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Could One Have Five? Synthesis and Structure of $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$ and Its Conjugate Acid

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Rhenium forms monomeric phosphine hydride complexes in a broad range of oxidation states: $HReL_5$,[1] H_3ReL_4,[2] H_5ReL_3, and H_7ReL_2.[3] Also known is the hydride-rich dimer $H_8Re_2L_4$[3,4] (Re≡Re distance 2.538 (4) Å), the only known compound with four hydrides bridging a metal–metal bond. Following an analysis of this unusual linkage, the Hoffmann group speculated[5] about still higher numbers of hydrides flanking an M_2 unit and posed the question that forms the title of the present report. They concluded that a system of the sort $M_2(\mu\text{-}H)_5L_6^+$ "should be most stable for a metal with up to a d^4 configuration". We describe here results bearing on this possibility.

Reaction of $Re_2H_8P_4$ (P≡PMe_2Ph) with 2 equiv of $P(OCH_2)_3CEt$ (P′) in benzene cleanly produces $Re_2H_4P_4P'_2$ (**1**). The X-ray structure[6,7] of this compound (all hydrogens were refined) reveals an unusual asymmetric structure (Figure 1a), in contrast to the centrosymmetric $P_3HM(\mu\text{-}H)_2MHP_3$ structures assumed by $M_2H_4(PMe_3)_6$, M = Mo[8] and Ru.[9] In $Re_2H_4P_4P'_2$, the two metal atoms have different coordination numbers (7 and 6) and formal oxidation states. The structure is based on the union of an octahedron ($(\mu\text{-}H)_3ReL_3$ at Re2) and a pentagonal bipyramid ($L_3HRe(\mu\text{-}H)_3$ at Re1) via a triangular face of each. A Re≡Re triple bond is required to give the dimer a 36 valence electron count. The metal–metal distance in $Re_2H_4P_4P'_2$ (2.597 (1) Å) is very close to that of the triply bridged triple bond in $Re_2H_6P_5$ (2.589 (1) Å).[10]

Protonation of $Re_2H_4P_4P'_2$ provides access to a molecule of the stoichiometry considered by Hoffmann:[5] $M_2H_5L_6^+$. Treatment of **1** with excess $HBF_4{\cdot}Et_2O$ in benzene at room temperature gives $[Re_2H_5P_4P'_2][BF_4]$ (**2**) as a red oil. The X-ray structure[11,12] (Figure 1b) was determined at −160 °C by using crystals grown from THF/Et_2O. All hydrogen positions were refined. This represents the first structural determination of a multimetal conjugate acid/base pair in which the proton is added/removed at a terminal site.[13] The formal metal–metal bond order is not required to change upon protonation, and the metal–metal separation (2.605 (2) Å) does not lengthen to any chemically significant extent. It is evident that one does not form five hydride bridges in the ground state of *this* d^4–d^4 dimer. The actual structure represents a symmetrization of the neutral dimer (**1**), since the cation is composed of two face-sharing pentagonal bipyramids and possesses an idealized C_2 axis.

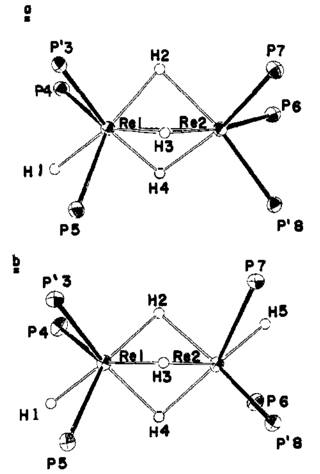

Figure 1. ORTEP views of the inner coordination spheres of (a) $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$ and (b) $Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2^+$ (P = PMe_2Ph, P′ = $P(OCH_2)_3CEt$). The approximately planar pentagon about Re(1) in $Re_2H_4P_4P'_2$ is composed of P4, P5, H1, H2, and H3. The additional planar pentagon in $Re_2H_5P_4P'_2{}^+$ is composed of P6, P7, H3, H4, and H5. Figure b is a view down the idealized C_2 symmetry axis passing through H3 and the Re≡Re midpoint. The effect of protonation on the remainder of the structure is best seen in the P6–Re2–P7 angle, which enlarges from 96.8° in **1** to 122.5° in **2**. All angles from P′ to P in both compounds are within the range 89.4–93.1°.

Since both **1** and **2** are stable above 25 °C, it is possible to examine their solution structure and dynamics. Consistent with the fact that compound **1** has no symmetry, four Re–H resonances are observed[14] at −48 °C. By +57 °C, these have coalesced to a single broad resonance, indicating the occurrence of hydride migration to all four environments. This migration occurs in a manner that makes the two ends of the molecule equally likely to have a terminal hydride, since the $^{31}P\{^1H\}$ spectrum[14] at +80 °C is a single AX_2 pattern ($^2J_{PP'}$ = 35 Hz). However, the phosphine methyl protons appear as two chemically shifted doublets at +57 °C, indicating that the diastereotopy of the methyl groups within one ReP_2P' unit is retained during the hydride migration. This is most simply accomplished by maintaining the basic (nonplanar) feature of *fac* stereochemistry of the ReP_2P' units throughout the hydride migration. Also, the effective mirror symmetry of the $Re_2P_4P'_2$ framework under conditions of rapid hydride migration (i.e., the PMe_2Ph ligands show one ^{31}P and only two methyl ^1H chemical shifts) indicates that such migration occurs concomitant with internal rotation of the phosphorus atoms at the two ends of the dimer.[15]

Compound **2** shows (−60 °C) three hydride resonances[16] and one ^{31}P ABX pattern consistent with the solid state C_2 symmetry. At +16 °C, the $^{31}P\{^1H\}$ pattern has transformed to A_2X, and the two bridging hydride ^1H NMR resonances have coalesced but remain distinct from the (now broad) terminal hydride triplet (coupled only to the two "local" PMe_2Ph ligands). The phosphine methyl proton resonances[17] change from three chemical shifts (one

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(6) Crystallographic data (−176 °C): *a* = 17.347 (8) Å, *b* = 12.722 (5) Å, *c* = 11.977 (5) Å, *α* = 104.81 (1)°, *β* = 97.39 (1)°, *γ* = 102.32 (1)°, *V* = 2449.11 Å^3; *Z* = 2 in space group $P\bar{1}$; R_F = 3.6%, R_{wF} = 3.6% for 7524 observed reflections using anisotropic thermal parameters for all nonhydrogen atoms. All hydrogens were refined isotropically.

(7) Selected structural parameters: Re–P, 2.294 (2)–2.367 (2) Å; Re–P′, 2.192 (2)–2.229 (2) Å; Re–H1, 1.70 (8) Å; Re–H (bridge), 1.78 (8)–1.99 (10) Å.

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(11) Crystallographic data (−160 °C): *a* = 11.507 (5) Å, *b* = 40.543 (24) Å, *c* = 10.792 (4) Å, *β* = 92.52 (2)°, *V* = 5029.92 Å^3; *Z* = 4 in space group $P2_1/n$; R_F = 4.5%, R_{wF} = 4.4% for 5400 observed reflections using anisotropic thermal parameters for all nonhydrogen atoms. All hydrogens were refined isotropically.

(12) Selected structural parameters: Re–P, 2.336 (3)–2.368 (3) Å; Re–P′, 2.224 (3)–2.233 (3) Å; Re–H (terminal), 1.32 (12)–1.61 (12) Å; Re–H (bridge), 1.63 (12)–1.98 (12) Å.

(13) This is a comment on structure; we have no evidence to show unequivocally that the added proton does indeed occupy a terminal position in the kinetic product.

(14) Re–H 220-MHz NMR (toluene-d_8) δ −3.9 (br s, 1), −6.1 (br s, 1), −7.4 (br s, 1), −7.9 (br t, *J* = 57 Hz, 1); $^{31}P\{^1H\}$ NMR (at +80 °C, toluene-d_8 δ −2.1 (d), +104.6 (t). The hydride resonance at δ −7.9 is assigned to the terminal hydride, by comparison to the spectrum of $Re_2H_6P_5$.[10]

(15) Compare to the rotation in an unbridged M≡M species: Chisholm, M. H.; Rothwell, I. P. *J. Am. Chem. Soc.* **1980**, *102*, 5950.

(16) Re–H NMR (CD_2Cl_2) δ −5.93 (br s, 1), −6.75 (br s, 2), −8.67 (br t, *J* = 53 Hz, 2); $^{31}P\{^1H\}$ NMR (−88 °C, CD_2Cl_2) δ −2.5 (d, *J* = 42 Hz), +3.5 (d, *J* = 45 Hz), +104.9 (t, *J* = 43 Hz).

(17) 220-MHz ^1H NMR of PMe protons (CD_2Cl_2) δ (at −60 °C) 1.48 (d, *J* = 9 Hz, 6), 1.63 (d, *J* = 9 Hz, 6), 2.18 (d, *J* = 9 Hz, 12); (at +35 °C) 1.93 (d, *J* = 9 Hz, 12), 1.89 (d, *J* = 9 Hz, 12).

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accidental degeneracy) at −60 °C to two at +35 °C, consistent with the effective internal rotation also found in **1**.

Protonation of a neutral metal hydride is often followed by dihydrogen elimination to yield a (quasi-) unsaturated cation.[18,19] The present observation of an isolable product of protonation of $Re_2H_4P_4P'_2$ is particularly interesting in view of the fact that a stable (18-electron) product of dihydrogen elimination, $Re_2H_3P_4P'_2{}^+$, would appear to be available merely by forming a Re–Re quadruple bond.[20]

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Supplementary Material Available: Table of positional and thermal parameters for compounds **1** and **2** (4 pages). Ordering information is given on any current masthead page.

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[20] Compare the protonation of $Ru_2H_4(PMe_3)_6$ in ref 9.

Generation of Titanocene and Rhodocene Cations in the Gas Phase by a Novel Metal-Switching Reaction

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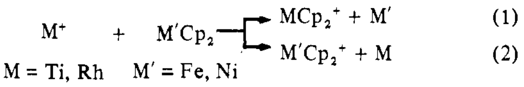
Cyclopentadienyl groups have been known to form interesting complexes with transition metals ever since the first report of ferrocene, bis(η^5-cyclopentadienyl)iron, in 1951.[1] Of particular interest are the "sandwich" compounds, called metallocenes, where a transition metal is π bonded on either side to a Cp (Cp = $C_5H_5^-$) ligand. While neutral metallocene analogues of Ni, Cr, V, and Co are known to be isostructural with $FeCp_2$, other transition metals have proven elusive to prepare as the sandwich complex.[2] Perhaps the most notable example is "titanocene", which is now thought to exist as a dimer in the condensed phase.[3]

We report the generation of titanocene and rhodocene cations by a novel metal-switching reaction (reaction 1) between Ti^+ and Rh$^+$ and two common metallocenes, $FeCp_2$ and $NiCp_2$. Charge exchange (reaction 2) is the only other major competing reaction observed. Fe^+ was also reacted with nickelocene but only underwent charge exchange (reaction 2).



$$M^+ + M'Cp_2 \longrightarrow \begin{cases} MCp_2{}^+ + M' & (1) \\ M'Cp_2{}^+ + M & (2) \end{cases}$$

M = Ti, Rh   M′ = Fe, Ni

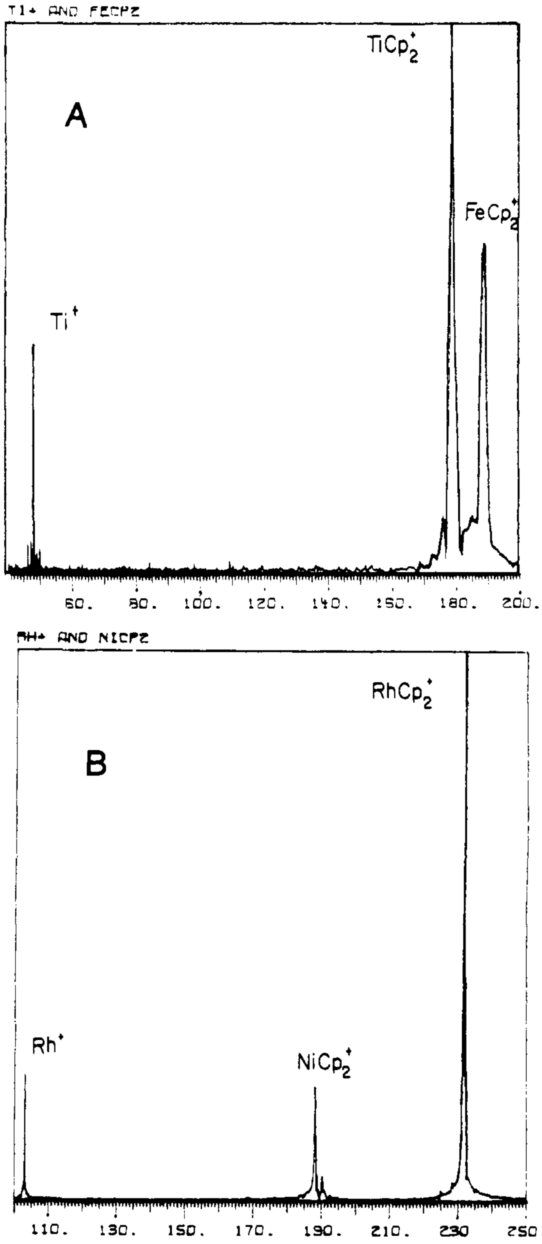


Figure 1. Fourier-transformed mass spectra arising from single laser pulses with (A) Ti^+ trapped for 3 s in the presence of ferrocene (8K transformation) and (B) Rh^+ trapped for 1 s in the presence of nickelocene (64K transformation). The pressure in both cases is $\sim 3 \times 10^{-7}$ torr.

Ion cyclotron resonance (ICR) spectrometry has proven to be a powerful tool for investigating organometallic reactions in the gas phase.[4-8] The recent application of Fourier transform techniques to ICR[8,9] has improved both the resolution and mass range of this mass spectrometric method. The experiments described here were performed on a prototype Nicolet FTMS-1000 spectrometer utilizing a 0.9-T magnetic field. The simple atomic metal ions were formed by a Quanta Ray Nd:YAG laser that produced a 530-nm beam (frequency doubled), which was focused onto a pure metal plate in the ICR cell.[4] The metal ions were trapped in the presence of the sample gas for times ranging from 100 ms to several seconds and products were detected mass spectrometrically. Figure 1 illustrates typical mass spectra taken from single laser shots. Clean metal surfaces exposed by laser

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