spectrum of the pure solid at low temperature, while in Figure 2 we show the absorption spectrum. The emission excitation spectrum at 77 K in hydrocarbon glass was identical with the absorption spectrum in the wavelength range 250–450 nm.

The half-width of the emission is extraordinarily temperature sensitive, increasing by about 50% between 20 and 80 K, for the solid. It continues to increase at higher temperatures, up to the highest temperature, ≈250 K, at which emission can be detected with our instrumentation.[1] The thermal variation is probably due to hot-band (second-moment) effects[3] involving the anticipated very low excited state $\nu(Re_2)$, although thermal population of several spin-orbit components[7] might also be involved.

No emission has been detected from fluid solutions of the rhenium dimers. The most important factor appears to be the rigidity of the medium, as weak emission is detectable even at room temperature for poly(methyl methacrylate) films containing the dimers (emission lifetime 4.8 μs at 293 K for the dppm complex).

The emissive state is likely to be the $^3(d\sigma \rightarrow d\sigma^*)$ state. The lowest energy absorption reported for $Re_2(CO)_{10}$ is the $^1(d\sigma \rightarrow d\sigma^*)$ transition at 312 nm;[8] transitions of the type $^1(d\pi \rightarrow d\sigma^*)$ appear to lie at higher energy of $d\sigma \rightarrow d\sigma^*$ for the third-row compound. For the compound $Re_2(dmpm)_2(CO)_6$, we assign the band at 342 nm (ϵ 12 400) to the $^1(d\sigma \rightarrow d\sigma^*)$ transition. The pronounced narrowing of the band at lower temperature is characteristic[3] of this transition. The dppm derivative shows an analogous band at 325 nm (ϵ 8000). The lower energy of this band relative to $Re_2(CO)_{10}$ is consistent with other studies of phosphine derivatives.[8,9] Thus, it is unlikely that $^3(d\pi \rightarrow d\sigma^*)$ states are responsible for the emissions of the Re_2 compounds, and, by extension, the previously characterized emissions (vide supra) of d^7–d^7 compounds are likely also from $^3(d\sigma \rightarrow d\sigma^*)$ states because of their very similar characteristics.[10] The energy of the emission is quite consistent with previous estimates[4,5] of the energy of $^3(d\sigma \rightarrow d\sigma^*)$, the large singlet–triplet splitting being attributable to the ionic nature of the singlet state. Excitation into the $^1(d\sigma \rightarrow d\sigma^*)$ absorption with polarized light yields polarized emission,[11] $I/I \approx 0.7$. Since $^1(d\sigma \rightarrow d\sigma^*)$ is molecular z-polarized, the observed emission polarization ratio less than one implies the emission to be x,y-polarized which is also consistent with a $^3(d\sigma \rightarrow d\sigma^*)$ assignment (spin-orbit components $A_1 + E$ in D_4 symmetry).

In conclusion, we find that the $^3(d\sigma \rightarrow d\sigma^*)$ state of d^7–d^7 singly metal–metal bonded complexes may be a long-lived (emissive) excited state if metal–metal dissociation is prevented. Photochemical studies of these molecules are in progress in conjunction with Professor David Tyler at the University of Oregon. Initial results indicate that efficient reaction occurs with halocarbons which suggests that metal–metal dissociation may still occur in a fluid medium.

Acknowledgment. We thank Dr. Joe Perry for assistance in performing lifetime measurements. The research described in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

Registry No. I, 90624-20-7; $Re_2(dppm)_2(CO)_6$, 95648-63-8.

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(7) Effects due to thermal population of spin-orbit states have been noted for the emissive triplet state of $Pt_2(P_2O_5H_2)^{4-}$: Rice, S. F.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 4571–4575.

(8) Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042–6046.

(9) Stiegman, A. E.; Miskowski, V. M.; Tyler, D. R.; Christoph, G. G., to be submitted for publication.

(10) The assignment of the very weak 400 nm (ϵ 400) absorption feature (Figure 2) exhibited by both Re dimers, which is also present in the excitation spectra, is uncertain. The weakness of the transition and the fact that it is not present in the spectra of analogous phosphine bridged manganese dimers suggests that it is a single–triplet absorption. The transition is too high in energy to be the emissive $^3(d\sigma \rightarrow d\alpha^*)$ state (this would give an unreasonably large Stokes shift) but may be the spin forbidden analogy of one of the higher energy $^1(d\pi–d\alpha^*)$ states (which are probably responsible for the bands to higher energy of $^1(d\sigma–d\sigma^*)$, see Figure 2). Unfortunately the weakness of the band prevented accurate determination of its polarization ratio.

(11) The polarization ratio is $(I_{vv} \cdot I_{hh})/(I_{vh} \cdot I_{hv})$.

Luminescence from a Novel Mixed-Valence Dirhodium Fluorophosphine Complex

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Fluorophosphine ligands coordinated to transition-metal complexes can engender unique oxidation–reduction chemistry. The dual function of fluorophosphines as good σ-donating and strong π-accepting ligands[1–4] is manifested in their ability to stabilize transition metals in several oxidation states.[5] Moreover, although the physical and chemical properties of electronically excited fluorophosphine complexes have yet to be defined, exhaustive spectroscopic studies of many other classes of transition-metal complexes during the past decade have demonstrated that ligands possessing low-lying π-accepting orbitals are effective in stabilizing metal complexes in long-lived lowest energy excited states.[6–13] Owing to our interest in developing new photoredox chemistry, we have begun investigations of fluorophosphine complexes in view of their demonstrated redox and anticipated excited-state properties. We now report the synthesis and spectroscopy of a long-lived, highly emissive binuclear complex in which a bidentate fluorophosphine ligand stabilizes rhodium in two different oxidation states, Rh(II) and Rh(0). Interestingly, our data suggest that the emissive excited state is primarily metal-localized with little metal-to-ligand charge-transfer character.

The previously reported $Rh_2(\mu\text{-}Cl)_2(PF_3)_4$ complex[14] reacts immediately with methylaminobis(difluorophosphine)[15] in benzene at room temperature. Addition of hexane to the resulting red-orange solution produces an orange solid. A dichloromethane solution of this compound layered with hexane yields red-orange prismatic crystals which have been identified by crystallographic analysis to be $Rh_2[(F_2P)\text{-}N(CH_3)\text{-}(PF_2)]_3Cl_2(PF_3)$ (**1**).[16] The molecular structure of **1**, represented by the ORTEP diagram shown

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(1) Nixon, J. F. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 41–141.

(2) Savariault, J.-M.; Serafini, A.; Pelissier, M.; Cassoux, P. *Theor. Chim. Acta* **1976**, *42*, 155–161.

(3) (a) Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064–4065. (b) Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. *J. Am. Chem. Soc.* **1983**, *105*, 7033–7037.

(4) (a) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1978**, *17*, 1585–1588. (b) Avanzino, S. C.; Chen, H.-W.; Donahue, C. J.; Jolly, W. L. *Inorg. Chem.* **1980**, *19*, 2201–2205.

(5) (a) King, R. B. *Acc. Chem. Res.* **1980**, *13*, 243–248. (b) Chaloyard, A.; El Murr, N.; King, R. B. *J. Organomet. Chem.* **1980**, *188*, C13–C15. (c) Newton, M. G.; Pantaleo, N. S.; King, R. B.; Lotz, T. J. *J. Chem. Soc., Chem. Commun.* **1978**, 514–515.

(6) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711–743.

(7) Henderson, L. J., Jr.; Fronczek, F. R.; Cherry, W. R. *J. Am. Chem. Soc.* **1984**, *106*, 5876–5879.

(8) (a) Kober, E. M.; Marshall, J. L.; Dressick, W. J.; Sullivan, B. P.; Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 2755–2763. (b) Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104–2109.

(9) Finlayson, M. F.; Ford, P. C.; Watts, R. J. *J. Phys. Chem.* **1986**, *90*, 3916–3922 and references therein.

(10) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381–2392.

(11) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244.

(12) Adamson, A. W.; Fleischauer, P. D. *Concepts of Inorganic Photochemistry*; Wiley-Interscience: New York, 1975.

(13) Crosby, G. A. *J. Chem. Educ.* **1983**, *60*, 791–796.

(14) Bennett, M. A.; Patmore, D. J. *Inorg. Chem.* **1971**, *10*, 2387–2395.

(15) Nixon, J. F. *J. Chem. Soc. A* **1968**, 2689–2692.

(16) (a) Crystal data for $Rh_2[(F_2P)\text{-}N(CH_3)\text{-}(PF_2)]_3Cl_2(PF_3)$ (**1**): orthorhombic, $P2_12_12_1$; $a = 9.620$ (2) Å, $b = 12.755$ (2) Å, $c = 19.564$ (3) Å; $V = 2400.4$ (6) Å^3; $Z = 4$, $D_{calcd} = 2.40$ g/cm^3. A Nicolet P3F diffractometer was used to collect 9542 data ($2° \leq \theta \leq 32.5°$) at 27 ± 1 °C of which 4889 data were unique; 3880 data with $I > 3\sigma(I)$ were used in refinement. Structure refined to $R = 0.026$ and $R_w = 0.025$, GOF = 1.20; highest final difference peak, 0.6 e/Å^3 [0.9 Å from Rh(2)]. (b) The $P2_12_12_1$ space group requires the existence of two enantiomorphic structures; differences between the two enantiomorphs were slight (no thermal parameter differed by more than 1σ and no bond distance differed by more than 0.005 Å). The enantiomorph in this manuscript was favored because its refinement yielded better GOF (1.20 versus 1.26) and R_w (0.025 versus 0.027) values.

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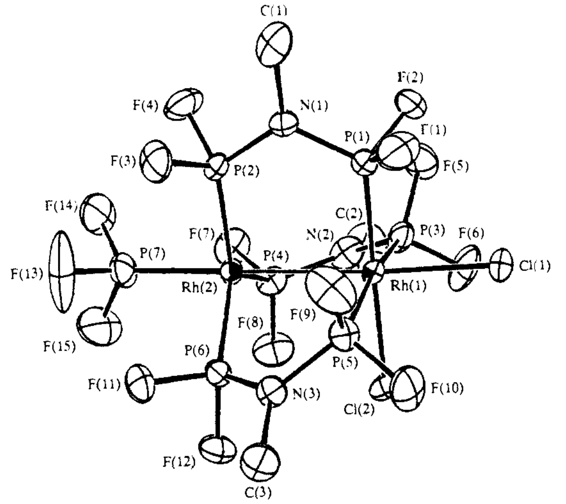

Figure 1. ORTEP drawing of $Rh_2[(F_2P)\text{-}N(CH_3)\text{-}(PF_2)]_3Cl_2(PF_3)$ (**1**) with 30% probability thermal ellipsoids. For clarity hydrogen atoms are not shown. Selected bond distances (Å) and angles (deg) not mentioned in the text are as follows: Rh(1)–Cl(1) = 2.431 (2), Rh(1)–Cl(2) = 2.385 (2), Rh(1)–P(1) = 2.183 (2), Rh(1)–P(5) = 2.251 (2), Rh(1)–P(3) = 2.258 (2), Rh(2)–P(7) = 2.168 (2), Rh(2)–P(2) = 2.209 (2), Rh(2)–P(6) = 2.254 (2), Rh(2)–P(4) = 2.248 (2), Rh(2)–Rh(1)–Cl(1) = 176.46 (6), P(1)–Rh(1)–Cl(2) = 178.32 (8), P(1)–Rh(1)–P(5) = 94.74 (8), P(1)–Rh(1)–P(3) = 97.05 (8), Rh(1)–Rh(2)–P(7) = 179.24 (7), P(2)–Rh(2)–P(4) = 124.43 (8), P(4)–Rh(2)–P(6) = 118.65 (8).

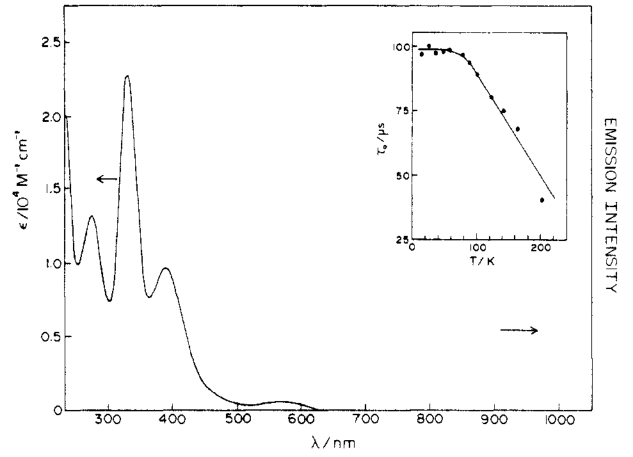

Figure 2. Electronic absorption spectrum (—) of **1** dissolved in CH_2Cl_2 at room temperature, and corrected emission spectrum (···, λ_{exc} = 365 nm) of solid **1** at 77 K. The temperature dependence of the emission lifetime of crystalline **1** is shown in the inset. Lifetimes were measured with the third harmonic of a Nd:YAG laser (λ_{exc} = 355 nm).

in Figure 1, is without precedent in rhodium chemistry. The most striking feature is the unsymmetrical disposition of chloride and phosphine ligands about the metal core. The phosphorus atoms of the three bridging fluorophosphine and the terminal trifluorophosphine ligands compose a trigonal bipyramid at the Rh(0) metal center. Conversely, the coordination geometry about Rh(II) is octahedral with the two axial coordination sites occupied by a chloride atom and the other rhodium atom.[17] In order to accommodate this coordination asymmetry about the metal core, two of the bridging ligands are rotated considerably from an eclipsed conformation [P(1)–Rh(1)–Rh(2)–P(2) = −4.8 (1)°; P(3)–Rh(1)–Rh(2)–P(4) = 22.8 (1)°; P(5)–Rh(1)–Rh(2)–P(6) = −26.4 (1)°]. The twisted conformation of a bidentate phosphine containing one bridgehead atom is unusual but not unique. The binuclear complexes $Rh_2Cl_2(O_2CCH_3)_2(dppm)_2{\cdot}2CH_3CN$[18] and $Re_2Cl_4(dppm)_2$[19] contain bis(diphenylphosphino)methane ligands in considerably twisted conformations and the methylaminobis(difluorophosphine) ligands in $[CH_3N(PF_2)_2]_3Co_2L_2$ complexes are twisted 30° about the metal–metal axis.[20] The Rh···Rh separation of 2.785 (1) Å is consistent with the presence of a direct Rh–Rh single bond.[18,21-23]

The electronic absorption spectrum of **1** dissolved in dichloromethane exhibits bands at 570 ($\epsilon_{max} = 5.73 \times 10^2$), 386 ($\epsilon$ 9.51×10^3), 328 (ϵ 2.29×10^4), and 270 nm (ϵ 1.31×10^4 M^{-1} cm^{-1}) (Figure 2). Excitation with frequencies coincident with the absorption manifold of solids and low-temperature glasses of **1** results in red luminescence. The emission spectrum, illustrated in Figure 2, remains vibrationally featureless at temperatures as low as 10 K. Although luminescence is detected from crystalline **1** over a wide temperature range (inset of Figure 2), solutions of the binuclear complex do not luminesce. The long emission lifetime of **1** is a signature of phosphorescence.

The structural and spectroscopic properties of **1** can be understood within the context of simple electronic structural considerations. Straightforward molecular orbital arguments[26,27] suggest that six electrons of the d^7 $Rh(II)Cl_2P_3$ group fragment reside in orbitals of $\pi(d_{xz},d_{yz})$ and $\delta(d_{xy})$ symmetries with the remaining electron occupying the higher energy d_{z^2} orbital. Similarly, the odd electron of the d^9 $Rh(0)P_4$ fragment also resides in the d_{z^2} orbital with eight d electrons stabilized in the lower energy $\pi(d_{xz},d_{yz})$ and $\delta(d_{xy},d_{x^2-y^2})$ orbitals. Formulation of the observed Rh–Rh single bond results directly from the overlap of the d_{z^2} orbitals of each metal center; in this regard, the electron count of the $Rh_2(II,0)$ d^7–d^9 complex is best represented as $(d^6)d^1$–$d^1(d^8)$. Within this framework, **1** is electronically analogous to the more conventional $(d^6)d^1$–$d^1(d^6)$ (e.g., $Mn_2(CO)_{10}$,[28] $Rh_2(O_2CR)_4$[21,29]) and $(d^8)d^1$–$d^1(d^8)$ (e.g., $Co_2(CO)_8$[30]) complexes and bridges the gap of this metal–metal single-bonded series.

On the basis of this simple molecular orbital model, the lowest energy excited states of **1** should be derived from $d\sigma \rightarrow d\sigma^*$ and $d\pi \rightarrow d\sigma^*$ excitations. Indeed, the maxima and intensities of the absorption bands of **1** correspond well with those of the $d\sigma \rightarrow d\sigma^*$ and $d\pi \rightarrow d\sigma^*$ transitions of other singly bonded metal–metal complexes.[24] Moreover, the luminescence properties of **1** are characteristic of metal–metal $d\sigma^*$ emission, which has only recently been observed for the first time with studies of d^7–d^7 $Pt_2(pop)_4X_2^{4-}$ (pop = $(HO_2P)_2O$, X = Cl, Br, SCN) complexes.[31] Similar to the Pt₂(III,III) complexes, deactivation of the $d\sigma^*$ excited state of **1** by metal–metal bond cleavage is prevented by the ligands bridging the binuclear core. Although dissociation of the axial ligands from the metal core should efficiently deactivate the $d\sigma^*$

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[17] Mixed-valence $Rh_2(II,0)$ cores are unusual in rhodium chemistry. See, for example: (a) Haines, R. J.; Meintjies, E.; Laing, M. *Inorg. Chim. Acta* **1979**, *36*, L403–L404. (b) Ladd, J. A.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1984**, *23*, 2318–2323.

[18] Cotton, F. A.; Dunbar, K. R.; Verbruggen, M. G. *J. Am. Chem. Soc.* **1987**, *109*, 5498–5506.

[19] Barder, T. J.; Cotton, F. A.; Dunbar, K. R.; Powell, G. L.; Schwotzer, W.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 2550–2554.

[20] King, R. B.; Chang, M.; Newton, M. G. *J. Organomet. Chem.* **1985**, *296*, 15–30.

[21] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley-Interscience: New York, 1982.

[22] Cowie, M.; Mague, J. T.; Sanger, A. R. *J. Am. Chem. Soc.* **1978**, *100*, 3628–3629.

[23] The resonance Raman spectrum (λ_{exc} = 406.7 nm) of **1** is typical of binuclear singly bonded rhodium complexes exhibiting three intense, low-frequency lines at 167, 253, and 352 cm^{-1}.[24] While it is tempting to ascribe the lowest frequency mode to ν(Rh–Rh) by analogy to other Rh–Rh complexes,[25] assignments of metal–metal and metal–ligand modes of singly bonded binuclear rhodium complexes are not well-established.[21,25]

[24] Miskowski, V. M.; Smith, T. P.; Loehr, T. M.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 7925–7934.

[25] Agaskar, P. A.; Cotton, F. A.; Falvello, L. R.; Han, S. *J. Am. Chem. Soc.* **1986**, *108*, 1214–1223.

[26] Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; Chapters 15–19.

[27] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

[28] Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042–6047.

[29] Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73–166.

[30] Abrahamson, H. B.; Frazier, C. C.; Ginley, D. S.; Gray, H. B.; Lilienthal, J.; Tyler, D. R.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 1554–1556.

[31] Stiegman, A. E.; Miskowski, V. M.; Gray, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 2781–2782.

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 $[M(\eta^2\text{-}H_2)(H)(\textit{meso-}\text{ or }\textit{rac-}\text{tetraphos-1})]^+$, M = Fe, Os

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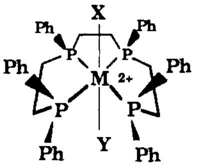
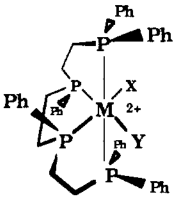
In order to better understand the hydrogen atom exchange between the η^2-dihydrogen ligand[1-10] and the hydride ligand in the complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(PR_2CH_2CH_2PR_2)_2]^+$, R = Ph, M = Fe (**1Fe**), Ru (**1Ru**), R = Et, M = Fe (**2Fe**), Ru (**2Ru**), Os (**2Os**),[3] we have 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]



I

meso ligand



II

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*-tetraphos)$]BF_4$, **3Fe**,[16] (eq 1)

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

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*-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*-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*-tetraphos)$]BPh_4$, **3Os**,[20] is readily prepared directly from the

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[1] (a) Kubas, G. J. *Acc. Chem. Res.*, in press. (b) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000–7009, and references therein.

[2] Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037, and references therein.

[3] (a) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780–3782. (b) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581–5582.

[4] Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645–3651, and references therein.

[5] (a) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675–1676. (b) Conroy-Lewis, F. M.; Simpson, S. J. *Ibid.* **1986**, 506–507.

[6] Sweany, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 6986–6991, and references therein.

[7] Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865–5867.

[8] Bianchini, C.; Mealli, C.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548–5549.

[9] Clark, H. C.; Hampden Smith, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 3829–3830.

[10] Theoretical studies: (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705–710. (b) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587–6592. (c) Burdett, J. K.; Pourian, M. R. *Organometallics* **1987**, *6*, 1684–1691.

[11] King, R. B. *Acc. Chem. Res.* **1972**, *5*, 177.

[12] Bosnich, B.; Jackson, W. G.; Wild, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 8269–8280.

[13] Brown, J. M.; Canning, L. R. *J. Organomet. Chem.* **1984**, *267*, 179–190.

[14] See Supplementary Material.

[15] Another complex with inequivalent trans hydrides is $IrH_3\{N(SiMe_2CH_2PPh_2)_2\}$: Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682–684.

[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).

[17] Ghilardi, C. A.; Midollini, S.; Sacconi, L.; Stoppioni, P. *J. Organomet. Chem.* **1981**, *205*, 193–202.

[18] Purchased from Strem Chemical Company.

[19] Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, *896*, 2605.