excited state, this nonradiative decay process is apparently circumvented by low temperatures. We are currently investigating the chemistry of electronically excited **1** and we are also extending our studies to include investigations of the excited-state chemistry of d^7–d^7 and d^9–d^9 dirhodium fluorophosphine complexes.

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Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, anisotropic temperature factors, least-squares planes, and torsion angles for **1** (12 pages); tables of observed and calculated structure factors for **1** (55 pages). Ordering information is given on any current masthead page.

Stereochemical Control of the Exchange of Hydrogen Atoms between Hydride and Dihydrogen Ligands in the Complexes $[M(\eta^2\text{-}H_2)(H)(meso\text{- or }rac\text{-tetraphos-1})]^+$, M = Fe, Os

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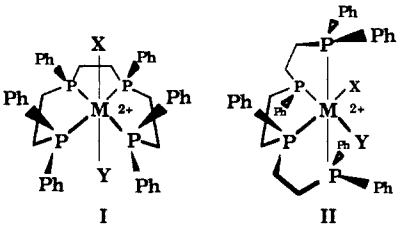
In order to better understand the hydrogen atom exchange between the η^2-dihydrogen ligand[1-10] and the hydride ligand in the complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(PR_2CH_2CH_2PR_2)_2]^+$, R = Ph, M = Fe (**1Fe**), Ru (**1Ru**), R = Et, M = Fe (**2Fe**), Ru (**2Ru**), Os (**2Os**),[3] we have examined the behavior of other iron group complexes containing four phosphorus donor sets. We describe here several noteworthy aspects of the chemistry involving the tetraphos-1 ligands, *meso*- or *rac*-$PPh_2(CH_2CH_2PPh)_2CH_2CH_2PPh_2$.[11] (1) *meso*-Tetraphos-1 holds the hydride and dihydrogen ligands trans to each other and prevents exchange of hydrogens on the NMR time scale in the title complexes. (2) There is the intriguing possibility of isomers based on the fact that one axial site is more crowded than the other (site X in structure I). (3) The meso ligand favors cis-β[12] stereochemistry in $OsCl_2$(*meso*-tetraphos) which activates it to reaction with H_2 under very mild conditions. (4) *rac*-Tetraphos-1 forces the H and H_2 ligands to go cis in the osmium complex so that there is extremely rapid intramolecular exchange of hydrogen atoms. The propensity for the meso ligand to give trans and the rac to give cis complexes has already been reported.[13] The complex $[Rh(H_2)(\text{tetraphos-2})]^+$ has recently been made.[8]



meso ligand rac ligand

The precursor to the iron dihydrogen complex is *trans*-FeH_2(*meso*-tetraphos)[14] (structure I, M = Fe; X, Y = H^-). This complex has two inequivalent trans hydride ligands with $^2J(H,H)$ of 18.2 Hz.[15] It was protonated with HBF_4 in ether to give the complex *trans*-$[Fe(\eta^2\text{-}H_2)H(meso\text{-tetraphos})]BF_4$, **3Fe**,[16] (eq 1)

$$trans\text{-}FeH_2(meso\text{-tetraphos}) + HBF_4{\cdot}Et_2O \rightarrow trans\text{-}[Fe(\eta^2\text{-}H_2)H(meso\text{-tetraphos})]BF_4 \quad (1)$$

in a similar preparation to **1Fe**. Curiously we have not been able to prepare **3Fe** by direct reaction of [FeH(*meso*-tetraphos)]Br[17] and $NaBPh_4$ with 1 atm H_2. The ^{31}P NMR spectrum of **3Fe** in THF shows the expected AA'XX' pattern for structure I. The ^1H NMR spectrum of **3Fe** at 293 K is like that of the other η^2-H_2 complexes **1** and **2** when no intramolecular exchange of H ligands is taking place. Thus the barrier to exchange must be much higher than that of the similar bisdiphosphine complex **1Fe**. The presence of the H–H bond was verified in the case of **3Fe** by observing the $^1J(H,D)$ coupling of 32.3 Hz for the isotopomer *trans*-$[Fe(\eta^2\text{-}HD)H(meso\text{-tetraphos})]BF_4$. This was prepared by reacting *trans*-FeH_2(*meso*-tetraphos) with HBF_4 in excess D_2O. It appears that the deuteriation is stereospecific since only one isomer with one HD coupling is observed. Arguments based on steric hindrance of the reaction would suggest a product with structure I with X = H^-, Y = HD. The site of deuteriation is a hydride; ^2H NMR spectra gives no evidence for *trans*-$[Fe(\eta^2\text{-}H_2)D(meso\text{-tetraphos})]BF_4$. Solutions of **3Fe** in acetone under Ar lose H_2 over a period of several hours.

The precursors to the osmium complexes are the dichlorides cis-β-$OsCl_2$(*meso*-tetraphos)[14] and cis-α-$OsCl_2$(*rac*-tetraphos)[14] (structure II, X, Y = Cl^-) which are prepared from $[Os_2Cl_3(PPh_2Et)_6]Cl{\cdot}2H_2O$ and the commercially available meso/rac mixture[18] by a method similar to that of Chatt and Hayter.[19] The two are easily separated since the rac ligand complex is much less soluble than the other. The complex *trans*-$[Os(\eta^2\text{-}H_2)H(meso\text{-tetraphos})]BPh_4$, **3Os**,[20] is readily prepared directly from the

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(16) **3Fe**: light beige powder, 80% yield; FAB MS, calcd for $C_{42}H_{45}{}^{56}FeP_4$ 729.3, obsd 729 (M^+); δ (^1H, 293 K, CD_2Cl_2) –9.77 (br s, H_2, T_1 = 32 ms), –16.72 (quintet, J (H,P) = 44.4 Hz, T_1 = 612 ms); δ (^{31}P versus 85% H_3PO_4, THF) 130.3 (P_X), 89.6 (P_A) (P_A–P_X–P_X–$P_{A'}$, $J_{AX} = J_{A'X'}$ = 58 Hz, $J_{AA'}$ = 19, $J_{XX'}$ = 0).
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dichloride precursor in an unusual reaction in THF at 293 K for 24 h (eq 2). **3Os** can also be prepared from *trans*-OsHCl-*cis*-β-$OsCl_2$(*meso*-tetraphos) + $NaBPh_4$ + $2H_2$ →

trans-[Os(η^2-H_2)H(*meso*-tetraphos)]BPh_4 + NaCl + HCl (2)

(*meso*-tetraphos),[14] $NaBPh_4$, and H_2 in a similar preparation to **2Os**. The distinctive AA'XX' pattern in the ^{31}P NMR spectrum confirms the trans structure. The ^1H NMR spectrum in the high field region at 293 K is consistent with the octahedral structure I in which the η^2-H_2 ligand is trans to the terminal hydride as observed in the crystal structure of **1Fe**. Triplets with ^1J(H,D) couplings of 26.4 Hz grow in the ^1H NMR spectrum with time because of intermolecular H^+/D^+ exchange with acetone-d_6 to give isotopomers containing HD.[21] In contrast to **2Os** where the rate of intramolecular exchange of H atoms is 3000 s^{-1} at room temperature, exchange in **3Os** is slow on the NMR time scale at 293 K.

The T_1 values measured at 200 MHz for the H_2 ligands of the complexes (32 ms for **3Fe**, 49 ms for **3Os**) are shorter than those of comparable complexes **1** and **2** extrapolated to room temperature by use of the known temperature dependences of these T_1 values.[22] For example the H_2 of **1Fe** has a T_1 of ~40 ms and that of **2Os** has a T_1 of ~340 ms at 200 MHz. This information combined with the larger ^1J(H,D) couplings for **4** argues for shorter H-H bonds in these tetraphos complexes relative to bis-diphosphine complexes.

cis-α-OsH_2(*rac*-tetraphos)[14] (structure II, X, Y = H^-) reacts with HBF_4 in ether to give a complex formulated as *cis*-α-[Os(η^2-H_2)H(*rac*-tetraphos)]BF_4, **4Os**.[23] The assignment of cis-α

cis-α-OsH_2(*rac*-tetraphos) + HBF_4·Et_2O →

cis-α-[Os(η^2-H_2)H(*rac*-tetraphos)]BF_4 (3)

geometry of the tetraphos ligand comes from the typical A_2X_2 ^{31}P NMR spectrum[23] and a preliminary X-ray diffraction study.[24] The three hydridic protons at −8.15 ppm remain equivalent to 180 K, and no HD couplings are observed for deuteriated analogues.

The T_1 of the hydridic resonances of **4Os** passes through a minimum value of 160 ms at 252 K, 400 MHz. Crabtree and Hamilton[25] and ourselves[22] have recently described how T_1 measurements can be used to determine the H-H distances of η^2-dihydrogen ligands in transition-metal complexes in solution. We calculate that the H-H distance falls in the range of 1.25-1.6 Å assuming (1) the limits of rapid and no rotation of the H_2 ligand, respectively, (2) dipolar relaxation predominates, (3) the terminal hydride has a T_1 of 600 ms, (4) exchange is of the type $(H_2)(H^*) \rightleftarrows (HH^*)(H)$.[14] Thus some degree of H-H bonding is present although the structure must be close to that of a seven-coordinate trihydride where H-H distances of ≥2 Å are expected. A long, weak H-H bond presumably facilitates H atom exchange,[3a] since $[Ir(H_2)(H)(PPh_3)_2(bq)]^+$ which also has cis H_2 and H ligands and a shorter H-H bond than **4Os** has a higher barrier to exchange.[2] An alternative formulation, *cis*-α-[Os(η^3-H_3)(*rac*-tetraphos)]BF_4, is also possible although for an H_3^- ligand two different types of H atoms and hence two chemical shifts might be expected.[26] Dihydrogen in **4Os** is easily displaced by CH_3CN in boiling CH_3CN/CH_2Cl_2 solution in 2 h to give *cis*-α-[Os(CH_3CN)(H)(*rac*-tetraphos)]BF_4.[14]

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Supplementary Material Available: Characterization of the complexes by FAB MS, C, H analyses, ^1H and ^{31}P NMR as well as calculations based on T_1 values (3 pages). Ordering information is given on any current masthead page.

(20) **3Os**: only characterized in solution since it is extremely difficult to crystallize; FAB MS calcd for $C_{42}H_{45}{}^{192}OsP_4$ 865.4, obsd 861 (M^+ − 4 H); δ (^1H, 293 K, acetone-d_6, 200 MHz) −6.36 (br s, H_2, T_1 = 49 ms) −11.21 (quintet, J(H,P) = 18.9 Hz, T_1 = 650 ms); δ (^{31}P versus 85% H_3PO_4, THF) 80.1 (m), 32.5 (m) (AA'XX', J_{AX} = 185 Hz).

(21) [Os(HD)H(*meso*-tetraphos)]$^+$: δ (^1H, 293 K, acetone-d_6) −6.36 (^1J(H,D) = 26.4 Hz), −11.25 (^2J(H,P) = 18 Hz); [Os(HD)(D)(*meso*-tetraphos)]$^+$: −6.28 (^1J(H,D) = 26.4 Hz).

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(23) **4Os**: white powder, 42% yield; FAB MS, calcd for $C_{42}H_{45}{}^{192}OsP_4$ 865.4, obsd 861 (M^+ − 4 H); Ir (Nujol) 2043 (vw), 2016 (vw), 1983 (vw) cm^{-1} (Os-H); δ (^1H, 252 K, CD_2Cl_2, 400 MHz) −8.20 (quintet, J(H,P) = 12.1 Hz, T_1 = 160 ms which is the minimum value; δ (^{31}P versus 85% H_3PO_4, acetone) 81.0 (s), 40.2 (s). Anal. Calcd for $C_{42}H_{45}BF_4OsP_4$·CH_2Cl_2: C, 49.87; H, 4.57. Found: C, 49.43; H, 4.23.

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X-ray Absorption of *Azotobacter vinelandii* Vanadium Nitrogenase

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Evidence for the existence of a vanadium-containing nitrogenase has existed for more than half a century,[1] but progress in understanding this enzyme has only come recently.[2] In 1980, Bishop and co-workers proposed that an alternative nitrogen-fixing enzyme exists in *Azotobacter vinelandii*[3] and subsequently proposed that vanadium was involved.[4] In 1986, Robson et al. demonstrated clearly that the alternate nitrogenase from *Azotobacter chroococcum*, Ac1*, contained vanadium[5] instead of molybdenum. Hales et al. have shown that vanadium is also found in the *Azotobacter vinelandii* alternative component I, Av1'.[6]

The molybdenum and vanadium nitrogenase proteins are similar in many respects. Like the molybdenum enzyme, both Ac1* and Av1' exhibit an EPR spectrum characteristic of a species with an $S = {}^3/_2$ ground state;[7,8] Av1' also contains the so-called P-clusters.[9] Additionally Ac1* has recently been shown to possess

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