

Supplementary Information

Remarkably Stable Chelating Bis-*N*-Heterocyclic Carbene Adducts of Phosphorus(I) Cations

Justin F. Binder, Ala'aeddeen Swidan, Martin Tang, Jennifer H. Nguyen and Charles L.B.
Macdonald*

Department of Chemistry and Biochemistry, University of Windsor,

Windsor, Ontario, Canada N9B 3P4

General Remarks	S2
Synthetic Procedures	S2
Crystallographic Details	S8
Computational Information	S17
References	S37

General Remarks

All manipulations were carried out using standard inert atmosphere techniques. All chemicals and reagents were purchased from Sigma-Aldrich and used without further purification. Deuterated solvents were dried according to literature procedure when necessary, and all other solvents were dried over a series of Grubbs'-type columns and degassed prior to use.¹ Cyclic triphosphenium bromide $[(\text{dppe})\text{P}^{\text{I}}][\text{Br}]^2$ and 1,1'-dialkyl-3,3'-methylenediimidazolium bromide salts³ were synthesized according to literature procedures. NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz, Bruker Avance Ultrashield 300 MHz or Bruker Avance DPX 300 MHz spectrometers. Chemical shifts are reported in ppm relative to internal standards for ^1H and ^{13}C (the given deuterated solvent) and external standards for ^{11}B ($\text{BF}_3 \cdot \text{OEt}_2$), ^{19}F (CCl_3F) and ^{31}P (85% H_3PO_4). Coupling constants $|J|$ are given in Hz. Melting points were recorded on samples sealed in glass capillaries under dry N_2 using an Electrothermal[®] Melting Point Apparatus. HR-ESI-MS and EA were performed by the University of Windsor Mass Spectrometry Service Laboratory using Micromass LCT and Perkin Elmer 2400 combustion CHN analyzer. Cyclic voltammetry was performed in dry MeCN solutions using a $[\text{NBu}_4][\text{PF}_6]$ (0.1 M) electrolyte with analyte concentration of about 0.01 M. A glassy carbon electrode, a platinum wire, and an Ag/AgCl electrode were used as the working, auxiliary, and reference electrodes, respectively. The experiments were run with a scan rate of 100mV/s and a sensitivity of 100 $\mu\text{A}/\text{V}$ and the potentials reported are referenced to ferrocene/ferrocenium ($E_{1/2} = 0.0 \text{ V}$).

Synthetic Procedures

General synthesis of $[\text{R}^{\text{LP}}][\text{Br}]$

A solution of $[\text{K}][\text{N}(\text{SiMe}_3)_2]$ in THF (20 mL) is added to a suspension of an equimolar amount of the given imidazolium salt in THF (20 mL) at -78°C . After allowing the reaction mixture to warm to -30°C over a period of 30 minutes, the pale yellow solution is again cooled to -78°C and filtered cold. To the filtrate is added $[(\text{dppe})\text{P}][\text{Br}]$, and the mixture is allowed to slowly warm to room temperature. The resulting orange precipitate is filtered and washed with THF (3 x 20 mL) and dried under reduced pressure. Recrystallization by slow evaporation of acetonitrile yields crystals suitable for X-ray diffraction.

Alternative synthesis of [^RLP][Br]

The method described above can be altered to facilitate synthesis on larger scales. While the reaction is essentially quantitative by NMR spectroscopy, some product is lost during workup, giving slightly lower isolated yields (≈70-83%). Products from this preferred procedure have identical spectroscopic properties to those collected using the former procedure. A cold solution of [K][N(SiMe₃)₂] in THF is added to a suspension of an equimolar quantity of the given imidazolium salt in THF at -78 °C and allowed to stir for 2 hours at -78 °C. A cold suspension of [(dppe)P][Br] in THF is then added to the mixture at -78 °C and allowed to stir for an additional hour before being allowed to warm to room temperature. All volatiles are then removed under reduced pressure and acetonitrile is added to the resulting residue. The orange acetonitrile solution is then filtered through celite and pumped dry under reduced pressure. Toluene or diethyl ether is added to the residue and the mixture is sonicated to yield an orange suspension. The mixture is then filtered to collect the precipitated product, which is washed with toluene or diethyl ether and dried under reduced pressure.

Data for [^{Me}LP][Br]

Reagents: [K][N(SiMe₃)₂] (425 mg, 2.130 mmol); 1,1'-dimethyl-3,3'-methylenediimidazolium dibromide (300 mg, 0.887 mmol); [(dppe)P][Br] (450 mg, 0.883 mmol). **Yield:** 60% (152 mg, 0.529 mmol). **Mp:** 170°C (dec.). **³¹P{¹H} NMR (CDCl₃) δ:** -83.3 (s). **¹³C{¹H} NMR (CDCl₃) δ:** 34.97 (d, CH₃, ³J_{CP} = 11.3), 59.12 (s, NCH₂N), 119.93 (s, CH_{imid}), 122.65 (s, CH_{imid}), 160.94 (d, PCN, ¹J_{CP} = 76.9). **¹H NMR (CDCl₃) δ:** 3.61 (d, 6H, CH₃, ⁴J_{PH}), 6.66 (d, 2H, NCH₂N, ⁴J_{PH} = 0.9), 7.19 (m, CH_{imid}), 7.83 (m, CH_{imid}). **Elemental Analysis:** calcd. for C₉H₁₂N₄PBr: C, 37.65; H, 4.21; N, 19.52, found: C, 37.83; H, 4.32; N, 18.18. **HR-ESI-MS:** calcd. for C₉H₁₂N₄P [M - Br]⁺ m/z = 207.0800, found: 207.0802.

Data for [^{Bn}LP][Br]

Reagents: [K][N(SiMe₃)₂] (122 mg, 0.612 mmol); 1,1'-dibenzyl-3,3'-methylenediimidazolium dibromide (150 mg, 0.306 mmol); [(dppe)P][Br] (120 mg, 0.236 mmol). **Yield:** 97% (100 mg, 0.228 mmol). **Mp:** 205°C (dec.). **³¹P{¹H} NMR (CD₃CN) δ:** -81.8 (s). **¹³C{¹H} NMR (CD₃CN) δ:** 51.62 (d, ArCH₂N, ³J_{CP} = 10.9), 59.53 (s, NCH₂N), 119.72 (s, CH_{imid}), 122.31 (s, CH_{imid}), 128.01 (s, Ar), 128.66 (s, Ar), 129.04 (s, Ar), 134.63 (s, Ar), 161.04 (d, PCN, ¹J_{CP} = 75.9). **¹H NMR (CD₃CN) δ:** 5.07 (s, 4H,

ArCH₂N), 5.94 (s, 2H, NCH₂N), 7.30 (m, 10H, CH_{Ar}), 7.39 (s, CH_{imid}), 7.41 (s, CH_{imid}). **Elemental Analysis:** calcd. for C₂₁H₂₀N₄PBr: C, 57.41; H, 4.59; N, 12.75, found: C, 57.53; H, 4.75; N, 12.71. **HR-ESI-MS:** calcd. for C₂₁H₂₀N₄P [M – Br]⁺ *m/z* = 359.1425, found: 359.1423.

Data for [ⁿBuLP][Br]

Reagents: [K][N(SiMe₃)₂] (142 mg, 0.711 mmol); 1,1'-di-*n*-butyl-3,3'-methylenediimidazolium dibromide (150 mg, 0.355 mmol); [(dppe)P][Br] (153 mg, 0.300 mmol). **Yield:** 81% (90 mg, 0.242 mmol). **Mp:** 155°C (dec.). **³¹P{¹H} NMR (CD₃CN) δ:** -83.1 (s). **¹³C{¹H} NMR (CD₃CN) δ:** 13.77 (s, CH₃), 20.19 (s, CH₂CH₂CH₃), 31.59 (s, CH₂CH₂CH₂), 48.99 (d, NCH₂CH₂, ³J_{CP} = 10.4), 60.23 (s, NCH₂N), 120.27 (s, CH_{imid}), 122.88 (s, CH_{imid}), 161.38 (d, PCN, ¹J_{CP} = 75.6). **¹H NMR (CD₃CN) δ:** 0.93 (t, 6H, CH₃, ³J_{HH} = 7.5), 1.33 (tq, 4H, CH₂CH₂CH₃, ³J_{HH} = 7.5), 1.75 (p, 4H, CH₂CH₂CH₂, ³J_{HH} = 7.5), 3.87 (t, NCH₂CH₂, ³J_{HH} = 7.5), 5.99 (s, 2H, NCH₂N), 7.24 (s, CH_{imid}), 7.36 (s, CH_{imid}). **Elemental Analysis:** calcd. for C₁₅H₂₄N₄PBr: C, 48.53; H, 6.51; N, 15.09, found: C, 48.86; H, 6.39; N, 14.95. **HR-ESI-MS:** calcd. for C₁₅H₂₄N₄P [M – Br]⁺ *m/z* = 291.1739, found: 291.1736.

Synthesis of [^{Me}LP][OTf]

TMS-OTf (0.253 mL, 1.398 mmol) was added via syringe to a stirring suspension of [^{Me}LP][Br] (403 mg, 1.398 mmol) in toluene (40 mL). The solution immediately turned a darker colour, after which an oily orange solid crashed out. After ten minutes of further stirring, any volatiles were removed under reduced pressure yielding a light orange powder. Recrystallization by slow evaporation of dichloromethane yielded crystals suitable for X-ray diffraction. **Yield:** 86% (432 mg, 1.209 mmol). **³¹P{¹H} NMR (CD₃CN) δ:** -85.0 (s). **¹⁹F{¹H} NMR (CD₃CN) δ:** -79.45 (s, CF₃). **¹³C{¹H} NMR (CD₃CN) δ:** 35.74 (d, CH₃, ³J_{CP} = 12.7), 60.9 (d, CH₂, ³J_{CP} = 2.5), 120.22 (d, J_{CP} = 3.8), 122.46 (q, CF₃, ¹J_{CF} = 320.7), 124.46 (d, J_{CP} = 1.6), 162.21 (d, PCN, ¹J_{CP} = 73.3). **¹H NMR (CD₃CN) δ:** 3.52 (s, 6H, CH₃N), 5.86 (s, 2H, NCH₂N), 7.18 (m, CH_{imid}), 7.22 (m, CH_{imid}). **Elemental Analysis:** calcd. for C₁₀H₁₂F₃N₄O₃PS: C, 33.71; H, 3.40; N, 15.73, found: C, 33.45; H, 3.34; N, 13.56. **HR-ESI-MS:** calcd. for C₉H₁₂N₄P [M – OTf]⁺ *m/z* = 207.0800, found: 207.0798. **Cyclic Voltammetry:** *E_p(ox)* = +0.341 V

Synthesis of [^{Bn}LP][OTf]

TMS-OTf (0.062 mL, 0.341 mmol) was added via syringe to a stirring suspension of [^{Bn}LP][Br] (150 mg, 0.341 mmol) in toluene (20 mL). The solution immediately turned a darker colour, after which an oily orange solid crashed out. After ten minutes of further stirring, any volatiles were removed under reduced pressure yielding a light orange powder. **Yield:** 98% (171 mg, 0.336 mmol). **³¹P{¹H} NMR (CDCl₃) δ:** -81.2 (s). **¹⁹F{¹H} NMR (CDCl₃) δ:** -78.38 (s, CF₃). **¹³C{¹H} NMR (CDCl₃) δ:** 52.23(d, CH₂, ³J_{CP} = 10.8), 59.01 (d, CH₂, ³J_{CP} = 3.1), 120.06 (d, J_{CP} = 3.4), 120.73 (q, CF₃, ¹J_{CF} = 320.3), 121.95 (s, Ar), 128.41 (d, J_{CP} = 2.0), 129.113 (s, Ar), 129.30 (s, Ar), 133.43 (s, Ar), 160.92 (d, PCN, ¹J_{CP} = 77.6). **¹H NMR (CDCl₃) δ:** 5.01 (s, 4H, ArCH₂N), 6.20 (s, 2H, NCH₂N), 7.10 (m, CH_{imid}), 7.28-7.35 (m, 10H, Ar), 7.50 (m, CH_{imid}). **Elemental Analysis:** calcd. for C₂₁H₂₀N₄PSO₃F₃: C, 51.97; H, 3.96; N, 11.02, found: C, 52.8; H, 4.15; N, 10.83.

Synthesis of [^{Bn}LP][BPh₄]

A solution of [Na][BPh₄] (183 mg, 0.535 mmol) in THF (10 mL) was added to a stirring suspension of [^{Bn}LP][Br] (235 mg, 0.535 mmol) in THF (10 mL) and allowed to stir overnight. The mixture was then filtered through celite, and the filter-cake was washed with THF (2 x 5 mL). Removal of THF was done under reduced pressure, and the resulting residue was suspended in toluene (20 mL), collected by filtration, washed with toluene (3 x 5 mL) and dried under reduced pressure to yield the product. Recrystallization by slow evaporation of THF or dichloromethane yielded crystals suitable for X-ray diffraction. **Yield:** 98% (354 mg, 0.522 mmol). **³¹P{¹H} NMR (CD₂Cl₂) δ:** -81.9 (s). **¹³C{¹H} NMR (CD₂Cl₂) δ:** 52.29(d, CH₂, ³J_{CP} = 11.6), 58.59 (s, CH₂), 119.55 (d, J_{CP} = 3.5), 121.54 (s, Ar), 122.55(s, Ar), 126.28(d, J_{CP} = 2.6), 128.53 (s, Ar), 129.35 (s, Ar), 129.55 (s, Ar), 133.72 (s, Ar), 136.24(s, Ar), 160.81 (d, PCN, ¹J_{CP} = 76.5), 164.45 (q, BPh_{ipso}, ¹J_{CB} = 49.2). **¹¹B NMR (CD₂Cl₂) δ:** -6.15 (s). **¹H NMR (CD₂Cl₂) δ:** 4.07 (s, 2H, NCH₂N), 4.86 (s, 4H, ArCH₂N), 6.27 (m, CH_{imid}), 6.64 (m, CH_{imid}), 6.85(m, 4H, BPh₄), 7.00 (m, 8H, BPh₄), 7.24 (m, Ar), 7.44 (m, Ar), 7.46 (br, 8H, BPh₄). **Elemental Analysis:** calcd. for C₄₅H₄₀N₄PB: C, 79.65; H, 5.94; N, 8.26, found: C, 79.4; H, 6.21; N, 7.63. **HR-ESI-MS:** calcd. for C₂₁H₂₀N₄P [M – BPh₄]⁺ *m/z* = 359.1425, found: 359.1420.

Synthesis of $[\text{Au}(\text{MeLP})_2][\text{OTf}]_2[\text{Cl}]$

A solution of $[\text{MeLP}][\text{OTf}]$ (154 mg, 0.431 mmol) in dichloromethane (10 mL) was added to a suspension of AuCl (50 mg, 0.215 mmol) in dichloromethane (15 mL). The reaction mixture was stirred overnight, after which all volatiles were removed under reduced pressure. Acetonitrile (5 mL) was added to the residue, resulting in a yellow solution which was filtered. To the stirring filtrate was added dichloromethane (20 mL), which resulted in the formation of a yellow precipitate. This was collected by filtration, washed with dichloromethane (2 x 2 mL) and allowed to dry under reduced pressure. Recrystallization by slow evaporation of acetonitrile yielded colorless to yellow crystals suitable for X-ray diffraction. **Yield:** 35% (70 mg). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN) δ : -86.2 (s). $^{19}\text{F}\{^1\text{H}\}$ NMR (CD_3CN) δ : -79.46 (s, CF_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ : 36.80 (d, CH_3 , $^3J_{\text{CP}} = 11.7$), 61.28 (d, CH_2 , $^3J_{\text{CP}} = 3.4$), 122.44 (q, CF_3 , $^1J_{\text{CF}} = 320.8$), 122.81 (d, $J_{\text{CP}} = 3.1$), 125.79 (s), 154.42 (d, PCN, $^1J_{\text{CP}} = 56.1$). ^1H NMR (CD_3CN) δ : 3.71 (s, 6H, CH_3N), 6.17 (s, 2H, NCH_2N), 7.34 (m, CH_{imid}), 7.47 (m, CH_{imid}). **Elemental Analysis:** calcd. for $\text{C}_{20}\text{H}_{24}\text{AuClF}_6\text{N}_8\text{O}_6\text{P}_2\text{S}_2$: C, 25.42; H, 2.56; N, 11.86, found: C, 25.79; H, 2.31; N, 10.22. **HR-ESI-MS:** the tricationic complex was not observed but the ligand was confirmed; calcd. for $\text{C}_9\text{H}_{12}\text{N}_4\text{P}$ $m/z = 207.0800$, found: 207.0798.

When the reaction is done with a 1:1 ratio of $[\text{MeLP}][\text{OTf}]$ (150 mg, 0.420 mmol) to AuCl (98 mg, 0.422 mmol), ^1H and ^{13}C NMR spectra show a mixture of $[\text{Au}(\text{MeLP})_2][\text{OTf}]_2[\text{Cl}]$ and one other product in the crude material **Crude Yield:** 74% (184 mg collected) (the additional resonances are given but unassigned): $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN) δ : 37.77 (s), 124.54 (s), 127.58 (s). ^1H NMR (CD_3CN) δ : 4.15 (s), 7.63 (m), 7.78 (m).

Summary of NMR and IR Studies on Reactions of $[\text{MeLP}]^+$ salts with Rhodium Complexes

An orange solution of $[\text{MeLP}][\text{OTf}]$ (100 mg, 0.280 mmol) in acetonitrile (2 mL) was added to a yellow solution of $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})_2]$ (54 mg, 0.139 mmol) in acetonitrile (2 mL). The reaction mixture immediately turned dark brown. THF (15 mL) was added to the reaction mixture, and the brown precipitate was collected by filtration and washed with THF (2 x 2 mL). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the precipitate showed a broad resonance at -21.1 ppm along with minor peaks at -6.3 ppm and 4.3 ppm. The IR spectrum of the precipitate reveals a single broad absorption at 1992 cm^{-1} ; no other peaks are observed in the carbonyl region. These data suggest that $[\text{MeLP}]^+$ cations react with $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})_2]$ with the elimination of CO to produce either: centrosymmetric dimers of the form *trans*- $[(\text{MeLP})\text{Rh}(\text{CO})(\mu\text{-$

$\text{Cl})_2^{2+}$, solvent complexes of the form $[(^{\text{Me}}\text{LP})\text{Rh}(\text{CO})\text{Cl}(\text{solvent})]^{1+}$, or Vaska's-like complexes of the form $[(^{\text{Me}}\text{LP})_2\text{Rh}(\text{CO})\text{Cl}]^{2+}$. For the product isolated from the 2:1 reaction of $[(^{\text{Me}}\text{LP})][\text{OTf}]$ with $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})_2]$, microanalysis suggests that the product is indeed *trans*- $[(^{\text{Me}}\text{LP})\text{Rh}(\text{CO})(\mu\text{-Cl})_2][\text{OTf}]_2$ (calcd. for $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{F}_6\text{N}_8\text{O}_8\text{P}_2\text{Rh}_2\text{S}_2$: C, 25.28; H, 2.31; N, 10.72, found: C, 25.29; H, 2.24; N, 9.14.) The addition of excess $[(^{\text{Me}}\text{LP})][\text{OTf}]$ to that complex produces a brown solution with a very broad signal in the ^{31}P NMR signal at ca. -66 ppm but this complex appears to be very labile in solution and decomposes even in the solid state.

The addition $[(^{\text{Me}}\text{LP})][\text{OTf}]$ in acetonitrile to $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ results in no reaction as determined by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which features a broad resonance at around 30.6 ppm at 313 K (consistent with the $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ starting material) that sharpens to give a doublet at 29.9 ppm ($^1J_{\text{P-Rh}} = 121$ Hz) at 233 K and a singlet which appears between at -86.8 at 233 K and -80.5 ppm at 313 K (this signal is consistent with $[(^{\text{Me}}\text{LP})]^+$).

An orange solution of $[(^{\text{Bn}}\text{LP})][\text{BPh}_4]$ (23 mg, 0.052 mmol) in acetonitrile (2 mL) was added to a yellow solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (10 mg, 0.026 mmol) in acetonitrile (2 mL). The reaction mixture immediately turned dark brown. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this solution features one resonance at -17.3 ppm. The IR spectrum of the evaporated reaction mixture showed a single broad absorption at 1992 cm^{-1} in the carbonyl region. Treatment of this solution with excess PPh_3 results in the appearance of a broad resonance at 30.7 ppm and a singlet at -82.4 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum; the observed chemical shifts are consistent with the displacement of $[(^{\text{Bn}}\text{LP})]^+$ by PPh_3 . The IR spectrum of the evaporated mixture reveals an intense, sharp carbonyl absorption at 1974 cm^{-1} , which is also consistent with the production of $\text{Rh}(\text{PPh}_3)_2(\text{CO})(\text{Cl})$.

Overall, solubility problems and lability of the complexes hinder the analysis of the complexation experiments with rhodium(I); the signals for the complexes in solution ^1H and ^{13}C NMR spectra were always broad and EPR experiments did not reveal the presence of any paramagnetic species. Regardless of the actual identity of the products in solution, the ligand exchange reactions indicate unambiguously that the $[(^{\text{R}}\text{LP})]^+$ cations are weaker ligands than PPh_3 and the chemical behavior and physical data from the complexes suggest that the electronic properties of the ligands are perhaps most comparable to those of some phosphites or α -cationic phosphine ligands.⁴ This assessment is bolstered by less-ambiguous evidence from the computational investigation of nickel carbonyl complexes (described below) which suggest that $[(^{\text{Me}}\text{LP})]^+$ cations have electronic effects that are almost identical to those of PH_3 . An attempt to gauge the donor ability of the cations using cyclic voltammetry investigations reveal that $[(^{\text{Me}}\text{LP})][\text{OTf}]$ has an oxidation potential of around +0.341 V (vs. Fc^0/Fc^+), which is predictably intermediate between

those found for NHC_2P_2 systems⁵ and α -cationic phosphine ligands⁴; unfortunately, the oxidation potentials for this P^{I} phosphanido-type donor does not appear to be directly comparable to those of P^{III} phosphines in regard to donor ability.

Crystallographic Details

Crystals for investigation were covered in Nujol[®], mounted into a goniometer head, and then rapidly cooled under a stream of cold N_2 of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXII software suite⁶ on a Bruker Photon 100 diffractometer using a graphite monochromator with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). For each sample, a hemisphere of data was collected using 10 or 30 seconds/frame at 173 K. APEXII software was used for data reductions and SADABS⁷ was used for absorption corrections (semi-empirical from equivalents). Structures were solved and refined using the SHELX⁸ suite of programs as implemented by WinGX⁹. Validation of the structures was conducted using PLATON.¹⁰ For the compound $[\text{B}^{\text{n}}\text{LP}][\text{BPh}_4]\cdot\text{THF}$, the disordered THF solvent was modeled as a 50/50 mixture of two superimposed orientations in which the ADP values and corresponding bond distances in each model were restrained to be similar. For the compound $[\text{B}^{\text{n}}\text{LP}][\text{BPh}_4]\cdot\text{DCM}$, a single “peak” representing a small amount of residual electron density (ca. $2.2 \text{ e}^- \text{ \AA}^{-3}$) may suggest the possibility of a small disordered component corresponding to the dichloromethane solvent of crystallization; the magnitudes of all of the other maxima and minima were well below $1.0 \text{ e}^- \text{ \AA}^{-3}$ so no attempt was made to model this disorder. For the compound $[\text{Au}^{\text{Me}}\text{LP}]_2 [\text{OTf}]_2 [\text{Cl}]$, the disorder present in the triflate anion was modeled as a mixture of two superimposed orientations (each featuring appropriately constrained ADPs and bond distances) and refined to give a roughly 82/18 ratio of occupancies; the only residual electron density greater than $1.0 \text{ e}^- \text{ \AA}^{-3}$ was located between the disordered F atom positions within the anion.

Table S1 Summary of crystal data and structure refinement

Compound	3 ^[MeLP] [Br]·MeCN	[^{BnLP}][Br]	[^{BnLP}][BPh ₄]·THF	[^{BnLP}][BPh ₄]·DCM	[^{MeLP}][OTf]	[Au(^{MeLP}) ₂][OTf] ₂ [Cl]
CCDC	1042843	1042844	1042846	1042847	1042845	1042848
Empirical formula	C ₂₉ H ₃₉ Br ₃ N ₁₃ P ₃	C ₂₁ H ₂₀ BrN ₄ P	C ₄₉ H ₄₈ BN ₄ OP	C ₄₆ H ₄₂ BCl ₂ N ₄ P	C ₁₀ H ₁₂ F ₃ N ₄ O ₃ PS	C ₂₀ H ₂₄ AuClF ₆ N ₈ O ₆ P ₂ S ₂
Formula Weight	902.37	439.29	750.69	763.51	356.27	944.95
Temperature (K)	173(2)	173(2)	173(2)	153(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P -1	P 21/c	P -1	P -1	P -1	C 2/c
Unit cell dimensions:						
a (Å)	10.1735(3)	12.2417(10)	11.0003(4)	11.0120(4)	8.2477(3)	20.7657(7)
b (Å)	12.6747(4)	4.8288(4)	13.6439(5)	13.4813(5)	8.4833(3)	14.6302(7)
c (Å)	16.2901(5)	33.910(3)	14.0585(5)	13.8114(4)	10.7821(4)	13.2427(5)
α (°)	83.7780(10)	90	77.876(2)	78.513(2)	97.8660(10)	90
β (°)	72.5960(10)	98.281(3)	79.118(2)	77.1380(10)	104.3960(10)	123.628(2)
γ (°)	73.1770(10)	90	87.493(2)	87.889(2)	93.2520(10)	90
Volume (Å ³)	1918.05(10)	1983.6(3)	2025.82(13)	1958.84(12)	720.59(5)	3349.9(2)
Z	2	4	2	2	2	4
Density (Mg/m ³)	1.562	1.471	1.231	1.294	1.642	1.874
Absorption coeff. (mm ⁻¹)	3.320	2.166	0.111	0.246	0.387	4.772
F(000)	908	896	796	800	364	1840
Crystal Size (mm ³)	0.231 x 0.209 x 0.117	0.090 x 0.078 x 0.033	0.350 x 0.300 x 0.210	0.270 x 0.263 x 0.205	0.332 x 0.236 x 0.125	0.21 x 0.101 x 0.079

θ range for data collection (°)	2.900 to 27.913	3.147 to 27.491	2.878 to 28.499	2.944 to 27.500	2.886 to 35.661	3.025 to 27.500
Index ranges	-13 ≤ h ≤ 13 -16 ≤ k ≤ 16 -21 ≤ l ≤ 21	-15 ≤ h ≤ 15 -6 ≤ k ≤ 6 -42 ≤ l ≤ 43	-14 ≤ h ≤ 14 -18 ≤ k ≤ 18 -18 ≤ l ≤ 18	-14 ≤ h ≤ 14 -17 ≤ k ≤ 17 -17 ≤ l ≤ 17	-10 ≤ h ≤ 13 -13 ≤ k ≤ 13 -17 ≤ l ≤ 17	-26 ≤ h ≤ 26 -18 ≤ k ≤ 18 -17 ≤ l ≤ 17
Reflections collected	36505	34945	93422	67652	19018	61590
Independent reflections	9153	4384	10259	8984	6604	3862
R_{int}	0.0494	0.0573	0.0483	0.0499	0.0408	0.0393
Completeness to θ	99.9	99.8	99.9	99.8	99.8	99.8
Absorption correction	Semi-empirical from equivalents					
Max. and Min. Transmission	0.678 and 0.542	0.931 and 0.861	0.977 and 0.933	0.951 and 0.866	0.953 and 0.813	0.686 and 0.558
Refinement method	Full-matrix least-squares on F^2					
Data / restraints / parameters	9153 / 0 / 439	4384 / 0 / 244	10259 / 37 / 550	8984 / 0 / 487	6604 / 0 / 201	3862 / 18 / 212
Goodness-of-fit on F^2	1.028	1.057	1.038	1.039	1.042	1.069
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0318$ $wR2 = 0.0647$	$R1 = 0.0320$ $wR2 = 0.0641$	$R1 = 0.0524$ $wR2 = 0.1356$	$R1 = 0.0560$ $wR2 = 0.1545$	$R1 = 0.0530$ $wR2 = 0.1229$	$R1 = 0.0293$ $wR2 = 0.0798$
R indices (all data)	$R1 = 0.0502$ $wR2 = 0.0718$	$R1 = 0.0537$ $wR2 = 0.0703$	$R1 = 0.0696$ $wR2 = 0.1503$	$R1 = 0.0695$ $wR2 = 0.1660$	$R1 = 0.0815$ $wR2 = 0.1377$	$R1 = 0.0308$ $wR2 = 0.0810$
Largest diff. peak and hole (e \AA^{-3})	0.500 and -0.329	0.367 and -0.258	0.570 and -0.449	2.152 and -0.782	0.642 and -0.373	1.634 and -1.171

$R1(F)$: $\{\Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\Sigma(F_o))$. $wR2(F^2)$: $\{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|^2)^2\}^{1/2}$ where w is the weight given to each reflection

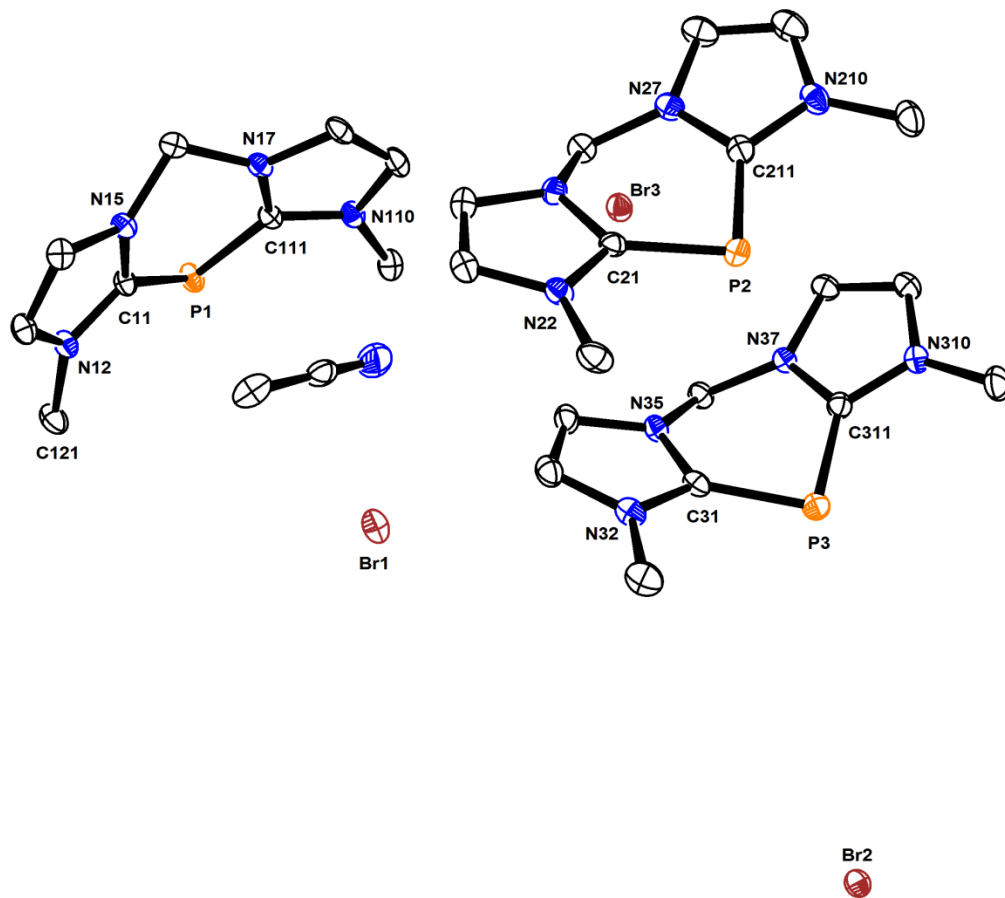


Fig. S1 Thermal ellipsoid plot (30% probability surface) of $3[\text{M}^e\text{LP}][\text{Br}] \cdot \text{MeCN}$. Hydrogen atoms are omitted for clarity.

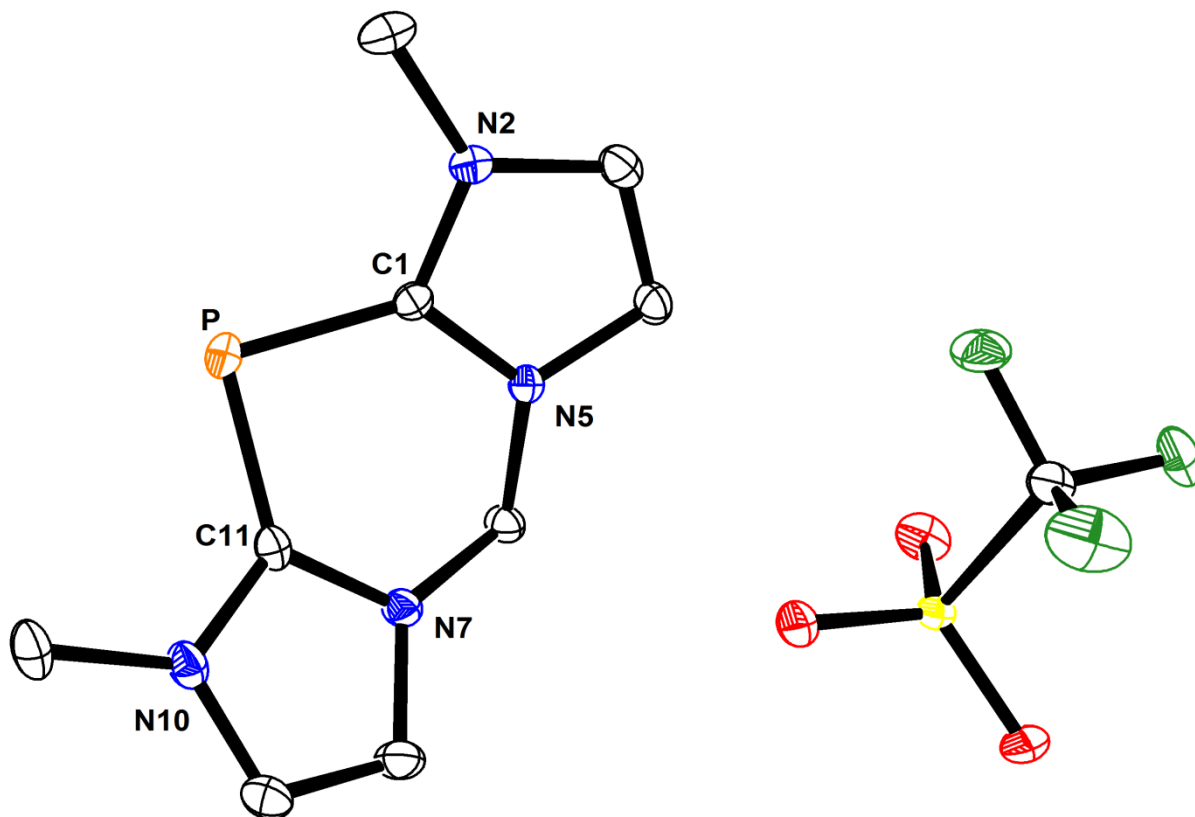


Fig. S3 Thermal ellipsoid plot (30% probability surface) of [^{Me}LP][OTf]. Hydrogen atoms are omitted for clarity.

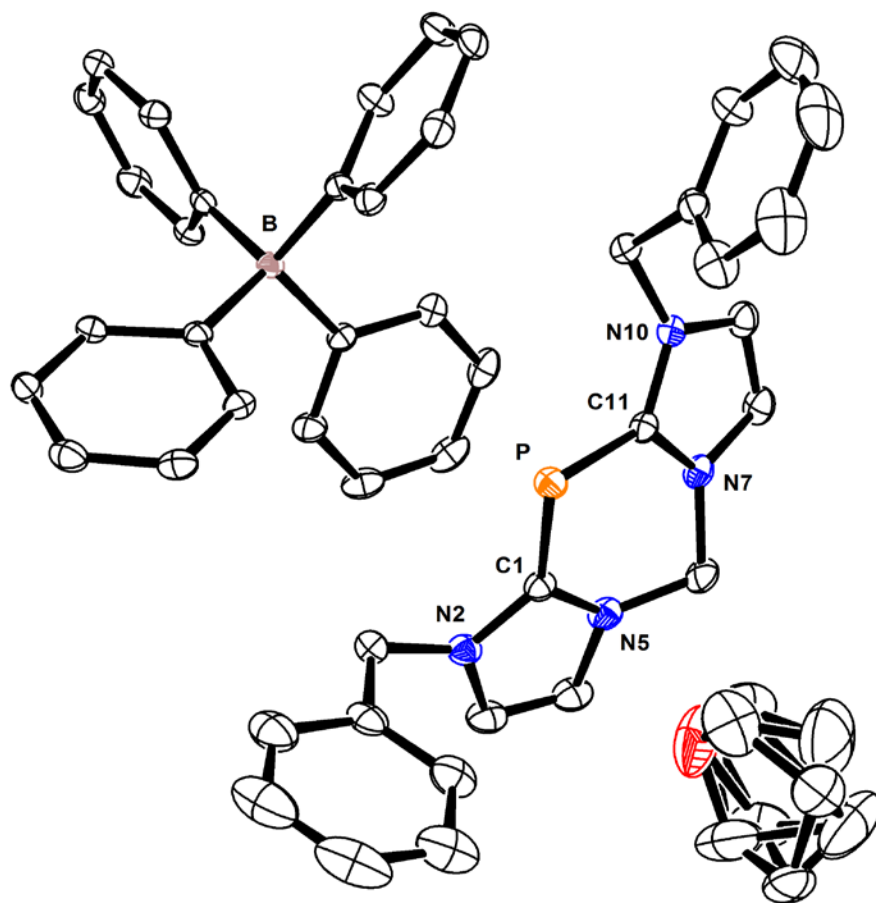


Fig. S4 Thermal ellipsoid plot (30% probability surface) of $[\text{BnLP}][\text{BPh}_4] \cdot \text{THF}$. Hydrogen atoms are omitted for clarity.

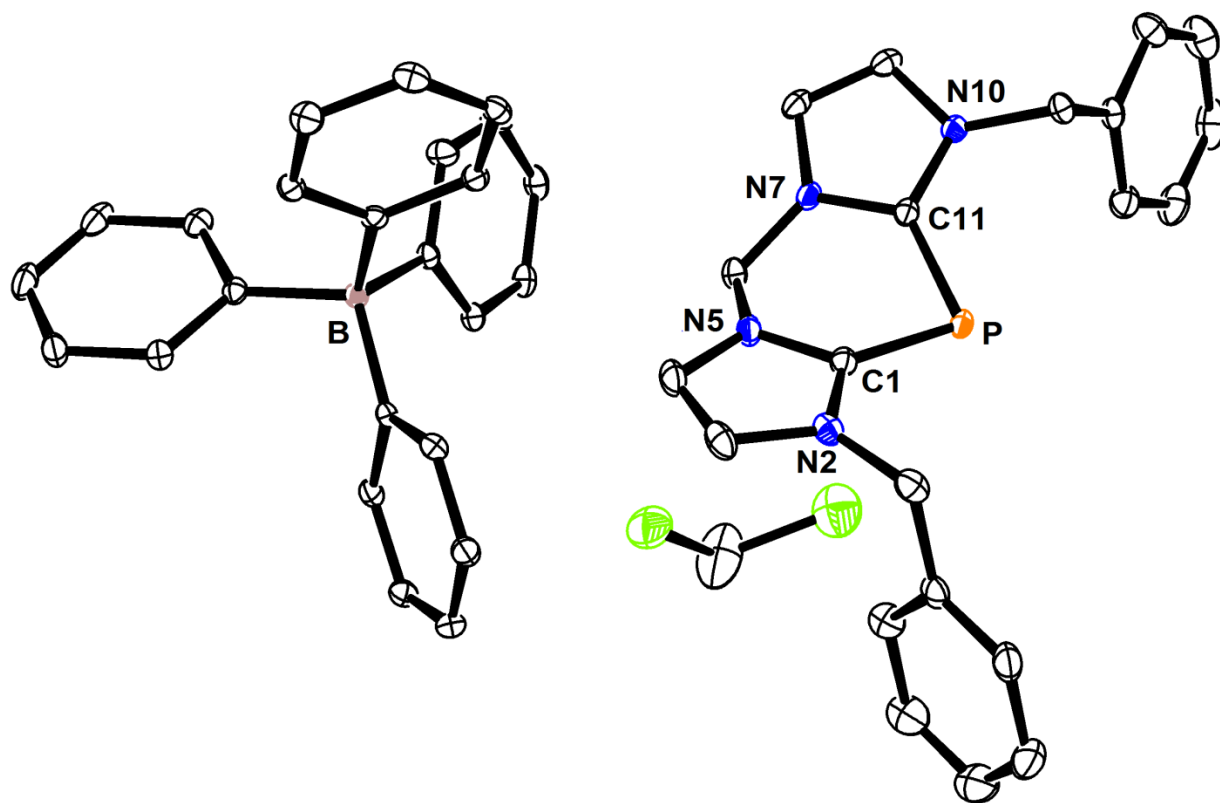


Fig. S5 Thermal ellipsoid plot (30% probability surface) of $[\text{MeLP}][\text{BPh}_4] \cdot \text{DCM}$. Hydrogen atoms are omitted for clarity.

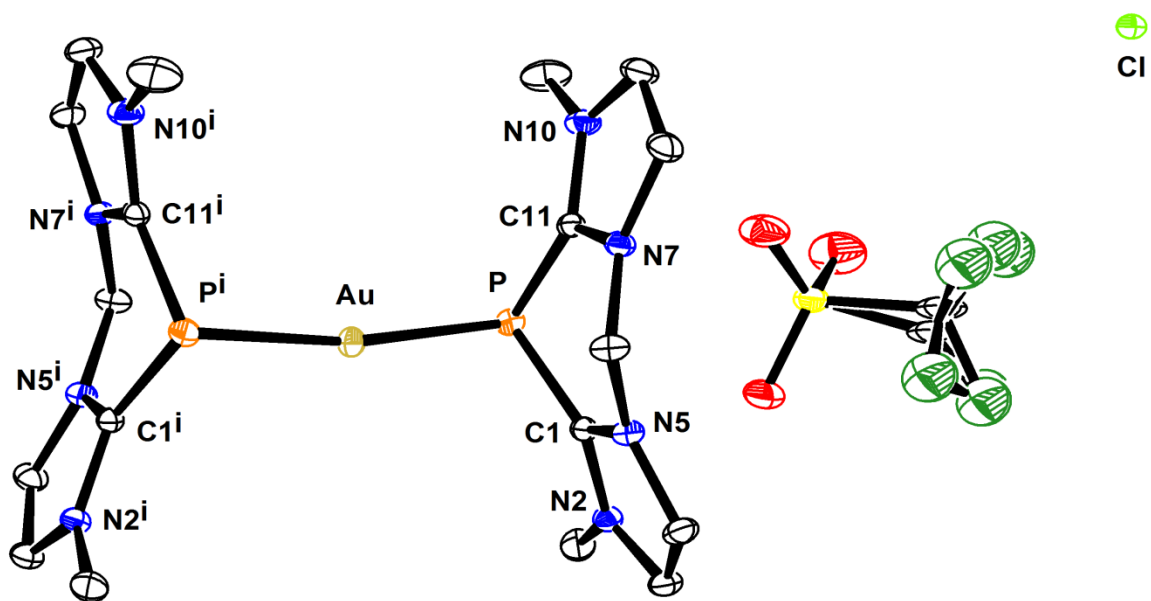


Fig. S6 Thermal ellipsoid plot (30% probability surface) of $[\text{Au}(\text{MeLP})_2][\text{OTf}]_2[\text{Cl}]$. Hydrogen atoms are omitted for clarity.

Computational Information

General Remarks

Calculations were performed with the Gaussian 09 suite of programs¹¹ using Compute Canada's Shared Hierarchical Academic Research Computing Network (SharcNet). All model complexes were fully optimized with no symmetry constraints using the PBE1PBE density functional theory (DFT) method¹²⁻¹⁴ in conjunction with the TZVP basis sets^{15,16} for all s- and p-block atoms; Ni atoms were modeled using the SDD effective core potential and associated basis set.¹⁷ Frequency calculations were performed at the same level of theory in order to confirm that the optimized structures were minima on the potential energy hypersurface, to determine thermochemical information, and to compare the frequencies of vibrational modes. Natural bond order (NBO) analyses¹⁸ to determine orbital contributions, Wiberg Bond Indices and orbital energies were obtained using the routine included in the Gaussian distributions.¹⁹ TD-DFT calculations on the optimized structures were conducted using the PBE1PBE DFT method using the 6-311+G(2d,p) basis sets for all atoms.²⁰ Geometry optimizations were started using models in which the relevant phosphorus, nitrogen and carbon atoms were placed at the positions found experimentally using X-ray crystallography and the hydrogen atoms were placed in geometrically appropriate positions using Gaussview.²¹ Details of the calculated results, including Cartesian coordinates are presented in the following sections; any readers interested in further information regarding these calculations are encouraged to contact the principal investigator (cmacd@uwindsor.ca).

Table S2. Summary of Calculated Results for Some Phosphamethine Cyanine Model Compounds

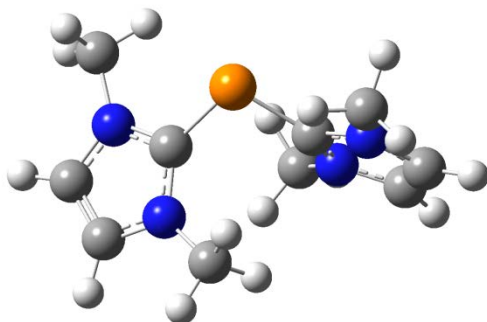
Model	N_{imag}	E_{HOMO} (eV)	E_{LUMO} (eV)	$E_{\text{H-L}}$ (eV)	UV-vis (nm)	$LP_{\text{(P)}}^a$ (NBO)	$E_{\text{deloc.}}^b$ (kcal mol ⁻¹)	$r_{\text{C-P}}$ (Å)	$\alpha_{\text{C-P-C}}$ (°)
$[(\text{Me}^{\text{H}}\text{NHC}^{\text{H}})_2\text{P}]^+$	0	-8.65	-4.12	4.53	351.95 314.01 265.80	2	64.64	1.809	99.23
$[\text{H}_2\text{C}(\text{Me}^{\text{H}}\text{NHC}^{\text{H}})_2\text{P}]^+$	0	-8.87	-4.27	4.61	336.93 271.97 268.21	2	96.53	1.7951	91.73
$[(\text{Me}^{\text{H}}\text{NSHC}^{\text{H}})_2\text{P}]^+$	0	-9.20	-5.46	3.74	388.35	1	n/a	1.7833	103.91

a. Number of lone pairs assigned to the phosphorus atom in the lowest energy configuration determined by the NBO analysis. b. Stabilization energy associated with delocalization of the π -lone pair on P with the adjacent π -bonds as determined by the NBO analysis.

Table S3. Summary of Calculated Metrical Parameters and Carbonyl Vibrational Modes for Model L-Ni(CO)₃ Complexes.

Model	N_{imag}	$\nu(\text{CO})$ (cm ⁻¹)	$\nu(\text{CO})$ (cm ⁻¹)	$\nu(\text{CO})$ (cm ⁻¹)	$r_{\text{P-Ni}}$ (Å)	$r_{\text{Ni-C}}$ (Å)	$r_{\text{C-O}}$ (Å)
$[\text{H}_2\text{P-Ni}(\text{CO})_3]^+$	0	2093	2025	2025	2.3525	1.7704-1.7773	1.1517-1.1519
$\text{H}_3\text{P-Ni}(\text{CO})_3$	0	2188	2125	2125	2.2296	1.7998-1.8000	1.1381-1.1381
$\text{Me}_3\text{P-Ni}(\text{CO})_3$	0	2171	2108	2108	2.2305	1.7927-1.7929	1.1404-1.1405
$\text{Ph}_3\text{P-Ni}(\text{CO})_3$	0	2174	2113	2113	2.2473	1.7952-1.7953	1.1396-1.1396
$[\text{H}_2\text{C}(\text{Me}^{\text{H}}\text{NHC}^{\text{H}})_2\text{P-Ni}(\text{CO})_3]^+$	0	2187	2135	2115	2.3122	1.7946-1.8185	1.1344-1.1392

Acyclic model [$(^{\text{Me}}\text{NHC}^{\text{H}})_2\text{P}^+$]:



```
1\1\GINC-SAW54\FOpt\RPBE1PBE\TZVP\C10H16N4P1(1+)\CMACD\14-Oct-2014\0\
```

```
# PBE1PBE/TZVP scf=tight opt freq pop=(full,nboread) test\Optimization of P(MeNHCH)2 acyclic  
cation\1,1\P,-0.0000496071,-1.8012722169,-0.0
```

```
001382017\C,-1.3741111511,-0.6291610028,-0.1029153904\N,-2.5695495497,  
-0.8359368293,0.5010156469\N,-1.5405792522,0.4744155876,-0.8750618963\  
C,-3.4706185544,0.1240251317,0.1079690315\C,-2.8247451075,0.9519701248  
, -0.7406111312\C,-2.8713433874,-1.9330401419,1.4007296466\C,-0.5645082  
011,0.9970228029,-1.8074313641\C,1.3740168146,-0.6291699469,0.10271294  
5\N,2.5694506128,-0.8358934111,-0.5012452197\N,1.5404857691,0.47435042  
54,0.8749388183\C,3.4705198201,0.124040742,-0.1081305467\C,2.824648206  
9,0.9519231609,0.7405115058\C,2.8712585803,-1.9329503662,-1.4010106368  
\C,0.5644205243,0.9968924387,1.8073507137\H,-1.953411999,-2.2274703705  
,1.9105347221\H,-3.2602145862,-2.7895645952,0.8478427663\H,-3.61108499  
58,-1.6026101812,2.1283791444\H,0.1582545458,1.6463308119,-1.310236224  
4\H,-1.085214637,1.5664252112,-2.5752533443\H,-0.0403078162,0.15934785  
98,-2.2695196957\H,3.2602579544,-2.7894498583,-0.8481756099\H,1.953304  
403,-2.2274479233,-1.91073534\H,3.6109001393,-1.6024415109,-2.12872689  
66\H,1.0851410774,1.566133944,2.5752829146\H,-0.1582721327,1.646334188  
3,1.3102273257\H,0.0401383436,0.1591856857,2.269286989\H,-4.4869400968  
,0.1368841158,0.464011248\H,-3.1664120003,1.8317818093,-1.2593781952\H
```

,3.166312875,1.8317003363,1.2593386302\H,4.4868347881,0.1369364883,-0.
 4641904552\\Version=EM64L-G09RevD.01\State=1-A\HF=-950.1877404\RMSD=8.
 714e-09\RMSF=7.604e-06\Dipole=0.0000176,1.1499539,0.0000397\Quadrupole
 =18.4007872,-9.3118421,-9.0889451,0.0001837,-4.8693487,-0.0000377\PG=C
 01 [X(C10H16N4P1)]\@\@

Zero-point correction= 0.261932 (Hartree/Particle)
 Thermal correction to Energy= 0.277930
 Thermal correction to Enthalpy= 0.278874
 Thermal correction to Gibbs Free Energy= 0.218075
 Sum of electronic and zero-point Energies= -949.925808
 Sum of electronic and thermal Energies= -949.909811
 Sum of electronic and thermal Enthalpies= -949.908866
 Sum of electronic and thermal Free Energies= -949.969665

NBO results:

1. (1.96125) BD (1) P 1 - C 2

(34.07%) 0.5837* P 1 s(15.06%)p 5.60(84.31%)d 0.04(0.63%)

0.0000 0.0000 0.3858 0.0415 -0.0004
 0.0000 -0.6996 -0.0434 -0.0016 -0.0001
 -0.5898 -0.0134 0.0002 0.0001 -0.0604
 0.0103 0.0023 0.0699 -0.0064 -0.0029
 -0.0083 -0.0364

(65.93%) 0.8120* C 2 s(39.24%)p 1.55(60.73%)d 0.00(0.03%)

0.0000 0.6258 -0.0267 -0.0095 0.0001
 0.6260 -0.0349 -0.0170 0.4456 -0.0170
 -0.0191 -0.1203 0.0144 0.0012 0.0134

-0.0037 -0.0022 0.0012 -0.0093

2. (1.96125) BD (1) P 1 - C 9

(34.07%) 0.5837* P 1 s(15.06%)p 5.60(84.31%)d 0.04(0.63%)

0.0000 0.0000 0.3858 0.0415 -0.0004

0.0000 0.6996 0.0434 0.0016 -0.0001

-0.5898 -0.0134 0.0002 -0.0001 0.0604

-0.0103 -0.0023 -0.0699 -0.0064 0.0029

-0.0083 -0.0364

(65.93%) 0.8120* C 9 s(39.24%)p 1.55(60.73%)d 0.00(0.03%)

0.0000 0.6258 -0.0267 -0.0095 0.0001

-0.6260 0.0349 0.0170 0.4456 -0.0170

-0.0191 0.1203 -0.0144 -0.0012 -0.0134

-0.0037 0.0022 0.0012 -0.0093

56. (1.92607) LP (1) P 1 s(70.29%)p 0.42(29.66%)d 0.00(0.04%)

0.0000 -0.0005 0.8383 -0.0142 0.0001

0.0000 0.0000 0.0000 0.0000 0.0004

0.5446 0.0003 -0.0005 0.0000 -0.0002

0.0000 0.0000 0.0000 0.0016 0.0000

0.0175 0.0103

57. (1.51950) LP (2) P 1 s(0.00%)p 1.00(99.77%)d 0.00(0.23%)

0.0000 0.0000 -0.0001 0.0000 0.0000

0.0000 -0.0753 -0.0141 -0.0041 0.0000

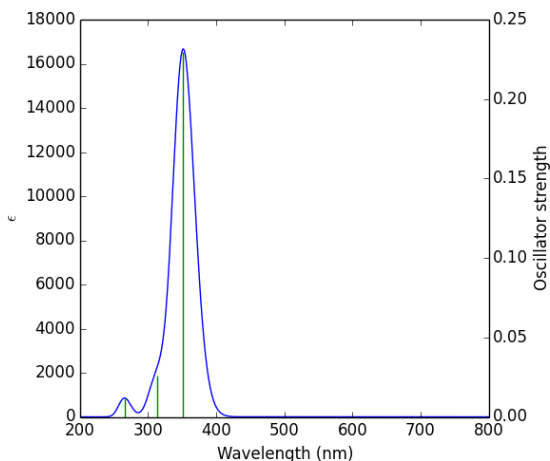
0.0004 0.0000 0.0000 0.0000 0.9955

-0.0276 0.0007 0.0170 0.0000 -0.0444

0.0000 0.0000

57. LP (2) P 1 /352. BD*(2) C 2 - N 3 64.64 0.09 0.069

TD-DFT results:



Excitation energies and oscillator strengths:

Excited State 1: Triplet-A 2.8117 eV 440.96 nm f=0.0000 $\langle S^{*2} \rangle = 2.000$

59 -> 60 0.70221

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -950.068257950

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 3.2035 eV 387.03 nm f=0.0000 $\langle S^{*2} \rangle = 2.000$

59 -> 61 0.68923

Excited State 3: Singlet-A 3.5228 eV 351.95 nm f=0.2294 $\langle S^{*2} \rangle = 0.000$

59 -> 60 0.69922

Excited State 4: Singlet-A 3.9484 eV 314.01 nm f=0.0257 $\langle S^{*2} \rangle = 0.000$

59 -> 61 0.68714

Excited State 5: Triplet-A 3.9992 eV 310.03 nm f=0.0000 <S**2>=2.000

57 -> 62 0.17471

58 -> 63 0.22330

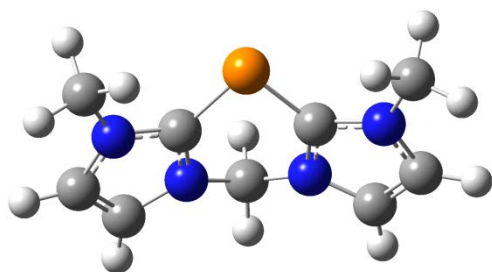
59 -> 62 0.58592

59 -> 64 -0.18485

Excited State 6: Singlet-A 4.6647 eV 265.80 nm f=0.0118 <S**2>=0.000

59 -> 62 0.69669

Cyclic model [H₂C(^{Me}NHC^H)₂P]⁺:



1\1\GINC-SAW18\FOpt\RPBE1PBE\TZVP\C9H12N4P1(1+)\CMACD\14-Oct-2014\0\#

PBE1PBE/TZVP scf=tight opt freq pop=(full,nboread) test\Optimization
of P(MeNHCH)2CH2 cation\1,1\P,-0.0000451712,-1.9239035122,0.53973330
15\C,1.2882616625,-0.7092052315,0.2446674463\N,2.5693980486,-0.9621956
178,-0.0889604871\N,1.1725217968,0.6403278733,0.2788390774\C,3.2543996
874,0.2254290081,-0.2476673932\C,2.3860761974,1.2314961527,-0.01983918
26\C,3.1235785679,-2.2916556384,-0.2612728566\C,0.0000159276,1.2780862
515,0.8208140077\C,-1.2883272798,-0.709162367,0.2447521239\N,-2.569484

8683,-0.9621156552,-0.0888247991\N,-1.1725414882,0.6403677072,0.278906
3097\C,-3.2544499576,0.2255297255,-0.2475340805\C,-2.3861142782,1.2315
699566,-0.0196342836\C,-3.1237083344,-2.2915595707,-0.2611218521\H,2.3
885054325,-2.921315235,-0.7651660592\H,3.3765482146,-2.7312724622,0.70
48978561\H,4.0193227492,-2.2249720825,-0.8753150352\H,-2.3886731103,-
.921234513,-0.7650507794\H,-3.3766489928,-2.731178259,0.7050559104\H,-
4.0194759885,-2.224848427,-0.875126716\H,0.0000252341,2.332899524,0.55
1604453\H,0.000042781,1.171844798,1.9140597632\H,-4.2961501484,0.24997
941,-0.5199364511\H,-2.5202567128,2.2997917483,-0.04775646\H,2.5202391
809,2.2997143,-0.0480038803\H,4.2960998099,0.2498460964,-0.5200726933\
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F=7.672e-06\Dipole=0.0000037,1.0066691,-0.2954383\Quadrupole=20.449159
7,-1.0699573,-19.3792024,-0.0003048,-0.0008483,2.7806553\PG=C01 [X(C9H
12N4P1)]\@

Zero-point correction=	0.213516 (Hartree/Particle)
Thermal correction to Energy=	0.226121
Thermal correction to Enthalpy=	0.227065
Thermal correction to Gibbs Free Energy=	0.174146
Sum of electronic and zero-point Energies=	-909.498182
Sum of electronic and thermal Energies=	-909.485578
Sum of electronic and thermal Enthalpies=	-909.484634
Sum of electronic and thermal Free Energies=	-909.537553

NBO results:

1. (1.96070) BD (1) P 1 - C 2

(33.66%) 0.5802* P 1 s(14.81%)p 5.71(84.53%)d 0.04(0.66%)

0.0000 -0.0001 0.3828 0.0387 0.0015
0.0001 0.7023 0.0411 0.0045 0.0001
0.5876 0.0110 0.0016 -0.0001 -0.0701
-0.0061 0.0002 0.0688 -0.0187 -0.0162
-0.0083 -0.0349

(66.34%) 0.8145* C 2 s(38.76%)p 1.58(61.21%)d 0.00(0.03%)

0.0000 0.6221 -0.0221 -0.0056 0.0003
-0.5641 0.0363 0.0217 -0.5040 0.0175
0.0191 0.1933 -0.0104 -0.0058 0.0137
-0.0057 -0.0044 0.0009 -0.0067

2. (1.96070) BD (1) P 1 - C 9

(33.66%) 0.5802* P 1 s(14.81%)p 5.71(84.53%)d 0.04(0.66%)

0.0000 -0.0001 0.3828 0.0387 0.0015
-0.0001 -0.7023 -0.0411 -0.0045 0.0001
0.5876 0.0110 0.0016 -0.0001 -0.0701
-0.0061 0.0002 -0.0688 0.0187 -0.0162
-0.0083 -0.0349

(66.34%) 0.8145* C 9 s(38.76%)p 1.58(61.21%)d 0.00(0.03%)

0.0000 0.6221 -0.0221 -0.0056 0.0003
0.5641 -0.0363 -0.0217 -0.5040 0.0175
0.0191 0.1933 -0.0104 -0.0058 -0.0137
0.0057 -0.0044 0.0009 -0.0067

51. (1.94978) LP (1) P 1 s(70.49%)p 0.42(29.47%)d 0.00(0.04%)

0.0000 -0.0006 0.8395 -0.0130 -0.0006
0.0000 0.0000 0.0000 0.0000 -0.0002
-0.5328 0.0037 -0.0003 0.0002 0.1036

0.0033 -0.0005 0.0000 0.0000 0.0088

0.0158 0.0075

52. (1.43165) LP (2) P 1 s(0.12%)p99.99(99.61%)d 2.37(0.28%)

0.0000 0.0000 0.0331 0.0079 0.0009

0.0000 0.0000 0.0000 0.0000 0.0000

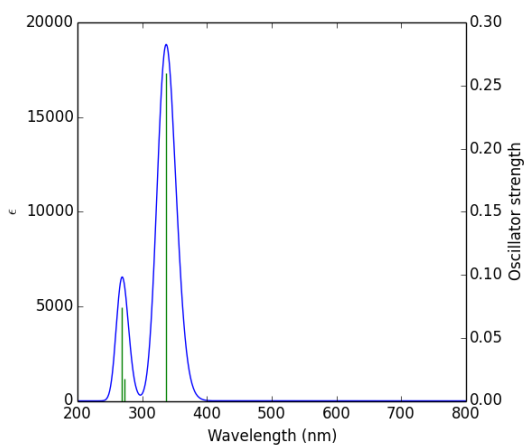
-0.1403 0.0165 0.0017 0.0000 -0.9877

0.0244 0.0035 0.0000 0.0000 -0.0495

0.0038 0.0168

52. LP (2) P 1 /313. BD*(2) C 2 - N 3 96.53 0.09 0.082

TD-DFT results:



Excitation energies and oscillator strengths:

Excited State 1: Triplet-A 2.8485 eV 435.26 nm f=0.0000 <S**2>=2.000

54 -> 55 0.70336

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -909.593014092

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Triplet-A 3.5657 eV 347.71 nm f=0.0000 <S**2>=2.000

54 -> 56 0.59312

54 -> 57 0.29960

54 -> 59 -0.19137

Excited State 3: Singlet-A 3.6798 eV 336.93 nm f=0.2600 <S**2>=0.000

54 -> 55 0.69843

Excited State 4: Triplet-A 3.8397 eV 322.90 nm f=0.0000 <S**2>=2.000

53 -> 58 0.23313

54 -> 56 -0.26846

54 -> 57 0.56682

Excited State 5: Singlet-A 4.5588 eV 271.97 nm f=0.0176 <S**2>=0.000

54 -> 58 -0.34824

54 -> 60 0.57926

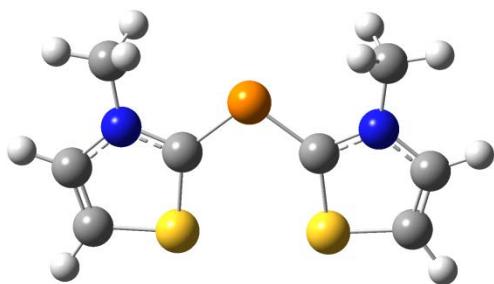
54 -> 62 -0.17066

Excited State 6: Singlet-A 4.6226 eV 268.21 nm f=0.0739 <S**2>=0.000

54 -> 56 0.65759

54 -> 57 -0.22758

Acyclic thiazolium model [$(\text{MeNSHC}^{\text{H}})_2\text{P}^+$]:



1\1\GINC-SAW283\FOpt\RPBE1PBE\TZVP\C8H10N2P1S2(1+)\CMACD\29-Jan-2015\0

\#\ PBE1PBE/TZVP scf=tight opt freq pop=(full,nboread) test\Optimizat

ion of P(MeNSHCH)₂ acyclic cation\1,1\P,0.0225273065,1.1986042349,0.1

319738583\C,-1.3733325285,0.0992243674,0.2840958764\N,-2.5922435358,0.

6381430704,0.5238851167\C,-3.6227537159,-0.2666863268,0.6293199181\C,-

3.2360911682,-1.5416262823,0.4743028346\C,-2.7967407473,2.0735398098,0

.6602112482\C,1.3980093382,0.1053004046,-0.1729135602\N,2.6269988505,0

.6495883646,-0.3372135387\C,3.6407158801,-0.2508143794,-0.5683732543\C

,3.2303020436,-1.5275509949,-0.5911613974\C,2.8582047998,2.0859946435,

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2,2.4567620214,1.4952590379\H,-3.8514176982,2.2598756073,0.8475915001\

H,2.2767758959,2.592117692,-1.0465941743\H,2.5662070208,2.4677777961,0

.7067161393\H,3.9163861659,2.2769535414,-0.4346382828\H,-4.6226518888,

0.0936318033,0.820140716\H,-3.8404147646,-2.4340438948,0.5104926206\H,

3.8180625871,-2.4173813918,-0.751364859\H,4.6473582863,0.1138992542,-0

.7087050149\S,-1.5307798996,-1.6220747433,0.1870179904\S,1.5234158354,

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305137\Quadrupole=27.4531107,-4.6137685,-22.8393422,0.2969205,-8.53051

88,1.3554469\PG=C01 [X(C8H10N2P1S2)]\@\

Zero-point correction= 0.173334 (Hartree/Particle)
 Thermal correction to Energy= 0.186715
 Thermal correction to Enthalpy= 0.187659
 Thermal correction to Gibbs Free Energy= 0.131865
 Sum of electronic and zero-point Energies= -1556.936817
 Sum of electronic and thermal Energies= -1556.923436
 Sum of electronic and thermal Enthalpies= -1556.922492
 Sum of electronic and thermal Free Energies= -1556.978286

NBO results:

1. (1.96973) BD (1) P 1 - C 2

(33.67%) 0.5802* P 1 s(16.74%)p 4.94(82.62%)d 0.04(0.64%)

0.0000 0.0000 0.4060 0.0504 0.0007
 0.0001 -0.7027 -0.0343 -0.0039 -0.0001
 -0.5754 -0.0089 -0.0020 0.0000 0.0001
 0.0000 0.0000 0.0708 0.0000 0.0000
 0.0010 -0.0379

(66.33%) 0.8145* C 2 s(39.57%)p 1.53(60.39%)d 0.00(0.04%)

0.0000 0.6290 0.0097 -0.0044 -0.0001
 0.6601 0.0167 -0.0121 0.4092 0.0136
 -0.0114 0.0001 0.0000 0.0000 0.0161
 0.0000 0.0000 0.0011 -0.0107

2. (1.73957) BD (2) P 1 - C 2

(61.23%) 0.7825* P 1 s(0.00%)p 1.00(99.67%)d 0.00(0.33%)

0.0000 0.0000 0.0000 0.0000 0.0000
 0.0000 0.0001 0.0000 0.0000 0.0000

0.0000 0.0000 0.0000 0.0010 0.9983
-0.0067 -0.0009 0.0000 -0.0145 -0.0557
0.0000 0.0000

(38.77%) 0.6227* C 2 s(0.00%)p 1.00(99.98%)d 0.00(0.02%)

0.0000 0.0000 0.0000 0.0000 0.0000
0.0001 0.0000 0.0000 -0.0002 0.0000
0.0000 0.9996 0.0084 0.0209 0.0000
0.0121 0.0096 0.0000 0.0000

3. (1.96973) BD (1) P 1 - C 7

(33.67%) 0.5802* P 1 s(16.74%)p 4.94(82.62%)d 0.04(0.64%)

0.0000 0.0000 0.4060 0.0504 0.0007
-0.0001 0.7027 0.0343 0.0039 -0.0001
-0.5754 -0.0089 -0.0020 0.0000 -0.0001
0.0000 0.0000 -0.0708 0.0000 0.0000
0.0010 -0.0379

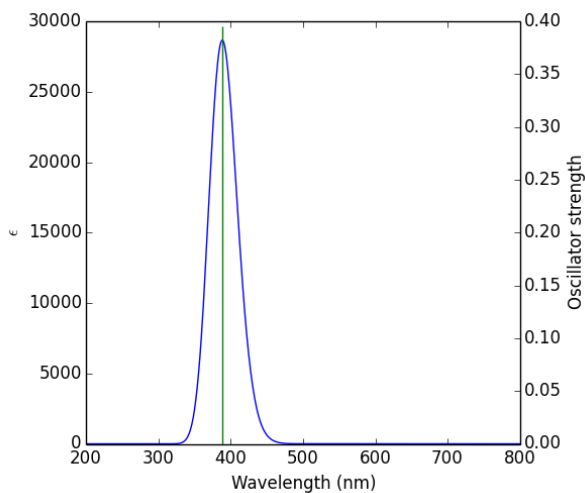
(66.33%) 0.8145* C 7 s(39.57%)p 1.53(60.39%)d 0.00(0.04%)

0.0000 0.6290 0.0097 -0.0044 -0.0001
-0.6601 -0.0167 0.0121 0.4092 0.0136
-0.0114 0.0000 0.0000 0.0000 -0.0161
0.0000 0.0000 0.0011 -0.0107

54. (1.92411) LP (1) P 1 s(66.93%)p 0.49(33.03%)d 0.00(0.03%)

0.0000 -0.0006 0.8179 -0.0196 -0.0002
0.0000 0.0000 0.0000 0.0000 0.0003
0.5747 -0.0085 -0.0039 0.0000 0.0000
0.0000 0.0000 0.0000 0.0000 0.0000
0.0136 0.0119

TD-DFT results:



Excitation energies and oscillator strengths:

Excited State 1: Triplet-A 2.0743 eV 597.73 nm f=0.0000 $\langle S^{*2} \rangle = 2.000$

59 -> 60 0.70648

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1557.03963703

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.1926 eV 388.35 nm f=0.3955 $\langle S^{*2} \rangle = 0.000$

59 -> 60 0.70239

Excited State 3: Triplet-A 3.1976 eV 387.74 nm f=0.0000 $\langle S^{*2} \rangle = 2.000$

58 -> 60 -0.13445

58 -> 65 0.10154

59 -> 61 0.67279

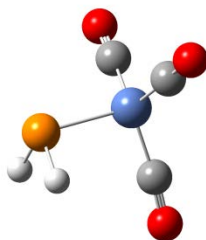
Excited State 4: Triplet-A 3.7358 eV 331.88 nm f=0.0000 <S**2>=2.000
59 -> 62 0.69953

Excited State 5: Singlet-A 3.8895 eV 318.77 nm f=0.0000 <S**2>=0.000
59 -> 62 0.70427

Excited State 6: Singlet-A 4.3823 eV 282.92 nm f=0.0000 <S**2>=0.000
59 -> 63 0.69875

Nickel Carbonyl Complexes:

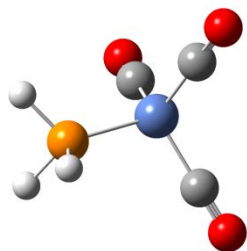
$[\text{H}_2\text{P-Ni}(\text{CO})_3]^-$:



```
1\1\GINC-SAW193\FOpt\RPBE1PBE\Gen\C3H2Ni1O3P1(1-)\CMACD\06-Feb-2015\0\  
\# PBE1PBE/gen pseudo=read scf=tight opt freq pop=(full,nboread) test\  
\Optimization of H2P-Ni(CO)3 anion complex\|-1,1\Ni,-0.041260322,0.501  
7759153,-0.4916313941\P,0.2168818454,-1.3177349899,0.9770572349\C,1.62  
88190684,0.9129745343,-0.9130436354\C,-0.875156532,1.639174802,0.58989  
60088\C,-1.0182462401,-0.1816430984,-1.8003299975\O,2.7296128224,1.147  
8366255,-1.1577846732\O,-1.4092244885,2.2926316247,1.3736545112\O,-1.6  
565482067,-0.6671030326,-2.6272329555\H,-1.1175252252,-1.4189448228,1.  
4963418812\H,0.6678420183,-0.6348508281,2.1564094697\\Version=EM64L-G0  
9RevD.01\State=1-A\HF=-853.1485145\RMSD=7.201e-09\RMSF=3.386e-05\Dipol
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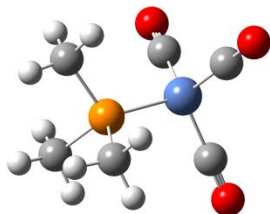

e=-0.1937693,0.823364,-0.4533086\Quadrupole=1.2410697,-1.5587506,0.317
6809,0.9843065,-0.0272409,1.182861\PG=C01 [X(C3H2Ni1O3P1)]\@

H₃P-Ni(CO)₃:



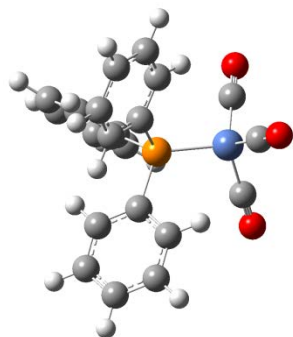
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BE1PBE/gen pseudo=read scf=tight opt freq pop=(full,nboread) test\Opt
imization of H3P-Ni(CO)3 complex\0,1\Ni,-0.0600162257,0.4649761481,-0
.3902598093\P,0.1622864251,-1.2234579879,1.0487630883\C,1.6005603759,0
.9425507053,-0.8938472214\C,-0.9059764621,1.7895285587,0.4869620774\C,
-1.0318178972,-0.1535765814,-1.7733886899\O,2.6429020812,1.2581060312,
-1.2243812382\O,-1.4400777698,2.6380441344,1.0255472072\O,-1.645571701
4,-0.5269925738,-2.6560826695\H,-0.9823560428,-1.8636759655,1.59196532
09\H,0.8409891773,-1.0351259376,2.2812777158\H,0.8446423595,-2.4090797
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MSD=4.464e-09\RMSF=2.756e-05\Dipole=0.1225606,-0.9321296,0.7943756\Qua
drupole=-2.289165,1.6992276,0.5899374,-0.5334829,0.4572977,-3.4553158\
PG=C01 [X(C3H3Ni1O3P1)]\@

Me₃P-Ni(CO)₃:



```
1\1\GINC-SAW69\FOpt\RPBE1PBE\Gen\C6H9Ni1O3P1\CMACD\06-Feb-2015\0\# PB
E1PBE/gen pseudo=read scf=tight opt freq pop=(full,nboread) test\Opti
mization of Me3P-Ni(CO)3 complex\0,1\Ni,-0.0179156824,0.444665745,-0.
4030948758\P,0.1725543315,-1.2277475242,1.0603477393\C,1.6487556495,0.
903424461,-0.8783221781\C,-0.8695855713,1.7735426704,0.4469662134\C,-0.
9650891711,-0.1901425171,-1.7867361463\C,1.0255565761,-0.8325058961,2
.641495336\C,-1.4005944992,-1.972451848,1.6559891632\C,1.101102851,-2.
7094821183,0.4893021208\O,2.7121722227,1.1884621538,-1.1758248075\O,-1
.4114723889,2.6139880964,0.9952356315\O,-1.5682335969,-0.6025766539,-2
.6623775517\H,2.0358360142,-0.4794652396,2.4280018151\H,1.0791474035,-
1.7031485384,3.3001982961\H,0.4881349767,-0.029692813,3.1491756448\H,0
.6157667988,-3.1195425755,-0.3979207449\H,1.1480480363,-3.4797760306,1
.2633381408\H,2.1147666781,-2.4144219325,0.2130316184\H,-1.2187133263,
-2.7805887884,2.3689999962\H,-2.0063704646,-1.2005237454,2.1333736126\
H,-1.9608369775,-2.3627122756,0.8045351662\Version=EM64L-G09RevD.01\S
tate=1-A\HF=-971.5545939\RMSD=9.806e-09\RMSF=6.530e-05\Dipole=0.155994
6,-1.3695331,1.1988748\Quadrupole=-1.6494651,1.1593372,0.4901279,-0.32
57388,0.2872925,-2.4903947\PG=C01 [X(C6H9Ni1O3P1)]\@
```

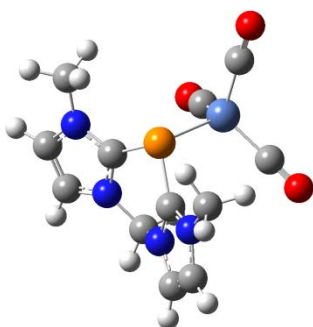
Ph₃P-Ni(CO)₃:



```
1\1\GINC-SAW280\FOpt\RPBE1PBE\Gen\C21H15Ni1O3P1\CMACD\09-Feb-2015\0\#\n
PBE1PBE/gen pseudo=read scf=tight opt freq pop=(full,nboread) test\O\n
ptimization of Ph3P-Ni(CO)3 complex\0,1\Ni,2.1535358006,-0.0024473032\n
,0.0024837418\P,-0.0937138688,-0.000616787,0.0012700988\C,2.6816837719\n
,0.5078402992,-1.6356304805\C,2.677597601,-1.6774568163,0.3800819527\C\n
,2.680113395,1.1604903544,1.2647716031\O,3.0274339117,0.8277315447,-2.\n
6733353095\O,3.0206554408,-2.7368841494,0.622220331\O,3.0248509796,1.8\n
987874977,2.0614769742\C,-0.8802437628,-0.4981736684,-1.587961465\C,-0\n
.2930158017,-1.5378681121,-2.3085919761\C,-2.0251724585,0.1151486659,-\n
2.0911918312\C,-0.8521932447,-1.9699664969,-3.5013436742\H,0.612393584\n
7,-2.0046279679,-1.9346894367\C,-2.577196337,-0.3117348401,-3.29200056\n
72\H,-2.4846888486,0.9332837354,-1.548217248\C,-1.9951558236,-1.355710\n
689,-3.9964951711\H,-0.3871067641,-2.7804913803,-4.0514297685\H,-3.465\n
255825,0.1768300385,-3.6778852579\H,-2.4271565377,-1.6863079659,-4.934\n
5866702\C,-0.8795065581,1.625234941,0.3638383203\C,-2.0188405274,1.756\n
7216041,1.1544743431\C,-0.2961460768,2.7677945426,-0.1833919893\C,-2.5\n
692038224,3.0107516574,1.3855686888\H,-2.4757973621,0.8791017538,1.597\n
638213\C,-0.8537804815,4.0173500825,0.0392265521\H,0.6051334411,2.6759\n
491026,-0.7805509394\C,-1.9912000414,4.1412869736,0.8264568444\H,-3.45
```

2839943,3.1023315924,2.0076958986\H,-0.3915978062,4.8977550697,-0.3933
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 68459351,1.2263977367\C,-2.0287747707,-1.8670291432,0.9456024806\C,-0.
 2958681078,-1.2341063373,2.4871224134\C,-2.582915648,-2.6935443838,1.9
 14457643\H,-2.4881948128,-1.80408705,-0.0343132512\C,-0.8571712123,-2.
 0510814339,3.4564615121\H,0.6107857839,-0.6794219483,2.7054556959\C,-2
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 ,-3.4312636073,3.9254805649\\Version=EM64L-G09RevD.01\State=1-A\HF=-15
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 286,-0.0130915\PG=C01 [X(C21H15Ni1O3P1)]\@

$[\text{H}_2\text{C}^{\text{Me}}\text{NHC}^{\text{H}}]_2\text{P-Ni}(\text{CO})_3]^+$:



1\1\GINC-SAW193\FOpt\RPBE1PBE\Gen\C12H12N4Ni1O3P1(1+)\CMACD\06-Feb-201
 5\0\# PBE1PBE/gen pseudo=read scf=tight opt freq pop=(full,nboread) t
 est\Optimization of LP-Ni(CO)3 cation complex\1,1\P,6.3847147097,5.0
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 85035476,7.4851191904,2.9101066161\N,5.2407600256,6.092357817,4.550386

218\C,4.6016414786,8.1085161936,4.0024504255\H,4.2119537578,9.11117010
98,3.9480203973\C,4.6402178913,7.2380612832,5.0330391505\H,4.295923289
2,7.3308437609,6.0494069003\C,5.6929640901,4.9494828186,5.306107021\H,
6.7696562006,5.047314644,5.491309138\H,5.1510891487,4.8955275732,6.248
2825554\C,5.0727014146,2.5100287342,5.0089379954\H,4.752352582,2.34512
74201,6.0239718158\C,5.1918728477,1.6579707194,3.968997478\H,4.9908127
124,0.6018411872,3.9037940389\C,5.8080442915,3.6687629369,3.2384986825
\N,5.4549875644,3.7508084133,4.5391834098\N,5.6348993568,2.3854132141,
2.8838706526\C,5.3325670204,8.0764394895,1.5932057884\H,6.2940678631,8
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2837189005,7.2858701025,0.8439700435\C,5.9044405256,1.8493542971,1.560
769699\H,5.6725227471,2.6120075347,0.8167440852\H,5.2707888072,0.98043
66711,1.3943033969\H,6.9532306404,1.5621140813,1.4736877457\Ni,8.63210
16022,5.2398126031,2.6780782706\C,8.8568659072,6.8361973143,3.46647594
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,7.8529857176,3.9632703416\O,9.4456442461,2.9679902319,4.3467622598\|V
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56,15.8511972,-3.8750416,-2.5059497,-7.0976316,-0.4697876\PG=C01 [X(C1
2H12N4Ni1O3P1)]\@

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