

proceeds without isomerization of the anti,syn complex **4** to syn,syn form **9**.

The transformation of **5** into 11-deoxy-PGE<sub>1</sub> (**7**) was carried out in the following way. Alkylation of the tetrahydropyranyl ether of **5** with 1-iodo-7,7-(1,3-dioxolane)heptane (NaH in DMF at 50 °C for 4 h) gave the alkylated product **18** in 45% yield. The lactone **18** was converted into the ester **19** in three steps (KOH in MeOH, CH<sub>2</sub>N<sub>2</sub>, and *t*-BuMe<sub>2</sub>SiCl/imidazole) and the desulfonation of **19** [5% Na(Hg) Na<sub>2</sub>HPO<sub>4</sub> in EtOH at room temperature for 12 h] gave the ester **20** in 93% yield. Conversion of the ester **20** to the aldehyde **21** (*i*-Bu<sub>2</sub>AlH in THF at -50 °C, Me<sub>2</sub>SO/(COCl)<sub>2</sub>) and then Et<sub>3</sub>N, overall yield 86%), cyanohydrin formation (Me<sub>3</sub>SiCN/KCN-18-crown-6 at 0 °C, PhCH<sub>2</sub>NMe<sub>3</sub>F in THF/H<sub>2</sub>O at 0 °C for 30 min), and the protection of the cyanohydrin [CH<sub>2</sub>=CHOEt/pyridinium *p*-toluenesulfonate (PPTS) in CH<sub>2</sub>Cl<sub>2</sub>] gave **22** in 95% overall yield. Removal of the silyl group (*n*-Bu<sub>4</sub>NF in THF at room temperature for 3 h) and the tosylation of the resulting alcohol (TsCl/Et<sub>3</sub>N in CH<sub>2</sub>Cl<sub>2</sub>) gave **23** in 89% overall yield. Cyclization of the protected cyanohydrin **23** was carried out<sup>4</sup> in 95% yield in refluxing THF with sodium bis(trimethylsilyl)amide. Removal of the hydroxy protecting groups in **24** (PPTS in MeOH at 40 °C for 3 h), followed by base treatment (K<sub>2</sub>CO<sub>3</sub> in MeOH at room temperature for 30 min), gave **25** in 90% overall yield. Hydrolysis of the acetal (0.1 N HCl in acetone), re-protection of the allyl alcohol (CH<sub>2</sub>=CHOEt/PPTS in CH<sub>2</sub>Cl<sub>2</sub>), followed by oxidation of the aldehyde (AgNO<sub>3</sub>/aqueous KOH in EtOH at room temperature for 5 h), and removal of the ethoxyethyl group (0.1 N HCl in acetone) gave 11-deoxy-PGE<sub>1</sub> (**7**). Esterification of **7** with diazomethane gave the methyl ester of 11-deoxy PGE<sub>1</sub>, which was identical in all respects (NMR, TLC, HPLC) with an authentic sample.<sup>9</sup>

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**Registry No.** (**±**)-**1**, 83918-40-5; **2**, 5436-04-4; **3**, 824-11-3; (**±**)-**5**, 83918-41-6; (**±**)-**5** (THP ether), 83918-42-7; (**±**)-**6**, 83918-43-8; (**±**)-**7**, 34603-80-0; (**±**)-**7** (methyl ester), 34603-79-7; (**±**)-**8**, 83918-44-9; (**±**)-**10**, 83946-23-0; (**±**)-**11**, 83918-45-0; **12**, 40365-61-5; (**±**)-**13**, 83918-46-1; (**±**)-**14**, 83918-47-2; **15**, 83918-48-3; (**±**)-**16**, 83918-49-4; (**±**)-**17**, 83946-24-1; **18**, 83918-50-7; **19**, 83918-51-8; **20**, 83928-39-6; **21**, 83928-40-9; **21** (cyanohydrin), 83928-41-0; **22**, 83928-42-1; **23** (R = H), 83928-43-2; **23**, 83928-44-3; **24**, 83918-52-9; **24** (diol), 83918-53-0; (**±**)-**25**, 83918-54-1; **25** (protected aldehyde), 83918-55-2; (**±**)-*erythro*-6-bromo-5-hydroxy-1-[(tetrahydropyran-2-yl)oxy]undec-3(*Z*)-ene, 83946-25-2.

(9) We are indebted to Ono Pharmaceutical Co. for providing an authentic sample of **7**.

## Transition-Metal Insertion into Naked Metal Cluster Poly-anions

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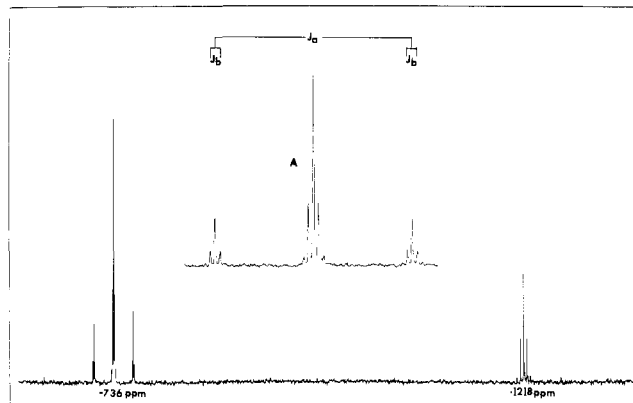
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Recently, considerable interest has developed in the study of naked metal clusters. Species that have been known for decades in solution such as Sn<sub>9</sub><sup>4-</sup> and Sb<sub>7</sub><sup>3-</sup> have been isolated in the solid state and characterized.<sup>1</sup> The nature of these species in solution

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**Figure 1.** <sup>119</sup>Sn NMR spectrum of the mixture K<sub>4</sub>[Sn<sub>9</sub>] and K<sub>4</sub>-[(PPh<sub>3</sub>)<sub>2</sub>PtSn<sub>9</sub>]. Spectrum A was achieved by using a smaller window: J<sub>a</sub> ≡ J<sub>195Pt-119Sn</sub>, J<sub>b</sub> ≡ J<sub>119Sn-117Sn</sub>. Chemical shifts are referenced to tetramethyltin.

has also been studied,<sup>2</sup> and they appear to be fluxional. Many new species have been synthesized, for example, Sn<sub>4</sub><sup>2-</sup>, Sn<sub>5</sub><sup>2-</sup>, Pb<sub>5</sub><sup>2-</sup>, Sn<sub>8</sub>Tl<sup>2-</sup>, Sn<sub>9-x</sub>Ge<sub>x</sub><sup>4-</sup>, (x = 0-9), Sn<sub>x</sub>Pb<sub>9-x</sub> (x = 0-9), Tl<sub>2</sub>Te<sub>2</sub><sup>2-</sup>, Ge<sub>9</sub><sup>4-</sup>, and others.<sup>1,9</sup> Despite this activity, however, no metal cluster containing a transition metal in addition to a main-group metal has yet been reported. The extreme sensitivity of these polyanions toward oxygen together with the difficulty of isolating pure homogeneous species from solution has greatly hindered progress toward this objective. However, <sup>119</sup>Sn and <sup>207</sup>Pb NMR spectroscopy has proven to be a sensitive and reliable investigative tool for species in solution. With this technique, for the first time clear evidence of the existence of compounds that contain a transition metal bonded to a naked metal cluster moiety has been obtained.

Earlier attempts to obtain naked cluster species such as Sn<sub>x</sub>M<sub>z</sub><sup>q-</sup>, where M is a transition metal, by extracting alloys of composition K<sub>y</sub>Sn<sub>x</sub>M<sub>z</sub> with ethylenediamine (en) have been unsuccessful.<sup>10</sup> This result is not surprising since metal clusters have many points of similarity with boron hydrides,<sup>11</sup> and in boron chemistry, compounds involving a naked transition metal are not known. However, metal-ligand moieties are very common in metalloborane and metalloheteroborane chemistry.

Addition of the zerovalent platinum complex, Pt(PPh<sub>3</sub>)<sub>4</sub>, to a solution of K<sub>4</sub>[Pb<sub>9</sub>] in en, in an equimolar ratio, causes a slow but gradual change in color of the solution from dark red-brown to green brown. The solution was investigated at both 18.7 and 74.8 MHz by <sup>207</sup>Pb NMR. The <sup>207</sup>Pb NMR spectra displayed only a triplet at 27.1 ppm and a singlet at 1154.1 ppm, upfield from 1 M Pb(NO<sub>3</sub>)<sub>2</sub>.<sup>12</sup> The singlet was assigned to Pb<sub>9</sub><sup>4-</sup> by comparison with an authentic sample of this anion in en. The frequency separation between the two outermost peaks of the triplet is independent of the applied field and this, together with the relative areas of the triplet (1:4:1), leads us to propose that this compound is a lead cluster containing a platinum atom of the form Pb<sub>x</sub>PtL<sub>y</sub><sup>q-</sup> (J<sub>195Pt-207Pb</sub> = 4122 Hz). Because of the fluxionality of this species in solution no indication of the value of x is possible from <sup>207</sup>Pb NMR.

(1) Belin, C. H. E.; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163-7169 and references therein.

(2) Rudolph, R. W.; Wilson, W. L.; Parker, F.; Taylor, R. C.; Young, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 4629-4630.

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(5) Burns, R. C.; Corbett, J. *J. Am. Chem. Soc.* **1982**, *104*, 2804-2810.

(6) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2627-2632.

(7) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2482-2487.

(8) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 632-635.

(9) Belin, C. H. E. *J. Am. Chem. Soc.* **1980**, *102*, 6036-6040.

(10) Rudolph, R. W.; Buslee, W. R.; Cooper, V. A., unpublished results. In the formula K = potassium, M = transition metal, and q, x, y, and z are integers.

(11) See, for instance: Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1-66.

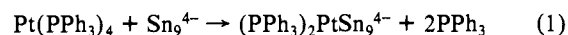
(12) Due to the fluxional nature of Pb<sub>9</sub><sup>4-</sup> in solution, all chemical environments are equivalent.

The reaction of  $\text{Pt}(\text{PPh}_3)_4$  with  $\text{K}_4[\text{Sn}_9]$  in en, in an equimolar ratio, causes the solution to change from deep orange-red to dark brown. The solution was investigated by  $^{119}\text{Sn}$  NMR, and only two sets of resonances at 1218 and 736 ppm upfield from tetramethyltin (TMT) were observed (see Figure 1). The quintet at  $-1218$  ppm is assigned to  $\text{Sn}_9^{4-}$  by comparison with an authentic sample of this anion in en. The triplet in the triplet of quintuplets at  $-736$  ppm and with intensities 1:4:1 we assign, as in  $\text{Pb}_x\text{PtL}_y^{q-}$ , to one platinum per cluster. Each of the components is further split by the  $^{117}\text{Sn}$  and  $^{115}\text{Sn}$  present in the sample. ( $J_{^{119}\text{Sn}-^{117}\text{Sn}} = 79$  Hz). Unlike lead, spin-spin coupling is observable for tin even when all chemical environments are averaged by a rapid intramolecular process due to the fortuitous occurrence of three magnetically active isotopes each of spin  $1/2$ . The relative ratio of the areas is 0.06:0.33:1:0.33:0.06 while the expected values for a cluster of nine tin atoms are 0.04:0.31:0.31:0.04.<sup>13a</sup>

Due to the similarity of  $\text{Pb}_9^{4-}$  and  $\text{Sn}_9^{4-}$  and comparable reaction conditions, it is logical to expect that both compounds have the same stoichiometry, i.e.,  $\text{L}_2\text{PtPb}_9^{4-}$  and  $\text{L}_2\text{PtSn}_9^{4-}$ . The 4- charge is the only plausible value since there has not been any variation in the content of tin (and presumably lead). On the other hand, formal negative oxidation states of platinum, which could lead to a closo cluster, occur very rarely in other platinum compounds and, to our knowledge, only when carbonyl ligands are present.<sup>13b</sup>

Unlike the composition of the core, which seems to be a well-defined  $\text{PtPb}_9$  or  $\text{PtSn}_9$  moiety, the nature of the ligand L is uncertain. The  $^{31}\text{P}$  NMR of the  $\text{L}_x\text{PtSn}_9^{4-}$  cluster solution 2 days after mixing the reagents shows a triplet with areas 1:4:1 ( $J_{^{195}\text{Pt}-^{31}\text{P}} = 5220$  Hz) at 147 ppm and a singlet due to a free

triphenyl phosphine at  $-6$  ppm.<sup>17</sup> The ratio of the intensities is very close to 1:1, which indicates the reaction



After the solution stood for a few weeks, only the free triphenylphosphine absorption was observed. This is attributed to the total, or partial, substitution of  $\text{PPh}_3$  by the less bulky en.<sup>15a</sup> This partial substitution by en is supported by the  $^{31}\text{P}$  NMR of  $\text{L}_2\text{PtPb}_9^{4-}$ , which as well as the free  $\text{PPh}_3$ , has a triplet of triplets with relative intensities of 1:4:1 at  $+308$  ppm. ( $J_{^{195}\text{Pt}-^{31}\text{P}} = 6218$  Hz and  $^3J_{^{195}\text{Pt}-^{31}\text{P}} = 419$  Hz).<sup>15b</sup> An extensive search to find the  $^{195}\text{Pt}$  NMR resonances was not successful.

Attempts to obtain crystals of X-ray structure determination are underway. The  $\text{Pt}(\text{PPh}_3)_2$  moiety being considered has a framework electron contribution of two electrons, as does tin.<sup>16</sup> The total number of electrons is then  $24 + 2n + 4$ . Consequently, a nido structure similar to  $\text{B}_{10}\text{H}_{14}$ <sup>17</sup> is predicted, the metal occupying one of the positions of the open mouth.

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(13) (a) This slight discrepancy is attributed to partial overlap of the signals, which clearly favors the smaller peaks with respect to the central peak. (b) A referee has questioned our assignment of a nido count,  $\text{L}_2\text{PtM}_9^{4-}$ , rather than a closo count,  $\text{L}_2\text{PtM}_9^{2-}$ . We have found that addition of 2,2,2-crypt to a solution of the compound in question results in the disappearance of the  $^{207}\text{Pb}$  and  $^{119}\text{Sn}$  NMR signals and the evolution of  $\text{H}_2$  gas. Analysis of the crystals results show them to be closo in nature. These results strongly suggest the original solution species to be nido.

(14) Free  $\text{PPh}_3$  was assigned after comparison with an authentic sample of  $\text{PPh}_3$  in en. All chemical shifts were obtained compared to  $\text{PPh}_3$ , which was assumed to have  $\delta -6$  referenced to  $\text{PO}_4\text{H}_3$  (80%).

(15) (a) Either a precipitation process, which would exaggerate the proportions of free  $\text{PPh}_3$  with respect to  $\text{PPh}_3$  attached to Pt, or the partial decomposition of  $(\text{PPh}_3)_2\text{PtSn}_9^{4-}$  to an insoluble phase would also explain the  $^{31}\text{P}$  NMR. (b) The solution remained free of solid phases, and the  $^{207}\text{Pb}/^{119}\text{Sn}$  NMR spectra remained unchanged over the time period investigated.

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(17) Tippe, A.; Hamilton, W. C. *Inorg. Chem.* **1969**, *8*, 464-470.

## Book Reviews

**Solubility in Inorganic Two-Component Systems.** By M. Broul (Chemopetrol-Research Institute of Inorganic Chemistry, Usti nad Labem), J. Nyvlt (Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague), and O. Sohnel (Chemopetrol-Research Institute of Inorganic Chemistry, Usti nad Labem, Czechoslovakia). Elsevier Scientific Publishing Company, Amsterdam, The Netherlands. 1981. 7 + 569 pp. \$90.25.

This book begins with a theoretical introduction consisting of a brief discussion of temperature dependence of solubility, concentration units, smoothing of experimental data, evaluation of data on solution supersaturation, material and heat balance of crystallization, temperature dependence of solubility in a three-component system, and crystallographic and structural characterization of substances. This is followed by a list of symbols and a brief discussion of how the data were tabulated.

The major part of this book consists of tables in which temperature-concentration data of some 500 inorganic substances are evaluated (listed alphabetically in a formula index). A page is devoted to each substance and consists of such information as temperature-concentration data tables, along with a solubility equation describing the tabulated data. Temperature coefficient of solubility data, crystal lattice parameters, and crystal modification parameters are included when available. The temperature range for each substance varies with the substances in the 0-100 °C range with tabulations given at 0.1 °C intervals. Older solubility data (up through the 1950's or 1960's) were obtained from Linke and Seidell ("Solubilities of Inorganic and Metalorganic Compounds", Van Nostrand, New York; 1958, American Chemical Society: Washington, 1965). More recent data were obtained from the original papers.

The available data appear to be carefully evaluated by the authors and

this book should be a valuable guide to various workers involved in liquid-phase water systems at moderate temperature. The book is important in its convenience of having under one cover data that are otherwise widely distributed and varied in nature in the original literature. It is thus much more useful than the usual brief solubility information found in chemical handbooks. The reviewer would like to have seen included data on hydrolysis such as pH values.

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**Chronicles of Drug Discovery. Volume I.** Edited by Jasjit S. Bindra and Daniel Lednicer. John Wiley and Sons, New York. 1982. XIII + 283 pp. \$32.50.

The scientific approaches, the consideration of chemical factors, and the utilization of experimental results which lead to the discovery of a new drug are seldom available in the scientific literature. This volume provides an account of scientific investigations which led to the discovery of 12 useful drugs in the past 15 years. These accounts of drug development should provide interesting material for teachers of courses in medicinal chemistry and should be read by chemists considering a career in the pharmaceutical industry.

While individual chapters deal with the discovery of a single drug, most provide an insight into research on compounds of that therapeutic class. Individual chapters describe research which culminated in the discovery of a histamine ( $\text{H}_2$ ) antagonist, two unique antipsychotics, two antihypertensives, a diuretic, two peripherally acting analgetics-antiinflammatories, two antibiotics, an anthelmintic, and an agent for the treatment of schistosomiasis.