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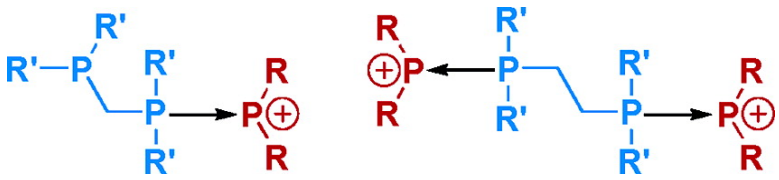

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Diphosphine−Phosphenium Coordination Complexes Representing Monocations with Pendant Donors and Ligand Tethered Dications

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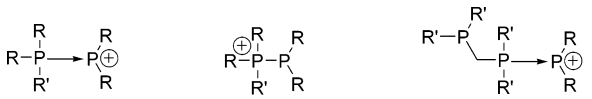
Abstract: Homoatomic P−P coordinate bonding is exploited to prepare the first examples of triphosphorus monocations and tetraphosphorus dications using dimethylphosphenium or diphenylphosphenium Lewis acceptors with diphosphinomethane, diphosphinoethane, diphosphinohexane, or diphosphinobenzene ligands. Solid-state structures and spectroscopic characterization data for complexes involving bis(diphenylphosphino)methane ligands show coordination of only one donor site of the diphosphine ligand in the monocations, and chelate complexation is not observed. Tetraphosphorus dications are observed with longer diphosphines, in which the ligand tethers two phosphenium acceptors. The structural preferences between monocations with pendant phosphines and tethered dications are dependent on intramolecular steric interactions and the flexibility of the tether.

Introduction

Notwithstanding the reputation of phosphines as ligands in the coordination chemistry of metals and electron-deficient nonmetals, complexes of phosphorus(III) centers as Lewis acceptors[1] have been reported with arene,[2] carbene,[3−7] amine,[8−12] imine,[9,13,14] nitrile,[15] halide,[15] urea,[16] phosphine,[17−25] thiourea,[16] gallane,[26] or selenourea donors.[16] This diverse array of ligand types highlights the synthetic utility of P(III) Lewis acceptors for E−P bond formation.



1a R = Me or Ph; R' = Me, Ph or Cl

1b

2a: R = Me; R' = Ph
2b: R = Ph; R' = Ph

Coordination complexes of phosphenium (R_2P^+) acceptors have been most extensively developed.[1] Inter-[17,23,24] and intramolecular[18,22,27−29] phosphine−phosphenium complexes

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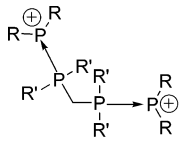
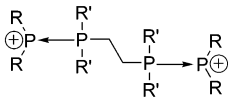
represent examples of complexes involving homoatomic coordinate bonding that is essentially unique to phosphorus (one example of Sb−Sb).[30] Although the geometry of each phosphorus center in derivatives of **1** is consistent with a phosphinophosphonium **1b** bonding description, facile ligand exchange reactions implicate the Lewis acid−base definition **1a**.[24] Consequently, the coordination chemistry of the phosphenium unit is potentially broad, but is currently limited to monoligand complexes that are typical for p-block Lewis acids (e.g., H_3B-NH_3, in contrast to transition metal complexes ML_n, $n = 1-6$).

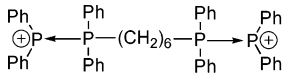


3a: R = Me; R' = Me
3b: R = Ph; R' = Me



4a: R = Ph; R' = Me
4b: R = Ph; R' = Ph

Bifunctional (and multifunctional) ligands offer a means of diversification for the coordination chemistry of acceptor sites that are restricted to a single ligand. Application of this approach to diphosphine−phosphenium systems has realized the first examples of triphosphorus monocations defined by complexes of phosphenium cations with a diphosphinomethane ligand (**2**), and tetraphosphorus dications defined by complexes of two phosphenium units tethered by a diphosphinomethane (**3**), diphosphinoethane (**4**), diphosphinohexane (**5**), or diphosphinobenzene (**6**) ligand. The observations demonstrate the preference for pendant (**2**) and tethered (**3**, **4**, **5**, **6**) arrangements over the corresponding chelate complexes (**7**, **8**).



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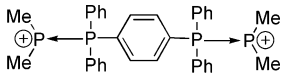

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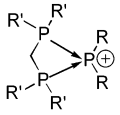

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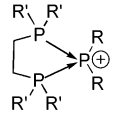

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Experimental

General. All manipulations were carried out in a nitrogen-filled Innovative Technologies drybox. All solvents were distilled prior to use and dispensed in the drybox. Dichloromethane was dried at reflux over calcium hydride, phosphorus pentoxide, and then calcium hydride. Hexane was dried at reflux over potassium, and diethyl ether was dried at reflux over sodium/benzophenone. Dimethylchlorophosphine, triphenylphosphine, diphenylchlorophosphine, gallium chloride, and trimethylsilyltrifluoromethanesulfonate (TMS-OTf), bis(diphenylphosphino)methane (dppm), bis(dimethylphosphino)methane (dmpm), 1,2-bis(diphenylphosphino)ethane (dppe), and 1,2-bis(dimethylphosphino)-ethane (dmpe) were purchased from Aldrich Chemical Co., and bis-(diphenylphosphino)hexane (dpph) and 1,4-bis(diphenylphosphino)benzene (1,4-dppb) were purchased form Kodak Chemical Co. All reagents were used as received without further purification. Derivatives of **1** were prepared *in situ* by literature procedures.[24] IR spectra were recorded on a Bruker VECTOR 22 FT-IR using Nujol mulls and are reported with ranked intensities in parentheses. Solution NMR data were obtained on a Bruker AC-250 NMR spectrometer at room temperature unless otherwise indicated. Chemical shifts are reported in ppm relative to a reference standard [85% H_3PO_4 (^{31}P)], and *J* values are reported in Hz. Crystalline samples were obtained by vapor diffusion. The sample (0.050−0.100 g) was dissolved in a minimal amount of CH_2Cl_2 in an uncapped 1 dram vial, which was placed inside a 4 dram vial containing Et_2O or pentane. The larger vial was capped tightly, and the system was allowed to stand at room temperature until crystals of suitable quality formed. Crystals were placed under oil (perfluoropolyether or Paratone) and placed in a cold stream of N_2. X-ray diffraction data (Table 2) were collected at 193(2) K on a Bruker PLATFORM diffractometer with a sealed tube generator and a SMART 1000 CCD detector using graphite-monochromated Mo Kα ($\lambda = 0.71073$) radiation.

Preparative Procedures.

[Me_2P-dppm] **2a** [OTf]. Me_2PCl (20 μL, 0.25 mmol) was added to a solution of TMS-OTf (22.9 μL, 0.13 mmol) in CH_2Cl_2 (2 mL) and stirred for 45 min at room temperature. A solution of dppm (0.049 g, 0.126 mmol) was added, and the reaction mixture was stirred for 8 h. A white powder precipitated on addition of pentane (5 mL). Crystals were obtained using vapor diffusion (CH_2Cl_2/Et_2O), 0.055 g, 73%; mp 185 °C. Anal. Calcd. for $C_{28}H_{28}F_3O_3P_3S$ (Found): C 56.57 (55.22), H 4.75 (4.72). IR: 469(16), 483(10), 514(14), 533(15), 636 (5), 689(7), 703(9), 723(11), 740(3), 757(12), 779(13), 902(17), 996(19), 1030(2), 1069(20), 1107(8), 1149(4), 1193(18), 1222(6), 1261(1).

[Me_2P-dppm] **2a** [$GaCl_4$]. Me_2PCl (20 μL, 0.253 mmol) was added to a solution of $GaCl_3$ (0.022 g, 0.126 mmol) in CH_2Cl_2 (1−2 mL) and stirred for 45 min at room temperature. A solution of dppm (0.049 g, 0.126 mmol) was added, and the reaction mixture was stirred for 6−8 h. On addition of pentane (5 mL) the solution became cloudy. A white powder was filtered after ~10 h of stirring and recrystallized from CH_2Cl_2 by vapor diffusion with Et_2O as clear, block-shaped crystals 0.076 g, 92%; mp 130−133 °C. Anal. Calcd. for $C_{27}H_{28}Cl_4GaP_3$ (Found): C 49.36 (49.35), H 4.30 (4.60). IR: 382(1), 478(7), 526(12), 666(11), 685(6), 695(5), 706(8), 722(2), 735(3), 745(4), 761(10), 775(13), 895(18), 950(15), 996(16), 1023(19), 1076(17), 1107(9), 1307(14).

[Ph_2P-dppm] **2b** [OTf]. A solution of dppm (0.086 g, 0.22 mmol) in CH_2Cl_2 (3 mL) was added to a stirred solution (over 45 min) of [$Ph_2(Cl)P-PPh_2$][OTf] (0.22 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 10 h at room temperature, and addition of pentane (5 mL) gave a white precipitate, yield 0.078 g, 49%; mp 80−82 °C. Elemental analyses were not determined. IR: 637(2), 691(6), 728(11), 740(7), 752(8), 761(13), 997(15), 1031(4), 1099(14), 1147(10), 1155(9), 1223(12) 1265(1), 1275(3), 1439(5).

[Ph_2P-dppm] **2b** [$GaCl_4$]. A solution of dppm (0.024 g, 0.056 mmol) in CH_2Cl_2 (3 mL) was added to a stirred solution of [$Ph_2(Cl)P-PPh_2$]-[$GaCl_4$] (0.111 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 10 h at room temperature. Addition of pentane (5 mL) resulted in the formation of a white precipitate, yield 0.018 g, 58%; mp 78 °C. Anal. Calcd. for $C_{37}H_{32}Cl_4GaP_3$ (Found): C 56.89 (57.36), H 4.13 (4.11). IR: 369(1), 451(4), 688(6), 740(9), 798(8), 918(12), 941(13), 998(11), 1023(3), 1092(5), 1186(15), 1261(7), 1309(14), 1437(12), 1586(10).

[Me_2P-dmpm$-PMe_2$] **3a** [$GaCl_4$]$_2$. A solution of dmpm (0.034 g, 0.063 mmol) in CH_2Cl_2 (3 mL) was added dropwise (over 5 min) to a stirred solution of [$Me_2(Cl)P-PMe_2$][$GaCl_4$] (0.252 mmol) in CH_2Cl_2 (3 mL), giving a white precipitate. After being stirred for 10 h at room temperature, the reaction mixture was filtered, and addition of pentane (5 mL) resulted in formation of a white precipitate, yield 0.041 g, 95%; mp 149 °C. Anal. Calcd. for $C_9H_{26}Cl_8Ga_2P_4$ (Found): C 15.87 (15.94), H 3.85 (3.59). IR: 368(2), 382(1), 811(10), 898(3), 926(4), 949(6), 1116(9), 1030(7), 1408(5), 2360(8).

[Me_2P-dmpm$-PMe_2$] **3a** [OTf]$_2$. A solution of dmpm (0.034 g, 0.250 mmol) in CH_2Cl_2 (5 mL) was added dropwise (over 5 min) to a stirred solution of [$Me_2(Cl)P-PMe_2$][OTf] (0.253 mmol) in CH_2Cl_2

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Table 1. ^{31}P NMR Data, δ (ppm),[a] J_{PP} (Hz), and P−P Distances (Å) for Derivatives of **1**, **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5**, **6**, **9**, **10**, **11**, and **12**

	^{31}P NMR (CH_2Cl_2)		^{31}P NMR (CP-MAS)			
compound (cation structure type)	δ	$^1J_{PP}$	δ	$^1J_{PP}$	P–P[g]	ref
$[Ph_2P(Cl)-PPh_2][GaCl_4]$ (**1**)	78 (d) 3 (d)	—[b]	—[e]	—[e]	2.205(4)	24
$[Ph_3P-PPh_2][GaCl_4]$ (**1**)	13 (d) −12 (d)	340	15 −17	323	2.220(6)	24
$[Ph_3P-PPh_2][OTf]$ (**1**)	15 (d) −10 (d)	—[b]	13 −22	350	2.230(1)	24
$[Cy_3P-PPh_2][OTf]$ (**1**)	15 (d) −10 (d)	361	13 −22	372	2.220(1)	24
$[Me_3P-PPh_2][OTf]$ (**1**)	15 (d) −23 (d)	289	17 −29	281	2.187(2)	24
$[Me_2P-dppm][GaCl_4]$ (**2a**)	26 (dd) −28 (dd) −60 (dd)	301[d] ^{2}J, 64 ^{3}J, 45	—[e]	—[e]	2.219(2)	this work
$[Me_2P-dppm][OTf]$ (**2a**)	28 (dd) −25 (dd) −60 (dd)	293 ^{2}J, 60 ^{3}J, 50	—[e]	—[e]	2.213(2)	this work
$[Ph_2P-dppm][GaCl_4]$ (**2b**)	21 (dd) −22 (dd) −30 (m)	318 ^{2}J, 63 ^{3}J, 53	—[e]	—[e]	—	this work
$[Ph_2P-dppm][OTf]$ (**2b**)	20 (dd) −24 (dd) −30 (m)	315 ^{2}J, 62 ^{3}J, 55	—[e]	—[e]	2.163(1)	this work
$[Me_2P-dmpm-PMe_2][GaCl_4]_2$ (**3a**)	—[f]	—	24 −64	288	—	this work
$[Ph_2P-dmpm-PPh_2][GaCl_4]_2$ (**3b**)	20 (d) −23 (d)	320[d]	15 −16	334	2.204(2)	this work
$[Ph_2P-dmpm-PPh_2][OTf]_2$ (**3b**)	20 −23	324[d]	26, −17 19, −24	306 321	2.233(1) 2.202(1)	this work
$[Ph_2P-dmpe-PPh_2][GaCl_4]_2$ (**4a**)	10 (d) −22 (d)	—	22 −15	349	2.201(1)	this work
$[Ph_2P-dmpe-PPh_2][OTf]_2$ (**4a**)	17 (d) −25 (d)	297[d]	—[c]	—[c]	2.217(2) 2.209(2)	this work, 33
$[Ph_2P-dppe-PPh_2][GaCl_4]_2$ (**4b**)	20 (d) −26 (d)	—[b]	22 −32	341	2.217(2)	this work
$[Ph_2P-dppe-PPh_2][OTf]_2$ (**4b**)	21 (d) −33 (d)	322[d]	—[c]	—[c]	2.219(1)	this work, 33
$[Ph_2P-dpph-PPh_2][GaCl_4]_2$ (**5**)	20 (d) −24 (d)	318[d]	—[e]	—[e]	2.211(1)	this work, 33
$[Me_2P-dppb-PMe_2][GaCl_4]_2$ (**6**)	25 (d) −55 (d)	309	—[e]	—[e]	2.197(3) 2.208(3)	this work
$[NEt_2(Me)P-P(Me)N(Me)C(O)N(Me)][Cl]$ (**9**)	60 (d) −1 (d)	241	—	—	2.191(2)	28
$[Ph_3P-P-PPh_3][AlCl_4]$ (**10**)	30 (d) −174 (t)	502	—	—	2.137(6) 2.128(6)	20
$[P-dppe]_2[SnCl_6]$ (**11**)	64 (d) −231 (t)	445	—	—	2.205(1)	34
$[Ph_3P-P(H)-PPh_3][AlCl_4]_2$ (**12**)	23 (d) −120 (t)	286	—	—	2.205(1)	35

[a] For each compound, the first ^{31}P δ value listed is assigned to the tetracoordinate (donor sites) phosphorus center based on the those of phosphonium cations, e.g., Ph_4P^+ ($\delta \approx 20$ ppm). The second ^{31}P δ value listed is assigned to the tricoordinate (acceptor sites) phosphorus center based on established values for Ph_3P ($\delta = -5$ ppm), Ph_2P-PPh_2 ($\delta = -15$ ppm), and Me_3P ($\delta = -62$ ppm). [b] Not observed, broad signals at room temperature. [c] Two crystallographically distinct cations, doublets overlap and appear as triplets in the CP-MAS spectrum. [d] 193 K. [e] Not measured. [f] Sparingly soluble. [g] Compare also P−P = 2.217(2) Å in Ph_2P-PPh_2.[32]

(3 mL). A white precipitate was formed upon combining the reagents. After being stirred for 10 h at room temperature, pentane was added (5 mL) to give a white precipitate, yield 0.11 g, 79%; mp 103−106 °C. Anal. Calcd. for $C_9H_{26}F_6O_6P_4S_2$ (Found): C 23.75 (23.57), H 4.71 (4.82). IR: 638(3), 858(12), 862(11), 871(13), 915(15), 960(10), 1030(2), 1160(4), 1226(5), 1260(1), 1303(6), 1418(8), 1436(9), 1455(7), 1558(14).

$[Ph_2P-dmpm-PPh_2]$ **3b** $[OTf]_2$. A solution of dmpm (0.015 g, 0.111 mmol) was added to a stirred solution of $[Ph_2(Cl)P-PPh_2][OTf]$ (0.223 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 10 h at room temperature. Pentane was added (10 mL) to the solution, giving a white precipitate, which was recrystallized by vapor diffusion (CH_2Cl_2/hexanes), yield, 0.064 g, 72%; mp 151−153 °C. Anal. Calcd. for $C_{31}H_{34}F_6O_6P_4S_2$ (Found): C: 46.27 (45.04) H: 4.26 (4.01). IR: 222(11), 247(4), 280(5), 303(13), 516(7), 638(3), 693(6), 745(14), 1031-(2), 1160(12), 1227(9), 1261(1), 1437(10), 1457(8).

$[Ph_2P-dmpm-PPh_2]$ **3b** $[GaCl_4]_2$. A solution of dmpm (0.015 g, 0.111 mmol) was added to a stirred solution of $[Ph_2(Cl)P-PPh_2][GaCl_4]$ (0.223 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 10 h at room temperature. Addition of pentane (5 mL) resulted in formation of a white precipitate, which was recrystallized (clear, colorless blocks) by vapor diffusion (CH_2Cl_2/hexanes), yield 0.077 g, 74%; mp 154−157 °C. Anal. Calcd. for $C_{29}H_{34}Cl_8Ga_2P_4$ (Found): C 37.39 (37.47), H 3.68 (3.69). IR: 364(5), 383(1), 476(14), 503(12), 693(4), 736(2), 748(6), 797(13), 922(3), 951(9), 997(11), 1083(10), 1159(15), 1294(8), 1307(7).

$[Ph_2P-dmpe-PPh_2]$ **4a** $[OTf]_2$. A solution of dmpe (0.007 g, 0.050 mmol) was added via automatic pipet to a solution of $[Ph_3P-PPh_2]$-

Table 2. Crystal Data

	[Me_2P–dppm] **2a** [OTf]	[Me_2P–dppm] **2a** [$GaCl_4$]	[Ph_2P–dppm] **2b** [OTf]	[Ph_2P–dmpm–PPh_2] **3b** [$GaCl_4$]$_2$	[Ph_2P–dmpm–PPh_2] **3b** [OTf]$_2$	[Ph_2P–dppe–PPh_2] **4b** [$GaCl_4$]$_2$
compound formula	$C_{28}H_{28}F_3O_3P_3S$	$C_{27}H_{28}Cl_4GaP_3$	$C_{38}H_{32}F_3O_3P_3S$	$C_{29}H_{34}Cl_8Ga_2P_4$	$C_{31}H_{34}F_6O_6P_4S_2$	$C_{50}H_{44}Cl_8Ga_2P_4$
fw (g mol^{-1})	594.47	656.92	718.61	929.48	804.58	1191.77
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1$	$C2/c$	$C2/c$	$P2_1/n$
a (Å)	13.394(2)	10.8925(4)	8.2272(3)	23.017(6)	27.845(2)	11.901(1)
b (Å)	15.506(2)	11.9222(4)	21.982(1)	9.523(3)	10.863(1)	19.006(1)
c (Å)	15.183(2)	12.5883(4)	10.2503(4)	18.060(5)	26.383(2)	12.614(1)
α (deg)	–	80.674(1)	–	–	–	–
β (deg)	114.473(2)	78.371(1)	110.830(1)	94.016(5)	112.326(1)	109.699(1)
γ (deg)	–	70.066(1)	–	–	–	–
V (Å^3)	2870.2(6)	1497.51(9)	1732.6(1)	3949.1(18)	7286.5(9)	2686.0(3)
Z	4	2	2	4	8	2
D_c (Mg m^3)	1.376	1.457	1.377	1.563	1.467	1.474
R ($I > 2\sigma(I)$)	0.0654	0.0397	0.0322	0.0649	0.0462	0.0305
wR ($I > 2\sigma(I)$)	0.1800	0.1040	0.0755	0.1806	0.1171	0.0790
GOF S	1.027	1.036	1.042	1.038	1.014	1.045

	[Ph_2P–dppe–PPh_2] **4b** [OTf]$_2$	[Ph_2P–dmpe–PPh_2] **4a** [OTf]$_2$	[Ph_2P–dmpe–PPh_2] **4a** [$GaCl_4$]$_2$	[Ph_2P–dpph–PPh_2] **5** [$GaCl_4$]$_2$	[Me_2P–dppb–PMe_2] **6** [$GaCl_4$]$_2$
compound formula	$C_{53}H_{46}Cl_2F_6O_6P_4S_2$	$C_{32}H_{36}F_6O_6P_4S_2$	$C_{30}H_{36}Cl_8Ga_2P_4$	$C_{54}H_{52}Cl_8Ga_2P_4$	$C_{34}H_{36}Cl_8Ga_2P_4$
fw (g mol^{-1})	1151.80	818.61	943.51	1247.88	991.55
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$I2/a$	$P2_1/c$
a (Å)	9.397(1)	8.637(1)	9.542(1)	30.395(4)	23.018(1)
b (Å)	12.863(1)	13.544(2)	9.821(1)	10.120(1)	17.817(1)
c (Å)	13.668(1)	15.742(2)	11.794(1)	19.465(2)	16.799(1)
α (deg)	119.801(2)	96.528(3)	73.331(1)	–	–
β (deg)	95.700(2)	93.131(3)	88.757(1)	105.829(2)	106.903(1)
γ (deg)	104.239(2)	99.431(2)	73.198(1)	–	–
V (Å^3)	1340.5(2)	1799.8(4)	1011.391)	5760(1)	6592.0(6)
Z	1	2	2	4	6
D_c (Mg m^3)	1.427	1.511	1.549	1.439	1.499
R ($I > 2\sigma(I)$)	0.0597	0.0741	0.0323	0.0503	0.0790
wR ($I > 2\sigma(I)$)	0.1676	0.2012	0.0884	0.1320	0.2446
GOF S	1.023	1.030	1.048	1.019	1.027

[OTf] (0.060 g, 0.099 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was stirred for 24 h at room temperature. Reduction of the volume to 2 mL by evaporation under vacuum and subsequent addition of hexane (5 mL) resulted in separation of an oil from the mother liquor. Vigorous stirring overnight gave a white precipitate, yield 0.025 g, 63%; mp 167−170 °C. Anal. Calcd. for $C_{32}H_{36}F_6O_6P_4S_2$ (Found): C 46.95 (46.67), H 4.43 (4.54). IR: 516(18), 571(20), 634(7), 693(15), 704(19), 723(13), 744(8), 912(11), 959(14), 997(17), 1028(5), 1088(16), 1152(19), 1183(6), 1201(12), 1221(10), 1249(3), 1283(4), 1377(2), 1462(1); colorless needle-shaped crystals were obtained using vapor diffusion (CH_2Cl_2/Et_2O) and were spectroscopically identical to the precipitate.

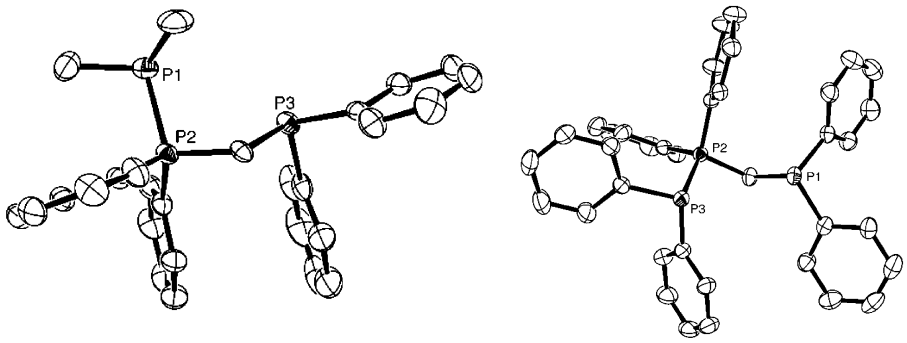
[Ph_2P−dmpe−PPh_2] **4a** [$GaCl_4$]$_2$. A solution of dmpe (0.020 g, 0.13 mmol) in CH_2Cl_2 (3 mL) was added dropwise (over 5 min) to a stirred solution of [Ph_2P(Cl)−PPh_2][$GaCl_4$] (0.26 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 1 h at room temperature. Reduction of the volume to 2 mL by evaporation under vacuum and addition of Et_2O (5 mL) gave a white precipitate, which was recrystallized by vapor diffusion (CH_2Cl_2/Et_2O) at −30 °C, yield 0.074 g, 61%; mp 108−110 °C. Elemental analyses were not determined.

[Ph_2P−dppe−PPh_2] **4b** [$GaCl_4$]$_2$. A solution of dppe (0.032 g, 0.099 mmol) in CH_2Cl_2 (3 mL) was added dropwise (over 5 min) to a stirred solution of [Ph_2(Cl)P−PPh_2][$GaCl_4$] (0.20 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred for 1 h at room temperature. The volume was reduced to 2 mL by evaporation under vacuum, and Et_2O was added (5 mL) to give a white precipitate, which was recrystallized (clear, colorless, needles) by vapor diffusion (CH_2Cl_2/Et_2O) at −30 °C, yield 0.091 g, 77%; mp 94−95 °C. Elemental analyses were not determined. IR: 247(10), 279(9), 371(2), 471(6), 497(7), 689(3), 730(1), 891(8), 997(5), 1108(4).

[Ph_2P−dppe−PPh_2] **4b** [OTf]$_2$. A solution of dppe (0.020 g, 0.050 mmol) in CH_2Cl_2 (3 mL) was added dropwise (over 5 min) to a solution of [Ph_3P−PPh_2][OTf] (0.060 g, 0.099 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 12 h at room temperature. Reduction of the volume to 2 mL by evaporation under vacuum (2 mL) and subsequent addition of hexane (5 mL) gave a fine white crystalline precipitate, yield 0.085 g, 74%; mp 193−195 °C. Anal. Calcd. for $C_{53}H_{46}Cl_2F_6O_6P_4S_2$ (Found): C 55.26 (57.26), H 4.03 (4.30). IR: 633(11), 658(15), 694(5), 723(1) 801(13), 881(14), 973(9), 996(8), 1028(4), 1097(6), 1150(3), 1263(2), 1584(12), 2670(10), 2726(7); clear colorless needlelike crystals were obtained by vapor diffusion (CH_2Cl_2/Et_2O) and were spectroscopically identical to the precipitate.

[Ph_2P−dpph−PPh_2] **5** [$GaCl_4$]$_2$. A solution of dpph (0.023 g 0.049 mmol) in CH_2Cl_2 (2 mL) was added to a solution of [Ph_2PCl−PPh_2]-[$GaCl_4$] (0.099 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was stirred for 24 h at room temperature. Reduction of the volume to 2 mL by evaporation under vacuum and the addition of hexane (5 mL) gave a fine white precipitate, yield 0.049 g, 79%; mp 64−67 °C. Anal. Calcd. for $C_{54}H_{52}Cl_8Ga_2P_4$ (Found): C 51.98 (51.01), H 4.20 (4.25). IR: 279(10), 356(9), 373(8), 688(7), 722(4), 742(3), 1104(5), 1377(2), 1461(1), 1670(3); colorless needlelike crystals were obtained using vapor diffusion (CH_2Cl_2/Et_2O) and were spectroscopically identical to the precipitate.

[Me_2P−dppb−PMe_2] **6** [$GaCl_4$]$_2$. A solution of dppb (0.085 g, 0.190 mmol) in CH_2Cl_2 (2 mL) was added to a solution of [Me_2(Cl)P−PMe_2]-[$GaCl_4$] (0.126 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 24 h at room temperature. Reduction of the volume to 2 mL by evaporation under vacuum and the addition of hexanes (5 mL) gave a fine white precipitate, yield 0.179 g, 95%; mp 174 °C. Anal. Calcd.



[Me_2P-dppm][OTf] [Ph_2P-dppm][OTf]

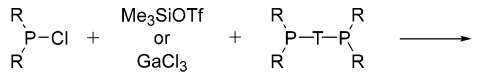
Figure 1. Representative views of the cations in the solid-state structures of [Me_2P−dppm] **2a** [OTf] and [Ph_2P−dppm] **2b** [OTf]. Ellipsoids are drawn to 50% probability. Hydrogen atoms and anions are not shown.

for $C_{34}H_{36}Cl_8Ga_2P_4$ (Found): C 41.18 (42.92), H 3.66 (3.94). IR: 383(2), 471(15), 507(12), 533(4), 578(7), 687(5), 743(6), 833(14), 893(11), 953(9), 996(10), 1012(13), 1100(3), 1117(8), 1438(1); clear colorless crystalline needles were grown using vapor diffusion (CH_2Cl_2/Et_2O) and were spectroscopically identical to the precipitate.

Results and Discussion

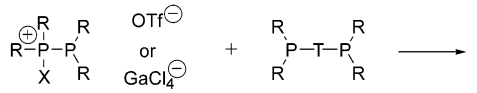
Phosphine−phosphenium donor−acceptor cationic complexes (**1**) represent readily accessible sources of dimethyl- (Me_2P^+) or diphenyl-phosphenium (Ph_2P^+) cationic units by virtue of facile ligand exchange reactions.[1,24] The introduction of traditional diphosphine ligands (dppm, dmpm, dppe, dmpe, dpph, dppb; see Experimental Section for abbreviations) offers the possibility of accessing monocationic complexes with a pendant phosphine (**2**), dications incorporating two phosphenium Lewis acids (**3**, **4**, **5**, and **6**) or chelate complexes (**7** and **8**), as observed in the diverse chemistry that is established for transition metal−diphosphine complexes.[31]

(1)



R = Ph or Me; T = CH_2, C_2H_4, C_6H_{12}, C_6H_4; X = Cl or Ph

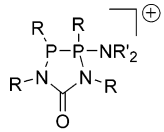
(2)



Equimolar combinations of dimethyl- or diphenyl-chlorophosphines with trimethylsilyltrifluoromethanesulfonate (Me_3SiOTf) or gallium chloride and a diphosphine (reaction mixture **1**) show ^{31}P NMR signals that are assigned to structure types **2**, **3**, **4**, **5**, or **6** representing new P−P bonded complexes. The same P−P bonded complexes are observed (by ^{31}P NMR spectroscopy) in reaction mixtures of the corresponding diphosphines with tetrachlorogallate (gallate) or trifluoromethanesulfonate (triflate) salts of the appropriate phosphine−phosphenium cations (reaction mixture **1**) $[Me_2P(Cl)-PMe_2]^+$ (as a source of $[Me_2P]^+$), $[Ph_2P(Cl)-PPh_2]^+$, or $[Ph_3P-PPh_2]^+$ (as a source of $[Ph_2P]^+$) (reaction mixture **2**). Distinct ^{31}P NMR signals are also observed for the ligands that are eliminated in reaction mixture **2**, Me_2PCl (δ = 99 ppm), Ph_2PCl (δ = 81 ppm), and Ph_3P (δ = −5 ppm), respectively. The P−P bonded products **2**, **3**, **4**, **5**, or **6** are formed quantitatively in all reaction mixtures (**1** and **2**), independent of the counteranion ([$GaCl_4$] or [OTf]) or the imposed reaction stoichiometry.

Gallate and triflate salts of **2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **5**, and **6** that are observed in reaction mixtures (by ^{31}P NMR spectroscopy) have been isolated and identified, as listed in Table 1. Ionic formulations have been confirmed for most derivatives by X-ray crystallographic studies (Table 2). The structures of the cations in gallate salts are essentially identical to those in the corresponding triflate salts. Figure 1 shows representative solid-state structural views of monocationic adducts **2** involving dppm with Me_2P^+ (**2a**) or Ph_2P^+ (**2b**). One P−P bond is observed with a consequential pendant phosphine that is more than 3.6 Å from the acceptor phosphenium site, rather than a chelate interaction of type **7**, involving two equivalent P−P distances. Examples of 1:1 complexes involving dppe, dmpe, dpph, or dppb have not been observed. Figure 2 shows representative solid-state structural views of dications of **3b**, **4a**, **4b**, **5**, and **6** involving two P−P bonds that associate two phosphenium units (R_2P^+) by a tethered diphosphine ligand (dmpm **3b**, dppe **4b**, dmpe **4a**, dpph **5**, dppb **6**).

Complexes of type **2** involving a pendant phosphine are only observed with the dppm ligand, and four examples have been characterized. Analogous monocationic complexes with longer organic tethers have not been observed. The dppm ligand is not observed to engage two phosphenium acceptors to form dications. Nevertheless, three examples of **3** are observed with the more basic dmpm ligand. Tethered dications are also observed with dmpe (**4a**), dppe (**4b**), dpph (**5**), and dppb (**6**).



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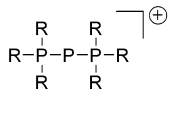

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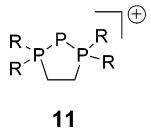

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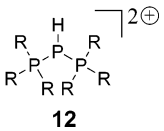

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The P−P distances in derivatives of **2**, **3**, **4**, **5**, and **6** (Table 1) are comparable with those in Ph_2P-PPh_2,[32] phosphine−

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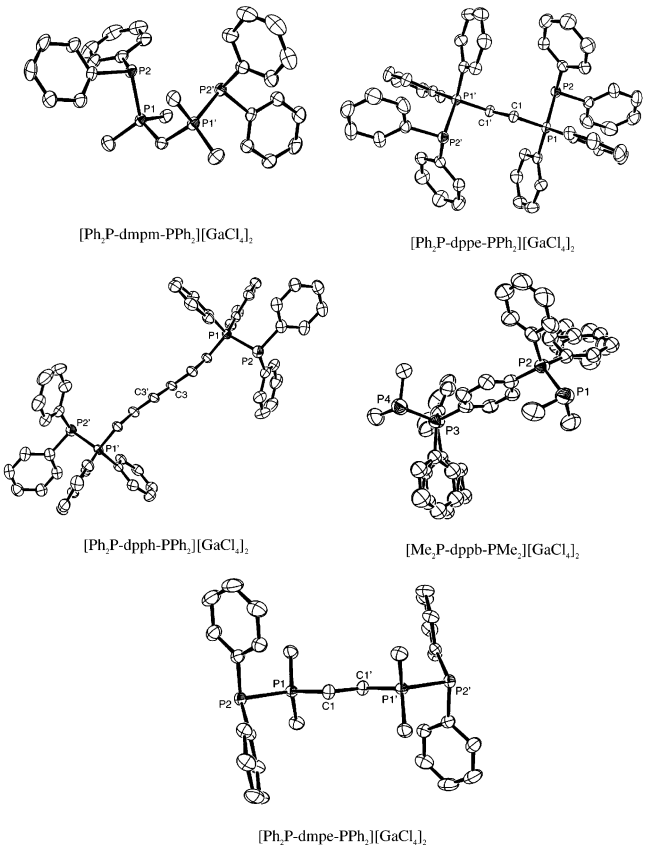

Figure 2. Representative views of dications in the solid-state structures of [$Ph_2P-dmpm-PPh_2$] **3b** $[GaCl_4]_2$, [$Ph_2P-dppe-PPh_2$] **4b** $[GaCl_4]_2$, [$Ph_2P-dpph-PPh_2$] **5** $[GaCl_4]_2$, [$Me_2P-dppb-PMe_2$] **6** $[GaCl_4]_2$, and [$Ph_2P-dmpe-PPh_2$] **4a** $[GaCl_4]_2$. Ellipsoids are drawn to 50% probability. Hydrogen atoms and anions are not shown. The phenyl groups in [$Me_2P-dppb-PMe_2$] **6** $[GaCl_4]_2$ are disordered, and the carbon atoms of these groups have been split over two positions with equal occupancy.

phosphenium cations of type **1**,[24] intramolecular complexes of type **9**,[27−29,36] and triphosphorus cations of type **10**,[20,35] **11**,[34,37] and **12**,[34,37] defining a remarkably narrow range despite differences in molecular charge and the coordination number at each phosphorus center. The pyramidal geometry about the three-coordinate phosphorus centers (acceptor sites) in all cations is consistent with a phosphine-like environment, and the donor phosphorus centers have a phosphonium-like, distorted tetrahedral geometry.

The dicationic complexes **3b** involving two Ph_2P^+ units tethered by dmpm (as gallate and triflate salts) contrast the pendant arrangements observed for dppm with both Me_2P^+ (**2a**) and Ph_2P^+ (**2b**). The 1:1 stoichiometry observed for [$Me_2P-dppm$] **2a** [OTf] and [$Ph_2P-dppm$] **2b** [OTf] may be due to the relatively lower basicity of the donor sites in the phenylated ligand (dppm) in comparison with those in dmpm. In addition, π-stacking of the phenyl substituents on the ligand, shown in Figure 1, likely limits flexibility of the P−C−P ligand backbone imposing steric restrictions on the second donor site and contributing to the preference for the structure of **2a** and **2b**.

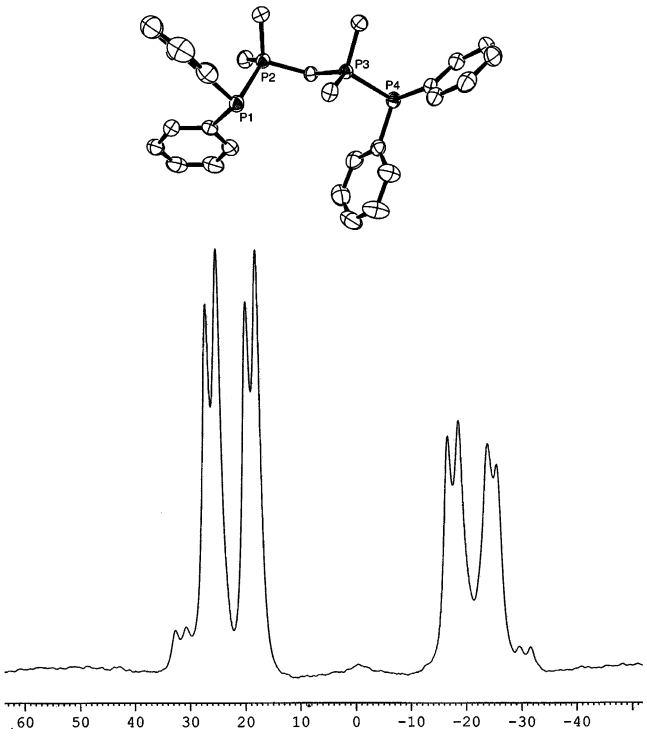

Figure 3. Solid-state structure and ^{31}P CP-MAS NMR spectrum of the dication in [$Ph_2P-dmpm-PPh_2$] **3b** $[OTf]_2$. Ellipsoids are drawn to 50% probability. Hydrogen atoms and anions are not shown. Four distinct doublets in the NMR spectrum are assigned to P(1), P(2), P(3), and P(4) in the cation. $^3J_{PP}$ and $^4J_{PP}$ coupling are not observed in the spectra obtained in the solid state or in solution.

Although a bis-phosphenium salt [$Ph_2P-dmpm-PPh_2$] **3b** $[OTf]_2$ is observed for the methylated diphosphinomethane ligand (dmpm), steric restrictions associated with the relatively short backbone of the ligand are evidenced by the significant difference in P−P distances and four distinct ^{31}P chemical shifts observed in the solid-state NMR spectrum (Figure 3). This crystallographic nonsymmetry is not unique for the cation in **3b**, although the differences in P−P bonds are more pronounced than those in the other nonsymmetric structure of [$Me_2P-dppb-PMe_2$] **6** $[GaCl_4]_2$. The two distinct P−P bond distances listed for [$Ph_2P-dmpe-PPh_2$] **4a** $[OTf]_2$ arise from two crystallographically distinct cations in the asymmetric unit, each with an inversion center at the central C−C bond in the tether, that are manifested in the ^{31}P solid-state NMR spectrum as two sets of overlapping doublets. In general, the longer organic tethers in diphosphinoethane, diphosphinohexane, and diphosphinobenzene ligands are expected to impose less steric restrictions on the donor sites in comparison to the diphosphinomethane ligands, so that NMR data for solid samples of all other bis-phosphenium complexes are consistent with those observed in solution.

All dicationic complexes (**3**, **4**, **5**, **6**) adopt an anti-configuration of the P−P coordinate bonds with torsional angles of 180°, except for complexes of dmpm. Although steric factors are likely prominent, the anti-configuration also maximizes the distance between Lewis acceptors. Observation of monocationic 1:1 complexes (**2**) for dppm corresponds with the relatively weak donor phosphine sites in comparison with the methylated derivative dmpm, which forms only derivatives of **3**, independent of the type of phosphenium acceptor. Therefore, the relative

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Lewis acidity of Me_2P^+ and Ph_2P^+ is not expressed in the series of complexes.

Phosphorus-31 NMR chemical shifts (Table 1) for each phosphorus center in derivatives of **2**, **3**, **4**, **5**, and **6** are consistent with established, distinctive shifts for phosphine−phosphenium cations **1**.[24] Moreover, the tricoordinate sites (acceptor sites) exhibit ^{31}P δ values that are consistent with those of phosphines, Ph_3P ($\delta = -5$ ppm), Ph_2P-PPh_2 ($\delta = -15$ ppm), and Me_3P ($\delta = -62$ ppm), and the tetracoordinate sites (donor sites) exhibit ^{31}P δ values that are consistent with those of phosphonium cations, for example, Ph_4P^+ ($\delta \approx 20$ ppm).[38] Salts of **2a** and **2b** exhibit AMX coupling patterns with typical values for $^1J_{PP}$, $^2J_{PP}$, and $^3J_{PP}$. All tethered complexes (**3**, **4**, **5**, and **6**) show AB coupling patterns (two doublets) with $^1J_{PP}$ values that are typical for P−P bonded complex cations.[39]

The versatile P−P homoatomic coordination chemistry provides a facile, high-yield synthetic methodology toward polyphosphorus cations and dications, which have comparisons with established polyphosphorus anions.[40,41] The observations represent the diversification of P−P coordination chemistry in terms of multinuclear donors and demonstrate the potential for extended systems. Nevertheless, in contrast to the diverse structures observed for transition metal−diphosphine complexes,[31] the apparent preference for open chain structures over chelate complexes indicates a limitation in the accommodation of multiple donors at the electron-rich phosphine acceptor site.

Conclusions

Facile ligand exchange reactions at phosphenium Lewis acceptors provide a versatile synthetic approach to diphosphine−phosphenium P−P bonded complexes. Monocations with open chain structures represented by **2** are observed, as well as dication tethered complexes represented by **3**, **4**, **5**, and **6**. Chelate complexes **7** and **8** have not been observed. The structural preferences are dependent on intramolecular steric interactions and flexibility of the tether.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Killam Foundation, the Canada Research Chairs Program, the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund, and the Walter C. Sumner Foundation for funding, the Atlantic Region Magnetic Resonance Centre for use of instrumentation, and Dr. M. Lumsden (ARMRC) for the collection of solid-state NMR data.

Supporting Information Available: Crystallographic information (PDF, CIF) for all of the compounds presented above. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0452121

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