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metal to the end-on-bonded dihalogen.

Note that the Pt $4f_{7/2}$ binding energy values of the four platinum complexes of $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$ are to the lower end of the range known for Pt compounds, whereas the N 1s binding energies (400.2–400.5 eV) are to the higher end of the range observed in N-containing organometallic compounds.[20,23] This is consistent with the hard-donor nature of the nitrogen ligand used.

In summary, application of XPS to organometallic platinum compounds is not straightforward but the use of short measuring times, cooled samples, and monochromatized X-rays can provide reliable XPS spectra. The application of this approach to the trapped intermediate $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$, found to contain a divalent platinum center, illustrates the usefulness of this technique.

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# Syntheses of the Seven-Metal Carbide Cluster $[PPN]_2[Os_3Ni_4C(CO)_{15}]$ and of $[PPN]_2[Os_3Ni_3C(CO)_{13}]$

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## Introduction

Clusters containing Ni, Pd, and Pt often have fewer electrons for their geometries than predicted by traditional electron-counting rules such as the polyhedral skeletal electron pair theory (PSEPT).[1,2] For example, $[Pt_3(CO)_6]^{2-}$[3] has only 44 electrons, although PSEPT predicts that it should be a 48-electron cluster. The large d to p promotion energy for Pt atoms results in the destabilization of cluster orbitals having platinum p character and, consequentially, in a decrease in the electron count for many Pt clusters.[4] Extended Hückel calculations on the 48-electron cluster $Fe_3(CO)_{12}$ show that 9 predominantly s and p metal orbitals and 3 d orbitals interact with the 12 CO ligands to give 24 filled cluster orbitals.[5] In $[Pt_3(CO)_6]^{2-}$ only 22 cluster orbitals are filled, because two high-lying e″ orbitals do not interact with CO ligands to form bonding orbitals. Similarly, in heterometallic clusters, the replacement of an $M(CO)_3$ fragment with an isolobal $PtL_2$ fragment may result in a decrease in the number of electrons required for a closed-shell configuration, but many heterometallic Pt clusters, for example $Pt_2Os_4(CO)_{12}(COD)_2$ (COD = 1,5-cyclooctadiene), obey traditional electron-counting rules such as PSEPT.[4,6]

The ketenylidene clusters $[PPN]_2[M_3(CO)_9CCO]$ react through redox condensation to form a variety of mixed-metal carbide clusters.[7,8] We report here the redox condensation of $[PPN]_2[Os_3(CO)_9CCO]$ and $Ni(CO)_4$ to form the seven-metal, 100-electron carbide cluster $[PPN]_2[Os_3Ni_4C(CO)_{15}]$.

**Table I.** X-ray Crystal Structure Data for $[PPN]_2[Os_3Ni_4C(CO)_{15}]$

| | | | |
|---|---|---|---|
| formula | $C_{88}H_{60}N_2P_4O_{15}Os_3\text{-}Ni_4\cdot 2C_4H_8O$ | $Z$ | 2 |
| | | $d$(calcd), g cm$^{-3}$ | 1.775 |
| $M_r$ | 2459.00 | $\mu$(Mo K$\alpha$), cm$^{-1}$ | 50.69 |
| cryst size, mm | 0.600 × 0.400 × 0.300 | radiation (λ, Å) | Mo K$\alpha$ (0.710 69) |
| cryst syst | triclinic | scan type | $\omega$–$\theta$ |
| space group | $P\bar{1}$ | $2\theta$ range, deg | 2–47 |
| $a$, Å | 13.395 (5) | no. of unique data | 13 562 |
| $b$, Å | 13.606 (6) | no. of unique data, $I > 3\sigma(I)$ | 10 210 |
| $c$, Å | 25.343 (8) | | |
| $\alpha$, deg | 88.18 (3) | no. of params | 637 |
| $\beta$, deg | 85.35 (3) | $R(F)$ | 0.081 |
| $\gamma$, deg | 89.31 (3) | $R_w(F)$ | 0.097 |
| $V$, Å$^3$ | 4601 (5) | GOF | 3.76 |

## Experimental Section

***Warning!*** In these reactions, the very highly toxic $Ni(CO)_4$ is produced as an intermediate.

**General Procedures.** All manipulations were carried out with the use of standard Schlenk techniques under an atmosphere of prepurified $N_2$.[9] Solids were handled in a Vacuum Atmospheres drybox with a Dri-train recirculator. The use of clamped O-ring ware permitted slightly positive pressures in the reaction vessels. Solvents were distilled from appropriate drying agents before use.[10] Solution infrared spectra were recorded on a Bomem MB-Series FTIR spectrometer at 2-cm$^{-1}$ resolution with 0.1 mm path length $CaF_2$ solution cells. $^{13}C$ NMR spectra of $^{13}C$-labeled compounds were recorded on a Varian XL-400 spectrometer operating at 100.58 MHz. The solvent was used as an internal reference. FAB mass spectra, obtained by $Cs^+$ bombardment of samples in a *m*-nitrobenzyl alcohol matrix, were recorded by Dr. D. L. Hung of Northwestern University Analytical Services Laboratory. Elemental analysis was done by Elbach Analytical Laboratories, Engelskirchen, Germany. $[PPN]_2[Os_3(CO)_9CCO]$ (I) was prepared by a literature method.[11] $Ni(COD)_2$ (Strem Chemicals) and CO were used as received.

**Synthesis of $[PPN]_2[Os_3Ni_4C(CO)_{15}]$ (II).** A 100-mL Schlenk flask was charged with 200 mg (0.103 mmol) of $[PPN]_2[Os_3(CO)_9CCO]$ and 200 mg (0.727 mmol) of $Ni(COD)_2$. THF (20 mL) was added, and the flask was fitted with a condenser. The suspension was freeze–pump–thaw degassed and CO (8 psig) was introduced. The flask was refluxed under a slow purge of $N_2$, while the ketenylidene dissolved and the suspension darkened from orange to brown. After 1.5 h, the solvent was removed in vacuo, along with excess $Ni(CO)_4$, which was destroyed. The dark brown product was extracted with 20 mL of THF. Slow diffusion of pentane into the extract produced black crystals: yield 205 mg (86%); IR (THF) 2042 (vw), 1993 (vs), 1966 (s), 1953 (m), 1917 (w), 1889 (w), 1811 (m) cm$^{-1}$; $^{13}C$ NMR (−20 °C, $CD_2Cl_2$) 333.1 (carbide), 256.3 (1), 210.4 (1), 209.2 and 209.1 (together, 4), 194.4 (3), 184.3 ppm (6). Anal. Calcd: C, 46.9; H, 3.12; Os, 23.2; Ni, 9.55. Found: C, 45.77; H, 3.31; Os, 25.15; Ni, 10.55.

**Synthesis of $[PPN]_2[Os_3Ni_3C(CO)_{13}]$ (III).** A 50-mL Schlenk flask was charged with 150 mg (0.0648 mmol) of II, and 10 mL of THF was added. The solution was freeze–pump–thaw degassed, and 5 psig of CO was introduced. The solution in the sealed flask lightened to a bronze color on stirring for 15 min. The solvent was then removed in vacuo, and the product was extracted with 10 mL of THF. Brown plates were grown by slow diffusion of 25 mL of diethyl ether into a solution of cluster in 10 mL of $CH_2Cl_2$: yield 45 mg (32%); IR (THF) 2026 (vw), 1981 (vs), 1965 (s), 1901 (w), 1823 (w) cm$^{-1}$; $^{13}C$ NMR (20 °C, $CD_2Cl_2$) 366.5 (carbide), 226.6 (1), 201.5 (3), 191.8 ppm (9); $^{13}C$ NMR (−115 °C, 2:1 $CF_2ClH$–$CD_2Cl_2$) 366.0 (carbide), 227.6 (1), 200.5 (3), 193.0 (6), 188.2 ppm (3); FAB mass spectrum P at *m/z* 1125 with broad fragment ion envelopes at *m/z* 1097, 1067, 1039, 1011, 982, and 955. Anal. Calcd: C, 46.9; H, 2.75; Os, 25.9; Ni, 8.00. Found: C, 46.53; H, 3.00; Os, 25.70; Ni, 7.64. The cluster was sometimes contaminated with unreacted $[PPN]_2[Os_3Ni_4C(CO)_{15}]$.

**Crystal Structure of $[PPN]_2[Os_3Ni_4C(CO)_{15}]$.** Crystals of II were grown by recrystallization in a diffusion tube from THF layered with pentane. The crystal habit was prismatic with poorly developed faces. The crystal was mounted on a glass fiber using oil (Paratone-N, Exxon)

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**Table II.** Positional Parameters for Significant Atoms in $[PPN]_2[Os_3Ni_4C(CO)_{15}]$

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Os1 | 0.34491 (6) | 0.39258 (5) | 0.18280 (3) |
| Os2 | 0.42158 (6) | 0.50629 (5) | 0.26468 (3) |
| Os3 | 0.31835 (6) | 0.33019 (6) | 0.28950 (3) |
| Ni1 | 0.2853 (2) | 0.6451 (2) | 0.2361 (1) |
| Ni2 | 0.2231 (2) | 0.5504 (2) | 0.1681 (1) |
| Ni3 | 0.1666 (2) | 0.4192 (2) | 0.2374 (1) |
| Ni4 | 0.2295 (2) | 0.5118 (2) | 0.3054 (1) |
| O211 | 0.400 (1) | 0.499 (1) | 0.0774 (5) |
| O212 | 0.220 (1) | 0.242 (1) | 0.1324 (6) |
| O213 | 0.533 (1) | 0.266 (1) | 0.1742 (6) |
| O221 | 0.521 (1) | 0.675 (1) | 0.1989 (6) |
| O222 | 0.448 (1) | 0.572 (1) | 0.3758 (6) |
| O223 | 0.614 (1) | 0.386 (1) | 0.2644 (7) |
| O231 | 0.295 (1) | 0.353 (1) | 0.4081 (5) |
| O232 | 0.155 (1) | 0.178 (1) | 0.2816 (7) |
| O233 | 0.487 (1) | 0.181 (1) | 0.2971 (6) |
| O511 | 0.282 (1) | 0.836 (1) | 0.2826 (7) |
| O521 | 0.084 (1) | 0.535 (1) | 0.0859 (6) |
| O531 | 0.007 (1) | 0.336 (1) | 0.1824 (6) |
| O541 | 0.203 (1) | 0.609 (1) | 0.4059 (6) |
| O551 | 0.243 (1) | 0.756 (1) | 0.1418 (6) |
| O552 | 0.025 (1) | 0.450 (1) | 0.3264 (6) |
| C | 0.284 (2) | 0.502 (1) | 0.2323 (7) |
| C211 | 0.375 (2) | 0.466 (1) | 0.1191 (8) |
| C212 | 0.267 (1) | 0.299 (1) | 0.1531 (7) |
| C213 | 0.460 (2) | 0.312 (1) | 0.1783 (7) |
| C221 | 0.481 (2) | 0.616 (2) | 0.2237 (8) |
| C222 | 0.435 (2) | 0.554 (2) | 0.3324 (8) |
| C223 | 0.540 (2) | 0.428 (2) | 0.2651 (8) |
| C231 | 0.301 (2) | 0.349 (2) | 0.3633 (9) |
| C232 | 0.217 (2) | 0.238 (2) | 0.2830 (8) |
| C233 | 0.427 (2) | 0.238 (1) | 0.2922 (7) |
| C511 | 0.282 (2) | 0.762 (2) | 0.2650 (9) |
| C521 | 0.138 (2) | 0.543 (2) | 0.117 (1) |
| C531 | 0.067 (2) | 0.365 (2) | 0.2064 (8) |
| C541 | 0.213 (2) | 0.570 (2) | 0.3651 (8) |
| C551 | 0.252 (2) | 0.684 (2) | 0.1678 (8) |
| C552 | 0.103 (2) | 0.457 (2) | 0.3009 (8) |

and transferred to the cold stream (−120 °C) of an Enraf-Nonius CAD4 diffractometer with a Mo K$\alpha$ radiation source. A summary of the data collection is given in Table I. Unit cell constants were determined by least-squares refinement of the setting angles of 25 unique reflections. Lorentz polarization and analytical absorption corrections were performed with transmission between 0.08 and 0.30. A decay correction was not applied, as the intensities of the three reflections monitored showed negligible variation.

Calculations were performed with the Texsan 5.0 crystallographic software package on a Micro Vax 3600 computer. The structure was solved by the direct methods technique (Shelxs-86), with full-matrix least-squares refinement. Carbon atoms were refined with isotropic thermal parameters; the remaining non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were varied in "idealized" positions. The four THF molecules cocrystallized with the cluster were refined as if all five atoms were carbons, because the oxygens could not be differentiated. The maximum and minimum peaks on the final difference map corresponded to 7.43 and −6.47 e/Å$^3$ and were in the vicinity of the metal atoms. The final positional parameters of significant atoms are listed in Table II.

## Results and Discussion

$[PPN]_2[Os_3(CO)_9CCO]$ and $Ni(CO)_4$, generated in situ, form the seven-metal carbide cluster $[PPN]_2[Os_3Ni_4C(CO)_{15}]$ (II), the largest cluster thus far synthesized by redox condensation of small metal carbonyls with ketenylidene clusters. The reactive species is presumably $Ni(CO)_{4-n}$, a product of the facile thermolysis of $Ni(CO)_4$.[12] Compound II loses nickel under CO, forming $[PPN]_2[Os_3Ni_3C(CO)_{13}]$ (III) and $Ni(CO)_4$, observed in the infrared spectrum of the reaction mixture. Unlike I, $[PPN]_2[M_3(CO)_9CCO]$ (M = Fe, Ru) react with $Ni(CO)_4$ to form directly the six-metal carbide clusters $[PPN]_2[M_3Ni_3C(CO)_{13}]$ (M = Fe, Ru).[7b,8]

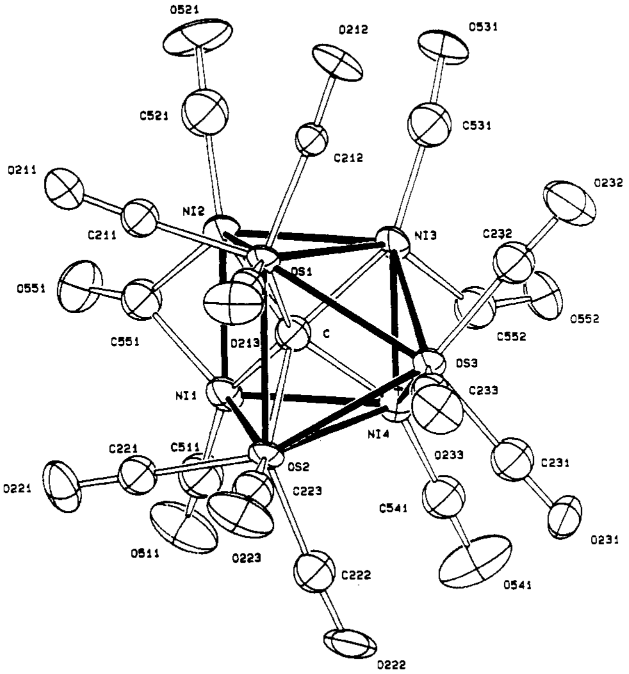

**Figure 1.** ORTEP drawing of $[PPN]_2[Os_3Ni_4C(CO)_{15}]$. Ellipsoids are drawn at the 50% probability level.

The observed isotope distribution of the parent ion in the FAB mass spectrum of III agrees with the distribution expected for $[PPN]_2[Os_3Ni_3C(CO)_{13}]$

$$R_p = \sum|I_o - I_c|/\sum I_o = 0.099$$

$I_o$ and $I_c$ are calculated and observed intensities, respectively. The most intense peak corresponds to the parent minus one CO.

The room-temperature solution $^{13}C$ NMR spectrum of $[PPN]_2[Os_3Ni_3C(CO)_{13}]$ has three resonances in the carbonyl region at 226.6, 201.5, and 191.7 ppm. These peaks can be assigned to a bridging carbonyl, the terminal carbonyls on the Ni atoms, and the terminal carbonyls on the Os atoms, respectively. The intermetallic site exchange of carbonyls is slow on the NMR time scale at room temperature. Above −105 °C, the resonance at 191.7 ppm splits into two broad resonances at 193 (6 CO) and 188 ppm (3 CO). The cluster retains $C_{3v}$ symmetry in the absence of intermetallic and intrametallic exchange of carbonyls. This slowing of the turnstile rotation was not observed for $[PPN]_2[M_3Ni_3C(CO)_{13}]$ (M = Fe, Ru) to which III is analogous.[7b,8] Like $[PPN]_2[Ru_3Ni_3C(CO)_{13}]$, the 86-electron cluster III has an electron-precise closed octahedral geometry in solution, although $[PPN]_2[Ru_3Ni_3C(CO)_{13}]$ was observed to have a formally electron-deficient opened structure in the solid state.[8] It was postulated that the observed difference between the solid-state and solution geometries of $[PPN]_2[Ru_3Ni_3C(CO)_{13}]$ was caused either by metal fluxionality in solution or by distortions resulting from packing effects.[8]

The ORTEP drawing of II, Figure 1, reveals that the carbide ligand sits in the center of a trigonal prism consisting of two Os atoms and four Ni atoms. The third Os atom caps a square face consisting of two Ni and two Os atoms and is not bonded to the carbide (Table III). Those Ni–Ni bonds bridged by CO are approximately 0.15 Å shorter than unbridged bonds, as is found for clusters such as $[Ni_3(CO)_6]_2^{2-}$,[13] and $[Ni_7C(CO)_{12}]^{2-}$.[14] Os–Os and Os–Ni distances are comparable to those found in $[Os_{10}C(CO)_{24}]^{2-}$ (mean 2.88 Å in octahedron, 2.79 (1) Å to capping Os)[15] and $[Os_3NiH_2(CO)_{10}(PPh_3)_2]^-$ (2.605 (1)–2.733

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**Table III.** Selected Bond Distances and Angles for $[PPN]_2[Os_3Ni_4C(CO)_{15}]$

| | Bond Distances (Å) | | |
|---|---|---|---|
| Os1–C | 2.09 (2) | Ni2–C | 1.97 (2) |
| Os2–C | 2.08 (2) | Ni3–C | 1.94 (2) |
| Os3···C | 2.76 (2) | Ni4–C | 1.94 (2) |
| Ni1–C | 1.95 (2) | | |
| Ni1–Ni2 | 2.392 (3) | Ni2–Ni3 | 2.542 (4) |
| Ni1–Ni4 | 2.560 (4) | Ni3–Ni4 | 2.382 (3) |
| Os1–Os2 | 2.888 (1) | Os2–Ni1 | 2.733 (3) |
| Os1–Os3 | 2.804 (1) | Os2–Ni4 | 2.695 (3) |
| Os1–Ni2 | 2.715 (3) | Os3–Ni3 | 2.760 (3) |
| Os1–Ni3 | 2.688 (3) | Os3–Ni4 | 2.757 (3) |
| Os2–Os3 | 2.809 (2) | | |
| | Bond Angles (deg) | | |
| Os2–Os1–Os3 | 59.12 (4) | Os2–Ni1–Ni2 | 95.1 (1) |
| Os2–Os1–Ni2 | 84.97 (6) | Os2–Ni1–Ni4 | 61.10 (8) |
| Os2–Os1–Ni3 | 84.51 (6) | Ni2–Ni1–Ni4 | 90.3 (1) |
| Os3–Os1–Ni2 | 108.32 (7) | Os1–Ni2–Ni1 | 95.4 (1) |
| Os3–Os1–Ni3 | 60.28 (6) | Os1–Ni2–Ni3 | 61.39 (8) |
| Ni2–Os1–Ni3 | 56.12 (8) | Ni1–Ni2–Ni3 | 89.5 (1) |
| Os1–Os2–Os3 | 58.95 (4) | Os1–Ni3–Os3 | 61.96 (6) |
| Os1–Os2–Ni1 | 84.56 (6) | Os1–Ni3–Ni2 | 62.49 (9) |
| Os1–Os2–Ni4 | 84.69 (6) | Os1–Ni3–Ni4 | 95.7 (1) |
| Os3–Os2–Ni1 | 107.85 (7) | Os3–Ni3–Ni4 | 64.37 (9) |
| Os3–Os2–Ni4 | 60.08 (6) | Ni2–Ni3–Ni4 | 90.9 (1) |
| Ni1–Os2–Ni4 | 56.27 (8) | Os2–Ni4–Os3 | 62.02 (6) |
| Os1–Os3–Os2 | 61.93 (4) | Os2–Ni4–Ni1 | 62.63 (9) |
| Os1–Os3–Ni3 | 57.77 (6) | Os2–Ni4–Ni3 | 95.1 (1) |
| Os1–Os3–Ni4 | 85.16 (6) | Os3–Ni4–Ni1 | 114.8 (1) |
| Os2–Os3–Ni3 | 84.72 (7) | Os3–Ni4–Ni3 | 64.47 (9) |
| Os2–Os3–Ni4 | 57.89 (6) | Ni1–Ni4–Ni3 | 89.3 (1) |
| Ni3–Os3–Ni4 | 51.15 (7) | | |

(1) Å),[16] respectively. Ni–C distances are comparable to those found in $[PPN]_2[Ru_3Ni_3C(CO)_{13}]$ (1.85 (1)–1.96 (1) Å)[8] and $[Ni_7C(CO)_{12}]^{2-}$, although in $[Ni_7C(CO)_{12}]^{2-}$ the carbide appears to be bonded to all seven nickel atoms ($Ni_{cap}$–C = 1.95 Å, Ni–Ni 1.94–2.09 Å).[14] Os–C distances are similar to those in $[Os_{10}C(CO)_{24}]^{2-}$ (mean 2.04 (3) Å)[15] and $[Os_6C(CO)_{16}(MeCCMe)]$ (mean 2.04 (2) Å).[17]

The solution $^{13}C$ NMR spectra of II are consistent with its solid-state structure. The carbide resonance occurs at 333.5 ppm. Peaks at 256.3 and 210.4 ppm may be assigned to the bridging carbonyls on the Ni atoms. Resonances at 209.2 and 209.1 ppm are assigned to the terminal carbonyls on the Ni atoms, and those at 194.4 and 184.3 ppm belong to terminal carbonyls on the Os atoms. A plane of symmetry runs through the capping Os perpendicular to the square faces of the trigonal prism for the static molecule. Broadening of the carbonyl resonances at 20 °C indicates that exchange of all carbonyls occurs at elevated temperatures. At −90 °C, broadening of resonances at 194.4 and 184.3 ppm indicates slowing of intrametal CO exchange.

The geometry of II may be viewed as a condensation of a trigonal prism (90 e) and a square pyramid (74 e) sharing a square face (64 e).[18] Thus, II is expected by PSEPT to have 100 electrons, 90 + 74 − 64, and is electron precise. Although other geometries are more common, four other clusters are known to adopt this same metal configuration.[14,18]

Factors determining the geometry of a cluster include its electron count[1,4] and the site preferences of interstitial atoms.[19] Other observed geometries for seven-metal clusters include a trigonal prism capped on a triangular face (102 e), a capped octahedron (98 e), an edge-bridged capped square pyramid (100 e), an edge-bridged octahedron (100 e), and a tricapped tetrahedron (96 e).[1] Unlike many mixed-metal clusters containing Pt metals, II adopts a geometry expected for its electron count. Clusters with Ni are more often electron precise than those with Pd or Pt, however.[1] In compound II, the Os atom prefers the capping site of the cluster, although it might be expected that, in the formation of a heptametallic cluster, nickel might cap one face, leaving all three Os–carbide bonds intact. Apparently, under the synthetic conditions, site preferences of the metal atoms, rather than kinetic factors, determine the final metal arrangement.

It has been suggested that in heterometallic clusters M–L and M–M bond strengths determine thermodynamic metal site preferences.[19] When M–L bonding does not vary between the alternative metal arrangements, the structure which maximizes the total M–M bond strength is favored. Heats of vaporization indicate that the average M–M bond strength in the metal, $\bar{M}$, is greater for osmium than for nickel (Ni, $\bar{M}$ = 71 kJ/mol; Os, $\bar{M}$ = 132 kJ/mol).[20,21] The configuration of metals found in II maximizes Os–Os and Os–Ni bonding, at the expense of weaker Ni–Ni bonding.

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**Supplementary Material Available:** Full lists of positional parameters and bond distances and angles (13 pages); a structure factor table (69 pages). Ordering information is given on any current masthead page.

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# Two Salts of Bis(ethanol)(*meso*-tetraphenylporphinato)iron(III). Molecular Structures and Magnetic Susceptibilities

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Six-coordinate iron(III) porphyrinates with neutral, weak-field, oxygen donor axial ligands have been generally found to have an $S = {}^5/_2$ (high-spin) ground state.[2,3] Interestingly, Gans et al. have synthesized and characterized a bis(ethanol) complex of $Fe^{III}TPP$ that *almost* fits this pattern.[4] This species, $[Fe(TPP)(EtOH)_2]BF_4$,[5] has been described by a quantum mechanical admixture of spin quartet ($S = {}^3/_2$) and spin sextet ($S = {}^5/_2$) states, with the sextet lying about 200 cm⁻¹ lower.[6] This

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[5] Abbreviations used: TPP and OEP, dianions of *meso*-tetraphenylporphyrin and octaethylporphyrin; EtOH, ethanol; THF, tetrahydrofuran; TMSO, tetramethylene sulfoxide.

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