

# Synthesis and Characterization of $[\eta^4\text{-P}_7\text{Ni}(\text{CO})]^{3-}$ , $[\eta^4\text{-HP}_7\text{Ni}(\text{CO})]^{2-}$ , and $[\eta^2\text{-P}_7\text{PtH}(\text{PPh}_3)]^{2-}$ : Two Electronically Equivalent Protonated Zintl Ion Complexes with Markedly Different Structures

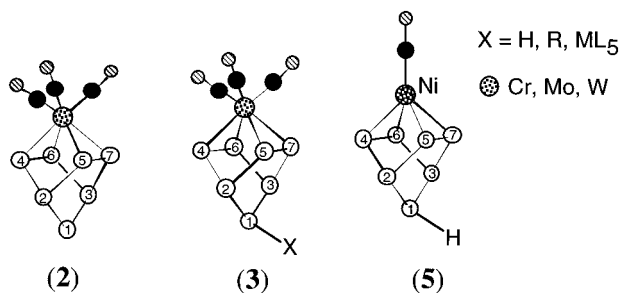
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In previous studies, we<sup>1,2</sup> and others<sup>3</sup> have described the reactions of the  $\text{E}_7^{3-}$  Zintl ions (**1**)<sup>4</sup> with group 6  $\text{M}(\text{CO})_3$  precursors to give the  $[\eta^4\text{-E}_7\text{M}(\text{CO})_3]^{3-}$  ions (**2**) where  $\text{E} = \text{P}, \text{As}, \text{Sb}$  and  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ . The electronic structures of compounds **2** are characterized by high-lying ligand-based orbitals that are predominately lone pairs localized on the E(1) atom.<sup>2</sup> Thus protonations,<sup>2,5</sup> alkylations,<sup>6</sup> and subsequent metallations<sup>5b</sup> occur at the E(1) site to give generic  $[\eta^4\text{-XE}_7\text{M}(\text{CO})_3]^{n-}$  ions (**3**) where  $\text{X} = \text{R}, \text{H}$ ,  $n = 2$  and  $\text{X} = \text{ML}_5$ ,  $n = 3$ . The  $\text{E}_7$  ligands of compounds **2** and **3** have a pronounced distortion from an idealized norbornadiene-type geometry; namely a  $\sim 0.3$  Å difference in the  $\text{E}(4)\cdots\text{E}(5)$  and  $\text{E}(6)\cdots\text{E}(7)$  nonbonded contacts.

The goal of the present study was to determine if  $[\eta^4\text{-E}_7\text{ML}]^{3-}$  complexes that are electronically equivalent and isostructural to compounds **2** could be prepared with group 10 metals and whether they too would be susceptible to ligand-based electrophilic attack at the E(1) site. When  $\text{E} = \text{Sb}$ , a trinickel *nido*- $[\text{Sb}_7\text{Ni}_3(\text{CO})_3]^{3-}$  polyhedral cluster is isolated in good yield<sup>7</sup> that is structurally quite different from compounds **2** and **3**. Herein we report the synthesis, structure, and



characterization of the norbornadiene-like  $[\eta^4\text{-P}_7\text{Ni}(\text{CO})]^{3-}$  ion (**4**), its conjugate acid  $[\eta^4\text{-HP}_7\text{Ni}(\text{CO})]^{2-}$  (**5**), and the electronically equivalent  $\text{Pt}(\text{PPh}_3)$  complex  $[\eta^2\text{-P}_7\text{PtH}(\text{PPh}_3)]^{2-}$  (**6**). Complexes **5** and **6** are formally conjugate acids of 18-electron  $[\text{P}_7\text{ML}]^{3-}$  ions, yet the structures and sites of hydrogen attachment are markedly different in the two cases.

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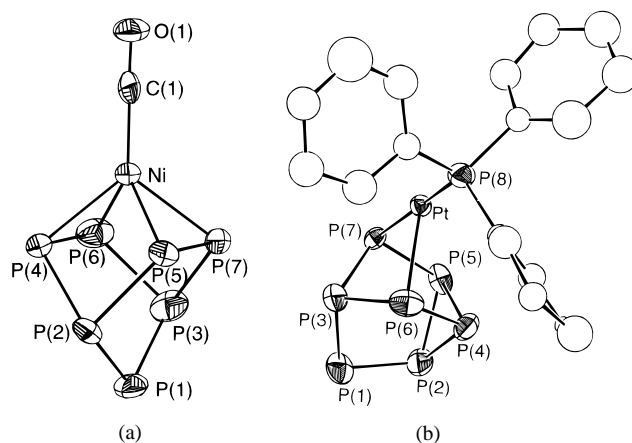
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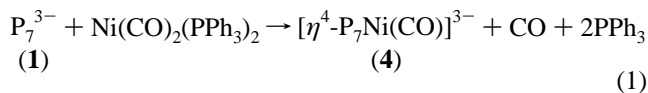
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**Figure 1.** (a) ORTEP drawing of the  $[\eta^4\text{-P}_7\text{Ni}(\text{CO})]^{3-}$  ion (**4**). Selected bond distances (Å): Ni–C(1) 1.77(1), Ni–P(6) 2.327(3), Ni–P(7) 2.328(3), Ni–P(4) 2.326(3), Ni–P(5) 2.300(3), P(5)–P(7) 2.127(3), P(4)–P(6) 2.128(4), P(4)⋯P(5) 2.952(5), P(6)⋯P(7) 3.005(5), P(1)–P(2,3) 2.144(5) (av), P(2)–P(4,5) 2.22(1) (av), P(3)–P(6,7) 2.23(2) (av). (b) ORTEP drawing of the  $[\eta^2\text{-P}_7\text{PtH}(\text{PPh}_3)]^{2-}$  ion (**av**). Selected bond distances (Å) and angles (deg): Pt–P(6) 2.42(1), Pt–P(7) 2.40(1), Pt–P(8) 2.23(1); P(7)–Pt–P(8) 174.5(4), P(6)–Pt–P(8) 98.6(4), P(6)–Pt–P(7) 78.2(4), P(2)–P(1)–P(3) 97.3(6).

Ethylenediamine solutions of  $\text{K}_3\text{P}_7$  react with  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  to give the  $[\eta^4\text{-P}_7\text{Ni}(\text{CO})]^{3-}$  ion (**4**) according to eq 1. Addition of 3 equiv of 2,2,2-crypt and excess  $(n\text{-C}_4\text{H}_9)_4\text{PBr}$  to the en solution gives crystalline  $[\text{K}(2,2\text{-crypt})][\text{K}(2,2\text{-crypt})]_2[\text{P}_7\text{Ni}(\text{CO})]^{3-}$  in 49% yield based on  $\text{P}_7^{3-}$ . Salts of **4** are orange–red



in color and are very air and moisture sensitive in solution and in the solid state. Complex **4** has been characterized by IR, <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopic studies, microanalysis, and single-crystal X-ray diffraction.<sup>8</sup> The ORTEP drawing of **4** (Figure 1a) shows the virtual  $\text{C}_{2v}$  symmetry of the ion that comprises a norbornadiene-like  $\text{P}_7^{3-}$  fragment bound  $\eta^4$  to the Ni(CO) center. Unlike the ions **2** and **3** described previously, the  $\text{P}_7$  cage of **4** is highly symmetrical with equivalent P(4)⋯P(5) and P(6)⋯P(7) separations of 2.98(3) Å (av). The Ni–P distances average 2.32(2) Å and are longer than typical Ni–P distances in zero valent nickel phosphine complexes (2.15–2.29 Å).<sup>9</sup> The Ni–C contact of 1.77(1) Å is typical of zero valent nickel carbonyl complexes ( $\sim 1.75$  Å, av)<sup>9,10</sup> even though the  $\nu(\text{CO})$  IR band at 1785  $\text{cm}^{-1}$  (KBr pellet) is highly red shifted relative to other zero valent nickel carbonyl complexes. The remainder of the structure is quite similar to

(8) Crystal data for  $[\text{K}(2,2\text{-crypt})][\text{K}(n\text{-Bu})_4\text{P}]_2[\text{P}_7\text{Ni}(\text{CO})]$ : monoclinic,  $\text{C}2/c$ ,  $a = 51.40(2)$  Å,  $b = 16.097(4)$  Å,  $c = 16.164(4)$  Å,  $\beta = 101.17(2)^\circ$ ,  $V = 13121(6)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.253$   $\text{g cm}^{-3}$  at 153 K. The structure was successfully refined against  $|F^2|$  using 3684 reflections [ $I > 2\sigma(I)$ ] to  $R(F) = 0.063$  and  $R_w(F^2) = 0.157$  (unit weights). Anal. calcd for  $\text{C}_{51}\text{H}_{108}\text{N}_2\text{O}_7\text{K}_2\text{P}_9\text{Ni}$ : C, 49.48; H, 8.79; N, 2.26; P, 22.52. Found: C, 49.91; H, 8.34; N, 2.38; P, 22.77. Selected NMR data for **4**: <sup>31</sup>P NMR (81.0 MHz, DMF-*d*<sub>7</sub>)  $\delta$  (ppm) = 101 (~tp, 1P, P(1)), 25 (m, 2P, P(2,3)), –124 (m, 4P, P(4–7)); <sup>13</sup>C NMR (100.6 MHz, DMF-*d*<sub>7</sub>)  $\delta$  = 198 (<sup>2</sup> $J_{\text{C–P}} = 8.5$  Hz).

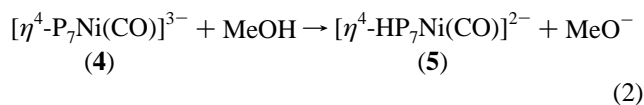
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those of **2**.<sup>2</sup> The symmetrical nature of the P<sub>7</sub> unit in **4** suggests that the observed asymmetries in complexes **2**<sup>1-3</sup> and **3**<sup>6</sup> result from specific orbital interactions between the M(CO)<sub>3</sub> fragments and the E<sub>7</sub><sup>3-</sup> ligands and are not due to inherent electronic instabilities<sup>2</sup> of 24-electron [η<sup>4</sup>-E<sub>7</sub>ML<sub>n</sub>]<sup>3-</sup> compounds.

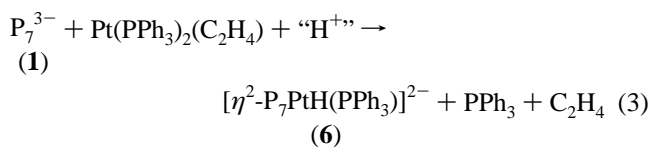
The <sup>31</sup>P NMR spectrum of **4** shows three second-order resonances in a 4:2:1 integral ratio<sup>8</sup> that are consistent with the solid state structure and are characteristic of C<sub>2v</sub> metal-bound norbornadiene-like P<sub>7</sub> units with AA'A''A'''MM'X spin systems.<sup>2</sup> The <sup>13</sup>C NMR spectrum shows a single pentet at 198 ppm (J<sub>P-C</sub> = 8.5 Hz) indicating that the Ni(CO)-P<sub>7</sub><sup>3-</sup> dissociation is not occurring on the NMR time scale.

Slow addition of 1 equiv of MeOH to DMF-*d*<sub>7</sub> solutions of **4** at -50 °C results in the formation of the [η<sup>4</sup>-HP<sub>7</sub>Ni(CO)]<sup>2-</sup> ion (**5**) according to eq. 2. Adding more than 1 equiv or warming to room temperature results in rapid decomposition of the complex to give as yet unidentified compounds. Equation



2 chemistry appears to be virtually quantitative by <sup>31</sup>P NMR spectroscopy, but **5** has not been isolated as a crystalline solid thus far. Compound **5** has C<sub>s</sub> point symmetry with a metal-bound norbornadiene-like P<sub>7</sub> unit, as evidenced by the characteristic AA'BB'MM'X <sup>31</sup>P NMR spin pattern.<sup>11</sup> The spectrum is similar to those of [η<sup>4</sup>-RP<sub>7</sub>W(CO)<sub>3</sub>]<sup>2-</sup> and [η<sup>4</sup>-HP<sub>7</sub>M(CO)<sub>3</sub>]<sup>2-</sup> where M = Cr, W.<sup>5,6</sup> Proton-coupled <sup>31</sup>P NMR experiments clearly show that the proton is attached to the unique phosphorus atom P(1). These data indicate that the structure of **5** is analogous to that of [η<sup>4</sup>-HP<sub>7</sub>Cr(CO)<sub>3</sub>]<sup>2-</sup> (see previous drawings).

Ethylenediamine solutions of K<sub>3</sub>P<sub>7</sub> also react with Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>) in the presence of 3 equiv of 2,2,2-crypt to give the [η<sup>2</sup>-P<sub>7</sub>PtH(PPh<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> ion (**6**) as the [K(2,2,2-crypt)]<sup>+</sup> salt in 46% yield according to eq 3. The reaction is quite reproducible; however, the source of the proton in eq 3 is currently not known.



Compound **6** is dark red in color and is moderately air and moisture sensitive in the solid state and solution. It has been characterized by IR, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopic studies, microanalysis, and single-crystal X-ray diffraction.<sup>12</sup> The

(11) Selected NMR data for **5**: <sup>31</sup>P NMR (81.0 MHz, DMF-*d*<sub>7</sub>) δ (ppm) = 58 (~tdp, 1P, <sup>1</sup>J<sub>P-H</sub> = 167 Hz, P(1)), 39 (m, 2P, P(2,3)), -133 (m, 2P, P(4,5)), -160 (m, 2P, P(6,7)).

(12) Crystal data for [K(2,2,2-crypt)]<sub>2</sub>[P<sub>7</sub>PtH(PPh<sub>3</sub>)<sub>2</sub>]: orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 17.088(1) Å, *b* = 19.900(1) Å, *c* = 20.030(2) Å, *V* = 6811(1) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 1.468 g cm<sup>-3</sup> at 298 K. The structure was successfully refined against |*F*| using 3144 reflections [*I* > 3σ(*I*)] to *R*(*F*) = 0.082 and *R*<sub>w</sub>(*F*) = 0.099 where *w* = (σ<sup>2</sup>*F* + 0.04*F*<sup>2</sup>)<sup>-1</sup>. Anal. calcd for C<sub>56</sub>H<sub>96</sub>N<sub>6</sub>O<sub>12</sub>K<sub>2</sub>P<sub>8</sub>Pt: C, 42.94; H, 6.18; N, 5.37; P, 15.82. Found: C, 42.11; H, 5.90; N, 4.81; P, 16.13. Selected NMR data for **6**: <sup>31</sup>P{<sup>1</sup>H} NMR (81.0 MHz, DMF-*d*<sub>7</sub>) δ (ppm) = 58 (m, <sup>1</sup>J<sub>P-Pt</sub> = 2720 Hz, <sup>2</sup>J<sub>P-P</sub> ≈ 8 Hz, PPh<sub>3</sub>); <sup>1</sup>H NMR (400.1 MHz, DMF-*d*<sub>7</sub>) δ = -10.1 (m, <sup>1</sup>J<sub>Pt-H</sub> = 1080 Hz, <sup>2</sup>J<sub>P-H</sub> ≈ 14 Hz).

ORTEP drawing of **6** (Figure 1b) reveals the virtually unperturbed, nortricyclic P<sub>7</sub><sup>3-</sup> fragment that is bound η<sup>2</sup> to the square planar [PtH(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> center. The hydride ligand was not located in the X-ray structure but is evident from the <sup>1</sup>H NMR spectrum (Pt-H, δ = -10.1 ppm, <sup>1</sup>J<sub>Pt-H</sub> = 1080 Hz, <sup>2</sup>J<sub>P-H</sub> ≈ 14 Hz).<sup>12</sup> It clearly occupies the fourth site in the Pt coordination sphere in the position *trans* to P(6). The two Pt-P bonds to P(6) and P(7) average 2.41(2) Å and are significantly longer than typical Pt-P bonds to phosphines (2.2–2.3 Å (av),<sup>13</sup> Pt-P(8) = 2.23(1) Å). The Pt-P(4) and Pt-P(5) separations of >3.3 Å are nonbonding. The ion has C<sub>1</sub> symmetry in the solid state, but <sup>31</sup>P NMR studies show fluxional behavior in solution that remains rapid on the NMR time scale at -60 °C in DMF-*d*<sub>7</sub> at 202 MHz. The persistence of the <sup>2</sup>J<sub>H-P</sub> coupling to the P<sub>7</sub> cage at 25 °C (observed in the <sup>1</sup>H NMR spectrum) indicates that an intramolecular fluxional process is operative, such as an η<sup>2</sup>-η<sup>1</sup>-η<sup>2</sup> “walk” of the [PtH(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> unit around the P<sub>7</sub><sup>3-</sup> cage.

As previously mentioned, the source of the H<sup>+</sup> in eq 3 is currently not known. On the basis of similar reactions conducted in the same en solvent and the reproducibly high isolated yields of **6**, we do not believe that adventitious protio impurities in the solvent serve as the hydrogen source. The hydride could originate from a Pt-based hydrogen abstraction process involving the C<sub>2</sub>H<sub>4</sub> ligand, a solvent molecule, or a [K(2,2,2-crypt)]<sup>+</sup> ion to generate a [PtH(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> type species *before* coordination to the P<sub>7</sub><sup>3-</sup> cluster. Regardless of the mechanism of formation, both **5** and **6** represent formal protonation products of the electronically equivalent complexes **4** and the putative [η<sup>4</sup>-P<sub>7</sub>Pt(PPh<sub>3</sub>)<sub>3</sub>]<sup>3-</sup> ion, respectively. Compounds **5** and **6** are electronically equivalent (*i.e.* Ni(CO) and Pt(PPh<sub>3</sub>) are both 12-electron fragments) but have very different structural motifs: namely the site of attachment of H<sup>+</sup> and the mode of P<sub>7</sub> coordination. Clearly the enhanced stability of Pt(II) hydrides vs Ni(II) hydrides<sup>14</sup> is influential in the product differentiation; however the role of the ligands (CO vs PPh<sub>3</sub>) is not clear at this time, and further investigations are warranted. It is interesting to note that the first stable metal-free protonated polyphosphide salt was only recently isolated.<sup>15</sup>

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**Supporting Information Available:** A complete listing of positional parameters, thermal parameters, and bond distances and angles for [K(2,2,2-crypt)]<sub>2</sub>[(*n*-Bu)<sub>4</sub>P]<sub>2</sub>[P<sub>7</sub>Ni(CO)] and [K(2,2,2-crypt)]<sub>2</sub>[P<sub>7</sub>PtH(PPh<sub>3</sub>)<sub>2</sub>] (45 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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