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Intramolecular Hydrogen-Bonded Tertiary Phosphines as 1,3,5-Triaza-7-phosphaadamantane (PTA) Analogues

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New cationic trialkylphosphines $[P(CH_2NH_2R)\{CH_2N(R)CH_2N(R)CH_2\}]^+$ (R = $C_6H_5CH_2$, **a**; 4-$FC_6H_4CH_2$, **b**), as their Cl^- (**1a**, **1b**), SbF_6^- (**2a**, **2b**), and PF_6^- (**3a**, **3b**) salts, are described. The phosphine framework is conformationally locked, in the solid state, through pairs of intramolecular N−H···N hydrogen bonds which are maintained in the Ru^{II} and Rh^{III} complexes **4** and **5**. Phosphines **1a**−**3b** can be considered as charged variants of the well-known PTA ligand.

Introduction

The ability by which tertiary phosphines can be modified undoubtedly remains a major reason why this ligand class continues to find spectacular success in many branches of chemistry. Considerable recent interest has focused on the aliphatic caged tertiary phosphine 1,3,5-triaza-7-phosphaadamantane (hereafter abbreviated PTA), which has been shown to possess many desirable attributes including water solubility.[1] Synthetic routes for modifying the adamantanoid framework of PTA such as protonation or alkylation of the tertiary nitrogen atoms or upper or lower rim functionalization have been reported.[2,3] Consequently, numerous applications of PTA and their derivatives in biomedicine,[4] coordination and organometallic chemistry,[4,5] and catalysis,[6] especially in aqueous media, have been realized. One aspect of PTA not previously investigated is the ability to manipulate the nitrogen centers, for example, by changing the alkyl or aryl substituents yet *preserving* the tertiary amine character as opposed to quaternization[3b] or forming boronated species.[5c] One approach by which this could be accomplished is to envisage removal of two "upper-rim" methylene (N−CH_2−N) groups from PTA, thereby allowing different R groups on nitrogen to be incorporated. Using suitable noncovalent interactions, such as intramolecular H-bonding, would allow for retention of the adamantane core. As part of ongoing studies in our group, we have recently developed highly functionalized (di)tertiary phosphines with regiospecific H-bonding capabilities.[7] Herein a simple concept for the synthesis of novel cationic trialkylphosphines, with stereoelectronic properties similar to those of PTA, and a preliminary exploration of their late transition metal chemistries are reported. All new compounds have been character-

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(1) Daigle, D. J.; Pepperman, A. B.; Vail, S. L. *J. Heterocycl. Chem.* **1974**, *11*, 407–408.

(2) For recent examples of PTA functionalization, see: (a) Erlandsson, M.; Gonsalvi, L.; Lenco, A.; Peruzzini, M. *Inorg. Chem.* **2008**, *47*, 8–10. (b) Wong, G. W.; Lee, W.-C.; Frost, B. J. *Inorg. Chem.* **2008**, *47*, 612–620. (c) Huang, R.; Frost, B. J. *Inorg. Chem.* **2007**, *46*, 10962–10964. (d) Wong, G. W.; Harkreader, J. L.; Mebi, C. A.; Frost, B. J. *Inorg. Chem.* **2006**, *45*, 6748–6755. (e) Zablocka, M.; Duhayon, C. *Tetrahedron Lett.* **2006**, *47*, 2687–2690. (f) Darensbourg, D. J.; Yarbrough, J. C.; Lewis, S. J. *Organometallics* **2003**, *22*, 2050–2056.

(3) For the chemistry of open cage ligands related to PTA, see: (a) Mena-Cruz, A.; Lorenzo-Luis, P.; Romerosa, A.; Serrano-Ruiz, M. *Inorg. Chem.* **2008**, *47*, 2246–2248. (b) Mena-Cruz, A.; Lorenzo-Luis, P.; Romerosa, A.; Saoud, M.; Serrano-Ruiz, M. *Inorg. Chem.* **2007**, *46*, 6120–6128. (c) Krogstad, D. A.; Ellis, G. S.; Gunderson, A. K.; Hammrich, A. J.; Rudolf, J. W.; Halfen, J. A. *Polyhedron* **2007**, *26*, 4093–4100. (d) Phillips, A. D.; Bolaño, S.; Bosquain, S. S.; Daran, J.-C.; Malacea, R.; Peruzzini, M.; Poli, R.; Gonsalvi, L. *Organometallics* **2006**, *25*, 2189–2200. (e) Darensbourg, D. J.; Ortiz, C. G.; Kamplain, J. W. *Organometallics* **2004**, *23*, 1747–1754.

(4) For recent medicinal examples using PTA and related ligands, see: (a) Gossens, C.; Tavernelli, I.; Rothlisberger, U. *J. Am. Chem. Soc.* **2008**, *130*, 10921–10928. (b) Miranda, S.; Vergara, E.; Mohr, F.; de Vos, D.; Cerrada, E.; Mendía, A.; Laguna, M. *Inorg. Chem.* **2008**, *47*, 5641–5648. (c) Vock, C. A.; Renfrew, A. K.; Scopelliti, R.; Juillerat-Jeanneret, L.; Dyson, P. J. *Eur. J. Inorg. Chem.* **2008**, 1661–1671. (d) Dutta, B.; Scolaro, C.; Scopelliti, R.; Dyson, P. J.; Severin, K. *Organometallics* **2008**, *27*, 1355–1357. (e) Leyva, L.; Sirlin, C.; Rubio, L.; Franco, C.; Le Lagadec, R.; Spencer, J.; Bischoff, P.; Gaiddon, C.; Loeffler, J.-P.; Pfeffer, M. *Eur. J. Inorg. Chem.* **2007**, 3055–3066. (f) Dillinger, S. A. T.; Schmalle, H. W.; Fox, T.; Berke, H. *Dalton Trans.* **2007**, 3562–3571. (g) Bergamini, P.; Bertolasi, V.; Marvelli, L.; Canella, A.; Gavioli, R.; Mantovani, N.; Mañas, S.; Romerosa, A. *Inorg. Chem.* **2007**, *46*, 4267–4276. (h) Dorcier, A.; Ang, W. H.; Bolaño, S.; Gonsalvi, L.; Juillerat-Jeannerat, L.; Laurenczy, G.; Peruzzini, M.; Phillips, A. D.; Zanobini, F.; Dyson, P. J. *Organometallics* **2006**, *25*, 4090–4096. (i) Dorcier, A.; Dyson, P. J.; Gossens, C.; Rothlisberger, U.; Scopelliti, R.; Tavernelli, I. *Organometallics* **2005**, *24*, 2114–2123. (j) Allardyce, C. S.; Dyson, P. J.; Ellis, D. J.; Heath, S. L. *Chem. Commun.* **2001**, 1396–1397.

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ized by a combination of spectroscopic and single crystal X-ray diffraction techniques.

Experimental Section

Materials. All manipulations and reactions were carried out under aerobic conditions. Dichloromethane was previously distilled over CaH_2 and diethyl ether over sodium/benzophenone, and tetrakis(hydroxymethyl)phosphonium chloride (THPC) was recrystallized from 2-propanol before use.[8] All other solvents and chemicals were obtained from commercial suppliers and used without further purification. The dinuclear metal compounds $\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2$ and $\{RhCl_2(\eta^5\text{-Cp*})\}_2$ were prepared according to published procedures.[9,10]

Instrumentation. Fourier transform infrared (FT-IR) spectra were recorded within pressed KBr pellets over the range of 4000−200 cm^{-1} using a Perkin-Elmer system 2000 FT spectrometer. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX-400 FT spectrometer with chemical shifts (δ) reported relative to external tetramethylsilane (TMS) or 85% H_3PO_4. Coupling constants (J) were recorded in hertz. All NMR spectra were recorded in dmso-d^6 solutions at about 298 K. Elemental analyses (Perkin-Elmer 2400 CHN or Exeter Analytical, Inc., CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry. Mass spectra for **1a**−**5** were analyzed (JEOL SX102 instrument) by fast atom bombardment (FAB) in a positive ionization mode using a 3-nitrobenzyl alcohol (NOBA) matrix. Compounds **6a** and **6b** were analyzed (Finnigan MAT 95XP) by low-resolution FAB (LSIMS) in positive ionization mode using CH_2Cl_2 as the solvent and a NOBA matrix.

Preparation of 1a. To a solution of THPC (3.83 g, 20.1 mmol) in EtOH (100%, 75 mL) was added dropwise $C_6H_5CH_2NH_2$ (8.94 g, 83.4 mmol). During the addition, heat was generated, and thick white fumes were observed. After about 5 min, the solution became clear. The mixture was stirred for 2 h at room temperature (frequently some unwanted "sticky" material was formed which was separated from the solution by decantation) and the volume reduced on a rotary evaporator to approximately a quarter of the original volume. The resulting crystalline solid was filtered and dried under vacuum. Yield: 7.60 g (86%). Selected data is as follows. $^{31}P\{^1H\}$ NMR: −55.0 ppm. ^1H NMR: 9.55 (br, NH_2, 2H), 7.59−7.01 (m, arom. H, 15H), 4.21 (s, CH_2, 2H), 3.42−3.38 (m, CH_2, 8H), 3.18 (d, $^2J_{PH}$ 13.6, CH_2, 2H), 2.65 (t, CH_2, 2H) ppm. FT-IR: 3028 and 2781 (br, NH and CH) cm^{-1}. FAB-MS: m/z 404 [M − Cl]. Anal. Calcd for $C_{25}H_{31}N_3PCl$: C, 68.24; H, 7.12; N, 9.55. Found: C, 68.25; H, 7.10; N, 9.58.

Preparation of 1b. To a solution of THPC (2.85 g, 14.9 mmol) in EtOH (100%, 55 mL) was added dropwise 4-$FC_6H_4CH_2NH_2$ (7.77 g, 62.0 mmol). The mixture was stirred for 2 h at room temperature and the volume reduced on a rotary evaporator to approximately a quarter of the original volume. The resulting crystalline solid was filtered and dried under vacuum. Additional crops of **1b** were obtained when the filtrate was allowed to stand for more than 24 h. Yield: 6.11 g (83%). Selected data is as follows. $^{31}P\{^1H\}$ NMR: −55.2 ppm. ^1H NMR: 7.62−6.93 (m, arom. H, 12H), 4.21 (s, CH_2, 2H), 3.29 (multiplicity could not fully be assigned as a result of overlap with residual solvent peaks, CH_2), 3.18 (d, $^2J_{PH}$ 13.8, CH_2, 2H), 2.67 (t, CH_2, 2H) ppm. FT-IR: 3044 and 2821 (br, NH and CH) cm^{-1}. FAB-MS: m/z 458 [M − Cl]. Anal. Calcd for $C_{25}H_{28}F_3N_3PCl$: C, 60.78; H, 5.73; N, 8.51. Found: C, 60.56; H, 5.58; N, 8.41.

Preparation of 2a. A solution of $Na(SbF_6)$ (0.18 g, 0.69 mmol) in the minimum volume of high performance liquid chromatography (HPLC) grade CH_3OH was added to a solution of **1a** (0.20 g, 0.45 mmol) in HPLC grade CH_3OH (10 mL). The solution was stirred at room temperature for 30 min. Concentration of the solution, under reduced pressure, and addition of distilled water afforded a colorless precipitate which was filtered and dried under vacuum. Yield: 0.28 g (97%). Selected data is as follows. $^{31}P\{^1H\}$ NMR: −55.2 ppm. ^1H NMR: 9.01 (br, NH_2, 2H), 7.49−6.92 (m, arom. H, 15H), 4.22 (s, CH_2, 2H), 3.57−3.41 (multiplicity could not fully be assigned as a result of overlap with residual solvent peaks, CH_2), 3.10 (d, $^2J_{PH}$ 12, CH_2, 2H), 2.66 (t, CH_2, 2H) ppm. FT-IR: 3064, 3031, and 2808 (s, NH and CH), 654 (vs, SbF) cm^{-1}. FAB-MS: m/z 404 [M − SbF_6]. Anal. Calcd for $C_{25}H_{31}N_3PSbF_6 \cdot 0.5H_2O$: C, 46.25; H, 4.98; N, 6.47. Found: C, 46.35; H, 4.80; N, 6.46.

Preparation of 2b. A solution of $Na(SbF_6)$ (0.16 g, 0.61 mmol) in the minimum volume of HPLC grade CH_3OH was added to a solution of **1b** (0.20 g, 0.40 mmol) in HPLC grade CH_3OH (10 mL). The solution was stirred at room temperature for 30 min. Concentration of the solution, under reduced pressure, and addition of distilled water afforded a colorless precipitate which was filtered and dried under vacuum. Yield: 0.21 g (73%). Selected data is as follows. $^{31}P\{^1H\}$ NMR: −55.0 ppm. ^1H NMR: 8.95 (br, NH_2, 2H), 7.57−6.98 (m, arom. H, 12H), 4.22 (s, CH_2, 2H), 3.84−3.50 (multiplicity could not fully be assigned as a result of overlap with residual solvent peaks, CH_2), 3.10 (d, $^2J_{PH}$ 13.6, CH_2, 2H), 2.67 (t, CH_2, 2H) ppm. FT-IR: 3052, 2953, 2830, 2799, and 2730 (m, NH

(5) For recent examples of PTA coordination complexes, see: (a) Serrano Ruiz, M.; Romerosa, A.; Sierra-Martin, B.; Fernandez-Barbero, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8665–8669. (b) Tu, X.; Nichol, G. S.; Wang, R.; Zheng, Z. *Dalton Trans.* **2008**, 6030–6038. (c) Bolaño, S.; Albinati, A.; Bravo, J.; Caporali, M.; Gonsalvi, L.; Male, L.; Rodríguez-Rocha, M. M.; Rossin, A.; Peruzzini, M. *J. Organomet. Chem.* **2008**, *693*, 2397–2406. (d) Jaremko, L.; Kirillov, A. M.; Smoleński, P.; Lis, T.; Pombeiro, A. J. L. *Inorg. Chem.* **2008**, *47*, 2922–2924. (e) Mena-Cruz, A.; Lorenzo-Luis, P.; Romerosa, A.; Serrano-Ruiz, M. *Inorg. Chem.* **2008**, *47*, 2246–2248. (f) Marchi, A.; Marchesi, E.; Marvelli, L.; Bergamini, P.; Bertolasi, V.; Ferretti, V. *Eur. J. Inorg. Chem.* **2008**, 2670–2679. (g) Smoleński, P.; Dinoi, C.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *J. Organomet. Chem.* **2008**, *693*, 2338–2344. (h) Mebi, C. A.; Frost, B. J. *Inorg. Chem.* **2007**, *46*, 7115–7120. (i) Mohr, F.; Falvello, L. R.; Laguna, M. *Eur. J. Inorg. Chem.* **2006**, 3152–3154. (j) Wang, Z.; Liu, J.; He, C.; Jiang, S.; Åkermark, B.; Sun, L. *Inorg. Chim. Acta* **2007**, *360*, 2411–2419. (k) Frost, B. J.; Bautista, C. M.; Huang, R.; Shearer, J. *Inorg. Chem.* **2006**, *45*, 3481–3483. (l) Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* **2004**, *248*, 955–993. (m) Darensbourg, D. J.; Robertson, J. B.; Larkins, D. L.; Reibenspies, J. H. *Inorg. Chem.* **1999**, *38*, 2473–2481.

(6) (a) Erlandsson, M.; Landaeta, V. R.; Gonsalvi, L.; Peruzzini, M.; Phillips, A. D.; Dyson, P. J.; Laurenczy, G. *Eur. J. Inorg. Chem.* **2008**, 620–627. (b) Korthals, B.; Göttker-Schnetmann, I.; Mecking, S. *Organometallics* **2007**, *26*, 1311–1316. (c) Xu, X.; Wang, C.; Zhou, Z.; Tang, X.; He, Z.; Tang, C. *Eur. J. Org. Chem.* **2007**, 4487–4491. (d) Ruiz, J.; Cutillas, N.; López, F.; López, G.; Bautista, D. *Organometallics* **2006**, *25*, 5768–5773. (e) Krogstad, D. A.; DeBoer, A. J.; Ortmeier, W. J.; Rudolf, J. W.; Halfen, J. A. *Inorg. Chem. Commun.* **2005**, *8*, 1141–1144. (f) Mejia-Rodriguez, R.; Chong, D.; Reibenspies, J. H.; Soriaga, M. P.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2004**, *126*, 12004–12014. (g) Darensbourg, D. J.; Joó, F.; Kannisto, M.; Kathó, A.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* **1994**, *33*, 200–208.

(7) (a) Smith, M. B.; Dale, S. H.; Coles, S. J.; Gelbrich, T.; Hursthouse, M. B.; Light, M. E.; Horton, P. N. *CrystEngComm* **2007**, *9*, 165–175. (b) Dann, S. E.; Durran, S. E.; Elsegood, M. R. J.; Smith, M. B.; Staniland, P. M.; Talib, S.; Dale, S. H. *J. Organomet. Chem.* **2006**, *691*, 4829–4842. (c) Elsegood, M. R. J.; Smith, M. B.; Staniland, P. M. *Inorg. Chem.* **2006**, *45*, 6761–6770. (d) Smith, M. B.; Dale, S. H.; Coles, S. J.; Gelbrich, T.; Hursthouse, M. B.; Light, M. E. *CrystEngComm* **2006**, *8*, 140–149.

(8) Frank, A. W.; Drake Jr., G. L. *J. Org. Chem.* **1972**, *37*, 2752–2755.

(9) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233–241.

(10) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228–234.

and CH), 653 (vs, SbF) cm^{-1}. FAB-MS: *m/z* 458 [M − SbF_6]. Anal. Calcd for $C_{25}H_{28}N_3PSbF_9 \cdot 0.5H_2O$: C, 42.70; H, 4.16; N, 5.98. Found: C, 42.46; H, 3.90; N, 5.87.

Preparation of 3a. A solution of K(PF_6) (0.13 g, 0.71 mmol) in the minimum volume of HPLC grade CH_3OH was added to a solution of **1a** (0.20 g, 0.45 mmol) in HPLC grade CH_3OH (10 mL). The solution was stirred at room temperature for 30 min. Concentration of the solution, under reduced pressure, and addition of distilled water afforded a colorless precipitate which was filtered and dried under vacuum. Yield: 0.18 g (72%). Selected data is as follows.$^{31}P\{^1H\}$ NMR: −54.6, −144.2 ppm, ($^1J_{PF}$ 711, PF_6^-). ^1H NMR: 9.02 (br, NH_2, 2H), 7.49−7.01 (m, arom. H, 15H), 4.23 (s, CH_2, 2H), 3.85−3.41 (multiplicity could not fully be assigned as a result of overlap with residual solvent peaks, CH_2), 3.10 (d, $^2J_{PH}$ 14, CH_2, 2H), 2.67 (t, CH_2, 2H) ppm. FT-IR: 3030 and 2809 (w, NH and CH), 842 (vs, PF) cm^{-1}. FAB-MS: *m/z* 404 [M − PF_6]. Anal. Calcd for $C_{25}H_{31}N_3P_2F_6$: C, 54.64; H, 5.70; N, 7.65. Found: C, 55.03; H, 5.61; N, 7.68.

Preparation of 3b. A solution of K(PF_6) (0.11 g, 0.60 mmol) in the minimum volume of HPLC grade CH_3OH was added to a solution of **1b** (0.20 g, 0.40 mmol) in HPLC grade CH_3OH (10 mL). The solution was stirred at room temperature for 30 min. Concentration of the solution, under reduced pressure, and addition of distilled water afforded a colorless precipitate which was filtered and dried under vacuum. Yield: 0.20 g (83%). Selected data is as follows.$^{31}P\{^1H\}$ NMR: −54.4, −144.2 ppm, ($^1J_{PF}$ 714, PF_6^-). ^1H NMR: 9.00 (br, NH_2, 2H), 7.58−6.98 (m, arom. H, 12H), 4.22 (s, CH_2, 2H), 3.84−3.51 (multiplicity could not fully be assigned as a result of overlap with residual solvent peaks, CH_2), 3.12 (d, $^2J_{PH}$ 13.6, CH_2, 2H), 2.67 (t, CH_2, 2H) ppm. FT-IR: 3077, 3042, 3007, 2949, 2820 (m, NH and CH), 848 (vs, PF) cm^{-1}. FAB-MS: *m/z* 458 [M − PF_6]. Anal. Calcd for $C_{25}H_{28}N_3P_2F_9 \cdot H_2O$: C, 48.32; H, 4.88; N, 6.76. Found: C, 48.21; H, 4.51; N, 6.72.

Preparation of $RuCl_2(\eta^6$-*p*-Cymene)(2a) (4). To a stirred solution of $\{RuCl_2(\eta^6$-*p*-cymene)$\}_2$ (0.030 g, 0.049 mmol) in CH_2Cl_2 (10 mL) was added **2a** (0.063 g, 0.10 mmol) as a solid in one portion. The solution was stirred for 30 min, the volume reduced to about 1−2 mL under reduced pressure, and Et_2O (10 mL) added. The suspension was stirred for 30 min and the solid collected on a glass sinter and dried under vacuum. Yield: 0.080 g (91%). Selected data is as follows. $^{31}P\{^1H\}$ NMR: 7.3 ppm. ^1H NMR: 8.98 (br, NH_2, 2H), 7.53−6.99 (m, arom. H, 15H), 5.94 (dd, $^3J_{PH}$ 8, C_6H_4, 4H), 4.29 (s, CH_2, 2H), 4.02 (d, $^2J_{PH}$ 4.8, CH_2, 2H), 3.80−3.71 (m, CH_2, 4H), 3.45 (partially obscured by solvent, CH_2), 2.62 (sept, $^3J_{PH}$ 6.8, $CH(CH_3)_2$, 1H), 1.96 (CH_3, 3H), 1.14 (d, $^3J_{PH}$ 6.8, $CH(CH_3)_2$, 6H) ppm. FT-IR: 3060 and 2967 (w, NH and CH), 660 (vs, SbF) cm^{-1}. FAB-MS: *m/z* 710 [M − SbF_6]. Anal (bulk material). Calcd for $C_{35}H_{45}N_3PSbF_6RuCl_2 \cdot 3.5CH_2Cl_2$: C, 37.18; H, 4.22; N, 3.38. Found: C, 37.17; H, 4.00; N, 3.24. A single crystal X-ray determination of **4** showed 1.67 CH_2Cl_2 molecules present in the crystal lattice.

Preparation of $RhCl_2(\eta^5$-Cp*)(2a) (5). To a stirred solution of $\{RhCl_2(\eta^5$-Cp*)$\}_2$ (0.030 g, 0.050 mmol) in CH_2Cl_2 (10 mL) was added **2a** (0.062 g, 0.10 mmol) as a solid in one portion. The solution was stirred for 30 min, the volume reduced to about 1−2 mL under reduced pressure, and Et_2O (10 mL) added. The suspension was stirred for 30 min and the solid collected on a glass sinter and dried under vacuum. Yield: 0.090 g (98%). Selected data is as follows. $^{31}P\{^1H\}$ NMR: 4.6 ppm, $^1J_{RhP}$ 144. ^1H NMR: 7.51−6.91 (m, arom. H, 15H), 4.37 (s, CH_2, 2H), 4.10 (s, CH_2, 2H), 3.76 (d, $^2J_{PH}$ 12.4, CH_2, 4H), 3.22 (multiplicity could not fully be assigned as a result of overlap with residual solvent peaks, CH_2), 1.67 (s, η^5-Cp*, 15H) ppm. FT-IR: 3031 (br, NH and CH), 660 (vs, SbF) cm^{-1}. FAB-MS: *m/z* 712 [M − SbF_6]. Anal (bulk material). Calcd for $C_{35}H_{46}N_3PSbF_6RhCl_2 \cdot CH_2Cl_2$: C, 41.81; H, 4.68; N, 4.06. Found: C, 41.46; H, 4.50; N, 4.07. A single crystal X-ray determination of **5** showed two CH_2Cl_2 molecules present in the crystal lattice.

Preparation of *trans*-$RhCl(CO)(1a)_2$ (6a). To a stirred solution of $\{RhCl(CO)_2\}_2$ (0.030 g, 0.080 mmol) in CH_2Cl_2 (10 mL) was added **1a** (0.14 g, 0.32 mmol) as a solid in one portion. The dark orange solution immediately went pale yellow, and a yellow solid was deposited within about 10 min. The suspension was stirred for 30 min, the volume reduced to about 1−2 mL under reduced pressure, and Et_2O (10 mL) added. The solid was collected on a glass sinter and dried under vacuum. Yield: 0.14 g (88%). As a result of the extreme insolubility of **6a** in both nonpolar and polar solvents, no meaningful NMR (^1H, ^{31}P) data could be obtained for this compound. FT-IR: 1979 (CO) cm^{-1}. LSI-MS: *m/z* 1009 [M − 2H − Cl]. Anal. Calcd for $C_{51}H_{62}N_6OP_2RhCl_3 \cdot 1.25CH_2Cl_2$: C, 54.45; H, 5.65; N, 7.29. Found: C, 54.28; H, 5.40; N, 7.46.

Preparation of *trans*-$RhCl(CO)(1b)_2$ (6b). To a stirred solution of $\{RhCl(CO)_2\}_2$ (0.030 g, 0.080 mmol) in CH_2Cl_2 (10 mL) was added **1b** (0.15 g, 0.30 mmol) as a solid in one portion. The dark orange solution immediately went pale yellow, and a yellow solid was deposited within about 10 min. The suspension was stirred for 30 min, the volume reduced to about 1−2 mL under reduced pressure, and Et_2O (10 mL) added. The solid was collected on a glass sinter and dried under vacuum. Yield: 0.16 g (93%). As a result of the extreme insolubility of **6b** in both nonpolar and polar solvents, no meaningful NMR (^1H, ^{31}P) data could be obtained for this compound. FT-IR: 1979 (CO) cm^{-1}. LSI-MS: *m/z* 1117 [M − 2H − Cl]. Anal. Calcd for $C_{51}H_{56}N_6OP_2F_6RhCl_3 \cdot CH_2Cl_2$: C, 50.40; H, 4.72; N, 6.78. Found: C, 50.63; H, 4.70; N, 6.94.

X-ray Crystallography. Suitable crystals of **1b** were obtained by allowing an ethanol filtrate, obtained from the reaction of THPC with 4-$FC_6H_4CH_2NH_2$, to stand for several days. Crystals of **2b** and **3a** were obtained upon layering CH_2Cl_2 solutions with petroleum ether (bp 40−60 °C) over several days. Slow diffusion of petroleum ether (bp 40−60 °C) into a $CDCl_3/CH_2Cl_2$ solution gave X-ray quality crystals of **4**·1.67CH_2Cl_2. Vapor diffusion of Et_2O into a CH_2Cl_2 solution gave suitable crystals of **5**·2CH_2Cl_2.

Measurements for **1b**, **2b**, **3a**, and **4**·1.67CH_2Cl_2 were made on a Bruker Apex 2 CCD diffractometer, at 150 K, using graphite-monochromated radiation from a sealed tube Mo Kα source (λ = 0.71073 Å). Diffraction data for **5**·2CH_2Cl_2 was collected, at 120 K, using a rotating anode source and a Bruker-Nonious Roper CCD camera. Narrow frame ω scans were employed for **1b**, **2b**, **3a**, and **4**·1.67CH_2Cl_2, and ϕ and ω scans were used for **5**·2CH_2Cl_2. Intensities were corrected semi-empirically for absorption on the basis of symmetry-equivalent and repeated reflections. The structures were solved by direct methods (Patterson synthesis for **4**·1.67CH_2Cl_2) and refined on F^2 values for all unique data by full-matrix least-squares. Table 1 gives further details. All non-hydrogen atoms were refined anisotropically. N*H* hydrogens for **2b**, **3a**, and **4** had coordinates freely refined with U_{eq} set to 1.2U_{eq} of the carrier atom, while the remaining hydrogen coordinates were constrained using a riding model with U_{eq} set to 1.2U_{eq} of the carrier atom (1.5U_{eq} for methyl hydrogen). In **4**·1.67CH_2Cl_2, one of the CH_2Cl_2 molecules was modeled as disordered over two sets of positions. This disorder was refined with restraints on geometry and anisotropic displacement parameters. The major component was equal to 66.0(3)%. In **5**·2CH_2Cl_2, the SbF_6^- counterion was found to be disordered over two sets of positions and was refined as above, the major component equal to 80.7(5)%. Programs used were COL-

Table 1. Details of the X-ray Data Collections and Refinements for Compounds **1b**, **2b**, **3a**, **4**·1.67CH_2Cl_2, and **5**·2CH_2Cl_2

	1b	**2b**	**3a**	**4**·1.67CH_2Cl_2	**5**·2CH_2Cl_2
formula	$C_{25}H_{28}ClF_3N_3P$	$C_{25}H_{28}F_9N_3PSb$	$C_{25}H_{31}F_6N_3P_2$	$C_{36.67}H_{48.33}Cl_{5.33}F_6N_3PRuSb$	$C_{37}H_{50}Cl_6F_6N_3PRhSb$
M	493.92	694.22	549.47	1087.65	1119.13
cryst dimens (mm^3)	0.40 × 0.34 × 0.23	0.27 × 0.21 × 0.04	0.50 × 0.21 × 0.15	0.31 × 0.22 × 0.11	0.16 × 0.10 × 0.04
cryst morphology, color	block, colorless	plate, colorless	block, colorless	block, orange	plate, orange
cryst syst	orthorhombic	triclinic	orthorhombic	triclinic	monoclinic
space group	*Ama*2	$P\bar{1}$	*Pbca*	$P\bar{1}$	$P2_1/n$
a (Å)	13.7194(15)	8.5038(12)	17.9476(5)	12.9426(5)	8.9106(3)
b (Å)	18.513(2)	8.8389(13)	15.8400(5)	14.0425(5)	14.7367(4)
c (Å)	9.5476(10)	19.082(3)	19.1365(6)	14.7175(6)	30.8857(9)
α (deg)		77.019(2)		65.2785(5)	
β (deg)		78.879(2)		70.5853(5)	95.887(2)
γ (deg)		84.880(2)		66.5392(5)	
V ($Å^3$)	2425.0(5)	1369.8(3)	5440.3(3)	2184.23(15)	4034.3(2)
Z	4	2	8	2	4
μ (mm^{-1})	0.265	1.147	0.220	1.383	1.578
θ range (deg)	2.20−28.97	2.23−24.76	2.02−30.55	1.67−30.55	2.99−27.55
measured reflns	10554	10538	62276	25887	47660
independent reflns	2932	4663	8335	13047	9116
observed reflns ($F^2 > 2\sigma(F^2)$)	2902	4154	6759	11295	6545
R_{int}	0.0216	0.0227	0.0291	0.0183	0.0658
$R1$ [$F^2 > 2\sigma(F^2)$][a]	0.0546	0.0259	0.0377	0.0377	0.0830
$wR2$ [all data][b]	0.1281	0.0675	0.1091	0.1033	0.2031
largest difference map features (e·$Å^3$)	0.388, −0.621	0.838, −0.759	0.408, −0.316	1.863, −1.184	1.389, −0.648

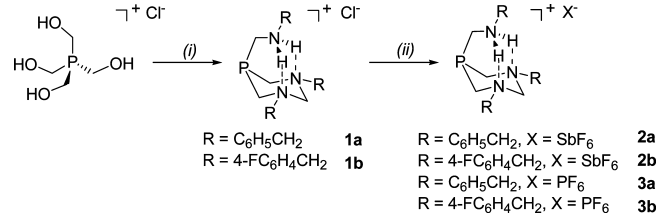
[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

LECT[11] or Bruker AXS APEX 2[12] for diffractometer control, DENZO[13] or SAINT[14] for frame integration, Bruker SHELXTL[15,16] for structure solution, refinement, and molecular graphics, and local programs. Disordered molecules of CH_2Cl_2 (for **5**·2CH_2Cl_2) were modeled by the Platon Squeeze procedure.[17]

Results and Discussion

Commercially available THPC ([$P(CH_2OH)_4$]Cl) has previously been shown to react with primary aromatic amines, through a series of condensation and elimination steps, to give aniline based tertiary phosphines.[8,18] In contrast, we have found when more basic benzylic amines such as $C_6H_5CH_2NH_2$ and 4-$FC_6H_4CH_2NH_2$ are reacted with THPC (ca. 4:1 ratio), crystalline cationic chloride salts **1a** and **1b** are obtained in high yields (typical nonoptimized yields >80%, Scheme 1). Using this procedure we have successfully synthesized batches of **1a** at the 5−10 g scale. Anion metathesis of **1a** or **1b** with $Na(SbF_6)$ or $K(PF_6)$ in CH_3OH at room temperature gave the corresponding salts **2a**−**3b** in excellent yields (72−97%). Compounds **1a**−**3b** have been fully characterized by spectroscopic and analytical methods.

Scheme 1. Preparation of Salts **1a**−**3b**[a]



[a] Key, reagents and conditions: (i) 4.1 equiv of $C_6H_5CH_2NH_2$ or 4.2 equiv of 4-$FC_6H_4CH_2NH_2$, C_2H_5OH, and (ii) $Na(SbF_6)$ or $K(PF_6)$, CH_3OH.

In particular, the $^{31}P\{^1H\}$ NMR spectra (dmso-d^6) of **1a**−**3b** showed a single phosphorus resonance around δ_P −55 ppm, some 40 ppm downfield with respect to PTA [δ_P −96.2 ppm, D_2O].[2a] At ambient temperature, **1a**−**3b** possess good solubility in CH_2Cl_2, CH_3OH, and dmso but were found to be insoluble in H_2O. Furthermore, in the solid state, **1a**−**3b** are air stable but slowly oxidize in dmso-d^6 solution over about 24 h.

The X-ray structures of **1b** (Figure 1), **2b** (Supporting Information), and **3a** (Figure 2) have been determined. Compound **1b** was found to lie across a crystallographic mirror plane that bisects the ammonium group of the cation and the methylene diamine bridge (mirror plane runs through [P(1)/C(1)/N(1)/C(2)/C(3)/C(6)/F(1)/C(8)]. Inspection of the intracage P−C bond lengths and P−C−N bond angles reveals close similarities with those of PTA.[19] The C−P−C angles within the P−C−N−C−N−C ring in **1b**, **2b**, and **3a** are in the range of 97.78(5)−99.4(2)° and are slightly enlarged in comparison with PTA [C−P−C, 96.1(1)°].[19] The most significant structural

(11) Hooft, R. W. W. *COLLECT: Data Collection Software*; Nonius B. V., 1998.
(12) *APEX 2: User Manual*; Bruker AXS Inc.: Madison, WI, 2005.
(13) Otwinowski, Z.; Minor, W. DENZO. In *Methods in Enzymology, Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276, pp 307−326.
(14) *SAINT: Software for CCD Diffractometers*; Bruker AXS Inc.: Madison, WI, 2001.
(15) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
(16) Sheldrick, G. M. *SHELXTL User Manual*, v.6.10; Bruker AXS Inc.: Madison, WI, 2001.
(17) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.
(18) (a) Hatnean, J. A.; Raturi, R.; Lefebvre, J.; Leznoff, D. B.; Lawes, G.; Johnson, S. A. *J. Am. Chem. Soc.* **2006**, *128*, 14992–14999. (b) Han, H.; Elsmaili, M.; Johnson, S. A. *Inorg. Chem.* **2006**, *45*, 7435–7445. (c) Keen, A. L.; Doster, M.; Han, H.; Johnson, S. A. *Chem. Commun.* **2006**, 1221–1223. (d) Han, H.; Johnson, S. A. *Organometallics* **2006**, *25*, 5594–5602.
(19) (a) Jogun, K. H.; Stezowski, J. J.; Fluck, E.; Weidlein, J. *Phosphorus Sulfur Relat. Elem.* **1978**, *4*, 199–204. (b) Marsh, R. E.; Kapon, M.; Hu, S.; Herbstein, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *58*, 62–77.

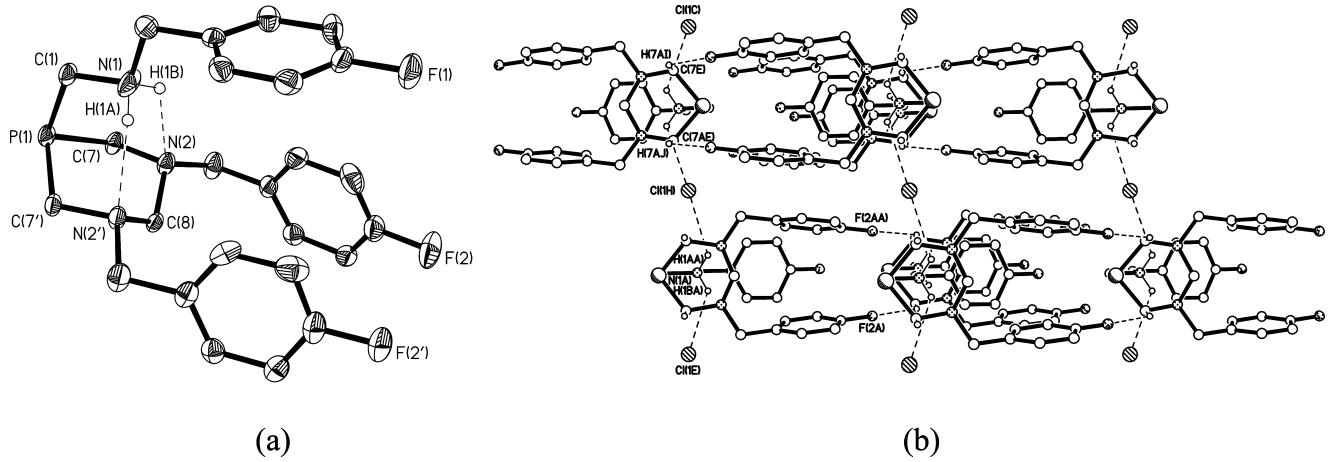


Figure 1. (a) Oak Ridge thermal ellipsoid plot (ORTEP) of the cation in **1b**. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.841(5), P(1)−C(7) 1.847(3); P(1)−C(1)−N(1) 116.2(3), P(1)−C(7)−N(2) 113.8(2). Thermal ellipsoids are drawn at the 50% probability level. (b) Packing plot of **1b** viewed along the *c*-axis showing the H-bonded sheet pattern.

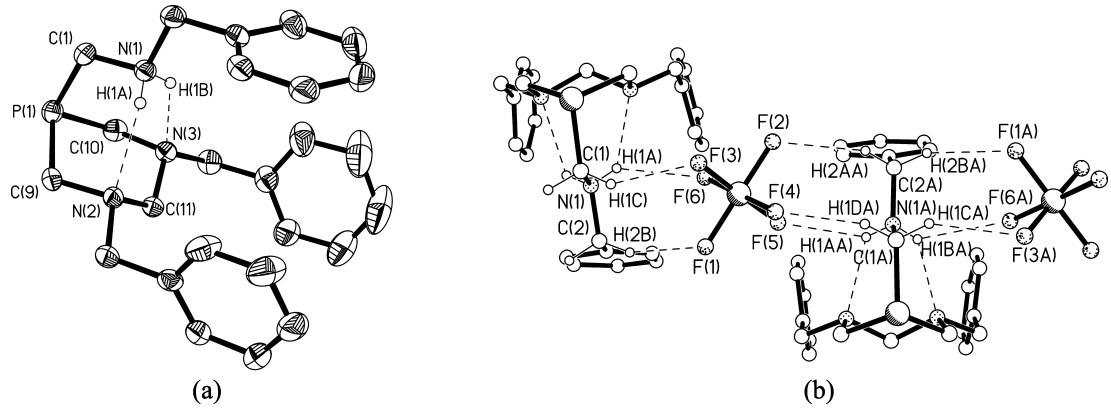
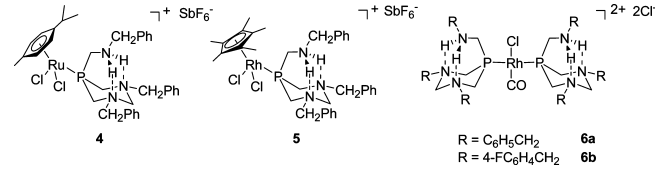


Figure 2. (a) ORTEP of the cation in **3a**. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.8490(12), P(1)−C(9) 1.8359(12), P(1)−C(10) 1.8366(13); P(1)−C(1)−N(1) 116.70(7), P(1)−C(9)−N(2) 114.09(7), P(1)−C(10)−N(3) 113.53(7). Thermal ellipsoids are drawn at the 50% probability level. (b) Packing plot of **3a** viewed along the *c*-axis showing the 1-D chain pattern.

feature observed in **1b**, **2b**, and **3a** is the presence of a pair of intramolecular hydrogen bonds between N(1)−H(1A)···N(2 or 2′) and N(1)−H(1B)···N(2 or 3) [**1b**, N(1)···N(2) 2.915(5) Å, H(1B)···N(2) 2.27 Å, N(1)−H(1B)···N(2) 126°; **2b**, N(1)···N(2) 2.804(3) Å, H(1A)···N(2) 2.14(3) Å, N(1)−H(1A)···N(2) 138(3)° and N(1)···N(3) 2.841(3) Å, H(1B)···N(3) 2.20(3) Å, N(1)−H(1B)···N(3) 130(2)°; and **3a**, N(1)···N(2) 2.8506(13) Å, H(1A)···N(2) 2.241(15) Å, N(1)−H(1A)···N(2) 128.7(12)° and N(1)···N(3) 2.8234(13) Å, H(1B)···N(3) 2.154(15) Å, N(1)−H(1B)···N(3) 132.9(12)°]. Various additional weak intermolecular H-bonding contacts exist between the cations and the Cl^-, SbF_6^-, or PF_6^- counterions leading to infinite 1-D chains or 2-D sheet structures (see Supporting Information for further details).

The single crystal data highlight three key findings regarding the N−H···N hydrogen-bonded framework[20] in the cations of **1b**, **2b**, and **3a**, namely, (i) while all synthetic reactions were performed in alcohol solvents (CH_3OH or C_2H_5OH) or required water for precipitation, no disruption of the N−H···N intramolecular hydrogen-bonded motif was apparent under the experimental or crystallization conditions employed; (ii) the core structure of each cation is independent of the counteranion (Cl^-, SbF_6^-, or PF_6^-) even though the potential for alternate hydrogen-bonding arrangements involving these anions is possible; and (iii) the absence of N−H···F−C contacts, albeit rarely observed,[21] shows that the three electronegative fluorines in the 4-position (**1b** and **2b**) do not disrupt the N−H···N hydrogen-bonding array found here.

Dyson and co-workers[4h,j] have previously shown that half-sandwich organometallic Ru^{II} and Rh^{III} compounds of PTA can be synthesized. To assess whether **2a** could function as a similar *P*-monodentate ligand, the piano-stool complexes **4** and **5** were prepared in high yields. Reassuringly, the coordination chemical shifts for **4** ($\Delta\delta_P$ 62 ppm) and **5** ($\Delta\delta_P$ 60 ppm) were found to closely match those of $RuCl_2(\eta^6$-*p*-cymene)(PTA) ($\Delta\delta_P$ 60 ppm) and $RhCl_2(\eta^5$-Cp*)(PTA) ($\Delta\delta_P$ 65 ppm),[4h,j] suggesting comparable stereoelectronic properties.



X-ray analyses of **4** and **5** have been performed (Figure 3). The M−P, M−Cl(1), and M−Cl(2) (M = Ru or Rh) parameters for **4** and **5** are similar to those of analogous complexes with PTA.[2b,4h,j] Moreover, upon coordination of

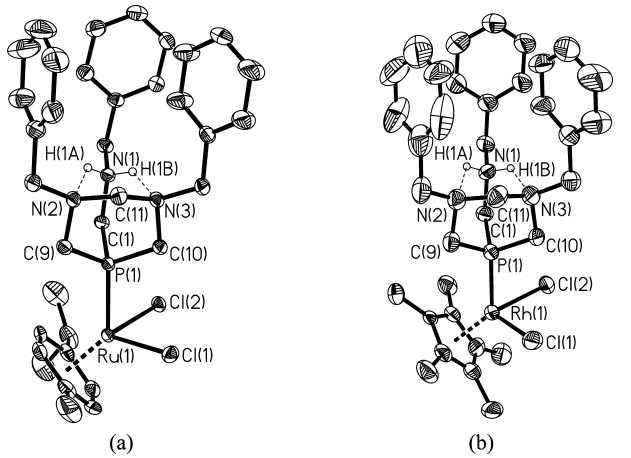


Figure 3. (a) ORTEP of the cation in **4**. Selected bond lengths (Å) and angles (deg): Ru(1)−Cl(1) 2.4064(7), Ru(1)−Cl(2) 2.4103(6), Ru(1)−P(1) 2.3293(6), Ru(1)−C_{av} 2.210(3), P(1)−C(1) 1.843(2), P(1)−C(9) 1.831(3), P(1)−C(10) 1.828(2); Cl(1)−Ru(1)−Cl(2) 88.00(2), Cl(1)−Ru(1)−P(1) 87.60(2), Cl(2)−Ru(1)−P(1) 83.75(2), P(1)−C(1)−N(1) 115.07(16), P(1)−C(9)−N(2) 110.35(16), P(1)−C(10)−N(3) 111.74(16). (b) ORTEP of the cation in **5**. Selected bond lengths (Å) and angles (deg): Rh(1)−Cl(1) 2.406(2), Rh(1)−Cl(2) 2.424(2), Rh(1)−P(1) 2.2851(19), Rh(1)−C_{av} 2.188(8), P(1)−C(1) 1.834(7), P(1)−C(9) 1.836(8), P(1)−C(10) 1.830(7); Cl(1)−Rh(1)−Cl(2) 92.67(8), Cl(1)−Rh(1)−P(1) 88.85(7), Cl(2)−Rh(1)−P(1) 83.37(7), P(1)−C(1)−N(1) 115.4(5), P(1)−C(9)−N(2) 110.1(5), P(1)−C(10)−N(3) 110.0(5).

the phosphine **2a**, there are minimal differences in the P−C and P−C−N metric parameters with respect to **1b**, **2b**, or **3a**. As seen previously for **1b**, **2b**, or **3a**, pairs of intramolecular N−H···N hydrogen bonds are once again maintained upon complexation [**4**, N(1)···N(2) 2.894(3) Å, H(1A)···N(2) 2.22(3) Å, N(1)−H(1A)···N(2) 130(3)° and N(1)···N(3) 2.840(3) Å, H(1B)···N(3) 2.24(3) Å, N(1)−H(1B)···N(3) 128(3)°; **5**, N(1)···N(2) 2.952(9) Å, H(1A)···N(2) 2.34 Å, N(1)−H(1A)···N(2) 124° and N(1)···N(3) 2.851(8) Å, H(1B)···N(3) 2.18 Å, N(1)−H(1B)···N(3) 129°]. Additional weak H-bonding interactions link molecules into dimer pairs (Supporting Information) and is a feature that has recently been observed in cationic dimeric Ru^{II} complexes of PTA.[22]

The electronic properties of **1a** and **1b** have been evaluated through preparation of the square-planar dicationic Rh^{I} carbonyl complexes **6a** (88%) and **6b** (93%) from $Rh_2(CO)_4(\mu-Cl)_2$ and the appropriate ligand. Both Rh^{I} compounds displayed poor solubility in common solvents preventing full characterization. However, FT-IR spectra of **6a** and **6b** were recorded as KBr pellets and showed, in each case, a single terminal carbonyl band at ν_{CO} 1979 cm^{-1}. These findings suggest the electronic properties of **1a** (R = $CH_2C_6H_5$) and **1b** (R = 4-$CH_2C_6H_4F$) are similar despite the different para substituents. Although no direct comparisons between the FT-IR data for **6a** and **6b** with the known neutral complexes *trans*-$RhCl(CO)(L)_2$ [L = PTA, ν_{CO} 1963 cm^{-1} (chloroform); L = "lower-rim" trisubstituted analogues of PTA, ν_{CO} 1978−1987 cm^{-1} (chloroform)][2c,23] can be drawn, **1a** and **1b** can be viewed as possessing similar electron donating properties to this series of PTA ligands.

Concluding Remarks

In summary, we have shown how simple modification of the PTA core can be achieved in which noncovalent interactions maintain the rigid cage structure in the solid state. Further studies are in progress and directed toward understanding the properties of this ligand family in aqueous and organic media, their coordination chemistry, and potential catalytic or medicinal applications.

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Supporting Information Available: X-ray data for **1b**, **2b**, **3a**, **4**·1.67CH_2Cl_2, and **5**·2CH_2Cl_2 in CIF format and additional figures and details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) (a) Allen, F. R. *Acta Crystallogr., Sect. B* **2002**, *58*, 380–388. (b) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746–749.
(21) Dunitz, J. D.; Taylor, R. *Chem.—Eur. J.* **1997**, *3*, 89–98.
(22) Bolaño, S.; Ciancaleoni, G.; Bravo, J.; Gonsalvi, L.; Macchioni, A.; Peruzzini, M. *Organometallics* **2008**, *27*, 1649–1652.
(23) Pruchnik, F. P.; Smoleński, P.; Raksa, I. *Pol. J. Chem.* **1995**, *69*, 5–8.