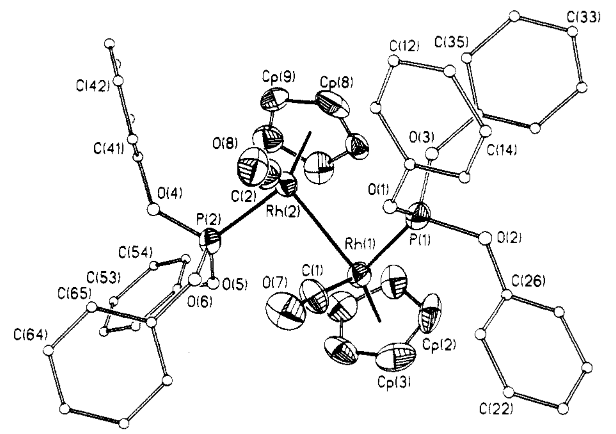

Figure 1. Cation structure and labeling scheme for $[CpRh(CO)P(OPh)_3]_2^{2+}$. Thermal ellipsoids are shown at the 50% probability level. Bond distances (Å): Rh(1)–Rh(2), 2.814 (1); P(1)–Rh(1), 2.258 (4); P(2)–Rh(2), 2.252 (4); Rh(1)–C(1), 1.88 (1); Rh(2)–C(2), 1.86 (1); Rh(1)–CENT(1), 1.873 (6); Rh(2)–CENT(2), 1.876 (7). Bond angles (deg): P(1)–Rh(1)–C(1), 89.8 (4); P(1)–Rh(1)–CENT(1), 128.6 (3); CENT(1)–Rh(1)–C(1), 126.8 (6); P(2)–Rh(2)–C(2), 90.4 (4); P(2)–Rh(2)–CENT(2), 125.5 (4); CENT(2)–Rh(2)–C(2), 128.6 (7); CENT(1)–Rh(1)–Rh(2)–CENT(2), −62.2 (6).

$(OPh)_3]$ cations joined by a Rh–Rh bond (Figure 1). The phosphite groups occupy essentially transoid positions, the P(1)–Rh(1)–Rh(2)–P(2) dihedral angle being 150.5°. The carbonyls are therefore rotated by 29.6° from an eclipsed position. The Rh–Rh bond length of 2.814 Å is somewhat longer than that of Rh metal[13] but is still consistent with the presence of a single metal–metal bond. There are very few compounds known with Rh–Rh bonds unsupported by bridging ligands.[14] Two binuclear isocyanide structures appear to have the greatest relevance to the present structure. The Rh(I) complex $(CNPh)_8Rh_2^{2+}$ has a very long Rh–Rh bond (3.193 Å),[15] but a much shorter distance (2.785 Å) is found in the formal Rh(II) analogue $(CNR)_8Rh_2I_2^{2+}$.[16]

The trimethylphosphine complex $CpRh(CO)PMe_3$ (**2**) also forms a metal–metal bonded dication, $\mathbf{2}_2^{2+}$, upon oxidation. The peak potentials for the oxidation of **2** and the reduction of $\mathbf{2}_2^{2+}$ are +0.32 and −0.23 V, respectively. The dication was poorly soluble, leading to voltammetric difficulties (e.g., electrode passivation) but easy isolation of $\mathbf{2}_2^{2+}$ from coulometric experiments. When millimolar solutions of **2** in CH_2Cl_2 were electrolyzed, pure red microcrystals of $[CpRh(CO)PMe_3]_2[PF_6]_2$ were obtained.[17]

Two aspects of these results deserve some comment at this stage of our investigations. First, it has now been demonstrated that cationic 17-electron complexes differing only in the coordinated phosphine can undergo metal–metal as well as ligand–ligand coupling. On the subject of the unsupported M–M bond, two recent reports are relevant. The osmocenium dimer $[Cp_2Os]_2^{2+}$ is formed when osmocene is treated with the two-electron oxidant Ce(IV).[18] This reaction most likely involves comproportionation of Cp_2Os^{2+} and Cp_2Os, with dimer formation proceeding through the coupling of two Cp_2Os^+ radicals. Comproportionation of $Ni(CNMe)_4{}^n$ (n = 0, 2+), leads to the Ni–Ni bonded dication $[Ni_2(CNMe)_8]^{2+}$ also through the likely intermediacy of the Ni(I) monocation $Ni(CNMe)_4{}^+$.[19] It appears that one-electron oxidation should be considered as a general strategy for the synthesis of charged complexes with unsupported metal–metal bonds. Second, it is not yet clear why the $P(OPh)_3$ and PMe_3 derivatives **1** and **2** behave differently than the PPh_3 derivative, which forms the fulvalene complex. Molecular orbital calculations[20,21] and photoelectron spectroscopy data[22] have shown that the HOMO in CpRh(CO)L complexes is $1b_1$, an admixture of the cyclopentadienyl $e_1{}^+$ and metal d_{xz}. The latter is oriented in the right direction to account for the observed M–M coupling. Experiments on the oxidation of other complexes with bulky phosphines are proceeding to see if steric effects are the reason for the lack of a stable metal–metal bonded dimer arising from the oxidation of $CpRh(CO)PPh_3$.

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Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, anisotropic thermal parameters, and H-atom coordinates (7 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Dynamics of Hydrogen Migrations in $(H)Fe_2(ethene)^+$ and $(H)Fe_2(propene)^+$ in the Gas Phase

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Summary: The dynamics of hydrogen migration in $(H)Fe_2(ethene)^+$ and $(H)Fe_2(propene)^+$ systems are investigated in the gas phase by using Fourier transform mass spectrometry along with specific isotopic labeling. The results suggest small barriers for reversible insertion into allylic C–H bonds for $(H)Fe_2(propene)^+$ with substantially larger barriers for either reversible vinylic C–H bond insertion or reversible olefin insertion/β-elimination processes.

Studying the dynamics of fundamental hydrogen migrations of organometallic species is of paramount importance in catalysis.[1] For example, the reversible insertion of an olefin into a metal–hydrogen bond, process 1, has been postulated as a key component in many catalytic cycles (e.g., hydroformylation,[2] hydrogenation,[3] and olefin isomerization[4]) which kinetic studies have revealed, in general, to be facile and reversible.[5] In addition to the above reversible β-hydrogen insertion, the reversible insertion into vinylic C–H bonds of ethene (process 2)[6,7] as well as reversible insertion into allylic C–H bonds of propene (process 3)[8] are also possible modes for hydrogen migrations.

$$(H)M(CH_2{=}CH_2) \rightleftharpoons M(-CH_2{-}CH_3) \qquad (1)$$

$$(H)M(ethene) \rightleftharpoons (H)_2M(-CH{=}CH_2) \qquad (2)$$

$$(H)M(propene) \rightleftharpoons (H)_2M(allyl) \qquad (3)$$

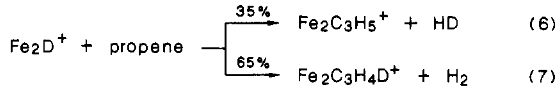
The dynamics of these hydrogen migrations can be explored by using gas-phase ion techniques along with specific isotopic labeling. In this paper we describe the reactions of the triatomic species, Fe_2H^+ (Fe_2D^+), with ethene and propene, focusing on the hydrogen migrations involved in these systems. In this case, hydrogen migrations are driven by the energy derived from coordination of the alkene to Fe_2H^+ (Fe_2D^+) which we estimate to be ~40 kcal/mol.[9] The kinetics of these hydrogen migrations, studied by monitoring isotopic (H/D) scrambling, can yield insights into both the mechanism involved in the (H/D) scrambling as well as the nature of the potential energy surface for the hydrogen migrations, processes 1–3. This methodology is analogous to studies involving multiple proton transfers within an ion–dipole complex as a method for probing potential energy surfaces.[10]

The reactant triatomic species, Fe_2H^+ (Fe_2D^+), was generated by using a Nicolet FTMS-1000 Fourier transform mass spectrometer[11,12] in a two-step process involving initial protonation (deuteriation) of $Fe(CO)_5$ by CH_5^+ (CD_5^+) yielding both $HFe(CO)_5^+$ ($DFe(CO)_5^+$) and $HFe(CO)_4^+$ ($DFe(CO)_4^+$). $HFe(CO)_4^+$ ($DFe(CO)_4^+$) undergoes a facile reaction with $Fe(CO)_5$ generating $HFe_2(CO)_8^+$ ($DFe_2(CO)_8^+$) which is unreactive with $Fe(CO)_5$. Collisional activation (CA)[13,14] of $HFe_2(CO)_8^+$ ($DFe_2(CO)_8^+$) results in facile eliminiation of the carbonyls yielding Fe_2H^+ (Fe_2D^+) which is subsequently isolated by swept double resonance ejection pulses.[12] This method undoubtedly results in the formation of Fe_2H^+ (Fe_2D^+) with a distribution of internal energies. The CA target gas (methane) pressure was high (~1×10^{-5} Torr) relative to the alkene pressure (~3×10^{-8} Torr),[15] therefore, in order to allow this excess energy to be dissipated by thermalizing collisions with methane prior to reaction with the alkenes. Observation of linear first-order kinetics upon reaction is evidence that these ions are indeed thermalized. Finally, $Fe(CO)_5$ was admitted into the vacuum chamber via a pulsed solenoid inlet valve[16] allowing it to be pumped from the chamber within 500 ms permitting these studies to be performed without complicating side reactions with $Fe(CO)_5$.

Ethene reacts with Fe_2D^+ yielding the symmetric exchange product Fe_2H^+ exclusively, process 4, with a rate constant of $(8.0 \pm 1.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Comparison with the Langevin collision frequency[17] of 1.0×10^{-9} cm^3 molecule^{-1} s^{-1} indicates that ~8% of the collisions result in exchange. In contrast propene reacts with Fe_2H^+ exclusively by dehydrogenation, process 5, with a rate constant of $(8.7 \pm 1.7) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (average dipole orientation rate = 1.1×10^{-9} cm^3 molecule^{-1} s^{-1}).[17] Substantial scrambling of the label is observed in the dehydrogenation of propene by Fe_2D^+, reactions 6 and 7, with essentially none (<1%) of the symmetric exchange product, Fe_2H^+, observed. In addition, Fe_2H^+ reacts with propene-2-d_1, yielding exclusive elimination of H_2, reaction 8.

$$Fe_2D^+ + C_2H_4 \rightarrow Fe_2H^+ + C_2H_3D \qquad (4)$$

$$Fe_2H^+ + propene \rightarrow Fe_2C_3H_5^+ + H_2 \qquad (5)$$



$$Fe_2D^+ + propene \xrightarrow{35\%} Fe_2C_3H_5^+ + HD \qquad (6)$$

$$Fe_2D^+ + propene \xrightarrow{65\%} Fe_2C_3H_4D^+ + H_2 \qquad (7)$$

$$Fe_2H^+ + propene\text{-}2\text{-}d_1 \xrightarrow{100\%} Fe_2C_3H_4D^+ + H_2 \qquad (8)$$

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$$ND_3^+ + C_2H_4 \rightarrow ND_3H^+ + C_2H_3$$

which has a reported rate constant of $1.3 \pm 20\% \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}. (Smith, D.; Adams, N. G. *Chem. Phys. Lett.* **1980**, *76*, 418). Propene pressure was measured by using the ethene calibration along with the ionization cross sections of ethene and propene.

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The scrambling observed in reaction 4 may proceed by either reversible insertion of an olefin into a metal–hydrogen bond, process 1, or by reversible insertion into vinylic C–H bonds of ethene, process 2. Labeling studies clearly cannot distinguish these two processes in this case. A single vinylic insertion/deinsertion (process 2) or ethene insertion (process 1) would result in exchange rates of 50% of 67%, respectively, of the collision rate with complete scrambling by multiple insertions yielding an exchange efficiency of 80% (assuming no isotope effects). The observed exchange efficiency of 8% for process 4 implies that a maximum of 16% of the collisions result in reaction. This slow rate of exchange is indicative of substantial barriers for both processes 1 and 2.[10]

Reaction with propene is quite different with facile dehydrogenation, process 5, and substantial scrambling is observed with Fe_2D^+, processes 6 and 7. If facile, reversible vinylic insertions were responsible for the scrambling in processes 6 and 7, then reaction of Fe_2H^+ with propene-2-d_1 should yield a 1:1 ratio of H_2 vs HD elimination whereas facile, reversible alkene insertion, process 1, should scramble all hydrogens yielding an H_2:HD elimination ratio of 71%:29%. Both processes 1 and 2 would result in scrambling of the C2 hydrogen on propene. Absence of HD elimination for reaction of Fe_2H^+ with propene-2-d_1 reveals that the C2 hydrogen on propene is not scrambled; therefore, neither process 1 nor process 2 can account for these results. These results, however, can be rationalized by invoking rapid interconversion of a hydrido propene complex with a dihydrido allyl species by reversible insertion across allylic C–H bonds, process 3. Such a scrambling process would render the C2 hydrogen unexchangeable as observed in reaction 8. Complete scrambling of the five terminal hydrogens of propene in reactions 6 and 7 would yield a dehydrogenation distribution consisting of 33% HD and 67% H_2 elimination which is observed. This suggests that the barrier for the reversible insertion of Fe_2H^+ into an allylic C–H bond of propene is very small since it must be traversed several times prior to dehydrogenation.

Additional aspects of the dehydrogenation process 5 can be investigated by monitoring H/D exchange of $Fe_2C_3H_5^+$ with D_2 where *only* four hydrogens are exchangeable, process 9. This exchange is slow with a rate constant for

$$Fe_2(CH_2CHCH_2)^+ \xrightarrow[-4HD]{4D_2} Fe_2(CD_2CHCD_2)^+ \qquad (9)$$

the first exchange roughly 1/10 of the Langevin collision rate.[18] These exchanges can again be rationalized by invoking initial addition of deuterium to the metal centers followed by reversible conversion of the dideuterioallyl species with a deuteriopropene complex resulting in elimination of HD. This scrambling accounts for the four exchangeable hydrogens in $Fe_2C_3H_5^+$ where the C2 hydrogen remains unexchanged as has previously been observed for $CpRh(allyl)^+$.[19] This was substantiated by monitoring H/D exchange of $Fe_2C_3H_4D^+$, formed in reaction 8, with D_2 where *all* four hydrogens undergo exchange, indicating the C2 hydrogen is clearly the unique, unexchangeable hydrogen.

These results demonstrate that the dynamics of hydrogen migrations on small transition-metal centers can be probed by using gas-phase ion techniques. The origin of the barriers to ethene insertion into an Fe–H bond or insertion into a vinylic C–H bond is unclear for these systems at this time, however, they may be simply due to spin multiplicity restrictions.[20] Such an argument has been used to account for the stability of $Cp_2Mo(H)(C_2H_4)^+$ which does not undergo unimolecular ethene insertion into the M–H bond forming an alkyl species.[21] Additional work in this area concerning these very fundamental and important hydrogen migrations as a function of cluster size and ligand environment should yield important insights into the the factors affecting these arrangements and is currently being pursued in our laboratory.

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Registry No. $(H)Fe_2(ethene)^+$, 112022-66-9; $(H)Fe_2(propene)^+$, 112022-67-0.

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[18] It was impossible to accurately measure the H/D exchange rate; however, it clearly is quite slow and was estimated to proceed at 1/10 the Langevin collision frequency.

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Molecular Structure of $\{Cp_2Ti(PMe_3)\}_2(\mu\text{-}N_2)$, a Titanocene Dinitrogen Complex

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Summary: Treatment of benzene solutions of bis(trimethylphosphine)titanocene, $Cp_2Ti(PMe_3)_2$ (**1**), with 1 atm of N_2 results in formation of an equilibrium mixture containing ca. 30% of $\{Cp_2Ti(PMe_3)\}_2(\mu\text{-}N_2)$ (**2**), a bridging dinitrogen complex of titanocene. Compound **2** can be isolated in 56% yield by stirring a petroleum ether slurry of **1** under N_2 and filtering. The solid-state structure of **2**, as determined by single-crystal X-ray diffraction methods, exhibits a relatively long N–N bond and short Ti–N bonds, consistent with substantial back-bonding from the titanium centers to the coordinated dinitrogen.

The coordination and reduction of molecular nitrogen by group 4 metallocenes has been the subject of intense study and some controversy.[1] Much of the ambiguity surrounding this chemistry stems from the instability and resulting complexity of the parent "titanocene". Three research groups have reported the preparation of unstable dimeric nitrogen complexes of composition $\{Cp_2Ti\}_2N_2$ (Cp $\equiv \eta^5\text{-}C_5H_5$), however, the properties of the compounds vary and their relationship is not clear.[2] Although the work

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