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]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 80-06331) and the M. H. Wrubel Computer Center. We are particularly grateful to Cleveland Refractory Metals for material support.

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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[18] (a) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1716. (b) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1204.

[19] Trogler, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 6459.

[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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Received December 14, 1981

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).

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

$$M = Ti, Rh \quad M' = Fe, Ni$$

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

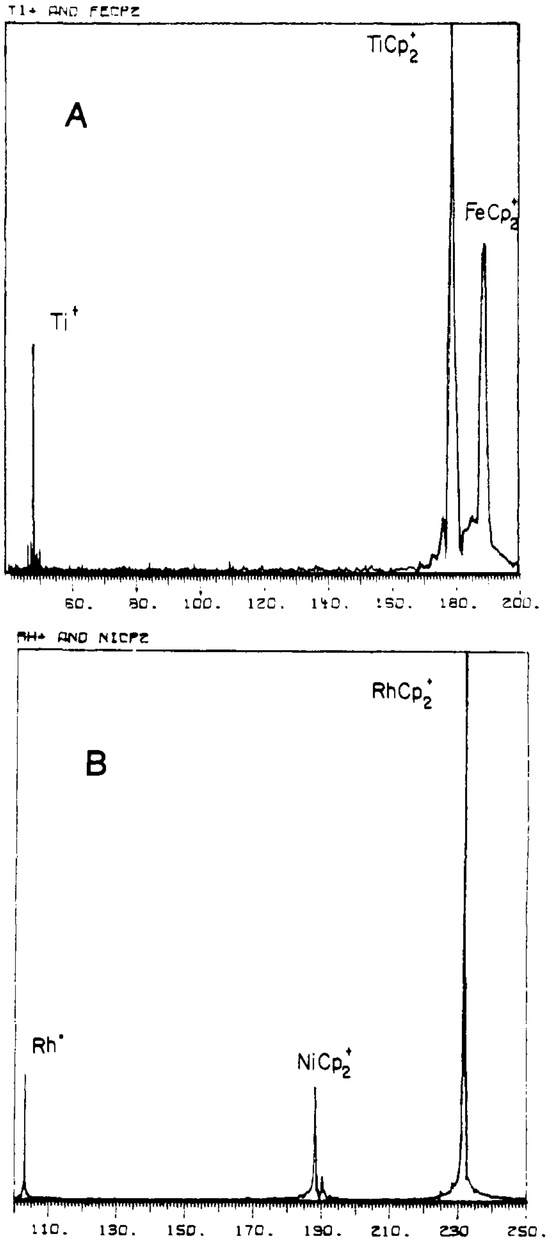

Figure 1. Fourier-transformed mass spectra arising from single laser pulses with (A) Ti^+ trapped for 3 s in the presence of ferrocene (8K transformation) and (B) Rh^+ trapped for 1 s in the presence of nickelocene (64K transformation). The pressure in both cases is ~3 × 10^{-7} torr.

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[1] Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125.

[2] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; pp 1163–1167 (1980).

[3] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; pp 706–708.

[4] (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641.

[5] (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (b) Allison, J.; Freas, R. B.; Ridge, D. P. *Ibid.* **1979**, *101*, 1332.

[6] Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794.

[7] (a) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449. (b) Corderman, R. R.; Beauchamp, J. L. *Ibid.* **1976**, *98*, 3998. (c) Foster, M. S.; Beauchamp, J. L. *Ibid.* **1975**, *97*, 4808.

[8] Parisod, G.; Comisarow, M. B. *Adv. Mass Spec.* **1980**, *8*, 212.

[9] (a) Marshall, A. B.; Comisarow, M. B.; Parisod, G.; *J. Chem. Phys.* **1979**, *71*, 4434. (b) Comisarow, M. B. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *37*, 251.

0002-7863/82/1504-2320$01.25/0

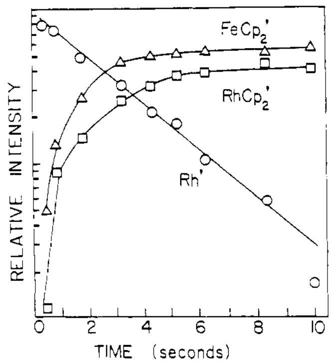

Figure 2. Temporal variation of ion abundance for the Rh$^+$–ferrocene system. The pressure is $\sim 10^{-7}$ torr.

Table I. Relative Product Distributions for the Primary Reactions of Ti$^+$ and Rh$^+$ with Ferrocene and Nickelocene

reaction		rel product dist, %	
M$^+$	M'Cp$_2$	MCp$_2^+$ [a]	M'Cp$_2^+$ [b]
Ti$^+$	FeCp$_2$	63	37
Ti$^+$	NiCp$_2$	40	60
Rh$^+$	FeCp$_2$	43	57
Rh$^+$	NiCp$_2$	83	17

[a] Metal switching. [b] Charge Exchange.

desorption are prone to adsorb neutrals which are vaporized by the next laser shot.[10] This produces a localized high-pressure gradient in the cell that varies from shot to shot. So that representative pressures could be recorded, several rapid laser pulses were used to remove surface-adsorbed gases, followed by a single laser pulse from which the Fourier transform mass spectrum was recorded.

The primary reaction trends for the four systems investigated are similar. In all cases the two metallocene products come up together in time and dominate after a few seconds, as exemplified by Figure 2. Reaction 1 dominated in the Rh$^+$/NiCp$_2$ and Ti$^+$/FeCp$_2$ cases while reaction 2 prevailed in the Rh$^+$/FeCp$_2$ and Ti$^+$/NiCp$_2$ cases. Product distributions are listed in Table I. The reactions with Rh$^+$ are in general greater than 3 times faster than the corresponding Ti$^+$ reactions and range from about 10^{-10} cm^3 molecule^{-1} s^{-1} for Rh$^+$ with FeCp$_2$ to about 10^{-9} cm^3 molecule^{-1} s^{-1} for Rh$^+$ with NiCp$_2$, compared to the Langevin rate constant for both of these reactions of 1.5×10^{-9} cm^3 molecule^{-1} s^{-1}. The observed rate constants are only good within a factor of 2, however, due to the uncertainty in the pressure. The observation of only minor amounts of MCp$^+$ or M'Cp$^+$ provides evidence for the stability of these gas-phase metallocene complexes. The TiCp$_2^+$ is observed to react further with ferrocene and nickelocene to form the mixed dimer species TiFeCp$_4^+$ and TiNiCp$_4^+$, whereas the analogous reactions are not observed for RhCp$_2^+$.

The reaction of Fe$^+$ with FeCp$_2$ to form FeCp$_2^+$ was previously confirmed by ICR[7] and probably results from charge exchange. Similarly, in our experiments Fe$^+$ reacts with nickelocene to give only the charge-exchange product NiCp$_2^+$. This result is not unusual since Fe has a higher ionization potential (IP = 7.87 eV)[11] than either FeCp$_2$ (IP = 7.0 eV)[11] or NiCp$_2$ (IP = 6.8 eV).[11] In the case of Ti (IP = 6.82 eV)[11] reaction 2 suggests that some Ti$^+$ may be formed either in an electronically excited state or with excess kinetic energy since its ground-state ionization potential is lower than that of either FeCp$_2$ or NiCp$_2$. Since these differences in IP are relatively small, metal switching (reaction 1) may be seen as competitive with charge exchange. Interestingly, the ionization potential of ground-state Rh (IP = 7.46 eV)[11] is greater than that of the two metallocenes, yet behavior similar to that of the Ti$^+$ reactions is observed. Since no charge exchange is observed between either TiCp$_2^+$ or RhCp$_2^+$ with NiCp$_2$, the upper limit for the ionization potentials of both TiCp$_2$ and RhCp$_2$ can be set at the ionization potential of NiCp$_2$, 6.8 eV.[11] This value is also consistent with not observing any Fe$^+$ or Ni$^+$ in reaction 1.

While there is no evidence that these metallocenes have the symmetrical sandwich structures, the lack of any significant fragmentation implies that both Cp rings remain intact. Further investigations into the gas-phase chemistry of TiCp$_2^+$ and RhCp$_2^+$ may provide some insights as to their actual structures. Finally, these metal-switching reactions may provide a novel method for synthesizing metallocenes and other organometallic compounds. We are currently studying the generality of these reactions with metal ions above atomic number 20 and by varying the neutral metal complexes. In addition to ferrocene and nickelocene, substituted ferrocenes and nickelocenes and other organometallic compounds such as dibenzenechromium, $(C_6H_6)_2Cr$, as well as phthalocyanines and other cyclic and macrocyclic metal chelates will be examined.

Acknowledgment is made to the Department of Energy (DE-AC02-80ER10689) for supporting this research and the National Science Foundation (CHE-8002685) for providing funds to purchase the FTMS. In addition, G.D.B. thanks Chevron for providing Fellowship support.

Registry No. Titanocene cation, 54873-35-7; rhodocene cation, 37205-11-1; FeCp$_2$, 102-54-5; NiCp$_2$, 1271-28-9.

Cyclization of Vinyl Radicals: A New Versatile Method for the Construction of Five- and Six-Membered Rings

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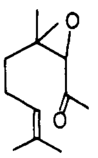
Received November 16, 1981

We report a new method of ring formation that we believe has considerable potential in synthesis. We previously made the suggestion that the cyclizations observed when certain unsaturated acyloxiranes react with hydrazine (cf. **1** → **2**) might involve an intermediate vinyl radical.[1] Regardless of the merit of this suggestion, it seemed to us that the possibility of forming rings by intramolecular addition of a vinyl radical to a double bond deserved to be explored. This appeared particularly true because such a process would result in the formation of a ring that would have a double bond at a predictable position (cf. **3** → **4** and **5** → **6**). This could then serve as the site of further synthetic operations.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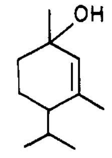
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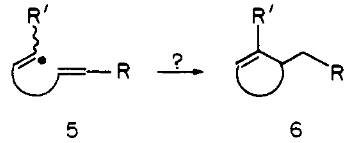

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[10] For a general discussion of laser/surface interactions see: Ready, J. F. "Effects of High Power Laser Radiation"; Academic Press: New York, 1971.

[11] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, supplement no. 1.

[1] Stork, G.; Willard, P. G. *J. Am. Chem. Soc.* **1977**, *99*, 7067.