Synthesis, Structure, and Coordination Chemistry of the Bicyclic π-Acid Phosphatri(3-methylindolyl)methane

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Reaction of tri(3-methylindolyl)methane (**1**) with PCl_3 in the presence of triethylamine produces the bicyclic π-acid phosphatri(3-methylindolyl)methane (**2**). The unconstrained analogue tri(*N*-3-methylindolyl)phosphine (**3**) was synthesized by reaction of lithium 3-methylindolide with PCl_3. Both **2** and **3** are stable to hydrolysis, alcoholysis, and aerial oxidation. Reactions of **2** with ^{t}BuOOH, S_8, or Se powder under forcing conditions produce the chalcogenide derivatives **2**═O (**4**), **2**═S (**5**), and **2**═Se (**6**), respectively. Tri(*N*-3-methylindolyl)phosphine selenide (**7**) and Se═P(*N*-pyrrolyl)$_3$ (**8**) were synthesized by reaction of Se powder with **3** and P(*N*-pyrrolyl)$_3$, respectively. The reaction of **2** with Rh(acac)$(CO)_2$ (acac = acetylacetonate) under forcing conditions yields Rh(acac)(CO)(**2**) (**9**), whereas Rh(acac)(CO)(**3**) (**10**) was synthesized by reaction of **3** with Rh(acac)$(CO)_2$ under mild conditions. Spectroscopic data for **6**−**10** were used to assess the electronic properties of **2** and **3**. Reduced σ-basicity of **2** and **3** is indicated by lack of their reactivity with methyl iodide. Furthermore, comparison of the $^1J_{P-Se}$ values of **6**−**8** shows the parent phosphines to be slightly stronger σ-bases than P$(OPh)_3$, but much weaker than triaminophosphines. In addition, comparison of the ν_{CO} data of **9** and **10** with those of known Rh(acac)(CO)(PR_3) complexes shows **2** is a stronger π-acid than P(*N*-pyrrolyl)$_3$ and P$(OPh)_3$, while **3** has π-acceptor properties similar to P$(OPh)_3$. The molecular structures of compounds **2**, **4**, and **9** were determined by X-ray crystallography.

Introduction

Organophosphorus ligands with enhanced π-acidity relative to triaryl phosphites may have potential applications in several homogeneous catalytic reactions. Reaction rates in rhodium-catalyzed hydroformylation of alkenes, for example, increase with increasing π-acidity of the organophosphorus ligands.[1] Currently, bulky triaryl phosphites are the π-accepting ligands of choice in catalytic applications, but the effects of even greater π-acidity on catalyst activity are poorly explored and development of new π-accepting ligands is of current interest.[2,3]

To be useful, new π-accepting ligands should be stable to hydrolysis, alcoholysis, and aerial oxidation and should also be readily derivatized to fine-tune steric, electronic, and solubility properties. Pyrrolylphosphines[3−9] have exceptional promise in this regard. The P−N bonds of P(*N*-pyrrolyl)$_3$ are stable to hydrolysis and alcoholysis, and P(*N*-pyrrolyl)$_3$ does not react with methyl iodide. Lack of reactivity with methyl iodide indicates weak σ-basicity of P(*N*-pyrrolyl)$_3$, a fact further substantiated by enthalpies of reaction with $Rh_2Cl_2(CO)_4$.[8] P(*N*-pyrrolyl)$_3$ is also a stronger π-acceptor than P$(OPh)_3$ and arylphosphines based on ν_{CO} values for series of $RhCl(CO)(L)_2$ and Rh(acac)(CO)(L) complexes.[3,7−9] π-Acidity has been further enhanced with 3,4-biscarboxyethyl substitution on the pyrrolyl rings.[7]

As reported by Moloy and Petersen,[3] the unique electronic properties of pyrrolylphosphines can be explained by the strong electron-withdrawing ability of pyrrolyl substituents. This electron-withdrawing ability is attributed to the high electronegativity of nitrogen, significantly enhanced by extensive delocalization of the nitrogen lone pair into the aromatic π-system and onto the pyrrolyl carbons. Delocalization reduces the availability of the nitrogen lone pair for π-donation to phosphorus.

Indolyl substituents also have strong electron-withdrawing ability, but with greater steric requirements than pyrrolyl substituents. However, indolylphosphines have received little attention. There has been a single report on mono-, di-, and tri(*N*-indolyl)phosphines[10] and another article describing the synthesis of tri(*N*-indolyl)-

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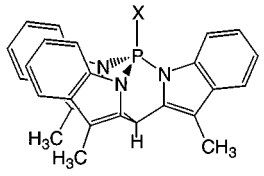
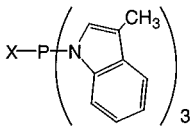
phosphine oxide.[11] Tri(*N*-indolyl)phosphine was also noted in a footnote by Moloy and Petersen,[3] but no synthetic details or characterization was reported. The only coordination complex reported is a 3,3′-dimethyl-1,1′-bis(diphenylphosphino)-2,2′-biindole complex of palladium.[12] We are aware of no additional coordination chemistry or catalytic studies involving indolylphosphines, and there has been no discussion of their electronic properties aside from a reported oxidation potential for 3,3′-dimethyl-1,1′-bis(diphenylphosphino)-2,2′-biindole.[12]

In addition to moderation of σ-basicity and enhancement of π-acidity by use of electron-withdrawing substituents, a reduction in phosphine basicity can also be achieved with increasing constraint of the angles at phosphorus as imposed by a mono- or bicyclic framework. Seminal studies by Verkade and co-workers[13−18] on electronic properties of a series of phosphites demonstrated that σ-basicity decreases and π-acidity increases with decreasing O−P−O angles as determined by $^1J_{P-Se}$,[13,14] ν_{CO},[15] and ν_{BH} data[15,16] for corresponding series of selenides, metal carbonyl complexes, and borane adducts, respectively. Reduced basicity has also been observed for $P(CH_3NCH_2)_3CCH_3$ in comparison to noncyclic triaminophosphines on the basis of $^{31}P-^{77}Se$ coupling constants, the magnitude of which increases with decreasing phosphine basicity.[13−15]

Herein, we report the use of tri(3-methylindolyl)-methane (**1**) in the preparation of the π-acidic, bicyclic phosphine **2**. The π-acidity of **2** benefits from both the electron-withdrawing ability of indolyl substituents and reduction of phosphine basicity by constraint at phosphorus as imposed by the tri(3-methylindolyl)methane framework. The synthesis, characterization, and reactivity of **2**, the unconstrained analogue **3**, and their chalcogenide derivatives **4**−**7** are reported. Electronic properties of **2** are assessed by spectroscopic data for **6** and Rh(acac)(CO)(**2**), and the data are compared with those for **3**, P(*N*-pyrrolyl)$_3$, and several phosphines and phosphites.



X = lp (**2**), O (**4**), S (**5**), Se(**6**)



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Experimental Section

General Procedures. All reactions were performed under an inert atmosphere of purified nitrogen using standard inert-atmosphere techniques unless specified otherwise. THF and hexanes were distilled from sodium benzophenone ketyl prior to use. Toluene and xylenes were distilled from sodium. Methanol and dichloromethane were degassed by nitrogen purge. $CDCl_3$ was dried by storage over activated molecular sieves. $RhCl_3 \cdot xH_2O$ and selenium powder were purchased from Strem Chemicals, Inc. and used as received. Phosphorus trichloride, 3-methylindole, and triethyl orthoformate were purchased from Aldrich and used as received. *tert*-Butyl hydroperoxide (5.0−6.0 M in decane) was purchased from Aldrich and diluted to twice its volume with degassed decane. Tri(3-methylindolyl)methane (**1**),[19] $Rh(acac)(CO)_2$,[20] and P(*N*-pyrrolyl)$_3$[3] were prepared as described previously. Solution NMR spectra were recorded on a Varian VXRS400 spectrometer using $CDCl_3$ as the internal lock. Chemical shifts are reported relative to TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Infrared spectra were recorded on a Nicolet FT-IR 5DX infrared spectrometer. High-resolution mass spectrometric analyses were performed by the Mass Spectrometry Laboratory at The Ohio State University, Columbus, OH. Low-resolution mass spectral *m*/*z* values are reported for the predominant peak in the isotope pattern. Elemental analyses were performed by the Instrumentation Center in Arts and Sciences, The University of Toledo, Toledo, OH.

Preparation of Phosphatri(3-methylindolyl)methane (2). Tri(3-methylindolyl)methane (10.0 g, 24.8 mmol) was placed in a 500 mL three-neck flask. The flask was then charged with 180 mL of THF and 11 mL of NEt_3 (8.0 g, 79.0 mmol). The yellow solution was cooled to −78 °C, and 2.5 mL of PCl_3 (3.94 g, 28.6 mmol) was added via syringe. A cloudy precipitate formed immediately. The mixture was warmed to room temperature and then heated to reflux for 24 h. The thick yellow suspension was filtered to remove the precipitated solids, which were washed with THF (4 × 30 mL) until the washings were colorless. The combined yellow filtrates were taken to dryness in vacuo, yielding a yellow solid residue. The solid was washed with methanol (100 mL), filtered in air, then washed with cold methanol (4 × 25 mL) and cold hexanes (2 × 25 mL). The crude yellow product was recrystallized twice by dissolution in the minimum amount of hot toluene (25 mL) followed by the addition of methanol (50 mL). The white microcrystalline solid was isolated by filtration and washed with cold methanol and cold hexanes. Yield: 6.20 g, 14.4 mmol, 58%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, 3H, H7, $^3J_{HH}$ = 8 Hz), 7.41 (d, 3H, H4, $^3J_{HH}$ = 8 Hz), 7.21 (t, 3H, H6, $^3J_{HH}$ = 8 Hz), 7.10 (t, 3H, H5, $^3J_{HH}$ = 8 Hz), 5.89 (s, 1H, CH), 2.39 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 137.18 (d, C7a, $^2J_{PC}$ = 19.5 Hz), 134.66 (s, C2), 130.15 (d, C3a, $^3J_{PC}$ = 4.2 Hz), 122.90 (s, aryl), 120.89 (s, aryl), 119.37 (s, aryl), 112.70 (d, C7, $^3J_{PC}$ = 6.2 Hz), 111.02 (s, C3), 31.58 (s, CH), 8.51 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ 22.3 (s). MS (EI) *m*/*z* (assignment, relative intensity): 431 (M^+, 100), 416 (M^+ − CH_3, 11), 400 (M^+ − P, 7), 301 (M^+ − C_9H_8N, 25). HRMS (EI) *m*/*z* for $C_{28}H_{22}N_3P$ (M^+): calcd 431.1551; found 431.1548. Anal. Calcd for $C_{28}H_{22}N_3P$: C, 77.94; H, 5.14; N, 9.74. Found: C, 77.54; H, 5.06; N, 9.67.

Preparation of Tri(*N*-3-methylindolyl)phosphine (3). 3-Methylindole (5.0 g, 38.1 mmol) was placed in a 250 mL three-neck flask. The flask was charged with 40 mL of THF and 10 mL of hexanes. The resulting clear, colorless solution was cooled to −78 °C, and ^{n}BuLi (1.6M hexane solution) (24 mL, 38.4 mmol) was added via syringe. A white precipitate

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formed immediately. The mixture was warmed to room temperature and stirred for 15 min, then cooled to −20 °C, and 1.2 mL of PCl_3 (1.89 g, 13.7 mmol) was added via syringe. The mixture was allowed to warm to room temperature and then refluxed for 5 h. The solution was cooled to room temperature and filtered through Celite to remove precipitated solids, which were washed with THF (2 × 10 mL). The combined filtrates were taken to dryness in vacuo. The residue was dissolved in toluene and filtered to remove any remaining LiCl. The solvent was removed from the filtrate in vacuo. The residue was then recrystallized from THF/hexanes at −25 °C. The white fibrous solid was isolated by filtration, washed with cold hexanes, and dried in vacuo. Yield: 3.30 g, 7.83 mmol, 62%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57−7.52 (m, 6H, aryl), 7.24−7.18 (m, 6H, aryl), 6.80 (m, 3H, CH), 2.25 (s, 9H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 139.53 (d, C7a, $^2J_{PC}$ = 20.3 Hz), 131.81 (d, C3a, $^3J_{PC}$ = 3.7 Hz), 124.16 (d, C2, $^2J_{PC}$ = 1.7 Hz), 123.22 (s, aryl), 121.34 (s, aryl), 119.31 (s, aryl), 117.43 (s, C3), 111.78 (d, C7, $^3J_{PC}$ = 15.4 Hz), 9.89 (s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ 64.8 (s). MS (EI) *m/z* (assignment, relative intensity): 421 (M^+, 23), 291 ($M^+ - C_9H_8N$, 100), 161 ($M^+ - 2C_9H_8N$, 7), 130 ($M^+ - 2C_9H_8N - P$, 31). HRMS (EI) *m/z* for $C_{27}H_{24}N_3P$ (M^+): calcd 421.1709; found 421.1708. Anal. Calcd for $C_{27}H_{24}N_3P$: C, 76.94; H, 5.74; N, 9.97. Found: C, 76.27; H, 5.88; N, 9.59.

Preparation of Phosphatri(3-methylindolyl)methane Oxide (4). To a solution of **2** (0.50 g, 1.16 mmol) in 15 mL of toluene was added ^{t}BuOOH (0.6 mL of 2.5−3.0 M solution in decane, approximately 1.5 equiv). The resulting solution became black in color and was stirred at room temperature for 110 h. The solvents and volatiles were removed in vacuo, yielding a dark gray residue. The residue was dissolved in CH_2Cl_2 and purified by chromatography on a silica gel column (7 cm × 2 cm). The isolated white solid was recrystallized from hot toluene by addition of methanol. The white crystalline solid was isolated by filtration, washed with cold methanol (2 × 5 mL) and cold hexanes (2 × 5 mL), and dried in vacuo. Yield (as **4**·0.5C_7H_8): 0.25 g, 0.56 mmol, 48%. IR ($\nu_{P=O}$, cm^{-1}): 1319 (CH_2Cl_2); 1314 (KBr). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, 3H, H7, $^3J_{HH}$ = 8 Hz), 7.41 (d, 3H, H4, $^3J_{HH}$ = 8 Hz), 7.27 (t, 3H, H6, $^3J_{HH}$ = 8 Hz), 7.17 (t, 3H, H5, $^3J_{HH}$ = 8 Hz), 5.85 (s, 1H, CH), 2.38 (s, 9H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 136.23 (d, C7a, $^2J_{PC}$ = 3.7 Hz), 134.57 (d, C2, $^2J_{PC}$ = 3.7 Hz), 129.96 (d, C3a, $^3J_{PC}$ = 11.2 Hz), 124.18 (s, aryl), 122.06 (s, aryl), 119.46 (s, aryl), 112.70 (s, C7), 111.02 (d, C3, $^3J_{PC}$ = 6.1 Hz), 31.35 (d, CH, $^3J_{PC}$ = 4.5 Hz), 8.60 (s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ −11.4 (s). MS (EI) *m/z* (assignment, relative intensity): 447 (M^+, 100), 432 ($M^+ - CH_3$, 32), 417 ($M^+ - 2CH_3$, 2), 384 ($M^+ - PO - CH_3 - H$, 6), 318 ($M^+ - C_9H_8N$, 2). HRMS (EI) *m/z* for $C_{28}H_{22}N_3OP$ (M^+): calcd 447.1501; found 447.1516. Anal. Calcd for $C_{28}H_{22}N_3OP$·0.5C_7H_8: C, 76.66; H, 5.31; N, 8.51. Found: C, 76.24; H, 5.24; N, 8.38.

Preparation of Phosphatri(3-methylindolyl)methane Sulfide (5). A solution of **2** (0.50 g, 1.16 mmol) and sulfur powder (0.60 g, 1.87 mmol) in 20 mL of xylenes was refluxed for 8 days. Solvent and volatiles were removed in vacuo, leaving a green solid residue, which was recrystallized in air three times from hot toluene by addition of methanol. The pale yellow crystalline solid was isolated by filtration, washed with cold methanol (2 × 5 mL) and cold hexanes (2 × 5 mL), and dried in air. Yield: 0.314 g, 0.677 mmol, 58%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.34 (d, 3H, H7, $^3J_{HH}$ = 8 Hz), 7.40 (d, 3H, H4, $^3J_{HH}$ = 8 Hz), 7.23 (t, 3H, H6, $^3J_{HH}$ = 8 Hz), 7.16 (t, 3H, H5, $^3J_{HH}$ = 8 Hz), 5.86 (s, 1H, CH), 2.38 (s, 9H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 137.10 (d, C7a, $^2J_{PC}$ = 5.8 Hz), 134.53 (s, C2), 130.23 (d, C3a, $^3J_{PC}$ = 10.8 Hz), 123.80 (s, aryl), 121.99 (s, aryl), 119.35 (s, aryl), 112.58 (s, C7), 109.79 (d, C3, $^3J_{PC}$ = 5.0 Hz), 31.01 (s, CH), 8.45 (s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ 21.5 (s). MS (EI) *m/z* (assignment, relative intensity): 463 (M^+, 100), 431 ($M^+ - S$, 33), 416 ($M^+ - S - CH_3$, 5), 400 ($M^+ - S - P$, 8), 301 ($M^+ - S - C_9H_8N$, 15). HRMS (EI) *m/z* for $C_{28}H_{22}N_3PS$ (M^+): calcd 463.1272; found 463.1263. Anal. Calcd for $C_{28}H_{22}N_3PS$: C, 72.55; H, 4.78; N, 9.06. Found: C, 71.87; H, 4.90; N, 9.01.

Preparation of Phosphatri(3-methylindolyl)methane Selenide (6). A solution of **2** (0.510 g, 1.18 mmol) and selenium powder (0.220 g, 2.79 mmol) in 20 mL of toluene was refluxed for 5 days. The reaction solution was filtered through Celite, and the solvent and volatiles were removed in vacuo from the pale yellow filtrate. The resulting residue was recrystallized in air three times from hot toluene by addition of methanol. The white crystalline product was isolated by filtration, washed with cold methanol (2 × 5 mL) and cold hexanes (2 × 5 mL), and dried in air. Yield: 0.358 g, 0.70 mmol, 59%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.56 (d, 3H, H7, $^3J_{HH}$ = 8 Hz), 7.40 (d, 3H, H4, $^3J_{HH}$ = 8 Hz), 7.23 (t, 3H, H6, $^3J_{HH}$ = 8 Hz), 7.17 (t, 3H, H5, $^3J_{HH}$ = 8 Hz), 5.89 (s, 1H, CH), 2.38 (s, 9H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 137.44 (d, C7a, $^2J_{PC}$ = 6.6 Hz), 134.62 (s, C2), 130.27 (d, C3a, $^3J_{PC}$ = 10.3 Hz), 123.63 (s, aryl), 122.06 (s, aryl), 119.28 (s, aryl), 112.54 (s, C7), 109.54 (d, C3, $^3J_{PC}$ = 4.9 Hz), 31.00 (s, CH), 8.37 (s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ 12.3 ($^1J_{PSe}$ = 1008 Hz). MS (EI) *m/z* (assignment, relative intensity): 511 (M^+, 22), 431 ($M^+ - Se$, 100), 416 ($M^+ - Se - CH_3$, 13), 400 ($M^+ - Se - P$, 8), 301 ($M^+ - Se - C_9H_8N$, 29). HRMS (EI) *m/z* for $C_{28}H_{22}N_3P^{80}Se$ (M^+): calcd 511.0716; found 511.0717. Anal. Calcd for $C_{28}H_{22}N_3PSe$: C, 65.89; H, 4.34; N, 8.23. Found: C, 65.91; H, 4.20; N, 8.13.

Preparation of Tri(*N*-3-methylindolyl)phosphine Selenide (7). A solution of **3** (0.500 g, 1.19 mmol) and selenium powder (0.235 g, 2.99 mmol) in 20 mL of toluene was refluxed for 18 h. The reaction solution was filtered through Celite, and the solvent and volatiles were removed in vacuo from the clear colorless filtrate. The resulting residue was recrystallized in air from toluene/hexanes at −25 °C. The light gray crystalline product was isolated by filtration, washed with cold hexanes (2 × 5 mL), and dried in vacuo. Yield: 0.501 g, 1.00 mmol, 84%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, 3H, H7, $^3J_{HH}$ = 8 Hz), 7.54 (d, 3H, H4, $^3J_{HH}$ = 8 Hz), 7.25 (t, 3H, H6, $^3J_{HH}$ = 8 Hz), 7.16 (t, 3H, H5, $^3J_{HH}$ = 8 Hz), 6.57 (dd, 3H, CH, $^4J_{HH}$ = 0.8 Hz, $^3J_{PH}$ = 4.0 Hz), 2.21 (d, 9H, CH_3, $^4J_{HH}$ = 0.8 Hz). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 137.56 (d, C7a, $^2J_{PC}$ = 5.0 Hz), 132.92 (d, C3a, $^3J_{PC}$ = 8.2 Hz), 124.87 (d, C2, $^2J_{PC}$ = 5.8 Hz), 124.02 (s, aryl), 122.68 (s, aryl), 119.45 (s, aryl), 117.99 (d, C3, $^3J_{PC}$ = 7.8 Hz), 114.88 (s, C7), 9.66 (s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ 28.2 ($^1J_{PSe}$ = 943 Hz). MS (EI) *m/z* (assignment, relative intensity): 501 (M^+, 16), 421 ($M^+ -$ Se, 14), 371 ($M^+ - C_9H_8N$, 5), 291 ($M^+ - Se - C_9H_8N$, 100), 240 ($M^+ - 2C_9H_8N$, 18), 161 ($M^+ - Se - 2C_9H_8N$, 9), 130 ($M^+ - Se - 2C_9H_8N - P$, 97). HRMS (EI) *m/z* for $C_{27}H_{24}N_3P^{80}Se$ (M^+): calcd 501.0873; found 501.0878. Anal. Calcd for $C_{27}H_{24}N_3PSe$: C, 64.80; H, 4.83; N, 8.40. Found: C, 64.95; H, 4.81; N, 8.21.

Preparation of Tri(*N*-pyrrolyl)phosphine Selenide (8). A solution of tri(*N*-pyrrolyl)phosphine (0.500 g, 2.18 mmol) and selenium powder (0.430 g, 5.45 mmol) in 20 mL of toluene was heated to 75 °C for 19 h. The reaction solution was filtered through Celite, and the solvent and volatiles were removed in vacuo from the clear colorless filtrate. The resulting residue was recrystallized in air from pentane at −25 °C. The white crystalline product was isolated by filtration, washed with cold pentane (2 × 5 mL), and dried in air. Yield: 0.466 g, 1.51 mmol, 69%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.79 (m, 6H, Hα), 6.39 (m, 6H, Hβ). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 123.65 (d, Cα, $^2J_{PC}$ = 6.6 Hz), 114.24 (d, Cβ, $^3J_{PC}$ = 9.9 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 MHz): δ 43.0 ($^1J_{PSe}$ = 970 Hz). MS (EI) *m/z* (assignment, relative intensity): 309 (M^+, 67), 229 ($M^+ -$ Se, 20), 177 ($M^+ - 2C_4H_4N$, 18), 162 ($M^+ - Se - C_4H_4N$, 100), 111 ($M^+ - 3C_4H_4N$, 35), 97 ($M^+ - Se - 2C_4H_4N$, 13). HRMS (EI) *m/z* for $C_{12}H_{12}N_3P^{80}Se$ (M^+): calcd 308.9934; found

308.9925. Anal. Calcd for $C_{12}H_{12}N_3PSe$: C, 46.77; H, 3.92; N, 13.64. Found: C, 46.80; H, 3.89; N, 13.54.

Preparation of Rh(acac)(CO)(2) (9). A solution of Rh(acac)$(CO)_2$ (0.100 g, 0.387 mmol) and **2** (0.167 g, 0.387 mmol) in 12 mL of THF was refluxed for 5 h. During reflux, a slow stream of N_2 was passed through the yellow-orange solution to remove displaced CO from the reaction flask. After cooling, the reaction solution was filtered and the solvent was removed in vacuo. The crude product was recrystallized from a toluene/methanol (1/2 v/v) solution by cooling to −25 °C overnight. The precipitated yellow solid was isolated by filtration and washed with cold hexanes (3 × 5 mL). Yield: 0.182 g, 0.275 mmol, 71%. IR (ν_{CO}, cm^{-1}): 2024 (CH_2Cl_2); 2020 (KBr). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.96 (d, 3H, H7, $^3J_{HH}$ = 8 Hz), 7.40 (d, 3H, H4, $^3J_{HH}$ = 8 Hz), 7.19 (t, 3H, H6, $^3J_{HH}$ = 8 Hz), 7.13 (t, 3H, H5, $^3J_{HH}$ = 8 Hz), 5.91 (s, 1H, CH), 5.84 (s, 1H, CH), 2.39 (s, 9H, CH_3), 2.35 (s, 3H, CH_3), 2.03 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 188.02 (s, C═O), 186.12 (s, C═O), 185.33 (dd, Rh−CO, $^1J_{RhC}$ = 71.4 Hz, $^2J_{PC}$ = 33.6 Hz), 137.66 (d, C7a, $^2J_{PC}$ = 10.8 Hz), 135.26 (s, C2), 130.37 (d, C3a, $^3J_{PC}$ = 7.8 Hz), 122.63 (s, aryl), 121.38 (s, aryl), 118.91 (s, aryl), 114.03 (d, C7, $^3J_{PC}$ = 2.1 Hz), 109.15 (d, C3, $^3J_{PC}$ = 2.5 Hz), 102.05 (d, CH, $^4J_{PC}$ = 2.1 Hz), 31.23 (d, CH, $^3J_{PC}$ = 2.5 Hz), 27.48 (d, CH_3, $^4J_{PC}$ = 7.0 Hz), 26.88 (s, CH_3), 8.36 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ 65.9 (d, $^1J_{RhP}$ = 242.7 Hz). Anal. Calcd for $C_{34}H_{29}N_3O_3PRh$: C, 61.73; H, 4.42; N, 6.35. Found: C, 61.14; H, 4.57; N, 6.19.

Preparation of Rh(acac)(CO)(3) (10). To a solution of Rh(acac)$(CO)_2$ (0.065 g, 0.252 mmol) in 10 mL of THF was added **3** (0.106 g, 0.251 mmol). The yellow solution was stirred at room temperature for 1 h. The solvent was removed in vacuo. The crude product was recrystallized from hexanes by cooling to −25 °C overnight. The precipitated yellow solid was isolated by decantation of the supernatant solution and washed with cold hexanes (3 × 3 mL). Yield: 0.151 g, 0.231 mmol, 92%. IR (ν_{CO}, cm^{-1}): 2005 (CH_2Cl_2); 2004, 1989 (KBr). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, 3H, H7, $^3J_{HH}$ = 8 Hz), 7.51 (d, 3H, H4, $^3J_{HH}$ = 8 Hz), 7.19 (d, 3H, H2, $^3J_{PH}$ = 4 Hz), 7.16 (t, 3H, H6, $^3J_{HH}$ = 8 Hz), 7.03 (t, 3H, H5, $^3J_{HH}$ = 8 Hz), 5.37 (s, 1H, CH), 2.25 (s, 9H, CH_3), 2.06 (s, 3H, CH_3), 1.05 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 187.32 (s, C═O), 186.34 (s, C═O), 186.26 (dd, Rh−CO, $^1J_{RhC}$ = 75.3 Hz, $^2J_{PC}$ = 30.5 Hz), 138.84 (d, C7a, $^2J_{PC}$ = 5.0 Hz), 132.42 (d, C3a, $^3J_{PC}$ = 5.7 Hz), 125.73 (d, C2, $^2J_{PC}$ = 8.8 Hz), 123.30 (s, aryl), 121.85 (s, aryl), 119.10 (s, aryl), 117.21 (d, C3, $^3J_{PC}$ = 7.1 Hz), 114.55 (d, C7, $^3J_{PC}$ = 3.3 Hz), 101.08 (s, CH), 27.37 (d, CH_3, $^4J_{PC}$ = 7.8 Hz), 25.37 (s, CH_3), 9.79 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ 97.4 (d, $^1J_{RhP}$ = 248.0 Hz). Anal. Calcd for $C_{34}H_{29}N_3O_3PRh$: C, 60.84; H, 4.80; N, 6.45. Found: C, 60.81; H, 4.85; N, 6.30.

Reaction of 2 and 3 with Methyl Iodide. Compound **2** (0.500 g, 1.16 mmol) and **3** (0.500 g, 1.16 mmol) were dissolved in 12 mL of toluene in separate Schlenk flasks. To each solution was added methyl iodide (0.4 mL, 6.43 mmol) via syringe. The reaction solutions were stirred at room temperature for 2 days. No precipitate formed in either reaction during this time. The solvent and volatiles were removed in vacuo, and the remaining white solid residues were identified as unreacted **2** and **3**, respectively, by ^1H and ^{31}P NMR spectroscopy.

Reaction of 2 and 3 with Methanol. Approximately 10 mg each of **2** and **3** were dissolved in $CDCl_3$ in separate NMR tubes, followed by addition of 2 drops of wet methanol to each solution. The NMR tubes were allowed to stand at room temperature and monitored by ^1H and ^{31}P NMR spectroscopy over a period of 5 days. During this time, **2** and **3** were unchanged.

Crystallographic Analyses. Crystals of **2** suitable for X-ray diffraction analysis were grown from a 1/1 hexane/dichloromethane solvent mixture by slow evaporation at room temperature. Crystals of **9** were grown from a 1/1 methanol/toluene solution at 0 °C. Preliminary examination and data collection were carried out at room temperature for **2** and **9** on a Siemens SMART Platform diffractometer. Intensity data were collected using 0.3° ω-scans at three different ϕ-settings corresponding to a nominal sphere of data. The intensities of the reflections were corrected for absorption and decay (SADABS).[21] Equivalent reflections were averaged, and all unique data were used for additional calculations. The structures were solved by Patterson synthesis (SHELXS-86)[22] for **9** and by direct methods (SHELXS-86)[22] for **2**. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares on F^2 using all unique data (SHELXL-93).[23] The hydrogen atoms in **2** were located and refined with isotropic thermal parameters. The hydrogen atoms in **9** were included with idealized geometry. Crystallographic data are summarized in Table 1.

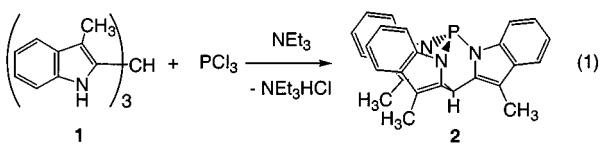
Table 1. Crystal Data and Structure Refinement Details for 2 and 9

	2	**9**
formula	$C_{28}H_{22}N_3P$	$C_{34}H_{29}N_3O_3PRh$
fw	431.46	661.48
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a, Å	12.2880(6)	15.5613(7)
b, Å	11.0127(4)	11.7666(6)
c, Å	17.4327(8)	17.4200(7)
β, deg	99.3520(10)	110.073(2)
V, Å^3	2327.71(18)	2995.9(2)
Z	4	4
D_{calcd}, g cm^{-3}	1.231	1.467
temp, °C	20(2)	20(2)
μ, mm^{-1}	0.138	0.356
λ, Å	0.71073	0.56087
transm coeff	0.720−0.992	0.414−0.997
2θ limits, deg	4.4−60.1	2.2−40.0
total no. of data	16 890	19 363
no. of unique data	6163	5676
no. of obsd data	3785	3450
no. of params	377	379
$R_1{}^a$ (F, $I > 2\sigma(I)$)	0.0464	0.0476
$wR_2{}^b$ (F^2, all data)	0.1319	0.1254
max, min peaks, e/Å^3	0.170, −0.241	0.445, −0.630

^{a} $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Results and Discussion

Synthesis, Characterization, and Chalcogenide Derivatives of 2 and 3. The constrained phosphine **2** was synthesized by reaction of tri(3-methylindolyl)methane (**1**) with PCl_3 in the presence of NEt_3 (eq 1), similar to the method used by Moloy and Petersen to synthesize P(N-pyrrolyl)$_3$.[3] Recrystallization from hot

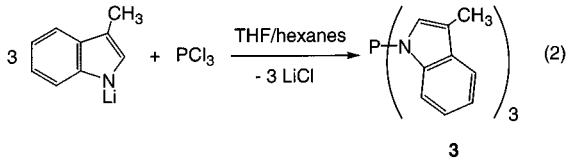


(1)

toluene and methanol gave **2** as a white crystalline solid in 58% yield. Attempts to synthesize the unconstrained tri(N-3-methylindolyl)phosphine (**3**) by the same method were not successful, but treatment of 3-methylindole with ^{n}BuLi in THF/hexanes, followed by addition of

(21) Sheldrick, G. M. *SADABS*; Absorption Correction Program; University of Göttingen: Göttingen, Germany, 1996.
(22) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(23) Sheldrick, G. M. *SHELXL-93*; Program for Refinement of Crystal Structures, University of Göttingen: Göttingen, Germany, 1993.

PCl_3, resulted in the desired phosphine in 62% yield (eq 2). P(*N*-indolyl)$_3$ was previously synthesized by Frenzel and co-workers in a similar manner from PF_3.[10] Compounds **2** and **3** have been characterized by mass spectrometry and NMR spectroscopy, as well as X-ray crystallography for **2**.



3

The ^{13}C NMR spectra of **2** and **3** provide valuable information for elucidating the structure of each phosphine. The magnitude of $^{31}P-^{13}C$ coupling constants is known to depend on the proximity of the coupled carbon atom to the phosphorus lone pair. Coupling is large when the carbon atom is close to the lone pair and small when the carbon atom is remote. This lone pair orientation effect is most obvious in rigid bicyclic phosphines such as phosphatriptycene[24] and 1,6-diphosphatriptycene.[25] The $^{31}P-^{13}C$ coupling constants of the rigid bicyclic phosphine **2** similarly exhibit lone pair orientation effects consistent with the constraint imposed by the tri(3-methylindolyl)methane framework. As expected, $^2J_{P-C7a}$ is large (19.5 Hz), while $^2J_{P-C2}$ is negligible (~0 Hz), and $^3J_{P-C7}$ (6.2 Hz) is larger than $^3J_{P-C3}$ (~0 Hz) and $^3J_{P-C3a}$ (4.2 Hz). Similar coupling effects have also been observed in ortho-substituted triphenylphosphines due to the steric interactions caused by the ortho substituents.[26] Thus, the steric interactions of the bulky 3-methylindolyl groups of the unconstrained phosphine **3** should result in $^{31}P-^{13}C$ coupling constants of a nature similar to that of **2**. This is indeed the case, with $^2J_{P-C7a}$ being large (20.3 Hz) compared with $^2J_{P-C2}$ (1.7 Hz), and $^3J_{P-C7}$ (15.4 Hz) is much larger than both $^3J_{P-C3}$ (~0 Hz) and $^3J_{P-C3a}$ (3.7 Hz). The coupling constants for **3** are very similar to those reported for P(*N*-indolyl)$_3$.[10]

^{31}P NMR data for **2** and **3** are also informative. The ^{31}P chemical shift of **2** (22.3 ppm) is shifted considerably upfield of that for **3** (64.8 ppm), P(*N*-indolyl)$_3$ (67.7 ppm), and P(*N*-pyrrolyl)$_3$ (79.6 ppm), due to the increased s character of the phosphorus lone pair that results from a decrease of the N−P−N angles upon constraint of the 3-methylindolyl substituents by the bridgehead methine group of **2**. A similar upfield shift has been found upon decreasing the size of the bridgehead atom, and thus the C−P−C angles, in the series 1,6-diphosphatriptycene (−43 ppm),[27] phosphatriptycene (−64 ppm),[25] and azaphosphatriptycene (−80 ppm)[28] when compared to their parent, PPh_3 (−8 ppm).

The molecular structure of **2** was further confirmed by X-ray crystallography. An ORTEP diagram of **2** is shown in Figure 1. Selected bond distances and angles are given in Table 2. The structure consists of a central bicyclic framework with the bridgehead phosphorus atom bonded to the nitrogen atoms of the 3-methylindolyl groups. The sum of the N−P−N angles of **2** is 285.3°, considerably less than the sum for P(*N*-pyrrolyl)$_3$ (301.2°)[6] and P(*N*-indolyl)$_3$ (299.8°),[10] though the sum is comparable to the sum of the C−P−C angles in the constrained aryl phosphines 3-*tert*-butyl-9,10-dihydro-9,10-*o*-benzeno-9-phosphaanthracene (284.9°)[29] and 1,6-diphosphatriptycene (290.9°).[30] The P−N bond distances in **2** average 1.708 Å, which is similar to the average P−N bond distances in P(*N*-pyrrolyl)$_3$ (1.696 Å),[6] P(*N*-indolyl)$_3$ (1.709 Å),[10] and P(*N*-pyrazolyl)$_3$ (1.714 Å).[31] The three 3-methylindolyl groups are planar within experimental error, but the molecule deviates from the expected pseudo 3-fold symmetry due to the slight rotation of one 3-methylindolyl group with respect to the bicyclic core framework. The rotation results in the N(3) methylindolyl group forming an angle of 12.3(1)° with the P(1)−N(3)−C(31)−C(1) plane. The rotation also results in an increased P(1)−N(3) bond distance of 1.7157(14) Å and a slight deviation in N(3) from the planarity expected for an sp^2-hybridized nitrogen atom, indicated by the sum of the angles around N(3) (357.5°). The sum of the angles around N(1) and N(2) are 360° and 359.8°, respectively. Interestingly, the phosphorus atom is contained in a pocket formed by the rigid tri(3-methylindolyl)methane framework. The phosphorus atom lies 0.750(1) Å below the plane defined by C(17)−C(27)−C(37).

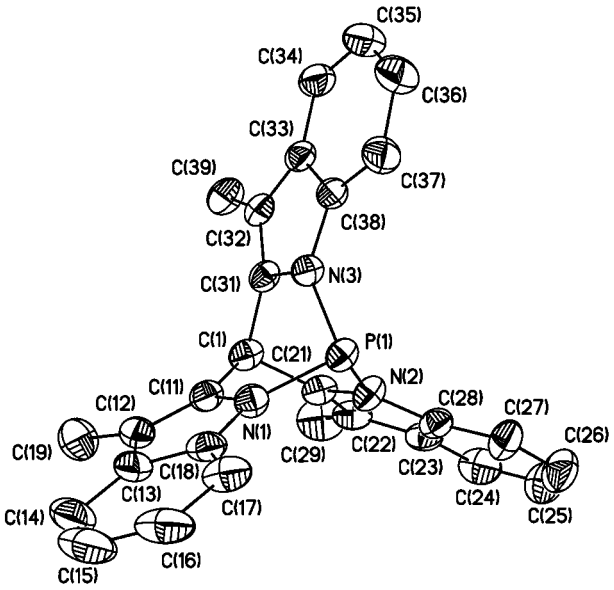


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2

distances		angles	
P(1)−N(1)	1.7055(16)	N(1)−P(1)−N(2)	95.01(7)
P(1)−N(2)	1.7041(14)	N(1)−P(1)−N(3)	94.62(7)
P(1)−N(3)	1.7157(14)	N(2)−P(1)−N(3)	95.67(7)

(24) Jongsma, C.; de Kleijn, J. P.; Bickelhaupt, F. *Tetrahedron* **1974**, *30*, 3465.
(25) Sørensen, S.; Jakobsen, H. J. *Org. Magn. Reson.* **1977**, *9*, 101.
(26) Sørensen, S.; Hansen, R. S.; Jakobsen, H. J. *J. Am. Chem. Soc.* **1972**, *94*, 5900.
(27) Weinberg, K. G.; Whipple, E. B. *J. Am. Chem. Soc.* **1971**, *93*, 1801.
(28) Hellwinkel, D.; Schenk, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 987.
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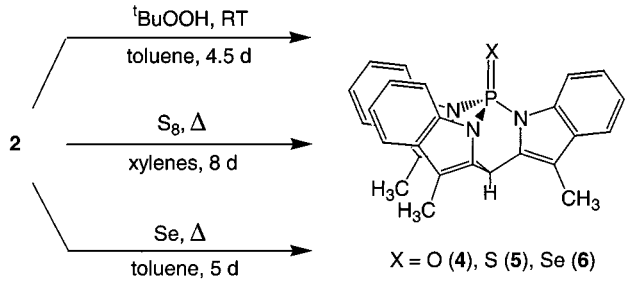
(30) Schomburg, D.; Sheldrick, W. S. *Acta Crystallogr.* **1975**, *B31*, 2427.
(31) Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr.* **1975**, *B31*, 2731.

Scheme 1

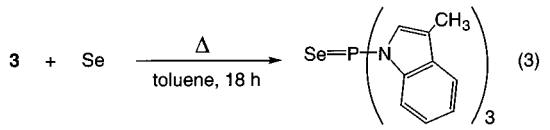


Both **2** and **3** are stable to aerial oxidation, and the P−N bonds are stable to moisture and methanol. In fact, attempts to dissolve **2** or **3** in refluxing methanol or ethanol were unsuccessful and did not result in any reaction of **2** or **3** with the alcohol as indicated by ^{1}H and ^{31}P NMR spectroscopy. In addition, reaction with CH_3I did not result in the formation of the corresponding phosphonium salt, indicative of the reduced σ-basicity of both phosphines. The same stability and lack of reactivity with CH_3I was found for P(*N*-pyrrolyl)$_3$.[5] In addition, **2** was unchanged after an attempted vacuum sublimation at 150 °C, attesting to its thermal stability.

Although **2** is not prone to aerial oxidation, it is oxidized by ^{t}BuOOH, S_8, or Se powder over long reaction times and at high temperatures to give the chalcogenide derivatives **4**−**6** in yields of 48, 58, and 59%, respectively (Scheme 1). The harsh conditions required for these oxidations may be attributed at least in part to the rigid steric bulk of the constrained tri(3-methylindolyl)-methane framework. The compositions of **4**−**6** were confirmed by elemental analysis and high-resolution mass spectrometry. NMR and IR spectroscopy confirmed the atom connectivity. Most notably, the ^{1}H NMR spectra of **4**−**6** are similar to that for **2** except that the doublet at 7.64 ppm assigned to H7 in **2** becomes progressively deshielded for **4** (7.92 ppm), **5** (8.34 ppm), and **6** (8.56 ppm) with increasing size of the chalcogenide atom. The IR spectrum of **4** shows $\nu_{P=O}$ at 1319 cm^{-1}, which compares well to that of the constrained amino phosphoryl compound O=P(CH_3NCH_2)$_3$CCH_3 (1285 cm^{-1})[16] and the constrained phosphate ester O=P(OCH_2)$_3$C(*n*-pentyl) (1327 cm^{-1}).[18] The high stretching frequencies of P=O in these constrained compounds can result from an augmentation of P=O π-bonding due to an increase in the positive charge on the phosphorus atom as a result of the imposed constraint of the molecules.[18] Additionally, **4** has been characterized crystallographically, confirming the structure of **4** to be similar to **2**, but solvent disorder and high residuals do not permit a discussion of bond distances and angles.[32]

Electronic Properties of 2 and 3. Lack of reactivity of **2** and **3** with CH_3I suggests that these new phosphines are poor σ-bases and probably good π-acceptors as anticipated by the P(*N*-pyrrolyl)$_3$ precedent. Electronic properties and the effects of constraint by the tri(3-methylindolyl)methane fragment were further assessed in a qualitative fashion by comparison of $^1J_{P-Se}$ and ν_{CO} values for a series of phosphine selenides and Rh(acac)(CO)(PR_3) complexes, respectively. The magnitude of the ^{31}P−^{77}Se coupling constant in selenophosphates and phosphine selenides provides a measure of σ-basicity of the parent phosphites and phosphines through an inverse relationship between σ-basicity and the value of $^1J_{P-Se}$. Previous work by Verkade and coworkers has demonstrated a decrease in σ-basicity, as indicated by increasing values of $^1J_{P-Se}$, with increasing geometrical constraint for a series of phosphites.[14] Reduced σ-basicity was also observed for P(CH_3NCH_2)$_3$-CCH_3 in comparison with the noncyclic tris(dimethylamino)phosphine, based again on ^{31}P−^{77}Se coupling constants of the respective selenide derivatives.[14]

The selenide derivatives of **3** and P(*N*-pyrrolyl)$_3$ were synthesized for comparison of their $^1J_{P-Se}$ values with that for **6**. Reactions of **3** and P(*N*-pyrrolyl)$_3$ with excess Se powder in refluxing toluene gave **7** (eq 3) and Se=P(*N*-pyrrolyl)$_3$ (**8**) in yields of 84% and 69%, respectively.



7

The structures and compositions of **7** and **8** were confirmed by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P), high-resolution mass spectrometry, and elemental analysis. Of particular interest is the magnitude of the ^{31}P−^{77}Se coupling in the ^{31}P NMR spectra of **6**−**8**, which decreases in the order **6** > **8** > **7**. The larger $^1J_{P-Se}$ value for **6** (1008 Hz) than for **7** (943 Hz) is consistent with decreased σ-basicity of **2** upon constraint of the 3-methylindolyl substituents. Larger ^{31}P−^{77}Se coupling for **8** (970 Hz) than for **7** is as expected since the pyrrolyl group is a slightly better electron-withdrawing substituent than is the indolyl group. Further comparison shows the ^{31}P−^{77}Se coupling constants for **6**−**8** are slightly less than those for Se=P(OPh)$_3$ ($^1J_{P-Se}$ = 1025 Hz)[33] and several constrained selenophosphates, and considerably larger than those for triaminophosphine selenides (784−854 Hz; Table 3).[14,33−37] Thus, **2**, **3**, and P(*N*-pyrrolyl)$_3$ are slightly more basic than triphenyl phosphite and constrained phosphites and less basic than triaminophosphines based on this measure of σ-basicity. The selenide derivative of P(*N*-indolyl)$_3$ has not been reported, so the basicity of this phosphine cannot be compared by this measure, but its ^{31}P−^{77}Se coupling constant is expected to be similar to that of **7**.

Electronic properties were also assessed by using ν_{CO} data for a series of Rh(acac)(CO)(L) complexes. Given the steric bulk of **2**, we sought to compare IR data for monosubstituted complexes rather than the disubstituted RhCl(CO)(PR_3)$_2$ complexes studied by Moloy and

(32) Crystal data for **4**: $C_{28}H_{22}N_3OP\cdot CH_2Cl_2$, monoclinic, *Cc* (No. 9), a = 16.454(2) Å, b = 15.1066(17) Å, c = 22.0460(8) Å, β = 107.982(7)°, V = 5212.2(9) Å^3, Z = 8, D_{calc} = 1.246 g/cm^3, T = 20 °C. Of 15 011 data collected (maximum 2θ = 52°, Mo Kα, μ = 0.233 mm^{-1}), 6988 were unique. The final residuals for 681 parameters refined against 4829 unique data with $I > 2\sigma(I)$ were R_1 = 0.0682 and wR_2 = 0.2338 (all data).

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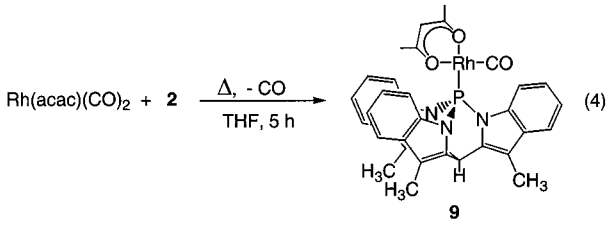
Table 3. $^{31}P-^{77}Se$ Coupling Constants for Selenophosphates and Phosphine Selenides

	$^1J_{31P-77Se}$ (Hz)	reference
Se=P(OCH$_2$)$_2$COMe	1099	14
Se=P(OCH$_2$)(O(CH$_2$)$_2$CHO)	1058	34
Se=P(OCH$_2$)$_3$CCH$_3$	1053	14
Se=P(OCH$_2$)(O(CH$_2$)$_3$CHO)	1046	35
Se=P(OPh)$_3$	1025	33
Se=P(OCH$_2$CH$_2$O)(OMe)	1011	14
6	1008	this work
8	970	this work
Se=P(OMe)$_3$	954	14
7	943	this work
Se=P(OEt)$_3$	935	36
Se=P(O^{n}Pr)$_3$	933	36
Se=P(NMeCH$_2$)$_3$CCH$_3$	854	14
Se=P(NMe$_2$)$_3$	784	14
Se=PPh$_3$	735	37

Petersen for P(*N*-pyrrolyl)$_3$.[3] Recently, Ziolkowski and co-workers reported the synthesis of monosubstituted Rh(acac)(CO){P(*N*-pyrrolyl)$_3$} from Rh(acac)(CO)$_2$.[9] Similarly, the reaction of **2** with Rh(acac)(CO)$_2$ resulted in the formation of Rh(acac)(CO)(**2**) (**9**), which was isolated in 71% yield (eq 4). As with the synthesis of chalcogenide



(4)

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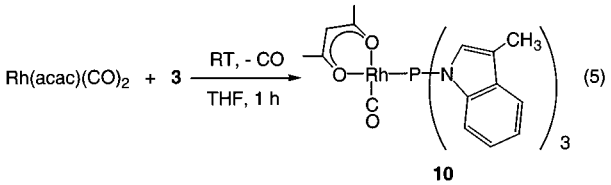
derivatives **4**−**6**, the reaction required forcing conditions. Substitution of one carbonyl ligand occurred only after 5 h in refluxing THF with a nitrogen purge to remove the liberated CO. Previously, for the bulky phosphines P(2-CH$_3$OC$_6$H$_4$)$_3$ and P{2,4,6-(CH$_3$O)$_3$C$_6$H$_2$}$_3$, refluxing hexane was required to form the respective Rh(acac)(CO){P(2-CH$_3$OC$_6$H$_4$)$_3$} and Rh(acac)(CO){P(2,4,6-(CH$_3$O)$_3$C$_6$H$_2$)$_3$} complexes.[38] The vigorous conditions required for substitution of one carbonyl ligand of Rh(acac)(CO)$_2$ by sterically hindered phosphorus ligands are in contrast to facile substitution at room temperature for less sterically hindered phosphines. In fact, the unconstrained phosphine **3** reacts with Rh(acac)(CO)$_2$ in THF at room temperature to form Rh(acac)(CO)(**3**) (**10**) in 91% yield (eq 5). Thus, the lack of a bridgehead methine group in **3** allows rotation of the 3-methylindolyl groups about the P−N bonds, therefore reducing the steric bulk of **3**.



(5)

10

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Table 4. Carbonyl Stretching Frequencies for Rh(acac)(CO)L Complexes

L	ν_{CO} (cm^{-1}) (CH$_2$Cl$_2$)	reference
2	2024	this work
P(NC$_4$H$_4$)$_3$	2012	39
P(OPh)$_3$	2008	39
3	2005	this work
PPh(NC$_4$H$_4$)$_2$	2002	39
P(OCH$_2$CH$_2$O)(OEt)	1996	40
PPh$_2$(NC$_4$H$_4$)	1990	39
P(*p*-CF$_3$C$_6$H$_4$)$_3$	1986	39
P(OCH$_2$CH$_2$O)(NEt$_2$)	1982	40
P(*p*-FC$_6$H$_4$)$_3$	1980	39
PPh$_3$	1978	39
P(OCH$_2$CH$_2$NEt)(NEt$_2$)	1974	40

The strong π-acceptor properties of **2** and **3** are suggested by comparing the solution IR spectra of **9** and **10** with those for a series of analogous monosubstituted Rh(acac)(CO)L complexes (Table 4).[39,40] The ν_{CO} value of 2024 cm^{-1} for **9** is much higher than for L = P(OPh)$_3$ (2008 cm^{-1})[39] and L = P(*N*-pyrrolyl)$_3$ (2012 cm^{-1}),[39] indicating **2** is a stronger π-acceptor than both P(OPh)$_3$ and P(*N*-pyrrolyl)$_3$. The ν_{CO} value for **10** (2005 cm^{-1}) is less than that of **9**, as expected due to the absence of substituent constraint in **3**, but is comparable to that of Rh(acac)(CO){P(OPh)$_3$}. This comparison suggests that **3** has similar π-acceptor properties to P(OPh)$_3$.

Solid-state IR data (KBr) are in good agreement with the solution IR data. The carbonyl stretch for **9** (2020 cm^{-1}) occurs at higher frequency than do the carbonyl stretches reported for Rh(acac)(CO){P(*N*-pyrrolyl)$_3$} (2012 cm^{-1})[9] and Rh(acac)(CO){P(OPh)$_3$} (2006 cm^{-1}).[41] Interestingly, the solid-state IR spectrum of **10** shows two carbonyl stretches at 2004 and 1989 cm^{-1}. This was surprising, as the NMR spectra of **10** indicate only one species to be present. A similar result was reported by Roodt et al. for Rh(acac)(CO)PPh$_2$Fc (PPh$_2$Fc = ferrocenyldiphenylphosphine), for which the solid-state IR spectrum also displayed two peaks.[42] Solution of the molecular structure by X-ray crystallography revealed two independent molecules with slightly different Rh−C−O angles. The solid-state IR data was attributed to electronic factors induced by packing effects.[42] A similar situation may exist for **10**, and efforts are underway to structurally characterize **10** by X-ray crystallography.

Molecular Structure of 9. Steric and electronic properties of **2** were further assessed from the molecular structure of **9** as determined by X-ray crystallography (Figure 2, Table 5). Compound **9** is comprised of an approximately square planar Rh atom ligated by **2**, a carbonyl, and a chelating acac ligand. The Rh(1) atom deviates only slightly from the expected square planar geometry, lying 0.074(2) Å out of the plane defined by the atoms bonded to it. The sum of the angles about Rh(1) is 359.8°. The Rh(1)−P(1) bond distance of 2.1783(12) Å is slightly greater than that found in Rh(acac)-

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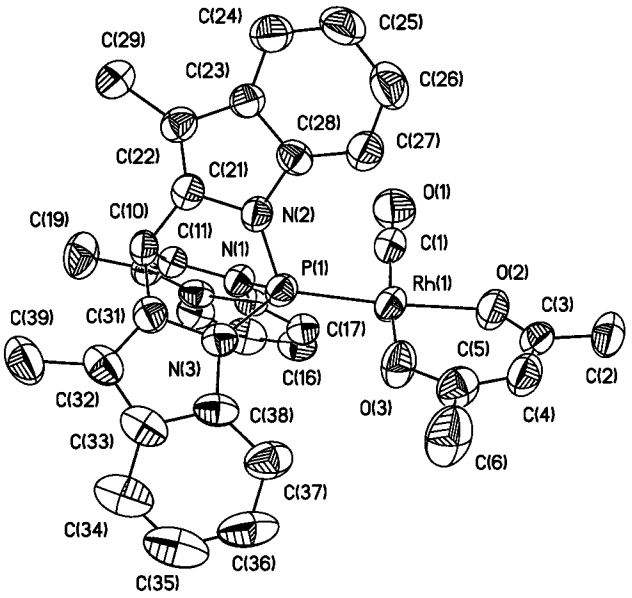

Figure 2. ORTEP drawing of **9**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) for 9

	Distances		
Rh(1)−P(1)	2.1783(12)	Rh(1)−O(2)	2.043(3)
Rh(1)−O(3)	2.015(3)	Rh(1)−C(1)	1.847(6)
P(1)−N(1)	1.725(4)	P(1)−N(2)	1.705(4)
P(1)−N(3)	1.710(4)	O(1)−C(1)	1.124(6)
	Angles		
P(1)−Rh(1)−O(2)	174.91(10)	P(1)−Rh(1)−O(3)	94.71(9)
P(1)−Rh(1)−C(1)	88.34(14)	O(2)−Rh(1)−O(3)	89.95(12)
O(2)−Rh(1)−C(1)	86.79(16)	O(3)−Rh(1)−C(1)	172.42(19)
Rh(1)−P(1)−N(1)	119.55(13)	Rh(1)−P(1)−N(2)	113.48(12)
Rh(1)−P(1)−N(3)	128.36(14)	N(1)−P(1)−N(2)	97.59(18)
N(1)−P(1)−N(3)	96.32(18)	N(2)−P(1)−N(3)	95.24(18)
Rh(1)−C(1)−O(1)	174.6(5)		

(CO){P(OPh)$_3$} (2.170(1) Å),[43] Rh(acac)(CO){P(*N*-pyrrolyl)$_3$} (2.166(1) Å),[9] Rh(acac)(CO){P(OCH$_2$CH$_2$O)(OEt)} (2.165(3) Å),[44] and Rh(acac){P(OPh)$_3$}$_2$ (2.147(2), 2.156(2) Å),[45] but much shorter than that observed for the phosphine complex Rh(acac)(CO)(PPh$_3$) (2.244(2) Å).[46] The shorter Rh−P bond distance for **9** than for Rh(acac)(CO)(PPh$_3$) reflects the stronger π-acceptor properties of ligand **2**, whereas the slightly greater Rh−P distance for **9** than for the corresponding P(OPh)$_3$ and P(*N*-pyrrolyl)$_3$ complexes is a manifestation of the greater steric demand of **2**. In support of this interpretation of the data, a cone angle of 191° was calculated for **2** using the method of Müller and Mingos[47] and the crystallographic data for **9**. Elongation of the Rh−O bond distance trans to **2** (2.043(3) Å) compared with that trans to CO (2.015(3) Å) indicates that **2** also has a greater trans influence than does CO. Similar Rh−O bond distances (2.054(2), 2.016(2) Å) were found for Rh(acac)(CO){P(*N*-pyrrolyl)$_3$},[9] but a much greater difference in Rh−O distances (2.087(4), 2.029(5) Å) was observed for Rh(acac)(CO)(PPh$_3$).[45] This suggests that the trans influence of **2** is less than that of PPh$_3$ and comparable to P(*N*-pyrrolyl)$_3$.

The rigid 3-fold framework and large cone angle of **2** have produced structural distortions in **9** due to steric interactions between **2** and the CO and acac ligands. The Rh(1)−C(1)−O(1) bond angle of 174.6(5)° deviates slightly from linearity, as the carbonyl ligand is bent away from the proximate N(1) methylindolyl group of **2**, with C(1)−C(17) and C(1)−C(18) distances of 3.161(7) and 3.378(6) Å, respectively. The O(1)−C(17) distance is 3.357(6) Å, with O(1) lying 0.180(7) Å above the P(1)−C(1)−O(2)−O(3) plane. The acac ligand is in close proximity to the N(3) methylindolyl group of **2**, with O(3) at a distance of 3.057(6) Å from C(37). This interaction results in a P(1)−Rh(1)−O(3) bond angle of 94.71(9)°. The corresponding angle in Rh(acac)(CO){P(*N*-pyrrolyl)$_3$} is 90.2(1)° due to the smaller steric demands of P(*N*-pyrrolyl)$_3$.[9] In addition, the planar acac ligand lies at an angle of 5.7(1)° from the P(1)−C(1)−O(2)−O(3) plane, away from the N(3) methylindolyl group. The sum of the N−P−N angles is 289.2° for **2** due to the opening of the N−P−N angles upon coordination to the Rh atom. The Rh−P−N bond angles indicate how **2** has adjusted to the square planar environment of the Rh atom. The Rh(1)−P(1)−N(2) angle of 113.48(12)° shows the N(2) methylindolyl group, almost perpendicular to the square plane, bent toward the Rh atom to minimize the interaction of the remaining methylindolyl arms with the acac and CO. The Rh(1)−P(1)−N(1) (119.55(13)°) and Rh(1)−P(1)−N(3) (128.36(14)°) angles demonstrate this adjustment, as does the movement of the N(3) methylindolyl group away from the larger acac ligand, placing the N(1) group closer to the smaller CO ligand. To further minimize interactions, both the N(1) and N(3) methylindolyl groups are bent with respect to the bicyclic framework of the phosphorus ligand. The N(1) methylindolyl group is bent 12.7(2)° from the P(1)−N(1)−C(11)−C(10) plane, away from the CO ligand, and the N(3) methylindolyl group is bent 10.0(2)° from the P(1)−N(3)−C(31)−C(10) plane, away from the acac ligand. Therefore, the two groups bend toward each other, decreasing the angle between them to 95.9(1)°. This also opens the angles of each with the N(2) methylindolyl group to 131.1(1)° and 131.9(1)°, respectively, to accommodate the square planar Rh(acac)(CO) unit. All these steric interactions result in an O(2)−Rh(1)−P(1)−C(10) torsion angle of 25.8(14)°.

Conclusions

The π-acidic phosphine phosphatri(3-methylindolyl)methane (**2**) and its unconstrained analogue tri(*N*-3-methylindolyl)phosphine (**3**) are easily synthesized in good yield from tri(3-methylindolyl)methane and 3-methylindole, respectively. In contrast with the P−O bonds of common phosphites, the P−N bonds of **2** and **3** are stable to hydrolysis and alcoholysis. These indolylphosphines are weak σ-bases comparable to alkyl phosphites and slightly stronger than the aryl phosphite P(OPh)$_3$. They are also exceptional π-acceptor ligands, with **2** being a more potent π-acid than P(OPh)$_3$ and P(*N*-pyrrolyl)$_3$, while **3** has π-acceptor properties similar

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to $P(OPh)_3$. Constraint of the N−P−N angles in **2** by the tri(3-methylindolyl)methane framework results in decreased σ-basicity and increased π-acidity compared with **3**. The constrained substituents have also greatly influenced the steric properties of **2**, which has an estimated cone angle of 191°. Studies to further assess the electronic and steric properties of rigid **2** and unconstrained **3** and their utility in coordination chemistry and catalytic applications are currently in progress.

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Supporting Information Available: Tables of crystal data and refinement details, positional and thermal parameters, complete bond distances and angles, and fully labeled ORTEP diagrams for **2**, **4**, and **9**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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