In contrast, cyclooctane desorbs molecularly from Pt(111) and does not undergo dehydrogenation or ring contraction. All of the C_8 alkenes except COT give multiple low-temperature H_2 desorption peaks and one high-temperature H_2 desorption peak near 620 K. Auger electron spectroscopy indicates that heating a saturation coverage of any of the C_8 alkenes to 800 K leaves about 15% of a monolayer of carbon, or about $^1/_4$ of the amount of carbon generated by heating a saturation coverage of ethylene on Pt(111).[13,14]

The similar temperatures at which benzene is formed from the different C_8 alkenes suggest that these reactions proceed via a common intermediate. One possibility is that the first step in the conversion of cyclic C_8H_{8+2n} alkenes to benzene is dehydrogenation to COT. Support for this suggestion has been obtained from high-resolution electron energy loss spectra (HREELS) of 1,5-COD and COT on Pt(111): at 220 K (which is above the multilayer desorption temperature), both molecules retain their tub-shaped structures and are bound to the surface in an η^4 fashion (Figure 2).[15-20] By 370 K, however, both 1,5-COD and COT react to form the *same* species on the surface. In the ν_{CH} region, only one peak, at ~3005 cm^{-1}, is observed in the HREEL spectrum. This band and those at 890 and 480 cm^{-1} are consistent with the presence on the surface of a planar, dianionic η^8-COT ring.[16,21,22]

Upon further heating, the most significant reaction channel is decomposition of the η^8-COT molecules to benzene and acetylene. Subsequently, the acetylene rapidly converts to surface acetylide (—C≡CH), as shown by the presence of peaks at 3090 (ν_{CH}) and 832 cm^{-1} (β_{CH}) in the HREEL spectra of a surface which was flashed to 560 K.[23] At least two mechanisms could account for the formation of benzene and acetylene from the η^8-COT intermediate: (1) rearrrangement to bicyclo[4.2.0]octa-1,3,5-triene[24] followed by a [2 + 2] cycloreversion reaction to give acetylene and benzene or (2) complete decyclization of COT to four acetylene molecules, some of which then cyclotrimerize to benzene.[25] We have distinguished these possibilities by carrying out a crossover experiment. A mixture of COT and COT-d_8 was coadsorbed onto a Pt(111) surface, and the benzene that desorbed between 400 and 530 K was analyzed by IDMS. No benzene-d_2 or benzene-d_4 was found to be present; instead, the desorbed benzene consisted almost exclusively of the -d_0 and -d_6 isotopomers.[26] The lack of crossover rules out the complete decyclization mechanism but is consistent with the rearrangement/cycloreversion pathway.

Further studies of the reactions of cyclic and bicyclic hydrocarbons on Pt(111) surfaces are underway.

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(11) For example, 1,5-COD and 1,3-COD both give two desorption features: the first, at 405 K, consists of COT, while the second, at 445 K, consists of benzene. In contrast, cyclooctene on Pt(111) gives three separate TPD features: the desorbing flux consists of a mixture of COE and 1,3-COD between 325 and 380 K, a mixture of COT and benzene between 380 and 450 K, and benzene exclusively above 450 K. On a polycrystalline Pt foil, COT and 1,5-COD give a benzene TPD peak at 455 K.

(12) For mass spectra of all of the C_6 and C_8 hydrocarbons, see: *Atlas of Mass Spectral Data*; Stenhagen, E., Abrahamsson, S., McLafferty, F. W., Eds.; Interscience: New York, 1969; Vol. 1. No C_2 or C_4 decomposition products were detected for any of the compounds studied.

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Ligand-Stabilized Giant Palladium Clusters: Promising Candidates in Heterogeneous Catalysis

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Large transition-metal clusters and colloids deserve notice for different reasons. They may serve as objects for the study of quantum size effects and the formation of metallic states,[1] and they are ideal candidates for catalytic processes.[2] Established methods for the preparation of large metal clusters and colloids on various supports[3-6] lead to a more or less broad size distribution.

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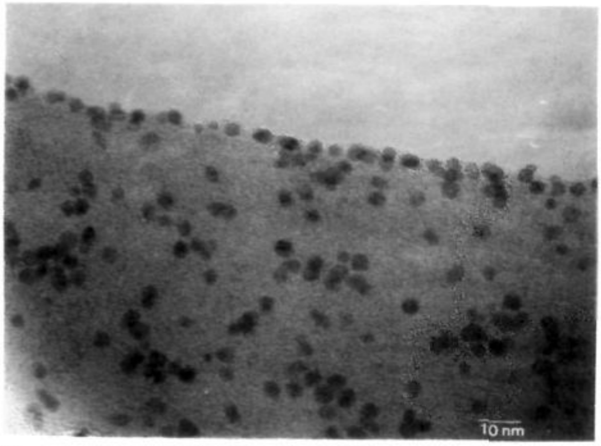

Figure 1. Mixture of Pd7/8 cluster particles.

A recent example is the synthesis of nanoscale platinum clusters in glassy carbon, showing a size range of 6–30 Å.[7] In contrast, ligand-stabilized clusters are provided with the advantage of being predominantly uniform. The largest ligand-stabilized cluster with satisfactory characterization was described by Moiseev et al. in 1985[8] and in a modified version by us.[9] It is formed when Pd(II) acetate is reduced by hydrogen in acetic acid solution and in the presence of appropriate ligands, followed by the careful addition of oxygen to coordinate free surface atoms. The yields of the cluster with the idealized formula $Pd_{561}phen_{36}O_{200\pm10}$ (phen = phenanthroline) in our synthesis is below 10%. In search of the other 90% of the palladium, we now found a mixture of mainly two different clusters with diameters of 31.5 and 36.0 Å. In a typical experiment, a solution of 2.32 g of $Pd(OAc)_2$ (1.03×10^{-2} mol) and 0.25 g of phen·H_2O (0.13×10^{-2} mol) in 800 ml of acetic acid is treated with gaseous hydrogen under vigorous stirring at room temperature. In the course of 10–12 min, 2.4 moles of H_2 per mole of Pd is used, and 0.65 mole of O_2 per mole of Pd is then needed to cover uncoordinated surface Pd atoms by oxygen. It is assumed that a part of the hydrogen is dissolved in the Pd particles and is removed then by the reaction with oxygen. There is no indication (NMR) that the final products contain hydrogen. The black reaction mixture is centrifuged at 4300 revolutions per minute. Repeated washing with acetic acid and drying under vacuum gives 1.157 g of the air-stable cluster mixture (90.7%). It is soluble in a water–pyridine mixture (10:1). The filtrate of the centrifugation contains the Pd_{561} cluster, which can be isolated by addition of the 3–4-fold amount of benzene, followed by centrifugation at 5000 revolutions per minute.

By studying the particle size distribution in several electron micrographs, the sizes found were approximately 31.5 and 36.0 Å, while about 10% were smaller or bigger. Atomic resolution images, recorded at electron acceleration voltages of 300 and 400 kV and at a structural resolution of 1.6 Å, show that most of the clusters are crystalline with an almost cuboctahedral shape. The number of (111) planes of atoms are most frequently 15 and 17 (cf. Figure 1). Using the terminology of full-shell clusters, these numbers correspond well with seven-shell, Pd7, or eight-shell, Pd8, clusters. The images of the clusters show that the structure is most of the time the cubic close packed (fcc) type, as in the bulk metallic Pd, but structural defects occur frequently.

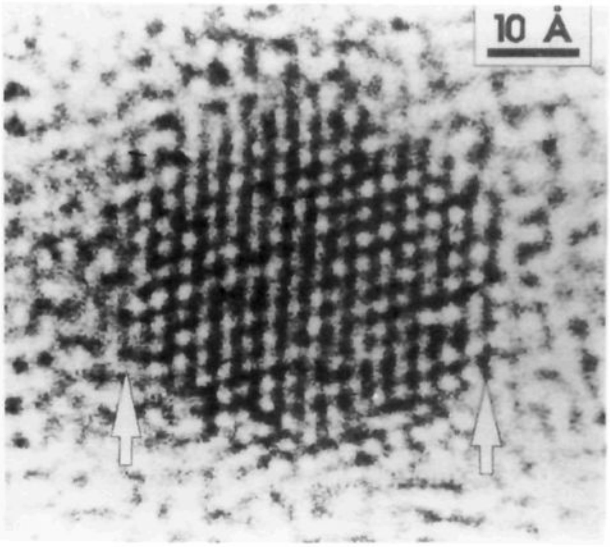

Figure 2. Cluster of palladium with 17 (111) layers of atoms. The outer layers are marked with arrows, showing the cuboctahedral shape of a cubic close packed structure. The HREM image is recorded along [110]. The cluster is supported on amorphous carbon.

Figure 2 shows a single eight-shell cluster particle with an almost perfect cuboctahedral shape.

The elementary analysis[10] of a microscopically investigated sample (30% Pd7, 62% Pd8) together with model studies enabled the calculation of idealized formulas for the two cluster types: $Pd_{1415}phen_{60}O_{\sim1100}$ (Pd7) and $Pd_{2057}phen_{84}O_{\sim1600}$ (Pd8). However, as these cluster molecules are only available as a mixture, these formulas are burdened with a portion of uncertainty. Nevertheless, the experimental analytical values agree well if the microscopic evaluation is accepted. Attempts to separate Pd7 from Pd8 by means of ultracentrifugation failed as did attempts by chromatographic methods.

Not only HRTEM but also X-ray powder diffractions prove the fcc structure of the clusters. The 111, 200, 220, 311, and 222 reflexions can be observed, and their positions agree well with those of bulk palladium.

Solutions of Pd7/Pd8 are well suited to prepare heterogeneous catalysts with metal particles of two different but very similar sizes. TiO_2 adsorbs the cluster molecules up to 5 wt % spontaneously from a water–pyridine (10:1) solution. BET measurements of the undoped, 1% doped, and 5% doped TiO_2 show that the original distribution of the micropore radii (7.6–35 Å) is reduced considerably with 1 wt % of Pd7/Pd8 and has almost completely disappeared with 5 wt % of the cluster material. γ-Al_2O_3 is much less suited as a support, as only 0.3 wt % of the cluster material is adsorbed.

A novel method for catalyst preparation uses aqueous solutions of Pd7/Pd8 to hydrolyze $Ti(OC_3H_7)_4$ in 2-propanol. $TiO_2 \cdot nH_2O$ is precipitated together with molecularly dispersed Pd7 and Pd8. A content of 1.1 wt % as a maximum is possible. This catalyst is almost as active as if the same amount of cluster molecules were adsorbed on the surface. It may be advantageous, if it is stressed mechanically, e.g., by vigorous stirring. If the surface is damaged, then new active surfaces are continuously reformed.

Preliminary experiments with Pd7/8 on TiO_2 and Al_2O_3 show these materials to be powerful catalysts in various olefin hydrogenation reactions. Diolefins like 1,3-cyclooctadiene or dicyclo-

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[10] Analytical data calculated (found) for a microscopically investigated mixture of 30% $Pd_{1415}(C_{12}H_8N_2)_{60}O_{1123}$ and 62% $Pd_{2057}(C_{12}H_8N_2)_{84}O_{1632}$: C, 4.71 (5.14 ± 0.03); H, 0.27 (0.42 ± 0.05); N, 0.91 (0.84 ± 0.02); O, 10.03 (9.98 ± 0.21); Pd, 84.08 (83.62 ± 0.11).

pentadiene can be semihydrogenated selectively. 1-Hexyne is transformed to 1-hexene with 98% yield.

All hydrogenation processes are definitely heterogeneously catalyzed, as no case has been observed where the filtered products showed catalytic activities. The activities of repeatedly used catalyst samples turned out to be absolutely constant.

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Modulation of Photoinduced Electron-Transfer Reactivity by Intramolecular Folding

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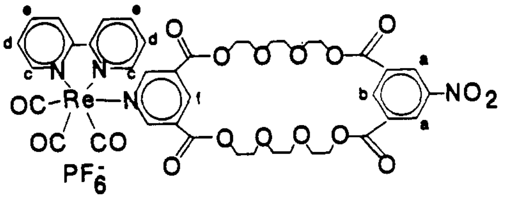
Rates of electron transfer (ET) between molecule-based donors (D) and acceptors (A) are known to depend strongly on DA separation distance, for both Franck–Condon (solvent reorganization) and electronic (orbital overlap) reasons.[1] Distances are often fixed, therefore, by linking D and A (covalently) with molecular bridges.[2] If the bridge structure is flexible, however, a range of distances can still result.[3] Recently we reported on ET from a photoexcited donor $(\mathrm{Re(CO)_3(bpy)(py)})^+$ (bpy is 2,2'-bipyridine, py is pyridine)) to an electron acceptor (nitrobenzene, NB), where the two are connected by a flexible crown ether-based link (see assembly **1**).[4] The initial experiments were performed in nitromethane as solvent, and the results were consistent with reactivity from a single conformational form. We now report experiments in methylene chloride as solvent which clearly demonstrate the existence of two structural forms. The two are interrelated by intramolecular folding and can be reversibly interconverted via changes in temperature. Importantly, the two forms exhibit marked differences in ET reactivity.



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The likely existence of two structural forms was initially indicated by variable temperature kinetics measurements. Figure 1 shows an ln rate/inverse temperature plot for intramolecular redox quenching of the $\mathrm{Re^{II}\bar{p}y}$ fragment of **1** by pendant NB.[5] Notably, the plot is biphasic with a transition temperature of ~280 K. From the high-temperature slope, ΔH_{ET}^* is 1.4 kcal mol^{-1}; from the high-T intercept, the preexponential factor A_{ET} is 3×10^6 s^{-1}. In contrast, from the low-T measurements, ΔH_{ET}^* and A_{ET} are 9 kcal mol^{-1} and 2×10^{12} s^{-1}, respectively. Despite the kinetic differences, however, no shift in steady-state emission energy (or bandwidth) with temperature was seen.[6]

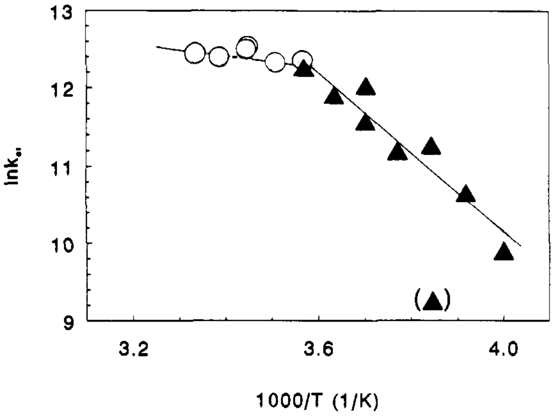

Figure 1. Logarithm of rate constant for intramolecular electron transfer ($\bar{\mathrm{p}}$y → NB; see Scheme I) vs inverse temperature in deoxygenated CH_2Cl_2 as solvent. (Data point in parentheses was omitted from the low-T fit.)

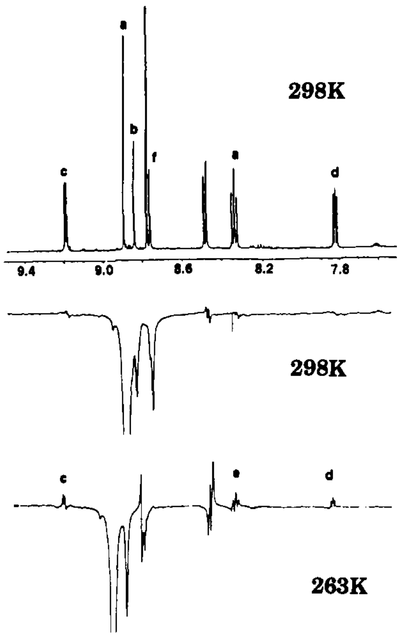

Figure 2. Proton NMR (top) and 1-D NOE (middle and bottom) spectra for **1** (aromatic region) and CD_2Cl_2 at 298 and 263 K (600-MHz Bruker spectrometer).

Confirmation that the biphasic kinetics are related to a temperature-dependent, secondary structural change was obtained by 1-D NOE in CD_2Cl_2 (Figure 2).[7] At 263 K, irradiation of

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[5] Rate constants were obtained[4] by comparing luminescence lifetimes for **1** with those for an equivalent assembly featuring a redox-inactive pyridine moiety in place of nitrobenzene (assembly **3** in ref 4) and by ascribing the differences to an intramolecular ET decay pathway. Representative data: $T = 299.5$ K, $\tau(1) = 680$ ns, $\tau(3) = 820$ ns, $k_{ET} = 2.5 \times 10^5$ s^{-1}; $T = 298$ K, $\tau(1) = 750$ ns, $\tau(3) = 900$ ns, $k_{ET} = 2.2 \times 10^5$ s^{-1}; $T = 260$ K, $\tau(1) = 860$ ns, $\tau(3) = 920$ ns, $k_{ET} = 7.6 \times 10^4$ s^{-1}.

[6] UV absorption spectra were also unchanged in energy, although a very slight increase in extinction accompanied cooling. No unusual changes were seen in the vicinity of the transition temperature.

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