the Pt-DGC materials are significantly more stable under the reaction conditions for H^+ reduction than bulk platinum. The current density for H^+ reduction with the Pt-DGC sample decays by less than 20% after 1 h of electrolysis. In contrast, pure platinum electrodes mounted in glass decayed by 75% over the same period, to current densities lower than those of the Pt-DGC samples despite the low atomic percentage of platinum present in the Pt-DGC materials. Dioxygen reduction was also studied on the thin-film Pt-DGC, bulk platinum, and GC, as shown in Figure 2B. At both pH 7 and pH ~0, the incorporation of nanoscale platinum particles reduced the overpotential for dioxygen reduction by about 800 mV *and resulted in a voltammetric response similar to that of pure platinum.*

Assessments of the catalytic efficiency of our initial Pt-DGC thin films indicate similar current densities to those of electroformed platinum microparticles (measured in micrograms of Pt per square centimeter of geometric electrode area).[5a–c,g] However, we have prepared Pt-DGC films with up to 2 orders of magnitude lower platinum loadings without sacrificing catalytic activity.

Pt-DGC materials differ fundamentally from electroformed platinum particles in polymer films. The average particle diameter of ca. 16 Å for Pt-DGC is much smaller than the typical 600 Å observed for electroformed platinum. The DGC matrix is conducting at all potentials and is quite stable at elevated temperatures or in harsh chemical environments. The rigid sp^2-carbon matrix may not only prevent particle coalescence but also adsorb potential poisons. We are continuing to explore the properties of these Pt-DGC materials and their use on a variety of substrates.

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Registry No. 1, 101848-54-8; **2**, 12120-15-9; Pt, 7440-06-4; C, 7440-44-0; O_2, 7782-44-7; H^+, 12408-02-5; $HClO_4$, 7601-90-3.

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(16) These Pt-DGC materials show greatly increased H^+ reduction current relative to the PtO_2-doped GC reported previously.[9a]

Gas-Phase Reaction of Iron Carbonyl Cations with Atomic Hydrogen and Atomic Nitrogen

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Whereas a large number of ion–molecule reactions, as well as various atom–molecule reactions, have been studied in the gas phase, there is a scarcity of experimental data concerning the reactivity of ions with free atoms such as hydrogen[1] or nitrogen[2] or with radical species. In the case of metal or metal-containing ions, no information has been reported on their reactions with atoms.

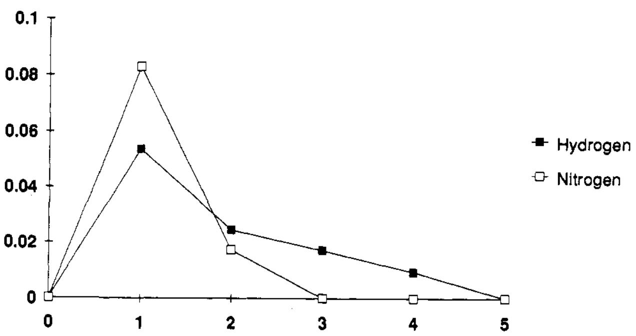

Figure 1. Extent of formation of $HFe(CO)_{n-1}^+$ from $Fe(CO)_n^+$ and hydrogen atoms (H_2 pressure: 1.5×10^{-3} Torr) and of $NFe(CO)_{n-1}^+$ from $Fe(CO)_n^+$ and nitrogen atoms (N_2 pressure: 6.5×10^{-4} Torr) as a function of the number n of CO ligands. The extent of formation is defined as the ratio of product ion intensity to total ion current.

Interest in the knowledge of such processes is two-fold. (i) Astrophysical: Free atoms, the most abundant of which being $H^\bullet$, are important components of the interstellar medium, and electropositive elements such as transition metals are likely efficiently photoionized to positive ions; therefore metal ions might react with free atoms or with radicals under interstellar conditions and perhaps play the role of catalysts.[3] (ii) Chemical: Reactions of free atoms with metal-containing ions may lead to new organometallic species or provide useful thermochemical data.

We report here our first results concerning the reactivity of iron carbonyl cations with molecular and atomic hydrogen or nitrogen. The reactions involving atomic species can be summarized in the following equations:

$$Fe(CO)_n^+ + H^\bullet \rightarrow HFe(CO)_{n-1}^+ + CO \qquad n = 1\text{–}4 \quad (1)$$

$$Fe(CO)_n^+ + N^\bullet \rightarrow NFe(CO)_{n-1}^+ + CO \qquad n = 1,2 \quad (2)$$

Ions were generated by electron impact on $Fe(CO)_5$ in the EI/CI source of a multiquadrupole MS/MS/MS instrument,[4] mass-selected by the first analyzer, and guided to the collision cell with an average kinetic energy of approximately 2 eV.[5] Hydrogen (respectively nitrogen) atoms were obtained by dissociation of molecular hydrogen (respectively nitrogen) in a microwave discharge at a pressure of ca. 1 Torr; these atoms were injected through a flow restriction in the second collision cell of the spectrometer.[6] The pressure in the collision cell was in the range 0.2–2 mTorr. Under such conditions the gas flow is relatively slow, allowing most of the electronically and vibrationally excited molecules produced in the discharge to be quenched before reaching the cell;[7] in counterpart, atom recombination prevents

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(5) The corresponding center-of-mass collision energies, depending on reactant masses, vary between 0.01 and 0.07 eV (0.2–1.6 kcal/mol) for atomic and molecular hydrogen and between 0.1 and 0.7 eV (3–15 kcal/mol) for atomic and molecular nitrogen.

(6) The discharge was effected in a 7-mm-diameter Pyrex tube, with a frequency of 2.45 GHz and a power of 60 W. About 10 cm separated the discharge zone from the end of the tube, from which a 0.4-mm-diameter hole, followed by a 30-cm-length, 4-mm-diameter Teflon tube, led to the collision cell.

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the occurrence of high dissociation fractions.[8] The reaction products were detected by scanning the third analyzer. All the experiments were carried out with the discharge successively off and on.

Bare iron cation Fe^+ did not react with molecular hydrogen, nor with molecular nitrogen; the cross section reported for the reaction of hydrogen with Fe^+ ions produced by EI on $Fe(CO)_5$ is ca. 2×10^{-18} cm^2 at low collision energy,[9b] which is too low to be detected under our reaction conditions. In the presence of atomic hydrogen or nitrogen (discharge on), no reaction was observed either; it is not surprising, since collisional stabilization of short-lived diatomic intermediates such as FeH^+ or FeN^+ is very unlikely at the pressure used, while radiative association is far too slow.[3]

The major reaction observed between $Fe(CO)_n^+$ and molecular hydrogen or nitrogen was fragmentation to $Fe(CO)_{n-1}^+$, with an extent of 3–10% of the total ion current at 1.5×10^{-3} Torr in the case of H_2, and 20–30% at 6.5×10^{-4} Torr in the case of N_2.[10]

For $n = 1$ or 2, the reaction with H_2 provided a second product of interest: FeH_2^+ from $FeCO^+$, $Fe(CO)H_2^+$ from $Fe(CO)_2^+$, with an extent of ca. 1%. We have yet no structural information on these ions; they may be simple association complexes between Fe^+ or $FeCO^+$ ions and H_2 molecule, similar to the known compound LiH_2^+.[12] Similar complexes with N_2 are possibly formed from reaction of $Fe(CO)_n^+$ with N_2, since the binding affinities of alkali cations for N_2 are larger than for H_2;[12b] these products cannot be detected since they are isobaric with the reactant ions.

The only other ions detected in the reaction mixtures were present in small amounts and arose from reaction of $Fe(CO)_n^+$ with oxygen and water impurities: for $n = 1$, these ions were FeO^+,[13] $FeOH^+$,[14] FeH_2O^+,[14] and FeO_2^+.[15] CO-containing byproducts were similarly formed from other $Fe(CO)_n^+$ ions: $Fe(CO)_{n-1}OH^+$ (n = 1–4), $Fe(CO)_{n-1}H_2O^+$ (n = 1–4), $Fe(CO)_{n-1}O_2^+$ (n = 1–3).

With the discharge on, a new product appeared in addition to the preceding ones, corresponding to replacement of a CO ligand by a H atom (eq 1) or a N atom (eq 2). The observed reaction extents amount to several percent, which correspond to quite efficient reactions since (i) the fractional dissociation of molecules to atoms is probably small[8] and (ii) the atom beam is introduced perpendicularly to the axis of the collision cell, so that ion–atom reactions are likely to occur only in a small fraction of the total cell length (about 1 cm instead of 12 cm), contrary to ion–molecule reactions.

In both cases the reaction efficiency decreased with the number n of CO ligands, as shown in Figure 1. This trend is more pronounced in the case of nitrogen atoms, which give no detectable product for n = 3–5. For $n = 1$ these reactions were carried out at variable pressure. In both cases the reaction extent (defined as the ratio of FeH^+ or FeN^+ to total ion current) was roughly proportional to pressure.

Although we have yet no experimental evidence of their structure, it seems likely that in all these compounds the hydrogen or nitrogen atom is bound directly to iron, by analogy with FeH^+ and FeN^+ obtained for $n = 1$.

FeH^+ has previously been obtained from endothermic reaction of Fe^+ with H_2;[9] its measured bond energy is 48.9 ± 1.4 kcal/mol,[9b] in agreement with theoretical studies.[16] Since the bond energy of $FeCO^+$ is 39.3 ± 2.0 kcal/mol,[11] reaction 1 should be exothermic by ca. 10 kcal/mol for $n = 1$.

A reaction similar to reaction 1 has been reported in aqueous solution. It involves formation of CuH^+ from hydrated Cu^+ and H atoms produced by pulse radiolysis.[17]

No experimental characterization of FeN^+ or of any transition-metal nitride cation had yet been reported; the closest related species experimentally known is $FeNH^+$.[18] The FeN^+ ion, like FeH^+, might be present in certain stars.[19] A theoretical study[20] predicts a bond energy of 24 kcal/mol for FeN^+, which is significantly less than in the nitride cations of the earlier transition metals.[21] In this case reaction 2 would be endothermic by ca. 15 kcal/mol for $n = 1$, which seems surprising in view of its efficiency.

The CO-containing hydride or nitride product ions are also new species. Their structure and reactivity are under investigation.

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(7) The flow through the hole, estimated either from hole diameter or from pump delivery, is in the range 10–100 mL s^{-1}, corresponding to a 0.05–0.5-s average residence time of the gas in the tube downstream from the discharge. This allows quenching of metastable electronic states of H_2, all of which have radiative lifetimes shorter than a few milliseconds,[7a] and collisional quenching of vibrationally excited H_2 (except the $v = 1$ level, for which only partial quenching can be expected).[7b] In the case of nitrogen, the long-lived excited state $A^3\Sigma_u^+$ is probably formed, but as it is very efficiently quenched by nitrogen atoms ($k = 3 \times 10^{-11}$ cm^3 atom^{-1} s^{-1}), this state is actually not detected downstream from a microwave discharge.[7c] (a) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold Company: New York, 1979; pp 240–253 and references cited therein. (b) Cacciatore, M.; Capitelli, M.; Billing, G. D. *Chem. Phys. Lett.* **1989**, *157*, 305–308. (c) Vidaud, H.; Wayne, R. P.; Yaron, M.; Von Engel, A. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1185–1193.

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This study is being extended to other metal ions and other free atoms. Preliminary experiments indicate that chromium carbonyl and tungsten carbonyl ions behave similarly to iron carbonyl ions toward hydrogen and nitrogen atoms.

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Catalytic Palladium-Mediated Tetraene Carbocyclizations: The Cycloisomerizations of Acyclic Tetraenes to Cyclized Trienes

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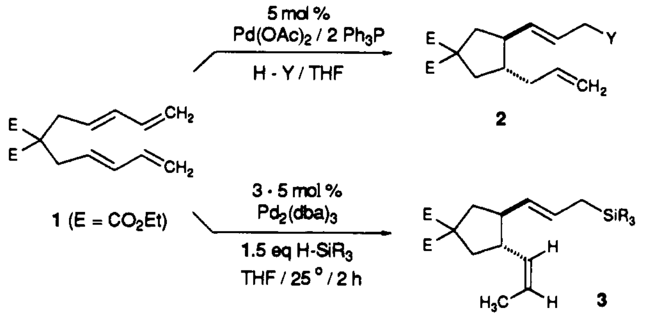
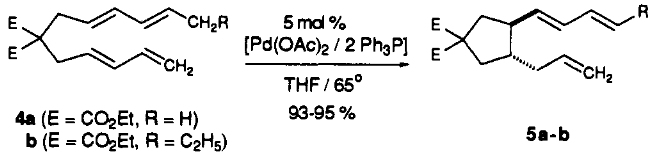
Among the more important new catalytic strategies for the construction of common organic ring systems are the transition-metal-mediated carbocyclizations[1] of substrates containing two or more elements of unsaturation. For example, catalytic transition-metal-mediated cycloisomerization reactions are under development which effect intramolecular cyclizations via formal cycloaddition,[2-6] hydrovinylation,[7-9] and ene[10-14] reaction pathways. We recently initiated a study of the catalytic transition-metal-mediated carbocyclizations of certain tetraene substrates containing within their structures two 1,3-diene subunits. Such substrates are appealing as synthetic intermediates in that they are readily accessible,[15] are reasonably robust,[16] and leave functionality in the cyclized product that is useful for further synthetic transformation. To date, we have reported two novel palladium-catalyzed tetraene cyclizations. One bond construction involves the cyclization of simple symmetric tetraenes (e.g., **1**) with incorporation of a "protic" H-Y trapping reagent (e.g., H-Y = HOR, HNR_2, HS(O)Ar, RCH_2NO_2, $H_2C(CO_2R)_2$) to afford products with the general structure **2**.[19,20] The second mode of cyclization leads to compounds of general structure **3** and is observed when "nonprotic" trapping reagents (e.g., hydrosilanes, tin hydrides, disilanes) are employed.[21] Both cyclization modes follow directly from what is known for the palladium-catalyzed dimerization of 1,3-butadiene and are in effect intramolecular variants of butadiene telomerization reactions.[22]



An issue critical to the synthetic utility of palladium-catalyzed tetraene cyclizations is whether efficient control elements can be found to direct the regioselective cyclization of unsymmetrical tetraene substrates, since substrates in which the two 1,3-diene subunits are differently substituted can potentially react via a number of regioisomeric reaction pathways. We therefore prepared tetraene **4a** and investigated some of its palladium-catalyzed chemistry. Treatment of **4a** with 5 mol % $Pd(OAc)_2$ and 10–15 mol % Ph_3P (THF, 65 °C, 12 h) in the absence of any trapping reagent affords triene **5a** with notable efficiency (95% chemical yield) and selectivity (>95% isomeric purity). Triene **5a** is the net result of palladium-catalyzed carbocyclization followed by apparent intramolecular transfer of an allylic hydrogen.[23] The overall transformation of an acyclic tetraene to a cyclized triene defines a new palladium-mediated reaction mode of tetraenes.[24,25]



Carbocyclization of **4a** affords predominantly the trans relative stereochemistry between substituents on the newly formed cyclopentane ring (vide infra) and predominantly the *E* geometry for the newly formed diene side chain. In a similar fashion, tetraene **4b** readily undergoes palladium-catalyzed cycloisomerization in refluxing THF to afford triene **5b** (93% yield, >93% isomeric purity). Of particular note in this latter example is the predominant *E,E* geometry of the newly formed 1,4-disubstituted 1,3-diene subunit within the upper side chain.

In contrast to **4a** and **4b**, alcohol **6** reacts only slowly (>24 h) in refluxing THF. We find that a variety of other solvents are suitable for these palladium-catalyzed cyclizations (e.g., 2-propanol, acetonitrile, toluene) and that it is often beneficial to add 5–10 equiv of triethylamine as a cocatalyst.[26] Palladium-catalyzed reaction of **6** proceeds more readily in acetonitrile/Et_3N (11 h) to afford a 1.6:1 mixture of **7a**:**7b** (66% yield). Confirmation of the trans relative stereochemistry of the side chains and

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