where, even if two overlapping cross peaks are resolved, they cannot be unambiguously assigned to either of two possible proton–proton NOEs. Another particularly useful feature of the 4D experiment is the possibility of identifying NOEs between protons with identical chemical shifts. Consider the two cross peaks originating from a NOE between the protons HA and HB in the molecular fragment CA–HA...HB–CB. When $\Omega_{HB} = \Omega_{HA} = \Omega_X$, the cross peaks between these protons will resonate on the diagonal in 2D and 3D NOE spectroscopy. In the 4D experiment, the cross peaks are found at the coordinates (f_1,f_2,f_3,f_4) $(\Omega_{CA},\Omega_X,\Omega_{CB},\Omega_X)$ and $(\Omega_{CB},\Omega_X,\Omega_{CA},\Omega_X)$ distinct from the diagonal peaks at $(\Omega_{CA},\Omega_X,\Omega_{CA},\Omega_X)$ (HA) and $(\Omega_{CB},\Omega_X,\Omega_{CB},\Omega_X)$ (HB), provided that $\Omega_{CA} \neq \Omega_{CB}$.[5] An example of this case is given in panel I of Figure 1, where a strong cross peak (arrow) is seen on the virtual diagonal,[6] showing an NOE between two protons that have identical chemical shifts but are attached to carbons with different shifts. Many methyl–methyl NOE cross peaks resonate close to or at the diagonal in 2D and 3D spectroscopy. Such peaks are readily identified in the 4D experiment (panel J), which is extremely important for the determination of the 3D structure of the hydrophobic core of proteins, where many methyl–methyl contacts occur.

In summary, it is demonstrated here that four-dimensional ^{13}C-resolved NOE spectroscopy yields spectra of greatly enhanced resolution. This method allows for the study of larger proteins by NMR and will contribute to the improvement of the quality of tertiary structures derived from NMR data. The same four-dimensional "double chemical shift labeling" method can be applied to H–C–C–H experiments[4] and to ^{15}N-resolved NOE spectra.[1a-c]

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(5) Note that inversion symmetry exists in the 4D data which can be exploited to enhance the S/N ratio and/or to reduce the final data size.

(6) Residual diagonal signals are observed in the "nondiagonal" planes due to ridges which were insufficiently suppressed. However, true cross peaks could be distinguished from the ridges by their symmetry relationships.

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Characterization of High-Nuclearity Platinum Carbonyl Cluster Anions by ^{252}Cf-Plasma Desorption Mass Spectrometry: Formation of Gas-Phase $[Pt_{26}(CO)_x]_n$ Monocharged Ion Oligomers (n = 1–20) from Solid-State $[Pt_{26}(CO)_{32}]^{2-}$ Dianions

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The great potential of mass spectroscopy for characterizing giant-sized metal clusters was first demonstrated by Fackler, McNeal, Winpenny, and Pignolet,[2] who used ^{252}Cf-plasma desorption mass spectrometry (PDMS)[3] to analyze the Schmid $Au_{55}(PPh_3)_{12}Cl_6$ cluster (14 165 amu).[4] Its formulation and its proposed two-shell Au_{55} cuboctahedral structure were based on molecular weight determinations, elemental analyses, NMR, Mössbauer spectroscopy, magnetic and conductivity measurements, and high-resolution transmission electron microscopy (HRTEM);[4] the lack of single crystals prevented characterization by X-ray diffraction. The recent analysis of ^{252}Cf-PD positive-ion mass spectra of several samples led to the reformulation[2] of this gold cluster with a Au framework patterned after the Teo cluster-of-clusters model[5] for vertex-sharing centered icosahedra.

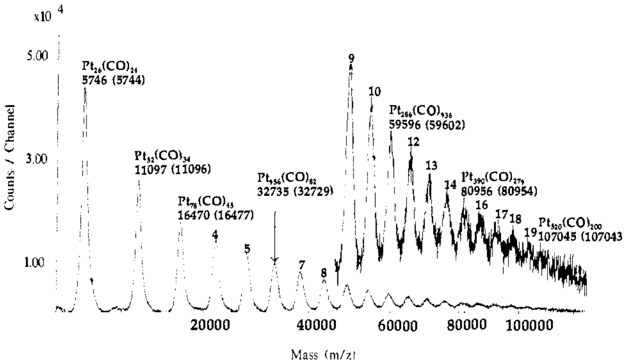

Figure 1. ^{252}Cf plasma desorption positive-ion mass spectrum of $[PPh_3Me]^+{}_2[Pt_{26}(CO)_{32}]^{2-}$. The major peak in both the positive- and negative-ion mass spectra is due to a monocharged parent ion Pt_{26} core; its peak maximum in this spectrum at m/z 5746 corresponds most closely to the partially decarbonylated $[Pt_{26}(CO)_{24}]^+$ ion (5744 u). The other high-mass peaks are readily attributed to monocharged $[Pt_{26}(CO)_x]_n{}^+$ oligomers (labeled up to n = 20).

The above work inspired us to investigate whether ^{252}Cf-PDMS of high-nuclearity platinum carbonyl cluster anions would provide meaningful spectral data.[6-11] Previous attempts to obtain FAB and laser desorption mass spectra of several triangular platinum carbonyl $[Pt_3(CO)_6]_n{}^{2-}$ clusters (n = 2–5)[12,13] had been unsuccessful. Reported herein is a preliminary account of mass spectral

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(6) Spectroscopic characterization of platinum carbonyl cluster anions has previously been limited primarily to infrared analysis of the carbonyl stretching region; however, the carbonyl band shapes and frequencies often do not provide an unambiguous means either for assessing sample purity or for differentiating different platinum cluster species from one another.[7-9] Although a comprehensive analysis of variable-temperature ^{13}C and ^{195}Pt NMR spectra of several $[Pt_3(CO)_6]_n{}^{2-}$ dianions (n = 2–5) was performed by Heaton and co-workers,[10] ^{13}C NMR spectroscopy of the closest packed platinum carbonyl clusters has not yielded meaningful data, due possibly to residual paramagnetic effects.[11]

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measurements[14] carried out on samples of the $[Pt_9(CO)_{18}]^{2-}$, $[Pt_{24}(CO)_{30}]^{2-}$, $[Pt_{26}(CO)_{32}]^{2-}$, and $[Pt_{38}(CO)_{44}]^{2-}$ dianions and the $[Pt_{19}(CO)_{22}]^{4-}$ tetraanion.[15,16] Both positive- and negative-ion mass spectra of these cluster anions are of interest in that (1) they emphasize that ^{252}Cf-PDMS is an excellent tool to probe platinum stoichiometry of high-nuclearity platinum carbonyl anions because the parent ion platinum core peak is the strongest signal observed in each sample, and (2) they all display high-mass ion peaks corresponding to oligomers of the parent ion platinum core fragment in each anion.

Figure 1 presents a positive-ion mass spectrum of the $[PPh_3Me]^+$ salt of the $[Pt_{26}(CO)_{32}]^{2-}$ dianion which contains a three-layer (7:12:7) hcp Pt_{26} core of pseudo-D_{3h} symmetry.[15,17] This positive-ion mass spectrum exhibits an extraordinary series of high-mass, monocharged $[Pt_{26}(CO)_x]_n^+$ peaks which extend from m/z 5746 for the major Pt_{26} core peak ($n = 1$) to m/z 107 045 for the Pt_{520} core peak ($n = 20$). This latter peak corresponds to the highest m/z ion to be detected by ^{252}Cf-PDMS. Each of these high-mass peaks consists of a complex envelope due not only to the different number (x) of carbonyl ligands attached to the platinum core for a given value of n but also to the various isotopic combinations[18] for a given molecular formula. Thus, the envelope of the major parent ion peak ranges from the fully decarbonylated species at the low-mass limit to the fully carbonylated cluster at the high-mass limit with the peak centroid most nearly conforming to the $[Pt_{26}(CO)_{24}]^+$ ion (5744 u). A similar pattern of monocharged parent ion and oligomer ion peaks is observed in the negative-ion spectrum as well. The extent of self-condensation of the Pt_{26} core is most remarkable and indicates strong cluster aggregation.

^{252}Cf-PDMS of different salts of the other platinum carbonyl anions also provided highly desirable information. It is particularly noteworthy that mass spectra of the $[Pt_{24}(CO)_{30}]^{2-}$ and $[Pt_{38}(CO)_{44}]^{2-}$ dianions also exhibited high-mass peaks corresponding to oligomerization of their parent ion ccp platinum cores. In contrast, mass spectra of the $[Pt_9(CO)_{18}]^{2-}$ dianion and $[Pt_{19}(CO)_{22}]^{4-}$ tetraanion displayed high-mass peaks involving only a small amount of dimerization ($n = 2$) of their non closest packed platinum cores. Mass spectra of the former complex also contained peaks due to the addition of Pt_3 units.

The negative-ion spectrum of the $[(Ph_3PCH_2C_5H_4)Fe(C_5H_5)]^+$ salt of the $[Pt_9(CO)_{18}]^{2-}$ dianion, whose idealized D_{3h} symmetry involves an eclipsed superposition of three $Pt_3(CO)_3(\mu_2\text{-}CO)_3$ building blocks, contained an intense parent ion envelope corresponding to $[Pt_9(CO)_x]^-$ with clearly resolvable peaks differing by carbonyl units varying from $x = 4$ to $x = 16$ with the principal peak centered at $x = 8$. Of prime interest was the occurrence of a multiplet set of monoanion peaks for Pt_{12}, Pt_{15}, Pt_{18}, and Pt_{21} cores. A slightly more intense peak envelope was observed for the dimeric $[Pt_{18}(CO)_x]^-$ multiplet ($n = 2$) than for the $[Pt_{12}(CO)_x]^-$ and $[Pt_{15}(CO)_x]^-$ multiplets. The fact that a spectroscopic (near-IR/near-UV) analysis[19] revealed that controlled oxidation of the $[Pt_9(CO)_{18}]^{2-}$ dianion in THF solution with the $[FeCp_2]^+$ cation gave not only the Chini–Longoni $[Pt_{12}(CO)_{24}]^{2-}$, $[Pt_{15}(CO)_{30}]^{2-}$, and $[Pt_{18}(CO)_{36}]^{2-}$ dianions[12,13] but also the previously unknown $[Pt_{21}(CO)_{42}]^{2-}$ and $[Pt_{24}(CO)_{48}]^{2-}$ dianions is consistent with these gas-phase species likewise being composed of trigonal-prismatic stacks of platinum triangles.

This work illustrates the general applicability of ^{252}Cf-PDMS for analyzing a wide variety of high-nuclearity anionic metal clusters. Furthermore, it represents a new evolution in the application of the high-mass capabilities of ^{252}Cf-PDMS, which has heretofore been limited to compounds of biological interest. Further work in progress includes studies of the effects of sample dilution on the formation of gas-phase oligomer ions from the solid-state $[Pt_{26}(CO)_{32}]^{2-}$ dianions and the determination of the fragmentation patterns for other triangular $[Pt_3(CO)_6]_n^{2-}$ dianions.

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(14) ^{252}Cf-PDMS was performed on solid samples that had been electrosprayed as ca. 10^{-3} M solutions onto a thin Au/Al-coated Mylar polyester film. The samples were initially weighed inside a Vacuum Atmospheres glovebox and then transferred to a N_2-purged glovebag enclosing the inlet probe, where they were dissolved in either THF or acetonitrile. A detailed description of the time-of-flight instrument (locally designed and constructed) with the ^{252}Cf-plasma desorption ionization probe and the data acquisition system is given elsewhere.[3]

(15) Descriptions and figures of the platinum core geometries of these clusters are given elsewhere.[16]

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(18) The naturally occurring isotopes of platinum are ^{190}Pt (0.01%), ^{192}Pt (0.79%), ^{194}Pt (32.9%), ^{195}Pt (33.8%), ^{196}Pt (25.3%), and ^{198}Pt (7.2%).

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Promotion of Electron Transfer by Protonation of Nitrogen-Centered Free Radicals. The Addition of Radicals to Iminium Ions[1]

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Chain reactions between alkylmercury halides and some electron-deficient alkenes $[CH_2{=}CH(EWG)]$ involving eq 1 have been reported, e.g., with EWG = $PhSO_2$ or $(EtO)_2P(O)$.[2] Although α,β-unsaturated carbonyl compounds react inefficiently with RHgCl when photostimulated, reactions occur readily in the presence of iodide ion in Me_2SO by virtue of electron transfer between the adduct enolyl radical and $RHgI_2^-$, eq 2.[3,4] However, adduct radicals from α,β-unsaturated nitriles do not undergo this reaction efficiently.

$$RCH_2CH(EWG)^\bullet + RHgCl \rightarrow RCH_2CH(HgCl)EWG + R^\bullet \qquad (1)$$

$$RCH_2\dot{C}HC(O)Y + RHgI_2^- \rightarrow RCH_2CH{=}C(O^-)Y + R^\bullet + HgI_2 \qquad (2)$$

We have found that intermediate adduct radicals such as $RCH(R^1)\dot{C}(Y)C{\equiv}N \leftrightarrow RCH(R^1)C(Y){=}C{=}\dot{N}$ or $RCH_2\dot{C}(R^1)C(Y){=}NR^2 \leftrightarrow RCH_2C(R^1){=}C(Y)\dot{N}R^2$, although often unreactive in reaction 1 or 2, will undergo chain propagation reactions with $RHgI/I^-$ in the presence of proton donors such as *p*-toluenesulfonic acid (PTSA), eqs 3 and 4. In the absence of

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