Table I. Reaction of Me_3NBH_2COOX (X = H, Na, Me) with Various Hydrides

hydride	no. of molar equiv	conditions	results
X = Me			
Et_4NBH_4[11]	2	CH_2Cl_2/reflux/64 h	no reaction[a]
$NaBH_4$	4	diglyme/reflux/60 h	no reaction[b]
$NaBH_4$/MeOH[12]	2.5	diglyme/reflux/1 h[c]	no reaction[a]
K-Selectride ($KB[CH(CH_3)C_2H_5]_3H$)	2	THF/rt/72 h	trace amount of $Me_3NBH_2CH_3$[d] remaining unreacted[b]
		reflux/16 h	same results
$LiAl(O\text{-}{}^tBu)_3H$	2	THF/reflux/24 h	small amount of $Me_3NBH_2CH_3$[d] remaining unreacted
$NaAlH_2Et_2$	2	Et_2O/rt/24 h	$NaBH_3CH_3$
$LiAlH_4$	1 or 2	Et_2O/rt/1 h	$LiBH_3CH_3$ + trace $Me_3NBH_2CH_3$
X = H			
$NaBH_4$	2	THF/reflux/1.5 h	Me_3NBH_3[b,e]
$LiAlH_4$	2	Et_2O/rt/1 h	$LiBH_3CH_3$, some $Me_3NBH_2CH_3$
	1	Et_2O/−78 °C/6 h	$LiBH_3CH_3$, Me_3NBH_2COOLi
$LiAl(O\text{-}{}^tBu)_3H$	2	THF/reflux/72 h	Me_3NBH_2COOLi
X = Na			
$NaBH_4$	2	THF/reflux/4 h	no reaction[b]
NaH	2	THF/reflux/48 h	decomposition to species without B–H bonds, small amount of Na_2BH_3COO and unreacted starting material
Vitride	2	THF/reflux/19 h	MBH_3CH_3
$LiAlH_4$	2	THF/rt/24 h	MBH_3CH_3

[a] Hydride reagent completely decomposed. [b] Some decomposition of hydride reagent. [c] The reaction mixture was refluxed for 1 h prior to addition of MeOH and then refluxed for another 1 h. [d] Since $Me_3NBH_2CH_3$ is very volatile, some of it may have escaped during the reaction. [e] Me_3NBH_3 is probably formed by the displacement reaction of diborane (generated as follows: $Me_3NBH_2COOH + NaBH_4 \rightarrow Me_3NBH_2COONa + H_2 + {}^1/_2B_2H_6$) with $Me_3NBH_2COOH(Na)$. Since no Na_2BH_3COO was observed, the displacement product, $BH_2COOH(Na)$, must degrade quickly before it can convert to **1**.

preparation of $Me_3NBH_2CH_3$ and subsequently $NH_3BH(CH_3)$-CONHEt,[10] the amide of the boron analogue of alanine (the first boron analogue of amino acids with a side chain). With NaH as the hydride source and X = Na, formation of small amounts of **1** was observed along with major decomposition.

Formation of **1**, MBH_3CH_3, and in some cases $Me_3NBH_2CH_3$ depends upon the rate of the following two reactions: (a) displacement of Me_3N by H^-; (b) reduction of the carbonyl group (Scheme II). In the case where X = Me (and reduction is observed), the reduction of carbonyl is much faster than displacement of Me_3N. Thus, formation of only $Me_3NBH_2CH_3$ (in small amounts) is observed upon reduction with K-Selectride ($KB[CH(CH_3)C_2H_5]_3H$ or $LiAl(O\text{-}{}^tBu)_3H$. With stronger hydride reagents, reaction b is followed by reaction a.

The carbonyl group in **2** is quite difficult to reduce, and when $NaAlH_2Et_2$ is used as the hydride source, both reactions proceed at a similar rate. The carbonyl group of **1**, formed by displacement of Me_3N from **2**, is even harder to reduce not only because of the negative charges on the adjacent atoms but also due to the insolubility of **1** in THF. From the data presented in Table I, it is also clear that the partially reduced species are very susceptible to reduction and are probably reduced as soon as they are formed.

In summary, a convenient synthesis of sodium boranocarbonate is described. Not only does it easily make available large amounts of **1** for biological studies and for selective reduction studies, but it also provides an easy source of BH_3CO for incorporation of boron into potential BNCT agents.

In pharmacological studies[13] in murine model screens, compound **1** has shown significant hypocholesterolemic[14] and anti-inflammatory[15] activity. These data will be published separately.

Acknowledgment. This research was supported by the Army Research Office.

Registry No. $Na_2(\mathbf{1})$, 17363-08-5; **2**, 103904-11-6; $NaAlH_2Et_2$, 17836-88-3; $Me_3NBH_2CH_3$, 52920-77-1; $NaBH_3CH_3$, 141344-69-6; $LiBH_3CH_3$, 52950-75-1; Me_3NBH_3, 75-22-9; $LiBH_3CH_3$, 52950-75-1; Me_3NBH_2COOLi, 141344-70-9; Me_3NBH_2COOMe, 91993-52-1; Me_3NBH_2COOH, 60788-33-2; Et_4NBH_4, 17083-85-1; $NaBH_4$, 16940-66-2; $KB[CH(CH_3)C_2H_5]_3H$, 54575-49-4; $LiAl(O\text{-}{}^tBu)_3H$, 17476-04-9; $LiAlH_4$, 16853-85-3; vitride, 22722-98-1.

Supplementary Material Available: Text giving a detailed synthesis of sodium carboxylatotrihydroborate (1 page). Ordering information is given on any current masthead page.

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Oxidation State of Platinum in Oxidative-Addition Reactions and η^1-I_2 Products from Dihalogen Reactions with Organoplatinum(II) Complexes, As Inferred from Monochromatic X-ray Photoelectron Spectroscopy

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Introduction

Continuing our investigations of oxidative-addition reactions, we have studied in detail the reactions of dihalogens, alkyl halides, and organotin(IV) complexes with various Pt(II) complexes containing the terdentate monoanionic ligand $[C_6H_3$-

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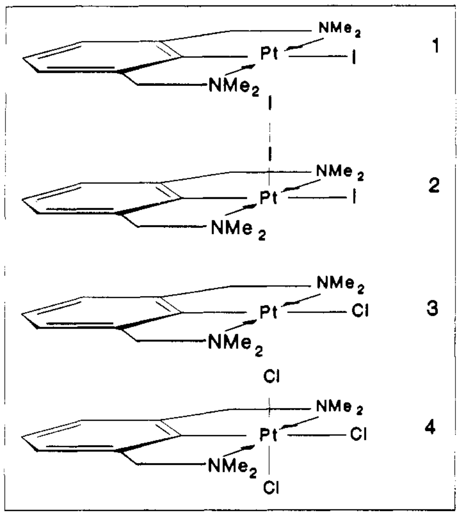

Figure 1. Structure of (1) [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}], (2) [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}(η^1-I_2)], (3) [PtCl{$C_6H_3(CH_2NMe_2)_2$-2,6}], and (4) [$PtCl_3${$C_6H_3(CH_2NMe_2)_2$-2,6}].

$(CH_2NMe_2)_2$-2,6].[1-4] In neutral complexes [PtX{$C_6H_3(CH_2NMe_2)_2$-2,6}], where the two hard N donor atoms are mutually trans, this ligand gives rise to tuned reactivity toward oxidative addition. In the resulting products, the ligand not only helps stabilize higher oxidation states but at the same time, through its rigidity, also restricts the number of possible ligand arrangements and rearrangements around the metal center. The latter two characteristics are especially important, since they can promote stabilization and hence isolation of reaction intermediates. This is well illustrated by the reactions of Cl_2 and I_2 with [PtX{$C_6H_3(CH_2NMe_2)_2$-2,6}] (X = Cl and I, respectively).[1,5-7] In the reaction with Cl_2, the Pt(IV) complex [$PtCl_3${$C_6H_3(CH_2NMe_2)_2$-2,6}], i.e. the oxidative addition product, is formed quantitatively, while, in the reaction with I_2, the process stops at the stage in which I_2 is η^1-coordinated to the metal center. This type of M–I_2 interaction is often described as the first step in the oxidative addition of dihalogens to d^8 metal centers, and the product [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}(η^1-I_2)][5,8,9] was the first isolated end-on-coordinated dihalogen metal complex; a few other examples have since been reported.[6,7,10]

For [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}(η^1-I_2)], questions arise as to the extent of the electron shift from the formally Pt(II) center to the end-on-coordinated, electrophilic I_2 molecule. The ^{1}H NMR spectrum of this η^1-I_2 addition complex unfortunately does not provide any information about whether the platinum center is Pt(II) or Pt(IV), since no satellites arising from Pt-H coupling constants are observed on the broad resonances. Combined spectroscopic solution studies provided evidence for fluxionality, but ambiguity remains about the exact nature of this unique species in solution. In this study, we report the use of monochromatic X-ray photoelectron spectroscopy (XPS) for determination and comparison of the Pt 4f binding energies of the Pt center in this species and some related organoplatinum complexes (Figure 1).

Table I. I/Pt, Cl/Pt, and N/Pt Peak Intensity Ratios of the Compounds Shown in Figure 1

	$I_{I\,3d}/I_{Pt\,4f}$	$I_{Cl\,2p}/I_{Pt\,4f}$	$I_{N1\,1s}/I_{Pt\,4f}$
[PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}]	2.13		0.23
[PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}(η^1-I_2)]	4.05		0.22
[PtCl{$C_6H_3(CH_2NMe_2)_2$-2,6}]		0.22	0.22
[$PtCl_3${$C_6H_3(CH_2NMe_2)_2$-2,6}]		0.59	0.24

Experimental Section

The organoplatinum compounds [PtX{$C_6H_3(CH_2NMe_2)_2$-2,6}] (X = Cl, I)[1,11] [$PtCl_3${$C_6H_3(CH_2NMe_2)_2$-2,6}],[3] and [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}(η^1-I_2)][9] were synthesized by following published procedures. Dilute solutions in dichloromethane (approximately 5 mg/mL) were prepared, and several droplets were left to dry on the stainless steel sample stubs of the XPS spectrometer. To minimize sample degradation due to exposure to electrons, heat, and X-rays, a monochromatic X-ray source was employed, and to prevent decomposition in the ultrahigh-vacuum (UHV) chamber, the samples were cooled to liquid-nitrogen temperature.

Spectra were obtained using a VG ESCALAB 200 spectrometer equipped with a monochromatic Al Kα X-ray source, a hemispherical analyzer with a five-channel detector, and a manipulator that can be cooled with liquid nitrogen. During measurement, the base pressure of the system was around 5×10^{-10} mbar. In order to minimize sample degradation effects, the XPS spectra were obtained as follows. First, the Pt 4f and C 1s lines (pass energy 20 eV) were recorded to establish the Pt 4f binding energy state of the platinum atom in the fresh sample. Subsequently, the N 1s, the Cl 2p or I 3d, and the C 1s peaks were recorded to determine precise binding energies of N 1s and Cl 2p or I 3d, followed by a broad-range scan (pass energy 100 eV) to measure peak intensity ratios. During all these measurements, the Pt 4f and C 1s signal were monitored to check for a stable binding energy of the Pt 4f doublet. All binding energies were determined by computer fitting of the measured spectra, and sample charging, typically between 0.5 and 3.5 eV, was corrected for by reference to the C 1s peak at 284.6 eV. Note that the C 1s signal is due not only to carbon in the complex but also to contaminant carbon from exposure of the sample to the air and the vacuum of the entry lock of the spectrometer. We estimate that the contaminant carbon accounts for roughly 50%–70% of the carbon signal. In particular, the inhomogeneous charging of the complexes leads to rather broad peaks and the fwhm varies slightly per sample. The values obtained for the binding energy have uncertainties of about 0.3 eV; this is the practical limit imposed by calibration errors, reproducibility, and instrumental resolution.

Results

Broad-energy-range scans (not shown) were used to obtain I 3d/Pt 4f, Cl 2p/Pt 4f, and N 1s/Pt 4f peak intensity ratios. These values should be consistent with the elemental stoichiometry of the complexes, and they thus provide a check of sample integrity under the measuring conditions employed. The measured intensity ratios are given in Table I. For the two Pt(II) complexes, the Pt(IV) product [$PtCl_3${$C_6H_3(CH_2NMe_2)_2$-2,6}], and the Pt–η^1-I_2 species, the N 1s/Pt 4f intensity ratios are equal to 0.23 ± 0.01. The ratios did not vary during measurements; i.e., the tridentate organic ligand does not evaporate from the samples in UHV. The Cl 2p/Pt 4f ratio value of the precursor Pt(II) complex [PtCl{$C_6H_3(CH_2NMe_2)_2$-2,6}] compared to that of the $Pt^{IV}Cl_3$ oxidative addition product is approximately 3 times higher; these peak ratios are expected because peak intensities are linear in concentrations. However, for the Pt–η^1-I_2 species, the I 3d/Pt 4f ratio is approximately twice that of [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}] whereas a factor of 3 would be expected. This indicates that the sample is an approximately 50%–50% mixture of [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}] and [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}(η^1-I_2)]. This, although not ideal, is nevertheless sufficient for determining the binding energy of the [PtI{$C_6H_3(CH_2NMe_2)_2$-2,6}(η^1-I_2)] compound, which is known to be labile in solution and to slowly lose I_2 when heated for extended periods under vacuum. Firm conclusions regarding the binding energies of the different I atoms however cannot be drawn.

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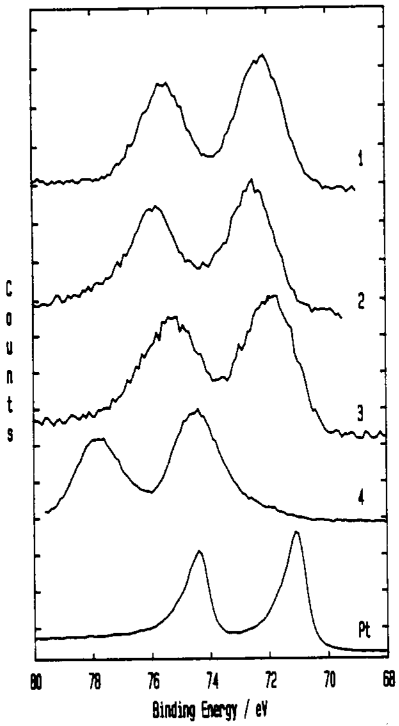

Figure 2. XPS spectra of the Pt 4f doublet of (1) $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, (2) $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$, (3) $[PtCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, (4) $[PtCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, and a clean platinum wire.

Table II. Binding Energies of the Compounds Shown in Figure 1

	Pt $4f_{7/2}$	C 1s	I $3d_{5/2}$	Cl 2p	N 1s
$[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	72.2	284.6	619.2		400.5
$[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$	72.5	284.6	619.1		400.3
$[PtCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	72.0	284.6		198.2	400.3
$[PtCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$	74.4	284.6		198.5	400.2

The exact position(s) of the Pt 4f peak(s) is (are) a direct indication of the platinum oxidation state. XPS spectra of the four organoplatinum complexes that cover the Pt 4f region are shown in Figure 2 together with a spectrum of a platinum metal wire reference for Pt(0). As Figure 2 shows, the Pt $4f_{7/2}$ peak of $[PtCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ appears at a binding energy approximately 2 eV higher than the corresponding peaks of $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ and $[PtCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (72.2 and 72.0 eV, respectively); these latter lie approximately 1 eV to the higher binding energy side of Pt(0). The species $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$ has a Pt $4f_{7/2}$ binding energy peak at 72.5 eV; i.e., its value is closely comparable to that of the Pt $4f_{7/2}$ peaks for the precursor Pt(II) species. On this basis, the metal atom in this $Pt\text{-}\eta^1\text{-}I_2$ species can be assigned a formal oxidation state of 2+.

A summary of the binding energies of the Pt $4f_{7/2}$ as well as the I $3d_{5/2}$, Cl 2p, and N 1s peaks is given in Table II. The binding energies of the N 1s, Cl 2p, and I 3d peaks are in agreement with those expected for these elements in the environments found in the complexes of Figure 1.

Discussion

During XPS measurements of platinum compounds, several investigators have reported sample degradation features in their spectra.[12-16] Our results show that worthwhile results can be obtained even for difficult samples if precautions are taken to avoid sample decomposition through exposure to electrons, heat, or X-rays in combination with the ultrahigh vacuum used. Although loss of Cl_2 from platinum complexes is reported in the literature,[13,14] our approach was successful for $[PtCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$. However, despite cooling the sample of the diiodine addition product $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$ with liquid nitrogen, some loss of diiodine could not be avoided; this lower stability relative to that of the other species is consistent with the description of this material as a "trapped" reaction intermediate on the path to the sterically unaccessible Pt(IV) product $[PtI_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$.

A Pt $4f_{7/2}$ binding energy of 72.5 eV for $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$ is consistent with the formal oxidation state of Pt(II). The binding energy is approximately 2 eV lower than that of Pt(IV) in $[PtCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, for which there is no doubt that the platinum occurs as Pt(IV). Several authors have reported an increase in binding energy of approximately 2 eV on going from Pt(II) to Pt(IV) with similar compounds.[12,13,16,17-20] Moddeman et al., for example, found a 2.4 eV higher Pt $4f_{7/2}$ binding energy for K_2PtCl_6 than for K_2PtCl_4.[19] For the organoplatinum compounds of $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$, the binding energy values of Pt $4f_{7/2}$ that can be assigned to formal Pt(II) and Pt(IV) are similar to those reported by other authors.[16,18,21-23]

However, one has to bear in mind that the oxidation state formalism used here is simply an artificial aid to systemization. According to the charge potential model,[24] the Pt $4f_{7/2}$ binding energy depends both on the charge on the platinum atom and on the intramolecular Madelung potential from the charges on all other atoms in the complex. In the closely related series of complexes we used, binding energy shifts can be interpreted in terms of different charges on the platinum and differences in Madelung potential due to the halogen atoms. This implies that if the metal center in the $Pt\text{-}\eta^1\text{-}I_2$ species were Pt(IV) instead of Pt(II), the charge on the $\eta^1\text{-}I_2$ iodine atom closest to platinum would have to be 3–4 times higher than that on a Cl atom in $[PtCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ to yield a binding energy of 72.5 eV. This amount of charge appears unrealistic, and we conclude that the Pt(II) assignment for the $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$ complex is consistent within the charge potential model.

Since the sample of $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$ partially degrades to $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ under the XPS measurement conditions employed, one expects to see two Pt 4f doublets with slightly different binding energies. However due to inhomogeneous charging, all peaks are rather broad and the fwhm varies slightly per sample. As a consequence, the expected difference is below the spectral resolution.

Despite the limitations in the accuracy of the binding energy values (ca. 0.3 eV), one finds a slightly higher binding energy of the Pt $4f_{7/2}$ peak for $[PtI\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\eta^1\text{-}I_2)]$ than for the Pt(II) complexes $[PtX\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (X = Cl, I). For the $Pt\text{-}\eta^1\text{-}I_2$ species, this indicates a lower electron density on the platinum atom, consistent with the proposed mechanism of its formation and its bonding description. The formation of this compound is the very first step in the oxidative addition of I_2 to a d^8 metal center whereby nucleophilic attack of the filled d_{z^2} orbital on the I_2 molecule leads to electron donation from the

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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	μ(Mo Kα), cm^{-1}	50.69
cryst size, mm	0.600 × 0.400 × 0.300	radiation (λ, Å)	Mo Kα (0.710 69)
cryst syst	triclinic	scan type	ω–θ
space group	$P\bar{1}$	2θ 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)		
α, deg	88.18 (3)	no. of params	637
β, deg	85.35 (3)	$R(F)$	0.081
γ, 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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