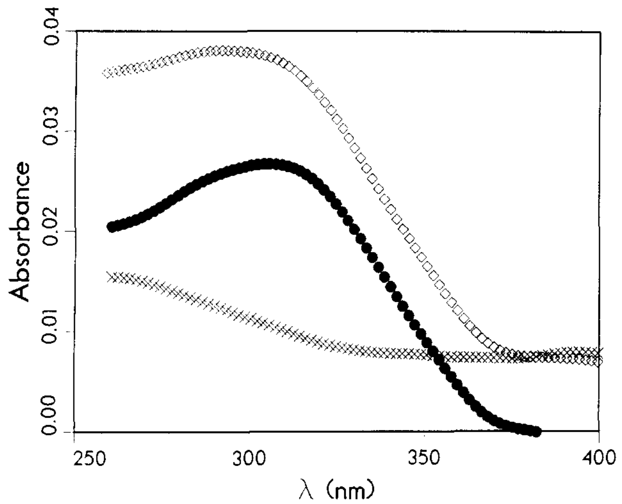


Figure 2. Derivation of Bk(II) spectrum: diamonds, spectrum at signal maximum obtained from data in Figure 1; crosses, spectrum of the ethanol radical from the blank experiment, containing the same (small) contribution from the hydrated electron absorption; filled circles, difference spectrum, ascribed to Bk(II).

to be characteristic of Bk(II). In order to obtain the undistorted shape of the Bk(II) spectrum, a correction was made for the absorption of the ethanol radical produced by the reaction of the OH radicals with the ethanol. Figure 2 shows the measured absorption spectrum at the time peak of the signal (diamonds), the absorption spectrum of the ethanol radical determined with a blank solution (crosses), and the difference spectrum (solid circles) with its absorption maximum at 310 nm and a molar absorptivity at this wavelength of $\epsilon = (2.3 \pm 0.2) \times 10^3$ cm^{-1} M^{-1}. We ascribe this spectrum to Bk(II). This assignment is consistent with theoretical considerations advanced by Carnall and Crosswhite(10) that would predict strong absorption in the visible and near-UV regions analogous to that observed for Tb^{2+}.

Bk(II) is in an unstable oxidation state in aqueous solution. Its rate of disappearance, determined from the time profile at 310 nm, is $(1.53 \pm 0.25) \times 10^5$ s^{-1}, a value to be compared to 9.7×10^4 s^{-1} for the disappearance of Am(II) and to 7×10^4 s^{-1} for that of Cf(II).

The logarithms of the rate constants for the oxidation of the divalent Am, Bk, and Cf (4.94, 5.18, and 4.85, respectively) are satisfactorily correlated with the values of the potentials for the +3/+2 couples. However, the value reported for the rate of disappearance of Cm(II) is smaller than that for any of these other divalent transplutonium ions in aqueous solution. This deviation from the systematics is particularly noticeable because of the estimated value of −3.7 V for the potential of the Cm^{3+}/Cm^{2+} couple and warrants further investigation.

Acknowledgment. We are indebted for the use of the ^{249}Bk to the Office of Basic Energy Sciences, Division of Chemical Sciences, USDOE, through the transplutonium element production facilities at Oak Ridge National Laboratory. We also gratefully acknowledge the technical assistance of D. F. Ficht and G. Cox, who operated the linear accelerator, and M. F. Williams, who ensured radiation safety for the operations.

Chemistry Division
Argonne National Laboratory
Argonne, Illinois 60439

J. C. Sullivan*
K. H. Schmidt
L. R. Morss
C. G. Pippin
C. Williams

Received October 14, 1987

---

(10) Carnall, W. T.; Crosswhite, H. M. In *The Chemistry of the Actinide Elements*, 2nd ed.; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; Vol. 2, pp 1260–1262.

Monomeric and Dimeric Ruthenium(II) η^2-Dihydrogen Complexes with Tricyclohexylphosphine Coligands

Sir:

We have recently described the preparation and some reactions of $RuH_6(PCy_3)_2$ (**1**), the first hexahydride of ruthenium.(1) Its exact structure was unknown. In view of the discovery of the η^2-H_2 ligand in thermally stable, group 6 metal complexes by Kubas' group(2,3) and later on in group 8 and 9 metal complexes by other groups,(4–14) we were led to reinvestigate the structure of **1** as well as those of other polyhydrido tricyclohexylphosphine complexes. We report here that **1** is likely to be the second thermally stable complex to contain two η^2-dihydrogen ligands. We have also characterized spectroscopically the first dinuclear complexes to contain an η^2-H_2 ligand.

---

(1) Chaudret, B.; Poilblanc, R. *Organometallics* **1985**, *4*, 1722–1726.
(2) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451–452.
(3) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I. Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000–7009 and references therein.
(4) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794–795.
(5) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1986**, *108*, 3124–3125.
(6) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037 and references therein.
(7) Crabtree, R. H.; Hamilton, D. G., submitted for publication.
(8) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581–5582.
(9) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780–3782.
(10) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506–507.
(11) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675–1676.
(12) Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R., submitted for publication.
(13) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548–5549.
(14) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865–5867.

0020-1669/88/1327-0598$01.50/0

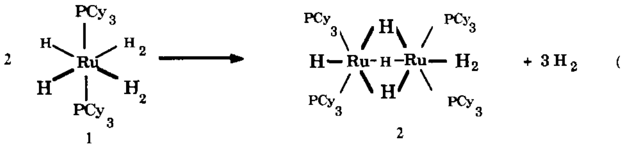
Table I. Longitudinal Relaxation Times (T_1) for the High-Field Resonances of the Complexes as a Function of Temperature

	temp, K	δ	integration	T_1, ms
$Ru(H_2)_2(H)_2(PCy_3)_2$	273	−7.9	6	80 ± 1^a
	203	−7.9	6	28 ± 3^a
$Ru(H_2)(H)_2(PCy_3)_3$	273	−9.1	4	36 ± 4^a
	203	−9.1	4	44 ± 15^a
$Ru_2(H_2)(H)_4(PCy_3)_4$	293	−12.5	6	88 ± 10^b

[a] 200 MHz; toluene-d_8 solvent. [b] 250 MHz; toluene-d_8 solvent.

In particular $RuH_6(PCy_3)_2$ (**1**) is isoelectronic to $[IrH_6(PCy_3)_2]^+$, which is actually likely to be *cis,cis,trans*-$[Ir(H_2)_2(H)_2(PCy_3)_2]^+$ based on the characteristically short T_1 values of its hydrogen ligands.[6] A related, thermally unstable complex *cis*-$Cr(H_2)_2(CO)_4$ has also been reported.[15,16] The reformulation of **1** as *cis,cis,trans*-$Ru(H_2)_2(H)_2(PCy_3)_2$ instead of $RuH_6(PCy_3)_2$ is most consistent with its spectra and chemistry. The infrared spectrum displays two strong bands of equal intensity at 1927 and 1890 cm^{-1} in agreement with the cis hydride structure. The ^1H NMR spectrum gives a broad singlet at −7.9 ppm from 190 to 310 K for the hydrogen ligands, which is consistent with a fluxional process involving interchange of hydrogens between hydride and η^2-H_2 sites.[6-9] The short, temperature-dependent T_1 value (Table I) for this resonance is indicative of H–H bonding and likely results from an averaging of a short T_1 for the η^2-H_2 ligands (four H atoms, each with a T_1 = 20 ms at 210 K) with a long T_1 for the terminal hydrides (two H atoms, each with $T_1 \sim$ 200 ms[6,7,9]). This averaging and temperature dependence of T_1 values has recently been demonstrated for the complexes $[Os(H_2)(H)(PEt_2CH_2CH_2PEt_2)_2]^{+}$[9] and $[Ir(H_2)(H)(C_{13}H_8N)(PR_3)_2]^{+}$[7] and proposed for other polyhydrido dihydrogen complexes.[7] The alternative formulation, $Ru(H)_4(H_2)(PCy_3)_2$ (two H atoms with T_1 = 10 ms, four with T_1 200 ms) does not account as well for the infrared bands and invokes the less common oxidation state, Ru(IV).

Complex **1** loses H_2 thermally (360 K) or photochemically in toluene to give the red complex $Ru_2(H_2)(H)_4(PCy_3)_4$ (**2**),[17] as in eq 1. Complex **2** gives a broad IR absorption in the solid state at 1550 cm^{-1} for bridging hydrides and a band at 2050 cm^{-1} for a terminal hydride. Like **1** this dinuclear complex is fluxional from 190 to 310 K showing a single broad peak at −12.5 ppm in the ^1H NMR spectrum that shifts to lower field and broadens upon cooling. The short T_1 value indicates the presence of H–H bonding in this fluxional complex. The complex reacts with N_2 to give a dinitrogen derivative ($\nu(N_2)$ = 2145 cm^{-1}).[18] A bioctahedral structure (eq 1) is proposed for **2** and the N_2 derivative when exchange processes are stopped on the basis of the solid-state structure of $Ru_2(H)_4(N_2)(PPh_3)_4$,[19] which can itself be prepared by reacting $Ru_2(H_2)(H)_4(PPh_3)_4$ with dinitrogen. This supports the ideas that a binding site for dinitrogen is also a binding site for dihydrogen and that when the dinitrogen stretching frequency falls in the range 2060–2150 cm^{-1}, then the corresponding η^2-dihydrogen adduct will be stable near room temperature.[20] The structure and fluxionality of **2** mirrors exactly that of the complex $Ru_2H_3(\mu\text{-}H)(\mu\text{-}Cl)_2(P(tol)_3)_4$[21] which likely should be reformulated as $Ru_2H(H_2)(\mu\text{-}H)(\mu\text{-}Cl)_2(P(tol)_3)_4$.[22]



1 2 (1)

The "tetrahydride" $Ru(H_2)(H)_2(PCy_3)_3$ (**3**)[1] actually contains an η^2-H_2 ligand like its triphenylphosphine congener $Ru(H_2)(H)_2(PPh_3)_3$.[5] Thus it also shows a broad peak at −9.1 ppm with a short T_1 value over a wide temperature range (two H with T_1 = 25 ms and two H with $T_1 \sim$ 200 ms at 210 K). The T_1 value goes through a minimum somewhere between 273 and 210 K just like the PPh_3 complex.[7] It shows a similar broad IR absorption, ν(Ru–H) = 1950 cm^{-1} in Nujol mulls. An interesting feature of **3** is that it has been shown to dissociate a phosphine in solution and insert into C–H bonds.[1] Thus the bulky PCy_3 ligand may dissociate from **3** more readily than does the η^2-H_2 ligand.

All of these complexes are too fluxional to observe slow exchange spectra in the proton NMR. Nevertheless the combination of data—terminal hydride stretches, ν(Ru–H), T_1 values, and analogies to other complexes of known structure—has allowed us to distinguish between hydrogen coordination modes and propose reasonable structures. The modes ν(H–H)[2,3] have not yet been detected.

Laboratoire de Chimie de Coordination du CNRS
Unite No. 8241 liée par convention à l'université Paul Sabatier
205 route de Narbonne
31077 Toulouse, France

Thérèse Arliguie
Bruno Chaudret*

Department of Chemistry and Scarborough Campus
University of Toronto
80 St. George Street
Toronto, Ontario, Canada M5S 1A1

Robert H. Morris
Andrea Sella

Received October 20, 1987

---

(15) Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645–3651.

(16) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374–2379.

(17) $Ru_2H(\mu\text{-}H)_3(H_2)(P(C_6H_{11})_3)_4$: IR ν(RuH) 2050 m br, 1525 m br cm^{-1}; ^1H NMR (C_7D_8, 303 K) δ −12.4 s, (210 K) − 10.2 vbr; ^{31}P NMR (C_7D_8, vs H_3PO_4) δ 81.1. Anal. Calcd: C, 65.03; H, 10.46; P, 9.32. Found: C, 65.6; H, 10.9; P, 8.9.

(18) $Ru_2H(\mu\text{-}H)_3(N_2)(P(C_6H_{11})_3)_4$: IR $\nu(RuN_2)$ 2145 s, ν(RuH) 1935 m cm^{-1}; ^1H NMR (C_7D_8, 303 K) δ −12.4 s. Anal. Calcd: C, 63.8; H, 10.0; N, 2.1; P, 9.1. Found: C, 62.5; H, 9.9; N, 2.2; P, 8.2.

(19) Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1727–1732.

(20) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674–2683.

(21) Dekleva, T. W.; Thornburn, I. S.; James, B. R. *Inorg. Chim. Acta* **1985**, *100*, 49–56.

(22) James, B. R., personal communication.