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New Polyhydride Anions and Proton-Hydride Hydrogen Bonding in Their Ion Pairs. X-ray Crystal Structure Determinations of Q[*mer*-$Os(H)_3(CO)(P^iPr_3)_2$], Q = [K(18-crown-6)] and Q = [K(1-aza-18-crown-6)]

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Abstract: The transition metal halides $Re(H_2)Br_2(NO)(P^iPr_3)_2$ and $MHCl(CO)(P^iPr_3)_2$, M = Ru, Os afforded the hydrido(tertiary phosphine)metalates $[ReH_3(NO)(P^iPr_3)_2]^-$ and $[MH_3(CO)(P^iPr_3)_2]^-$, M =Ru, Os in reactions with KH in the presence of crown ethers (2.2.2-crypt, 18-crown-6, 1-aza-18-crown-6) under H_2. The anionic hydrides $[RuH_3(PPh_3)_3]^-$ and $[MH_5(P^iPr_3)_2]^-$, M = Ru, Os were also efficiently prepared by this method. The trihydrides [K(18-crown-6)][$OsH_3(CO)(P^iPr_3)_2$] and [K(1-aza-18-crown-6)][$OsH_3(CO)(P^iPr_3)_2$] were characterized by single-crystal X-ray diffraction and possess the *mer* structure with two trans hydride ligands. Unlike the former structure, the latter is chain polymeric via CO···K^+ links and NH···HOs hydrogen bonds; this is the first one-dimensional network to be held together by proton−hydride bonding. The $[K(1\text{-aza-18-crown-6})]^+$ N−H IR band shift ($\Delta\nu$) indicates the increasing strength of hydrogen bonding with the following hydrides: $[ReH_3(NO)(P^iPr_3)_2]^-$ (102 cm^{-1}) < $[OsH_3(CO)(P^iPr_3)_2]^-$ (116 cm^{-1}) < $[RuH_3(CO)(P^iPr_3)_2]^-$ (136 cm^{-1}). The order of acidity of the conjugate acid forms follows a different trend: $Os(H_2)(H)_2(CO)(P^iPr_3)_2$ > $Re(H)_4(NO)(P^iPr_3)_2$ > $Ru(H_2)(H)_2(CO)(P^iPr_3)_2$. The crypt-containing cations interact weakly with the anions in [K(2.2.2-crypt)][$OsH_3(CO)(P^iPr_3)_2$] and [K(2.2.2-crypt)][$RuH_3(CO)(P^iPr_3)_2$] in toluene or tetrahydrofuran (THF). This results in the formation of only the *mer* isomers. Substantial ion-pairing between $[K(18\text{-crown-6})]^+$ and the trihydrides results in the stabilization of the *fac* isomers to a greater degree in toluene than in polar THF. Use of $[K(1\text{-aza-18-crown-6})]^+$ results in even greater stabilization of the *fac* isomers both in THF and toluene. Nuclear Overhauser effect (NOE) experiments reveal that NH···HM hydrogen bonds cause tighter ion pairing in this case.

Introduction

Weak *intramolecular* interactions between iridium(III) hydrides and hydrogen-bond donors, IrH···HX, X = N or O, were identified in the early 1990s as an important new type of hydrogen bond. [1−5] This led to the discovery of *intermolecular* interactions MH···HX in rhenium(V) polyhydrides in the solid state[6,7] and tungsten(0)[8] and ruthenium(II)[9,10] hydrides in solution. Further examples of intramolecular interactions MH···HX in iridium(III),[11−13] rhenium(V),[9,14] and Os(II)[15] have also been discovered. Recently, an intermediate with an RuH···HN interaction has been implicated in the catalytic asymmetric reduction of ketones.[16] Such interactions have similar strength, IR spectral characteristics,[7] and electronic structures[17] as conventional hydrogen bonds.

The MH···HX bonding has been described as electrostatic,[18] with the associated description of proton−hydride bonding,[3] and unconventional hydrogen bonding,[7] with associated description "dihydrogen bonding." To date such interactions have been studied in cationic and neutral metal hydride complexes. The present work utilizes anionic hydride complexes with the objective of enhancing the electrostatic component of the proton−hydride bond.

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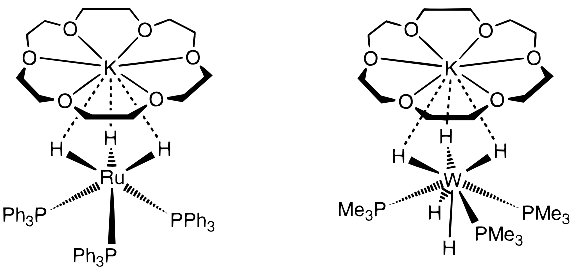

$[RuH_3(PPh_3)_3][K(18\text{-crown-}6)]$ $[WH_5(PMe_3)_3][K(18\text{-crown-}6)]$

Figure 1. Metal hydrides interacting with potassium-18-crown-6.

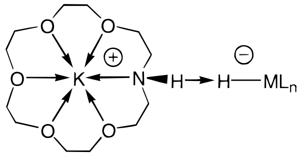

Figure 2. $[K(1\text{-aza-}18\text{-crown-}6)]^+$ as a hydrogen bond donor to an anionic hydride.

Ion pairing is an important aspect of anionic hydride chemistry which is also exploited in this work to enhance proton−hydride bonding. The interaction of metal cations with the carbonyl ligands of hydridocarbonylmetalates[19] is a well-known phenomenon. When no carbonyl ligands are present, the cation often interacts with the hydrides; here the potassium cation is displaced from the 18-crown-6 ring toward a triangle of three hydrides in the anions *fac*-$[RuH_3(PPh_3)_3]^-$ [20] and $[WH_5(PMe_3)_3]^-$ [21] (Figure 1).

In this work we utilize 1-aza-18-crown-6 coordinated to potassium for the first time in order that it might serve as a N−H hydrogen bond donor to the hydrides (Figure 2).

Anionic hydride complexes with few or no carbonyl ligands are required for our studies to avoid the formation of conventional MCO−HN hydrogen bonds. There are only a few examples of hydridophosphinemetalate complexes which do not contain carbonyl ligands; examples include *fac*-$[RuH_3(PPh_3)_3]^-$,[20,22] $[WH_5(PMe_3)_3]^-$,[21] $[RuH_2(C_6H_4PPh_2)(PPh_3)_2]^-$,[20,22] $[OsH_5(P^iPr_3)_2]^-$,[23] $[OsH_3(PMe_2Ph)_3]^-$,[24] and $[RuH_5(PPh_3)_2]^-$.[25,26] The most common method of preparation of such complexes is the deprotonation of neutral metal polyhydrides by use of a strong base such as KH or BuLi (eq 1).[27]

$$MH_xL_n + B^- \rightleftharpoons [MH_{x-1}L_n]^- + HB \qquad (1)$$

These preparations are challenging because the neutral hydride precursors are often difficult to prepare or isolate in good yield and the anionic hydride complexes are highly reactive strong bases.[24] Equation 1 is not a general preparative route because in certain cases suitable neutral hydride precursors do not exist or are very unstable with respect to H_2 loss. For instance, $[RuH_5(PPh_3)_2]^-$ could not be prepared by the deprotonation as in eq 1 because $RuH_6(PPh_3)_2$ has not been isolated.[25,26,36] Instead it was prepared in three steps from the reaction of $RuHCl(PPh_3)_3$ with potassium naphthalide to give $[RuH_2(PPh_3)_2(PPh_2C_6H_4)]^-$ which was then converted to $[RuH(PPh_3)_2(1,4\text{-}Ph_2\text{-}1,3\text{-butadiene})]^-$ and then the product.[25,26] Here we describe an alternative, attractive synthetic strategy that is based on the reaction of transition metal halide complexes with potassium hydride and suitable crown ether reagent.

Anionic hydrides species have interesting reactivity as strong nucleophiles and reductants.[19] Ruthenium anionic hydrides are catalyst precursors for the hydrogenation of ketones, aldehydes, esters, nitriles, and olefins under mild conditions.[28,29] An anionic zirconium hydride complex catalyzes the dehydrocoupling of primary phosphines.[30]

Results and Discussion

Preparation of Anionic Hydride Complexes. A useful route to the formation of hydridophosphinemetalates is the reaction of halide or hydridohalide precursors in tetrahydrofuran (THF) under H_2 with excess potassium hydride and one equivalent of crown, either 18-crown-6 or 1-aza-18-crown-6 (eq 2). These routes are economical in terms of use of the metal and phosphine ligand because the halide precursors can be obtained in high yield from commercially available reagents.

$$MH_xX_yL_z + (y + 1)KH + \text{crown} \rightarrow [K(\text{crown})][MH_{x+y+1}L_z] + yKX \qquad (2)$$

Neither KH nor KX are appreciably soluble in THF, so that the THF-soluble hydride complexes are easily separated from these salts. In this way the new complexes [K(18-crown-6)]-$[MH_3(CO)(P^iPr_3)_2]$, M = Ru (**1**), Os (**2**), and [K(18-crown-6)]-$[ReH_3(NO)(P^iPr_3)_2]$ (**3**), as white, oxygen and water sensitive solids, were prepared from the precursors $MHCl(CO)(P^iPr_3)_2$, M = Ru, Os[31] or $Re(H_2)Br_2(NO)(P^iPr_3)_2$[32] in yields of 71, 93, and 78%, respectively. The novel white compounds with proton−hydride bonds [K(1-aza-18-crown-6)]$[MH_3(L)(P^iPr_3)_2]$, M = Ru, L = CO (**4**) and M = Os, L = CO (**5**), and M = Re, L = NO (**6**) were prepared in high yield by use of the same precursors and the aza-crown. The 2.2.2-crypt ligand for potassium was also used as in eq 2 to produce complexes with minimal anion−cation interactions, namely [K(2.2.2 crypt)]-$[MH_3(CO)(P^iPr_3)_2]$, M = Ru (**7**), Os (**8**). In addition, the complex $RuCl_2(PPh_3)_3$[33] conveniently provides the known complex [K(18-crown-6)]$[RuH_3(PPh_3)_3]$ according to eq 2.[20] The pentahydride complexes [K(18-crown-6)]$[MH_5(P^iPr_3)_2]$, M = Ru and Os were also prepared in excellent yield as described elsewhere.[34] Many hydridometalates, including [K(18-crown-6)]$[RuH_3(PPh_3)_3]$ and the new complexes **1**−**6**, are capable of ion-pairing and are soluble in benzene and toluene.

The crown reagent is required because of the insolubility and consequently low reactivity of KH in THF. Our initial explora-

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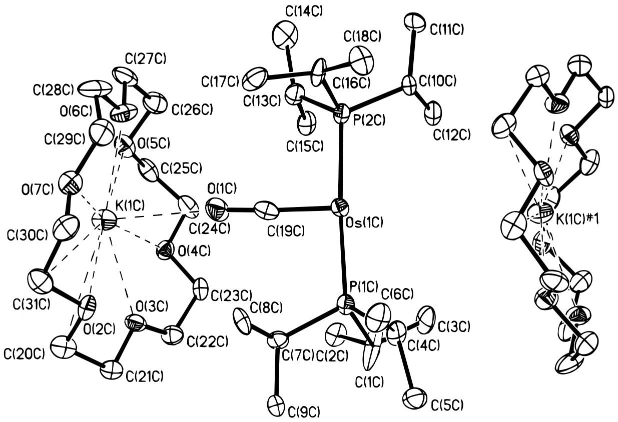

Figure 3. Molecular structure and atomic numbering of ion pair C of $[K(18\text{-crown-}6)][\textit{mer}\text{-}OsH_3(CO)(P^iPr_3)_2]$.

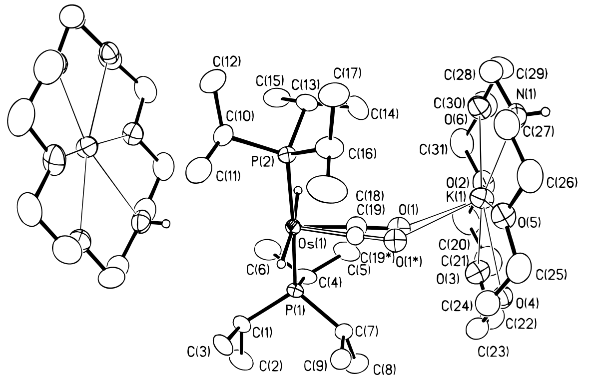

Figure 4. Molecular structure and atomic numbering of $[K(1\text{-aza-}18\text{-crown-}6)][\textit{mer}\text{-}OsH_3(CO)(P^iPr_3)_2]$.

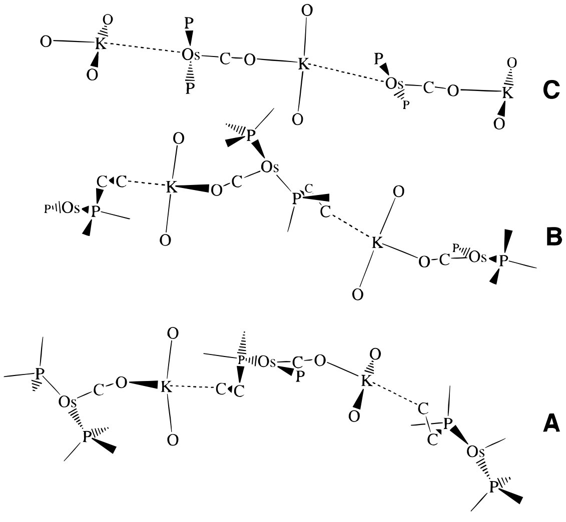

Figure 5. Three different chains of ion pairs of $[K(18\text{-crown-}6)][\textit{mer}\text{-}OsH_3(CO)(P^iPr_3)_2]$ defined by independent ion pairs A, B and C in the crystal lattice. The element symbols are approximately positioned where certain atoms are located to reveal the chains. Only the positions of atoms near to the plane which contains the three chain structures are shown.

tion of the $MH_xX_yL_z$/KH reactions in NMR tubes (sealed under H_2) showed that halide complexes could be partially converted to hydride complexes but not to anionic hydrides $[MH_{x+y+1}L_z]^-$.

The balanced eq 2 does not appear to require the involvement of H_2 gas as a hydride source; nevertheless we deliberately used 1 atm of H_2 for two reasons. First, eq 2 may not be representative of the actual reaction mechanism. The starting halides $MH_xX_yL_z$ are typically unsaturated, as are the kinetic products (hydrides) of their reactions with KH. Devoid of π-donor ligands, unsaturated hydrides are usually short-lived and would normally react with the solvent or decompose. Trapping such reactive species with dissolved H_2 should make the preparation more tractable when the supply of KH is limited by solubility. Second, unstable dihydrogen complexes are known in some cases to be intermediates in the synthesis. For example, $Os(H_2)(H)_2(CO)(P^iPr_3)_2$[35] was detected in an NMR-tube reaction of $OsHCl(CO)(P^iPr_3)_2$/3KH/18-crown-6 under nitrogen. Similar reactivity could be anticipated in the reactions of other halides in this work, and thus the formation of the labile dihydrogen complexes $Ru(H_2)_nH_{6-2n}(P^iPr_3)_2$ ($n = 1$ or 2), [36,37] $Ru(H_2)H_2(PPh_3)_3$,[38] $Ru(H_2)H_2(CO)(P^iPr_3)_2$,[39] and $ReH_4(NO)(P^iPr_3)_2$[32] is expected. In the absence of dissolved H_2 these complexes can lose coordinated dihydrogen and decompose (or exchange H_2 for N_2 under nitrogen). However it may turn out that Ar(g) is sufficient for some preparations.

In two cases our attempts to prepare anionic hydrides using the KH/18-crown-6/H_2 reaction failed. No reaction was observed for $OsHCl(CO)_2(P^iPr_3)_2$.[31] This and related OsX_2L_4 complexes are generally quite inert toward alumino- and borohydrides. The other case was $ReOCl_3(PPh_3)_2$, for which the reaction resulted in decomposition and extensive phosphine loss.

X-ray Diffraction Structure Determinations. The crystal structures of $[K(18\text{-crown-}6)][\textit{mer}\text{-}OsH_3(CO)(P^iPr_3)_2]$ (**2**) and $[K(1\text{-aza-}18\text{-crown-}6)][\textit{mer}\text{-}OsH_3(CO)(P^iPr_3)_2]$ (**5**) were determined in this work. Part of the ion-pair structure of each compound is displayed in Figures 3 and 4, respectively. The unit cell of $[K(18\text{-crown-}6)][\textit{mer}\text{-}OsH_3(CO)(P^iPr_3)_2]$ contains three crystallographically independent anion−cation pairs: A, B, and C. These ion pairs exist in three types of layers of chains of ion pairs as shown in Figure 5. One of them (C), shown in Figure 3, has the closest estimated distance (ca. 3.2 Å) between an undetected hydride on the anion of **2** and an atom of the next cation (a potassium ion). The other two ion pairs A and B have $K^+\cdots$methyl interactions as described below.

Both crystals have anions of similar octahedral structure. The trans Os−P bonds are of comparable length (Table 1). In each case a cis carbonyl ligand interacts with the potassium. For **5** the carbonyl ligand is disordered over two positions generating two structures indicated as **5** and **5*** in Table 1 with occupancies 38 and 62%, respectively. The Os−C distances of 1.81(1)−1.86(1) Å in **5** and **2** are comparable, as are the C−O bonds of 1.18(1)−1.22(1) Å. Electron density difference maps revealed the presence of the trans hydride ligands of **5** but not the hydride trans to the disordered carbonyl. The trans hydrides H(2Os) and H(3Os) refined with reasonable thermal parameters and with Os−H distances of 1.39(4) and 1.45(3) Å, respectively; however this accurate positioning might be coincidental considering the disorder in the $Os(H)_3(CO)$ plane (see Figure 6). A typical Os−H distance of neutral polyhydrides derived by neutron diffraction studies is 1.65 Å[40,41] and the average Os−H distance is 1.68(8) Å in the anion $\textit{fac}\text{-}[Os(H)_3(PMe_2Ph)_3]^-$ as determined by X-ray diffraction.[24] No hydrides were located for **2**. However, there is infrared evidence for their existence (see below).

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Table 1. Selected Bond Distances and Angles for Complexes **2** and **5**

	complex **2**				
	ion pair A	ion pair B	ion pair C	**5**	**5***
		bond distances (Å)			
Os(1)−C(19)	1.825(9)	1.826(9)	1.821(9)	1.81(1)	1.864(6)
Os(1)−P(2)	2.305(5)	2.307(4)	2.312(5)	2.3109(9)	2.3109(9)
Os(1)−P(1)	2.308(5)	2.315(5)	2.334(4)	2.3142(9)	2.3142(9)
O(1)−C(19)	1.22(1)	1.22(1)	1.22(1)	1.21(1)	1.18(1)
K(1)−O(1)	2.68(1)	2.65(1)	2.87(1)	2.480(8)	2.729(6)
K(1)−O(2)	2.87(2)	2.87(2)	2.92(1)	2.866(3)	2.866(3)
K(1)−O(3)	2.71(2)	2.72(2)	2.70(1)	2.808(3)	2.808(3)
K(1)−O(4)	2.87(2)	2.84(1)	2.85(1)	2.869(3)	2.869(3)
K(1)−O(5)	2.78(2)	2.78(1)	2.75(1)	2.764(3)	2.764(3)
K(1)−O(6)	2.87(2)	2.85(2)	2.74(1)	2.774(3)	2.774(3)
K(1)−O(7)	2.81(2)	2.82(2)	2.81(1)		
N(1)−K(1)				2.883(3)	2.883(3)
N(1)−H(1N)				0.82(4)	0.82(4)
Os(1)−H(2OS)				1.39(4)	1.39(4)
Os(1)−H(3OS)				1.45(3)	1.45(3)
		bond angles (deg)			
C(19)−Os(1)−P(2)	92.7(6)	91.7(6)	91.9(5)	91.5(4)	90.8(2)
C(19)−Os(1)−P(1)	100.3(6)	101.2(6)	92.2(5)	91.6(4)	93.7(2)
P(2)−Os(1)−P(1)	167.0(2)	167.0(2)	175.6(2)	173.62(3)	173.62(3)
C(19)−O(1)−K(1)	151(1)	149(1)	174(1)	157.5(8)	139.8(5)
O(1)−C(19)−Os(1)	174(2)	174(2)	177(2)	176(1)	178.3(6)
H(2OS)−Os(1)−H(3OS)				173(2)	173(2)
H(2OS)−Os(1)−C(19)				89(1)	103.2(12)
H(3OS)−Os(1)−C(19)				98(1)	83.0(12)
H(2OS)−Os(1)−P(2)				71(1)	71(1)
H(3OS)−Os(1)−P(2)				105(1)	105(1)
H(1N)−N(1)−C(27)				113(3)	113(3)
H(1N)−N(1)−C(28)				107(3)	107(3)
C(27)−N(1)−C(28)				113.0(4)	113.0(4)
H(1N)−N(1)−K(1)				107(3)	107(3)

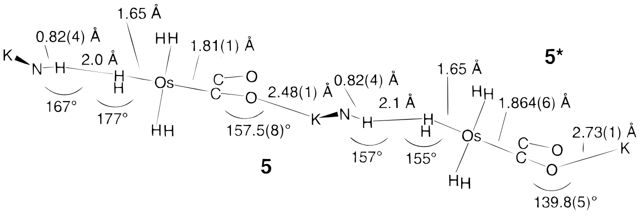

Figure 6. The zigzag chain of [K(1-aza-18-crown-6)][*mer*-$OsH_3(CO)(P^iPr_3)_2$]. Only the principal structural elements are shown to emphasize the polymeric nature in the solid state. In this view each N−H group is in the $Os(H)_3(CO)$ plane of the adjacent anion. The carbonyl ligand is disordered over two positions generating two structures indicated as **5** and **5*** with occupancies 38 and 62%, respectively. The hydrides are also assumed to be disordered as shown. The ion pair fragment on the left has bonds to ligands in **5**, whereas the ion pair fragment to the right has bonds to ligands in **5***.

In both cases the potassium cation bonds to the carbonyl oxygen instead of to the hydride ligands. Apparently the former configuration is more favorable than the alternative situation shown by other compounds (see Figure 1) in which the potassium interacts with three *fac* hydride ligands. Note that both the *mer* and *fac* isomers were present in the crystallization solution (see below) but only the *mer* isomer is observed in the solid state. The potassium to carbonyl K(1)···O(1) bond distances in **2** and **5** fall in a similar range of distances (2.65(1)−2.87(1) Å) as the K−O(crown) bonds (2.70(1)−2.92(1) Å) except for the 2.48(1) Å value for the disordered component **5**. The C(19)−O(1)···K(1) angles range from being almost linear (174(1)°) in **2**C to quite bent (139.8(5)°) in **5*** (Table 1). The linkage between an alkali metal cation and a carbonyl ligand of an anionic metal complex tends to be bent.[19]

The potassium cation in the C ion pair of **2** has the carbonyl oxygen to one side of the plane of the crown and the undetected hydride of a neighboring anion on the other side at a long distance (Figure 3; the Os(1C)−K(1C)#1 distance is 4.86 Å). With the assumption of an Os−H distance of 1.65 Å, the K···H separation is ca. 3.2 Å—substantially longer (by 0.35 Å) than in the examples of Figure 1. The K(1C) shows no significant deviation from the crown plane and the angles around Os(1C) are not far from octahedral (Table 1). The ion pairs C are arranged in a fairly linear fashion with a K(1)−O(1)−C(19) angle of 174(1)° and a C(19)−Os(1)−K(1)#1 angle of 171°. All of these data indicate that interactions between ion pairs C are weak.

As displayed in Figure 5, the potassium cations in the A and B ion pairs interact with the carbonyl oxygen on one side of the crown ether plane and hydrogens of the methyl group (C(9)-#1) of an adjacent phosphine ligand on the other side with K(1)−C(9)#1 distances of 3.41(2) in **2**A and 3.28(2) Å in **2**B. This creates the two serpentine chains A and B of Figure 5. The C(19)−Os(1)−P(1) and P(2)−Os(1)−P(1) angles in anions of **2**A and **2**B of about 101° and 167.0(2)°, respectively, are far from octahedral because of the interaction of the potassium with the methyl of the phosphine that contains P(1).

The ion pairs in **5** are oriented in a different fashion to those of **2** so that an N−H group can hydrogen bond to the (undetected) hydride in the next anion of the chain (Figure 6). The position of the hydrogen atom on nitrogen was located and refined with *d*(N−H) 0.82(4) Å; the angles around this nitrogen are close to tetrahedral (see Table 1). This X-ray experiment has underestimated this bond length by about 0.15 Å because N−H distances of 0.95−1.00 Å as determined by neutron diffraction are more typical.[6] If the 1.0 Å value is used, then the hydrogen is 3.5 Å from the osmium. The H···H separation can be estimated by placing the hydride trans to each position

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(40) $OsH_4(PMe_2Ph)_3$: Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

(41) $OsH_6(P^iPr_2Ph)_2$: Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930.

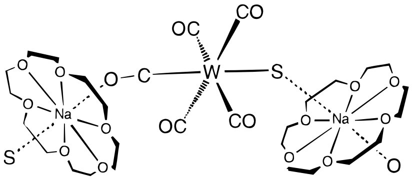

Figure 7. The one-dimensional network of crystalline [Na(18-crown-6)][W(CO)$_5$(SH)].

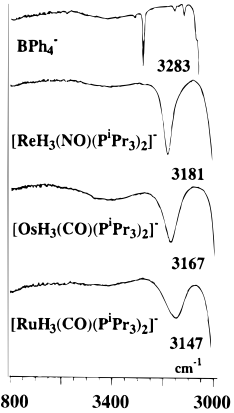

Figure 8. IR (Nujol) spectra in the N−H vibrational region of K(1-aza-18-crown-6)$^+$ with the anions shown.

of C(19) in **5** and **5***; Figure 6 shows these two possible situations. The resulting H···H distances are about 1.9 Å for **5** and 2.0 Å for **5***. If anionic Os−H bonds are longer than 1.65 Å, then these distances will be shorter. 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.[6] The N−H bond points at the hydride in **5** but is at an angle to the Os−H bond in **5*** (Figure 6). By contrast, the indole N−H appears to point at the middle of the Re−H bond in the rhenium system. We have characterized several intramolecular N−H···HIr bonds that have characteristics similar to those of the intermolecular interaction in **5**: the N−H points at the hydride on Ir giving H···H distances of 1.8 to 2.0 Å. [3,4,12,42]

Clearly, N−H···H−Os bonding is a dominant intermolecular interaction in **5**. The polymeric structure adopts a zigzag shape where every second potassium−azacrown cation must be rotated by 180° to keep the chain growing approximately perpendicular to the crown plane. The chaining mode (NH···HOsCO···K)$_n$ is more favorable than the alternative (NH···HOsH···K)$_n$ or (NH···OCOsH···K)$_n$ structural possibilities.

A polymeric system most resembling that in Figure 6 is shown in Figure 7. In [Na(18-crown-6)][W(CO)$_5$(SH)] the anion is linked to two sodium cations via the oxygen and sulfur atoms of the trans CO and SH ligands.[43] The coordination geometry of the Na$^+$ cation is hexagonal bipyramidal, with the [Na(18-crown-6)]$^+$ complex approximately planar.

Crystal structures are not available for [K(1-aza-18-crown-6)][RuH$_3$(CO)(P^{i}Pr$_3$)$_2$] and [K(1-aza-18-crown-6)][ReH$_3$(NO)(P^{i}Pr$_3$)$_2$], but on the basis of their similar infrared spectra we assume that they have solid-state structures similar to that of [K(1-aza-18-crown-6)][OsH$_3$(CO)(P^{i}Pr$_3$)$_2$].

Infrared Spectroscopy of Solid Samples. The N−H···H−M bonding can be easily identified by IR spectroscopy. Figure 8 demonstrates the characteristic broadening and shifting to lower wavenumber of the N−H bands in the spectra of the trihydrides prepared with [K(1-aza-18-crown-6)]$^+$. A sample of [K(1-aza-18-crown-6)]BPh$_4$ provides the value of $\nu_{N-H} = 3283$ cm^{-1} in the absence of hydrogen bonding. The magnitude of the band shift $\Delta\nu$ and the extent of broadening normally correlate with the strength of the bonding. [6,8] The peaks in Figure 8 become broader and shift to lower wavenumber in the order: [ReH$_3$(NO)-(P^{i}Pr$_3$)$_2$]$^-$ ($\Delta\nu$ 102 cm^{-1}) < [OsH$_3$(CO)(P^{i}Pr$_3$)$_2$]$^-$ ($\Delta\nu$ 116 cm^{-1}) < [RuH$_3$(CO)(P^{i}Pr$_3$)$_2$]$^-$ ($\Delta\nu$ 136 cm^{-1}). This is expected to be the order of increasing NH···HM bond strength. The reported band shift ($\Delta\nu$ 141 cm^{-1}) for the indole−ReH$_5$(PPh$_3$)$_3$ compound [6] with an NH···HRe separation of 1.73 Å is similar to that of the ruthenium complex. However, the comparison is suspect because of the different types of N−H bonds in the two systems.

Table 2. Selected IR (Nujol) Data in cm^{-1} for the *mer*-Trihydrides Q [MH$_3$L(P^{i}Pr$_3$)$_2$], M = Os, Ru, L = CO, and M = Re, L = NO

complex	M	Q	ν_{MH} and $\nu_{CO(NO)}$[a]	ν_{MH}[b]
mer-**1**	Ru	K(18-crown-6)$^+$	1835[c], 1813	1589
mer-**4**	Ru	K(1-aza-18-crown-6)$^+$	1849, 1808	1576
mer-**7**	Ru	K(2.2.2 crypt)$^+$	1847, 1834	1574
mer-**2**	Os	K(18-crown-6)$^+$	1855, 1811, 1734	1686
mer-**5**	Os	K(1-aza-18-crown-6)$^+$	1861, 1813, 1742	1695
mer-**8**	Os	K(2.2.2 crypt)$^+$	1884, 1836, 1763	1697
mer-**3**	Re	K(18-crown-6)$^+$	1745	1489
mer-**6**	Re	K(1-aza-18-crown-6)$^+$	1772, 1697	1488

[a] Strongly coupled vibrations of the *trans* ligands. [b] Assigned to the *trans* hydrides. [c] Shoulder.

The hydridorhenate **6** shows apparently the weakest bonding ($\Delta\nu$ 102 cm^{-1}). Surprisingly, the complex is a stronger Brönsted base in THF than the osmium analogue ($\Delta pK_a = 1.9$ for the conjugate acids, see below), although the H−Re bond involved in the hydrogen bonding may not be the most basic site (Table 5). [RuH$_3$(CO)(P^{i}Pr$_3$)$_2$]$^-$, which is slightly more basic than the rhenium trihydride ($\Delta pK_a = 0.5$ for the conjugate acids), is the most strongly bound on the basis of the band shift of 136 cm^{-1}.

The ν_{M-H} and $\nu_{C-O(N-O)}$ stretching wavenumbers in complexes **1**−**6** are reported in Table 2. A salient feature of the IR spectra is that the M−H vibrations in the anionic hydrides are as strong as the C−O (N−O) stretches. In the *mer*-trihydrides, the trans M−H and C−O (N−O) vibrations are too close in frequency to assign without isotopic labeling. Their positions clearly change with different counterions as expected for the vibrations of ligands involved in ion-pairing interactions. However, further interpretation is difficult.

The single broad bands observed in the range 1500−1700 cm^{-1} are tentatively assigned to the asymmetric H−M−H vibration of the trans hydride ligands. These are of unusually low frequency for hydrides of these metals and are relatively insensitive to the nature of the cation. The trans arrangement of hydrides is less common than the cis arrangement. A recent example of the *cis*- and *trans*-IrH$_2$(CO)L complexes (L = C$_6$H$_3$(CH$_2$P^{i}Pr$_2$)$_2$) also demonstrated a low $\nu_{M-H} = 1746$ cm^{-1} in the trans dihydride isomer vs $\nu_{M-H} = 1965$ and 2066 cm^{-1} in the cis dihydride.[44] The lower ν_{M-H} is indicative of the longer M−H distances caused by the high trans influence of the hydride ligands. The spectra of the osmium complexes in Table 2 display an extra band in the region between 1742 and 1763 cm^{-1} which is sharper but of similar intensity to the low-frequency band at about 1690 cm^{-1}. This might be the symmetrical H−Os−H

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(42) Xu, W.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **1996**, *35*, 1549.

(43) Cooper, M. K.; Duckworth, P. A.; Henrick, K.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1981**, 2357.

(44) Rybtchinski, B.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786.

Table 3. Selected NMR Data for the *mer*- and *fac*- Trihydrides Q $[MH_3L(P^iPr_3)_2]$ (M = Os, Ru, L = CO and M = Re, L = NO)

	M	Q	solvent	δ MH; ^2J(H, H), ^2J(H, P)	δ MH$_2$; ^2J(H, P)	δ ^{31}P
mer-**1**	Ru	K(18-crown-6)$^+$	THF-d_8	−9.97; 6.5, 28.0	−9.10; 20.9	101.3
mer-**4**	Ru	K(1-aza-18-crown-6)$^+$	THF-d_8	−9.90; 6.3, 28.3	−9.15; 20.8	100.7
mer-**7**	Ru	K(2.2.2 crypt)$^+$	THF-d_8	−10.00; 6.6, 28.0	−9.10; 20.9	101.5
mer-**1**	Ru	K(18-crown-6)$^+$	tol-d_8	broad pattern between δ −8.7 and −9.1		99.0
mer-**4**	Ru	K(1-aza-18-crown-6)$^+$	tol-d_8	broad pattern between δ −8.7 and −9.1		99.1
mer-**7**	Ru	K(2.2.2 crypt)$^+$	tol-d_8	−9.24; 5.7, 28.4	−8.37; 20.8	101.5
fac-**1**	Ru	K(18-crown-6)$^+$	THF-d_8	−8.82; 6.4, 22.9	−10.71, m^a	77.3
fac-**4**	Ru	K(1-aza-18-crown-6)$^+$	THF-d_8	−8.63; 6.3, 23.0	−10.82, m^a	76.3
fac-**1**	Ru	K(18-crown-6)$^+$	tol-d_8	−8.38; 6.3, 22.8	−10.51, m^a	77.4
fac-**4**	Ru	K(1-aza-18-crown-6)$^+$	tol-d_8	−8.18; 6.3, 22.8	−10.65, m^a	76.4
mer-**2**	Os	K(18-crown-6)$^+$	THF-d_8	−11.56; 6.3, 25.5	−11.77; 17.1	61.3
mer-**5**	Os	K(1-aza-18-crown-6)$^+$	THF-d_8	−11.49; 6.2, 25.8	−11.75; 17.1	61.3
mer-**8**	Os	K(2.2.2 crypt)$^+$	THF-d_8	−11.61; 6.4, 25.4	−11.81; 17.1	59.7
mer-**2**	Os	K(18-crown-6)$^+$	tol-d_8	−10.61; 6.1, 27.3	−11.10; 17.0	59.7
mer-**5**	Os	K(1-aza-18-crown-6)$^+$	tol-d_8	−10.63; 6.1, 27.4	−11.15; 17.0	59.6
mer-**8**	Os	K(2.2.2 crypt)$^+$	tol-d_8	−10.78; 6.4, 26.3	−11.01; 16.9	61.8
fac-**2**	Os	K(18-crown-6)$^+$	THF-d_8	−10.74; 6.3, 21.4	−12.46; ± 26.5, ∓ 70.8^a	39.7
fac-**5**	Os	K(1-aza-18-crown-6)$^+$	THF-d_8	−10.55; 6.4, 21.3	−12.56; m^a	−
fac-**2**	Os	K(18-crown-6)$^+$	tol-d_8	−10.24; 6.3, 21.3	−12.25; ± 26.4, ∓ 70.3^a	39.9
fac-**5**	Os	K(1-aza-18-crown-6)$^+$	tol-d_8	−10.06; 6.4, 21.3	−12.36; m^a	38.7
mer-**3**	Re	K(18-crown-6)$^+$	THF-d_8	−8.15; 8.3, 33.5	−5.59; 16.4	66.7
mer-**6**	Re	K(1-aza-18-crown-6)$^+$	THF-d_8	−8.23; 8.2, 33.8	−5.60; 16.2	66.7
mer-**3**	Re	K(18-crown-6)$^+$	tol-d_8	−7.66; −^{b}, 36.1	−5.14; 16	65.5
mer-**6**	Re	K(1-aza-18-crown-6)$^+$	tol-d_8	−7.73; −^{b}	−5.17; −^{b}	66.5
fac-**3**	Re	K(18-crown-6)$^+$	tol-d_8	−5.98; 7.3, 31.2	−4.71, m^a	44.8
fac-**6**	Re	K(1-aza-18-crown-6)$^+$	tol-d_8	−5.84; 7.4, 31.0	−4.91, m^a	44.1

[a] BB′XX′ part of the ABB′XX′ spin system. [b] Not resolved.

Table 4. Isomers and Equilibrium Constants Observed in the ^{1}H NMR Spectra of the Trihydrides $Q[MH_3(CO)(P^iPr_3)_2]$ and $Q[ReH_3(NO)(P^iPr_3)_2]$

complex	solvent	K(2.2.2 crypt)$^+$	K(18-crown-6)$^+$	K(1-aza-18-crown-6)$^+$
$[RuH_3(CO)(P^iPr_3)_2]^-$	THF-d_8	*mer*	*mer*/*fac*, 8.8	*mer*/*fac*, 2.4
	tol-d_8	*mer*	*mer*/*fac*, 0.29	*mer*/*fac*, 0.10
$[OsH_3(CO)(P^iPr_3)_2]^-$	THF-d_8	*mer*	*mer*/*fac*, 23.6	*mer*/*fac*, 6.1
	tol-d_8	*mer*	*mer*/*fac*, 0.41	*mer*/*fac*, 0.17
$[ReH_3(NO)(P^iPr_3)_2]^-$	THF-d_8	−	*mer*	*mer*/*fac*, 23
	tol-d_8	−	*mer*/*fac*, 6.2	*mer*/*fac*, 2.6

vibration which is made infrared active by coupling to other Os−H or C−O modes.

Solution NMR Data. The trihydrides **1**−**3** and **7**−**8** in THF show NMR spectra consistent with the *mer* structure. In the hydride region, the ^{1}H spin system is of the AB_2X_2 type, i.e., a triplet of triplets and a triplet of doublets; the $^{31}P\{^1H\}$ resonance is a singlet. Chemical shifts and coupling constants are collected in Table 3.

The osmium hydride T_{1min} times were measured for the crypt salt **8** in THF-d_8 (300 MHz): 254 (OsH) and 305 ms (OsH$_2$). The hydride···hydride dipolar contribution to the T_{1min} can be evaluated as $1/0.254 - 1/0.305 = 0.66$ s^{-1}, and the H···H distance as $5.81 \cdot (0.66 \cdot 300)^{-1/6} = 2.41$ Å.[45] Assuming that the Os−H bond length is 1.65 Å, the H−Os−H angle is estimated to be 94°. If the *trans*-Os−H bonds were elongated, e.g., 1.70 Å, the calculated angle would decrease to 92°. Thus, the hydride and heavy atoms positions (X-ray above) consistently indicate that *mer*-$[OsH_3(CO)(P^iPr_3)_2]^-$ possesses an octahedral structure.

The [K(2.2.2 crypt)]$^+$ salts **7** and **8** are only marginally soluble (ca. 3 mmol/L) in toluene and these solutions also show exclusively the *mer*-$[MH_3(CO)(P^iPr_3)_2]^-$ structures (Tables 3 and 4). The undissolved material becomes partially solvated and forms a separate viscous, oily phase that can be dispersed by shaking but settles quickly; i.e., it is not miscible with toluene. ^{1}H and ^{31}P NMR spectra of the freshly dispersed sample show, in addition to the expected resonances, broad and systematically low-field-shifted ^{1}H and ^{31}P NMR resonances of the second phase belonging to the same (*mer*) structural form. The related [K(18-crown-6)]$^+$ and [K(1-aza-18-crown-6)]$^+$ salts are, by contrast, very soluble in aromatic hydrocarbons. This is an important observation plainly indicating that the solubility of salts in nonpolar solvents is greatly determined by ion-pairing. As predicted, a potassium cation encapsulated in a cryptand ligand cannot form tight ion pairs.

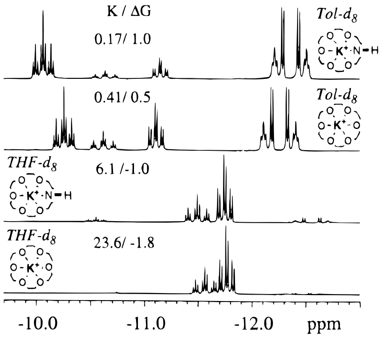

Figure 9. Solvent and counterion dependence of the hydride resonances of $[OsH_3(CO)(P^iPr_3)_2]^-$. Equilibrium constants K = *mer*-$[OsH_3(CO)(P^iPr_3)_2]^-$/*fac*-$[OsH_3(CO)(P^iPr_3)_2]^-$ and free energies, Δ*G* (kcal/mol), are given on the spectra.

In Figure 9 the ^{1}H NMR spectra of [K(18-crown-6)]-$[OsH_3(CO)(P^iPr_3)_2]$ and [K(1-aza-18-crown-6)]$[OsH_3(CO)(P^iPr_3)_2]$ show that ion-pairing results in isomerization and formation of *fac*-$[OsH_3(CO)(P^iPr_3)_2]^-$ and this becomes the major

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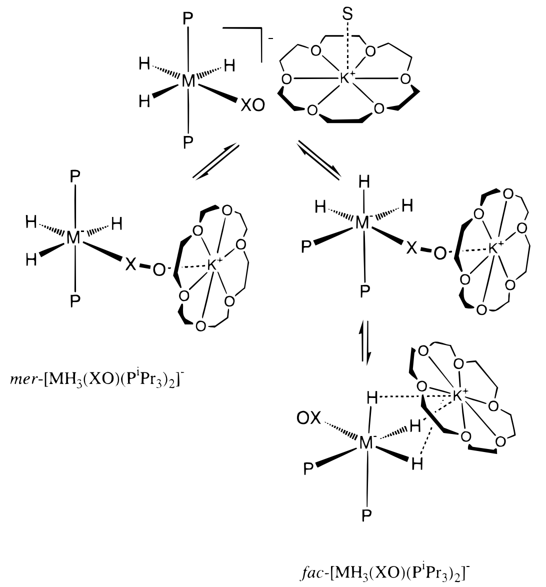
(45) Gusev, D. G.; Hübener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716 and references therein.

Scheme 1.



structural form in toluene. It is clearly distinguished by the ABB′XX′ pattern in the hydride region (Table 3). In polar THF the equilibrium strongly favors the *mer* isomer.

Scheme 1 gives an interpretation of the NMR observations. In THF solution the carbonyl−potassium interaction of the trihydrides Q[MH$_3$(CO)(P^{i}Pr$_3$)$_2$], Q$^+$ = [K(18-crown-6)]$^+$, and [K(1-aza-18-crown-6)]$^+$ may be weakened by coordination and solvation by THF (Scheme 1, top, S═THF). In toluene, which is less polar than THF, the *mer* form is predominantly paired (Scheme 1, left side) and the *fac* isomer apparently exists only in ion pairs (Scheme 1, right side).

The usual preference for the trans disposition of bulky P^{i}Pr$_3$ ligands should stabilize the *mer* over *fac* geometry. In the particular case of the trihydrides, the *mer* structure is probably destabilized by the trans hydrides.[46] If this is the case, the *fac* structure with all cis hydrides may approach the *mer* isomer in energy. Further stabilization in the *fac* form is certainly achieved by ion-pairing in solution, because it is favorably adapted for the strong facial coordination of the complex cation, as exemplified in Scheme 1.

Further insights are provided by comparison of the [K(1-aza-18-crown-6)]$^+$ and [K(18-crown-6)]$^+$ salts in Figure 9. The complex cation capable of hydrogen bonding substantially ($\Delta\Delta G$ = 0.5 to 0.8 kcal/mol, 293 K) increases the thermodynamic stability of the *fac* isomer. Variable temperature NMR studies of the salts in toluene show that the *mer* → *fac* isomerization is favored enthalpically by [K(1-aza-18-crown-6)]$^+$ vs [K(18-crown-6)]$^+$ ($\Delta H = -2.7$ vs -1.4 kcal/mol), while slightly disfavored entropically ($\Delta S = -5.5$ vs -3 eu). This can be attributed to a tighter pairing of [K(1-aza-18-crown-6)]$^+$ compared to [K(18-crown-6)]$^+$ because of H···H hydrogen bonding. There are only a few other examples[3,9,47] in which proton−hydride bonding influences the structure and reactivity of the hydride complex.

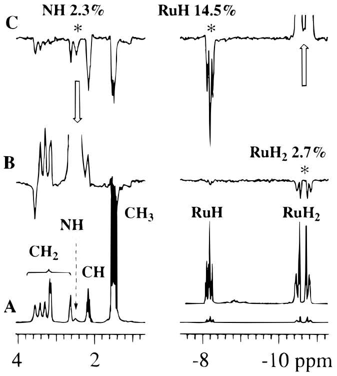


Figure 10. Regular ^{1}H (A) and difference ^{1}H NOE (B, C) spectra of [K(1-aza-18-crown-6)][*fac*-RuH$_3$(CO)(P^{i}Pr$_3$)$_2$] in toluene-d_8. The irradiated positions are indicated as well as the line assignment and observed enhancements. Low power was applied (DHP = 0, DLP = 1023). For the closely separated NH and CH lines ($\Delta\delta = 2.492-2.167 = 0.325$) the irradiation at δ 1.842 = 2.167−0.325 produced no enhancement in the difference spectrum.

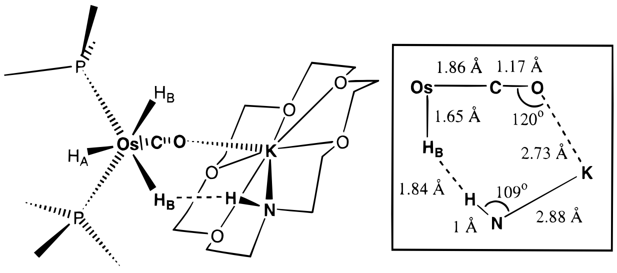


Figure 11. Selective K−O and H···H ion pairing interactions of [K(1-aza-18-crown-6)][*mer*-OsH$_3$(CO)(P^{i}Pr$_3$)$_2$] in nonpolar solvents

Similar trends were observed for all trihydrides Q[MH$_3$(CO)(P^{i}Pr$_3$)$_2$] and Q[ReH$_3$(NO)(P^{i}Pr$_3$)$_2$] of this work. A summary of the equilibrium data is given in Table 4. The tendency to adopt the *fac* structure increases in the order [ReH$_3$(NO)(P^{i}Pr$_3$)$_2$]$^-$ < [OsH$_3$(CO)(P^{i}Pr$_3$)$_2$]$^-$ < [RuH$_3$(CO)(P^{i}Pr$_3$)$_2$]$^-$. This order is expected to reflect a tighter ion-pairing and/or a smaller energy gap between the isomers.

The hydrogen-bonded *fac* isomers could not be characterized by X-ray and we sought additional solution NMR information to ascertain their structural features. The most stable *fac* compound in toluene is [K(1-aza-18-crown-6)][*fac*-RuH$_3$(CO)(P^{i}Pr$_3$)$_2$] (Figure 10, bottom) and so this was chosen for a difference nuclear Overhauser effect (NOE) experiment. The existence of direct dipolar interactions between the hydrides is clearly established in Figure 10. More important, irradiation of the NH signal resulted in the apparently preferential enhancement of the second-order RuH$_2$ resonance, indicating that these hydrogens are close in the ion-paired structure. In addition we note that the NH quintet at δ 0.92 in [K(1-aza-18-crown-6)]BPh$_4$ shifts to δ 2.19 in a solution of [K(1-aza-18-crown-6)][RuH$_3$(CO)(P^{i}Pr$_3$)$_2$]; it also broadens (width = 7.8 vs 4.2 Hz, all data in THF). This is typical of the ^{1}H NMR behavior of hydrogen-bonded NH protons.

A reasonable model for the *fac* trihydride paired with [K(1-aza-18-crown-6)]$^+$ can be assembled with the use of some distances provided by the structure of [K(1-aza-18-crown-6)][*mer*-OsH$_3$(CO)(P^{i}Pr$_3$)$_2$]. Figure 11 shows the cation coordinated to the carbonyl oxygen and forming a 1.8 Å H···H hydrogen bond to an adjacent hydride. The latter feature makes pairing of [K(1-aza-18-crown-6)]$^+$ tighter than that of [K(18-crown-6)]$^+$, increasing thermodynamic stability of the *fac* isomers in solution. The N−H hydrogen bond donor can bond to either of

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[46] A computational study with an appropriate model possessing small but good donor phosphines, e.g. [RuH$_3$(CO)(PMe$_3$)$_2$]$^-$, will be required to provide more quantitative data on the intrinsic electronic preferences in this system. It is unclear to what extent trans hydrides may be destabilizing, although it is commonly believed that they are.

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Table 5. Thermodynamic Data for Acid/Base Equilibria in THF

N	base[a]	conc., mmol/L	acid	conc., mmol/L	K	ΔpK_a
1	$[RuH_3(CO)(P^iPr_3)_2]^-$	38	$OsH_4(CO)(P^iPr_3)_2$	37	229	2.4
2	$[ReH_3(NO)(P^iPr_3)_2]^-$	38	$OsH_4(CO)(P^iPr_3)_2$	41	74	1.9

[a] As the $[K(18\text{-crown-}6)]^+$ salts

the two hydrides which are trans to phosphorus but cannot reach the hydride trans to carbonyl. This explains the preferential nuclear Overhauser enhancement of the second-order resonance of the hydrides trans to phosphorus.

Protonation of Anionic Hydrides. All of the anionic hydrides studied in this work are strong Brönsted bases. The conjugate acids, which are neutral complexes, can be obtained from the anionic hydrides by protonation with appropriate mild acids HX such as water or alcohols (eq 3).

$$Q[MH_{n-1}L_m] + HX \rightarrow MH_nL_m + QX \qquad (3)$$

This approach was applied in this work to prepare $Os(H_2)H_2(CO)(P^iPr_3)_2$[35] by reaction of its conjugate base anion with water. $OsH_6(P^iPr_3)_2$[48] and $RuH_6(P^iPr_3)_2$, a complex that is unstable with respect to H_2 loss and likely contains two dihydrogen ligands, were also prepared and isolated by similar protonation reactions of the anionic hydrides $[MH_5(P^iPr_3)_2]^-$.[34] The neutral osmium complexes can also be accessed by traditional "reduction" reactions with boro- and aluminohydrides,[48−50] whereas $Ru(H_2)_2(H)_2(P^iPr_3)_2$ was observed but not isolated previously.[37]

The relative basicity of the trihydridecarbonyl complexes has been determined in THF. This was done by reacting the dihydrogen complex $Os(H_2)H_2(CO)(P^iPr_3)_2$ with the anionic hydrides of Ru and Re and measuring the equilibrium constants by quantitative ^{31}P and ^1H NMR methods as reported in Table 5. A more extensive ranking of such acid−base equilibria will be reported elsewhere.[34] Therefore, the acidity of the conjugate dihydrogendihydride or tetrahydride complexes increases as $Ru(H_2)H_2(CO)(P^iPr_3)_2$ (ΔpK_a 2.4) < $Re(H)_4(NO)(P^iPr_3)_2$ (ΔpK_a 1.9) < $Os(H_2)H_2(CO)(P^iPr_3)_2$ (ΔpK_a 0). The anomalous ordering of the Ru complex being less acidic than the osmium complex was observed before in other comparable Ru vs Os dihydrogen complexes and was attributed to the stronger, shorter H−H bond in the Ru complex.[51] From other work we determined that the rhenium complex has the same pK_a as diphenylphosphine,[34] which is reported to have a pK_a in THF of 23.8 relative to 9-phenylfluorene at 18.5.[52]

Conclusions

Reaction of tertiary phosphine transition metal halides in THF under H_2 with KH in the presence of crown ethers serves as a high yield, convenient route to hydrido(tertiary phosphine)-metalates, including the new trihydrides $[MH_3(CO)(P^iPr_3)_2]^-$, M = Ru, Os and $[ReH_3(CO)(P^iPr_3)_2]^-$, and the known trihydride $[RuH_3(PPh_3)_3]^-$. This route in turn provides an efficient synthesis of neutral polyhydrides such as $Os(H_2)(H)_2(CO)(P^iPr_3)_2$. The *fac* isomers of the trihydride complexes are close in energy to the more stable *mer* structures that possess trans hydride ligands. Experiments, designed to compare the effects of the cations Q = $[K(2.2.2\text{-crypt})]^+$, $[K(18\text{-crown-}6)]^+$, and $[K(1\text{-aza-}18\text{-crown-}6)]^+$ on ion pairing, reveal that in solution the relative thermodynamic stability of the *fac* isomers is significantly enhanced on going from crypt to aza crown. The ion-paired $[K(1\text{-aza-}18\text{-crown-}6)][fac\text{-}MH_3L(P^iPr_3)_2]$ is further stabilized by inter-ion-pair M−H···H−N hydrogen bonding. This hydrogen bonding provides the first chain structure held together in the solid state by these unconventional hydrogen bonds.

Experimental Section

General. If not specified otherwise, all manipulations were carried out under N_2 with the use of standard Schlenk and glovebox techniques in dry, oxygen-free solvents. The inert-atmosphere glovebox was equipped with a vacuum line and a −30 °C refrigerator. All air- and moisture-sensitive solids were filtered in the glovebox using fritted funnels of which the part above the frit could be pressurized with a tightly inserted bulb or septum. ^1H NMR measurements were done at 300 MHz (Varian Gemini 300), and ^{13}C NMR spectra were recorded at 100.6 MHz (Varian Unity 400).

Equilibrium constants were determined by quantitative integration ^1H and (inverse-gated-decoupled) ^{31}P NMR (in nondeuterated THF when possible). T_1 measurements indicated that the ^{31}P T_1 times were in the range of 2−8 s for the complexes of this work. The recycling time (D1 + AT) was set to more than $3T_1$ in all ^1H measurements and when the ^{31}P T_1 was known, otherwise the time was set to 50 s.

P^iPr_3 was supplied by Organometallics, Inc., and KH, 18-crown-6, 1-aza-18-crown-6, 2.2.2 crypt, $o\text{-}C_6H_4(CH_2OH)_2$, and $RuCl_2(PPh_3)_3$ were supplied by Aldrich Chemical Co. $RuCl_3 \cdot nH_2O$ and $OsCl_3 \cdot nH_2O$ were obtained from Johnson Matthey, Inc. The compounds $MHCl(CO)(P^iPr_3)_2$, M = Ru, Os,[31] and $Re(H_2)Br_2(NO)(P^iPr_3)_2$,[32] were prepared according to literature procedures.

Microanalyses were performed under an inert atmosphere by the Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada. All samples were submitted in ampules sealed under N_2. For $[K(1\text{-aza-}18\text{-crown-}6)][BPh_4]$ and complexes **1**, **2**, **4**, and **6**, a second determination at a higher combustion temperature was requested with independently prepared and submitted samples (however, the sample was taken from the same bulk material as for the first determination). This was prompted by the systematic problem of substantially underestimated C%, although all H% and N% data were in very good agreement with the calculated values. We suspect that the low C% could result from the formation of metal carbides (upon thermal decomposition) and thus incomplete oxidation of carbon. Although the second determination did provide markedly improved C%, ruthenium complexes and $[K(1\text{-aza-}18\text{-crown-}6)]BPh_4$ remained low in carbon. The ^1H NMR measurements in all cases showed accurate integration.

$Q[RuH_3(CO)(P^iPr_3)_2]$, Q = $K(18\text{-crown-}6)^+$ (1), $K(1\text{-aza-}18\text{-crown-}6)^+$ (4), $K(2.2.2\ \text{crypt})^+$ (7). A typical preparation is described for **1**. THF (5 mL) was syringed against a flow of H_2 into a mixture of $RuHCl(CO)(P^iPr_3)_2$ (1.01 g, 2.08 mmol), KH (280 mg, 7 mmol), and 18-crown-6 (548 mg, 2.07 mmol). Stirring was continued for 1 h under H_2, then for 1 h under N_2. After the solids were filtered and washed with 1.5 mL of THF, the product was precipitated by addition of 13 mL of hexanes and the mixture was left at −30 °C for 20 h. The product was isolated by filtration, washed with 3 × 3 mL of hexanes, and dried in vacuo. Yield 1.1 g (71%). Anal. **1**. Calcd for $C_{31}H_{69}KO_7P_2Ru$: C, 49.25; H, 9.20. Found: C, 47.86; H, 9.18. **4**. Calcd for $C_{31}H_{70}KNO_6P_2Ru$: C, 49.32; H, 9.35; N, 1.86. Found: C, 46.72; H, 9.42; N, 1.80. **7**. Calcd for $C_{37}H_{81}KN_2O_7P_2Ru$: C, 51.19; H, 9.40; N, 3.23. Found: C, 48.34; H, 9.62; N, 3.10. The spectroscopic properties of these Ru(II) salts are listed below and in Tables 2 and 3.

$[K(18\text{-crown-}6)][$*mer*$\text{-}RuH_3(CO)(P^iPr_3)_2]$, *mer*-1. ^1H NMR (THF-d_8): δ −9.97 (tt, ^2J(H, P) = 28.0 Hz, ^2J(H, H) = 6.5 Hz, 1H, RuH); − 9.10 (td, ^2J(H, P) = 20.9 Hz, 2H, RuH); 1.22 (dt, ^3J(H, H) = 5.4 Hz, ^3J(H, P) = 13.5 Hz, 36H, CH_3); 1.83 (m, 6H, CH); 3.64 (s, 24 H,

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CH$_2$). ^{31}P NMR (THF-d_8): δ 101.3. ^{13}C NMR (THF-d_8): δ 21.62 (s, CH$_3$); 29.53 (virtual t, CH); 71.20 (s, CH$_2$); 214.77 (t, ^2J(C, P) = 11 Hz, CO).

[K(18-crown-6)][*fac*-RuH$_3$(CO)(P^{i}Pr$_3$)$_2$], *fac*-1. ^{1}H NMR (tol-d_8): δ −10.51 (m, 2H, RuH); −8.38 (tt, ^2J(H, P) = 22.8 Hz, ^2J(H, H) = 6.3 Hz, 1H, RuH); 1.50 and 1.55 (dd, ^3J(H, P) = 11.4 Hz, ^3J(H, H) = 7 Hz, 36H, CH$_3$); 2.23 (ds, ^3J(H, H) = ^2J(H, P) = 7 Hz, 6H, CH); 3.33 (s, 24H, CH$_2$). ^{31}P NMR (tol-d_8): δ 77.4. ^{13}C NMR (tol-d_8): δ 21.53 (s, CH$_3$); 29.98 (m, CH); 70.15 (s, CH$_2$); 213.98 (br. s, width = 15 Hz, CO).

Q[OsH$_3$(CO)(P^{i}Pr$_3$)$_2$], Q = K(18-crown-6)$^+$ (2), K(1-aza-18-crown-6)$^+$ (5), K(2.2.2 crypt)$^+$ (8). A typical preparation is described for **2**. THF (5 mL) was syringed against a flow of H$_2$ into a mixture of OsHCl(CO)(P^{i}Pr$_3$)$_2$ (645 mg, 1.12 mmol), KH (210 mg, 5.24 mmol) and 18-crown-6 (295 mg, 1.12 mmol). This was stirred for 0.5 h under H$_2$ and then for 1 h under N$_2$. After the solids were filtered and washed with 1.5 mL of THF, the product was precipitated by addition of 13 mL of hexanes. It was isolated by filtration, washed with 3 × 3 mL of hexanes, and dried in vacuo. Yield 882 mg (93%). Anal. **2**. Calcd for C$_{31}$H$_{69}$KO$_7$P$_2$Os: C, 44.06; H 8.23. Found: C, 44.45; H 8.49. **5**. Calcd for C$_{31}$H$_{70}$KNO$_6$P$_2$Os: C, 44.11; H, 8.36; N, 1.66. Found: C, 44.13; H, 8.66; N, 1.65. **8**. Calcd for C$_{37}$H$_{81}$KN$_2$O$_7$P$_2$Os: C, 46.42; H, 8.53; N, 2.93. Found: C, 46.16; H, 8.28; N, 2.90. The spectroscopic properties for the osmium salts are listed below and in Tables 2 and 3.

[K(18-crown-6)][*mer*-OsH$_3$(CO)(P^{i}Pr$_3$)$_2$], *mer*-2. ^{1}H NMR (tol-d_8): δ − 11.10 (td, ^2J(H, P) = 17 Hz, ^2J(H, H) = 6.1 Hz, 2H, OsH); −10.61 (tt, ^2J(H, P) = 27.3 Hz, 1H, OsH); 1.56 (m, 36H, CH$_3$); 2.24 (m, 6H, CH). ^{31}P NMR (tol-d_8): δ 59.7. ^{13}C NMR (THF-d_8): δ 22.04 (s, CH$_3$); 30.05 (virtual t, CH); 71.14 (s, CH$_2$); 197.84 (br, width = 20 Hz, CO).

[K(18-crown-6)][*fac*-OsH$_3$(CO)(P^{i}Pr$_3$)$_2$], *fac*-2. ^{1}H NMR (tol-d_8): δ −12.25 (m, ^2J(H, P) = ±70.3 Hz, m 26.4 Hz, 2H, OsH); −10.24 (tt, ^2J(H, P) = 21.3 Hz, ^2J(H, H) = 6.3 Hz, 1H, OsH); 1.52 and 1.46 (dd, ^3J(H, P) = 11.2 Hz, ^3J(H, H) = 7.2 Hz, 36H, CH$_3$); 2.23 (ds, ^3J(H, H) = ^2J(H, P) = 7.2 Hz, 6H, CH). ^{31}P NMR (tol-d_8): δ 39.9.

[K(2.2.2 crypt)][*mer*-OsH$_3$(CO)(P^{i}Pr$_3$)$_2$], *mer*-8. ^{1}H T_1 (300 MHz, THF-d_8, ms): OsH/OsH$_2$ 536/686 (−10 °C), 356/460 (−30 °C), 259/327 (−50 °C), 254/315 (−60 °C), 258/305 (−70 °C).

[K(1-aza-18-crown-6)][*mer*-OsH$_3$(CO)(P^{i}Pr$_3$)$_2$], *mer*-5. ^{1}H T_1 (THF-d_8, ms): OsH/OsH$_2$ 276/4348 (−40 °C), 252/319 (−50 °C), 248/301 (−60 °C).

[K(1-aza-18-crown-6)][*fac*-OsH$_3$(CO)(P^{i}Pr$_3$)$_2$], *fac*-5. ^{1}H T_1 (300 MHz, THF-d_8, ms): OsH/OsH$_2$ 203/237 (−40 °C), 187/210 (−50 °C), 211/229 (−60 °C).

OsH$_4$(CO)(P^{i}Pr$_3$)$_2$. [K(18-crown-6)][OsH$_3$(CO)(P^{i}Pr$_3$)$_2$] (300 mg, 0.36 mmol) was treated with 1.5 mL of water, and the product was washed with 3 × 1.5 mL of water; the washings were then removed with a pipet. The residue was dried under vacuum to give 112 mg (58%) of a white solid. Product identity was established by a comparison to the literature NMR data.[49]

Q[ReH$_3$(NO)(P^{i}Pr$_3$)$_2$], Q = K(18-crown-6)$^+$ (3), K(1-aza-18-crown-6)$^+$ (6). A typical preparation is described for **6**. THF (3 mL) was syringed against a flow of H$_2$ to a mixture of Re(H$_2$)Br$_2$(NO)(P^{i}Pr$_3$)$_2$ (250 mg, 0.36 mmol), KH (90 mg, 2.24 mmol), and 1-aza-18-crown-6 (113 mg, 0.43 mmol). Stirring was continued for 15 min at room temperature, then for 1.5 h at 40 °C. After the solids were filtered and washed with 1.5 mL of THF, the product was precipitated by addition of 16 mL of hexanes and left at −30 °C overnight. The product was isolated by filtration, washed with 3 × 1.5 mL of hexanes, and dried in vacuo. Yield 236 mg (78%). Anal. **3**. Calcd for C$_{30}$H$_{69}$KNO$_7$P$_2$Re: C, 42.74; H, 8.25; N, 1.66. Found: C, 42.47; H, 8.15; N, 1.65. **6**. Calcd for C$_{30}$H$_{70}$KN$_2$O$_6$P$_2$Re: C, 42.79; H, 8.38; N, 3.33. Found: C, 43.00; H, 8.50; N, 3.26. Spectroscopic properties of the crown and aza-crown (**mer-6, fac-6**) salts are listed in Tables 2 and 3. More properties of the crown salts are listed below.

[K(18-crown-6)][*mer*-ReH$_3$(NO)(P^{i}Pr$_3$)$_2$], *mer*-3. ^{1}H NMR (THF-d_8): δ −8.15 (tt, ^2J(H, P) = 33.5 Hz, ^2J(H, H) = 8.3 Hz, 1H, ReH); − 5.59 (td, ^2J(H, P) = 16.4 Hz, 2H, ReH); 1.23 (dt, ^3J(H, H) = 5.1 Hz, ^3J(H, P) = 13.9 Hz, 36H, CH$_3$); 2.01 (m, 6H, CH); 3.61 (s, 24 H, CH$_2$). ^{31}P NMR (THF-d_8): δ 66.7.

Table 6. Summary of Crystal Data, Details of Intensity Collection and Least-Squares Refinement Parameters for **2** and **5**

	2	**5**
empirical formula	C$_{31}$H$_{69}$KO$_7$OsP$_2$	C$_{31}$H$_{70}$KNO$_6$OsP$_2$
M_r	845.10	844.12
crystal size, mm	0.45 × 0.35 × 0.30	0.53 × 0.43 × 0.33
crystal class	monoclinic	monoclinic
space group	*Cc*	$P2_1/n$
temperature, K	173(2)	173(2)
a, Å	47.790(7)	11.595(3)
b, Å	11.517(2)	21.667(4)
c, Å	21.428(4)	16.676(3)
β, °	92.54(1)	104.61(2)
V, A^3	11782(3)	4054.2(14)
Z	12	4
D_{calc} g cm^{-3}	1.429	1.383
μ(MoKα), cm^{-1}	34.73	33.63
F(000)	5232	1744
ω scan width, °	0.67	0.62
range θ collected, °	2.04 to 27.00	2.52 to 30.00
independent reflections	12838	11662
no. observed data [$I > 2\sigma(I)$]	10394	8646
R_1 [$I > 2\sigma(I)$]^a	0.0560	0.0323
wR_2 (all data)	0.1367	0.0756
goodness of fit	1.035	0.951
parameters refined	1145	403
maximum peak in final ΔF map, eÅ^{-3}	3.505	0.835

^{a} Definition of R indices: $R_1 = \sum(F_o - F_c)/\sum(F_o)$; w$R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

[K(18-crown-6)][*fac*-ReH$_3$(NO)(P^{i}Pr$_3$)$_2$], *fac*-3. ^{1}H NMR (tol-d_8): δ −5.98 (tt, ^2J(H, P) = 31.2 Hz, ^2J(H, H) = 7.3 Hz, 1H, ReH); −4.71 (m, 2H, ReH); 1.45 and 1.53 (dd, ^3J(H, P) = 11.4 Hz, ^3J(H, H) = 7.1 Hz, 36H, CH$_3$); ca. 2.4 (m, overlapped with the CH resonance of the *mer*-isomer, 6H, CH); 3.28 (s, 24H, CH$_2$). ^{31}P NMR (tol-d_8): δ 44.8.

[K(18-crown-6)][RuH$_3$(PPh$_3$)$_3$]. A mixture of RuCl$_2$(PPh$_3$)$_3$ (800 mg, 0.83 mmol), KH (159 mg, 3.96 mmol), and 18-crown-6 (221 mg, 0.84 mmol) was stirred in 5 mL of THF for 2 h at 70 °C under H$_2$. The solids were filtered and washed with 2 × 1.5 mL of THF. The filtrate was not used in further isolation because it was substantially contaminated with a THF-soluble impurity (this impurity may originate from the [RuCl$_2$(PPh$_2$)$_2$]$_2$ dimer that forms on dissolving of RuCl$_2$(PPh$_3$)$_3$).[53] The solid was extracted with 35 mL of THF, and the resulting solution afforded a yellow precipitate after hexanes (80 mL) were added and the solution was left to stand at −30 °C overnight. The solution was filtered and washed with 3 × 6 mL of hexanes; yield 703 mg (71%). Product identity was established by a comparison to the literature NMR data.[20]

[HNEt$_3$][BPh$_4$]. NEt$_3$ (100 mg, 1 mmol) and CF$_3$COOH (225 mg, 2 mmol) were added to 1.5 mL of ethanol and mixed with another solution containing NaBPh$_4$ (338 mg; 1 mmol) in 3 mL of ethanol, affording a precipitate. The precipitate was separated by filtration, washed with 4 × 2 mL ethanol, and dried in vacuo, giving the product in 82% yield (340 mg). Anal. Calcd for C$_{30}$H$_{36}$BN: C, 85.50; H, 8.61; N, 3.32. Found: C, 85.57; H, 8.67; N, 3.28.

[K(1-aza-18-crown-6)][BPh$_4$]. [HNEt$_3$][BPh$_4$] (80 mg, 0.19 mmol) was added to a suspension containing KH (30 mg, 0.75 mmol) and 1-aza-18-crown-6 (50 mg, 0.19 mmol) in 3 mL of THF and the mixture was stirred for 0.5 h. The resulting suspension was filtered. Addition of hexanes (12 mL) afforded a precipitate that was separated by filtration, washed with 3 × 1.5 mL hexane, and dried in vacuo giving the product in 80% yield (95 mg). ^{1}H NMR (THF): δ 0.92 (qi, ^3J(H,H) = 8 Hz, NH), 2.63 (m, 4H, CH), 3.34 (m, 4H, CH), 3.49 (s, 16H, CH), 6.71, 6.87, 7.28 (m, 20H, BPh$_4$). Anal. Calcd for C$_{36}$H$_{45}$BNO$_5$: C, 74.22; H, 7.79; N, 2.40. Found: C, 70.22; H, 7.80; N, 2.21.

Crystal Structures. The complexes [K(18-crown-6)][OsH$_3$(CO)(P^{i}Pr$_3$)$_2$] **2** and [K(1-aza-18-crown-6)][OsH$_3$(CO)(P^{i}Pr$_3$)$_2$] **5** were crystallized in 5 mm NMR tubes from solutions of ca. 12 mg in THF layered with hexanes.

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A summary of selected crystallographic data are given in Table 6. Data for both compounds were collected on an Siemens P4 diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The intensities of three standard reflections measured every 97 reflections showed no decay. The data were corrected for Lorentz and polarization effects and absorption (semiempirical corrections from psi-scans).[54] Minimum and maximum absorption corrections were 0.4278 and 0.8259 for **2** and 0.3218 and 0.7809 for **5**.

The structures were solved and refined using the SHELXTL\PC[54] package. Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0305P)^2]$ for **5** and $1/[\sigma^2(F_o^2)+(0.0508P)^2+176.7P]$ for **2** where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms. In **2** there are three independent molecules in the asymmetric unit. None of the hydride atoms was located. In **2** the top three peaks in the final difference Fourier, which are greater than 3.0 eÅ^3 are within 1.0 Å of each of the three Os atoms; these are chemically unreasonable positions for hydrides. In **5** the hydride atoms in the equatorial plane of the Os, which are cis to the −C═O, group, were refined with isotropic thermal parameters. The hydride atom trans to the −C═O group is most likely disordered, corresponding to the disorder of the −C═O group itself (with occupancies of 0.38 for **5** and 0.62 for **5***), and was not located.

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Supporting Information Available: X-ray crystallographic tables for complexes **2** and **5** (21 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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