Water Soluble Diphosphine ligands based on 1,3,5-triaza-7-phosphaadamantane (PTA-PR₂): synthesis, coordination chemistry, and ruthenium catalyzed nitrile hydration[‡]

Jeremiah M. Sears, Wei-Chih Lee, Brian J. Frost*

Department of Chemistry, University of Nevada, Reno, Nevada 89557-0216, United States

[‡] Dedicated to the memory of Dr. Gene W. Wong a student, friend, and colleague.

ABSTRACT: Two chiral chelating 1,3,5-triaza-7-phosphaadamantane (PTA) derivatives were synthesized, in racemic form, by addition of ClPⁱPr₂ or ClP(NⁱPr)₂(CH₂)₂ to lithiated PTA. PTA-PⁱPr₂ (**1**) and PTA-P(NⁱPr)₂(CH₂)₂ (**2**) were isolated in good yield, 73 % and 56 % respectively, and fully characterized by multinuclear NMR spectroscopy, mass spectrometry, and X-ray crystallography. PTA-PⁱPr₂ is highly air sensitive, but stable and somewhat soluble in degassed water. PTA-P(NⁱPr)₂(CH₂)₂ (**2**) is air-stable, but decomposes in water over the course of hours. Two tungsten tetracarbonyl complexes were prepared by addition of the PTA-PR₂ to [W(CO)₄(pip)₂] and characterized by NMR and IR spectroscopies and X-ray crystallography in the case of [W(CO)₄(PTA-PⁱPr₂)]. Based on IR spectroscopy PTA-PⁱPr₂ (**1**) is more electron donating than PTA-P(NⁱPr)₂(CH₂)₂ (**2**) or the previously published PTA-PPh₂. Products isolated from the reaction of [(η⁶-toluene)RuCl₂]₂ with two equivalents of **1** were found to contain monodentate (κ¹), bidentate (κ²), and possibly bridging coordination modes of PTA-PⁱPr₂. These ruthenium complexes were explored as catalysts for aqueous phase nitrile hydration. Of the ruthenium explored [(η⁶-toluene)RuCl₂(κ¹-PTA-PⁱPr₂)] (**7**) was the most active towards nitrile hydration. In the presence of air at 100 °C **7** converted various nitriles to the respective amides with 43-99% conversions in 7 h.

Introduction

The hydration of nitriles to amides has been carried out by a wide range of metal complexes under a variety of conditions.[1–3] Ruthenium compounds

have been utilized as catalysts for nitrile hydration with [(η⁶-arene)RuCl₂PR₃] complexes as some of the most efficient and versatile catalysts with good substrate tolerance.[1–14] Ruthenium complexes of 1,3,5-triaza-7-phosphaadamantane (PTA)[11,12,15–17] and derivatives[10] have exhibited high activity and selectivity for the hydration of nitriles to amides. We have shown that some ruthenium complexes with PTA or PTA derivatives are active for nitrile hydration in the presence of air, removing the need to run these reactions under inert atmosphere.[10,16]

Scheme 1.

Our group,[10,18–20] and others,[21–30] have been interested in the development of derivatives of the water-soluble and air-stable phosphine 1,3,5-triaza-7-phosphaadamantane (PTA).[31,32] A variety of lower-rim (C₃N₃ ring) modified derivatives have been published involving opening of the cage,[21,22,23,25,27,33] expansion of the ring,[34,35] substitution of a methylene with SO₂,[24,36] or tri-substitution of the triazacyclohexane ring.[19] Up-

per-rim derivatives of PTA have been synthesized by addition of aldehydes, ketones, imines, and carbon dioxide to lithiated PTA (PTA-Li) resulting in the formation of carboxylates,[20] β -phosphino alcohols,[20,28,30] or β -amino phosphines;[10] Scheme 1. Our initial report describing the synthesis of PTA-Li included the synthesis of 6-(diphenylphosphino)-1,3,5-triaza-7-phosphaadamantane (PTA-PPh₂) by addition of ClPPh₂ to PTA-Li.[18] PTA-PPh₂ is a chiral and air-stable, but unfortunately water insoluble, phosphine ligand isolated in somewhat poor yield (10%).[18] Herein we report the synthesis of two new bisphosphine ligands of the type PTA-PR₂, and details of their coordination chemistry to tungsten carbonyl and a ruthenium(II) arene. In addition, a number of ruthenium complexes have been explored as aqueous phase catalysts for nitrile hydration.

Results and Discussion

The chiral phosphine ligands PTA-PⁱPr₂ (**1**) and PTA-P(NⁱPr)₂(CH₂)₂ (**2**) were synthesized, in racemic form, by addition of ClPⁱPr₂ or ClP(NⁱPr)₂(CH₂)₂ to a suspension of PTA-Li in THF (Scheme 2). PTA-PⁱPr₂ (**1**) was isolated in modest yield (56 %) and is soluble in common organic solvents e.g. hexanes, benzene, toluene, dichloromethane, chloroform, acetonitrile, and methanol. Unlike the previously reported water insoluble PTA-PPh₂, **1** is somewhat soluble in degassed water (S_{25}° = 13.3 mg/mL; 48.7 mM). PTA-P(NⁱPr)₂(CH₂)₂ (**2**) was isolated in 73 % yield and exhibited similar solubility characteristics as **1**, but is slightly less soluble in water (S_{25}° = ~10 mg/mL; ~30 mM). Both **1** and **2** exhibited similar water-solubility to the β -phosphino alcohols (PTA-CRR'OH; S_{25}° = ~2–11 mg/mL; 17.4–37.9 mM),[20,28] and higher water solubility than the β -amino phosphines (PTA-CRR'NHPh; S_{25}° = ~2.7–5 mg/mL; 6.5–14.2 mM) previously reported by us.[10] Peruzzini and co-workers reported that imidazole derivatives of PTA that are quite water soluble (0.4 – 1.2 M)[29] and we have reported a PTA-CO₂Li derivative that is highly soluble in water (3.8 M).[20]

Scheme 2. Reaction of PTA-Li with PR₂Cl.

PTA-PⁱPr₂ (**1**) readily oxidizes upon exposure to air in both the solid state or solution. Solid samples of PTA-P(NⁱPr)₂(CH₂)₂ (**2**) are stable in air; **2** oxidizes over the course of a week in solution. Oxygen free aqueous solutions (D₂O) of **2** decomposed, presumably via hydrolysis of the P–N bonds, within ~2 h as observed by ³¹P NMR spectroscopy. Aqueous samples of **1** were significantly more stable; ³¹P NMR spectra taken over the course of two weeks revealed PTA-PⁱPr₂ (**1**) slowly oxidizing to the phosphine oxide along with other decomposition/hydrolysis products apparent at longer times.

The ³¹P{¹H} NMR spectra for PTA-PⁱPr₂ and PTA-P(NⁱPr)₂(CH₂)₂ in CDCl₃ contained the expected pair of doublets at -3.31 ppm (PⁱPr₂) and -98.28 ppm (PTA) for **1** (d, ²J_{PP} = 50 Hz) and 100.36 ppm (P(NⁱPr)₂(CH₂)₂) and -100.18 ppm (PTA) for **2** (d, ²J_{PP} = 38 Hz); Table 1.

The phosphine oxides of **1** and **2**, O=PTA-O=PⁱPr₂ (**3**) and O=PTA-O=P(NⁱPr)₂(CH₂)₂ (**4**), were prepared by addition of H₂O₂ to the corresponding diposphine in CH₂Cl₂. As expected the ³¹P{¹H} NMR resonances of O=PTA-O=PⁱPr₂ (**3**) are shifted significantly from **1** and are observed as a pair of doublets centered at 57.70 and -8.32 ppm, ²J_{PP} = 5 Hz. Two broad resonances at 24.89 and -10.53 ppm were observed in the ³¹P{¹H} NMR spectrum for the cyclic amine derivative O=PTA-O=P(NⁱPr)₂(CH₂)₂ (**4**). These chemical shifts and coupling constants (²J_{PP}) are consistent with what has been previously observed for PTA-PPh₂ and O=PTA-O=PPh₂; Table 1. Oxidation of PTA-PPh₂ with H₂O₂ resulted in a ³¹P NMR spectrum containing two doublets at -1.4 and 34.3 ppm (²J_{PP} = 4 Hz) corresponding to O=PTA and O=PPh₂ phosphorus nuclei, respectively.[18] IR stretching frequencies, ν_{PO} , for **3** and **4** were observed between 1155 and 1185 cm⁻¹ consistent with PTA oxide (1167 cm⁻¹).[37,38]

Table 1. ³¹P{¹H} NMR chemical shifts and coupling constants for PTA-PR₂ compounds and oxides.

Complex	³¹ P{ ¹ H} ppm ^a	² J _{PP} Hz
PTA-P ⁱ Pr ₂	-3.3 (PR ₂)	50
(1)	-98.3 (PTA)	
PTA-P(N ⁱ Pr) ₂ (CH ₂) ₂	100.4 (PR ₂)	38
(2)	-100.2 (PTA)	
O=PTA-O=P ⁱ Pr ₂	57.0 (PR ₂)	5
(3)	-8.8 (PTA)	
O=PTA-O=P(N ⁱ Pr) ₂ (CH ₂) ₂	24.9 (PR ₂)	----
(4)	-10.5 (PTA)	
PTA-PPh ₂ ^{b,c}	-19.8 (PR ₂)	65

Complex	$^3\text{P}\{^1\text{H}\}$ ppm ^a	$^2J_{\text{PP}}$ Hz
	-100.1 (PTA)	
O=PTA-O=PPh ₂ ^{b,c}	34.3 (PR ₂) -1.4 (PTA)	4

a) in CDCl₃; b) in CD₂Cl₂; c) see ref [18]

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** contains six separate resonances between 47 and 77 ppm for the six carbons in the PTA cage with the PCHP carbon appearing as a doublet of doublets at 57.25 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** also contains 6 resonances for the six chemically distinct carbons in the PTA cage with the N-C-N carbons the most down-field between 69 and 76 ppm. The P-C-P carbon was observed as doublet of doublets centered at 63.9 ppm. The other P-C-N carbons for **2** were observed between 47 and 53 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The methine carbons of the isopropyl groups were observed as doublet of doublets at 23.29 and 21.87 ppm for **1** and as doublets for **2** at 52.15 and 50.43 ppm.

The proton NMR spectra for **1** and **2** are complicated and have been assigned utilizing ^1H - ^{13}C HMQC. The lower rim methylene groups for **1** and **2** were observed between 5.33-4.26 ppm and 5.11-4.36 ppm, respectively. The upper rim methine proton (PCHP) for both compounds was observed as a multiplet between 4.36 to 4.13 ppm. The other upper rim protons (PCH₂N) for **1** and **2** are observed between 4.26-3.83 ppm. The isopropyl resonances for **1** were found between 1.98-1.82 ppm (methine) and 1.25-1.05 ppm (methyl) whereas **2** displayed two methine resonances (3.32-3.24 ppm and 2.95-2.9 ppm) with methyl signals appearing between 1.14-1.07 ppm. The four protons from the ethyl bridge in **2** were observed between 3.24-3.01 ppm in the ^1H NMR spectrum.

The solid-state structures of **1** – **4** were determined by single crystal X-ray diffraction. Figures 1 – 4 contain the thermal ellipsoid representations of PTA- P^iPr_2 (**1**), PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ (**2**), O=PTA-O= P^iPr_2 (**3**), and O=PTA-O= $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ (**4**). Selected bond lengths and angles for **1** – **4** as well as the related PTA-PPh₂ may be found in Table 2. As observed with other upper-rim PTA derivatives the P-C₁ distance is slightly elongated relative to PTA (P-C_{ave} = 1.856 Å). [39] The P1-C1 distances for PTA- P^iPr_2 and PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ were found to be 1.873 Å slightly shorter than the 1.890(4) Å observed for PTA-PPh₂. [18] The P1-C2 (1.815(5) Å) and P1-C3 (1.832(4)

Å) distances in PTA-PPh₂; however, are slightly shorter than those observed for PTA- P^iPr_2 (1.857(3) and 1.852(3) Å) and PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ (1.872(1) and 1.869(1) Å). The P-C-P angle in PTA- P^iPr_2 , 113.36(15)°, and PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$, 115.41(6)°, were somewhat larger than observed in PTA-PPh₂ (108.79(18)°). The oxides, O=PTA-O= P^iPr_2 and O=PTA-O= $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$, had shorter P-C bonds (1.8155(14)-1.8374(1) Å) than PTA- P^iPr_2 or PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ (1.852(3) and 1.873(3) Å). This is consistent with the observed bond lengths in PTA/O=PTA and PTA-PPh₂/O=PTA-O=PPh₂. [18,39,40]

Fig. 1. Thermal ellipsoid representation (50% probability) of the R_{C1} enantiomer of PTA- P^iPr_2 (**1**) along with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity with the exception of those on C₁. Selected bond lengths: P2-C7 = 1.862(3); P2-C10 = 1.863(3) see Table 2 or SI for additional information.

Fig. 2. Thermal ellipsoid representation (50 % probability) of O=PTA-O= P^iPr_2 (**3**) along with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity with the exception of those attached to C₁. Only the R_{C1} enantiomers are shown; however, both R_{C1} and S_{C1} enantiomers are present. Selected bond lengths: P1-O1 = 1.4885(11); P2-O2 = 1.4942(12) see Table 2 or SI for additional information.

Fig. 3. Thermal ellipsoid representation (50 % probability) of PTA-P(NⁱPr)₂(CH₂)₂ (**2**) along with the atomic numbering scheme. Hydrogen atoms have been omitted with the exception of the stereogenic carbon, C₁. Only the R_{C1} enantiomer is shown; however, both R_{C1} and S_{C1} are present in the unit cell. Selected bond lengths and angles: P2–N₄ = 1.6965(10); P2–N₅ = 1.7286(10); N₄–P2–N₅ = 92.09(5) see Table 2 or SI for additional information.

Fig. 4. Thermal ellipsoid representation (50 % probability) of O=PTA–O=P(NⁱPr)₂(CH₂)₂ (**4**) along with the atomic numbering scheme. Hydrogen atoms have been omitted with the exception of the one on the chiral carbon, C₁. Only the S_{C1} enantiomer is shown for; however, both R_{C1} and S_{C1} are present in the unit cell. Selected bond lengths and angles: P1–O₁ = 1.4919(9); P2–O₂ = 1.4808(9); P2–N₄ = 1.6580(10); P2–N₅ = 1.6427(10); N₄–P2–N₅ = 94.96(5) see Table 2 or SI for additional information.

Insert Table 2 here

Tungsten carbonyl complexes of **1** and **2**.

Scheme 3.

Tungsten tetracarbonyl complexes [W(CO)₄(PTA-PⁱPr₂)] (**5**) and [W(CO)₄(PTA-P(NⁱPr)₂(CH₂)₂)] (**6**) were synthesized by addition of PTA-PⁱPr₂ (**1**) or PTA-P(NⁱPr)₂(CH₂)₂ (**2**) to a CH₂Cl₂ solution of *cis*-[W(CO)₄(pip)₂] and isolated as yellow solids (Scheme 3). **5** is soluble in CH₂Cl₂ and acetonitrile but insoluble in methanol and water; **6** is soluble in CH₂Cl₂ and insoluble in acetonitrile, water, and methanol. The molecular ion (M+H) was observed by HRMS at 565.0800 *m/z* for **5** (CH₃CN) and 621.1152 *m/z* for **6** (CH₂Cl₂/MeOH) with the isotopic distribution patterns calculated for these complexes.[41] [W(CO)₄(PTA-PⁱPr₂)] (**5**) and [W(CO)₄(PTA-P(NⁱPr)₂(CH₂)₂)] (**6**) both exhibited the expected two sets of doublets by ³¹P{¹H} NMR spectroscopy: 52.7 (PⁱPr₂) and –91.7 ppm (PTA) for **5** (CD₂Cl₂) and 121.61 (P(NⁱPr)₂(CH₂)₂) and –100.58 ppm (PTA) for **6** (CDCl₃). Tungsten satellites were observed for both complexes ¹J_{PR2-W} = 190 Hz and ¹J_{PTA-W} = 188 Hz for **5** and ¹J_{PR2-W} = 236 Hz and ¹J_{PTA-W} = 199 Hz for **6**, comparable to the those observed for [W(CO)₄(PTA-PPh₂)]^c, ¹J_{PTA-W} = 185 and ¹J_{PR2-W} = 201 Hz, and other [W(CO)₄(PR₃)₂] complexes, Table 3.[18]

Table 3. ³¹P{¹H} NMR chemical shifts and coupling constants for series of *cis*-[W(CO)₄L₂] complexes (L₂ = (PTA)₂, (PPh₃)₂, PTA-PPh₂, DPPM, PTA-PⁱPr₂, **2**) in CD₂Cl₂.

Complex	³¹ P{ ¹ H} NMR	² J _{PP} (Hz)	¹ J _{PW} (Hz)
[W(CO) ₄ (PTA-P ⁱ Pr ₂)] 5	52.7, –91.7	19	188, ^a 190 ^b
[W(CO) ₄] 6	121.6, –100.6	31	236, ^a 199 ^b
[W(CO) ₄ (PTA-PPh ₂)] ^c	20.8, –90.4	26	201, ^a 185 ^b
[W(CO) ₄ (PPh ₃)(PTA)] ^c	22.7, –80.3	21	236, ^a 218 ^b
[W(CO) ₄ (PTA) ₂] ^c	–76.5	-----	216
[W(CO) ₄ (PPh ₃) ₂] ^c	34.15	-----	235
[W(CO) ₄ (DPPM)] ^c	–21.9	-----	212

^a J_{PW} ; ^b J_{PTA-W} ; ^c see ref [18]

The IR spectra obtained for **5**, **6**, and $[W(CO)_4(PTA-PPh_2)]$ exhibit the expected four band pattern consistent with approximate C_{2v} symmetry. PTA- P^iPr_2 (**1**) is the most electron donating of the PTA- PR_2 derivatives as evidenced by the lowest A_1 ν_{CO} , Figure 5. A series of similar tungsten carbonyl phosphine complexes are listed in Table 3. **5** and **6** both exhibited lower IR stretching frequencies (ν_{CO}) than $[W(CO)_4(PTA-PPh_2)]$, $[W(CO)_4(PTA)_2]$, and $[W(CO)_4(PPh_3)(PTA)]$ indicating increased electron donation, Table 4.

Fig. 5. IR spectrum (ν_{CO} region) for **5** (—), **6** (—), and $[W(CO)_4(PTA-PPh_2)]$ (—) in dichloromethane.

Insert Table 4 here

The solid state structure of **5** was determined by single crystal X-ray diffraction, Figure 6. Crystals of $[W(CO)_4(PTA-P^iPr_2)]$ suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2 solution of **5**. As expected the geometry about the tungsten center is a distorted octahedron with four coordination sites occupied by carbonyl ligands and two *cis* coordination sites occupied by the two phosphorus atoms of **1**. The $W-P_{1PTA}$ distance of 2.504(1) Å in **5** is similar to that observed in $[W(CO)_4(PTA-PPh_2)]$ where $W-PTA = 2.4949(11)$ Å. The $W-P_{2iPr}$ distance of 2.561(1) Å is slightly longer than the comparable $W-P_{PPh_2} = 2.5349(12)$ Å. Bite angles ($\angle P-W-P$) for a series $[W(CO)_4(PR_3)_2]$ complexes are included in Table 4 and reveal similar bite angles among dppm 67.108(16)°, PTA- P^iPr_2 67.83(4)°, and PTA- PPh_2 68.18(4)°.

Fig. 6. Thermal ellipsoid representation (50 % probability) of $[W(CO)_4(PTA-P^iPr_2)]$ (**5**) with the atomic numbering scheme. Hydrogen atoms have been omitted except for that on the stereocenter C_5 . The SC_5 enantiomer is shown; however, both SC_5 and RC_5 are present in the unit cell. Selected Bond lengths (Å) and angles (deg): $W1-P1 = 2.504(1)$, $W1-P2 = 2.560(1)$, $W1-C1 = 1.971(5)$, $W1-C2 = 1.962(5)$, $W1-C3 = 2.042(5)$, $W1-C4 = 2.022(5)$, $P1-C5 = 1.837(5)$, $P2-C5 = 1.869(5)$, $P1-W1-P2 = 67.83(4)$, $P1-C5-P2 = 99.4(2)$, $C5-P1-W1 = 94.8(1)$, $C5-P2-W1 = 92.2(1)$, $C1-W1-P1 = 167.0(1)$, $C2-W1-P2 = 168.3(1)$, $C2-W1-P1 = 100.7(1)$, $C3-W1-P1 = 95.8(1)$, $C1-W1-P2 = 99.4(1)$, $C3-W1-P2 = 96.0(1)$, $C1-W1-C3 = 87.8(2)$, $C4-W1-C3 = 173.4(2)$.

Ruthenium arene complexes of PTA- P^iPr_2 .

Scheme 4.

Addition of 2 equivalents of PTA- P^iPr_2 (**1**) to a benzene solution of $[(\eta^6\text{-toluene})RuCl(\mu\text{-Cl})_2]_2$ results in precipitation of $[(\eta^6\text{-toluene})RuCl_2(\kappa^1\text{-PTA-}P^iPr_2)_2]$ (**7**) as an air-stable orange-brown solid in 90 % yield, Scheme 4. The $^3P\{^1H\}$ NMR spectrum of **7** in CD_2Cl_2 contains two doublets centered at 11.0 ($-P^iPr_2$) and -27.4 (PTA) ppm with a coupling constant $^2J_{PP} = 65$ Hz, (Figure 7). The >70 ppm shift for the PTA phosphorus along with the smaller shift (~15 ppm) of the P^iPr_2 chemical shift is consistent with coordination of only the PTA phosphorous to ruthenium. Compound **7** is not stable in solution forming both κ^2 and possibly bridging complexes over time, *vide infra*.

Fig. 7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\eta^6\text{-toluene})\text{RuCl}_2(\kappa^1\text{-PTA-P}^i\text{Pr}_2)]$ (**7**) in CDCl_2 .

Addition of two equivalents of PTA- P^iPr_2 (**1**) to a CH_2Cl_2 solution of $[(\eta^6\text{-toluene})\text{RuCl}(\mu\text{-Cl})_2]$ initially leads to formation of the κ^1 complex **7** as described above. Over the course of a few days we observe by NMR spectroscopy a shift from κ^1 to κ^2 coordination. Upon substitution of a chloride for the second phosphorus the complex now contains two chiral centers (C_1 and Ru_1). The diastereomeric pair is observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as two sets of doublets centered at 62.7 ($^2J_{\text{PP}} = 64$ Hz), 50.8 ($^2J_{\text{PP}} = 65$ Hz), -46.0 ($^2J_{\text{PP}} = 65$ Hz) and -54.3 ppm ($^2J_{\text{PP}} = 64$ Hz) (Fig. 8). The κ^2 complex $[(\eta^6\text{-toluene})\text{RuCl}(\kappa^2\text{-PTA-P}^i\text{Pr}_2)]\text{Cl}$ (**8**) was isolated as a red orange solid in an $\sim 3:5$ ratio diastereomeric ratio. Similar results are observed when **7** is dissolved in CD_2Cl_2 and monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy; the NMR resonances for **7** disappear and those for **8** grow in over a few days, Scheme 5. Mass analysis of the red-orange solid described above provides additional evidence for the generation of the κ^2 -PTA- P^iPr_2 complexes as well as the presence of dimers rising from PTA- P^iPr_2 bridging two Ru centers.[42] Coordination of PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ to $[\text{RuCl}_2(\eta^6\text{-toluene})]_2$ resulted in a series of multiplets by ^{31}P NMR spectroscopy which were not separable or isolable in our hands.[43]

Fig. 8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[(\eta^6\text{-toluene})\text{RuCl}(\kappa^2\text{-PTA-P}^i\text{Pr}_2)]\text{Cl}$ (**8**) in CD_2Cl_2 .

Scheme 5.

Complexes **7** and **8** are soluble in methanol, water, acetonitrile, dichloromethane, and chloroform and insoluble in hexane, benzene and diethyl ether. Yellow plates of **8** suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2 solution. A thermal ellipsoid representation of **8** is depicted in Figure 9 with selected bond lengths and angles. A piano stool geometry around ruthenium was observed with a chelating PTA- P^iPr_2 ligand, one chloride, and one η^6 -toluene. The Ru_1 -arene_{centroid} distance for **8** is 2.228(3) Å. The Ru-P bond length are 2.3024(10) Å and 2.3700(10) Å with the Ru-PTA bond length the shorter of the two. These distances are

comparable to the Ru-P lengths of 2.316(2) and 2.309(2) Å observed for $[(\eta^6\text{-cymene})\text{-RuCl}(\text{dppm})]\text{BF}_4$. [44] The distance between $\text{Ru}_1\text{-Cl}$ is 2.4030(8) Å, which is comparable to the Ru-Cl bond length of 2.397(2) Å in $[(\eta^6\text{-cymene})\text{-RuCl}(\text{dppm})]\text{BF}_4$ and other PTA derivative ruthenium arene complexes. The observed angles of **8** were 71.69(3)° for $\text{P}_1\text{-Ru}_1\text{-P}_2$ and 96.02(13)° for $\text{P}(1)\text{-C}(1)\text{-P}(2)$. These angles were slightly larger than angles of 71.29(6)° for P-Ru-P and 95.3(3)° for P-C-P in $[(\eta^6\text{-cymene})\text{-RuCl}(\text{dppm})]\text{BF}_4$. [44]

Fig. 9. Thermal ellipsoid representation (50 % probability) of $[(\eta^6\text{-toluene})\text{RuCl}(\kappa^2\text{-PTA-P}^i\text{Pr}_2)]\text{Cl}$ (**8**) with the atomic numbering scheme. Hydrogen atoms have been omitted except those attached to the stereocenter C_1 . Only the $\text{R}_{\text{C}_1}\text{R}_{\text{Ru}}$ enantiomer is shown; however, both $\text{R}_{\text{C}_1}\text{R}_{\text{Ru}}$ and $\text{S}_{\text{C}_1}\text{S}_{\text{Ru}}$ are present in the unit cell. Selected Bond lengths (Å) and angles (deg): $\text{Ru}_1\text{-P}_1 = 2.3024(10)$, $\text{Ru}_1\text{-P}_2 = 2.3700(10)$, $\text{Ru-Cl}_1 = 2.4029(10)$, $\text{Ru}_1\text{-arene}_{\text{centroid}} = 2.228(3)$, $\text{P}_1\cdots\text{P}_2 = 2.7317(5)$, $\text{P}_1\text{-Ru}_1\text{-P}_2 = 71.70(3)$, $\text{P}_1\text{-Ru}_1\text{-Cl}_1 = 88.95(3)$, $\text{P}_2\text{-Ru}_1\text{-Cl}_1 = 90.95(4)$, $\text{P}_1\text{-C}_1\text{-P}_2 = 96.06(18)$.

Catalytic Hydration of Nitriles.

In situ generated catalysts incorporating PTA- P^iPr_2 (**1**) or PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ (**2**) and either $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ or $[(\eta^6\text{-toluene})\text{RuCl}(\mu\text{-Cl})_2]$ were studied as aqueous phase nitrile hydration catalysts. The ruthenium starting material was combined with 1 or 2 equivalents of the PTA- PR_2 ligand. Due to the air sensitivity of the free ligands, these hydrations were performed under nitrogen in degassed water. The catalyst (5 mol%), nitrile, and water were combined in a culture tube at 100 °C and the reaction was monitored at 7 and 24 h by GC/MS (Table 5). *In situ* generated catalysts of **1** with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were at least two times less efficient than **1** with $[\text{RuCl}_2(\eta^6\text{-toluene})]_2$ at seven hours (Table 5 entries 3, 4, 6, and 7. This trend was not observed for *in situ* catalysts incorporating PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ (**2**) where high yields were observed with both $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $[\text{RuCl}_2(\eta^6\text{-toluene})]_2$ (Entry 5 and 8). Increased [PTA- P^iPr_2] (**1**)

resulted in higher conversions at seven hours; however, the catalysts incorporating **2** remained more efficient. $[(\eta^6\text{-toluene})\text{RuCl}_2(\kappa^1\text{-PTA-P}^i\text{Pr}_2)]$ **7** had comparable activity to the *in situ* catalyst incorporating two equiv. of **1** with $[\text{RuCl}_2(\eta^6\text{-toluene})]_2$ (Table 5, entries 7 and 10). With conversions of 94–98% in 7 hours, ligand **2** appears to be an excellent ligand for nitrile hydration; unfortunately, attempts to isolate a ruthenium arene complex with PTA- $\text{P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ have been unsuccessful.

Table 5. Catalytic hydration of benzonitrile in water.^a

Entry	Catalyst	Conv. ^b (%)
1	$[\text{RuCl}_2(\eta^6\text{-toluene})]_2$	0
2	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	54
3	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + 1 \text{ eq } \mathbf{1}^c$	23(79)
4	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + 2 \text{ eq } \mathbf{1}^c$	47(99)
5	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + 1 \text{ eq } \mathbf{2}^c$	94(99)
6	$[(\eta^6\text{-toluene})\text{RuCl}(\mu\text{-Cl})]_2 + 1 \text{ eq } \mathbf{1}^c$	80(99)
7	$[(\eta^6\text{-toluene})\text{RuCl}(\mu\text{-Cl})]_2 + 2 \text{ eq } \mathbf{1}^c$	94(99)
8	$[(\eta^6\text{-toluene})\text{RuCl}(\mu\text{-Cl})]_2 + 1 \text{ eq } \mathbf{2}^c$	98(99)
9	$[(\eta^6\text{-toluene})\text{RuCl}(\kappa^2\text{-PTA-P}^i\text{Pr}_2)]\text{Cl}$ (8)	85(99)
10	$(\eta^6\text{-toluene})\text{RuCl}_2(\kappa^1\text{-PTA-P}^i\text{Pr}_2)$ (7)	93(99)

^aConditions: benzonitrile (1 mmol), catalyst (5 mol %), H_2O (3 mL), 100 °C, in air. ^bGC calculated conversions to amide after 7 h (24 h yield in parentheses).

^cPrepared in a dry box with degassed water.

Complex **7** was one of the most active catalysts tested along with the *in situ* generated complexes derived from ligands **1** and **2** (Table 5, entries 7 and 8). Interestingly $[(\eta^6\text{-toluene})\text{RuCl}_2(\kappa^1\text{-PTA-P}^i\text{Pr}_2)]$ (**7**) was slightly more active towards nitrile hydration than $[(\eta^6\text{-toluene})\text{RuCl}(\kappa^2\text{-PTA-P}^i\text{Pr}_2)]\text{Cl}$ (**8**) see entries 9 and 10 in Table 5 as well as Table 1-S in supporting information.[41] The higher catalytic activity of **7** is attributed to the presence of a readily accessible coordination site through dissociation of a Cl^- . This hypothesis is backed by the rapid formation of bidentate and possibly bridging coordination modes for $[(\eta^6\text{-toluene})\text{RuCl}_2(\kappa^1\text{-PTA-P}^i\text{Pr}_2)]$ (**7**) in solution (*vide supra*). A mass spectrum of **7** obtained during

hydration of benzonitrile contained a m/z peak of 624.77 consistent with $[(\eta^6\text{-toluene})\text{RuCl}(\text{PTA-P}^i\text{Pr}_2)(\text{NCPh})(\text{H}_2\text{O})]^+$. The coordination/interaction of the nitrile and water supports the proposed mechanistic pathway for ruthenium catalyzed nitrile hydrations involving coordination of nitrile and close association of water.[45]

The catalytic activity of **7** was further investigated via a series of nitriles, Scheme 4 and Table 6. All nitriles were converted to amides with 43–99% conversions as determined by GC after 24 hours (36 – 98 % after 7 h). Upon completion of the hydration reaction, dark brown or black oily precipitates were observable in the aqueous solution. Subsequent workup included solvent evaporation of the reaction mixture and purification by column chromatography on silica gel using ethyl acetate as eluent to isolate the pure amides (18–92% isolated yields).

Substituted benzonitriles were successfully converted to the corresponding amides with comparable activity for the parent benzonitrile. The presence of an electron withdrawing group (Table 6 entry 4) resulted in a slightly more efficient conversion to the amide relative to a nitrile with an electron donating group (Table 6 entry 3). This result coincides with the predicted effect electron-withdrawing groups have on activating the nitrile carbon towards nucleophilic attack by water. [12,46] This effect is not absolute, as exceptions are reported. [47,48]

Limitations in the efficacy of $[(\eta^6\text{-toluene})\text{RuCl}_2(\kappa^1\text{-PTA-P}^i\text{Pr}_2)]$ (**7**) were found in the pyridyl and aliphatic nitriles (entries 4–5). Decreased efficiency of heteroaromatics is reported due to possible coordination of the heteroatom (nitrogen) to the metal.[49] The conversion (37%) of heptyl cyanide to the corresponding octyl amide after 7 hours was comparable to other ruthenium arene catalysts with PTA derivatives.[27] The hydration of acrylonitrile was initially difficult to ascertain, a result of both acrylonitrile and acrylamide exhibiting poor solubility in CH_2Cl_2 . Upon switching the extraction solvent to diethyl ether less than 1% of acrylonitrile was observed at 7 and 24 hours. The reaction was observed to only produce acrylamide and prolonged exposure (24 hours) to the catalytic conditions did not lead to the observance of polymerized products in the GC/MS spectrum. The reaction is considered complete within 7 hours, and the product was isolated with 18% yield (entry 7).

Overall these catalysts are comparable to other $[(\eta^6\text{-arene})\text{RuCl}_2(\text{PR}_3)]$ complexes which have exhibited average to excellent conversion in 1–20 h at 100 °C with a range of PR_3 ligands.[2,4,6,7,10,12,13,15] Unlike

the present example, in which the reaction is carried out in the presence of air, many of the previously reported catalytic reactions were carried out under nitrogen.

Scheme 4.

Table 6. Catalytic hydration of various nitriles by $[(\eta^6\text{-toluene})\text{RuCl}_2(\text{PTA-P}^i\text{Pr}_2)]$ (**7**).

Entry	Substrate	% Conv. ^b	% Yield ^c
1		93(99)	80
2		95(99)	76
3		88(99)	74
4		98(99)	92
5		36(46)	35
6		37(74)	56
7		99	18

^a Conditions: nitrile (1 mmol), catalyst (5 mol%), H_2O (3 mL), 100 °C, in air. ^b GC calculated conversions to amide after 7 h (24 h yield in parentheses). ^c Isolated by column chromatography.

Conclusion

PTA diphosphine derivatives **1** and **2** were synthesized in good yield and found to be somewhat water soluble. We observed evidence for κ^1 , κ^2 , and bridg-

ing coordination modes for the ligands. Chloride dissociation from $[(\eta^6\text{-toluene})\text{RuCl}_2(\kappa^1\text{-PTA-P}^i\text{Pr}_2)]$ (**7**) resulted in formation of a diastomeric mixture of the chelating isomer $[(\eta^6\text{-toluene})\text{RuCl}(\kappa^2\text{-PTA-P}^i\text{Pr}_2)]\text{Cl}$. $[(\eta^6\text{-toluene})\text{RuCl}_2(\kappa^1\text{-PTA-P}^i\text{Pr}_2)]$ (**7**) was found to be a highly active aqueous phase nitrile hydration catalyst with tolerance toward air and a variety of functional groups, some decomposition was observed during hydration. The elevated activity of **7** versus the $[(\eta^6\text{-toluene})\text{RuCl}(\kappa^2\text{-PTA-P}^i\text{Pr}_2)]\text{Cl}$ (**8**) was attributed to the ability of **7** to more easily dissociate a chloride ligand allowing for nitrile coordination. The presumably less favorable dissociation of a chloride from the cationic **8** likely slows down catalysis. *In situ* generated catalysts based on addition of $\text{PTA-P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ or $\text{PTA-P}^i\text{Pr}_2$ to RuCl_3 or $[(\eta^6\text{-toluene})\text{RuCl}(\mu\text{-Cl})_2]$ revealed that $\text{PTA-P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ is a highly active ligand for nitrile hydration. We are continue to attempt the isolation of $\text{PTA-P}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$ complexes.

Experimental

Materials and Methods: Unless otherwise noted, all manipulations were performed on a double-manifold Schlenk line under nitrogen or in a nitrogen-filled glovebox. Tetrahydrofuran (THF) and hexanes were freshly distilled under nitrogen from sodium/benzophenone. *n*-Butyllithium, *n*,*n*-diisopropylethylenediamine, trichlorophosphine, diisopropylchlorophosphine, benzonitrile, *p*-tolunitrile, *p*-methoxybenzonitrile, *p*-nitrobenzonitrile, 2-cyanopyridine, heptyl cyanide, acrylonitrile, and ruthenium trichloride trihydrate were purchased from commercial sources and used as received. NMR solvents were purchased from Cambridge Isotopes and used as received. Tetraakis(hydroxymethyl)phosphonium chloride was obtained from Cytec and used without further purification. 1,3,5-Triaza-7-phosphaadamantane (PTA),^[50] PTA-Li ,^[18] $\text{CIP}(\text{N}^i\text{Pr})_2(\text{CH}_2)_2$,^[51,41] $[\text{W}(\text{CO})_4(\text{Pip})_2]$,^[52] and $[(\eta^6\text{-toluene})\text{RuCl}_2]$ ^[53] were prepared as reported in literature. NMR spectra were recorded on a Varian NMR system 400 spectrometer. ^1H and ^{13}C NMR spectra were referenced to residual solvent relative to TMS. Phosphorus chemical shifts are relative to an external standard of 85% H_3PO_4 in D_2O . IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer in a 0.1 mm CaF_2 liquid cell. Electrospray ionization mass spectra (ESI-MS) were recorded on a Agilent GG230AA time-of-flight mass spectrometer with calibration performed with Agilent solution G1969-85000 with purine at 121 *m/z* and HP-0921 at 922 *m/z* prior to analysis (positive ion mode) and a Waters Micromass 20 ESI mass

spectrometer (positive ion mode). GC/MS analyses were obtained using a Varian CP 3800 GC (DB5 column) equipped with a Saturn 2200 MS and a CP 8410 auto-injector or an Agilent 7890A GC equipped with an Agilent 5975C inert MSD with triple axis detector and an Agilent 7693 autosampler. X-ray crystallographic data were collected at 100(±1) K on a Bruker APEX CCD diffractometer with Mo K α radiation (λ = 0.71073 Å) and a detector-to-crystal distance of 4.94 cm. Data collection was optimized utilizing the APEX 2 software with 0.5° scan width. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed using SAINTPLUS and corrected for absorption using SADABS. The structures were solved by direct methods and refined using SHELXTL, version 6.10.⁵⁴ All non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in calculated positions. Crystallographic data and data collection parameters are in Table 7. Nitrile hydrations were carried out in 16 mm x 125 mm culture tubes with a capacity of ca. 16 mL; Kimax (45066-16125) or Pyrex® (No. 99447).

Synthesis of 6-(diisopropylphosphino)-1,3,5-triaza-7-phosphaadamantane, PTA-PⁱPr₂ (**1**): Chlorodiisopropylphosphine (0.94 g, 5.97 mmol) was dissolved in THF and added to a THF suspension of PTA-Li (1.137 g, 6.97 mmol) at 0°C. The reaction was allowed to warm to room temperature, stirred overnight, and THF was removed under vacuum. The resulting residue was extracted under nitrogen with 20 mL hexanes and 10 mL degassed water at 0°C. The organic layer and subsequent hexanes washes (3 x 10 mL) were transferred to a dry flask and the volatiles removed under vacuum. The product was obtained in 73 % yield (1.19 g) as a flaky white air sensitive solid. ¹H NMR (400 MHz, CD₂Cl₂): δ 5.33-5.20 (m, 1H, NCH₂N), 4.65, 4.56 (AB quartet, J = 12 Hz, 4H, NCH₂N); 4.36-4.26 (m, 1H, P-CH-P; 1H, NCH₂N), 4.26-4.16 (m, 1H, PCH₂N), 4.16-3.99 (m, 2H, PCH₂N), 3.89 (ddt, J = 2 and 13 Hz, 1H, PCH₂N), 1.98-1.82 (m, 2H, PCHC), 1.25-1.05 (m, 12H, CCH₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 76.0 (s, NCH₂N), 74.2 (t, J_{PC} = 2 Hz, NCH₂N), 68.1 (dd, J_{PC} = 11 and 2 Hz, NCH₂N), 57.3 (dd, J_{PC} = 7 and 30 Hz, PCHP), 51.8 (d, J_{PC} = 22 Hz, PCH₂N), 47.6 (d, J_{PC} = 22 Hz, PCH₂N), 23.3 (dd, J_{PC} = 13 and 20 Hz, PCHC), 21.9 (dd, J_{PC} = 6 and 13 Hz, PCHC), 21.1 (dd, J_{PC} = 8 and 16 Hz, CCH₃), 20.7 (d, J_{PC} = 13 Hz, CCH₃), 19.7 (dd, J_{PC} = 4 and 8 Hz, CCH₃), 19.1 (d, J_{PC} = 10 Hz, C-CH₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ -3.31 (d, J_{PP} = 50 Hz, PⁱPr), -98.28 (d, J_{PP} = 50 Hz, PTA). HRMS (ESI, H₂O) m/z calc. C₁₂H₂₆N₃P₂: [M+H]⁺ 273.1524; found 273.1533. X-ray-quality crystals were obtained by slow evaporation of

a hexanes solution of **2**, resulting in the formation of clear colorless plates over the course of 4 days.

Synthesis of 6-(1,3-bis(2,6-diisopropyl)-1,3,2-diazaphosphino)-1,3,5-triaza-7-phosphaadamantane, PTA-P(NⁱPr)₂(CH₂)₂ (**2**): A THF solution (10 mL) of 2-chloro-1,3-diisopropyl-[1,3,2]diazaphospholidine (17.03 mmol, 1.88 g) was added to a THF solution (40 mL) of PTA-Li (1.698 g, 9.48 mmol) at 0°C. The reaction was allowed to warm to room temperature and stirred for an additional 1 hour after which time the solvent was removed under vacuum. The resulting residue was dissolved in hexanes (10 mL) and 0 °C degassed water (10 mL). The organic layer and subsequent hexanes washes (3 x 10 mL) were transferred to a dry flask and the volatiles removed under vacuum. The resulting yellow solid (1.68 g, 56 % yield) was used without further purification. ¹H NMR (400 MHz, CDCl₃): 5.11, 4.38 (AB quartet, J = 13 Hz, 2H, NCH₂N); 4.62, 4.38 (AB quartet, J = 13 Hz, 2H, NCH₂N); 4.54-4.44 (m, 2H, NCH₂N), 4.41-4.36 (m, 2H, NCH₂N), 4.21-4.13 (m, 1H, PCHP), 4.09-4.00 (m, 1H, PCH₂N), 3.94-3.87 (m, 1H, PCH₂N), 3.87-3.83 (m, 1H, PCH₂N), 3.75 (apparent doublet, J = 6 Hz, 1H, PCH₂N), 3.32-3.24 (m, 1H, NCHC), 3.24-3.01 (m, 4H, NCH₂CH₂N), 2.95-2.90 (m, 1H, NCHC), 1.14-1.07 (m, 12H, CCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 76.4 (dd, J_{PC} = 5 and 2 Hz, NCH₂N), 74.0 (t, J_{PC} = 3 Hz, NCH₂N), 68.9 (dd, J_{PC} = 10 and 3 Hz, NCH₂N), 63.9 (dd, J_{PC} = 35 and 33 Hz, PCHP), 52.5 (dd, J_{PC} = 23 and 2 Hz, PCH₂N), 52.2 (d, J_{PC} = 27 Hz, NCHC), 50.4 (d, J_{PC} = 18 Hz, NCHC), 49.0 (d, J_{PC} = 9 Hz, NCH₂CH₂N), 48.3 (dd, J = 22 and 1 Hz, PCH₂N), 47.8 (dd, J_{PC} = 6 and 3 Hz, NCH₂CH₂N), 23.4 (d, J_{PC} = 9 Hz, CCH₃), 22.8 (dd, J_{PC} = 13 and 2 Hz, CCH₃), 22.6 (d, J_{PC} = 10 Hz, CCH₃), 21.7 (dd, J_{PC} = 5 and 1 Hz, CCH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 100.36 (d, J_{PP} = 38 Hz, PN₂), -100.18 (d, J_{PP} = 38 Hz, PTA). HRMS (ESI, H₂O) m/z calc. C₁₄H₃₀N₅P₂: [M+H]⁺ 329.1898; found 329.1914. X-ray-quality crystals were obtained by slow evaporation of a hexanes solution, resulting in the formation of clear colorless plates over the course of 4 days.

Synthesis of 6-(diisopropylphosphino)-1,3,5-triaza-7-phosphaadamantane dioxide, O=PTA-(O)PⁱPr₂ (**3**): PTA-PⁱPr₂ (**1**) (0.10 g, 0.366 mmol) was dissolved in CH₂Cl₂ followed by the addition of three drops of 30 % H₂O₂. The reaction was immediately opened to air and the solvent evaporated with a draft of nitrogen. The resulting colorless solid (0.98 g, 88 % yield) was characterized without further purification. ¹H NMR (400 MHz, CDCl₃): δ 4.74-4.61 (m, 1H, PCH₂N), 4.45-4.31 (m, 2H, NCH₂N), 4.23-4.06 (m, 3H, PCHP, NCH₂N), 4.14, 5.24 (AB quartet, J = 14 Hz, 2H,

NCH₂N); 3.93–3.80 (m, 2H, PCH₂N), 3.74 (dd, $J = 15$ and 8 Hz, 1H, PCH₂N), 2.71–2.81 (m, 1H, P-CH-C), 2.35–2.44 (m, 1H, P-CH-C), 1.24–1.36 (m, 12H, C-CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 74.4 (dd, $J_{PC} = 1$ and 8 Hz, NCH₂N), 71.4 (d, $^3J_{PC} = 10$ Hz, NCH₂N), 67.7 (d, $^3J_{PC} = 10$ Hz, NCH₂N), 59.6 (dd, $J_{PC} = 55$ and 37 Hz, PCHP), 56.4 (dd, $J_{PC} = 51$ and 5 Hz, PCH₂N), 53.0 (d, $J_{PC} = 52$ Hz, PCH₂N), 27.9 (dd, $J = 59$ and 9 Hz, PCHC), 25.6 (dd, $J_{PC} = 61$ and 3 Hz, PCHC), 16.2 (dd, $J_{PC} = 18$ and 2 Hz, CCH₃), 15.4 (d, $^2J_{PC} = 7$ Hz, CCH₃), 15.04 (s, CCH₃), 15.01 (d, $^2J_{PC} = 1$ Hz, CCH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 57.04 (d, $^2J_{PP} = 5$ Hz, O=PⁱPr₂), -8.85 (d, $^2J_{PP} = 5$ Hz, O=PTA). IR ν_{PO} (CH₂Cl₂, cm⁻¹): 1185.5 (m), 1174.0 (m). X-ray-quality crystals were obtained by slow evaporation of a 1:5 CH₂Cl₂:hexanes solution resulting in the formation of clear colorless blocks over the course of 2 days.

Synthesis of 6-(CH₂)₂(NⁱPr)₂P-1,3,5-triaza-7-phosphaadamantane dioxide, O=PTA-OP(NⁱPr)₂(CH₂)₂ (**4**): PTA-P(NⁱPr)₂(CH₂)₂ (**2**) (0.100 mg, 0.304 mmol) was dissolved in CH₂Cl₂ followed by the addition of three drops of 30 % H₂O₂. The reaction was immediately opened to air and the solvent evaporated with a draft of nitrogen. The resulting colorless solid (0.987 g, 90 % yield) was characterized without further purification. ¹H NMR (400 MHz, CDCl₃): 4.64–4.50 (m, 1H, NCH₂N), 4.39 (dd, $J = 24$ and 13 Hz, 2H, NCH₂N), 4.11 (ddt, $J = 19$, 13, and 4 Hz, 3H, NCH₂N, NCHC), 4.09, 5.24 (AB quartet, $J = 14$ Hz, 2H, NCH₂N), 3.91 (dd, $J = 18$ and 14 Hz, 1H, PCHP), 3.85–3.75 (m, 2H, PCH₂N), 3.64 (td, $J = 13$ and 7 Hz, 2H, NCHC, PCH₂N), 3.32 – 3.19 (m, 2H, NCH₂C), 3.11–2.97 (m, 2H, NCH₂C), 1.19 (dd, $J = 7$ and 3 Hz, 6H, CCH₃), 1.12 (dd, $J = 15$ and 7 Hz, 6H, CCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 75.4 (dd, $J_{PC} = 12$ and 7 Hz, NCH₂N), 72.7 (d, $^3J_{PC} = 9$ Hz, NCH₂N), 69.1 (d, $J_{PC} = 38$ Hz, P-C-P), 67.9 (dd, $J_{PC} = 24$ and 13 Hz, NCH₂N), 57.5 (d, $J_{PC} = 7$ Hz, NCH₂N), 57.0 (d, $^2J_{PC} = 7$ Hz, PCH₂N), 53.4 (d, $J_{PC} = 53$ Hz, PCH₂N), 45.1 (d, $^2J_{PC} = 5$ Hz, NCHC), 44.3 (d, $^2J_{PC} = 5$ Hz, NCHC), 37.7 (dd, $J = 12$ and 3 Hz, NCH₂CH₂N), 21.6 (d, $^3J_{PC} = 7$ Hz, CCH₃), 21.5 (s, CCH₃), 21.2 (d, $^3J_{PC} = 4$ Hz, CCH₃), 21.0 (s, CCH₃). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 24.89 (bs, PR₂), -10.53 (bs, PTA). IR ν_{PO} (CH₂Cl₂, cm⁻¹): 1185.6(m) and 1169.8(m). X-ray quality crystals were obtained by slow evaporation of a 1:1 solution of CH₂Cl₂:hexanes resulting in the formation of clear and colorless plates over the course of 4 days.

Synthesis of [W(CO)₄(PTA-PⁱPr₂)] (**5**): PTA-PⁱPr₂ (**1**) (0.137 g, 0.5 mmol) was added to a degassed dichloromethane solution of *cis*-[W(CO)₄(NHC₅H₁₀)₂] (232 mg, 0.5 mmol). The solution was refluxed for two hours and the solvent was removed under va-

cuum. The resulting brown-yellow solid was dissolved in CH₂Cl₂ and filtered through a plug of silica gel. Methanol was added to the CH₂Cl₂ and the solution cooled to 0 °C resulting in the precipitation of **5** as a yellow crystalline solid (0.090 g, 32 % yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 4.95 (t, $^2J_{PH} = 12$ Hz, 1H, PCHP), 4.63 (d, $J = 13$ Hz, 6H, NCH₂N), 4.56–4.42 (m, 1H, PCH₂N), 4.42–4.31 (m, 1H, PCH₂N), 4.26 (ddd, $J = 15$, 10, and 5 Hz, 2H, PCH₂N); 4.09, 3.96 (AB quartet, $J = 15$ Hz, 2H, PCH₂N); 2.55 (dtd, $J = 14$, 7, and 3 Hz, 1H, PCHC), 2.40 (qd, $J = 14$ and 7 Hz, 1H, PCHC), 1.44–1.32 (m, 6H, CCH₃), 1.28–1.15 (m, 6H, CCH₃). ¹³C{¹H} NMR (100 MHz, CD₂Cl₂): δ 209.3 (dd, $^2J_{PC} = 24$ and 7 Hz, *trans*-CO), 208.8 (dd, $^2J_{PC} = 25$ and 7 Hz, *trans*-CO), 204.0 (t, $^2J_{PC} = 8$ Hz, *cis*-CO), 201.6 (t, $^2J_{PC} = 6$ Hz, *cis*-CO), 77.0 (t, $^3J_{PC} = 5$ Hz, NCH₂N) 74.9 (dd, $J_{PC} = 22$, and 10 Hz, PCHP), 73.4 (d, $^3J_{PC} = 6$ Hz, NCH₂N), 69.8 (d, $^3J_{PC} = 8$ Hz, NCH₂N), 55.9 (d, $J_{PC} = 15$ Hz, PCH₂N), 54.9 (d, $J_{PC} = 9$ Hz, PCH₂N), 29.8 (d, $J_{PC} = 14$ Hz, PCHC), 24.2 (dd, $J_{PC} = 13$ and 7 Hz, PCHC), 22.7 (d, $^2J_{PC} = 8$ Hz, CCH₃), 21.0 (d, $^2J_{PC} = 7$ Hz, CCH₃), 20.1 (s, CCH₃), 19.5 (d, $^2J_{PC} = 7$ Hz, CCH₃). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 52.7 (d, $^2J_{PP} = 19$ Hz, $J_{PW} = 190$ Hz, PⁱPr₂), -91.7 (d, $^2J_{PP} = 19$ Hz, $J_{PW} = 188$ Hz, PTA). IR ν_{CO} (CH₂Cl₂, cm⁻¹): 2012 (m), 1906 (sh), 1891 (vs), 1876 (sh). HRMS (ESI, CH₃CN) m/z calc. for C₁₆H₂₆N₃O₄P₂W: [M+H]⁺ 565.0787; found 565.0800. Crystals suitable for X-ray diffraction were obtained by slow evaporation of dichloromethane solution, resulting in light yellow blocks after a few days.

Synthesis of [W(CO)₄(PTA-P(NⁱPr)₂(CH₂)₂)] (**6**): PTA-P(NⁱPr)₂(CH₂)₂ (**2**) (0.035 g, 0.106 mmol) and *cis*-[W(CO)₄(NHC₅H₁₀)₂] (0.050 g, 0.107 mmol) were dissolved in 10 mL degassed dichloromethane and stirred for two days at room temperature. The solvent was removed and the resulting yellow solid dissolved in 3 mL dichloromethane and filtered through celite. Addition of 80 mL hexanes and placement in a freezer for 3 hours resulted in a precipitate. Filtration and subsequent drying *in vacuo* resulted in an 89 % yield of **6** as a yellow solid (0.598 g). ¹H NMR (400 MHz, CDCl₃): δ 5.10, 4.38 (AB quartet, $J = 13$ Hz, 2H, NCH₂N); 4.67, 4.38 (AB quartet, $J = 13$ Hz, 2H, NCH₂N); 4.56–4.45 (m, 2H, NCH₂N), 4.42–4.33 (m, 3H, PCHP; PCH₂N), 4.14–4.01 (m, 3H, NCHC; NCHC; PCH₂N), 3.95 (apparent doublet, $J = 14$ Hz, 1H, PCH₂N), 3.50 (tdd, $J = 10$, 7, and 3 Hz, 1H, NCH₂CH₂N), 3.20–2.97 (m, 3H, NCH₂CH₂N), 1.30 (d, $J_{HH} = 7$ Hz, 3H, CCH₃), 1.25 (d, $J_{HH} = 7$ Hz, 3H, CCH₃), 1.21 (d, $J_{HH} = 7$ Hz, 3H, CCH₃), 1.09 (d, $J_{HH} = 7$ Hz, 3H, CCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 208.9–208.4 (m, *trans*-CO), 208.3–207.8 (m, *trans*-CO), 204.8 (t, $^2J_{PC} = 7$ Hz, *cis*-CO), 203.0 (t, $^2J_{PC} = 6$ Hz,

cis-CO), 87.9 (dd, $^1J_{PC} = 19$ and 7 Hz, PCHP), 76.1 (t, $^3J_{PC} = 6$ Hz, NCH₂N), 73.2 (d, $^3J_{PC} = 7$ Hz, NCH₂N), 68.0 (d, $^3J_{PC} = 7$ Hz, NCH₂N), 55.2 (apparent singlet, PCH₂N), 55.1–55.0 (m, PCH₂N), 52.1 (d, $^2J_{PC} = 12$ Hz, NCHN), 46.5 (d, $^2J_{PC} = 14$ Hz, NCHN), 43.2 (d, $^2J_{PC} = 4$ Hz, NCH₂CH₂N), 42.2 (s, NCH₂CH₂N), 22.6 (d, $^3J_{PC} = 12$ Hz, CCH₃), 21.9 (d, $^3J_{PC} = 2$ Hz, CCH₃), 21.2 (d, $^3J_{PC} = 5$ Hz, CCH₃), 19.6 (d, $^3J_{PC} = 2$ Hz, CCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD₂Cl₂): δ 121.61 (d, $^2J_{PP} = 31$ Hz, $^1J_{PW} = 236$ Hz, PN₂), -100.58 (d, $^2J_{PP} = 31$ Hz, $^1J_{PW} = 199$ Hz, PTA). IR ν_{CO} (CH₂Cl₂, cm⁻¹): 2014 (m), 1915 (sh), 1894 (vs), 1871 (sh). HRMS (ESI, 1:1 CH₂Cl₂:MeOH) m/z calc. for C₁₈H₃₀N₅O₄P₂W: [M+H]⁺ 621.1162; found 621.1152.

Synthesis of [(η^6 -toluene)RuCl₂(κ^1 -PTA-PⁱPr₂)] (7): [(η^6 -C₆H₅CH₃)RuCl(μ -Cl)]₂ (0.106 g, 0.20 mmol) and PTA-PⁱPr₂ (1) (0.115 g, 0.42 mmol) were stirred in benzene (20 mL) overnight, during which time the product crashed out of solution. The reaction mixture was filtered and washed with hexane (3 $\times$ 10 mL). The solid was dried under reduced pressure to give an orange solid (0.967 g, 90% yield). ¹H NMR (400 MHz, CDCl₃) 5.56–5.45 (m, 2H, C₆H₅CH₃), 5.30 (d, $J_{\text{HH}} = 6$ Hz, 1H, C₆H₅CH₃), 5.26–5.21 (m, 1H, C₆H₅CH₃), 5.18 (t, $J = 5$ Hz, 1H, PCHP), 4.78 (d, $J_{\text{HH}} = 16$ Hz, 1H, C₆H₅CH₃), 4.69 (d, $J_{\text{HH}} = 5$ Hz, 1H, NCH₂N), 4.56–4.49 (m, 2H, NCH₂N), 4.48–4.40 (m, 2H, NCH₂N), 4.37–4.26 (m, 1H, NCH₂N; 2H, PCH₂N), 4.11 (dt, $J = 2$ and 15 Hz, 1H, PCH₂N), 3.88 (d, $J = 13$ Hz, 1H, PCH₂N), 2.21–2.04 (m, 2H, PCHC; 3H, C₆H₅CH₃), 1.27–1.07 (m, 12H, CCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD₂Cl₂): δ 11.17 (d, $^2J_{PP} = 65$ Hz, PⁱPr₂), -27.40 (d, $^2J_{PP} = 65$ Hz, PTA). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution of 7 over the course of a few days.

Synthesis of [(η^6 -toluene)RuCl(κ^2 -PTA-PⁱPr₂)]Cl (8): [(η^6 -C₆H₅CH₃)RuCl(μ -Cl)]₂ (0.106 g, 0.20 mmol) and PTA-PⁱPr₂ (1) (0.115 g, 0.42 mmol) were stirred in CH₂Cl₂ (20 mL) for 3 days, during which time the solvent evaporated. The residue was dissolved in a minimum of CH₂Cl₂, 60 mL diethyl ether was added, and the solution placed in a freezer for ~1 hour. The resulting precipitate was filtered and washed with diethyl ether (2 $\times$ 5 mL) providing 0.101 g (94 % yield) of an red-orange solid of 8 as a 3:5 mixture of diastereomers. ¹H NMR (400 MHz, CD₂Cl₂): δ 6.19–6.07 (m, 3H, C₆H₅CH₃), 5.86 (d, $J = 4$ Hz, 1H, C₆H₅CH₃), 5.69 (s, 1H, C₆H₅CH₃), 5.61 (d, $J = 4$ Hz, 1H, NCH₂N and PCH₂N), 5.38 (d, $J = 12$ Hz, 1H, PCHP), 4.76 (d, $J = 16$ Hz, 1H, PCH₂N), 4.64–4.31 (m, 8H, NCH₂N and PCH₂N), 2.33–2.16 (m, 2H, PCHC; 3H, C₆H₅CH₃); 1.65–1.37 (m, 12H, CCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR

(100 MHz, CD₂Cl₂): δ 93.0 (d, $^2J_{PC} = 8$ Hz, C₆H₅CH₃), 92.8 (d, $^2J_{PC} = 7$ Hz, C₆H₅CH₃), 92.5 (d, $^2J_{PC} = 8$ Hz, C₆H₅CH₃), 91.4 (s, C₆H₅CH₃), 79.7 (s, C₆H₅CH₃), 75.1 (t, $^3J_{PC} = 8$ Hz, NCH₂N), 73.8 (d, $^1J_{PC} = 8$ Hz, NCH₂N), 70.6 (d, $^3J_{PC} = 8$ Hz, NCH₂N), 70.0 (dd, $^1J_{PC} = 18$ and 26 Hz, PCHP), 55.2 (d, $^1J_{PC} = 8$ Hz, PCH₂N), 50.1 (d, $^1J_{PC} = 13$ Hz, PCH₂N), 21.7 (s, PCHC), 21.2 (t, $^1J_{PC} = 8$ Hz, PCHC), 20.6 (d, $^2J_{PC} = 8$ Hz, CCH₃), 20.2 (s, CCH₃), 19.7 (s, C₆H₅CH₃), 19.0 (s, CCH₃), 18.8 (s, CCH₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD₂Cl₂): δ 62.95 (d, $^2J_{PP} = 64$ Hz, PⁱPr₂), 51.30 (d, $^2J_{PP} = 65$ Hz, PⁱPr₂), -46.41 (d, $^2J_{PP} = 65$ Hz, PTA), -54.97 (d, $^2J_{PP} = 64$ Hz, PTA). HRMS (ESI, CH₃CN) m/z calc. for C₁₉H₃₃ClN₃P₂Ru: [M-Cl]⁺ 496.0914 and C₃₈H₆₆Cl₃N₆P₄Ru₂: [2M-Cl]⁺ 1027.1517; found 496.0914 and 1027.1501.

General procedure for catalytic nitrile hydration: A culture tube was charged with 1 mmol nitrile, 3 mL water, and 5 mol % ruthenium complex 7 or 8 sealed under air and heated to 100 °C. In the case of the *in situ* generated catalyst a culture tube containing RuCl₃·3H₂O (0.05 mmol) or [(η^6 -toluene)RuCl(μ -Cl)]₂ (0.05 mmol) was transferred to a dry box and 0.05 or 0.10 mmol phosphine was added along with 1.0 mmol nitrile and 3 mL degassed water. The culture tube was sealed, removed from the dry box, and stirred at 100 °C. Small aliquots (~50 μ L) were taken at 7 and 24 h, extracted with CH₂Cl₂ (3 $\times$ 2 mL) and the % conversion measured by gas chromatography. Isolated yields were obtained by evaporation of solvent followed by column chromatography on silica gel with ethyl acetate as eluent. GC/MS and ¹H NMR spectroscopic data of the product amides were compared to authentic samples.

AUTHOR INFORMATION

Corresponding Author

* To whom correspondence should be addressed. E-mail: Frost@unr.edu

ACKNOWLEDGMENT

The authors would like to thank Gene Wong and Jessica Vellucci for their initial work on this project. Funding

from the NSF CAREER program CHE-0645365 and NSF-REU program CHE-0552816 are gratefully acknowledged.

Table 2. Selected bond lengths (Å) and angles (deg) for **1**, **2**, and PTA-PPh₂.

	PTA-P ⁱ Pr ₂ (1)	PTA-P(N ⁱ Pr) ₂ (CH ₂) ₂ (2)	O=PTA- O=P ⁱ Pr ₂ (3)	O=PTA- O=P(N ⁱ Pr) ₂ (CH ₂) ₂ (4)	PTA-PPh ₂
P1-C1	1.867(2)	1.8729(12)	1.8292(14)	1.8374(11)	1.890(4)
P1-C2	1.847(3)	1.8717(13)	1.8165(15)	1.8176(12)	1.815(5)
P1-C3	1.850(3)	1.8690(14)	1.8155(14)	1.8240(12)	1.832(4)
P2-C1	1.895(2)	1.8917(12)	1.8396(13)	1.8392(11)	1.867(4)
N1-C1	1.489(3)	1.4905(15)	1.4997(17)	1.5032(14)	1.577(5)
N1-C4	1.466(3)	1.4723(15)	1.4784(19)	1.4761(15)	1.508(5)
N1-C5	1.464(3)	1.4783(16)	1.4741(19)	1.4825(14)	1.530(5)
N2-C6	1.470(3)	1.4703(17)	1.472(2)	1.4732(14)	1.477(5)
P1-C1-N1	110.45(15)	113.92(8)	108.34(9)	107.63(7)	116.1(2)
N1-C1-P2	110.88(16)	108.79(8)	112.47(9)	111.39(7)	109.8(2)
P1-C1-P2	113.70(13)	115.41(6)	113.85(7)	115.63(6)	108.79(18)

Table 4. IR ν_{CO} stretching frequencies and P-M-P angle for *cis*-[W(CO)₄L₂] complexes [L₂ = PTAPⁱPr₂ (1), PTA-P(NⁱPr)₂(CH₂)₂ (2), PTA-PPh₂, (PTA)₂, (PTA)(PPh₃), and dppm].

Complex	ν_{CO} , cm ⁻¹				P-M-P angle (deg)
	A ₁	A ₁	B ₁	B ₂	
[W(CO) ₄ (PTA-P ⁱ Pr ₂)] (5)	2012 (m)	1906 (sh)	1891 (vs)	1876 (sh)	67.83(4)
W(CO) ₄ (PTA-P(N ⁱ Pr) ₂ (CH ₂) ₂) (6)	2014 (m)	1915 (sh)	1894 (vs)	1871 (sh)	----
[W(CO) ₄ (PTA-PPh ₂)] ^a	2018 (m)	1916 (sh)	1899 (vs)	1881 (sh)	68.18(4)
[W(CO) ₄ (PTA) ₂] ^a	2018 (m)	1917 (sh)	1900 (vs)	1883 (sh)	100.66(5)
[W(CO) ₄ (PPh ₃)(PTA)] ^a	2017 (m)	1913 (sh)	1898 (vs)	1879 (sh)	100.60(4)
[W(CO) ₄ (dppm)] ^a	2018 (s)	1916 (sh)	1904 (vs)	1874 (s)	67.12(2)

^a see ref [18].

Table 7. Crystallographic Data for PTA-PⁱPr₂ (1), PTA-P(NⁱPr)₂(CH₂)₂ (2), O=PTA-O=PⁱPr₂ (3), O=PTA-O=P(NⁱPr)₂(CH₂)₂ (4), [W(CO)₄(PTA-PⁱPr₂)] (5), and [(η⁶-toluene)RuCl(κ²-PTA-PⁱPr₂)]Cl (8).

	1	2	3	4	5	8
Emp. formula	C ₁₂ H ₂₅ N ₃ P ₂ O _{0.5}	C ₁₄ H ₂₉ N ₃ P ₂	C ₁₂ H ₂₅ N ₃ O ₂ P ₂	C ₁₄ H ₂₉ N ₃ O ₂ P ₂	C ₁₆ H ₂₅ N ₃ O ₅ P ₂ W	C ₂₀ H ₃₅ Cl ₄ N ₃ P ₂ Ru
formula weight	281.29	329.36	305.29	361.36	585.18	622.32
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Rhombohedral	Monoclinic	Monoclinic	Monoclinic
space group	Pc	C2/c	R-3	C2/c	P2(1)/n	P2 ₁
<i>a</i> (Å)	5.94910(10)	19.8453(12)	27.2522(3)	36.9117(4)	10.3453(2)	15.0888(2)
<i>b</i> (Å)	18.0367(4)	6.2351(4)	27.2522(3)	6.01820(10)	9.9451(2)	11.2885(2)
<i>c</i> (Å)	7.2020(2)	27.9329(17)	10.93800(10)	18.1646(2)	20.3868(5)	15.5226(2)
α (deg)	90	90	90	90	90	90
β (deg)	109.8430(10)	102.564(3)	90	116.4390(10)	98.4730(10)	104.7120(10)
γ (deg)	90	90	120	90	90	90
volume (Å ³)	726.91(3)	3373.6(4)	7035.12(13)	3613.08(8)	2074.60(8)	2557.28(7)
<i>Z</i>	2	8	18	8	4	4
<i>D</i> _{calcd} (Mg/m ³)	1.285	1.297	1.297	1.329	1.874	1.616
abs coeff (mm ⁻¹)	0.289	0.260	0.281	0.257	5.754	1.170
cryst size (mm ³)	0.23×0.11×0.03	0.37×0.27×0.06	0.22×0.18×0.16	0.39×0.13×0.07	0.21×0.11×0.08	0.25×0.13×0.06
θ range (deg)	2.26 to 30.188	1.49 to 30.03	1.49 to 30.06	1.23 to 30.13	2.02 to 30.13	1.36 to 30.00
	-8 ≤ <i>h</i> ≤ 8	-27 ≤ <i>h</i> ≤ 27	-38 ≤ <i>h</i> ≤ 38	-51 ≤ <i>h</i> ≤ 52	-14 ≤ <i>h</i> ≤ 14	-19 ≤ <i>h</i> ≤ 21
index ranges	-25 ≤ <i>k</i> ≤ 25	-8 ≤ <i>k</i> ≤ 8	-37 ≤ <i>k</i> ≤ 38	-8 ≤ <i>k</i> ≤ 8	-14 ≤ <i>k</i> ≤ 11	-15 ≤ <i>k</i> ≤ 15
	-7 ≤ <i>l</i> ≤ 10	-39 ≤ <i>l</i> ≤ 39	-15 ≤ <i>l</i> ≤ 12	-24 ≤ <i>l</i> ≤ 25	-19 ≤ <i>l</i> ≤ 28	-21 ≤ <i>l</i> ≤ 21
reflns collected	12137	27445	24447	30225	36836	53104
indep reflns	3924	4929	4592	5339	6120	14756
	<i>R</i> _{int} = 0.0280	<i>R</i> _{int} = 0.0440	<i>R</i> _{int} = 0.0285	<i>R</i> _{int} = 0.0234	<i>R</i> _{int} = 0.0381	<i>R</i> _{int} = 0.0343
abs corr.	SADABS	SADABS	SADABS	SADABS	SADABS	SADABS
data/restr/para	3924 / 2 / 175	4929 / 0 / 190	4592 / 0 / 172	5339 / 0 / 208	6120 / 0 / 244	14756 / 1 / 542
GOF on <i>F</i> ²	1.043	1.046	1.040	1.097	1.050	1.039
final <i>R</i> indices	<i>R</i> ₁ = 0.0324	<i>R</i> ₁ = 0.0336	<i>R</i> ₁ = 0.0386	<i>R</i> ₁ = 0.0310	<i>R</i> ₁ = 0.0351	<i>R</i> ₁ = 0.0308
[<i>I</i> > 2σ(<i>I</i>)]	w <i>R</i> ₂ = 0.0747	w <i>R</i> ₂ = 0.0858	w <i>R</i> ₂ = 0.1001	w <i>R</i> ₂ = 0.0888	w <i>R</i> ₂ = 0.0851	w <i>R</i> ₂ = 0.0697
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0366	<i>R</i> ₁ = 0.0447	<i>R</i> ₁ = 0.0499	<i>R</i> ₁ = 0.0383	<i>R</i> ₁ = 0.0497	<i>R</i> ₁ = 0.0359
	w <i>R</i> ₂ = 0.0765	w <i>R</i> ₂ = 0.0937	w <i>R</i> ₂ = 0.1075	w <i>R</i> ₂ = 0.0993	w <i>R</i> ₂ = 0.0930	w <i>R</i> ₂ = 0.0727
CCDC	1043626	1043625	1043627	1043629	1043624	1043628

- 1 T. J. Ahmed, S.M.M. Knapp, D.R. Tyler, *Coord. Chem. Rev.* **255** (2011) 949-974.
- 2 R. Garcia-Alvarez, J. Francos, E. Tomas-Mendivil, P. Crochet, V. Cadierno, *J. Organomet. Chem.* **771** (2014) 93-104.
- 3 R. Garcia-Alvarez, P. Crochet, V. Cadierno, *Green Chem.* **15** (2013) 46-66.
- 4 S.M.M. Knapp, T.J. Sherbow, R.B. Yelle, L.N. Zakharov, J.J. Juliette, D.R. Tyler, *Organometallics* **32** (2013) 824-834.
- 5 S.M.M. Knapp, S.J. Sherbow, J.J. Juliette, D.R. Tyler, *Organometallics* **31** (2012) 2941 - 2944.
- 6 R. García-Álvarez, J. Díez, P. Crochet, V. Cadierno, *Organometallics* **29** (2010) 3955-3965.
- 7 A. Cavarzan, A. Scarso, G. Strukul, *Green Chem.* **12** (2010) 790-794.
- 8 S.M. Ashraf, I. Berger, A.A. Nazarov, C.G. Hartinger, M.P. Koroteev, E.E. Nifant'ev, B.K. Keppler, *Chem. Biodiversity* **5** (2008) 1640-1644.
- 9 S.M. Ashraf, W. Kandioller, M.-G. Mendoza-Ferri, A.A. Nazarov, C.G. Hartinger, B.K. Keppler, *Chem. Biodiversity* **5** (2008) 2060-2066.
- 10 W.-C. Lee, J.M. Sears, R.A. Enow, K. Eads, D.A. Krogstad, B.J. Frost, *Inorg. Chem.* **52** (2013) 1737 - 1746.
- 11 V. Cadierno, J. Díez, J. Francos, J. Gimeno, *Chem. Eur. J.* **16** (2010) 9808-9817.
- 12 S.E. García-Garrido, J. Francos, V. Cadierno, J.-M. Basset, V. Polshettiwar, *ChemSusChem.* **4** (2011) 104-111.
- 13 R. García-Álvarez, M. Zablocka, P. Crochet, C. Duhayon, J.-P. Majoral, V. Cadierno *Green. Chem.* **15** (2013) 2447 - 2456.
- 14 P. Crochet, V. Cadierno, *Dalton Trans.* **43** (2014) 12447-12462.
- 15 V. Cadierno, J. Francos, J. Gimeno, *Chem. Eur. J.* **14** (2008) 6601-6605.
- 16 W.-C. Lee, B.J. Frost, *Green Chem.* **12** (2012) 62 - 66.
- 17 E. Bolyog-Nagy, A. Udvardy, F. Joó, A. Katho, *Tet. Lett.* **55** (2014) 3615-3617.
- 18 G.W. Wong, J.L. Harkreader, C.A. Mebi, B.J. Frost, *Inorg. Chem.* **45** (2006) 6748 - 6755.
- 19 R. Huang, B.J. Frost, *Inorg. Chem.* **46** (2007) 10962 - 10964.
- 20 G.W. Wong, W.-C. Lee, B.J. Frost, *Inorg. Chem.* **48** (2008) 612 - 620.
- 21 a) V.I. Siele, *J. Heterocycl. Chem.* **14** (1977) 337-339; (b) E. Fluck, H. Weissgraeber, *J. Chem.-Ztg.* **101** (1977) 304.
- 22 B. Assmann, K. Angermaier, H. Schmidbaur, *J. Chem. Soc., Chem. Commun.* (1994) 941-942.
- 23 B. Assmann, K. Angermaier, M. Paul, J. Riede, H. Schmidbaur, *Chem. Ber.* **128** (1995) 891-900.
- 24 D.J. Darensbourg, J.C. Yarbrough, S.J. Lewis, *Organometallics* **22** (2003) 2050-2056.
- 25 D.J. Darensbourg, C.G. Ortiz, J.W. Kamplain, *Organometallics* **23** (2004) 1747-1754.
- 26 A. Mena-Cruz, P. Lorenzo-Luis, A. Romerosa, M. Saoud, M. Serrano-Ruiz, *Inorg. Chem.* **46** (2007) 6120-6128.
- 27 D.A. Krogstad, G.S. Ellis, A.K. Gunderson, A.J. Hammrich, J.W. Rudolf, J.A. Halfen, *Polyhedron* **26** (2007) 4093-4100.
- 28 M. Erlandsson, L. Gonsalvi, M. Peruzzini, *Inorg. Chem.* **47** (2008) 8-10.
- 29 D.A. Krogstad, A. Guerriero, A. Ienco, G. Manca, M. Peruzzini, G. Reginato, L. Gonsalvi, L. *Organometallics* **30** (2011) 6292-6302.
- 30 A. Guerriero, M. Erlandsson, A. Ienco, D.A. Krogstad, M. Peruzzini, G. Reginato, L. Gonsalvi, *Organometallics* **30** (2011) 1874-1884.
- 31 A.D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, *Coord. Chem. Rev.* **248** (2004) 955-993.
- 32 J. Bravo, S. Bolaño, L. Gonsalvi, M. Peruzzini, *Coord. Chem. Rev.* **254** (2010) 555-607.
- 33 A. Mena-Cruz, P. Lorenzo-Luis, A. Romerosa, M. Serrano-Ruiz, *Inorg. Chem.* **47** (2008) 2246 - 2248.
- 34 J. Navech, R. Kraemer, J.P. Majoral, *Tetrahedron Lett.* **21** (1980) 1449-1452.
- 35 M. Benhammou, R. Kraemer, H. Germa, J.P. Majoral, J. Navech, *J. Phosphorus Sulfur* **14** (1982) 105-119.
- 36 (a) D.J. Daigle, A.B. Pepperman Jr., G.J. Boudreaux, *Heterocycl. Chem.* **11** (1974) 1085-1086; (b) J.R. Delerno, R.J. Majeste, L.M. Trefonas, *J. Heterocycl. Chem.* **13** (1976) 757-760.
- 37 D.J. Daigle, A.B. Pepperman Jr., S.L. Vail, *J. Heterocycl. Chem.* **11** (1974) 407-408.
- 38 B.J. Frost, W.-C. Lee, K. Pal, T.H. Kim, D. VanDerveer, D. Rabinovich, *Polyhedron* **29** (2010) 2373-2380.
- 39 (a) K.H. Jogun, J.J. Stezowski, E. Fluck, J. Weidlein, *Phosphorus Sulfur* **4** (1978) 199-204. (b) R.E. Marsh, M. Kapon, S. Hu, F.H. Herbstein, *Acta Crystallogr., Sect. B* **B58** (2002) 62-77.
- 40 Complete bond lengths and angles are available in the supporting information.
- 41 See supporting information for additional details.
- 42 High resolution mass spectrometry of the red-orange solid contained two clusters of peaks at $m/z = 496.0914$ consistent with the κ^2 complex $[(\eta^6\text{-toluene})\text{RuCl}(\kappa^2\text{-PTA-P}^i\text{Pr}_2)]^+$ and $m/z = 1027.1501$ consistent with a bridging Ru dimer $[(\eta^6\text{-toluene})\text{RuCl}(\mu\text{-PTA-P}^i\text{Pr}_2)]_2\text{Cl}^+$ or $[(\eta^6\text{-toluene})\text{RuCl}(\mu\text{-PTA-P}^i\text{Pr}_2)\text{Ru}(\eta^6\text{-toluene})\text{Cl}(\kappa^1\text{-PTA-P}^i\text{Pr}_2)]\text{Cl}^+$.

-
- 43 The addition of two equivalents of PTA- $P(N^iPr)_2(CH_2)_2$ (**2**) to a CH_2Cl_2 solution of $[(\eta^6\text{-arene})RuCl(\mu\text{-Cl})]_2$ resulted in a brown solid containing multiple products. A $^{31}P\{^1H\}$ NMR spectrum revealed a number of doublets and triplets in benzene.
- 44 C. Daguenet, R. Scopelliti, P.J. Dyson, *Organometallics* **23** (2004) 4849–4857.
- 45 S.-L. Murahashi, H. Takaya, *Acc. Chem. Res.* **33** (2000) 225–233.
- 46 R. Ramón, N. Marion, S.P. Nolan, *Chem. Eur. J.* **15** (2009) 8695–8697.
- 47 K. Yamaguchi, M. Matsushita, N. Mizuno, *Angew. Chem. Int. Ed.* **43** (2004) 1576–1580.
- 48 A.Y. Kim, H.S. Bae, S. Park, S. Park, K.H. Park, *Catal. Lett.* **141** (2011) 685–690. (not for this manuscript—nanoparticle paper)
- 49 M. Muranaka, I. Hyodo, W. Okumura, T. Oshiki, *Catal. Today* **164** (2011) 552–555.
- 50 D.J. Daigle, *Inorg. Synth.* **32** (1998) 40–45.
- 51 (a) J. Krysiak, C. Lyon, A. Baceiredo, H. Gornitzka, M. Mikolajczyk, G. Bertrand, *Chem. Eur. J.* **10** (2004) 1982–1986.
(b) C. Stader, Dissertation, Universität Bayreuth, 1988.
- 52 D.J. Darensbourg, R.L. Kump *Inorg. Chem.* **17** (1978) 2680–2682.
- 53 M.A. Bennett, A.K. Smith, *J. Chem. Soc., Dalton Trans.* (1974) 233–241.
- 54 G.M. Sheldrick, *Acta Crystallogr., Sect. A* **64** (2008) 112–122.

Graphical Abstract for:

Water Soluble Diphosphine ligands based on 1,3,5-triaza-7-phosphaadamantane
(PTA-PR₂): synthesis, coordination chemistry, and ruthenium catalyzed nitrile
hydration

*Jeremiah M. Sears, Wei-Chih Lee, Brian J. Frost**

Two new 1,3,5-triaza-7-phosphaadamantane (PTA) derivatives PTA-PⁱPr₂ and PTA-P(NⁱPr)₂(CH₂)₂ were synthesized. Ruthenium arene complexes of these ligands were highly active catalysts for aqueous phase nitrile hydration. Reaction of PTA-PⁱPr₂ with [(η⁶-toluene)RuCl(μ-Cl)]₂ resulted in the formation of [(η⁶-toluene)RuCl₂(κ¹-PTA-PⁱPr₂)] which, over time, converted into the diastereomeric [(η⁶-toluene)RuCl(κ²-PTA-PⁱPr₂)](Cl).