11826 *J. Am. Chem. Soc.* **1998,** *120,* 11826−11827

Organizing Chain Structures by Use of Proton−Hydride Bonding. The Single-Crystal X-ray Diffraction Structures of [K(Q)][Os(H)$_5$(P^{i}Pr$_3$)$_2$] and [K(Q)][Ir(H)$_4$(P^{i}Pr$_3$)$_2$], Q = 18-Crown-6 and 1,10-Diaza-18-crown-6

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Received June 25, 1998

There are several recent reports of metal hydride complexes that form MH⋯HX “dihydrogen” [1] or “hydride−proton” [2] bonds with hydrogen bond donors HX in an intramolecular[3−7] or intermolecular[1,8−10] fashion. Such interactions have the strength, IR spectral characteristics,[1] and electronic structure[11] of conventional hydrogen bonds. All of these studies utilized neutral or cationic complexes. Some of us recently described the synthesis and properties of anionic hydrides [M(H)$_3$(CO)(P^{i}Pr$_3$)$_2$]$^-$, M = Ru, Os, that interact with cations [K(aza-18-crown-6]$^+$ via MCO−K and MH⋯HN bonds.[12] We show here that the cation [K(1,10-diaza-18-crown-6)]$^+$ organizes new anionic polyhydride complexes into a novel 1-dimensional chain in the solid state with crystallographically well-defined proton−hydride bonds in the case of the iridium complex. The [K(18-crown-6)]$^+$ salts with no hydrogen bonds have completely different structures. This new synthetic strategy is providing materials for the study of the influence of the ancillary ligands and the metal on these unique H⋯H bonds.

The complexes **1**−**3** were prepared in 70−80% yield by reacting OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$[13] or IrHCl$_2$(P^{i}Pr$_3$)$_2$[14] in THF under 1 atm of H$_2$ with excess potassium hydride and 1 equiv of either 18-crown-6 or 1,10-diaza-18-crown-6[15] (eq 1). Deprotonation of

$$\mathrm{MH}_x\mathrm{Cl}_2(\mathrm{P^iPr_3})_2 + 3\mathrm{KH} + \mathrm{Q} \xrightarrow{\mathrm{THF,\ H_2}} [\mathrm{K(Q)}][\mathrm{MH}_{x+3}(\mathrm{P^iPr_3})_2] + 2\mathrm{KCl} \qquad (1)$$

1, M = Os, x = 2, Q = 18-crown-6

2, M = Os, x = 2, Q = 1,10-diaza-18-crown-6

3, M = Ir, x = 1, Q = 18-crown-6

neutral polyhydrides such as IrH$_5$(P^{i}Pr$_3$)$_2$[14] provides a second method of preparation of such complexes as illustrated for complex **4** (eq 2, yield 63%). Complexes **1**−**4** are air- and water-sensitive, colorless salts.[16] The ^{1}H and ^{31}P NMR spectra of the osmium complexes **1** and **2** in THF-d_8[16] are consistent with a pentagonal bipyramidal structure with trans phosphines; the spectra are similar to those reported previously for **1** observed in situ.[17] However, **2** is much less soluble in THF than **1** presumably because of the propensity of **2** to form a one-dimensional solid (see below). Iridium tetrahydrido anions such as those in **3** and **4** have not been reported previously. Anions of **3** and **4** exist in THF as a mixture of cis and trans isomers in the ratio of 2:1 and 8:1, respectively. The influence of the type of cation on this ratio will be discussed in more detail elsewhere. The trans isomer in each case is characterized by a singlet in the ^{31}P{^{1}H} NMR spectrum and a triplet in the hydride region in the ^{1}H NMR spectrum.[16] The cis isomer gives a distinctive A$_2$BB′XX′ hydride resonance in the ^{1}H NMR and a singlet in the ^{31}P{^{1}H} NMR spectrum.[16] Interconversion of the isomers in THF-d_8 at 20° occurs readily but at a rate that is too slow to average NMR properties.

$$\mathrm{IrH}_5(\mathrm{P^iPr_3})_2 + \mathrm{KH} + \mathrm{Q} \xrightarrow{\mathrm{THF,\ H_2}} [\mathrm{K(Q)}][\mathrm{IrH}_4(\mathrm{P^iPr_3})_2] + \mathrm{H}_2 \qquad (2)$$

4, Q = 1,10-diaza-18-crown-6

The non-hydrogen atomic positions as determined by single-crystal X-ray diffraction of complexes **2** and **4** are very similar.[18] They consist of one-dimensional chains of alternating cations and anions (Figure 1). In both **2** and **4** the potassium diazacrown

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(16) Representative preparation of **1**: THF (5 mL) was injected against a flow of H$_2$ into a flask containing a mixture of OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$ (315 mg, 0.54 mmol), KH (76 mg, 1.9 mmol), and 18-crown-6 (143 mg, 0.54 mmol). After being stirred for 4 h, the mixture was filtered and the solids were washed with 1.5 mL of THF. The white product was then precipitated from the filtrate by the addition of 13 mL of hexanes, washed with 3 × 3 mL of hexanes, and dried in vacuo. Yield 80%. Selected ^{1}H NMR data (300 MHz, THF-d_8): **1** δ −12.42 (t, ^2J(HP) = 14.9 Hz, 5H, OsH). **2** −12.40 (t, ^2J(HP) = 14.8 Hz, 5H, OsH), 1.89 (qi, 2H, NH). **3** −15.62 (t, ^2J(HP) = 17.4 Hz, 4H, IrH, trans isomer), −14.79 (t of t, A$_2$ part of A$_2$BB′XX′ pattern, ^2J(H$_A$P$_X$) = 13.4 Hz, ^2J(H$_A$H$_B$) = 4.9 Hz, 2H, IrH, cis isomer), −15.45 (BB′ part, ^2J(H$_B$P$_X$) = ±120.0, ^2J(H$_{B'}$P$_X$) = ∓13.4 Hz, ^2J(H$_B$H$_{B'}$) = 2 Hz, ^2J(P$_X$P$_{X'}$) = 3 Hz, 2H, IrH, *cis* isomer). **4** −15.57 (t, ^2J(HP) = 17.2 Hz, 4H, IrH, *trans* isomer), −14.58 (t of t, A$_2$ part of A$_2$BB′XX′ pattern, ^2J(H$_A$P$_X$) = 13.4 Hz, ^2J(H$_A$H$_B$) = 4.9 Hz, 2H, IrH, *cis* isomer), −15.57 (BB′ part), 2.06 (qi, 2H, NH). ^{31}P{^{1}H} NMR (120.5 MHz, THF-d_8): **1** δ 64.0 (s). **2** 63.4 (s) **3** 65.7 (s, *trans*), 42.6 (s, *cis*). **4** 65.7 (s, *trans*), 42.6 (s, *cis*). IR (Nujol, cm^{-1}): **1** 1858, 1843 (OsH). **2** 1839 (OsH), 3184 (br, NH). **3** 1921 (IrH). **4** 1682 (IrH), 3148 (br, NH).

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(18) Crystal data: **1** C$_{34}$H$_{79}$KO$_7$OsP$_2$, monoclinic, $P2_1/n$, a = 10.571(1) Å, b = 33.950(1) Å, c = 11.991(1) Å, β = 92.99(1)°, V = 4298(2) Å^3, Z = 4, size 0.32 × 0.28 × 0.25 mm, T = 123 K, reflections collected 33450, $R(F)$ = 0.0565, $R(wF^2)$ = 0.0788 for 8708 independent reflections. **2** C$_{30}$H$_{73}$KN$_2$O$_4$OsP$_2$, monoclinic, $C2/c$, a = 19.7370(5) Å, b = 11.6714(1) Å, c = 17.1651(4) Å, β = 102.62(3)°, V = 3858.6(2) Å^3, Z = 4, size 0.25 × 0.15 × 0.08 mm, T = 150 K, reflections collected 20526, $R(F)$ = 0.0430, $R(wF^2)$ = 0.0861 for 5340 independent reflections. **3** C$_{30}$H$_{70}$IrKO$_6$P$_2$, triclinic, $P\bar{1}$, a = 9.012(3)°, b = 11.390(6)°, c = 20.502(8) Å, α = 73.88(3)°, β = 85.62(5)°, γ = 72.03(4)°, V = 1923(1) Å^3, Z = 2, size 0.52 × 0.42 × 0.31 mm, T = 173 K, reflections collected 3827, $R(F)$ = 0.0232, $R(wF^2)$ = 0.0505 for 3803 independent reflections. **4** C$_{30}$H$_{72}$IrKN$_2$O$_4$P$_2$, monoclinic, $C2/c$, a = 19.5469(5) Å, b = 11.6464(2) Å, c = 17.2179(5) Å, β = 102.81(3)°, V = 3822.2(2) Å^3, Z = 4, size 0.20 × 0.15 × 0.10 mm, T = 150 K, 14307 reflections collected, $R(F)$ = 0.0405, $R(wF^2)$ = 0.0554 for all 3889 independent reflections. Data for colorless **1**, **2**, and **4** were collected on a Nonius Kappa-CCD, and for **3** on a Siemans P4 diffractometer with Mo Kα radiation (λ 0.71073 Å). CCD data were integrated and scaled with the DENZO-SMN package. The structures were solved and refined with SHELXTL V5.0. The hydrides in **1**, **3**, and **4** were located and refined with isotropic thermal parameters.

10.1021/ja9822106 CCC: $15.00

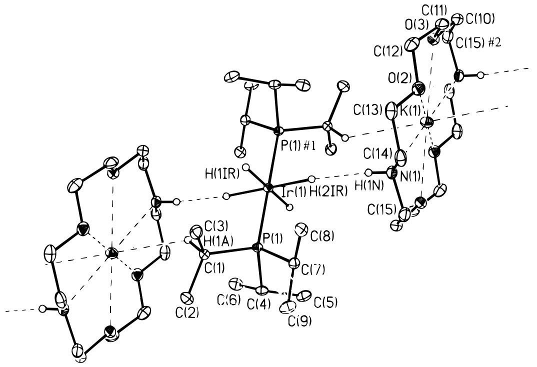

Figure 1. Proton−hydride and K···H interactions between ions of **4** (distances in Å and angles in deg). Ir−H(1IR) 1.54(3), Ir−H(2IR) 1.68(3), Ir−P 2.2606(8), K−O av 2.817(3), K−N 2.859(3), N−H(1N) 0.77(3), H(1N)···H(2IR) 2.07, K···H(1A) 2.99 Å, H(1IR)−Ir−H(2IR) 89(2), H(1IR)−Ir−P(1) 89(1), H(1IR)−Ir−P(1)#1 91(1), H(2IR)−Ir−P(1) 95(1), H(2IR)−Ir−P(1)#1 85(1); all trans angles 180.0°. In isomorphous **2**, a disordered OsH_5 unit replaces the IrH_4 unit. Os−P 2.2931(8), K−O av 2.814(6), K−N 2.878(3), N−H(1N) 0.96(5), H(1N)···Os 3.58.

cations are oriented so that the two NH groups are directed toward hydride ligands of two adjacent anions to form $H^{\delta+}\cdots H^{\delta-}$ bonds. For both complexes the transition metal and the potassium are on crystallographic centers of inversion. The potassium is in the plane of the crown and forms axial K···HC interactions of 3.0 Å with a hydrogen of two adjacent phosphine methine groups. The hydride ligands of **4** were located and refined while the hydrides of **2** were not located but probably would be disordered over 10 sites in a similar arrangement to the one reported previously in the neutron structure determination of $IrH_5(P^iPr_3)_2$ which also crystallizes with a center of inversion.[14] In **4** the trans hydrides involved in hydride−proton bonding have Ir(1)−H(2IR) distances of 1.68(3) Å. These distances compare favorably with the average Ir−H of 1.60 Å determined by neutron diffraction for neutral complexes. However, **4** might be expected to have longer Ir−H distances than the average because of the high trans influence of hydride and of their polarization by the protons on the nitrogens. The refined N−H distances are 0.96(5) Å in **2** and 0.77(3) Å in **4**. As is usual for X-ray diffraction, these distances are underestimated relative to the 1.00 Å average N−H value determined by neutron diffraction.[8,19] When 1.00 Å for N−H is used, the H···H distances in the proton−hydride bonds in **4** are about 1.85 Å, shorter than the crystallographically determined value of 2.07 Å. These distances are slightly longer than the NH···HRe distance of 1.73(1) Å that was determined for the hydrogen-bonded indole-$ReH_5(PPh_3)_3$ system by neutron diffraction.[8]

The crystalline structures of **1** and **3**[18] (Figure 2) which lack hydrogen-bond donors (except for C−H bonds) in the cation are very different from those of **2** and **4**, even though the conditions of crystallization (solvent etc) are similar. Complex **1** crystallizes with the cation $[K(THF)(18\text{-crown-}6)]^+$ and anion $[OsH_5(P^iPr_3)_2]^-$ in Van der Waal's contact. The pentagon of hydride ligands is clearly defined with an average Os−H distance of 1.56(4) Å. The closest distance between a hydride and a hydrogen on the crown is 2.4 Å. Complex **3** crystallizes with a cis anion and a cation oriented so that the potassium is out of the best plane through the oxygens of the crown by 0.8 Å and is sitting on three *fac* hydrides of the anion. It is noteworthy that $[IrH_4(P^iPr_3)_2]^-$ is predominantly cis in THF solution as the $[K(18\text{-crown-}6)]^+$ salt or the $[K(\text{diazacrown})]^+$ salt and is exclusively cis in the solid state in **3**. The cis configuration is favorable because it allows the potassium in the crown to ion pair on a trihydride face of the octahedron as observed previously for other anionic hydrides in the solid state[20,21] and it avoids having two pairs of trans hydrides. The trans geometry in the crystal of the $[K(\text{diazacrown})]^+$ salt is adopted to allow the formation of favorable NH···HIr contacts.

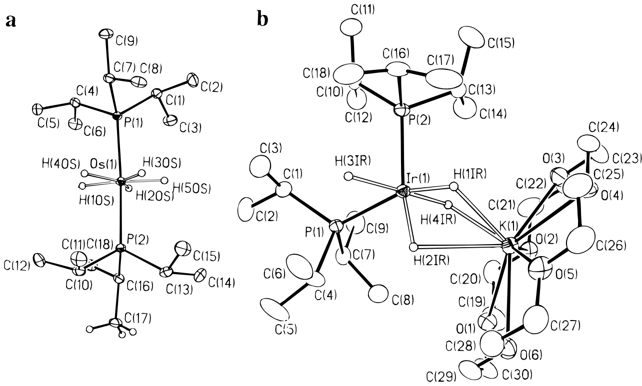

Figure 2. (a) The anion of **1**. (b) The ion-pair structure of **2**.

Proton−hydride bonding in **2** and **4** causes changes in the infrared spectra of powders compared to those of **1** and **3**.[16] The metal−hydride stretching wavenumbers are lower in the presence of proton−hydride interactions by about 10 cm^{-1} for **2** and 233 cm^{-1} for **4**. A lowering of ν(Ir−H) in some iridium complexes containing intramolecular proton−hydride bonds was previously proposed.[1] The effect is particularly pronounced for **4** where an extremely low mode at 1682 cm^{-1} is present because of the two sets of mutually trans hydrides. The N−H stretch[16] is broader and lowered by $\Delta\nu = 96$ cm^{-1} in **2** and 132 cm^{-1} in **4** relative to the average of the ν(N−H) of $[K(1,10\text{-diaza-}18\text{-crown-}6)]BPh_4$ (3282, 3278 cm^{-1}). A comparable $\Delta\nu = 141$ cm^{-1} was observed for the ReH···HX interaction in $ReH_5(PPh_3)_3$·indole.[1] The greater value of $\Delta\nu$ for **4** compared to **2** is consistent with the greater basicity of **4**. We have independently determined that the pK_a of $IrH_5(P^iPr_3)_2$ is at least 8 units greater than that of $OsH_6(P^iPr_3)_2$ in THF.[22] Therefore the more basic anionic hydride has the stronger proton−hydride interaction. A similar conclusion was reached in a study of intermolecular proton-hydride bonds with neutral hydrides in solution.[9] The properties of **1**−**4** in solution will be reported in due course.

Acknowledgment. This research was supported by an operating grant to R.H.M. from NSERC Canada and by an NSERC Postgraduate Scholarship to S.E.L. Johnson Matthey PLC is thanked for a loan of platinum metals.

Supporting Information Available: Preparation and spectroscopic and X-ray structure determination details for complexes **1**−**4** (33 pages; print/PDF). See any current masthead page for ordering information and Web access instructions.

JA9822106

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