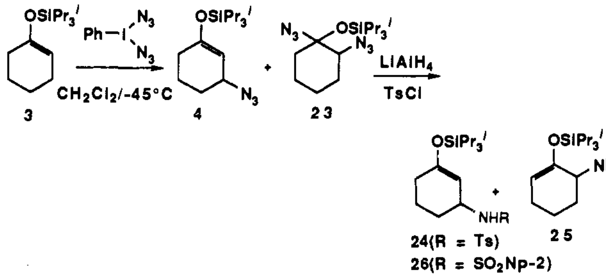
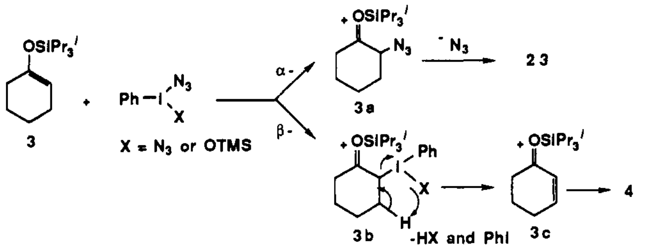
Scheme III



Scheme IV



In all cases, the reaction is complete within a few minutes at -15 °C, and the β-azido product is formed in very high yield. The only other products are iodobenzene and hexamethyldisiloxane, which are removed under vacuum. For entries 3 and 4, the β-azido compounds **8** and **10** are a 1:1 mixture of diastereomers. Particularly noteworthy is the conversion of **13** into the anomeric azide **14** (entry 6). The major azide **16** (6:1 epimers), entry 7, is assigned an axial configuration from the ^{1}H NMR coupling of the equatorial proton ($J_{a/e} = J_{e/e} = 6.5$ Hz).

Representative Experimental Procedure. To a suspension of iodosobenzene (2.64 g, 12 mmol) and 1-[(triisopropylsilyl)oxy]cyclohexene (**3**) (2.55 g, 10 mmol) in dichloromethane (100 mL) stirred under nitrogen and cooled to between -16 and -19 °C was added trimethylsilyl azide (3.19 mL, 24 mmol). After 15 min at -16 °C, the suspension became a clear solution and was allowed to warm to 25 °C. The solvent was removed in vacuo, and the resulting yellow oil was placed for 24 h under high vacuum. Flash chromatography of the oil using silica gel (230–400 mesh, 20 g) and hexane as eluent gave **4** (2.47 g, 84%) as a colorless oil after removal of the solvent.

A plausible mechanistic speculation is outlined in Scheme IV. The α-pathway is the conventional and expected reaction sequence. The β-pathway involves nucleophilic attack of **4** on the iodine atom in either **1** and/or **2** to give the oxonium ion **3b**. Elimination of HX (syn?) and PhI results in the α,β-unsaturated oxonium ion **3c**, which can add azide to give **4**. We have not detected any products resulting from 1,2-addition to **3c**, although in some cases trace amounts of α,β-unsaturated ketone is present in the crude product mixture, possibly formed by desilylation of **3c**.[6]

The scope and mechanism of this unusual new reaction is being studied, as are the potential uses of β-azido triisopropylsilyl enol ethers in synthesis.

Acknowledgment. The National Institutes of Health is thanked for support of this research (GM 32718). Rhône Poulenc is thanked for a graduate fellowship (J.L.). Dr. Vince Lynch (University of Texas at Austin) is thanked for the X-ray crystal structure of **26**.

Supplementary Material Available: Details of the X-ray structure determination of **26**, tables of fractional coordinates, isotropic thermal parameters, anisotropic thermal parameters, bond lengths and angles, and torsion angles, and spectral details for compounds **3–24**, **26**, and i/ii (32 pages). Ordering information is given on any current masthead page.

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(6) It is possible that **3c** is trapped by azide to give a 1,2-adduct (kinetic), which subsequently undergoes allylic rearrangement to the 1,4-adduct **4**. Gagneux, A.; Winstein, S.; Young, W. G. *J. Am. Chem. Soc.* **1960**, *82*, 5956. VanderWerf, C. A.; Heasley, V. L. *J. Org. Chem.* **1966**, *31*, 3534.

Nanoscale Platinum(0) Clusters in Glassy Carbon: Synthesis, Characterization, and Uncommon Catalytic Activity

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Received August 30, 1991

The preparation of nanoscale metal clusters is important because of their potential for high catalytic activity.[1] In addition, the synthesis of atomic to macrosized metal clusters is interesting from a fundamental viewpoint.[2] Successful methods for the preparation of metal clusters include metal ion reduction to give small crystallites on various surfaces[3] or colloidal dispersions,[4] metal ion reduction into polymer films coated on electrode surfaces,[5] decomposition of organometallic compounds,[6] evaporation of metals,[7] and sol–gel processes.[8] We expected that the incorporation of metals on the molecular level in a carbon precursor, followed by thermolysis, would result in a conductive, dimensionally stable carbon matrix containing metal particles of controlled composition, size, and catalytic activity. We report here the synthesis of nanoscale platinum(0) clusters in glassy carbon, the characterization of these materials, and their catalytic activity with respect to H$^+$ and dioxygen reduction.

We chose to incorporate platinum in a glassy carbon precursor by the reaction of poly(phenylenediacetylene) (**1**)[9] with (ethyl-

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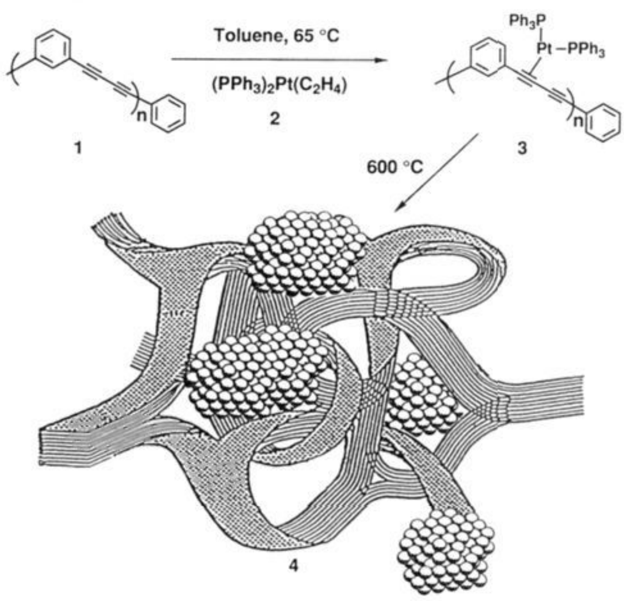
Scheme I



ene)bis(triphenylphosphine)platinum(0)[10] (**2**) (Scheme I).[11] The coordination of the platinum complex to the triple bond of the oligomer was carried out in approximately 1:4 and 1:2 ratios[12] of **2** to the butadiyne unit in **1** in toluene at 65 °C for 5 h. The resulting toluene-soluble oligomers[13] **3** were heated to 600 °C to give platinum-doped glassy carbon (Pt-DGC) as pellets or thin films on conventional glassy carbon. Raman analysis of Pt-DGC found bands at 1580 and 1360 cm^{-1}, which are consistent with the formation of an sp^2-hybridized carbon lattice similar to that found for conventional glassy carbon.[9a,14] X-ray photoelectron spectroscopic and microprobe analyses of Pt-DGC confirmed the incorporation of approximately 0.5–1 atom % of platinum(0) in glassy carbon. Transmission electron microscopic analysis (Figure 1A) of thin films of Pt-DGC found a narrow size distribution of clusters of platinum, with an average diameter of approximately 16 Å (Figure 1B).[15] Our interpretation of these analyses of Pt-DGC is that its idealized structure may be represented by **4**.

The electrocatalytic activity of the Pt-DGC materials was evaluated with H^+ reduction in 1 M $HClO_4$. From Figure 2A, curve iii, it is apparent that our synthetic GC is virtually inactive for H^+ reduction, as is conventional GC. Figure 2A, curve ii, shows that a 1 atom % Pt-DGC film of ca. 2-μm thickness on conventional GC has, within experimental error, the same overpotential for H^+ reduction as that found for pure polycrystalline platinum (Figure 2A, curve i).[16] In addition, we have found that

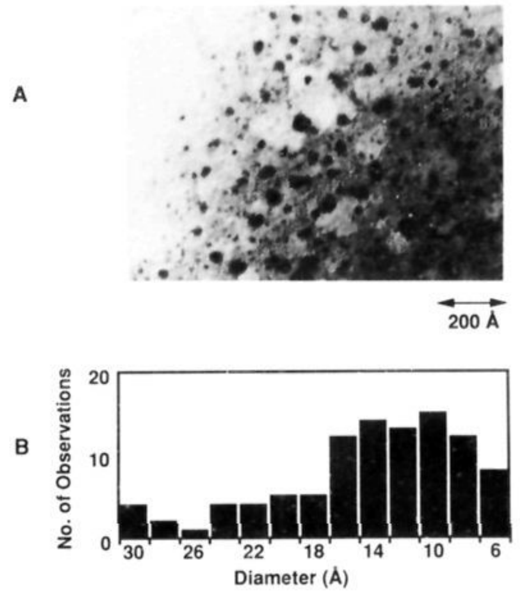


Figure 1. (A) Transmission electron micrograph of the edge of a film of Pt-DGC which was deposited onto a sodium chloride pellet and then lifted onto a copper microgrid. The dark spots represent platinum clusters. (B) Cluster diameter distribution measured from Figure 1A. Eighteen observations were recorded above 30 Å; due to the limit of resolution of the microscope (4.5 Å point-to-point), observations below 6 Å were not included in the calculation of the average diameter.

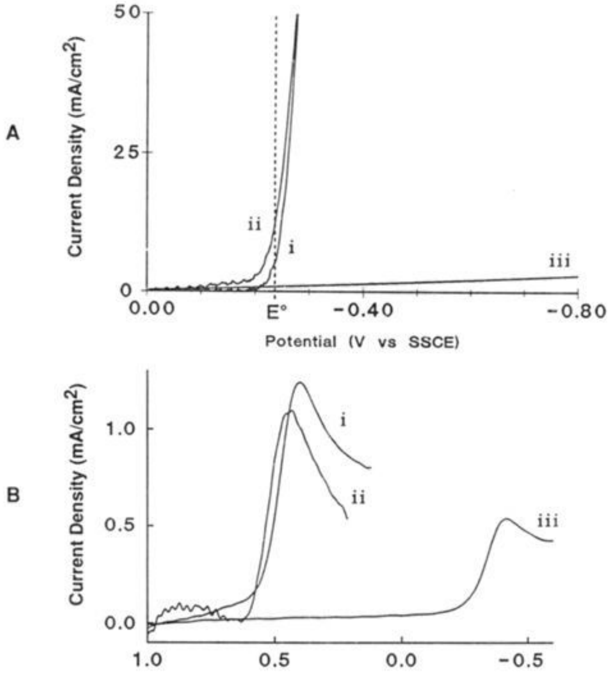


Figure 2. (A) Voltammogram for H^+ reduction in 1 M $HClO_4$, obtained at 50 mV/s. Electrode materials were as follows: i, bulk polycrystalline Pt mounted in a Kel-F holder; ii, 1 atom % Pt-DGC thin film on conventional GC; iii, synthetic GC without Pt doping. (B) Voltammograms for O_2-saturated 1 M $HClO_4$ buffer, 50 mV/s scan rate for the following: i, bulk polycrystalline Pt mounted in a Kel-F holder; ii, 1 atom % Pt-DGC thin film on conventional glassy carbon; iii, conventional GC.

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[12] The actual ratios were calculated from elemental analysis data and X-ray photoelectron spectroscopic analyses and were found to be 1:4.4 and 1:1.7, respectively.

[13] Spectral data for **3** (1:4.4): IR (KBr) 2150, 1720, 1580, 1470, 1420, 1190, 1150, 1090, 1020, 990 cm^{-1}; ^1H NMR (C_6D_6, 250.1 MHz) δ 6.8 (m), 7.65 (m) ppm; ^{13}C NMR (C_6D_6, 62.9 MHz) δ 131–137, 83, 76 ppm; ^{31}P NMR (C_6D_6, 101.3 MHz) δ 24.5, 25.5–26 ppm. Anal. Calcd: C, 75.8; H, 3.76; P, 4.92; Pt, 15.5. Found: C, 75.8; H, 3.89; P, 3.40; Pt, 16.5. Spectral data for **3** (1:1.7): IR (KBr) 2150, 1720, 1580, 1470, 1420, 1190, 1150, 1090, 1020, 990 cm^{-1}; ^1H NMR (C_6D_6, 250.1 MHz) δ 6.8 (m), 7.65 (m) ppm; ^{13}C NMR (C_6D_6, 62.9 MHz) δ 131–137, 83, 76 ppm; ^{31}P NMR (C_6D_6, 101.3 MHz) δ 24.5, 25.5–26 ppm. Anal. Calcd: C, 70.0; H, 3.92; P, 6.3. Found: C, 70.0; H, 4.18; P, 4.86.

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[15] Thin films of Pt-DGC were prepared by evaporation of **3** onto a sodium chloride disk to give ~2–3-μm-thick coatings. The disk was then heated at 1 °C/min to 600 °C for 6 h *in vacuo* in a quartz tube. The sodium chloride disk was dissolved, and the film was picked up on a copper grid and examined with a JEOL 200CX analytical electron microscope operating at 200 kV with a Tracor-Northern 2000 (Noran) EDX system. The images were processed using an Optimax V image analysis system.

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.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9007132) for their financial support of this work. We also thank Fort Fibres Optiques (Paris) for a scholarship to N.L.P. and the Campuswide Materials Research Program of The Ohio State University for partial support of this effort. We thank Dr. Hendrik Colijn of the Central Electron Optics Facility (OSU) for his assistance with the TEM analyses. D.C.A. was a National Need Fellow during the course of this work.

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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Received August 5, 1991

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.

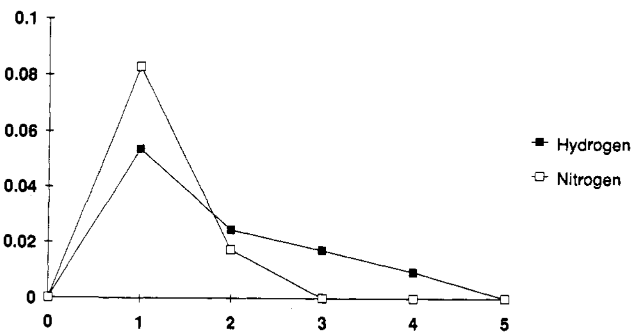

Figure 1. Extent of formation of $HFe(CO)_{n-1}^+$ from $Fe(CO)_n^+$ and hydrogen atoms (H_2 pressure: 1.5×10^{-3} Torr) and of $NFe(CO)_{n-1}^+$ from $Fe(CO)_n^+$ and nitrogen atoms (N_2 pressure: 6.5×10^{-4} Torr) as a function of the number n of CO ligands. The extent of formation is defined as the 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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[†] Laboratoires associés à l'Université Pierre et Marie Curie.

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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.