

# Water-Soluble Organometallic Compounds. 7.<sup>1</sup> Further Studies of 1,3,5-Triaza-7-Phosphaadamantane Derivatives of Group 10 Metals, Including Metal Carbonyls and Hydrides

Donald J. Darensbourg,\* Jeffrey B. Robertson, David L. Larkins, and Joseph H. Reibenspies

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

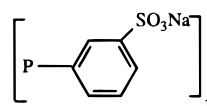
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The syntheses of Ni(PTA)<sub>4</sub> (**5**), Pd(PTA)<sub>4</sub> (**6**), and Pt(PTA)<sub>4</sub> (**8**) are accomplished through the reduction of the M<sup>II</sup>Cl<sub>2</sub> salts in water with excess 1,3,5-triaza-7-phosphaadamantane (PTA). The products are obtained as partially protonated derivatives with protonation occurring at the nitrogen atoms of the bound PTA ligands. Crystal structures illustrating the monoprotonated and bis-protonated derivatives of **8**, [Pt(PTA)<sub>3</sub>(PTAH)]Cl (1S) and [Pt(PTA)<sub>2</sub>(PTAH)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (2S), are reported. The crystal structure of an intermediate along the reduction pathway, [PdCl(PTA)<sub>3</sub>][Cl] (**7**), is also presented, showing a trans influence whereby the Pd–P bond length trans to the Cl<sup>−</sup> ligand is shorter, 2.238(3) Å, than the average Pd–P bond length cis to the Cl<sup>−</sup> ligand, 2.334(2) Å. Complex **8** is also protonated at the metal center to form [(H)Pt(PTA)<sub>4</sub>][X], where X = Cl<sup>−</sup>, BF<sub>4</sub><sup>−</sup>, HCO<sub>3</sub><sup>−</sup>, and C<sub>3</sub>H<sub>5</sub>CO<sub>2</sub><sup>−</sup>, through the addition of weak acids such as CO<sub>2</sub>/H<sub>2</sub>O, NH<sub>4</sub>Cl, PTAH<sup>+</sup>Cl<sup>−</sup>, HPy<sup>+</sup>BF<sub>4</sub><sup>−</sup>, and crotonic acid. Addition of strong acids such as HCl or HBF<sub>4</sub> results in protonation at the PTA ligands. Thereby, the Pt metal center is shown to have a pK<sub>a</sub> between 7.44 and 9.25. The bound PTA ligands on complex **8** have a pK<sub>a</sub> below 4.69 but above 2.12. Ni(CO)<sub>4−n</sub>(PTA)<sub>n</sub> derivatives are also reported for n = 3 (**9**), 2 (**10**), and 1 (**11**). Using IR data of **11**, PTA is determined to have an electronic parameter (χ) as defined by Tolman to be 15.3 cm<sup>−1</sup>, indicating PTA to be slightly less donating than PPh<sub>3</sub>, where χ = 12.8 cm<sup>−1</sup>. Complex **10** is crystallized out of a MeOH/ether solution maintained at −15 °C and characterized by X-ray crystallography. It is a distorted tetrahedron and has a crystallographically determined Tolman cone angle of PTA of 103°. Monitored reactions of Ni(PTA)<sub>4</sub> with CO in water via in situ IR techniques show that the rate observed for the dissociation of PTA to provide Ni(CO)(PTA)<sub>3</sub> is 7.92 × 10<sup>−4</sup> s<sup>−1</sup> at 20 °C. This rate, along with <sup>31</sup>P NMR results, indicates that the M<sup>0</sup>(PTA)<sub>4</sub> complexes exhibit little dissociation and slow exchange of the bound PTA ligands.

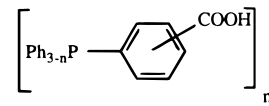
## Introduction

Although phosphine ligands containing sulfonated aryl groups (e.g., TPPTS, **1**) have dominated the ligands utilized in water-solubilizing organometallic derivatives, there is an increase in the number of investigations involving other types of substituents on phosphines which impart water solubility. For example, these include cationic ammonium groups (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup> and Cy<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>NMe<sub>3</sub><sup>+</sup>)<sup>2–5</sup> and carboxylated aromatic groups (**2**).<sup>6</sup> Among the nonionic aliphatic phosphine ligands which offer greater basicities are *tris*(hydroxymethylphosphine), P-(CH<sub>2</sub>OH)<sub>3</sub>,<sup>7,8</sup> (HOCH<sub>2</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>P(CH<sub>2</sub>OH)<sub>2</sub>,<sup>9</sup> and PTA (**3**).<sup>10–12</sup> It is also possible to alkylate or protonate one of the nitrogen

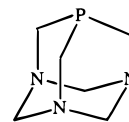
bases in the latter ligand to afford the ionic ligands PTAMe<sup>+</sup> and PTAH<sup>+</sup>, respectively, thus providing additional solubility properties in water.



**1** (TPPTS)



**2** (n = 1–3; *ortho*, *meta*, or *para*)



**3** (PTA)

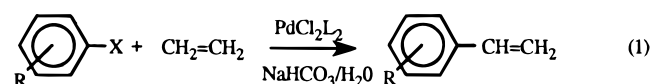
We have been extensively associated with the development of the PTA ligand in aqueous organometallic chemistry and catalysis.<sup>13–16</sup> Pertinent to these efforts it is of importance to

- \* Corresponding author. E-mail: djdarens@mail.chem.tamu.edu.
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- (10) PTA (1,3,5-triaza-7-phosphatrimethylene [3.3.1.1<sup>3,7</sup>] decane) is commonly referred to as 1,3,5-triaza-7-phosphaadamantane. Some authors prefer to condense this ligand's name to TPA.
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note that the 1,3,5-triaza-7-phosphaadamantane ligand was originally synthesized by Daigle et al. and was given the abbreviation PAA.<sup>17</sup> During the same time period Darensbourg and Daigle described in a report the synthesis and characterization of a variety of metal carbonyl derivatives of this ligand, where it was given the abridged designation PTA.<sup>18</sup> In addition, the X-ray structure of one of these derivatives, Mo(CO)<sub>5</sub>PTA, was subsequently reported,<sup>19</sup> followed by the X-ray structure of the free ligand, PTA.<sup>20</sup>

Recent efforts from our laboratories have focused on the group 10 metal derivatives of PTA.<sup>1</sup> In part the impetus for these investigations stems from the widespread use of related metal derivatives as catalysts or catalyst precursors in a variety of chemical transformations, many of which may be carried out in an aqueous medium. For example, carbon-carbon coupling reactions have been successfully performed in aqueous solution or aqueous-organic biphasic systems. In addition to the Heck reaction (eq 1),<sup>21</sup> several other cross-coupling reactions have



been carried out under these conditions, including Suzuki<sup>22</sup> and Stille<sup>23</sup> coupling processes. Carbonylation of benzyl chloride has also been shown to be catalyzed by water-soluble phosphine complexes of palladium in a biphasic system.<sup>24</sup> In all of these processes a zerovalent metal complex is the catalytically active species, which is often produced in situ from the corresponding M<sup>II</sup>X<sub>2</sub>L<sub>2</sub> derivative.

Herrmann and co-workers have prepared the homoleptic TPPTS complexes of the zerovalent group 10 metals where the coordination number of the metal was found to increase with increasing metal size, i.e., Ni(TPPTS)<sub>3</sub>, Pd(TPPTS)<sub>3</sub>, and Pt(TPPTS)<sub>4</sub>.<sup>25</sup> This trend is consistent with the greater steric requirements of the TPPTS ligand<sup>26</sup> as compared to PPh<sub>3</sub>,<sup>27</sup> where the analogous group 10 metal complexes exhibit four-coordination. More recently, Pringle and co-workers have synthesized and fully characterized the zerovalent group 10 metal derivatives M[P(CH<sub>2</sub>OH)<sub>3</sub>]<sub>4</sub>.<sup>7</sup> In addition there are several reports of water-soluble phosphine complexes of group 10 metals in the +2 oxidation state, including *cis*- and *trans*-PtCl<sub>2</sub>(TPPTS)<sub>2</sub>,<sup>25</sup> MCl<sub>2</sub>[P(CH<sub>2</sub>OH)<sub>3</sub>]<sub>2</sub> (M = Ni, Pd, Pt),<sup>7,28</sup> and hydroxy metal bis(phosphine) complexes of Pd and Pt.<sup>29</sup>

We have previously reported the synthesis of M(PTA)<sub>4</sub> (M = Ni, Pd, Pt) derivatives by several well-known procedures, i.e., Ni(cod)<sub>2</sub> plus PTA, reduction of PdCl<sub>2</sub> or PtCl<sub>2</sub> with hydrazine in the presence of PTA, and Pt(PPh<sub>3</sub>)<sub>4</sub>/PTA ligand exchange.<sup>1</sup> Herein, we wish to communicate a facile synthetic method for these metal derivatives from their respective halide salts in water using excess phosphine as reductant. In addition, the preparation of a series of Ni(CO)<sub>4-n</sub>(PTA)<sub>n</sub> (n = 1–3) complexes derived from the ligand substitution reactions of Ni(PTA)<sub>4</sub> and CO is described, along with the X-ray structure of one of these, Ni(CO)<sub>2</sub>(PTA)<sub>2</sub>. Finally, a water-soluble platinum hydride species originating from the reaction of Pt(PTA)<sub>4</sub> and weak acids (e.g., carbonic acid) has been synthesized and characterized by <sup>1</sup>H, <sup>31</sup>P, and <sup>195</sup>Pt NMR spectroscopies.

## Experimental Section

**Methods and Materials.** All reactions were performed under an inert atmosphere unless otherwise stated. NiCl<sub>2</sub> and PdCl<sub>2</sub> were purchased from Aldrich Chemicals and Johnson-Matthey Chemicals, respectively, and used without further purification. PtCl<sub>2</sub> was purchased from Strem Chemicals and Pressure Chemical and used without further purification. 1,3,5-triaza-7-phosphaadamantane (PTA) was synthesized according to the procedure developed by Daigle and co-workers.<sup>11</sup> CO was purchased from Matheson and Liquid Carbonic Specialty Gases. Crotonic acid and tetrafluoroboric acid were purchased from Aldrich. Ammonium chloride was purchased from J. T. Baker. CO<sub>2</sub> was purchased from Praxair. Hydrochloric acid and phosphoric acid were purchased from EM. All were used without further purification. PTAH<sup>+</sup>Cl<sup>-</sup> was prepared by treating PTA with an equimolar amount of 0.1 M HCl. The solvent was removed in vacuo to yield a white powder (<sup>31</sup>P NMR (D<sub>2</sub>O): δ = -91 ppm). Pyridinium tetrafluoroborate was prepared by treating pyridine with tetrafluoroboric acid in ether, followed by isolation of the precipitate. Water was degassed through a nitrogen purge for at least 45 min prior to use. Methanol was purchased from Fischer Scientific and stored over and distilled from Mg/I<sub>2</sub> prior to use. Ether was purchased from Fisher Scientific, stored over Na/benzophenone, and distilled before use. D<sub>2</sub>O, MeOH-*d*<sub>4</sub>, and THF-*d*<sub>8</sub> were purchased from Cambridge Isotopes Laboratories. D<sub>2</sub>O was stored in an airtight flask under N<sub>2</sub> at all times. MeOH-*d*<sub>4</sub> and THF-*d*<sub>8</sub> were stored in a drybox. <sup>31</sup>P NMR spectra were recorded on a Varian Unity 300 spectrometer, and 85% H<sub>3</sub>PO<sub>4</sub> (δ = 0.0 ppm) was used as an external reference. <sup>195</sup>Pt NMR spectra were recorded on a Varian XL200 broadband spectrometer employing aqueous K<sub>2</sub>PtCl<sub>4</sub> (δ = -1630 ppm) as an external reference. Infrared samples were recorded on a Mattson 6021 Galaxy Series FT-IR in a 0.01 mm CaF<sub>2</sub> cell for water samples and a 0.1 mm CaF<sub>2</sub> cell for MeOH samples. Monitored kinetic reactions were done using an ASi Applied Systems ReactIR 1000 Electronics Module. The pH measurements involving PTA were carried out at 25.0 ± 0.1 °C at a constant ionic strength (μ = 0.100 M) adjusted with KCl in doubly distilled, deionized water, with careful exclusion of oxygen and carbon dioxide. These experiments were performed by Dr. Tara Decuir in the laboratories of Professor A. Martell, employing the experimental setup and procedure previously described in detail.<sup>30</sup> Elemental analysis were carried out by Canadian Microanalytical Service, Ltd.

**Dichlorobis(1,3,5-triaza-7-phosphaadamantane)nickel(II), 4.** A 0.346 g (1.46 mmol) sample of NiCl<sub>2</sub> and 0.470 g (2.98 mmol) of PTA were weighed out into a Schlenk flask. Then 20 mL of MeOH was added, resulting in the formation of a blue solution. The solution was allowed to stir for 2 days during which time a red precipitate formed. The precipitate was collected on a sintered glass frit and washed with MeOH and ether. The powder was dried in vacuo, and 0.547 g (85%

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yield) of the product was isolated. Anal. Calcd for  $\text{NiCl}_2\text{P}_2\text{C}_{12}\text{H}_{24}\text{N}_6$ : C, 32.47; H, 5.45; N, 18.93. Found: C, 32.45; H, 5.42; N, 18.74.

**Tetrakis(1,3,5-triaza-7-phosphaadamantane)nickel(0), 5.** To 0.203 g (0.85 mmol) of  $\text{NiCl}_2$  and 0.739 g (4.71 mmol) of PTA was added 4 mL of  $\text{H}_2\text{O}$ . Immediately, the solution became a dark blue ink color. This color began to change to red as 8 mL of MeOH was added. The red/orange solution was allowed to stir for 8 h. During this time, the orange color faded and a white precipitate formed. The precipitate was collected on a sintered glass frit. It was washed three times with MeOH and twice with ether. It was allowed to dry in vacuo, and 0.436 g (74% yield) of the white product was isolated.  $^{31}\text{P}$  NMR revealed a singlet at  $-44.8$  ppm in  $\text{D}_2\text{O}$ .

**Tetrakis(1,3,5-triaza-7-phosphaadamantane)palladium(0), 6.** A 0.107 g portion of  $\text{PdCl}_2$  (0.680 mmol) and 0.534 g of PTA (3.4 mmol, 5 equiv) were weighed out into a Schlenk flask. The flask was evacuated and backfilled with nitrogen. Then 5 mL of distilled water was added via syringe. The resulting solution was a deep orange/brown color. It was allowed to stir overnight. The mixture was filtered through Celite to remove any metallic palladium, and then the solvent was removed. Twenty milliliters of MeOH was added, and the resulting mixture was filtered to yield a tan precipitate and a yellow filtrate. The solid was washed several times with 5 mL aliquots of MeOH, followed by a 5 mL aliquot of ether. The product was allowed to dry in vacuo. A 0.283 g (57% yield) portion of white/gray product was isolated.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -56.5$  ppm (s).

**[PdCl(PTA)<sub>3</sub>]Cl, 7.** The synthesis of this compound has been described previously.<sup>1</sup> Bright yellow needles were obtained from a methanol/0.1 M HCl solution of **7** (5:1 mL/mL) allowed to stand overnight. These needles were isolated and redissolved in methanol/0.1 M HCl. This solution was stored at 5 °C for 2 months until yellow crystals suited to X-ray diffraction appeared.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -47$  ppm.

**Tetrakis(1,3,5-triaza-7-phosphaadamantane)platinum(0), 8.** A 0.169 g portion of  $\text{PtCl}_2$  (0.637 mmol) and 0.600 g of PTA (3.82 mmol, 6 equiv) were weighed out into a Schlenk flask, and 10 mL of distilled water was added via syringe. Initially, the solution was an orange color and contained a precipitate. After a few hours the precipitate disappeared, and the orange color faded to yellow. The solution was allowed to stir for 2 days and was then filtered through Celite to remove any metallic platinum. The solution was taken to dryness in vacuo and 10 mL of MeOH was added to redissolve the solid. The addition of 20 mL of ether caused an off-white precipitate to form. This was collected on a sintered glass frit and washed extensively with ether and allowed to dry in vacuo. The solid (0.432 g) was isolated in a drybox.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -70$  ( $J_{\text{Pt-P}} = 3699$  Hz), and  $-80$  ppm ( $J_{\text{Pt-P}} = 2357$  Hz), showing a mixture of two products.

**Reaction of  $\text{PtCl}_2$  and PTA under Acidic Conditions.**  $\text{PtCl}_2$  (0.169 g, 0.635 mmol) and PTA (0.6 g, 3.82 mmol, 6 equiv) were combined in a Schlenk flask which was evacuated and backfilled with  $\text{N}_2$ . Initially, 10 mL of 0.1M HCl (degassed) was added to the flask, causing the formation of a clear, orange solution. After 15 min, another 30 mL of 0.1 M HCl was added. The solution immediately lost the orange color, which faded to a light yellow. After stirring for 2 days, the volume was removed in vacuo, and 20 mL of MeOH was added. The resulting white precipitate was isolated on a sintered glass frit.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -47$  ppm (broad).

**Reaction of  $\text{PtCl}_2$  and PTA under a  $\text{CO}_2$  Atmosphere.**  $\text{PtCl}_2$  (0.169 g, 0.635 mmol) and PTA (0.6 g, 3.82 mmol, 6 equiv) were weighed out into a 10 mL Schlenk flask.  $\text{H}_2\text{O}$  (3 mL) and  $\text{D}_2\text{O}$  (3 mL) were added under a nitrogen atmosphere. The solution was allowed to stir for 2 days.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -80$  ppm ( $J_{\text{Pt-P}} = 2361$  Hz).

**$^{31}\text{P}$  NMR Experiments of  $\text{Pt}(\text{PTA})_4$  Reactions with Acids.** **Pt(PTA)<sub>4</sub> +  $\text{H}_3\text{PO}_4$ .**  $\text{Pt}(\text{PTA})_4$  (30 mg  $3.65 \times 10^{-5}$  mol) was weighed out into a 5 mm NMR tube, and 1 mL of  $\text{D}_2\text{O}$  was added via syringe, followed by 2.47  $\mu\text{L}$  ( $3.6 \times 10^{-5}$  mol) of  $\text{H}_3\text{PO}_4$ .  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -70$  ppm ( $J_{\text{Pt-P}} = 3701$  Hz).

**Pt(PTA)<sub>4</sub> + Pyridinium Tetrafluoroborate.**  $\text{Pt}(\text{PTA})_4$  (30 mg,  $3.65 \times 10^{-5}$  mol) was weighed out into a 5 mm NMR tube, and 0.0142 g ( $7.30 \times 10^{-5}$  mol) of pyridinium tetrafluoroborate was dissolved in 1 mL of  $\text{D}_2\text{O}$  and cannulated into the NMR tube.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -80$  ppm ( $J_{\text{Pt-P}} = 2357$  Hz).

**Pt(PTA)<sub>4</sub> +  $\text{PTAH}^+\text{Cl}^-$ .**  $\text{Pt}(\text{PTA})_4$  (30 mg,  $3.65 \times 10^{-5}$  mol) was weighed out into a 5 mm NMR tube, and 0.021 g ( $1.09 \times 10^{-4}$  mol) of  $\text{PTAH}^+\text{Cl}^-$  was dissolved in 1 mL of  $\text{D}_2\text{O}$  and cannulated into the NMR tube.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -80$  ppm ( $J_{\text{Pt-P}} = 2357$  Hz).

**Pt(PTA)<sub>4</sub> +  $\text{CO}_2$ .**  $\text{Pt}(\text{PTA})_4$  (0.030 g,  $3.65 \times 10^{-5}$  mol) was weighed out into a 5 mm NMR tube, and 0.9 mL of  $\text{D}_2\text{O}$  was added.  $\text{CO}_2$  gas was bubbled through the solution for 5 min.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -74$  ( $J_{\text{Pt-P}} = 3604$  Hz),  $-80$  ppm ( $J_{\text{Pt-P}} = 2357$  Hz).  $-74$  ppm: $-80$  ppm ratio = 0.0300.

**Pt(PTA)<sub>4</sub> +  $\text{NH}_4\text{Cl}$ .**  $\text{Pt}(\text{PTA})_4$  (30 mg,  $3.65 \times 10^{-5}$  mol) was weighed out into a 5 mm NMR tube, and 0.0021 g ( $3.96 \times 10^{-5}$  mol) of  $\text{NH}_4\text{Cl}$  was dissolved in 1 mL of  $\text{D}_2\text{O}$  and cannulated into the NMR tube.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -74$  ( $J_{\text{Pt-P}} = 3591$  Hz),  $-80$  ppm ( $J_{\text{Pt-P}} = 2357$  Hz).  $-74$  ppm: $-80$  ppm ratio = 2.96.

**Pt(PTA)<sub>4</sub> +  $\text{C}_3\text{H}_5\text{CO}_2\text{H}$ .**  $\text{Pt}(\text{PTA})_4$  (0.030 g,  $6.0 \times 10^{-5}$  mol) was weighed out into a 5 mm NMR tube, and 0.012 g ( $1.39 \times 10^{-4}$  mol) of crotonic acid was weighed out into a Schlenk flask.  $\text{D}_2\text{O}$  (0.8 mL) was added to the Schlenk flask. This solution was cannulated into an NMR tube under an inert atmosphere.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -70$  ( $J_{\text{Pt-P}} = 3681$  Hz),  $-80$  ppm ( $J_{\text{Pt-P}} = 2357$  Hz).  $-80$  ppm: $-70$  ppm ratio = 3.88.

**Pt(PTA)<sub>4</sub> + 2,3-Dichlorophenol.**  $\text{Pt}(\text{PTA})_4$  (0.030 g,  $3.65 \times 10^{-5}$  mol) was weighed out into a 5 mm NMR tube. 2,3-Dichlorophenol (0.012 g,  $7.18 \times 10^{-5}$  mol) was weighed out into a Schlenk flask. An 0.8 mL amount of  $\text{D}_2\text{O}$  was added to the Schlenk flask. This solution was cannulated into an NMR tube under an inert atmosphere.  $^{31}\text{P}$  NMR ( $\text{D}_2\text{O}$ ):  $\delta = -74$  ppm,  $J_{\text{Pt-P}} = 3592$  Hz;  $\delta = -80$  ppm,  $J_{\text{Pt-P}} = 2355$  Hz;  $-80$  ppm: $-74$  ppm ratio = 1.5.

**Carbonyltris(1,3,5-triaza-7-phosphaadamantane)nickel(0), 9.**  $\text{Ni}(\text{PTA})_4$  (0.300 g, 0.457 mmol) was weighed out into a 100 mL Schlenk flask, and the flask was evacuated and back-filled with a CO atmosphere. To the flask was added 55 mL of methanol, and the resulting slurry was allowed to stir at room temperature. After 5 min, all of the precipitate had dissolved and the CO atmosphere was quickly replaced with a nitrogen atmosphere to prevent further substitution. The volume was reduced in vacuo until approximately one-third of the initial volume remained. During this time, a white solid precipitated out of solution. Ether (60 mL) was added and the flask was placed in the freezer overnight. The white precipitate was collected on a frit, washed with ether, and allowed to dry in vacuo. The product was isolated as a white powder (0.208 g, 85% yield) in a drybox. IR (MeOH):  $1945$   $\text{cm}^{-1}$ .  $^{31}\text{P}$  NMR (MeOH-*d*<sub>4</sub>):  $\delta = -47.2$  ppm (s). Anal. Calcd for  $\text{NiC}_{19}\text{N}_9\text{OH}_{36}\text{P}$ : C, 40.89; H, 6.50; N, 22.58. Found: C, 40.36; H, 6.43; N, 22.19.

**Dicarbonylbis(1,3,5-triaza-7-phosphaadamantane)nickel(0), 10.** In a typical synthesis,  $\text{Ni}(\text{PTA})_4$  (0.300 g, 0.437 mmol) was placed in a Schlenk flask, and 35 mL of MeOH was added under a CO atmosphere. The mixture was heated to 50 °C and allowed to stir overnight. The mixture was filtered through Celite and the MeOH removed in vacuo.  $\text{H}_2\text{O}$  (20 mL) was added, and the white precipitate which resulted was collected on a frit and washed with ether. After drying in vacuo overnight, the product (0.142 g, 76% yield) was isolate in the drybox as a white solid. IR (MeOH): 2012, 1956  $\text{cm}^{-1}$ .  $^{31}\text{P}$  NMR (MeOH-*d*<sub>4</sub>):  $\delta = -50.7$  ppm. Anal. Calcd for  $\text{NiC}_{14}\text{N}_6\text{O}_2\text{H}_{24}\text{P}_2$ : C, 39.19; H, 5.64; N, 19.59. Found: C, 38.92; H, 5.54; N, 19.44. Crystals of the product were grown by dissolving the isolated powder in a minimum amount of MeOH in a large test tube. The MeOH was then layered with ether and allowed to sit at room temperature for 3 days, at which time small feathery crystals grew. The tube was then placed in a freezer at  $-15$  °C. After approximately 1 week, crystals suitable for X-ray diffraction appeared.

**Tricarbonyl(1,3,5-triaza-7-phosphaadamantane)nickel(0), 11.**  $\text{Ni}(\text{PTA})_4$  (200 mg, 0.291 mmol) was weighed out into a 100 mL Schlenk flask. The flask was evacuated and backfilled with a CO atmosphere. Toluene (80 mL) was added, and CO was allowed to flow through the flask for approximately 0.5 h. The flask was then sealed off and heated to 50 °C in an oil bath. The reaction was monitored periodically for 1 week. The mixture was filtered through a sintered glass frit. The solvent was evaporated in vacuo, which yielded trace amounts of a yellow/white powder. IR (toluene): 2068, 1993  $\text{cm}^{-1}$ .

**Table 1.** Crystallographic Data and Data Collection Parameters for Complexes **7**, **10**, **1S**, and **2S**

complex	<b>7</b>	<b>10</b>	<b>1S</b>	<b>2S</b>
empirical formula	C <sub>19</sub> H <sub>42</sub> Cl <sub>2</sub> N <sub>9</sub> OP <sub>3</sub> Pd	C <sub>24</sub> H <sub>60</sub> ClN <sub>12</sub> O <sub>6</sub> P <sub>4</sub> Pt	C <sub>24</sub> H <sub>56</sub> B <sub>2</sub> F <sub>8</sub> N <sub>12</sub> O <sub>4</sub> P <sub>4</sub> Pt	C <sub>15</sub> H <sub>28</sub> N <sub>6</sub> NiO <sub>3</sub> P <sub>2</sub>
fw	682.83	967.26	1069.40	461.08
space group	<i>P2</i> <sub>1</sub> / <i>c</i>	<i>Fd</i> $\bar{3}$	<i>C2/c</i>	<i>Cmca</i>
<i>V</i> (Å <sup>3</sup> )	2856.3(10)	7818.5(13)	8478(3)	4119.5(14)
<i>Z</i>	4	8	8	8
<i>D</i> <sub>calc</sub> (Mg m <sup>3</sup> )	1.588	1.643	1.676	1.487
<i>a</i> (Å)	10.796(3)	19.8476(19)	25.079(5)	23.046(5)
<i>b</i> (Å)	21.255(3)	19.8476(19)	21.639(4)	7.508(2)
<i>c</i> (Å)	12.677(2)	19.8476(19)	17.325(4)	23.808(5)
$\alpha$ (deg)	90	90	90	90
$\beta$ (deg)	100.49(2)	90	115.61(3)	90
$\gamma$ (deg)	90	90	90	90
<i>T</i> (K)	293(2)	193(2)	173(2)	193(2)
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.036	3.874	8.349	1.125
wavelength (Å)	0.710 73	0.710 73	1.541 84	0.710 73
<i>R</i> <sub>F</sub> (%) <sup>a</sup>	5.71	5.70	8.28	4.98
<i>R</i> <sub>wF</sub> (%) <sup>a</sup>	17.40	11.32	17.71	13.13

$$^a R_F = \frac{\sum ||F_o| - |F_c||}{\sum F_o} \text{ and } R_{wF} = \left\{ \frac{\sum w(F_o - F_c)^2}{\sum wF_o^2} \right\}^{1/2}.$$

<sup>31</sup>P NMR (THF-*d*<sub>8</sub>):  $\delta = -54$  ppm. This complex was more readily prepared from the reaction of Ni(CO)<sub>4</sub> and PTA in toluene solution.

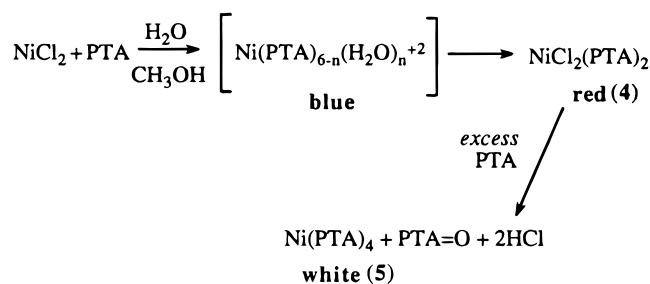
**Monitored Kinetics of Ni(PTA)<sub>4</sub> + CO in Water.** In a typical run, CO was bubbled through water for approximately 1 h, and 15 mL of this solution was transferred via syringe into the reaction vessel. The reaction vessel contained the IR probe and was maintained under an atmosphere of CO at a constant temperature via an external bath. The solution was then allowed to equilibrate to the desired temperature for 5 min. A total of 256 background scans were taken, and the instrument was setup to take 64 scans every 50 s. The run was started and four scans were taken before the Ni(PTA)<sub>4</sub> ( $2.33 \times 10^{-4}$  mol in 5 mL of degassed water) was introduced via syringe to the reaction vessel. The appearance of a product  $\nu$ (CO) band at 1945 cm<sup>-1</sup> was followed over time. The reaction was monitored until it was determined that all of the Ni(PTA)<sub>4</sub> had reacted to form Ni(CO)(PTA)<sub>3</sub>.

**X-ray Structural Determinations.** Crystal data and details of data collection are given in Table 1. In addition, crystallographically determined parameters for the singly and doubly protonated Pt(PTA)<sub>4</sub> derivatives, namely, [Pt(PTA)<sub>3</sub>(PTAH)](Cl) (**1S**) and [Pt(PTA)<sub>2</sub>(PTAH)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (**2S**), are contained in the Supporting Information. A yellow needle of [Pd(PTA)<sub>3</sub>Cl]Cl and a white needle of Ni(CO)<sub>2</sub>(PTA)<sub>2</sub> were mounted on glass fibers with epoxy cement at room temperature and cooled in a liquid nitrogen cold stream. Preliminary data collection was performed on a Nicolet R3m/v X-ray diffractometer (Mo K $\alpha$ ,  $\lambda = 0.71073$  Å radiation). Cell parameters were calculated from the least-squares fitting of the setting angles for 24 reflections.  $\omega$  scans for several intense reflections indicated acceptable crystal quality. Data were collected for  $4.0^\circ \leq 2\theta \leq 50^\circ$ . Three control reflections, collected every 97 reflections, showed no significant trends. Background measurements by stationary-crystal and stationary-counter techniques were taken at the beginning and end of each scan for half the total scan time. Lorentz and polarization corrections were applied to 4627 reflections for [Pd(PTA)<sub>3</sub>Cl]Cl and 1603 reflections for Ni(CO)<sub>2</sub>(PTA)<sub>2</sub>. A total of 4627 unique reflections for [Pd(PTA)<sub>3</sub>Cl]Cl and 1603 for Ni(CO)<sub>2</sub>(PTA)<sub>2</sub>, with  $|I| \geq 2.0\sigma(I)$ , were used in further calculations. The structure was solved by direct methods [SHELXS program package, Sheldrick (1993)]. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded;  $R = 6.35$ ,  $R_w = 18.82$ , and  $S = 1.036$  for [Pd(PTA)<sub>3</sub>Cl]Cl, and  $R = 4.98$ ,  $R_w = 13.13$ , and  $S = 1.021$  for Ni(CO)<sub>2</sub>(PTA)<sub>2</sub>. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Neutral-atom scattering factors and anomalous scattering correction terms were taken from *International Tables for X-ray Crystallography*.

## Results and Discussion

**Zerovalent Group 10 Metal M(PTA)<sub>4</sub> Derivatives.** The tetrakis(1,3,5-triaza-7-phosphaadamantane)nickel(0) complex was readily synthesized from the room-temperature reaction of NiCl<sub>2</sub> and excess PTA in an aqueous methanol solution (Scheme

### Scheme 1

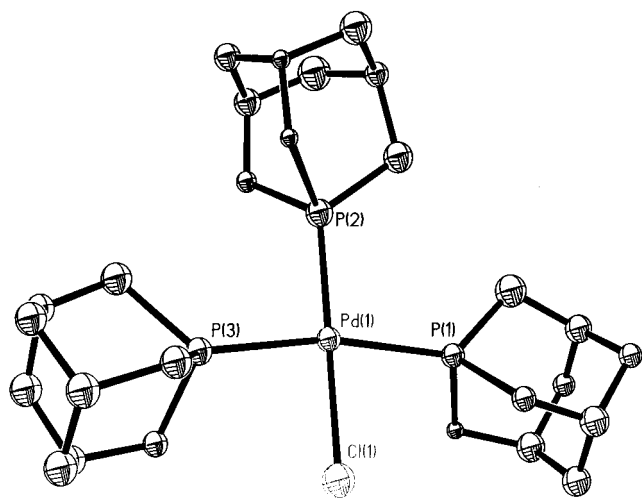


1). The reaction solution immediately turned blue followed by changing to red, subsequently resulting in a colorless solution. The identity of the blue transient species is most likely an octahedral Ni(II) complex containing PTA ligands bound via a nitrogen atom, since amine complexes of this type are characteristically blue in color.<sup>31</sup> Although there are *no* documented-complexes of PTA bound via a nitrogen atom, the measured  $pK_a$  of  $5.70 \pm 0.01$  of a nitrogen-bound proton in PTAH<sup>+</sup> would suggest it to be a suitable ligand toward Ni(II). Nevertheless, we observed no apparent reaction between NiCl<sub>2</sub> and the weaker nitrogen base analogue hexamethylenetetraamine ( $pK_a = 4.89$ ), in aqueous solution. The red intermediate has been identified as NiCl<sub>2</sub>(PTA)<sub>2</sub>, (**4**) by way of an independent synthesis of this derivative in anhydrous methanol. On the other hand, this latter Ni(II) derivative was shown to be quite unstable in an aqueous methanol solution with regard to forming the reduced Ni(PTA)<sub>4</sub> (**5**) species along with 1 equiv of PTA=O (<sup>31</sup>P NMR at  $-2.32$  ppm).

The Ni(PTA)<sub>4</sub> which was prepared by this route in a purified yield of 74% has a single <sup>31</sup>P NMR signal at  $-44.8$  ppm in D<sub>2</sub>O. This <sup>31</sup>P chemical shift is slightly downfield from that of Ni(PTA)<sub>4</sub> prepared in toluene/methanol from the ligand substitution reaction of Ni(cod)<sub>2</sub> and PTA of  $-45.7$  ppm.<sup>1</sup> This downfield shift is indicative of partially protonated PTA ligands in the nickel(0) product obtained in Scheme 1, which is consistent with the production of 2 equiv of HCl during this process. The completely protonated Ni(PTAH)<sub>4</sub><sup>+</sup> cation, prepared from Ni(PTA)<sub>4</sub> in 0.1 M HCl and crystallographically characterized, exhibits a <sup>31</sup>P NMR chemical shift further downfield at  $-41.9$  ppm.

The palladium analogue to complex **5** is similarly prepared from PdCl<sub>2</sub> and 5 equiv of PTA in an aqueous solution in a

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**Figure 1.** Molecular structure of complex **7** (thermal ellipsoids at 50% probability).

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Complex **7**

Pd(1)—Cl(1)	2.375(3)	N—C(ave) <sup>a</sup>	1.491[11]
Pd(1)—P(1)	2.330(2)	N—C(ave) <sup>b</sup>	1.472[11]
Pd(1)—P(2)	2.238(3)	P(1)—C(ave)	1.846[9]
Pd(1)—P(3)	2.338(2)	P(2)—C(ave)	1.852[8]
O(1M)—C(1M)	1.38(2)	P(3)—C(ave)	1.851[9]
Cl(1)—Pd(1)—P(1)	84.23(8)	P(1)—Pd(1)—P(2)	97.72(8)
Cl(1)—Pd(1)—P(2)	174.43(8)	P(1)—Pd(1)—P(3)	168.37(9)
Cl(1)—Pd(1)—P(3)	84.37(8)	P(2)—Pd(1)—P(3)	93.85(8)
Pd(1)—P(1)—C(ave)	118.8[3]	Pd(1)—P(3)—C(ave)	118.6[3]
Pd(1)—P(2)—C(ave)	119.1[3]		

<sup>a</sup> Carbon bonded to one nitrogen atom and one phosphorus atom.

<sup>b</sup> Carbon bonded to two nitrogen atoms.

yield of 57%. However, the synthesis of this derivative requires a longer reaction period of about 12 h. As in the case of the nickel complex, the <sup>31</sup>P NMR signal in D<sub>2</sub>O of this Pd(PTA)<sub>4</sub> (**6**) complex was downfield at −56.5 ppm relative to the unprotonated derivative (−58.7 ppm), again indicative of some protonation of the bound PTA ligands. Previously we have reported upon the reductive synthesis (PdCl<sub>2</sub> plus excess PTA) of the Pd(PTA)<sub>4</sub> complex in ethanol/water where a cationic Pd-(PTA)<sub>3</sub>Cl<sup>+</sup> intermediate species was isolated and characterized spectroscopically as its chloride salt.<sup>1</sup> Herein, we have obtained X-ray quality crystals of this derivative, complex **7**. The [Pd-(PTA)<sub>3</sub>Cl][Cl] salt was crystallized from methanol/water with one molecule each of CH<sub>3</sub>OH and H<sub>2</sub>O in the crystal lattice and shown to be isomorphous with its platinum analogue previously reported by Muir and co-workers.<sup>32</sup>

Yellow crystals suitable for X-ray diffraction were obtained from a concentrated aqueous methanol solution of complex **7** maintained at 5 °C for several days. These crystals were extremely air sensitive, turning orange followed by decomposition upon minimal exposure to moist air. Crystallographic data and data collection parameters are listed in Table 1. A thermal ellipsoid view of the cation of complex **7** is depicted in Figure 1, along with the atomic numbering scheme. Bond distances and bond angles of specific interest are found in Table 2. The geometry about the palladium center in the cation, Pd(PTA)<sub>3</sub>Cl<sup>+</sup>, is approximately square planar, where the average deviation from the plane defined by the four ligand and Pd atoms is

±0.062 Å. The Pd—P bond trans to the chloride ligand is observed to be significantly shorter, 2.238(3) Å, as compared to the average Pd—P bond length cis to the Cl<sup>−</sup> ligand, 2.334(2) Å. That is, the cation exhibits a notable *trans influence*, much like that seen in the platinum derivative.<sup>32</sup> The average Cl—Pd—P<sub>cis</sub> and P<sub>cis</sub>—Pd—P<sub>trans</sub> bond angles were found to be 84.30(8)° and 95.79(8)°, respectively, whereas the P<sub>cis</sub>—Pd—P<sub>cis</sub> bond angle was determined to be 168.37(9)°. The water molecule was shown to be involved in a hydrogen-bonding motif with the nitrogen atoms of adjacent cations (N⋯O distances are 2.863 and 2.913 Å with a N—O—N angle of 121.2°). Similarly, the chloride anion is hydrogen-bonded to methanol with a Cl⋯O distance of 3.098 Å and a C—O—Cl angle of 101.1°.

The reaction of platinum dichloride with excess PTA in an aqueous solution over the period of 2 days underwent a color change from orange to yellow prior to affording the off-white, zerovalent platinum complex. However, the definitive identification of the product(s) resulting from this reaction was not as straightforward as that of the other group 10 metals. That is, this process provided two platinum(0) species in an overall yield of 82%. These two platinum derivatives exhibited sharp, singlet <sup>31</sup>P NMR resonances in D<sub>2</sub>O at −70 (*J*<sub>Pt—P</sub> = 3699 Hz) and −80 ppm (*J*<sub>Pt—P</sub> = 2357 Hz) in a ratio of 1.7 to 1. The former <sup>31</sup>P signal is readily assignable to the expected product, a partially protonated at nitrogen Pt(PTA)<sub>4</sub> derivative. Recall that Pt(PTA)<sub>4</sub> and Pt(PTAH)<sub>4</sub><sup>4+</sup> have <sup>31</sup>P NMR chemical shifts at −74.5 and −69.1 ppm, respectively.<sup>1</sup>

Upon the addition of an aqueous solution of [Et<sub>4</sub>N][OH] to the mixture of platinum(0) species in water, a single <sup>31</sup>P resonance at −74.5 ppm appeared. Hence, both derivatives are related to Pt(PTA)<sub>4</sub> via a protonation process. It is important to reiterate here that the Pt(PTAH)<sub>4</sub>Cl<sub>4</sub> complex (crystals grown from Pt(PTA)<sub>4</sub> in 0.1 HCl) has been crystallographically defined to be a tetrahedral species with one N atom of each PTA ligand protonated as evidence by an analysis of the C—N bond distances in the bound PTA ligands.<sup>12</sup> Therefore, it follows that the other platinum derivative is protonated at an alternative site, most likely at the metal center. Indeed several research groups have reported zerovalent group 10 metal derivatives protonated at the metal site.<sup>7,33–36</sup>

From these observations it is evident that the kinetically controlled site of protonation of Pt(PTA)<sub>4</sub> is at the nitrogen atoms of the PTA ligands. That is, the addition of an excess of strong aqueous acids such as hydrochloric led to formation of the well-characterized Pt(PTAH)<sub>4</sub>Cl<sub>4</sub> derivative. However, if a much weaker acid is employed such as [PTAH][Cl] (*pK*<sub>a</sub> = 5.70) or carbonic acid (*pK*<sub>a</sub><sup>1</sup> = 6.37), the PTA ligands are not protonated and only the <sup>31</sup>P NMR resonance at −80 ppm is observed. [The bound PTA ligands would be anticipated to be less basic than those of free PTA, which we have determined to have a *pK*<sub>a</sub> of 5.70. For example, PTA=O has a measured *pK*<sub>a</sub> of 2.52.] It is of importance to note that in the synthesis of Pt(PTA)<sub>4</sub> by the aqueous reduction of PtCl<sub>2</sub> in excess PTA the HCl produced in this process is partially consumed by free PTA, thereby leading to two protonating reagents and subsequently two different protonated platinum species. From one of these preparations we have isolated crystals of a Pt(PTA)<sub>4</sub> complex protonated at one of the nitrogen atoms of PTA, i.e., [Pt(PTA)<sub>3</sub>(PTAH)][Cl] (**1S**), as determined by X-ray crystal-

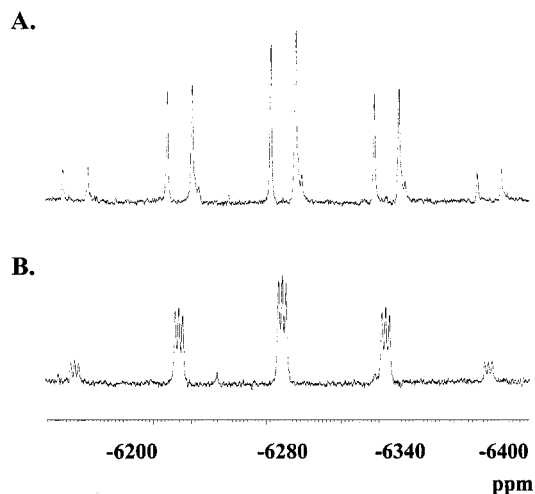
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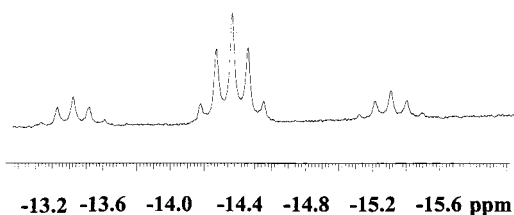
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**Figure 2.** (A)  $^{195}\text{Pt}$  NMR spectrum of  $[(\text{H})\text{Pt}(\text{PTA})_4][\text{Cl}]$  in 3:1  $\text{H}_2\text{O}/\text{D}_2\text{O}$ . (B)  $^{195}\text{Pt}$  NMR spectrum of  $[(\text{D})\text{Pt}(\text{PTA})_4][\text{Cl}]$  in  $\text{D}_2\text{O}$ .

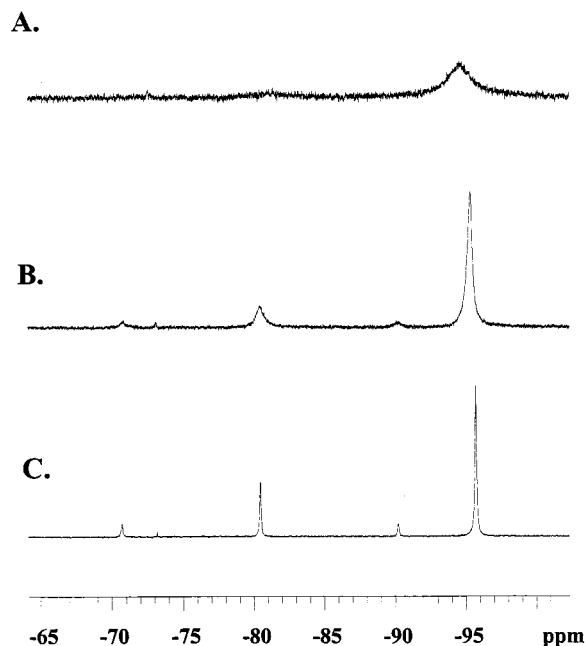


**Figure 3.**  $^1\text{H}$  NMR spectrum of  $[(\text{H})\text{Pt}(\text{PTA})_4][\text{Cl}]$  in 3:1  $\text{H}_2\text{O}/\text{D}_2\text{O}$ .

lography. Structural parameters for complex **1S** are essentially the same as those previously reported for the  $[\text{Pt}(\text{PTAH})_4][\text{Cl}]_4$  derivative.<sup>1</sup>

That this species is protonated at the platinum center is clearly demonstrated by both  $^{195}\text{Pt}$  and  $^1\text{H}$  NMR spectroscopies. Figure 2 depicts the  $^{195}\text{Pt}$  NMR spectra for the protonated and deuterated  $\text{HPt}(\text{PTA})_4^+$  species in water. As seen in Figure 2, superimposed on the platinum nucleus being split by four-equivalent phosphine ligands into a quintet ( $J_{\text{Pt-P}} = 2362$  Hz) are the Pt-H ( $J_{\text{Pt-H}} = 565$  Hz) and Pt-D ( $J_{\text{Pt-D}} = 87$  Hz) couplings. Although there is some overlap in the  $^{195}\text{Pt}$  NMR chemical shifts for Pt(II) and Pt(0) species, the chemical shift found for  $\text{HPt}(\text{PTA})_4^+$  at  $-6289$  ppm is more typical of a platinum(0) species. The  $^1\text{H}$  NMR spectrum of the  $\text{HPt}(\text{PTA})_4^+$  cation in water exhibits a signal at  $-14.3$  ppm split into a quintet by four magnetically equivalent phosphine ligands ( $^2J_{\text{P-H}} = 28.0$  Hz). In addition, the  $^{195}\text{Pt}$  satellites appear with a coupling constant of  $J_{\text{Pt-H}} = 567$  Hz (see Figure 3). Similarly, the  $^{31}\text{P}$  NMR spectrum of this derivative, a singlet at  $-80$  ppm in  $\text{H}_2\text{O}$ , displays a  $^2J_{\text{P-H}}$  value of  $28.0$  Hz. Furthermore, low-temperature  $^{31}\text{P}$  NMR spectra determined in  $\text{CD}_3\text{OD}$  revealed the phosphine ligands to be magnetically equivalent at temperatures as low as  $-80$  °C, indicative of a rapid *intramolecular* ligand exchange process. Correspondingly, at elevated temperatures in aqueous solution rapid *intermolecular* ligand exchange occurs between the  $\text{HPt}(\text{PTA})_4^+$  cation and free PTA, as evidenced by  $^{31}\text{P}$  NMR spectroscopy (see Figure 4).

All attempts to grow crystals of the  $[\text{HPt}(\text{PTA})_4][\text{X}]$  salt with various anions have thusfar been unsuccessful. For example, crystals of the partially protonated derivative,  $[\text{Pt}(\text{PTA})_2(\text{PTAH})_2][\text{BF}_4]_2$  (**2S**), were obtained from the reaction of  $\text{Pt}(\text{PTA})_4$  and  $[\text{PTAH}][\text{BF}_4]$  in water/methanol and characterized by X-ray diffraction (see the Supporting Information). The metric parameters determined were quite similar to those previously reported for the  $[\text{Pt}(\text{PTAH})_4][\text{Cl}]_4$  derivative.<sup>1</sup> Although we have



**Figure 4.** Variable temperature  $^{31}\text{P}$  NMR of  $[(\text{H})\text{Pt}(\text{PTA})_4][\text{BF}_4]$  and excess PTA in  $\text{D}_2\text{O}$  at (A)  $80$  °C, (B)  $65$  °C, and (C)  $25$  °C.

thusfar not obtained crystals of this platinum derivative protonated at the metal center, X-ray structures of several such species synthesized via  $\text{NaBH}_4$  reduction of Pt(II) derivatives have been reported.<sup>36–38</sup> These platinum cations display distorted trigonal bipyramidal or capped tetrahedral coordination in the solid state. Furthermore,  $^{31}\text{P}$  NMR studies reveal the phosphorus nuclei to be undergoing a rapid fluxional process on the NMR time scale, even at low temperatures. However, a static trigonal bipyramidal structure for the  $\text{HPt}[\text{P}(\text{CH}_2\text{OH})_3]_4^+$  derivative in  $\text{CD}_3\text{OD}$  has been assigned at  $-78$  °C on the basis of  $^{31}\text{P}$  NMR studies.<sup>7</sup> This increase in the barrier to intramolecular phosphine exchange in this instance is thought to result from hydrogen bonding between the coordinated  $\text{P}(\text{CH}_2\text{OH})_3$  ligands. In addition,  $^{31}\text{P}$  NMR studies of other platinum hydride derivatives obtained from  $\text{NaBH}_4$  reduction of Pt(II) complexes containing tripodal phosphine ligands reveal trigonal bipyramidal structures in solution.<sup>39–41</sup>

The metal site is more basic than the bound PTA nitrogen atoms and therefore the thermodynamic site for protonation of the  $\text{Pt}(\text{PTA})_4$  species in water. Nevertheless, rapid protonation of the nitrogen atoms of the PTA ligands of  $\text{Pt}(\text{PTA})_4$  by strong acids inhibits protonation at the metal center. Indeed when 1 equiv of aqueous  $\text{HCl}$  is slowly added dropwise to an aqueous solution of  $\text{Pt}(\text{PTA})_4$ , protonation occurs predominantly at the metal center. We have been able to better define the basicity of the metal center in  $\text{Pt}(\text{PTA})_4$  by employing acids of various strengths under conditions of kinetic control. In this manner the extent of protonation at the nitrogen atoms of PTA *vs* the platinum center as a function of the  $\text{p}K_a$  of the added acid was determined by  $^{31}\text{P}$  NMR ( $-70$  vs  $-80$  ppm signals, respectively). Of course, the fact that these processes are carried out

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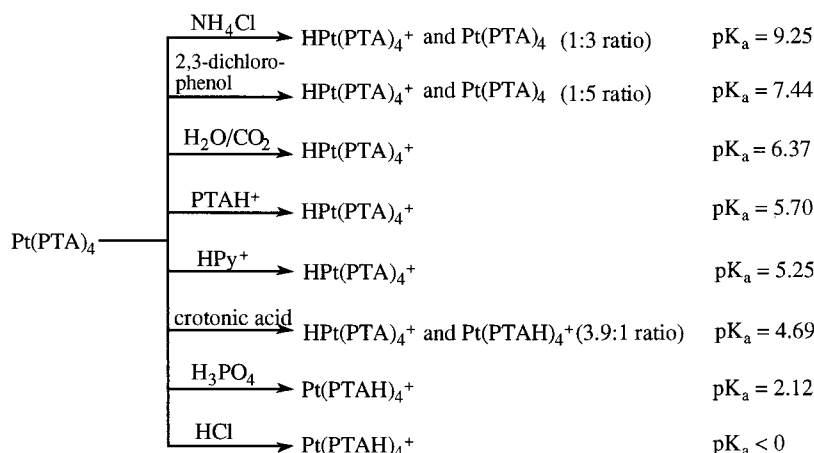
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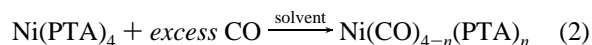
## Scheme 2



in water allows for the use of a wide range of well-defined acid strengths. The summary of our findings are shown in Scheme 2. As indicated by these results, the metal center in Pt(PTA)<sub>4</sub> is fairly basic with a pK<sub>a</sub> value greater than 7.44 but less than 9.25. We have tentatively defined the pK<sub>a</sub> of the metal protonated species to be 7.89 by the titration method described for free PTA.

**Carbonyl Derivatives of Ni(PTA)<sub>4</sub>.** In this study we have examined the production of carbonyl derivatives of Ni(PTA)<sub>4</sub> via ligand substitution reactions for two reasons. First, catalytic processes involving 18-electron catalyst precursors of Ni(PR<sub>3</sub>)<sub>4</sub> derivatives generally require phosphine dissociation prior to substrate binding and reacting; hence, it is important to establish the rates of PTA dissociation in aqueous solution. Second, the electronic and steric properties of the PTA ligand have been defined on the basis of comparisons with group 6 metal carbonyl derivatives.<sup>18,19</sup> The availability of Ni(CO)<sub>4-n</sub>(PTA)<sub>n</sub> complexes would allow for a more *direct* comparison with Tolman's parameters, which are based on an extensive series of Ni(CO)<sub>3</sub>PR<sub>3</sub> derivatives.<sup>27a</sup>

Synthesis of the carbonyl derivatives of Ni(PTA)<sub>4</sub> was accomplished by way of the reaction described in eq 2. The



initial substitution step is quite fast (vide infra). However, substitution of one PTA ligand by CO greatly retards the rate of dissociation of the second PTA ligand. That is, this latter substitution process takes place over a 12 h reaction period in methanol at 50 °C. The Ni(CO)(PTA)<sub>3</sub> product (**9**) is quite soluble in water, whereas the Ni(CO)<sub>2</sub>(PTA)<sub>2</sub> product (**10**) is only slightly water-soluble but very soluble in methanol. Substitution of a third PTA ligand by CO to provide Ni(CO)<sub>3</sub>PTA (**11**) occurs extremely slowly at ambient temperature in toluene/methanol, requiring about 1 week to go to completion. Complex **11** is not water-soluble and only slightly soluble in methanol, but is quite soluble in organic solvents such as THF or toluene. Alternatively, this complex is more readily prepared via the reaction of Ni(CO)<sub>4</sub> with 1 equiv of PTA, a process which takes place on the time scale of minutes. Hence, the successive replacement of the PTA ligands in Ni(PTA)<sub>4</sub> occurs at a decelerated rate, and concomitantly the reaction products possess greatly reduced solubilities in water and enhanced solubilities in nonpolar organic solvents.

These complexes were all characterized by  $\nu(\text{CO})$  infrared and <sup>31</sup>P NMR spectroscopies (see Table 3). As anticipated, the

**Table 3.** IR and NMR Data for Ni(CO)<sub>x</sub>(PTA)<sub>4-x</sub> Complexes

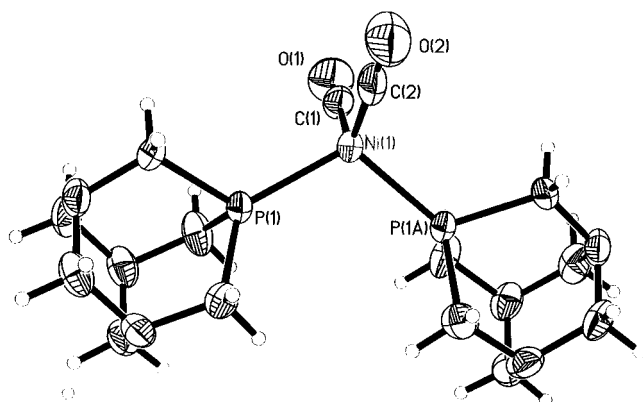
complex	IR( $\nu_{\text{CO}}$ ) (cm <sup>-1</sup> )	<sup>31</sup> P NMR (ppm)	solvent
Ni(PTA) <sub>4</sub>		-46	H <sub>2</sub> O
Ni(CO)(PTA) <sub>3</sub>	1945	-48	H <sub>2</sub> O
Ni(CO) <sub>2</sub> (PTA) <sub>2</sub>	2012	-50	MeOH
	1956		
	2001		THF
	1944		
	2006		CH <sub>2</sub> Cl <sub>2</sub>
	1946		
Ni(CO) <sub>3</sub> (PTA)	2069	-55	THF
	1994		
	2068		toluene
	1993		
	2071		CH <sub>2</sub> Cl <sub>2</sub>
	1997		

average  $\nu(\text{CO})$  value and the <sup>31</sup>P NMR chemical shift increase in frequency and shift upfield, respectively, with an increase in the number of CO ligands in the complex. The Tolman electronic parameter derived from the value of the  $\nu(\text{CO})$  A<sub>1</sub> band observed in CH<sub>2</sub>Cl<sub>2</sub> for Ni(CO)<sub>3</sub>PTA suggests that the PTA ligand is much less electron-donating than PMe<sub>3</sub>.<sup>42</sup> The  $\nu(\text{CO})$  vibrational modes exhibit significant shifts to lower frequencies in going from water or methanol as solvent to less polar organic solvents. For example, the symmetric and asymmetric  $\nu(\text{CO})$  vibrations in the Ni(CO)<sub>2</sub>(PTA)<sub>2</sub> derivative appear at 2012 and 1955 cm<sup>-1</sup> in H<sub>2</sub>O or MeOH and shift to 2001 (2006) and 1944 (1946) cm<sup>-1</sup> in THF (CH<sub>2</sub>Cl<sub>2</sub>). On the other hand, the calculated angle ( $\theta$ ) between the two CO ligands' Ni-C-O vectors determined from the absolute intensity ratio of the symmetric and asymmetric  $\nu(\text{CO})$  vibrations was found to be quite similar, i.e., 104.4° (THF), 103.2° (CH<sub>2</sub>Cl<sub>2</sub>), and 107.6° (MeOH).<sup>43</sup> These calculated angles are somewhat less obtuse than that experimentally observed in complex **10** in the solid state (117.5°) (vide infra). This underestimation of the calculated OC-Ni-CO angle is a consequence of an enhancement of the intensity of the symmetric  $\nu(\text{CO})$  vibrational mode relative to the asymmetric mode as a result of electronic migration in the phosphine-Ni  $\pi$ -bonding framework during the former vibration.<sup>43</sup>

The solid-state structure of one of these derivatives, complex **10**, was determined by X-ray crystallography. Crystals suitable for X-ray diffraction were obtained from a methanol solution of the complex layered with ether and maintained at -15 °C for several days. Crystallographic data and data collection

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**Figure 5.** Molecular structure of complex **10** (thermal ellipsoids at 50% probability).

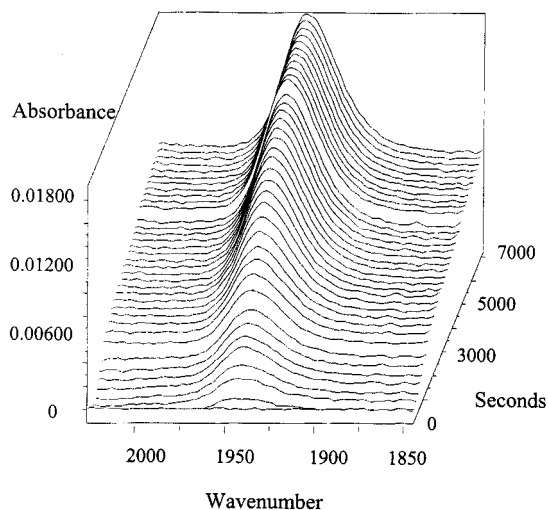
**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for Complex **10**

Ni(1)–C(1)	1.767(6)	N(3)–C(8)	1.467(6)
Ni(1)–C(2)	1.758(9)	N(2)–C(4)	1.479(6)
Ni(1)–P(1)	2.1853(13)	N(2)–C(6)	1.456(7)
Ni(1)–P(1)#1	2.1853(12)	N(2)–C(7)	1.463(6)
P(1)–C(3)	1.838(5)	N(1)–C(3)	1.472(6)
P(1)–C(4)	1.839(5)	N(1)–C(6)	1.478(7)
P(1)–C(5)	1.848(5)	N(1)–C(8)	1.468(6)
N(3)–C(5)	1.466(6)	O(3)–C(1M)	1.405(12)
N(3)–C(7)	1.458(6)	O(3)–C(1M)#2	1.405(12)
C(2)–Ni(1)–C(1)	117.5(3)	C(2)–Ni(1)–P(1)	110.56(12)
C(1)–Ni(1)–P(1)	103.43(13)	C(2)–Ni(1)–P(1)#1	110.56(12)
C(1)–Ni(1)–P(1)#1	103.43(13)	P(1)–Ni(1)–P(1)#1	110.96(8)
C(3)–P(1)–C(4)	97.5(2)	C(3)–P(1)–C(5)	96.9(2)
C(4)–P(1)–C(5)	96.1(2)	C(3)–P(1)–Ni(1)	115.7(2)
C(4)–P(1)–Ni(1)	126.1(2)	C(5)–P(1)–Ni(1)	118.9(2)
C(1M)–O(3)–C(1M)#2	131.3(13)		

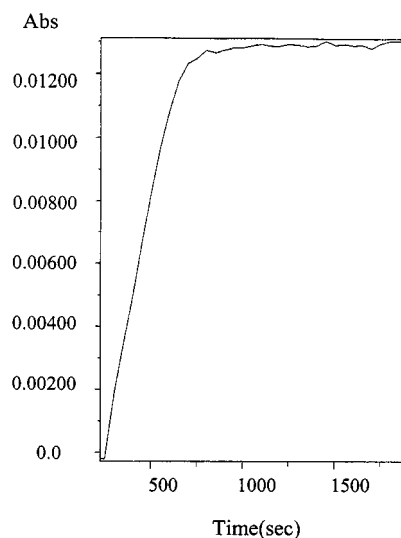
Symmetry transformations used to generate equivalent atoms: #1,  $-x, y, z$ ; #2,  $x, -y, -z + 1$ .

parameters are listed in Table 1. A thermal ellipsoid view of the complex is found in Figure 5, along with the atomic numbering scheme. Selected bond distances and bond angles are compiled in Table 4. The geometry about the nickel center is that of a slightly distorted tetrahedron with metal–ligand bond angles of C–Ni–P (ave.  $107^\circ$ ), P–Ni–P ( $110.96(8)^\circ$ ), and C–Ni–C ( $117.5(3)^\circ$ ). The average Ni–CO bond distance is  $1.763[8]$  Å and the Ni–P bond length is  $2.185(1)$  Å. These bonding parameters are consistent with those in other bisphosphine carbonyl derivatives of  $\text{Ni}(\text{CO})_4$ .<sup>44</sup> However, as would be anticipated on steric grounds, the P–Ni–P angles in the more bulky  $\text{PCy}_3$ <sup>44a</sup> and  $\text{PPh}_3$ <sup>44c</sup> derivatives are more obtuse at  $123^\circ$  and  $117^\circ$ , respectively. The corresponding Ni–P bond distances of  $2.261$  and  $2.221$  Å, respectively, are significantly longer than those observed herein for the PTA derivative with the Ni–C distances of  $1.746$  and  $1.763$  Å being quite similar for all three derivatives. The crystallographically defined Tolman cone angle as described in ref 19 was calculated to be  $103^\circ$ .

The rate of PTA substitution in  $\text{Ni}(\text{PTA})_4$  by carbon monoxide in aqueous solution was determined by employing an infrared probe for real time, in situ monitoring of the reaction's progress. The system consists of a dedicated interferometer, which is coupled through a stainless steel optical conduit with a ZnSe support element to a silicon disk probe (SiComp). This probe,



**Figure 6.** Overlay of IR spectra of  $\text{Ni}(\text{PTA})_4 + \text{CO}$  in  $\text{H}_2\text{O}$  at  $20^\circ\text{C}$ , and monitored appearance of  $\text{Ni}(\text{CO})(\text{PTA})_3 \nu(\text{CO})$  vibration at  $1945\text{ cm}^{-1}$ .

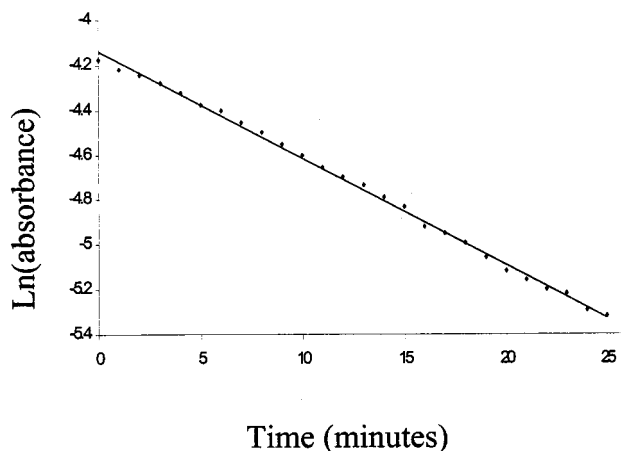


**Figure 7.** Reaction profile of  $\text{Ni}(\text{PTA})_4 + \text{CO}$  in  $\text{H}_2\text{O}$  at  $20^\circ\text{C}$ , and monitored appearance of  $\text{Ni}(\text{CO})(\text{PTA})_3 \nu(\text{CO})$  vibration at  $1945\text{ cm}^{-1}$ .

in turn, is inserted into a glass reaction vessel which is externally cooled or heated. The  $\nu(\text{CO})$  vibrational mode in the product,  $\text{Ni}(\text{CO})(\text{PTA})_3$ , at  $1945\text{ cm}^{-1}$  was used to follow the progress of the reaction (Figure 6). As depicted in Figure 7, substitution of a second PTA ligand in  $\text{Ni}(\text{CO})(\text{PTA})_3$  is much slower than that of the first, i.e., the absorbance for the  $1945\text{ cm}^{-1}$  peak increases and levels off with no diminution during the course of the substitution process. The reaction was shown to be first-order in metal complex, as indicated by the linearity of the logarithmic plot of  $(\text{Abs}_\infty - \text{Abs}_t)$  vs time (Figure 8). Consistent with the qualitative observations noted during the preparations of these carbonyl derivatives of  $\text{Ni}(\text{PTA})_4$ , the rate of PTA substitution in complex **10** is quite fast in water with a  $k_{\text{obs}} = 7.92 \times 10^{-4}\text{ s}^{-1}$  at  $20^\circ\text{C}$ . Because of the low solubility of CO in water, even at high pressure, the PTA substitutional process is retarded by small quantities of PTA ligand in solution, or in other words, the reaction product (PTA) retards the CO substitution process. The low solubility of CO in aqueous vs organic solvents is a real limitation in investigating mechanistic aspects of these process, e.g., the  $[\text{CO}]$  in water  $[(1.13\text{--}1.09) \times 10^{-3}\text{ M}]$  at  $1.2\text{--}10.5\text{ atm}$ <sup>45</sup> is not only much lower than that in organic solvents but does not vary significantly at modest

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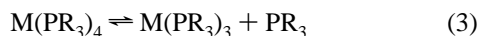




**Figure 8.** Ln(Abs<sub>∞</sub> - Abs<sub>t</sub>) vs *t* (min) plot of Ni(PTA)<sub>4</sub> + CO in H<sub>2</sub>O at 20 °C.

CO pressures. Nevertheless, in a reaction carried out in 1 equiv of PTA the measured rate constant was an order of magnitude smaller than that observed with *no* added PTA. This observation is totally consistent with a dissociative (D) pathway for the substitution of a phosphine ligand in an 18-electron metal complex by a weakly nucleophilic incoming CO ligand.<sup>46</sup>

The relatively slow rate of PTA dissociation in Ni(PTA)<sub>4</sub> in aqueous medium is consistent with the observation that, upon adding excess PTA to solutions of **5**, **6**, and **8**, sharp <sup>31</sup>P NMR signals are observed for both the complexes and free ligand. This is indicative of slow dissociative phosphine exchange on the NMR time scale. The aforementioned observation, coupled with the absence of a <sup>31</sup>P resonance for free PTA in the <sup>31</sup>P NMR spectra of M(PTA)<sub>4</sub> derivatives, is as anticipated for the dissociative equilibrium depicted in eq 3, which has been shown to be governed by steric rather than electronic effects.<sup>47</sup> That is, for the small, tight-binding PTA ligand in group 10 M(PTA)<sub>4</sub> species, there is little or no dissociation and slow exchange.



### Comments and Conclusions

Herein we have described the synthesis of water-soluble, zerovalent group 10 metal tetrakis-phosphine derivatives from the reaction of the corresponding metal(II) chloride salt and excess PTA in aqueous solution with concomitant production of PTA=O. These M(PTA)<sub>4</sub> derivatives were shown by <sup>31</sup>P NMR studies to have little to no phosphine dissociation and to undergo slow exchange with free PTA in water. Unlike the nickel and palladium derivatives, the Pt(PTA)<sub>4</sub> complex was found to be readily protonated at the metal center by weak aqueous acids such as carbonic acid and pyridinium tetrafluoroborate to provide [HPt(PTA)<sub>4</sub>][X] salts. The <sup>195</sup>Pt chemical

shift value of -6289 ppm suggests these complexes to be protonated Pt(0) derivatives as opposed to Pt(II) hydrides. By way of comparison with acids of well-defined p*K*<sub>a</sub> values in water, the p*K*<sub>a</sub> of this platinum hydride is estimated to be greater than 7.44 but less than 9.25. On the other hand, the p*K*<sub>a</sub> of the protonated nitrogen atoms of bound PTA ligands is less than 5.70. These protonated platinum salts were shown to possess magnetically equivalent phosphine ligands at a temperature as low as -80 °C in CD<sub>3</sub>OD by <sup>31</sup>P NMR, indicative of a fast *intramolecular* exchange processes. Furthermore, at elevated temperatures (>50 °C) fast *intermolecular* phosphine exchange between the HPt(PTA)<sub>4</sub><sup>+</sup> cation and free phosphine in aqueous solution was observed.

It is of interest to compare the p*K*<sub>a</sub> defined for the HPt(PTA)<sub>4</sub><sup>+</sup> cation in aqueous solution with other values determined in closely related complexes. For example, the water-soluble Pt-[P(CH<sub>2</sub>OH)<sub>3</sub>]<sub>4</sub> complex has been protonated by water which would indicate the platinum center to be much more basic than in the PTA analogue reported herein.<sup>7</sup> This in turn would dictate that the P(CH<sub>2</sub>OH)<sub>3</sub> ligand is a much better donor than PTA, for Angelici has shown that there is a strong correlation between the enthalpies of protonation (Δ*H*<sub>HM</sub>) of metal phosphine complexes and the phosphine's basicity.<sup>48</sup> Related to this, the p*K*<sub>a</sub> of HPt[P(OMe)<sub>3</sub>]<sub>4</sub><sup>+</sup> has been estimated at 11 in H<sub>2</sub>O from data determined in acetonitrile.<sup>49</sup> On the basis of our studies, this p*K*<sub>a</sub> value would appear to be *too high* since the P(OMe)<sub>3</sub> ligand is a weaker donor than PTA.

Finally, the synthesis and characterization of a series of Ni(CO)<sub>4-n</sub>(PTA)<sub>n</sub> derivatives has allowed for an assessment of the electronic and steric parameters for the PTA ligand according to Tolman's original definitions.<sup>27a</sup> That is, based on the *ν*-(CO) A<sub>1</sub> vibrational frequency of Ni(CO)<sub>3</sub>PTA in methylene chloride, the PTA ligand is shown to be less donating to the Ni(0) center than PPh<sub>3</sub>. This was a bit unexpected, since previous comparisons with molybdenum and iron carbonyl derivatives, as well as metal carbonyl cluster derivatives,<sup>50</sup> have suggested the PTA ligand to be similar to PMe<sub>3</sub>.<sup>18</sup> On the other hand, the steric requirements (cone angle) of PTA, as determined by X-ray crystallography for the Ni(CO)<sub>2</sub>(PTA)<sub>2</sub> derivative, was computed to be 103°. This value is indistinguishable from that defined for this parameter based on crystallographic data for the Mo-(CO)<sub>5</sub>PTA complex.<sup>19</sup>

**Acknowledgment.** Financial support of this research by the National Science Foundation (Grant 96-15866) and the Robert A. Welch Foundation is greatly appreciated. The experimental contributions of Dr. A. Kathó and Dr. Tara Decuir to this research effort are gratefully acknowledged.

**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determinations of complexes **7**, **10**, **1S**, and **2S**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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