Bisphosphine ligands containing two *o*-*N*,*N*-dimethylanilinyl substituents at each phosphorus atom

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Abstract: The synthesis and complete characterization of the family of tetra(amine)bisphosphine ligands (*o*-$NMe_2C_6H_4)_2P$-(X)-P(*o*-$NMe_2C_6H_4)_2$, where X = CH_2 (dmapm), $(CH_2)_2$ (dmape), and $CH(CH_2)_3CH$ (dmapcp), are described. Crystal structure data are compared with known, analogous bisphosphines containing *o*-pyridyl or phenyl substituents in place of the *o*-dimethylanilinyl groups. Several short, intramolecular C-H···N distances in the anilinyl derivatives may represent the presence of weak hydrogen bonds.

Key words: phosphine, amine, polydentate, hydrogen-bonding to N atoms.

Résumé : On décrit la synthèse et la caractérisation complète d'une famille de ligands tétra(amine)bisphosphine, (*o*-$NMe_2C_6H_4)_2P$-(X)-P(*o*-$NMe_2C_6H_4)_2$, dans lesquels X = CH_2 (dmapm), $(CH_2)_2$ (dmape) et $CH(CH_2)_3CH$ (dmapcp). On a comparé leurs structures cristallines à celles de bisphosphines connues, analogues, contenant des substituants *o*-pyridyle ou phényle à la place des groupes *o*-diméthylanilinyles. Plusieurs distances intramoléculaires C-H···N dans les dérivés anilinyles sont courtes et elles peuvent être le reflet de la présence de faibles liaisons hydrogènes.

Mots clés : phosphine, amine, polydentate, liaison hydrogène avec des atomes d'azote.

[Traduit par la Rédaction]

Introduction

The introduction of an amine moiety into a *mono*phosphine compound for use as a P-N ligand has a long history and dates from the 1940s; early examples include the 2-pyridylphosphines made by Mann and co-workers (1) and *o*-diphenylphosphino-*N*,*N*-dimethyl-aniline [$Ph_2P(o\text{-}C_6H_4NMe_2)$] reported by Venanzi and co-workers (2); we have used the latter extensively in some recent Ru chemistry (3). This aminophosphine is just one example of a wide range of bidentate, chelating P-N ligands (4). The incorporation of an amine functionality into a *bis*(phosphine) ligand is more recent and dates from about 25 years or so, an early example being that of Achiwa who incorporated two PPh_2 moieties into proline derivatives (5). The amino-bisphosphine systems, which have been reviewed (6), have been developed mainly with the aim of surmounting the severe problem in homogeneous catalysis of separating the catalyst from the reaction products. Approaches to solving this problem, including representative literature references, have been: (*i*) to "heterogenize" the homogeneous catalyst by incorporating it into an insoluble polymer via attachment through the N atom (5, 7–9); (*ii*) to solubilize the catalyst in water (in which the reactants and products are only slightly miscible) by quaternization of the N atom via protonation or alkylation (10–16); (*iii*) to water solubilize the catalyst via incorporation of a sulfonate group within an elaborated N-containing functionality (17); and (*iv*) to extract the catalyst post-reaction with aqueous acid in which the product does not dissolve (18, 19).

Our group here has reported extensively on the use of mono- and bis-phosphine ligands containing the *o*-pyridyl moiety, with the goal of developing platinum metal complexes rendered water soluble by protonation of the pyridyl N atom (20); examples include the compound $py_2P(CH_2)_2Ppy_2$ and the related $py_2P(C_5H_8)Ppy_2$, where py = *o*-pyridyl and C_5H_8 is a cyclopentane moiety bridging the two P atoms (cf. Fig. 1). We have now extended this theme by replacing the *o*-pyridyl group by the *o*-dimethylanilinyl group and report here on the synthesis of the new ligands dmapm (1,1-bis(di(*o*-*N*,*N*-dimethylanilinyl)phosphino)methane), dmape (1,2-bis(di(*o*-*N*,*N*-dimethylanilinyl)phosphino)ethane), and dmapcp (*rac*-

Received 6 March 2002. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 28 November 2002.

Dedicated to Tris Chivers, a close friend, fellow cricketer, squash player, and chemistry colleague for 35 years (at least for BRJ!).

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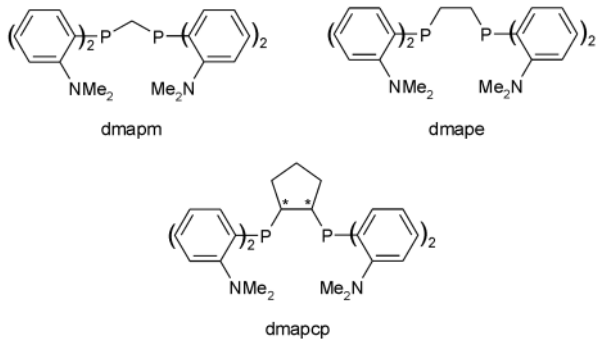
 DOI: 10.1139/V02-127

Fig. 1. Tetra(*o*-*N*,*N*-dimethylanilinyl)bisphosphines.



1,2-bis(di(*o*-*N*,*N*-dimethylanilinyl)phosphino)cyclopentane), illustrated in Fig. 1. Tóth and co-workers (11–15) have made related ligands, but bearing *para*-$C_6H_4(NMe_2)$ substituents, including chiral derivatives for catalytic asymmetric hydrogenation in water, once the N atoms have been quaternized; with these systems, simultaneous coordination to the same metal centre by both the P and N atoms of the same ligand is not possible, and there are no reports of bridging by these *para*-substituted ligands. Our new *ortho*-substituted ligands make the N atoms available for coordination to the same metal as the P atoms, as well as for providing convenient μ(P-N) environments; the extensive coordination chemistry of these ligands, particularly within Ru, Pd, and Pt systems, and their applications in catalysis (6, 21) will be published elsewhere. One benefit of excluding coordination chemistry from this article is that the findings presented amount to a contribution in main group chemistry, Tris Chivers's forte!

Experimental

General

Unless otherwise noted, synthetic procedures were performed using standard Schlenk techniques under a dry Ar or N_2 atmosphere. The precursors 1,1-bis(dichlorophosphino)methane and 1,2-bis(dichlorophosphino)ethane were purchased from commercial sources and stored in an N_2-filled glovebox, while 1,2-bis(dichlorophosphino)cyclopentane was made according to a literature procedure (22) and stored in a Schlenk tube under Ar. *N*,*N*-Dimethyl-*o*-bromoaniline was made by reaction of *o*-bromoaniline and dimethylsulfate according to a literature procedure (23); all other reagents were purchased from commercial sources and used as supplied. Solvents were dried and distilled under N_2 prior to use.

NMR spectra were recorded on a Bruker AV300 spectrometer (300.13 MHz for ^{1}H, 75.46 MHz for ^{13}C, 40.56 MHz for ^{15}N, 121.49 MHz for ^{31}P) at 300 K in $CDCl_3$. Residual solvent proton (^{1}H, δ 7.24 relative to external $SiMe_4$), solvent carbon (^{13}C, δ 77.0 relative to external $SiMe_4$), external $MeNO_3$ (^{15}N), or external $P(OMe)_3$ (^{31}P, δ 141.00 relative to 85% aq H_3PO_4), were used as references (*s* = singlet, *d* = doublet, *t* = triplet, *p* = pseudo). Downfield shifts were taken as positive. All *J*-values are given in Hz. Mass spectral and elemental analyses were conducted in the UBC Chemistry Department (B.C., Canada) by G. Eigendorf using a Kratos Concept II HQ mass spectrometer and by P. Borda using a Carlo Erba 1108 analyzer, respectively.

1,1-Bis(di(*o*-*N*,*N*-dimethylanilinyl)phosphino)methane, dmapm

To a solution of *n*-BuLi in hexanes (1.6 M, 16.5 mL, 26.4 mmol), cooled to –40°C on a dry ice – CH_3CN bath, was added *o*-bromo-*N*,*N*-dimethylaniline (5.05 g, 25.2 mmol) in Et_2O (20 mL) via cannula over 20 min. The yellow solution was stirred for 15 min and a white precipitate formed. The slurry was allowed to warm to room temperature (r.t.) and stirring was continued for 1 h. After the solution was cooled again to –40°C, 1,1-bis(dichlorophosphino)methane (1.33 g, 6.09 mmol) in Et_2O (15 mL) was added over 5 min. The resulting orange slurry was stirred for 15 min and then allowed to warm to r.t. Stirring was continued for 1 h and then HCl (~1 M, 50 mL) was added. The organic layer was removed and KOH (~2 M) was added dropwise to the aqueous layer to neutrality. The aqueous fraction was extracted with CH_2Cl_2 (3 × 20 mL) and the combined extracts were dried over $MgSO_4$. After removal of the solvent in vacuo, EtOH (15 mL) was added. The slurry was refluxed for 0.5 h, cooled to r.t., and the mixture filtered to give a white powder that was washed with cold EtOH (3 × 5 mL) and dried in vacuo. Yield: 1.84 g (54%). ^{1}H NMR δ: 2.23 (t, 2H, CH_2, $^2J_{HP}$ = 4.2), 2.68 (s, 24H, NCH_3), 7.02 (pt, 2H, Ar), 7.11 (pd, 4H, Ar), 7.25 (pt, 4H, Ar), 7.40 (pd, 4H, Ar). ^{13}C{^{1}H} NMR δ: 28.0 (t, *C*H_2, $^1J_{CP}$ = 26.2), 45.3 (s, N*C*H_3), 119.7 (s, *C*H), 124.2 (s, *C*H), 128.6 (s, *C*H), 132.3 (s, *C*H), 139.2 (s, *C*N), 157.1 (m, *C*P). ^{15}N NMR δ: –343.7 (s, *N*Me_2). ^{31}P{^{1}H} NMR δ: –36.0 (s). CI-MS *m*/*z*: 557 ([M–H]$^+$). Anal. calcd. for $C_{33}H_{42}N_4P_2$: C 71.2, H 7.6, N 10.1; found: C 71.0, H 7.8, N 9.9. Crystals of dmapm suitable for X-ray diffraction were grown from an acetone solution layered with hexanes.

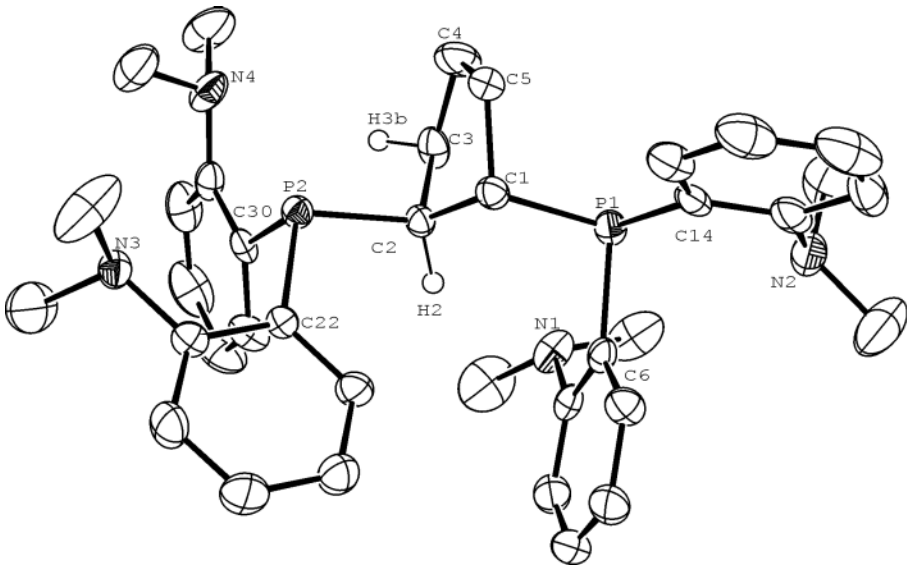
1,2-Bis(di(*o*-*N*,*N*-dimethylanilinyl)phosphino)ethane, dmape

The synthesis of this compound follows that of dmapm. Thus, reaction of *n*-BuLi (1.6 M, 17.4 mL, 27.8 mmol), *o*-bromo-*N*,*N*-dimethylaniline (5.56 g, 27.8 mmol), and 1,2-bis(dichlorophosphino)ethane (1.61 g, 6.94 mmol) gave 2.44 g (61%) of a white powder. ^{1}H NMR δ: 1.91 (pt, 4H, CH_2, $^2J_{HP}$ = 4.1), 2.62 (s, 24H, NCH_3), 6.94 (m, 8H, Ar), 7.09 (m, 4H, Ar), 7.22 (m, 4H, Ar). ^{13}C{^{1}H} NMR δ: 24.3 (s, *C*H_2), 45.2 (s, N*C*H_3), 119.8 (s, *C*H), 124.1 (s, *C*H), 128.8 (s, *C*H), 132.3 (s, *C*H), 136.9 (pt, *C*N, *J* = 9.5), 157.7 (pt, *C*P, *J* = 6.6). ^{15}N NMR δ: –343.8 (s, *N*Me_2). ^{31}P{^{1}H} NMR δ: –28.9 (s). CI-MS *m*/*z*: 571 ([M – H]$^+$). Anal. calcd. for $C_{34}H_{44}N_4P_2$: C 71.6, H 7.8, N 9.8; found: C 71.0, H 7.6, N 9.5. Crystals of dmape suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with EtOH.

Rac-1,2-bis(di(*o*-*N*,*N*-dimethylanilinyl)phosphino)cyclopentane, dmapcp

The synthesis of this compound corresponds to that of dmapm. Thus, reaction of *n*-BuLi in hexanes (1.6 M, 23.0 mL, 36.8 mmol), *o*-bromo-*N*,*N*-dimethylaniline (6.83 g, 34.1 mmol), and 1,2-bis(dichlorophosphino)cyclopentane (2.33 g, 8.57 mmol) at –40°C gave 2.72 g (52%) of a white powder. ^{1}H NMR δ: 1.51 (m, 2H, $C_{(4)}H_2$), 1.70 (m, 2H, $C_{(3/5)}H$H), 2.23 (m, 3H, $C_{(3/5)}H$H, C*H*), 2.55 (s, 12H, NCH_3), 2.60 (s, 12H, NCH_3, obscures C*H* protons), 6.49 (m, 2H, Ar), 6.71 (m, 2H, Ar), 6.96–7.28 (m, 12H, Ar). The ^{13}C{^{1}H} NMR spectrum shows a complicated pattern of signals due to coupling to phosphorus. Chemical shifts are presented

Fig. 2. Molecular structure of dmapcp (50% ellipsoids); H2 and H3b are labelled because they are discussed in the text.



and the number of lines in each signal are given in parentheses following the peak frequencies. $^{13}C\{^1H\}$ NMR δ: 24.6 (1, $C_{(4)}H_2$), 29.9 (3, $C_{(3/5)}H_2$), 40.4 (3, $C_{(1/2)}H$), 45.0 (2, NCH_3), 119.9 (2, *C*H), 124.1 (2, *C*H), 128.5 (1, *C*H), 133.1 (2, *C*H), 137.9 (9, *C*N), 157.8 (7, *C*P). ^{15}N NMR δ: –338.8 (s, NMe_2). $^{31}P\{^1H\}$ NMR δ: –25.6 (s). CI-MS *m/z* 611 ($[M–H]^+$). Anal. calcd. for $C_{37}H_{48}N_4P_2$: C 72.8, H 8.0, N 9.2; found: C 72.9, H 8.1, N 9.1. Crystals of dmapcp suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with EtOH. The labelling of the C atoms in the NMR corresponds to that shown in the crystal structure (Fig. 2).

X-ray crystallography of dmapm, dmape, and dmapcp

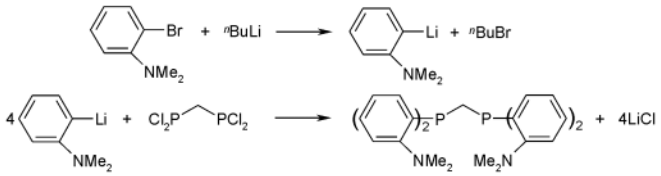
Suitable crystals were selected, mounted on a glass fibre using Paratone-N oil, and the unit frozen to –100°C. All measurements were made on a Rigaku/ADSC CCD area detector with graphite monochromated Mo Kα radiation. Selected crystallographic data appear in Table 1.[5] In each case the data were processed and corrected for Lorentz and polarization effects and absorption (24). Neutral atom scattering factors for all non-hydrogen atoms were taken from the *International Tables for X-ray Crystallography* (25, 26). All structures were solved by direct methods (27) and expanded using Fourier techniques (28). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not refined, but were included in calculated positions (with C—H = 0.98 Å) that were updated as the refinement progressed.

Results and discussion

Synthesis

The compounds dmapm, dmape, and dmapcp were prepared in a low-temperature, two-step, one-pot procedure in which *N*,*N*-dimethyl-2-lithioaniline is first generated by reaction of *n*-BuLi with *N*,*N*-dimethyl-2-bromoaniline, and then this is exposed to 0.25 mol equiv of the appropriate tetra(chloro)bisphosphine; Scheme 1 summarizes the method for dmapm. The compounds were isolated from the reaction mixture by extraction with dilute aq HCl and purified after neutralization by recrystallization from boiling EtOH. The syntheses are analogous to those used for syntheses of the related (pyridyl) mono- and bis(phosphine) ligands (20, 29–31). Of note, owing to the activating nature of the NMe_2 groups, the lithium exchange in step one of the synthesis proceeds with higher yields than for the deactivated pyridyl halides in the corresponding tetra(pyridyl)bisphosphine analogues (>50 vs. ~30%) (20). The new ligands are white, microcrystalline powders that are indefinitely air- and moisture-stable in the solid state and for prolonged periods in metal-free solution. They are freely soluble in chlorinated solvents and in dilute aq HCl, partially soluble in alcohols and Et_2O, and insoluble in hexanes.

Scheme 1.



The precursor 1,2-bis(dichlorophosphino)cyclopentane was made by reaction of cyclopentene, white phosphorus, and PCl_3 (22). This procedure results almost exclusively in the *trans* product and, because of this, dmapcp is produced as a racemic mixture of *R*,*R*- and *S*,*S*-enantiomers, as with

[5] Supplementary data (full crystal data and details on data collection and refinement have been deposited, along with tables of atomic coordinates, anisotropic thermal parameters, all bond lengths and angles, and torsion angles) may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 185016–185018 contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data for dmapm, dmape, and dmapcp.

	dmapm	dmape	dmapcp
Formula	$C_{33}H_{42}N_4P_2$	$C_{34}H_{44}N_4P_2$	$C_{37}H_{48}N_4P_2$
Formula weight	556.67	570.70	610.73
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	*Cc*(#9)	$P\bar{1}$(#2)	$P2_12_12_1$(#19)
a (Å)	12.076(2)	8.1849(4)	11.975(1)
b (Å)	19.674(2)	15.500(1)	14.9163(2)
c (Å)	14.341(3)	19.882(2)	19.8124(5)
α (°)	90	73.501(4)	90
β (°)	114.142(8)	81.052(1)	90
γ (°)	90	79.9046(9)	90
V (Å^3)	3109.1(8)	2364.9(3)	3539.2(3)
Z	4	3	4
$D_{calcd.}$ (g cm^{-3})	1.189	1.202	1.146
μ (Mo Kα) (mm^{-1})	0.168	0.167	0.153
T (°C)	–100	–100	–93
Total data collected	14209	21881	9864
Independent reflections	5977	10698	9864
R_1 (on F^2, all data)	0.073	0.077	0.0942
wR_2 (on F^2, all data)	0.097	0.083	0.0705

the 1,2-bis(diphenylphosphino)cyclopentane analogue, dppcp (22); the chirality designators refer to the absolute configurations of the methine C atoms 1 and 2 in the backbone of the ligand (Figs. 1 and 2).

Characterization

The dmapm, dmape, and dmapcp compounds have been fully identified by means of NMR spectroscopy of all the nuclei present (^{1}H, ^{13}C, ^{31}P, and ^{15}N), mass spectrometry, elemental analysis, and molecular structure determination by low-temperature X-ray diffraction.

The compounds show the expected chemical shifts in their ^{1}H NMR signals, but the multiplicity of the backbone protons needs comment. Whereas the CH_2 in dmapm gives the expected triplet due to H–P coupling ($^2J_{HP}$ = 4.2 Hz), the protons in dmape appear as a pseudo triplet, resulting from the overlapping of the expected doublet of doublets, as in the *o*-pyridyl analogue, dpype (30). In the case of the racemic dmapcp, only multiplets were observed for the cyclopentyl protons, and these are assigned by comparison with data for the *o*-pyridyl analogue, dpypcp (20); the assignments of the ^{13}C{^{1}H} signals are tentative and are also based on well-established data for dpypcp (20). The ^{31}P{^{1}H} NMR spectra show singlets at δ –36.0 (dmapm), –28.9 (dmape), and –25.6 (dmapcp); the values for the last two are about 20 ppm to higher fields than those of the *o*-pyridyl analogues (20, 30). The ^{15}N NMR signals for the NMe_2-type ligands appear in the δ –340 region.

It is constructive to consider structural features of dmapm, dmape, and dmapcp along with those of their phenyl analogues: bis(diphenylphosphino)methane, dppm (32), 1,2-bis(diphenylphosphino)ethane, dppe (33), and dppcp (see above) (22), and those we have determined for the pyridyl analogues dpype (20) and dpypcp (20, 34), respectively. As far as we are aware, the pyridyl analogue of dmapm has not been reported. The molecular structures of the three new compounds are, not surprisingly, very similar to those of their phenyl and pyridyl analogues.

Table 2. Selected bond lengths (Å) and angles (°) for dppm and dmapm with estimated standard deviations in parentheses.

	dppm[a]	dmapm
Bond lengths (Å)		
P1—C17	1.846(5)	1.854(3)
P2—C17	1.868(5)	1.844(3)
P1—C9	1.828(5)	1.835(2)
P1—C1	1.842(5)	1.856(2)
P2—C18	1.839(6)	1.843(3)
P2—C26	1.842(5)	1.843(3)
P1···P2	2.97(1)	3.099(3)
Bond angles (°)		
Σ<P1, Σ<P2[b]	306.3(6), 303.7(6)	301.5(3), 303.4(3)
P1-C17-P2	106.2(3)	113.9(1)
C1-P1-C17	101.7(2)	95.9(1)
C17-P2-C26	103.2(2)	98.9(1)

[a]Data taken from ref. 32.
[b]Sum of angles at P1 and P2.

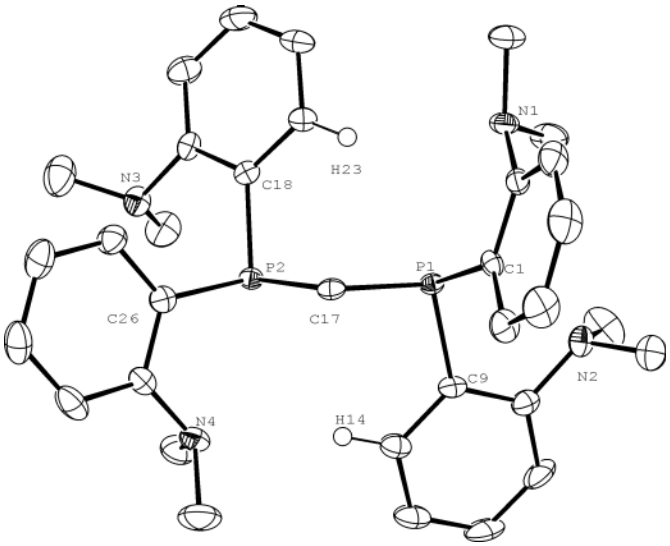
Table 2 lists some geometrical parameters for dmapm and dppm, and Fig. 3 shows the molecular structure of dmapm, which shows minor differences to that of dppm. The increased steric bulk of the NMe_2 substituents in dmapm leads to a different rotation of the arene moieties that induces two sub van der Waals contacts between N and H atoms in adjacent *N*,*N*-dimethylanilinyl moieties on each side of the molecule (N1···H23 = 2.65 Å and N4···H14 = 2.50 Å vs. the van der Waals contact of 2.75 Å (35)); the corresponding C···N bond lengths are 3.61 and 3.45 Å (larger than the 3.30 Å value for the sum of the radii), and the corresponding N···C-H angles are about 147 and 163°. These interactions may represent weak C-H···N hydrogen bonds, which do exist (35). This steric hindrance forces the molecule to "stretch", which leads to a 7° wider P-C-P angle (113.9°) and a longer P···P distance (3.099 Å) with respect to dppm. Also, the corresponding C-P-C angles are compressed in comparison to

Table 3. Selected bond lengths (Å) and angles (°) for dppe, dpype, and dmape with estimated standard deviations in parentheses.

	dppe[a]	dpype[b]	dmape(C_S)		dmape(C_1)
Bond lengths (Å)					
P3—C35	1.829(3)	1.842(3)	1.849(2)	P1—C1	1.858(2)
P3—C44	1.825(7)	1.845(3)	1.837(2)	P1—C3	1.847(2)
P3—C36	1.819(3)	1.849(3)	1.844(2)	P1—C11	1.846(2)
C35—C35*	1.521(7)	1.527(6)	1.538(4)	C1—C2	1.526(3)
P3···P3*	4.436(13)	4.453(9)	4.481(6)	P1···P2	4.508(6)
Bond angles (°)					
Σ<P1, Σ<P2[c]	304.2(12)	301.6(9)	300.0(5)	Σ<P1, Σ<P2	301.7(2), 301.3(2)
P1-C35-C35*	110.9(4)	110.4(3)	110.7(2)	P1-C1-C2	110.9(1)
				P2-C2-C1	113.7(1)
P-C-C-P	0.0	0.0	0.0	P-C-C-P	7.0

[a]Data taken from ref. 33; weighted mean of two independent measurements.
[b]Data taken from ref. 20.
[c]Sum of angles at P1 and P2.

Fig. 3. Molecular structure of dmapm (50% ellipsoids); H14 is labelled because it is discussed in the text.



those of dppm (C1-P1-C17 (95.9°) and C17-P2-C26 (98.9°) vs. 101.7° and 103.2°), which leads to slightly more "pyramidal" P atoms as defined by the sum of the angles at P1 and P2 (av 302.5 vs. av 304.9°). The P—C bond lengths within the two molecules are essentially the same.

The asymmetric unit cell of dmape contains 1.5 crystallographically independent molecules, 1 being in a general position and 1 lying on a centre of symmetry. The main difference (see Fig. 4) is that in the C_S molecule one of the phosphine groups is twisted 180° with respect to the other, whereas in the dissymmetric molecule both phosphine moieties are facing the same side, the *N*,*N*-dimethylanilinyl substituents taking gauche positions with respect to each other. The corresponding bond lengths and angles within each molecule differ only marginally (Table 3). While the centrosymmetric molecule exhibits a planar backbone with a P-C-C-P torsion angle constrained by symmetry to be –180°, the C_S molecule is slightly puckered with a corresponding torsion angle of 173°. The C_S molecule exhibits geometry very similar to that of the also centrosymmetrical analogues dppe and dpype. The pyramidal geometry at the P atom is not affected by the different aromatic substituents, but the average P—$C_{(aromatic)}$ bond lengths are longer in dmape (av 1.844 Å) and dpype (av 1.847 Å) than in dppe (av 1.822 Å), presumably reflecting electronic differences between the *ipso* carbons in the anilinyl and pyridyl moieties compared with those in the phenyl groups (the same difference is seen on comparing data for dmapm and dppm, see Table 2). The C_S molecule shows a short N6···H42 contact (2.53 Å) with C—N = 3.49 Å and an N···H-C angle of 165°, again indicative of a weak H-bonding interaction.

In the case of dmapcp, the backbone is puckered owing to the steric demand of the cyclopentyl ring (P-C-C-P, 168°) (Fig. 2). The four *N*,*N*-dimethylanilinyl moieties lead to steric crowding, inducing sub van der Waals contacts (and possible H-bonding) between two of the N atoms and the closest H atoms of the cyclopentyl backbone (N4···H3b (2.67 Å), C—N (3.49 Å), N···H–C (140.7°); and N1···H2 (2.53 Å), C—N (3.33 Å), N···H–C (136.4°)). These contacts might explain the relatively long P—$C_{(aliphatic)}$ bonds (1.882 and 1.879 Å) and the increased P—P distance (4.505 Å) compared with data for dppcp and dpypcp (Table 4). Accordingly, the P—$C_{(aromatic)}$ bonds of the strained *N*,*N*-dimethylanilinyl moieties are also slightly elongated compared with those of the non-interacting *N*,*N*-dimethylanilinyl groups: P1—C6 (1.852) vs. P1—C14 (1.837 Å) and P2—C30 (1.847) vs. P2—C22 (1.831 Å). The P—$C_{(aliphatic)}$ bonds are about 0.04 Å longer than the P—$C_{(aromatic)}$ bonds.

The unit cell of the dmapcp crystal chosen for the analysis shows that only the *S*,*S* enantiomer is present (chiral space group $P2_12_12_1$), implying a spontaneous resolution has taken place; other crystals must contain only *R*,*R* enantiomers, but no attempt was made to separate these by the Pasteur method of inspection. The analogous dppcp and dpypcp systems crystallize with both enantiomers in the unit cell. Apart from the slight distortions mentioned above, the *S*,*S* enantiomers of the three compounds exhibit a very similar overall molecular geometry (Table 4).

Coordination chemistry

As alluded to in the Introduction, the new ligands have revealed diverse coordination chemistry (6, 21). Established bonding modes include: (*i*) *P*,*P*-, *P*,*N*-, and *P*,*P*,*N*-coordination within d^8 square planar systems, including interconversions

Fig. 4. Structures of the dissymmetric (C_1) and symmetric (C_S) molecules of dmape (50% ellipsoids); H42 is labelled because it is discussed in the text.

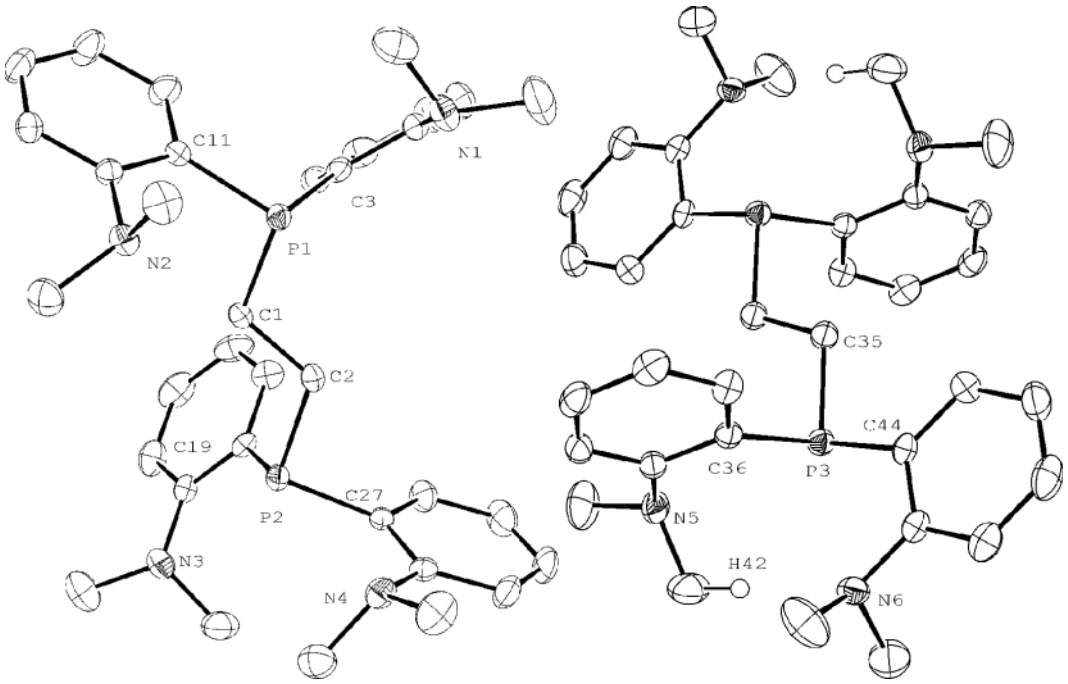


Table 4. Selected bond lengths (Å) and angles (°) for dpcp, dpypcp, and dmapcp with estimated standard deviations in parentheses.

	dppcp[a]	dpypcp[b]	dmapcp
Bond lengths (Å)			
P1—C1	1.866(2)	1.862(2)	1.882(3)
P1—C6	1.836(2)	1.850(2)	1.852(3)
P1—C14	1.833(2)	1.847(2)	1.837(3)
P2—C2	1.857(2)	1.863(2)	1.879(3)
P2—C22	1.833(2)	1.834(2)	1.831(3)
P2—C30	1.831(2)	1.854(2)	1.847(3)
C1—C2	1.546(2)	1.546(3)	1.537(3)
P1···P2	4.448(6)	4.457(7)	4.505(9)
Bond angles (°)			
Σ<P1, Σ<P2[c]	306.4(3), 304.6(3)	304.2(3), 303.8(3)	302.4(3), 299.1(3)
P1-C1-C2	109.2(1)	109.0(1)	108.5(1)
P2-C2-C1	109.8(1)	109.9(1)	111.3(1)
P-C-C-P	161.7	–164.3	168.2

[a]Data taken from ref. 22.
[b]Data taken from ref. 34.
[c]Sum of angles at P1 and P2.

between types sometimes involving loss of initially coordinated ancillary halides; (*ii*) *P*,*P*,*N*,*N*-coordination with the dmapm ligand that bridges metal–metal bonded systems of formally d^8 centres; and (*iii*) *P*,*P*,*N*,*N*- and *P*,*P*,*N*,*N*,*N*-coordination modes within Ru^{II}-d^6 octahedral systems. These findings will be reported in future publications.

Acknowledgments

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support, the Royal Society for a fellowship for M.B.S., and the Deutsche Forschungsgemeinschaft for a fellowship for U.L.

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