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Selective Synthesis, Characterization, and Spectroscopic Studies on a Novel Class of Reduced Platinum and Palladium Particles Stabilized by Carbonyl and Phosphine Ligands

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The chemistry and physics of small metal particles are presently attracting a great and diverse interest because of the special position of these species at the boundary between the molecular and metallic states.[1-6] Potential applications can be found in the fields of material science,[1] catalysis,[2] and biology.[3] Metal particles in colloidal solutions have been known for many years and were originally prepared and studied in water.[4] Recent work has extended metal colloid chemistry into nonaqueous solution, and these materials can now be prepared in several ways, such as metal complex salt reduction, metal vapor chemistry, and a promising method which we have been investigating recently, the decomposition of an organometallic precursor in the presence of a polymer.[5,6] This led us to attempt the stabilization of metal particles by simple classical ligands such as PPh_3, CO, or pyridine.

The pioneering work of Schmid, Moiseev, and co-workers has demonstrated the feasibility of preparing large clusters by partial reduction of inorganic complexes[7,8] in the presence of stabilizing ligands. A closed-shell structure, e.g., $Au_{55}(PPh_3)_{12}Cl_6$, $Rh_{55}[P(^tBu)_3]_{12}Cl_{30}$, $Ru_{55}[P(^tBu)_3]_{12}Cl_{20}$, $Pd_{561}Phen_{36}O_{200}$, or $Pd_{561}L_{60}(OAc)_{180}$ (L = Phen, bipy), was attributed to these species. These compounds, of which none has been isolated in single crystal form and which have been characterized by the methods of colloid chemistry (TEM, ultracentrifugation, EXAFS), all contain anionic ligands at their surfaces, implying that the surface layer may be partially oxidized. The large molecular cluster $Pd_{38}(\mu^3\text{-}CO)_4(\mu^2\text{-}CO)_{24}(PEt_3)_{12}$ has been prepared by the reaction of $Pd(OAc)_2$ with $Pd_{10}(CO)_{12}(PEt_3)_6$ and characterized by an X-ray crystal structure.[9] This communication describes the synthesis, from zero-valent palladium and platinum complexes, of small metal particles stabilized by triphenylphosphine and carbon monoxide with diameters corresponding to giant clusters. The size of the particles has been previously shown to be controlled by the nature and the quantity of ligands used for their preparation,[7] but we demonstrate for the first time that a modification of ligand concentration will induce a size modification in a given experiment.

We have previously shown[6] that the decomposition of $M(dba)_2$ (M = Pd, Pt; dba = dibenzylideneacetone) under CO or H_2 was a reproducible way of preparing metal particles in organic solutions. If, instead of a polymer, various amounts of PPh_3 ($[PPh_3]/[Pt]$ = 0.70, 0.57, 0.40, 0.20) are used during the decomposition of $Pt(dba)_2$ in THF, very small, nonagglomerated particles (ca. 13 Å) are formed, showing in each case a very narrow size distribution as monitored by TEM.[10] Solution infrared spectra of these particles show a ligand concentration dependence.[11] Thus increase in the phosphine concentration leads to a shift of the terminal CO stretch to low frequency and the disappearance of the band at 1868 cm^{-1} together with the appearance of a new one at 1811 cm^{-1}. This is due to the increased electron density on the particle, in agreement with the increased coverage of the particle surface with the good electron donor phosphine ligands. A change of coordination mode of CO, for example from doubly to triply bridging,[9] seems unlikely in this case. The ^{31}P NMR spectra of these solutions show two different sets of signals. The first, centered at 50.28 ppm, is a single complex multiplet showing $^1J_{^{195}Pt-^{31}P}$ (5130 Hz) and various $^2J_{^{195}Pt-^{31}P}$ and $^3J_{^{195}Pt-^{31}P}$. The second set of three resonances, at 45.75, 45.43, and 45.19 ppm, are of comparable intensity but vary according to phosphine concentration. The ^{195}Pt NMR spectra show two signals at –4315 and –4075 ppm. The former is coupled to phosphorus ($^1J_{^{195}Pt-^{31}P}$, 5130 Hz), whereas the latter is not. However, both signals show additional splittings of ca. 450 Hz which do not correspond to $^2J_{^{195}Pt-^{31}P}$ but could be due either to the presence of different sites fortuitously located at the same chemical shift difference in the Pt-coupled and Pt-noncoupled regions or to a direct $^1J_{^{195}Pt-^{195}Pt}$. Such direct $^{195}Pt-^{195}Pt$ couplings have been shown in metal–metal-bonded dinuclear platinum complexes and small trinuclear clusters to vary between 90 and

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(10) TEM images were obtained on a JEM 200 CX-T electron microscope operating at 200 keV. The samples were prepared according to the following procedure: the reaction mixture after colloid preparation was diluted 20 times in THF, and one drop of this solution was evaporated in air on a 2.3-mm copper grid previously covered with an amorphous carbon film and ionized.

(11) CO streching frequencies (intensities) vary as follows: $[PPh_3]/[Pt]$ = 018, 2066 (s), 1884 (m) cm^{-1}; $[PPh_3]/[Pt]$ = 0.38, 2054 (m), 2035 (m), 1868 (w), 1811 (w) cm^{-1}; $[PPh_3]/[Pt]$ = 0.57, 2040 (m), 2015 (m), 1827 (w), 1810 (w) cm^{-1}.

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9000 Hz;[12] it is therefore difficult to draw any conclusion at the present time. Further smaller couplings are observable. The sharpness of the ^{195}Pt resonances of the clusters is consistent with a molecular nature and a regular structure. Pt resonances in supported Pt particles as measured by solid-state NMR are notoriously broad, due to both their polydispersity and the irregular nature of their surfaces which gives rise to a broad range of resonance frequencies.[13] It is noteworthy that the size observed by TEM is similar to that observed for icosahedral systems containing 55 atoms.

When similar reactions were carried out starting with Pd(dba)$_2$ under CO in THF, ([PPh$_3$]/[Pd] = 0.25, 0.54, 0.85), particles of respectively 26.0 ± 4.5, 15.0 ± 3, and 12.5 ± 3 Å were formed with a broader size distribution as the particle size increased. The observed mean diameters correspond to those of closed-shell clusters of respectively 561, 147, and 55 atoms. The dependence of particle size with phosphine concentration is reproducible over several preparations. The particles were found to be stable for a limited period of time in the absence of CO in solution at room temperature. They can be kept at −18 °C for several weeks in the solid state after precipitation from THF/pentane. They can be easily redissolved, and TEM analysis does not show any sign of aggregation. Two preliminary experiments were carried out to determine the reactivity of these colloidal solutions and their potential use for chemical applications. First excess phosphine was added under CO to a solution characterized by TEM as containing 26-Å particles. The result is an important increase of the size dispersity and a decrease of the mean size to ca. 18 Å. The second experiment was a substitution reaction of CO by tBuNC over 15-Å particles. After complete substitution of CO, as monitored by IR spectroscopy, the particle sizes remained essentially the same, and ^{1}H NMR spectra of the resulting particles indicated a 2:1 ratio of tBuNC compared to PPh$_3$. Similar results, i.e., particle stabilization and size dependence upon ligand concentration, were observed when PCy$_3$ was used instead of PPh$_3$, whereas if pyridine was used some metal precipitation was observed during the decomposition of Pd(dba)$_2$. Furthermore, we observed by TEM a large distribution in size (mean size near 13.8 Å).[14] This demonstrates that pyridine is not as good as phosphines for the synthesis of metal particles of defined size.

The infrared spectra of the palladium particles show a phosphine concentration dependence which in the present case probably results essentially from a size dependence (Figure 1).[15] Well-defined bands corresponding to terminal, doubly, and possibly triply bridging CO groups are observed as in the platinum case. The situation of the colloids prepared in the presence of pyridine is very different since only broad bands are observed as in the case of palladium colloids in PVP,[6b] which suggests again (vide supra) that addition of phosphine favors the formation of defined species, whereas pyridine will only weakly coordinate to these particles. Interestingly, when left in THF solution, the particles lose CO as monitored by infrared spectroscopy. However, CO loss is reversible, and bubbling CO restores the initial spectrum. This phenomenon could account for the aggregation observed by TEM when the clusters are left in solution for several hours and even for metal precipitation when a solution is left standing at room temperature for several days.

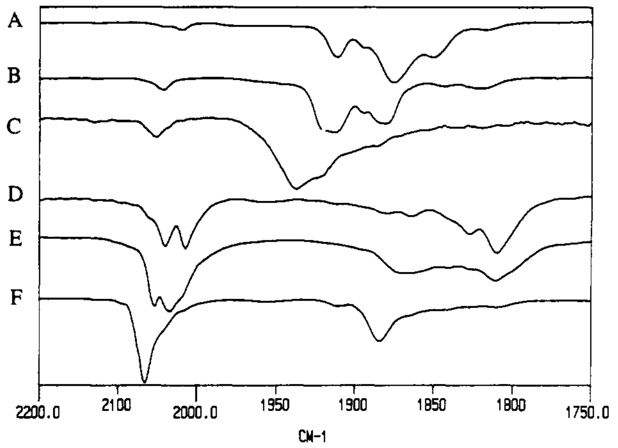

Figure 1. IR spectra of palladium and platinum particles stabilized by carbon monoxide and varying amounts of triphenylphosphine. A, P/Pd = 0.85; B, P/Pd = 0.54; C, P/Pd = 0.25; D, P/Pt = 0.57; E, P/Pt = 0.38; F, P/Pt = 0.18.

In summary, we report in this communication the synthesis of novel platinum and palladium particles containing only two electron-stabilizing ligands and no protecting oxidized layer but which can be studied by spectroscopic methods. The platinum particles are stable even in solution at room temperature for an extended period of time and show a defined and reproducible size. In icosahedral systems, such a size corresponds to two filled-shells, i.e., 55 atoms. The particles link strongly to phosphorus, as deduced from the lack of fluxionality observed in ^{31}P NMR and ^{195}Pt NMR. In contrast, the palladium particles are less stable and subject to size variations in solution even though the three mean sizes observed by TEM are well defined. It is likely that they correspond to metastable states during the nucleation process of metallic palladium. These particles are very reactive and are able to undergo simple reactions such as ligand addition, elimination, and substitution as well as more complex ones such as size modifications. Finally, the stability of the particles is related to the ligand affinity, as observed for the difference of behavior of palladium particles in the presence of PPh$_3$ and pyridine. The synthesis of such highly reactive, polymer-free colloidal solutions will be interesting in the fields of material science and homogeneous catalysis and as models of heterogeneous reactions.

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Supplementary Material Available: Transmission electron micrograph of platinum particles prepared by carbonylation of Pt(dba)$_2$ in THF in the presence of 0.41 equiv of PPh$_3$; histograms of platinum colloids at different L/M ratios; ^{31}P NMR spectra of platinum particles prepared by carbonylation of Pt(dba)$_2$ in THF in the presence of 0.70 equiv of PPh$_3$ at 32 and 81 MHz; ^{195}Pt NMR spectrum of platinum particles; transmission electron micrographs of palladium particles at different L/M ratios; histograms of palladium colloids at different L/M ratios; histograms of palladium colloids before and after addition of excess triphenylphosphine under carbon monoxide; histograms of palladium colloids before and after substitution of carbon monoxide by tBuNC (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(14) The particles containing pyridine as ligands were prepared like the one using PPh$_3$ by bubbling CO in a THF solution of Pd(dba)$_2$ containing 0.35, 0.60, or 0.80 mol % pyridine. Only the 0.35 mol % sample led to the observation of disperse particles, the two latter leading to agglomerates. The size distribution was found very broad (6–26 Å), with a mean size of 13.8 Å.

(15) CO streching frequencies (intensities) vary as follows: [PPh$_3$]/[Pd] = 0.25, 2052 (w), 1937 (s), 1923 (sh), 1889 (sh) cm^{-1}; [PPh$_3$]/[Pd] = 0.54, 2044 (w), 1920 (s), 1914 (s), 1895 (sh), 1881 (m) cm^{-1}; [PPh$_3$]/[Pd] = 0.85, 2020 (w), 1911 (m), 1895 (sh), 1875 (s), 1852 (m) cm^{-1}.