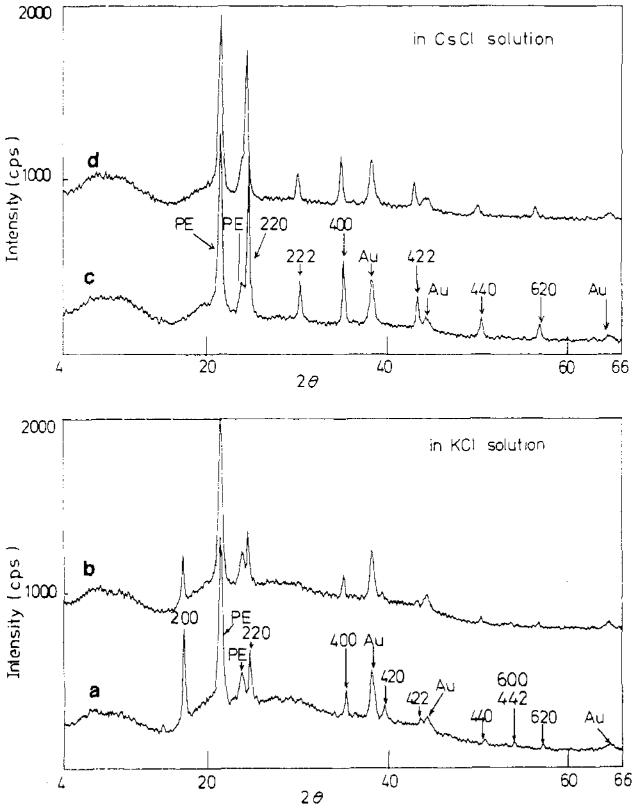

Figure 3. Typical X-ray diffraction patterns measured in situ from Prussian blue and its reduced forms prepared by electroreduction in KCl (a, b) and CsCl (c, d) solutions: (a, c) PB; (b, d) PB potentiostated at 0 V in KCl solution or −0.05 V in CsCl vs Ag/AgCl.

kali-metal ions of a larger atomic number. The diffraction intensities of the individual peaks changed as follows (as changes from a to b and from c to d in Figure 3): *hkl* of increasing peaks, 220 and 222; *hkl* of decreasing peaks, 200, 420, 442, and 600. These intensity changes show that the alkali-metal ions penetrate into the PB lattice because of the electroreduction.

It has been proposed that cations are inserted into PB after reduction without changing the lattice structure[11] or a_0.[2,16] In this measurement, no change in the cubic cell structure was observed after electroreduction. However, positions and intensities of the diffraction peaks changed with the potentials. They changed continuously with neither a peak split nor a long spacing reflection. Therefore, the cations must penetrate into the PB lattice and occupy a site randomly as though forming a solid solution. The lattice constants of the cubic cell at the various potentials are illustrated in Figure 4. They were obtained as the average values of a_0 from d spacings of four to eight diffraction peaks after correction using the 110 peak of gold ($2\theta = 38.19°$). In the case of Cs^+, a_0 was shifted with no electroreduction due to the penetration of Cs^+ as described above. During the oxidation of Everitt white, the lattice constants were changed almost reversibly, as shown by the open symbols in Figure 4. Under these experimental conditions, the separation of PB from the electrode, which has been reported in cyclic voltammetry measurements in LiCl and NaCl solutions,[4] was not observed. This may be due to using a soft electrode like cellulose instead of a conventional platinum electrode.

During the penetration of the cations, crystallographically larger cations increased a_0 more extensively. Increases in a_0 observed at −0.1 to 0 V from freshly prepared PB in the solution with no alkali-metal ion (a_0 = 10.16 Å indicated by the + symbol in Figure 4) were as follows: Li^+, 0.036 Å; Na^+, 0.094 Å; K^+, 0.082 Å; Rb^+, 0.116 Å; Cs^+, 0.152 Å (with errors of ±0.012 Å). Since the residual currents at the potentials less than 0.2 V were quite high, it was impossible to calculate precisely how many cations penetrated into a unit cell of PB. The source of the residual current was not identified completely, but it might be due to the high activity on the surface of the sputtered gold. Roughly estimated changes in the lattice constant by a charge of 1 faraday/mole of Fe in PB were 0.22 ± 0.06 Å for Na^+, K^+, Rb^+, and Cs^+ and 0.12 ± 0.04 Å for Li^+ from an a_0 vs charge plot (potential > 0.2 V) and a chemical analysis of the PB film. The ions penetrating with more difficulty into the lattice like Li^+ seemed to have a crystallographically small effect. Therefore, it is implied that there is a contribution from the kinetic effect in the easy penetration of ions with small Stokes radii.

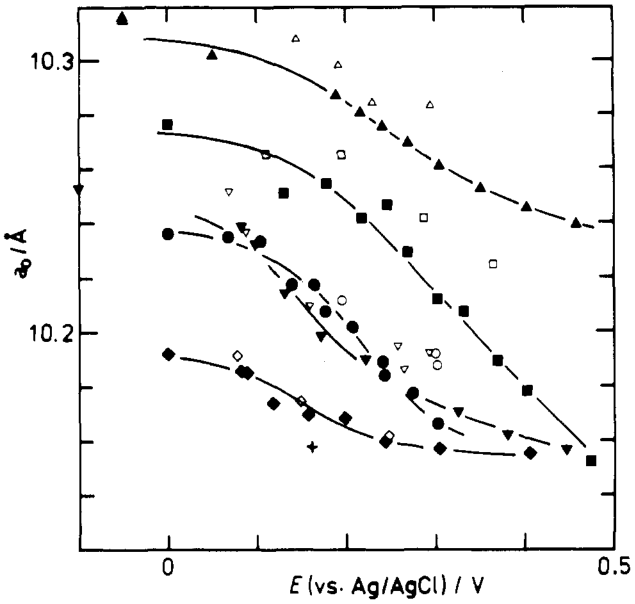

Figure 4. Lattice constant change of Prussian blue during the reduction in 1 M alkali-metal chloride solutions with 0.0001 N HCl: ▲, Cs; ■, Rb; ●, K; ▼, Na; ◆, Li; +, no alkali-metal chloride. (Open symbols show a_0 measured during the oxidation after the reduction of PB.)

In order to confirm these conclusions, it is important to measure a_0 vs charge instead of a_0 vs potential. This requires an appropriate electrochemical system that has a low residual current. Measurement of penetration of ammonium ion and tetraalkylammonium ions would also provide further evidence for the above conclusion. It is also necessary to calculate the structural parameters of PB containing alkali-metal ions to determine the penetrating position in the PB lattice. These studies are currently in progress.

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Registry No. $Fe_4[Fe(CN)_6]_3$, 14038-43-8; $[Fe(CN)_6]^{4-}$, 13408-63-4; CsCl, 7647-17-8; RbCl, 7791-11-9; KCl, 7447-40-7; NaCl, 7647-14-5; LiCl, 7447-41-8; Cs, 7440-46-2; Rb, 7440-17-7; K, 7440-09-7; Na, 7440-23-5; Li, 7439-93-2.

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NMR Studies of the Complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(Ph_2PCH_2CH_2PEt_2)_2]X$ (M = Fe, X = BPh_4; M = Os, X = BF_4): Evidence for Unexpected Shortening of the H–H Bond

Sir:

Several recent papers describe how changes in coligands adjacent to the η^2-dihydrogen ligand change the properties of this interesting ligand.[1-6] Only small changes were observed in early

Table I. 200-MHz ^{1}H NMR Data in the High-Field Region[a]

		η^2-H_2			M–H		
complex	ligand[b]	$\delta(H_2)$	T_1, ms	J(H,D), Hz	δ(H)[c]	T_1, ms	$\Delta G^{\ddagger}$(300 K), kcal mol^{-1}
1Fe	dppe	−8.0[d]	7	30	−12.9[d]	146	14.2
2Fe	dedppe	−9.2	7	32	−13.6	190	>15
3Fe	depe	−10.5	12	28	−14.6	302	13.0
2Os	dedppe	−8.3[e]	125[e]		−8.3[e]	125[e]	13.9[f]
		−8.1	(30)[g]	19	−9.1	(250)[g]	13.9[f]
3Os	depe	−10.0[e]	433[e]		−10.0[e]	433[e]	12.6
		−10.0	52	*h*	−9.7	260	12.6

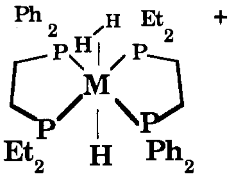
[a] In acetone-d_6 at 210 K unless otherwise noted. [b] Abbreviations: dppe = $Ph_2PCH_2CH_2PPh_2$, dedppe = $Et_2PCH_2CH_2PPh_2$, depe = $Et_2PCH_2CH_2PEt_2$. [c] Quintet unless otherwise noted; J(H,P) = 47 Hz for **1Fe**, **2Fe**, and **3Fe**; J(H,P) = 17.3 for **2Os** and 17.5 for **3Os**. [d] In CD_2Cl_2. [e] At 293 K; average value weighted 2:1 for the H_2 and H sites, respectively, because of exchange. [f] From the Eyring equation: $\Delta H^{\ddagger} = 8.8 \pm 0.5$ kcal/mol; $\Delta S^{\ddagger} = 17 \pm 4$ eu. [g] Estimated from the 293 K data by use of the equation $3/T_1^{\text{av}} = 1/T_1^{\text{MH}} + 2/T_1^{\text{MH}_2}$ and the known temperature dependence of T_1 values for **3Os**.[14] [h] Either the coupling is too small to resolve or exchange is destroying this coupling.[3a]

studies, where monodentate phosphines were altered.[1,2] More recent work showed that the H–H bond could be lengthened[3a] or completely broken[1b,4,5] by altering the properties of the diphosphine ligands or tetraphosphine ligand.[6] We report here a surprising and unexplained effect of changing the substitution on the diphosphine ligands in the complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(R_2PCH_2CH_2PR'_2)_2]^+$ (M = Fe, Os) from R and R′ = Ph (**1Fe**) to R = Ph, R′ = Et (**2Fe**, **2Os**) and to R and R′ = Et (**3Fe**, **3Os**). On the basis of electronic arguments one might expect complexes **2** to have properties intermediate between those of **1** and **3**. Instead, their H–H bonds are shorter than expected. NMR evidence (T_1, J(H,D) values) suggests that the H–H bonds lengthen in the order **2Fe** < **1Fe** < **3Fe** < **2Os** < **3Os**. Also the barriers to exchange of H atoms between η^2-H_2 and H ligands for complexes **2** are larger than those of **1** or **3**, but this is consistent with having to break a stronger H–H bond in **2** in order for the exchange to occur.[3a]

Complex **2Fe**[7] was prepared by reacting a solution of *trans*-$FeHCl(Et_2PCH_2CH_2PPh_2)_2$[8] in acetone with $NaBPh_4$ under 1 atm of H_2 in a fashion similar to that for **3Fe**:[3a]

$$trans\text{-}FeHCl(Et_2PCH_2CH_2PPh_2)_2 + NaBPh_4 + H_2 \rightarrow trans\text{-}[Fe(\eta^2\text{-}H_2)H(Et_2PCH_2CH_2PPh_2)_2]BPh_4 + NaCl \quad (1)$$

The ^{1}H NMR spectrum in the high-field region at room temperature is consistent with an octahedral structure in which the η^2-H_2 ligand is trans to the terminal hydride as observed in the crystal structure of **1Fe**:



There is a broad resonance characteristic of an H_2 ligand at a chemical shift that is intermediate between those of **1Fe** and **3Fe** (Table I), but its T_1 value at 210 K is equal to that of **1Fe** (7 ms) under similar conditions. The terminal hydride resonance is a quintet (J(P,H) = 47 Hz) with a chemical shift and a T_1 value intermediate between those of **1Fe** and **3Fe**. A surprising feature of **2Fe** is that, unlike the case for **1Fe** and **3Fe**, there is no intramolecular exchange of hydrogens according to ^{1}H NMR studies at 200 MHz, 323 K, and 1 atm of H_2 with acetone-d_6 as the solvent. Thus, $\Delta G^{\ddagger}$ for the process must be greater than 15 kcal mol^{-1}. The ^{31}P NMR spectral pattern is A_2X_2, so that only the isomer with PPh_2 groups trans to each other is present. The isotopomer $[Fe(\eta^2\text{-}HD)D(Et_2PCH_2CH_2PPh_2)_2]^+$ gives a characteristic 1:1:1 triplet with J(H,D) = 32 Hz, greater than the couplings observed for derivatives of **1Fe** and **3Fe** (Table I). This HD complex was prepared according to eq 1 by use of 1 atm of D_2. Thus, this large H–D coupling constant, the small T_1 value, and the high barrier to exchange are all consistent with **2Fe** having the shortest H–H bond of the three iron complexes. It must be shorter than 0.89 (11) Å, determined for **1Fe** by X-ray diffraction.[3b]

Complex **2Os**[9] was prepared in a sequence of three steps starting from $[Os_2Cl_3(PEt_2Ph)_6]Cl$.[10] First the latter was heated with neat diphosphine at 200 °C to give *cis*-$OsCl_2(Et_2PCH_2CH_2PPh_2)_2$,[11] which was then treated with $LiAlH_4$ (5 equiv) in THF and then ethanol to give *trans*-$OsH_2(Et_2PCH_2CH_2PPh_2)_2$.[12] The dihydride was protonated with HBF_4 in ether to give complex **2Os** (eq 2) in a fashion similar to that

$$trans\text{-}OsH_2(Et_2PCH_2CH_2PPh_2)_2 + HBF_4{\cdot}Et_2O \rightarrow trans\text{-}[Os(\eta^2\text{-}H_2)H(Et_2PCH_2CH_2PPh_2)_2]BF_4 \quad (2)$$

for the preparation of **1Fe**.[3b] The ^{1}H NMR spectrum of **2Os** at 210 K (Table I) is like that of the other η^2-H_2 complexes **1**–**3** when no intramolecular exchange of H ligands is taking place. The high-field resonances coalesce at approximately 290 K, 200 MHz to a broad singlet devoid of the J(H,P) coupling observed for **3Os**.[3a] The spectra were simulated in the same fashion as was done previously for **3Os**,[3a] and the $\Delta G^{\ddagger}$ value was found to be greater than that of **3Os** (Table I). In the simulation the chemical shifts of the H_2 and H ligands were temperature-dependent; both peaks shift downfield with increasing temperature but at different rates.[13] The broad peaks of the ^{31}P NMR spectrum of **2Os** at 293 K are consistent with a process involving the exchange of ^{31}P nuclei.

The most significant feature of the osmium complex is the very small coupling ^1J(H,D) of 19 Hz observed for the isotopomer *trans*-$[Os(\eta^2\text{-}HD)D(Et_2PCH_2CH_2PPh_2)_2]BF_4$. This is one of the

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(7) *trans*-$[Fe(\eta^2\text{-}H_2)H(Et_2PCH_2CH_2PPh_2)_2]BPh_4$ (**2Fe**): yellow-orange powder; 30% yield; ^{31}P NMR (vs 85% H_3PO_4, acetone-d_6) δ 101.3 (t) and 93.8 (t) (J(P,P) = 38 Hz) (one isomer present).

(8) *trans*-$FeHCl(Et_2PCH_2CH_2PPh_2)_2$: red powder; 70% yield; IR (Nujol) 1884 cm^{-1} (Fe–H); ^{1}H NMR (acetone-d_6) δ −29.93 (quintet, J(H,P) = 48 Hz); ^{31}P NMR (vs 85% H_3PO_4, acetone-d_6) δ 87.9 (t) and 79.9 (t) (J(P,P) = 44 Hz) (one isomer present). Anal. Calcd for $C_{60}H_{71}BFeP_4{\cdot}0.5CH_3OH$: C, 72.76; H, 7.37. Found: C, 72.64; H, 7.11.

(9) *trans*-$[Os(\eta^2\text{-}H_2)H(Et_2PCH_2CH_2PPh_2)_2]BF_4$ (**2Os**): white powder; variable yield ~30%; ^{31}P NMR (vs 85% H_3PO_4, acetone-d_6) δ 44.8 (b) and 41.0 (b).

(10) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, *896*, 2605.

(11) *cis*-$OsCl_2(Et_2PCH_2CH_2PPh_2)_2$: light yellow powder; 78% yield; ^{31}P NMR (vs 85% H_3PO_4, acetone-d_6) δ 10.0 (t) and 5.6 (t) (J(P,P) = 7.3 Hz).

(12) *trans*-$OsH_2(Et_2PCH_2CH_2PPh_2)_2$: light yellow powder; 32% yield; IR (Nujol) 1698 cm^{-1} (Os–H); ^{1}H NMR (acetone-d_6, 200 MHz) δ −21.4 (quintet, J(H,P) = 15.5 Hz, T_1 = 486 ms); ^{31}P NMR (vs 85% H_3PO_4, acetone-d_6) δ 55.8 (t) and 44.5 (t) (J(P,P) = 18.3 Hz).

(13) Earl, K. A. M.S. Thesis, University of Toronto, 1987.