dependence of rate on temperature $E_{act} < 2$ kcal/M. These results provide an interesting comparison with studies of hopping charge transport in molecularly doped Lexan.[31] In such studies where $\Delta G \geq 0.01$ V due to the electric field gradient, $E_{act} \geq 10$ kcal/M.

However, when all three of the reactions mentioned above were compared at room temperature and 77 K, a significant temperature dependence is observed, which is larger than expected from simple Marcus theory. We believe these lower reaction rates reflect the slow dielectric response of the β relaxation at low temperature, which may lead to a change in the effective frequency factor for reaction.[4,31]

Summary. We have observed long distance nonadiabatic electron (hole) transfer for the reactions $(Ru(LL)_3^{2+*} +$ organic reductants in rigid polycarbonate medium. The transfer distances appear to be larger than in the $Ru(LL)_3^{2+*}/MV^{+2}$ oxidative quenching reactions observed in rigid glycerol.[3a] The reactions in polycarbonate appear to be more accurately described by the superexchange mechanism, with the primary reaction path being hole transfer from the $Ru(LL)_3^{2+*}$ to the organic reductant mediated through positive solvent states. In the superexchange mechanism, the electronic damping factor α is proportional to ln V, where V is the hole binding energy of the Ru complexes. This mechanism gives more satisfactory results than conventional electron tunnelling theories, which predict $\alpha \propto V^{1/2}$, where V is the ionization energy of the organic reductant.

The temperature of these reactions in Lexan show predicted behavior from ~ 300 to 350 K. However, at low temperatures, these reactions tend to show "solvent controlled" rates which are a function of the dielectric response of the medium. This behavior has been observed in other systems.[4]

(31) Stolka, M.; Yanus, J.; Pai, D. *J. Phys. Chem.* **1984**, *88*, 4707.
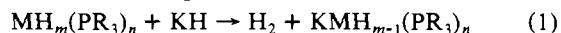
A Lipophilic Salt of a Transition-Metal Polyhydride: KOsH₃(PMe₂Ph)₃

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Abstract: The polyhydride OsH_4P_3 (P = PMe₂Ph) is deprotonated by KH in THF to yield K(fac-OsH₃P₃), characterized by ¹H and ³¹P NMR spectroscopy. This reaction also proceeds in aromatic solvents, and the ether-free product is soluble in benzene and toluene. Spectral properties in toluene are similar to those in THF but reveal subtle differences. The crystal structure of KOsH₃(PMe₂Ph)₃, crystallized from toluene, reveals the reason for the lipophilic character of this material. It consists of centrosymmetric $K_2Os_2H_6(PMe_2Ph)_6$ dimers composed of $(PhMe_2P)_3Os(\mu-H)_3K$ monomers (an intimate ion pair) bound into dimers by one additional hydride bridge from each K to one hydride hydrogen in the second monomer unit. Equally important to the dimerization is the enfolding of each K^+ by two phenyl rings of the second monomer unit with the result that the periphery of the molecule is entirely hydrocarbon in character. The hard acid/soft base character of the K^+/phenyl interaction is particularly surprising. Crystal data for KOsH₃(PMe₂Ph)₃ (at −160 °C) are the following: $a = 9.990$ (2) Å, $b = 22.867$ (8) Å, $c = 12.381$ (3) Å, $\beta = 111.44$ (1)° with $z = 4$ in space group $P2_1/n$.

In the course of studying the synthesis of *anionic* transition-metal polyhydride complexes by the deprotonation of neutral polyhydrides[1] with KH (eq 1), we have been accustomed to employing tetrahydrofuran as solvent, both to promote this polar

$$MH_m(PR_3)_n + KH \rightarrow H_2 + KMH_{m-1}(PR_3)_n \qquad (1)$$

reaction and also because we expected the polyhydride anion salt to be soluble in this solvent. While these expectations are born out for $OsH_4(PMe_2Ph)_3$ as the conjugate acid in eq 1, we were most surprised to find that this proton transfer also proceeds in toluene solvent *and* that the product has good solubility in this medium. We describe here the full characterization of KOsH₃(PMe₂Ph)₃ and the explanation of how such a material can achieve solubility in aromatic hydrocarbons. At the same time, this work provides a rare structural view of the manner in which contact ion pairs aggregate to larger units.

Experimental Section

General. All manipulations were carried out in an atmosphere of prepurified N₂ (BASF R-311 purification bed) with solvents dried over benzophenone ketyl (THF) or liquid NaK alloy (arenes). In order to avoid protonation of the very basic anion, glassware should be flamed under vacuum. Reliable spectroscopic measurements are best done in NMR tubes which have been prerinsed with a sacrificial charge of KOsH₃(PMe₂Ph)₃ solution. Alternatively, since the $OsH_3P_3^-/OsH_4P_3$ equilibrium is reversible, this conjugate pair in the presence of excess KH may be used to scavenge surface bound protons. ³¹P chemical shifts *downfield* of the 85% H₃PO₄ reference signal are given *positive* values.

K[fac-OsH₃(PMe₂Ph)₃]. To a THF solution of OsH₄(PMe₂Ph)₃ in an NMR tube was added a threefold excess KH powder (prepared from a 35% dispersion of KH in mineral oil by the procedure described in the literature),[2] and the solution was heated in a 70 °C oil bath for 12 h. ³¹P and ¹H (when reaction was done in THF-d_8) NMR spectra showed quantitative conversion to yellow K[fac-OsH₃(PMe₂Ph)₃]. The excess KH was easily removed by filtration; however, in the absence of KH, the product slowly transforms to OsH₄(PMe₂Ph)₃ on standing even in oven-dried glassware. Addition of H₂O to a THF solution of K[OsH₃-(PMe₂Ph)₃] gave immediate quantitative (³¹P NMR) conversion to OsH₄(PMe₂Ph)₃. The product also reacts rapidly with acetonitrile-d_3 to generate OsH$_x$D$_{4-x}$(PMe₂Ph)₃. NMR data for K[fac-OsH₃(PMe₂Ph)₃] follow: in tetrahydrofuran-d_8, ³¹P{¹H} NMR (30 °C) δ −30.1 (s), ¹H NMR (220 MHz, 16 °C) δ 7.89 (t, $J = 7$ Hz, 6 H, o-C₆H₅), 7.20 (m, 9 H, m- and p-C₆H₅), 1.54 ($J = 6$ Hz, 18 H, P–CH₃), −11.60 (m, 3 H, Os–H); in toluene-d_8 H 7.69 (br), 7.2 (br), 1.79 (br), −11.88 (m), ³¹P −32.5.

(1) Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8310.

(2) Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organometal. Chem.* **1978**, *154*, 337.

Table I. Crystal Data for KOsH$_3$(PMe$_2$Ph)$_3$

empirical formula	C$_{24}$H$_{33}$P$_3$KOs
color	yellow
crystal dimensions, mm	0.06 × 0.07 × 0.09
space group	$P2_1/n$
cell dimensions (at −160 °C; 34 reflections)	
a, Å	9.990 (2)
b, Å	22.867 (8)
c, Å	12.381 (3)
β, deg	111.44 (1)
molecules/cell	4
volume, Å^3	2632.55
calcd density, g/cm^3	1.632
wavelength, Å	0.71069
molecular weight	646.77
linear absorption coeff, cm^{-1}	51.952
max absorption	0.4300
min absorption	0.55
no. of unique intensities	6059
no. with $F > 3.00\sigma(F)$	5413
final residuals	
$R(F)$	0.0318
$R_w(F)$	0.0346
goodness of fit for the last cycle	0.81
max Δ/σ for last cycle	0.05

Table II. Fractional Coordinates and Isotropic Thermal Parameters for KH$_3$Os(PMe$_2$Ph)$_3$

	10^4x	10^4y	10^4z	$10B_{iso}$[b]
Os(1)	3934.9 (2)	1046.1 (1)	8270.3 (1)	8
K(2)	6087 (1)	706.4 (4)	1032 (1)	13
P(3)	1544 (1)	841 (1)	7672 (1)	11
P(4)	4580 (1)	654.9 (5)	6836 (1)	10
P(5)	3777 (1)	1992.2 (5)	7678 (1)	10
C(6)	515 (6)	1309 (2)	8307 (5)	19
C(7)	292 (6)	880 (3)	6149 (5)	22
C(8)	1005 (5)	119 (2)	8061 (4)	15
C(9)	365 (6)	−323 (2)	7256 (6)	23
C(10)	67 (7)	−869 (3)	7632 (7)	30
C(11)	418 (7)	−987 (3)	8786 (7)	29
C(12)	1053 (7)	−558 (3)	9589 (6)	27
C(13)	1363 (6)	−15 (2)	9237 (5)	18
C(14)	6378 (6)	814 (2)	6835 (5)	18
C(15)	3561 (6)	803 (2)	5285 (4)	18
C(16)	4635 (5)	9851 (2)	6812 (4)	13
C(17)	3401 (5)	9522 (2)	6206 (4)	14
C(18)	3403 (6)	−1083 (2)	6255 (5)	17
C(19)	4641 (6)	−1381 (2)	6915 (5)	19
C(20)	5884 (6)	−1070 (2)	7514 (5)	18
C(21)	5884 (5)	−463 (2)	7462 (4)	16
C(22)	2227 (6)	2293 (3)	6480 (5)	20
C(23)	3866 (6)	2555 (2)	8767 (5)	16
C(24)	5244 (5)	2250 (2)	7224 (4)	13
C(25)	5065 (5)	2358 (2)	6061 (4)	15
C(26)	6238 (6)	2484 (2)	5756 (5)	17
C(27)	7601 (6)	2523 (2)	6589 (5)	19
C(28)	7794 (5)	2423 (2)	7751 (5)	18
C(29)	6635 (5)	2286 (2)	8054 (4)	17
H(1)[a]	426 (9)	38 (4)	−112 (7)	30 (16)
H(2)	873 (9)	378 (4)	452 (7)	27 (15)
H(3)	49 (22)	360 (10)	383 (18)	71 (44)

[a] Fractional coordinates for hydrogen atoms are ×10^3. [b] Isotropic values for those atoms refined anisotropically are calculated with the formula given by Hamilton (Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609).

Crystal Structure. A nearly equidimensional crystal grown by slow cooling of a toluene solution was transferred to the goniostat with standard inert atmosphere handling techniques.[3] The sample was cooled to −160 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima which were indexable as monoclinic in the unique space group $P2_1/n$ (alternate setting of $P2_1/c$). Data were collected (graphite monochromator, −160 °C, 6° ≤ 2θ ≤ 55°) in the usual manner and

(3) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.
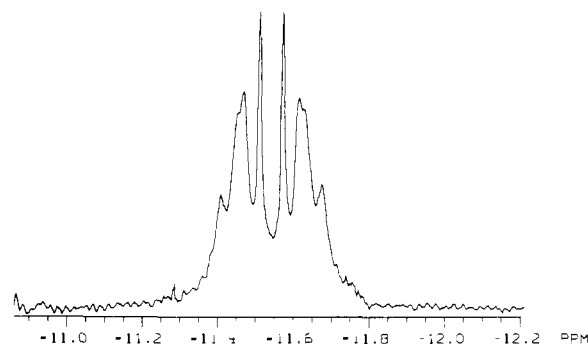
Figure 1. Hydride ^{1}H NMR (360 MHz) resonance of KOsH$_3$(PMe$_2$Ph)$_3$ in THF-d_8.
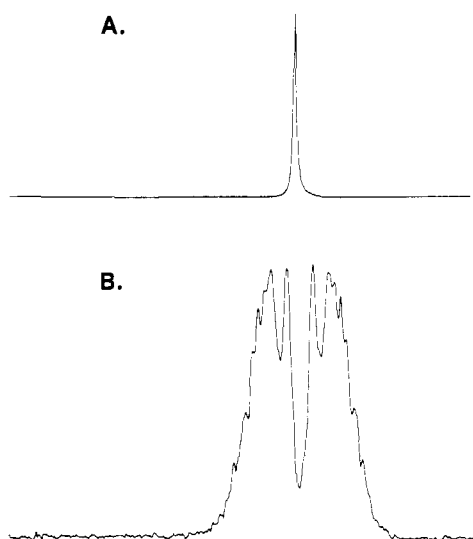
Figure 2. (A) ^{31}P{^{1}H} NMR spectrum (40.5 MHz) of KOsH$_3$(PMe$_2$Ph)$_3$ in THF-d_8. (B) Same as part A with selective coupling to only the hydride hydrogens.

corrected for Lorentz, polarization, background, and absorption. It should be noted that, while the crystal faces were poorly defined and the absorption correction is therefore an approximation, a definite improvement was seen in the agreement between equivalent data after correction. Parameters of the data collection and subsequent refinement are given in Table I.

The structure was solved by direct methods (MULTAN78) and Fourier techniques and refined by blocked full-matrix least-squares methods for $F > 3\sigma(F)$. All hydrogen atoms were located and refined. The difference Fourier used to locate the hydride hydrogens contained one peak (1.3 e/Å^3) at the Os position and three other peaks (1.1, 1.0, and 0.9 e/Å) within 1.0 Å of the Os. The next four peaks in the map included one near the K$^+$ as well as the three positions reported for H(1)–H(3). A final difference map was featureless, with the largest peak being at the Os position (1.2 e/Å^3).

The results of the structural study are shown in Tables II and III, as well as the figures. Additional data are available as Supplementary Material. Hydrogens in the phosphine ligands show C–H distances ranging from 0.82 (5) to 1.08 (7) Å.

Results

Synthesis and Characterization. The utility of KH in ether solvents for deprotonation of boron hydrides[4] and metal carbonyl hydride clusters[5] to form the anionic conjugate base has been described by the Shore group. We find that OsH$_4$P$_3$ (P ≡ PMe$_2$Ph) reacts with KH[6a] in tetrahydrofuran at 70 °C to quantitatively yield only the *fac* isomer of OsH$_3$P$_3^-$ (eq 2).

$$\text{OsH}_4\text{P}_3 + \text{KH} \rightarrow \text{K}[fac\text{-OsH}_3\text{P}_3)] + \text{H}_2 \qquad (2)$$
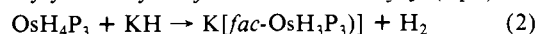
(4) Shore, S. G. *Pure Appl. Chem.* **1977**, *49*, 717.
(5) Inkrott, K. E.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 2817.
(6) (a) A substantial excess of KH is desireable in order to increase the rate of this heterogeneous reaction. (b) Potassium encapsulation by oxygen of coordinated phosphite has precedent: Burch, R. R.; Muetterties, E. L.; Thompson, M. R.; Day, V. W. *Organometallics* **1983**, *2*, 474.

KOsH₃(PMe₂Ph)₃

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Table III. Selected Bond Distances (Å) and Angles (deg) for KOsH₃(PMe₂Ph)₃

Os	H(1)	1.68 (8)	K	H1′	2.52
Os	H(2)	1.69 (7)	K	H1	2.73
Os	H(3)	1.66 (12)	K	H2	2.68
Os	P(3)	2.2756 (13)	K	H3	3.02
Os	P(4)	2.2816 (12)	K′	C8	3.297
Os	P(5)	2.2710 (13)	K′	C9	3.512
P(3)	C(6)	1.847 (5)	K′	C10	3.603
P(3)	C(7)	1.845 (6)	K′	C11	3.474
P(3)	C(8)	1.854 (5)	K′	C12	3.236
P(4)	C(14)	1.832 (5)	K′	C13	3.118
P(4)	C(15)	1.847 (5)	K′	C16	3.269
P(4)	C(16)	1.839 (5)	K′	C17	3.310
P(5)	C(22)	1.842 (6)	K′	C18	3.322
P(5)	C(23)	1.842 (5)	K′	C19	3.275
P(5)	C(24)	1.848 (5)	K′	C20	3.226
Os	K	3.397	K′	C21	3.217
Os	K′	4.10	K	K′	4.198

P(3)	Os	P(4)	103.14 (5)
P(3)	Os	P(5)	98.65 (4)
P(4)	Os	P(5)	97.38 (4)
P(5)	Os	K	119.10 (5)
P(3)	Os	K	118.90 (4)
P(4)	Os	K	116.02 (5)
H(3)	Os	K	63 (4)
H(1)	Os	K	58 (4)
H(2)	Os	K	51 (4)
Os	H1	K′	156 (5)
Os	P(3)	C(6)	115.02 (18)
Os	P(3)	C(7)	124.16 (18)
Os	P(3)	C(8)	117.96 (15)
Os	P(4)	C(14)	118.57 (18)
Os	P(4)	C(15)	122.13 (18)
Os	P(4)	C(16)	115.04 (14)
Os	P(5)	C(22)	123.70 (19)
Os	P(5)	C(23)	116.77 (18)
Os	P(5)	C(24)	115.63 (14)
P(3)	Os	H(1)	88.0 (26)
P(3)	Os	H(2)	83.1 (25)
P(3)	Os	H(3)	161 (4)
P(4)	Os	H(1)	86.0 (27)
P(4)	Os	H(2)	166.6 (25)
P(4)	Os	H(3)	92 (4)
P(5)	Os	H(1)	171.6 (26)
P(5)	Os	H(2)	93.3 (26)
P(5)	Os	H(3)	67 (4)
H(1)	Os	H(2)	82 (4)
H(1)	Os	H(3)	105 (5)
H(2)	Os	H(3)	85 (5)

Figure 3. ORTEP drawing of the [KOsH₃(PMe₂Ph)₃]₂ dimer viewed along the edge of the K₂Os₂ plane. Hydrogens on carbon have been omitted for clarity. Hydrides are open circles, cabons are open ellipses, and bonds to potassium are shown as single lines. The center of symmetry midway between the two K⁺ ions generates the second (primed) half of the dimer.

Figure 4. View perpendicular to the K₂Os₂ plane, showing the *fac*-H₃P₃ coordination of osmium and the three coordination of H1. Carbons enfolding K′ are labeled.

Consistent with the claim of *fac* geometry, the anion shows only one methyl resonance (a doublet, indicating an absence of virtual coupling and therefore cis phosphine stereochemistry), a ³¹P{¹H} singlet, and one hydride chemical shift; threefold symmetry is required by these data. The hydride resonance in the ¹H NMR (Figure 1) and the ³¹P NMR signal with selective coupling to the hydride ligands (Figure 2) both show the distinctive mirror-symmetric patterns characteristic of AA′A″ XX′X″ spin system of a *fac*-OsH₃P₃ octahedron. The hydride multiplet structure is virtually indentical with that of the isoelectronic and isostructural *fac*-IrH₃(PEt₂Ph)₃.[7] The osmium compound is exceptionally sensitive to proton sources, which act to cleanly regenerate OsH₄P₃.

Remarkably, if the above reaction is carried out with toluene as solvent, the deprotonation again occurs to give a soluble product, as evidenced by the growth of product resonances in both ¹H and ³¹P NMR spectra. The proton chemical shifts of K[OsH₃-(PMe₂Ph)₃] agree to within 0.3 ppm between THF-*d₈* and toluene-*d₈* solvent media. The only noteworthy point is that, relative to OsH₄(PMe₂Ph)₃, the salt has methyl resonances shifted upfield in THF but downfield in toluene. Particularly provocative is the fact that an alkali metal compound devoid of Lewis base ligands
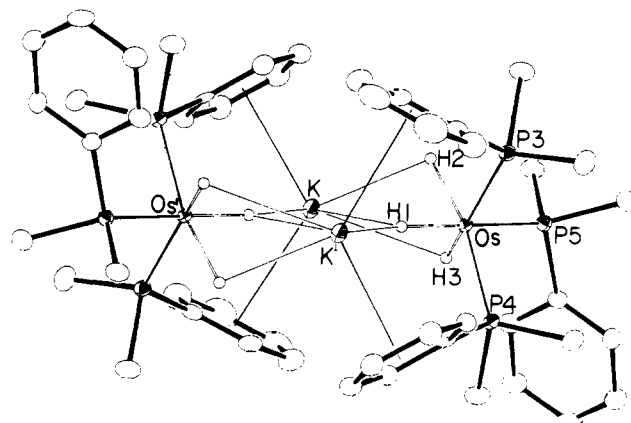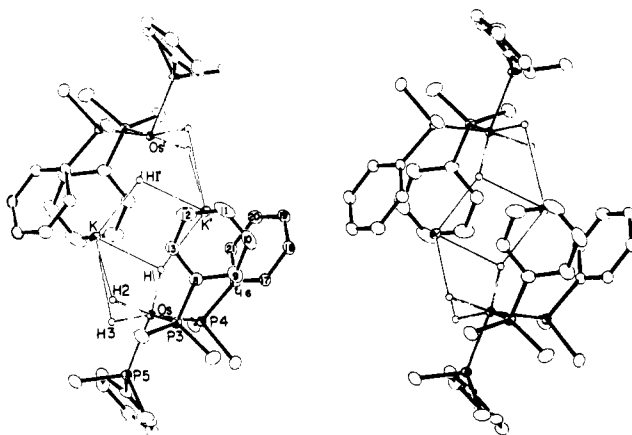
or donor atoms in pendant ligands[6b] can be hydrocarbon soluble.

In addition to the problem of how a charge-separated salt of composition KOsH₃(PMe₂Ph)₃ can achieve solubility in arenes, we formulated yet another question: Since our synthetic procedure in toluene, as well as the spectral data collected on the product, precludes any coordination of conventional Lewis bases (e.g., ethers) to K⁺ in KOsH₃(PMe₂Ph)₃, what then is the nature of the coordination environment about K⁺ in this compound? Specifically, even if there is intimate ion pairing between K⁺ and OsH₃(PMe₂Ph)₃⁻, how does K⁺ avoid a situation where all of its ligands lie in one hemisphere, with the other hemisphere about K⁺ naked? Such an anisotropic distribution of ligands about an electrophilic center is wholly improbable based on our studies of the products of transition-metal polyhydrides reacting with Cu⁺ and Ag⁺.[8,9]

Molecular Structure. The X-ray diffraction study of a crystal of KOsH₃(PMe₂Ph)₃ grown from toluene reveals (Figures 3 and 4) it to be comprised of the intimate ion pair (PMe₂P)₃Os(μ-H)₃K. The coordination geometry about osmium is the *fac* octahedral arrangement deduced spectroscopically. The potassium forms an intimate ion pair with this anion, making the P₃Os(μ-H)₃K notation appropriate. In spite of the symmetry-reducing interactions to be discussed below, the P₃OsK unit displays close to C₃ᵥ symmetry: Os–P distances (average value 2.28 Å), P–Os–P angles

(7) Jesson, J. P. In "Transition Metal Hydrides", Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; p 80.

(8) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 5137.

(9) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 6874.
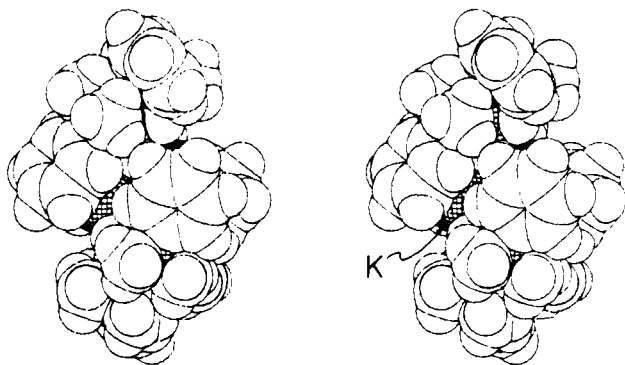
Figure 5. Stereo space-filling view of the dimer oriented as in Figure 4. One K$^+$ is the hatched atom indicated, while the other is veiled by the phenyl rings at right.

(99.7°), and P–Os–K angles (118.0°) are equivalent within their particular type. Both this last criterion and Figure 4 show that K$^+$ lies on the idealized C_3 axis of the *fac*-OsH$_3$P$_3$ unit.[10]

The monomeric intimate ion pair P$_3$Os(μ-H)$_3$K suffers from having the previously described three-coordinate *pyramidal* K$^+$. This unhappy angular configuration of too few ligands is alleviated not by coordinating solvent of crystallization (toluene) but rather by binding a second monomer unit (Figure 3 and 4). This dimerization occurs by pyramidal K$^+$ in one monomer unit interacting with one hydrogen (H1′) from the partner monomer unit. In addition, K$^+$ nestles into a cave created (see below) by two phenyl rings of the partner monomer. The partner monomer literally swallows the exposed back side of one K$^+$, and vice versa. The aggregation of P$_3$OsH$_3$K monomers into centrosymmetric dimers thus employs hard/hard (K/H) and hard/soft (K/phenyl) acid–base interactions to clothe K$^+$ in a lipophilic sheath. This is most readily seen in Figure 5, where the hydrocarbon periphery of K$_2$Os$_2$H$_6$(PMe$_2$Ph)$_6$ is revealed; the structural study thus clearly identifies the origin of the lipophilic nature of what we had naively considered to be a salt.

The dimerization is effected by an H1–K′ interaction which is approximately linear (∠Os–H1–K′ = 156°) and also short (K′–H1 = 2.52 Å). H1 thus becomes three coordinate. The cloaking of K$^+$ in a hydrocarbon environment involves rather symmetrical binding (Figure 4) to all six carbons of the phenyl ring comprised of C16–C21 (3.22–3.32 Å distant from K′). The perpendicular ring-to-plane distance here is 2.95 Å, and a line from K′ to the ring center of gravity intersects the ring plane at an angle of 87.4°. Because of a twist about the P–C8 bond, carbons C8–C13 span a wider range of K′–C distances (3.12–3.60 Å). The perpendicular ring-to-plane distance is 3.02 Å, and the corresponding line/plane angle is 79.0°. With the π-complexation of K$^+$ by the two phenyl groups established,[11] the coordination environment of K$^+$, (arene)$_2$K(η^3-H$_3$OsP$_3$)(H′), resembles that of zirconium in Cp$_2$ZrH(η^3-H$_3$OsP$_3$).[1]

As mentioned earlier, the interaction between P$_3$Os(μ-H)$_3$K subunits in the dimer has little effect on breaking the threefold symmetry of the subunit. The P–Os–P angle involving the two "phenyl–donor" interactions is slightly (5°) larger than the other two P–Os–P angles, but this is barely significant in comparison to two examples where phenyl complexation is absent: in *fac*-IrH$_3$(PMe$_2$Ph)$_3$[12] and Cp$_2$ZrCl[η^3-H$_3$Os(PMe$_2$Ph)$_3$],[1] P–Os–P angles range from 95.0 to 102.1°. There is no evidence, in KOsH$_3$(PMe$_2$Ph)$_3$ for unusual Os–P–C (Table III) or C–P–C angles, and it thus appears that potassium encapsulation by

phosphine phenyl groups occurs with no energetically costly distortion in the Os(PMe$_2$Ph)$_3$ unit. The important degree of freedom which permits this encapsulation is rotation about Os–P and P–C σ bonds. Both *fac*-IrH$_3$(PMe$_2$Ph)$_3$ and Cp$_2$ZrCl[η^3-H$_3$Os(PMe$_2$Ph)$_3$] show the in-phase orientation (A) of phenyl groups, while B is necessary in order to enfold K$^+$ at site "X".

A   B
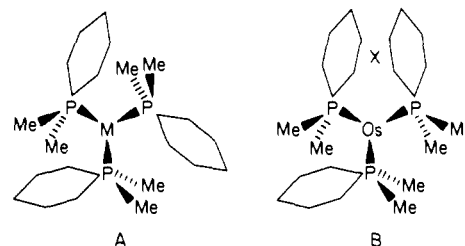
Discussion

Formation of the ion pair P$_3$Os(μ-H)$_3$K resembles the hydride-bridged condensation we have reported[8,9] between transition-metal polyhydrides and the group 11[26] electrophiles Cu$^+$ and Ag$^+$ (e.g., coordination, via hydride donation, of IrH$_3$P$_3$ to these monocations). The chemistry developed there revealed an aversion on the part of those electrophiles to accept highly anisotropic ligand binding (e.g., trigonal *pyramidal*), and instead, ligands were always drafted to complete tetrahedral or octahedral coordination geometries about the monocation. In the case of P$_3$Os(μ-H)$_3$K, this same principle operates, but ligation to the back side of K$^+$ in the monomer unit is achieved by donation from one hydride and two phenyl units of a second monomer unit. The fact that this linkage of two monomers into a dimer is complementary (i.e., each P$_3$Os(μ-H)$_3$K is both donor and acceptor, by virtue of the center of symmetry) makes this dimerization particularly efficient and apparently explains why it occurs to the exclusion of arene (solvent) coordination (e.g., P$_3$Os(μ-H)$_3$K(η^6-toluene)). It also naturally explains the exclusive facial H$_3$OsP$_3$ stereochemistry since only this isomer permits such efficient dimerization.

Although K$^+$ does not coordinate to arene solvent in the isolated solid, the structure found reveals that this electrophile is capable of binding to *neutral* aryl groups, in a hard acid/soft base linkage heretofore unanticipated. Thus, K$^+$/hydrocarbon bonding does not require that the hydrocarbon be anionic, as it is in (1,1,2,2-tetramethylenediamine)K(C$_{13}$H$_9$).[13] In fact, the K–C distances to carbons of the fluorenyl anion in this compound range from 3.04 to 3.68 Å (average value 3.32 Å), while those in KOsH$_3$-(PMe$_2$Ph)$_3$ range from 3.12 to 3.60 Å (average 3.39 Å). In the ionic lattice of KMe,[14] the K–C distance is 3.22 Å. Thus by a distance criterion, the K/phenyl interaction in KOsH$_3$(PMe$_2$Ph)$_3$ is every bit as strong as it is in more conventional charge-separated organopotassium compounds. Given the sandwich character of the K$^+$/phenyl interaction in KOsH$_3$(PMe$_2$Ph)$_3$, a comparison to the charge-delocalized intercalation compound potassium graphitate (KC$_8$) is appropriate.[15,16] This material involves alternating layers of potassium and graphite hexagons, with potassium centered above certain ring centers. The K–C distances in KC$_8$ are 3.06 Å. All of the distances cited here should be compared to the van der Waals "thickness" of a phenyl ring (i.e., the *nonbonding* distance perpendicular to the ring plane) of 3.35 Å; this is half the inter-layer distance in graphite.

Similar interactions have been observed between the smaller cation Na$^+$ and phenyl rings in Na(THF)(Et$_2$O)Na-(Et$_2$O)$_2$CrPh$_5$,[17] where the cations approach the *ipso* and *ortho* carbons of all five phenyl rings at distances of 2.63–2.95 Å.

(10) It is evident from Table III and Figure 4 that atom H3 is poorly located in an angular sense; it is too close to P5 and thus too far from H1 and K. The K–H3 distance (3.02 Å) is thus considerably longer than K–H1(2.73 Å) and K–H2 (2.68 Å). We feel that this is an artefactual result and assume that the three hydride bridges in fact have threefold symmetry.

(11) There is no perceptible distortion of phenyl carbon–carbon distances as a result of the K$^+$/phenyl binding.

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Analogous interactions (2.58–3.16 Å) are found in {[NaPh]₂-(THF)₂.₅]NiC₂H₄}₂.[18]

The K–H distances in [KH₃Os(PMe₂Ph)₃]₂, 2.52–3.02 Å, are comparable to those in K₂PtD₄ (2.879 Å)[19], KD (2.845 Å), and K₂ReH₉ (2.64–3.93 Å).[20]

Given the symmetry-reducing interactions in the K/Os ion pair dimer, the question arises as to what influence this has on the NMR spectra. Both ¹H and ³¹P NMR spectra give little evidence for a reduction of symmetry from C_{3v}. One may therefore conclude that the ion pairing is at least fluxional *within* the unit yielding time-averaged C_{3v} symmetry. However, note the following: (1) The altered chemical shift (and marked loss of multiplet resolution) of the methyl resonances on going from THF to toluene solvent suggests an influence of the instantaneous ion pair structure (e.g., Ph ring currents) on the average methyl environment. (2) The broadened (average) ortho phenyl pattern (in toluene relative to THF) is consistent with dynamic behavior. (3) The substantially reduced resolution in this hydride AA'A''XX'X'' NMR pattern may originate from the quadrupolar character of potassium. If so, this supports the idea that fluxionality is intra-unit, with no rapid exchange of potassium cations between (KOsH₃P₃)₂ dimers. (4) The coupling of hydride to only three phosphorus nuclei reveals that the fluxional process occurs with retention of local stereochemistry at each osmium and without hydride migration to another osmium (i.e., with retention of Os–H bonds).

Perhaps the most relevant comparison to KOsH₃(PMe₂Ph)₃ is to be made with K(Ph₃P)₂Ph₂PC₆H₄RuH₂·C₁₀H₈·Et₂O. (The ether and naphthalene molecules merely occupy lattice cavities and will therefore not be discussed further.[21]) An intimate ion pair exists between K⁺ and the ortho-metalated complex anion as sketched in I (Hydride ligands were not detected in the X-ray

I
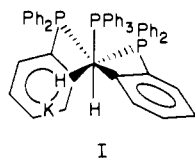
study, but their location is deduced from the assumption of octahedral geometry about ruthenium.) The molecule in I dimerizes

in the solid state, with K⁺ enfolded by the pendant phenyl sketched in I and by the ortho-metalated phenyl of the second monomer unit.[22] Potassium–carbon distances range from 2.97 to 3.59 Å. This compound shows longer K/Ru separations (3.62–4.08 Å) than the K/Os separations in KOsH₃(PMe₂Ph) (3.4–4.1 Å), a characteristic attributable to the fact that the former contains the K(μ-H)₂Ru unit while the latter contains K(μ-H)₃Os.

Finally, in a search for covalent K/Mo bonds, the compound (18-crown-6)KHMoCp₂ was synthesized and subjected to an X-ray structure determination.[23] The results (including K–Mo = 3.61 Å) were interpreted in terms of a hydride bridging these two metal atoms, with Mo–H = 1.66 Å and K–H = 2.80 Å. The solubility of this compound in hydrocarbons was not reported.

The ability of phenyl rings of coordinated phosphines to confer hydrocarbon solubility on anotherwise highly polar and predictably lipophobic "salt" of a transition-metal hydride complex invites comparison to crown ether solubilization of inorganic reagents (e.g., KMnO₄) in hydrocarbon solvents. However, the present example is exceptional in that conventional alkali metal cation ionophores always function by O or N lone pair donation. The potential to homogeneously employ highly electron rich ("hydridic") hydride complexes in reductions of hydrophobic organic substrates is an attractive feature of the K⁺/aryl coordination described here, and this potential has already been transformed into reality for one class of reductions.[24,25]

Supplementary Material Available: A listing of anisotropic thermal parameters, hydrogen atom parameters, and observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(22) The enveloping of K⁺ by phenyl rings in this compound thus differs from that in KOsH₃(PMe₂Ph)₃ in that a given potassium binds to one phenyl from each ruthenium anion.

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(26) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)