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Hydrogenation of $RhC_7H_6^+$ in the Gas Phase

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Addition of hydrogen to transition-metal complexes, as well as the catalytic hydrogenation of unsaturated organics, are well-known processes in solution and on surfaces. In the gas phase, H/D exchanges have been observed for transition-metal complexes using deuterium, presumably proceeding through initial addition of deuterium onto the metal followed by elimination of HD.[1-4] However, no hydrogenation processes have been reported in the gas phase. We report here the first observation of a *bimolecular* hydrogenation in the gas phase by the rhodium complex, $RhC_7H_6^+$, generating $RhC_7H_8^+$, which is apparently stabilized by infrared radiative stabilization.[5]

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer utilizing a 0.9-T magnetic field. The theory, instrumentation, and methodology of conventional ion cyclotron resonance (ICR)[6] and Fourier transform mass spectrometry (FTMS)[7] have been discussed at length elsewhere. Details of the laser ionization technique used to generate metal ions[8] and collision-induced dissociation (CID) experiments for ion structural studies[9-11] have previously been described.

Rh^+ reacts with toluene[3] to produce exclusively $RhC_7H_6^+$ (process 1). The same reaction with toluene-α-d_3 yields 70% D_2

$$Rh^+ + \text{toluene} \rightarrow RhC_7H_6^+ + H_2 \qquad (1)$$

loss and 30% HD loss. H/D exchange reactions using deuterium have been used to probe the structure of gas-phase metal ion complexes[1,2] and were used here for that purpose. The product of reaction 1 undergoes H/D exchanges when trapped in the presence of excess deuterium (Figure 1), but the unsymmetrical nature of the H/D exchanges highlighted by the deuterium distribution in the final products is indeed surprising. The results are readily explained, however, by invoking a competition between H/D exchange and the addition of D_2 where only the non-D_2-addition species undergoes exchanges (Scheme I). The hydrogenation of $RhC_7H_6^+$ was then tested by reaction with excess hydrogen (process 2) with complete hydrogenation observed. The

$$RhC_7H_6^+ + H_2 \rightarrow RhC_7H_8^+ \qquad (2)$$

$RhC_7H_6^+$ signal decays in a first-order fashion yielding a bimolecular rate constant of 6 ± 3 × 10^{-11} cm^3 molecule^{-1} s^{-1}. In addition, the hydrogenation product in reaction 2, $RhC_7H_8^+$, does not undergo any exchanges with deuterium. Hence, a competition between H/D exchanges and addition of D_2 clearly exists as suggested in Figure 1 and Scheme I. Interestingly, direct bimolecular hydrogenation of the phenyl ion, $C_6H_5^+$, has been reported.[12] While direct hydrogenation of the C_7H_6 moiety cannot be completely ruled out in this case, a metal-mediated hydrogenation seems most reasonable.

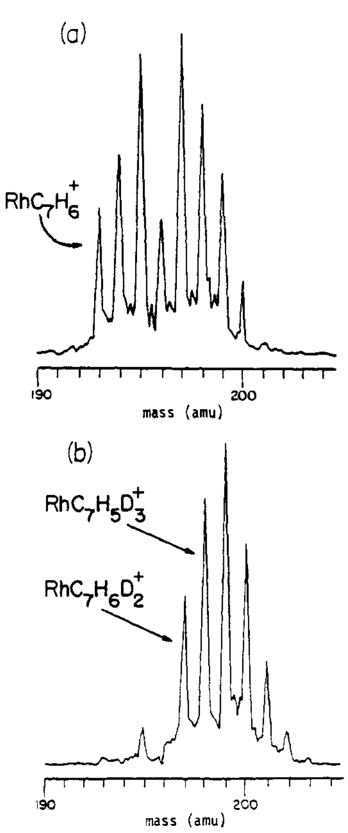
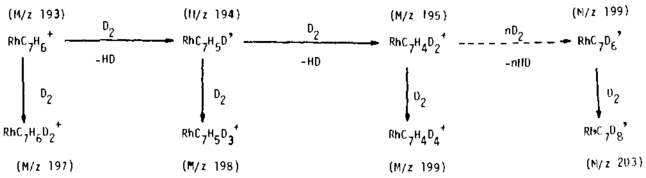


Figure 1. (a) Mass spectrum obtained when $RhC_7H_6^+$, generated in reaction 1, is trapped in the presence of 2 × 10^{-6} torr deuterium for 1.5 s. (b) Same conditions as (a) but trapped for 5 s. No change in the spectrum is seen when the trapping time is increased (from 5 to 15 s) indicating exchange and hydrogenation are complete. The small amount of *m*/*z* 195 observed corresponds to $Rh(CH_3Ph)^+$ arising from the reaction of $RhC_7H_6^+$ with background toluene.

Scheme I



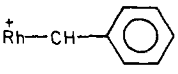
A variety of simple hydrocarbons were also found to hydrogenate $RhC_7H_6^+$. For example, ethane yields exclusively the hydrogenated species (reaction 3) with a rate constant of 8 ± 4

$$RhC_7H_6^+ + C_2H_6 \rightarrow RhC_7H_8^+ + C_2H_4 \qquad (3)$$

$$RhC_7H_6^+ + C_2H_6 \not\rightarrow Rh(C_7H_6)C_2H_4^+ + H_2 \qquad (4)$$

× 10^{-10} cm^3 molecule^{-1} s^{-1}. No reaction was seen for methane. Reaction 3 is interesting since gas-phase transition-metal ions generally react with alkanes to eliminate hydrogen and retain the olefin.[2,13] Complete absence of reaction 4 indicates that hydrogen incorporation into the C_7H_6 unit occurs prior to formation of a dihydride–olefin complex.

There are three reasonable structures for the $RhC_7H_6^+$ ions generated in reaction 1. Collision-induced dissociation of $RhC_7H_6^+$ yields predominantly RhC^+ with significant amounts of Rh^+ also



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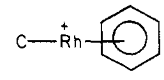

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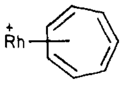

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Table I. Percentages of Neutral Losses from CID of $RhC_7H_8^+$ Complexes Accelerated to 20-eV Kinetic Energy[a,b]

neutral losses	$Rh(C_7H_8)^+$ [c]	$Rh(CH_3Ph)^+$ [d]	$Rh(c\text{-}C_7H_8)^+$ [d]
H_2	25	28	24
C_2H_2			18
$H_2 + C_6H_6$	57	56	56
C_7H_8	18	16	2

[a] Argon used as target at ~5×10^{-6} torr. [b] CID interaction time of 30 ms. [c] $RhC_7H_8^+$ generated from reactions 2 and 3. [d] Generated by displacement of ethylene from $RhC_2H_4^+$ by toluene and cycloheptatriene.

observed.[3] Benzene undergoes a condensation reaction with RhC^+ generating exclusively $RhC_7H_6^+$ (process 5). CID of this product

$$RhC^+ + C_6H_6 \rightarrow RhC_7H_6^+ \qquad (5)$$

yields exclusively RhC^+ with no Rh^+ produced suggesting formation of the carbide–benzene complex **2**. Furthermore, the product of reaction 5 does *not* add hydrogen, clearly eliminating the formation of structure **2** in reaction 1.

CID results indicate that the hydrogenated $RhC_7H_8^+$ products, formed in reactions 2 and 3, have the same structure. In addition their CID spectra are identical (same peaks, intensities, and energy dependence within experimental error) with those for $Rh(CH_3Ph)^+$ formed by ligand displacement reactions and distinguishable from CID of $Rh(c\text{-}C_7H_8)^+$ (Table I). Hence, hydrogenation of $RhC_7H_6^+$ generates formally a $Rh(CH_3Ph)^+$ complex. CID of $RhC_7H_6^+$, generated by reaction 1 with toluene-α-^{13}C, produces $Rh\text{-}^{12}C^+$ and $Rh\text{-}^{13}C^+$ in roughly a 6:1 ratio indicating nearly complete scrambling. This could arise if complexes **1** and **3** are in equilibrium. Lending some support to this possibility is the fact that phenylcarbenes have been found to undergo facile reversible rearrangement to cycloheptatrienylidenes in the gas phase at 250–600 °C[14] and have been treated theoretically.[15] One can rationalize that structure **3** may be undergoing H/D exchanges while hydrogenation of the phenylcarbene complex, **1**, produces the toluene complex.

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Registry No. Rh^+, 20561-59-5; CH_3Ph, 108-88-3.

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Low-Valent Transition-Metal Cyanides: A Crown Ether Strategy for the Development of Their Solution Chemistry

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That cyanide can stabilize the zero oxidation state in transition-metal complexes has been evident for over 40 years.[1,2] However, little is known concerning the reactivity of such complexes. Perhaps the primary barrier to the development of the chemistry of $M(CN)_x^{x-}$ complexes has been their solubility properties. These complexes are isolated as potassium salts, which are completely insoluble in all nonreactive solvents. The same is often true of the ionic reaction products. For example, $K_4Ni(CN)_4$[1] in acetonitrile suspension reacts with $PhC{\equiv}CPh$ as evidenced by a color change of the suspended solid. Examination of the product reveals that only a surface layer of $K_4Ni(CN)_4$ has reacted with the acetylene.

We now report a general strategy for dealing with this problem, which has enabled the first synthesis of organonickel cyanides from $K_4Ni(CN)_4$. 18-Crown-6 (**1**) has a profound influence on the course of several chemical reactions involving $K_4Ni(CN)_4$, in spite of its ineffectiveness as a solubilizing agent for $K_4Ni(CN)_4$ in MeCN.[3] Diphenylacetylene (1 equiv) reacts with $K_4Ni(CN)_4$ (1 equiv) in the presence of **1** (2 equiv) with CH_3CN or THF as solvent to give the novel blue-violet complex $(K^+\text{-}\mathbf{1})_2[Ni(CN)_2(PhC{\equiv}CPh)]$ (**2**) (50%) (eq 1). Complex **2** itself does not react

$$K_4Ni(CN)_4 + PhC{\equiv}CPh \xrightarrow[CH_3CN,\ \mathbf{1}]{} \underset{\mathbf{2}}{(K^+\text{-}\mathbf{1})_2[Ni(CN)_2(PhC{\equiv}CPh)]} \qquad (1)$$

with excess $PhC{\equiv}CPh$ nor are any organic products evident under the conditions examined thus far. IR and ^1H and ^{13}C NMR data are supportive of an alkyne symmetrically bound to a $Ni(CN)_2^{2-}$ moiety.[4] Compound **2** is the first organometallic complex (excluding carbonyls) to be prepared directly from $K_4Ni(CN)_4$. It is also the first member of the (alkyne)NiL_2 class where L = CN^- and the first anionic member.[5]

Efforts to extend this approach to other potential ligands revealed another aspect of the reactivity of $K_4Ni(CN)_4$. While H_2, CO_2, 1,3-butadiene, and 1,5-cyclooctadiene all failed to give evidence of complex formation, consumption of $K_4Ni(CN)_4$ in a slow reaction with MeCN was noted. The nature of this reaction was illuminated by the observation that benzaldehyde reacted under these conditions to give an unexpected product:

$$PhCHO + K_4Ni(CN)_4 + CH_3CN \xrightarrow[CH_3CN,\ 40\%]{\mathbf{1}} \underset{\mathbf{3}}{[(\eta^2\text{-}PhCH{=}CHCN)Ni(CN)_2](K\text{-}\mathbf{1})_2} \qquad (2)$$

The spectral evidence for the nature of **3** is straightforward[6a] and closely parallels that for the related $NiL_2(CH_2{=}CHCN)$[6b] and $((E)\text{-}PhCH{=}CHCN)Co(CN)_4^{3-}$[6c] complexes. The identity of **3** is confirmed by the observation that it can be prepared directly from (E)-cinnamonitrile by using the same crown ether method. The apparent implication of reaction 2 is that the $K_4Ni(CN)_4$ + **1** *combination* is a strong enough base to deprotonate acetonitrile (pK_a ~31)[7] to an appreciable extent. By contrast, "normal"

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(4) IR (Nujol mull) 2069 (s, $\nu_{C{\equiv}N}$), 2053 (s, $\nu_{C{\equiv}N}$), 1753 (m, br, $\nu_{C{\equiv}C}$), 1731 (m, br, $\nu_{C{\equiv}C}$), 1583 (s, $\nu_{C{=}C(Ph)}$); ^1H NMR (CD_3CN) δ 7.84–6.84 (m, 10 H), 3.60 (s, 48 H); ^{13}C NMR (CD_3CN) δ 140.6 (CN), 137.9 ($C{\equiv}C$), 128.9, 127.6, 123.2, 123.0 (Ph), 70.1 (18-crown-6). Anal. ($C_{40}H_{58}N_2O_{12}$-K_2Ni) C, H, N, Ni.

(5) An analogous reaction occurs with 3-hexyne, but the product has proven to be too unstable to fully characterize although apparently analogous by IR. Reaction with phenylacetylene does not appear to be analogous and as yet has not yielded tractable materials.

(6) (a) IR (Nujol mull) 2161 (s, [C=C]C≡N), 2081 (s, [Ni]C≡N), 2069 (s, [Ni]C≡N), 1590 (s), 1569 (w), ^1H NMR (CD_3CN) δ 6.90 (s, Ph), 3.62 (s, 18-crown-6), 2.68 (d, J = 9.75 Hz, HPhC=), 1.60 (d, J = 9.75 Hz, =C(CN)H); ^{13}C NMR δ 150.6 (NiCN), 128.9, 127.8, 124.1, 119.8 (Ph), 114.1 (nitrile CN), 70.2 (18-crown-6), 40.1 (PhHC=), 25.1 (=C(H)(CN)). (b) Tolman, C. A.; Seidel, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 2774–2780. Tolman, C. A.; English, A. D.; Manzer, L. E. *Inorg. Chem.* **1975**, *14*, 2353–2356. (c) Funabiki, T.; Hosomi, H.; Yoshida, S.; Tarama, K. *J. Am. Chem. Soc.* **1982**, *104*, 1560–1568.

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