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Electronic and steric Tolman parameters for proazaphosphatranes, the superbase core of the tri(pyridylmethyl)azaphosphatrane (TPAP) ligand†

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The Tolman electronic parameters (TEP) and cone angles were experimentally measured for a series of substituted proazaphosphatrane ligands by synthesizing their respective $\text{Ni}(\text{L}^{\text{R}})(\text{CO})_3$ complexes, where $\text{L} = \text{P}(\text{RNCH}_2\text{CH}_2)_3\text{N}$ and $\text{R} = \text{Me}$, *i*Pr, *i*Bu and Bz. The complexes $\text{Ni}(\text{L}^{\text{Me}})(\text{CO})_3$ (**1**), $\text{Ni}(\text{L}^{\text{iPr}})(\text{CO})_3$ (**2**), $\text{Ni}(\text{L}^{\text{iBu}})(\text{CO})_3$ (**3**) and $\text{Ni}(\text{L}^{\text{Bz}})(\text{CO})_3$ (**4**) display CO vibrational frequencies (A1 mode) at 2057.0, 2054.6, 2054.9 and 2059.1 cm^{-1} , respectively. The TEPs for the phosphine ligands in **1–3** are among the lowest measured, with values close to $\text{P}(\text{tBu})_3$ the most donating phosphine measured by Tolman. The cone angles of L^{R} measured in **1–4** are 152, 179, 200 and 207° for $\text{R} = \text{Me}$, *i*Pr, *i*Bu and Bz, respectively. The substituted proazaphosphatranes have larger cone angles compared to the analogous trialkyl substituted monophosphines. Our study demonstrates that while the cone angles have a significant dependence on R, all of the substituted proazaphosphatranes are strong electron donors. Additionally, in order to determine the electronic donor strength of our previously reported multidentate ligand, TPAP, $\text{Ni}(\text{TPAP})(\text{CO})_2$ (**5**) (TPAP = tris(2-pyridylmethyl)azaphosphatrane) and $\text{Ni}(\text{L}^{\text{Me}})_2(\text{CO})_2$ (**6**) were also synthesized and evaluated in a similar fashion.

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Introduction

Phosphines are ubiquitous ligands in transition metal synthesis¹ and catalysis,^{2,3} as their steric and electronic properties can be easily tuned *via* substituent modification.⁴ The relative stereoelectronic effects between phosphine ligands are most commonly evaluated by the Tolman electronic parameter (TEP) and cone angle.⁵

We recently reported a new tetradentate ligand bearing a modified proazaphosphatrane, tris(2-pyridylmethyl)-azaphosphatrane (TPAP).⁶ Although prior studies suggested that proazaphosphatranes (colloquially known as Verkade's superbases) are strong electron donor ligands,^{7–9} the Tolman parameters had never been measured. In this study, we experimentally measured the TEP and cone angle for a series of proazaphosphatranes (L) with various functionalities (L^{R} , $\text{R} = \text{Me}$, *i*Pr, *i*Bu, and Bz) by synthesizing the corresponding $\text{Ni}(\text{L}^{\text{R}})(\text{CO})_3$ complexes, shown in Chart 1 as compounds **1–4**. The TEP was evaluated by the infrared vibrational stretching frequencies of the CO bonds,¹⁰ and the cone angle was determined by X-ray crystallographic analysis.¹¹ Additionally, we evaluated the phos-

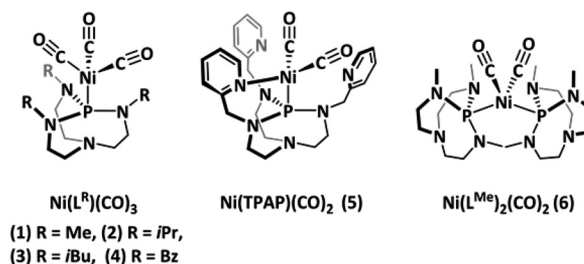


Chart 1

phine donor strength in TPAP by synthesizing the $\text{Ni}(\text{TPAP})(\text{CO})_2$ (**5**) complex and comparing its properties to $\text{Ni}(\text{L}^{\text{Me}})_2(\text{CO})_2$ (**6**).

The Tolman electronic parameters for the proazaphosphatranes in this study establish them as among the most electron donating phosphine ligands. The TEPs are comparable to $\text{P}(\text{tBu})_3$, the most donating phosphine measured by Tolman, and only recently exceeded by a series of imidazolin-2-ylidene-aminophosphines.¹² The cone angles are also larger compared to the equivalently substituted trialkyl phosphines. The combined electron donor strength and large steric size of proazaphosphatranes is likely an important factor in their successful use as ligands in Pd and Pt catalyzed C–C,^{13–16} C–N,^{9,17–22} and C–Si²³ bond coupling reactions.

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The quantification of Tolman parameters for proazaphosphatranes in this study permits the rational modification of steric and electronic properties for this synthetically modular class of ligands. Additionally, it establishes the strong electron donor character at the core of the multidentate TPAP ligand.

Results and discussion

Synthesis and structure of Ni(L^R)(CO)₃ complexes (1–4)

Bis(1,5-cyclooctadiene)nickel(0) was added to a solution of L^R (L = P(RNCH₂CH₂)₃N, R = Me, *i*Pr, *i*Bu and Bz) in THF. After stirring for 1 hour, CO gas (1 atm) was added and the respective products were isolated by recrystallization to furnish Ni(L^{Me})(CO)₃ (1), Ni(L^{*i*Pr})(CO)₃ (2), Ni(L^{*i*Bu})(CO)₃ (3), and Ni(L^{Bz})(CO)₃ (4) in 84, 87, 74 and 93% yield, respectively. The

identity of the diamagnetic complexes was determined by ¹H, ¹³C, and ³¹P NMR spectroscopy (shown as Fig. S1–S12 in the ESI†), and the purity was confirmed by elemental analysis.

Solution infrared spectra of 1–4 in CH₂Cl₂ contain two CO vibrational stretches (Fig. S13†), assigned to the A₁ and E modes. The A₁ resonances for 1–4 are 2057.0, 2054.6, 2054.9, and 2059.1 cm⁻¹, and the E resonances are 1977.7, 1974.7, 1975.3, and 1981.1 cm⁻¹, respectively. The values are also listed in Table 1.

Single crystals suitable for X-ray analysis were grown from a slow evaporation of pentane solutions of 2–4. Crystallographic data and selected bond distances and angles are given in Tables 2 and 3. The structures are shown in Fig. 1, and were used to determine the cone angles for L^R.

Most complexes prepared by Tolman were not structurally characterized. Instead, cone angles were determined by a space-filling CPK (Corey–Pauling–Koltun) model based on a tetrahedral coordination geometry and a P–Ni bond length of 2.28 Å.²⁴ Consistent with this model, the structures of 2–4 display near ideal tetrahedral geometries with τ₄ values of 0.977, 0.955, and 0.968, respectively, where τ₄ = 1 represents a tetrahedral geometry and τ₄ = 0 represents a square planar geometry.²⁵ The P–Ni distances of 2–4 are 2.2680(5), 2.2519(3) and 2.2424(5) Å, respectively. Although our P–Ni distances are slightly shorter, Tolman remarked that variations of up to 0.1 Å “seldom change the cone angle by more than 3 or 4°”.⁵ Therefore, we believe our structurally determined cone angles are consistent with the parameters originally reported by Tolman using the CPK model.

The values for the P–Ni bond lengths in 2–4 display an inverse relationship with Tolman’s cone angle parameters. Additionally, more electronegative substituents on the proaza-

Table 1 CO vibrational frequencies (in CH₂Cl₂) and cone angle of complexes 1–4 and selected Ni(CO)₃(PR₃) complexes

Complex	ν _{co} A ₁ (cm ⁻¹)	ν _{co} E (cm ⁻¹)	Cone angle (°)
Ni(CO) ₃ (L ^{Me}) (1)	2057.0	1977.7	152 ^a
Ni(CO) ₃ (L ^{<i>i</i>Pr}) (2)	2054.6	1974.7	179
Ni(CO) ₃ (L ^{<i>i</i>Bu}) (3)	2054.9	1975.3	200
Ni(CO) ₃ (L ^{Bz}) (4)	2059.1	1981.1	207
Ni(CO) ₃ (P(<i>t</i> Bu) ₃) ^b	2056.1	1971	182
Ni(CO) ₃ (P(Me) ₃) ^b	2064.1	1982	118
Ni(CO) ₃ (P(<i>i</i> Pr) ₃) ^b	2059.2	1977	160
Ni(CO) ₃ (P(<i>i</i> Bu) ₃) ^b	2059.7	—	143
Ni(CO) ₃ (P(Bz) ₃) ^b	2066.2	1986	165

^a Cone angle was measured from crystal structure of 6. ^b TEP values taken from Tolman *et al.*⁵

Table 2 Crystallographic data and refinement parameters for complexes 2–6

Complex	2	3	4	5	6
Formula	C ₁₈ H ₃₃ N ₄ O ₃ PNi	C ₂₁ H ₃₉ N ₄ O ₃ PNi	C ₃₀ H ₃₃ N ₄ O ₃ PNi	C ₂₆ H ₃₀ N ₇ O ₂ PNi	C ₂₀ H ₄₂ N ₈ O ₂ P ₂ Ni
Molar mass	443.16	485.24	587.28	562.25	547.27
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
<i>T</i> [K]	133(2)	88(2)	133(2)	88(2)	133(2)
<i>a</i> [Å]	9.4521(6)	10.4524(5)	9.7263(8)	12.8799(6)	8.5551(5)
<i>b</i> [Å]	16.0515(11)	17.9047(8)	23.412(2)	14.0169(7)	19.4034(12)
<i>c</i> [Å]	14.5677(10)	13.5993(6)	12.5881(11)	15.4714(7)	15.9663(1)
α [°]	90.00	90.00	90.00	90.00	90.00
β [°]	93.8772(8)	97.2348(6)	99.3160(10)	109.6630(10)	104.7970(10)
γ [°]	90.00	90.00	90.00	90.00	90.00
<i>V</i> [Å ³]	2205.2(3)	2524.8(2)	2828.6(4)	2630.3(2)	2562.5(3)
<i>Z</i>	4	4	4	4	4
<i>D</i> (calcd) [Mg m ⁻³]	1.335	1.277	1.379	1.420	1.419
μ(Mo–Kα) [mm ⁻¹]	0.977	0.859	0.781	0.836	0.916
Index range	–12 ≤ <i>h</i> ≤ 12 –21 ≤ <i>k</i> ≤ 21 –19 ≤ <i>l</i> ≤ 19	–14 ≤ <i>h</i> ≤ 13 –23 ≤ <i>k</i> ≤ 23 –18 ≤ <i>l</i> ≤ 18	–13 ≤ <i>h</i> ≤ 13 –32 ≤ <i>k</i> ≤ 31 –16 ≤ <i>l</i> ≤ 17	–17 ≤ <i>h</i> ≤ 16 –18 ≤ <i>k</i> ≤ 19 –20 ≤ <i>l</i> ≤ 21	–11 ≤ <i>h</i> ≤ 11 –25 ≤ <i>k</i> ≤ 25 –21 ≤ <i>l</i> ≤ 21
Reflection collected	24 569	31 264	70 276	32 415	62 910
Independent reflections	5360	6479	7270	6760	6562
Data/restraints/parameters	5360/0/250	6479/0/431	7270/0/352	6760/0/334	6562/0/304
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0359, 0.0749	0.0272, 0.0665	0.0400, 0.1283	0.0291, 0.0753	0.0232, 0.1097
<i>R</i> ₁ , w <i>R</i> ₂ [all data]	0.0544, 0.0810	0.0341, 0.0701	0.0470, 0.1393	0.0380, 0.0776	0.0242, 0.1122
GOF	1.220	1.029	1.168	1.045	1.056

Table 3 Selected distances and angles of 2–6

Complex	2	3	4	5	6 ^a
P–Ni (Å)	2.2680(5)	2.2519(3)	2.2424(5)	2.2121(4)	2.2320(3)
P...N1 (Å)	3.330	3.435	3.317	3.274	3.478
P–N2 (Å)	1.6927(14)	1.6899(11)	1.6879(13)	1.6837(12)	1.6892(9)
P–N3 (Å)	1.6900(14)	1.6885(11)	1.6824(13)	1.6880(12)	1.6902(9)
P–N4 (Å)	1.6894(14)	1.6876(11)	1.6890(13)	1.6919(12)	1.6939(9)
C–O1 (Å)	1.140(2)	1.1385(17)	1.146(2)	1.1541(18)	1.1500(15)
C–O2 (Å)	1.143(2)	1.1447(18)	1.140(2)	1.1482(17)	1.1506(14)
C–O3 (Å)	1.133(2)	1.1404(18)	1.142(2)	—	—
N2–P–Ni (°)	114.59(5)	113.93(4)	112.74(5)	118.80(4)	112.92(3)
N3–P–Ni (°)	113.96(5)	113.77(4)	114.01(5)	118.35(5)	120.25(3)
N4–P–Ni (°)	115.05(5)	115.12(4)	115.49(5)	106.32(4)	113.12(3)
N4–P–N3 (°)	103.34(7)	104.00(5)	105.32(6)	105.56(6)	102.74(5)
N3–P–N2 (°)	104.07(7)	104.18(5)	103.78(6)	103.28(6)	103.10(5)
N2–P–N4 (°)	104.46(7)	104.64(5)	104.32(6)	102.83(6)	102.71(4)

^a One of the two L^{Me} measurements in complex 6.

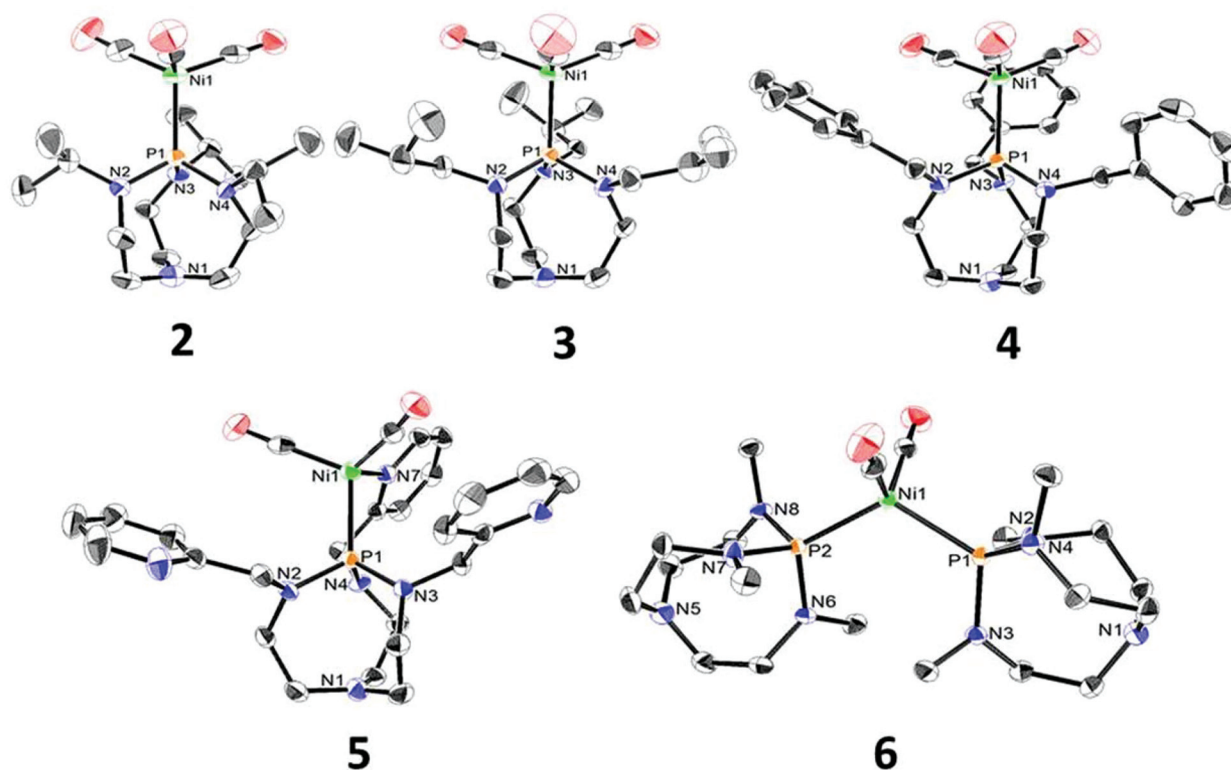


Fig. 1 Crystal structure of Ni(L^{iPr})(CO)₃ (2), Ni(L^{iBu})(CO)₃ (3), Ni(L^{Bz})(CO)₃ (4), Ni(TPAP)(CO)₂ (5) and Ni(L^{Me})₂(CO)₂ (6). Thermal ellipsoids drawn at 80% probability; hydrogen atoms are omitted for clarity. Carbon atoms from the minor part of a disorder in 3 are also omitted.

phosphatranes (R = Bz > *i*Bu > *i*Pr)²⁶ results in shorter P–Ni bond lengths. Our observed trend is consistent with Tolman's observation that more electronegative substituents increases the phosphorus s orbital character, which shortens the bond.⁵

Synthesis and structure of Ni(TPAP)(CO)₂ (5) and Ni(L^{Me})₂(CO)₂ (6) complexes

Complexes 5 and 6 were synthesized in a similar fashion as complexes 1–4. Bis(1,5-cyclooctadiene)nickel(0) was added to a

solution of TPAP in THF, which produced a green intermediate complex. Once CO gas (1 atm) was introduced, the color changed from dark green to colorless. The solvent was removed and recrystallization from diethyl ether resulted in Ni(TPAP)(CO)₂ (5) in 77% yield. The solution infrared spectrum of 5 in CH₂Cl₂ displays two CO vibrational stretches at 1981.7 and 1906.5 cm⁻¹ (Table 4 and Fig. S14[†]).

Ni(L^{Me})₂(CO)₂ (6) was synthesized from a 2 : 1 ratio of L^{Me} and bis(1,5-cyclooctadiene)nickel(0) in THF and an atmo-

Table 4 CO vibrational frequencies of complexes **5**, **6**, Ni(CO)₂(PTA)₂, Ni(CO)₂(P(Me)₃)₂, and Ni(CO)₂(P(*i*Pr)₃)₂ in CH₂Cl₂

Complex	ν_{CO} (cm ⁻¹)	ν_{CO} (cm ⁻¹)
Ni(CO) ₂ (TPAP) (5)	1981.7	1906.5
Ni(CO) ₂ (L ^{Me}) ₂ (6)	1976.8	1909.3
Ni(CO) ₂ (PTA) ₂ ³³	2006	1946
Ni(CO) ₂ (P(Me) ₃) ₂ ²⁴	1990 ^a	1926 ^a
Ni(CO) ₂ (P(<i>i</i> Pr) ₃) ₂ ²⁴	1984 ^a	1922 ^a

^a Measured in toluene.

sphere of CO gas. Upon exposure to CO the color changed from dark orange to colorless. The crude product was recrystallized from CH₂Cl₂ to give the product in 62% yield. The solution infrared spectrum of **6** in CH₂Cl₂ exhibits two CO vibrational stretches at 1976.8 and 1909.3 cm⁻¹ (Table 4 and Fig. S14[†]). Complexes **5** and **6** were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy (shown as Fig. S15–S20 in the ESI[†]), and the purity was confirmed by elemental analysis. Single crystals suitable for X-ray analysis were grown from slow evaporation of diethyl ether (**5**) or CH₂Cl₂ (**6**) solutions. The structures of **5** and **6**, shown in Fig. 1, display a tetrahedral geometry with τ_4 values of 0.885 and 0.971, respectively.²⁵ Crystallographic data for **5** and **6** and selected bond distances and angles are given in Tables 2 and 3.

Tolman electronic parameters and cone angles of Ni(L^R)(CO)₃ complexes (1–4)

The electronic and steric properties of the most strongly electron donating trialkyl substituted phosphines measured by Tolman⁵ are used as a comparison to the proazaphosphatranes summarized in Table 1 and shown in Fig. 2. The CO vibrational frequencies of 1–3 are similar to those reported for the most donating alkyl-phosphine ligand, P(*t*Bu)₃ (Ni(P(*t*Bu)₃)(CO)₃, ν_{CO} = 2056.1 cm⁻¹), while the CO vibrational frequencies of complex **4** were closer to those observed for the acyclic triaminophosphine ligand (Ni(P(NMe₂)₃)(CO)₃, ν_{CO} = 2061.9 cm⁻¹).²⁵

The trend in electron donor properties of the trisubstituted proazaphosphatranes follows the same trend as the trialkyl substituted phosphines originally measured by Tolman (stronger

donor > weaker donor: *i*Pr ≥ *i*Bu > Me > Bz). However, the overall strength of electronic donation for the proazaphosphatranes is greater than that of the equivalently substituted tertiary phosphine.

The greater overall donor strengths of the proazaphosphatranes are primarily due to replacement of the alkyl functionalities on the phosphine with alkyl-substituted amine donors. Amine substituents are known to increase the strength of electron donation when bound to phosphorus ligands. A prior study by Woollins *et al.* systematically investigated this effect on acyclic phosphines and determined that the strength of phosphorus electron donation increases after the first and second P–C bonds are replaced by P–N bonds.^{27,28} However, replacement of the third P–C bond with a P–N bond results in a decrease in the electron donor strength because the effect of a stronger σ donor is outweighed by the electron-withdrawing character of the more electronegative nitrogen atoms due to steric constraints. This phenomenon is observable in the X-ray crystal structure of acyclic tris(dialkylamino)phosphine ligands, where two of the nitrogen atoms are nearly planar (sum of angles at nitrogen ~360°) and one of the nitrogens is not (sum of the angles at nitrogen ~350°).^{29–31} As a result, the two planar nitrogen atoms can donate electron density to the phosphorus through their lone pairs, which are nearly orthogonal to the phosphorus lone pair. However, the third nitrogen only contributes electron-withdrawing character due to its orientation (*anti*) to the lone pair on phosphorus.³² In contrast, structural characterizations of the cyclic proazaphosphatranes in this study (Fig. 1) demonstrate that all three nitrogens bound to the phosphorus are nearly planar (sum of angles at nitrogen = 358 to 360°). Verkade *et al.* hypothesized that the rigid bicyclic framework of the proazaphosphatranes molecule constrains all three nitrogens to adopt this geometry, resulting in stronger overall electron-donating character compared to the previously studied acyclic tris(dialkylamino) phosphines.⁷

Overall, the proazaphosphatranes exhibit greater cone angles compared to the equivalent trialkyl substituted phosphines. In fact, L^{Bz} has a cone angle close to the highest cone angle (P(mesityl)₃ = 212°) measured by Tolman.⁵ The TEP vs. cone angle for L^R in 1–4 are graphed along with comparable phosphines in Fig. 2, which demonstrates that while the cone angle of proazaphosphatranes are highly substituent dependent, they all maintain their strong electron donating character.

Electronic donor strength of Ni(TPAP)(CO)₃ (**5**) and Ni(L^{Me})₂(CO)₂ (**6**)

In complex **5**, TPAP binds to Ni(0) in a bidentate fashion. Therefore, no direct comparison regarding the CO vibrational frequencies between **5** and 1–4 can be made. In an attempt to evaluate the electron donating properties of the phosphorus in TPAP to the proazaphosphatranes in 1–4, complex **6** was also synthesized. Complex **6** is coordinated with two CO molecules and two L^{Me} ligands. The CO vibrational frequencies of **5** and **6** are comparable (Table 4), but **5** has only one proazaphospha-

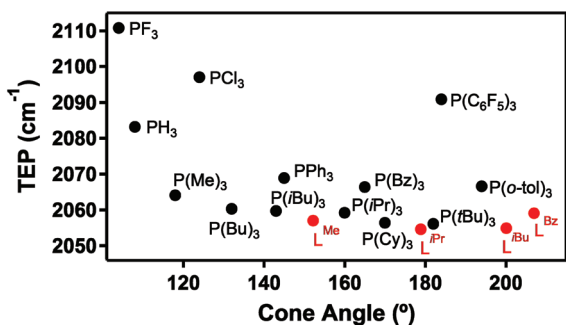


Fig. 2 Comparison of Tolman electronic parameter (TEP) and cone angles. Red dots (●) represent proazaphosphatranes measured herein and black dots (●) represent phosphines measured by Tolman.⁵

trane bound to Ni(0) along with a more weakly donating pyridine ligand. This indicates that the proazaphosphatrane in TPAP is at least as strong of an electron donor as L^{Me} . The CO vibrational frequencies of **5** and **6** are both lower than that of $Ni(CO)_2(PTA)_2$ ($PTA = 1,3,5$ -triaza-7-phosphaadamantane),³³ $Ni(CO)_2(P(Me)_3)_2$,²⁴ or $Ni(CO)_2(P(iPr)_3)_2$ ²⁴ (listed in Table 4), indicating that two L^{Me} and TPAP are stronger electron donors than two PTA, $P(Me)_3$ or $P(iPr)_3$ ligands. By comparing their respective dicarbonyl complexes, we expect the proazaphosphatrane in TPAP to be at least as electron donating as the monodentate derivatives. This conclusion is consistent with our observation that various alkyl substituents have a minimal effect on the overall donor strength for proazaphosphatranes.

Based on the similar steric profile of the benzyl substituents and the 2-methylpyridyls in TPAP, we believe the cone angle for the proazaphosphatrane in TPAP is most similar to that of L^{Bz} .

Experimental

General considerations

The complexes described below are air- and moisture-sensitive, and must be handled under an inert atmosphere of nitrogen using standard glovebox and Schlenk techniques. Unless otherwise noted, all procedures were performed at ambient temperature (21–24 °C). All solvents were sparged with argon and dried using a solvent purification system. Tetrahydrofuran, pentane, diethyl ether and dichloromethane were passed through two columns of neutral alumina. Compounds 2,8,9-tribenzyl-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (L^{Bz}), 2,8,9-tri(2-pyridinemethyl)-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (TPAP)⁶ and 2,8,9-triisopropyl-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (L^{iPr})³⁴ were synthesized according to established procedures. C_6D_6 was freeze-pump-thawed three times and dried over molecular sieves. 2,8,9-trimethyl-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (L^{Me}) was purchased from Sigma-Aldrich with unspecified purity; therefore further extraction with pentane was necessary to obtain the product in high purity. 2,8,9-Triisobutyl-2,3,8,9-tetraaza-1-phosphabicyclo[3,3,3]undecane (L^{iBu}), bis(1,5-cyclooctadiene)nickel(0) (98%), and carbon monoxide (100%) were purchased from commercial sources and used without further purification.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX500 spectrometer fitted with a TCI cryoprobe (^{13}C) or a DRX400 with a switchable QNP probe (1H and ^{31}P) in dry, degassed solvents. 1H NMR spectra were referenced to (tetramethylsilane) TMS using the residual proteo impurities of the solvent; ^{13}C NMR spectra were referenced to TMS using the natural abundance ^{13}C of the solvent; ^{31}P NMR spectra were referenced to H_3PO_4 using the Ξ scale with the corresponding 1H spectra. All chemical shifts are reported in the standard δ notation in parts per million; positive chemical shifts are to a higher frequency from the given reference. Infrared (IR) absorption measurements of the solution of **1–6** in

CH_2Cl_2 was taken in a OMNI-Cell CaF_2 sealed cell (1.00 mm) on a Thermo Scientific Nicolet iS5 spectrophotometer with an iD1 transmission attachment. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS elemental analyzer or on an Exeter Analytical, Inc. CE-440 Elemental Analyzer.

X-ray diffraction studies were carried out at the UCI Department of Chemistry X-ray Crystallography Facility on a Bruker SMART APEX II diffractometer. Data was collected at 88 K for **3** and **5** and 133 K for **2**, **4**, and **6** using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A full sphere of data was collected for each crystal structure. The APEX2 program suite was used to determine unit-cell parameters and for collection (30 s per frame scan time for a sphere of diffraction data). The raw frame data were processed and absorption corrected using the SAINT and SADABS programs, respectively, to yield the reflection data files. Structures were solved by direct methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97. The analytical scattering factors for neutral atoms were used throughout the analysis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at geometrically calculated positions and refined using a riding model, and their isotropic displacement parameters were fixed at 1.2 (1.5 for methyl groups) times the U_{eq} of the atoms to which they are bonded. For structure **3**, carbon atoms C(16), C(17) and C(18) were disordered and modeled using multiple components with partial site-occupancy-factors.

General synthesis of $Ni(L^R)(CO)_3$ complexes

In the glove box, a solution of bis(1,5-cyclooctadiene)nickel(0) (1 equiv.) in 5 mL of tetrahydrofuran was added to a solution of L^R (1 equiv.) in 5 mL of tetrahydrofuran. The solution was stirred for 1 hour at room temperature. The solution was then transferred to a 100 mL Schlenk flask and brought out of the glove box and filled with CO gas (1 atm). The solution was stirred overnight under a CO atmosphere, after which the solution became colorless. The solvent was removed under reduced pressure and the resulting light yellow solid was brought back into the glove box and dissolved in diethyl ether or pentane. Colorless crystals were grown from a slow evaporation of diethyl ether (**1**) or pentane (**2–4**).

Ni(L^{Me})(CO)₃ (1). L^{Me} (74.5 mg, 0.345 mmol) and bis(1,5-cyclooctadiene)nickel(0) (94.8 mg, 0.345 mmol). 84% Yield. 1H NMR (C_6D_6 , 400 MHz) $\delta = 2.39$ (br, 9H, CH_3NP), 2.47 (s, 6H, NCH_2CH_2NP), 2.50 (s, 6H, NCH_2CH_2NP). $^{13}C\{^1H\}$ NMR (C_6D_6 , 126 MHz) $\delta = 35.8$ (CH_3NP), 50.4 (NCH_2CH_2NP), 50.6 (NCH_2CH_2NP), 199 (CO). ^{31}P NMR (C_6D_6 , 162 MHz) $\delta = 136$. FTIR (CH_2Cl_2): $\nu = 2057.0$ (CO- A_1), 1977.7 (CO-E). Analytical Calculation for $C_{12}H_{21}N_4NiO_3P$: C, 40.15; H, 5.90; N, 15.61 Found: C, 39.67; H, 5.99; N, 15.15.

Ni(L^{iPr})(CO)₃ (2). L^{iPr} (194 mg, 0.647 mmol) and bis(1,5-cyclooctadiene)nickel(0) (178 mg, 0.647 mmol). 87% Yield. 1H NMR (C_6D_6 , 400 MHz) $\delta = 1.04$ (d, $J = 6.6$ Hz, 18H, $NCH(CH_3)_2$), 2.55–2.69 (A_2B_2 , 12H, NCH_2CH_2NP), 3.90 (septet, $J = 6.7$ Hz, 3H, $NCH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (C_6D_6 , 126 MHz) $\delta = 22.7$ ($NCH(CH_3)_2$), 39.9 (NCH_2CH_2NP), 49.7 ($NCH(CH_3)_2$), 54.8 (NCH_2CH_2NP), 199 (CO). ^{31}P NMR (C_6D_6 , 162 MHz) $\delta = 137$.

FTIR (CH₂Cl₂): $\nu = 2054.6$ (CO-A₁), 1974.7 (CO-E). Analytical Calculation for C₁₈H₃₃N₄NiO₃P: C, 48.79; H, 7.51; N, 12.64 Found: C, 48.75; H, 7.39; N, 12.58.

Ni(L^{iBu})(CO)₃ (3). L^{iBu} (195 mg, 0.569 mmol) and bis(1,5-cyclooctadiene)nickel(0) (157 mg, 0.569 mmol). 74% Yield. ¹H NMR (C₆D₆, 400 MHz) $\delta = 0.94$ (d, $J = 6.7$ Hz, 18H, NCH₂CH(CH₃)₂), 2.06 (septet, $J = 6.9$ Hz, 3H, NCH₂CH(CH₃)₂), 2.55 (t, $J = 4.8$ Hz, 6H, NCH₂CH₂NP), 2.82–2.67 (br, 12H, NCH₂CH₂NP, NCH₂CH(CH₃)₂). ¹³C{¹H} NMR (C₆D₆, 126 MHz) $\delta = 21.1$ (NCH₂CH(CH₃)₂), 28.8 (NCH₂CH(CH₃)₂), 48.2 (NCH₂CH₂NP), 50.3 (NCH₂CH₂NP), 55.4 (NCH₂CH(CH₃)₂), 199 (CO). ³¹P NMR (C₆D₆, 162 MHz) $\delta = 141$. FTIR (CH₂Cl₂): $\nu = 2054.9$ (CO-A₁), 1975.3 (CO-E). Analytical Calculation for C₂₁H₃₉N₄NiO₃P: C, 51.98; H, 8.10; N, 11.55 Found: C, 51.56; H, 7.94; N, 11.86.

Ni(L^{Bz})(CO)₃ (4). L^{Bz} (146 mg, 0.328 mmol) and bis(1,5-cyclooctadiene)nickel(0) (90.0 mg, 0.328 mmol). 93% Yield. ¹H NMR (C₆D₆, 400 MHz) $\delta = 2.45$ (t, $J = 4.8$ Hz, 6H, NCH₂CH₂NP), 2.68 (br, 6H, NCH₂CH₂NP), 4.31 (br, 6H, PhCH₂NP), 7.14 (m, 3H, *p*-Ph), 7.30 (t, $J = 7.7$ Hz, 6H, *m*-Ph), 7.40 (d, $J = 7.3$ Hz, 6H, *o*-Ph). ¹³C{¹H} NMR (C₆D₆, 126 MHz) $\delta = 46.7$ (NCH₂CH₂NP), 49.9 (NCH₂Ph), 50.7 (NCH₂CH₂NP), 128 (Ph), 128 (Ph), 129 (Ph), 139 (Ph), 198 (CO). ³¹P NMR (C₆D₆, 162 MHz) $\delta = 143$. FTIR (CH₂Cl₂): $\nu = 2059.1$ (CO-A₁), 1981.1 (CO-E). Analytical Calculation for C₃₀H₃₃N₄NiO₃P: C, 61.36; H, 5.66; N, 9.54 Found: C, 61.02; H, 5.64; N, 9.48.

Ni(TPAP)(CO)₂ (5). In the glove box, a solution of bis(1,5-cyclooctadiene)nickel(0) (13.8 mg, 0.050 mmol) in 5 mL of tetrahydrofuran was added to a solution of TPAP (22.5 mg, 0.050 mmol) in 5 mL of tetrahydrofuran. The solution was stirred for 1 hour at room temperature. The solution was then transferred to a 100 mL Schlenk flask and brought out of the glove box and filled with CO gas (1 atm). The solution was stirred overnight under a CO atmosphere, after which the color changed from dark green to colorless. The CO gas was removed under reduced pressure with four cycle of freeze-pump-thaw and the resulting light yellow solution was brought back into the glove box. The oil that remained after solvent evaporation was washed with cold pentane to yield a yellow solid. Yellow crystals of 5 were grown from a slow evaporation of diethyl ether to give the product in 77% yield. NMR studies of 5 were conducted in a J-Young tube, in 1 atm of CO gas. ¹H NMR (C₆D₆, 400 MHz) $\delta = 2.46$ (t, $J = 10.8$ Hz, 6H, NCH₂CH₂NP), 2.76 (br, 6H, NCH₂CH₂NP), 4.58 (br, 6H, PyrCH₂N), 6.67 (dd, $J = 7.1, 5.1$ Hz, 3H, Pyr), 7.25 (td, $J = 7.7, 1.7$ Hz, 3H, Pyr), 7.38 (d, $J = 7.8$ Hz, 3H, Pyr), 8.53 (m, 3H, Pyr). ¹³C{¹H} NMR (C₆D₆, 126 MHz) $\delta = 47.7$ (NCH₂CH₂NP), 50.2 (PyrCH₂N), 53.3 (NCH₂CH₂NP), 122 (Pyr), 122 (Pyr), 136 (Pyr), 150 (Pyr), 160 (Pyr), 198 (CO). ³¹P NMR (C₆D₆, 162 MHz) $\delta = 142$. FTIR (CH₂Cl₂): $\nu = 1981.7$ (CO), 1906.5 (CO). Analytical Calculation for C₂₆H₃₀N₇NiO₂P: C, 55.54; H, 5.38; N, 17.44 Found: C, 55.02; H, 5.19; N, 17.50.

Ni(L^{Me})₂(CO)₂ (6). In the glove box, a solution of bis(1,5-cyclooctadiene)nickel(0) (26.2 mg, 0.095 mmol) in 5 mL of tetrahydrofuran was added to a solution of L^{Me} (41.2 mg, 0.191 mmol) in 5 mL of tetrahydrofuran. The solution was stirred for 1 hour at room temperature. The solution was trans-

ferred to a 100 mL Schlenk flask, brought out of the glove box, and filled with CO gas (1 atm). The solution was stirred overnight under a CO atmosphere, during which time the color changed from dark orange to colorless. The solvent was removed under reduced pressure and the resulting light yellow solid was brought back into the glove box and washed with pentane. Colorless crystals of 6 were grown from a slow evaporation of dichloromethane to give the product in 62% yield. ¹H NMR (C₆D₆, 400 MHz) $\delta = 2.61$ (s, 18H, CH₃NP), 2.74 (d, $J = 8.7$ Hz, 24H, NCH₂CH₂NP). ¹³C{¹H} NMR (C₆D₆, 126 MHz) $\delta = 36.2$ (CH₃NP), 50.6 (NCH₂CH₂NP), 51.1 (NCH₂CH₂NP), 204 (CO). ³¹P NMR (C₆D₆, 162 MHz) $\delta = 144$. FTIR (CH₂Cl₂): $\nu = 1976.8$ (CO), 1909.3 (CO). Analytical Calculation for C₂₀H₄₂N₈NiO₂P₂: C, 43.90; H, 7.74; N, 20.48 Found: C, 43.51; H, 7.79; N, 20.49.

Conclusions

The first experimentally measured Tolman electronic parameters and cone angles for a series of proazaphosphatranes are presented. The proazaphosphatranes in this study display lower TEPs and greater cone angles compared to equivalently substituted trialkyl phosphines. The unique cyclic structure of the proazaphosphatranes contributes to its high donor strength, which is also greater than comparable acyclic triaminophosphines.

Another interesting feature of the proazaphosphatranes is the large effect that alkyl substitution plays on the cone angle while having a negligible effect on the electron donor strength. This property allows the steric bulk to be independently tuned. Lastly, the TEPs obtained from 1–4 were used to assess the electron donating ability of the modified proazaphosphatranes ligand, TPAP. Based on the experimental data, the proazaphosphatranes at the core of the multidentate TPAP ligand maintains its strong electronic donor properties, with steric effects similar to the benzyl-substituted proazaphosphatranes.

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