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Synthesis and coordination chemistry of neutral phospha(III)guanidines. Formation of 1-aza-3-phospha-4-metallacyclobut-1-ene rings at group 6 metals †

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The neutral phospha(III)guanidine compounds, $Ph_2PC\{NR\}\{NHR\}$ (**1a**, R = Cy; **1b**, R = ^{i}Pr), are reported. NMR spectroscopic data indicated the presence of the E_{syn} isomer in solution and structural studies confirmed this in the solid-state. Reaction of **1a** with $M(CO)_4(pip)_2$ [M = Mo, W; pip = piperidine] proceeded *via* displacement of the piperidine ligands to generate the complexes $M[Ph_2PC\{NCy\}\{NHCy\}](CO)_4$ (**2a**, M = Mo; **3a**, M = W). The X-ray structure of **2a** and **3a** were solved, showing the first structurally characterised examples of 1-aza-3-phospha-4-metallacyclobut-1-ene rings.

1 Introduction

Amidinate ligands, $[R'C\{NR\}_2]^-$ (R′ = alkyl, aryl) have found application in the synthesis of a diverse range of coordination compounds,[1] with much of the work focused on the easily prepared benzamidinate anion $[PhC\{NSiMe_3\}_2]^-$.[2] Substitution of the R′-group by an NR''_2 functionality gives the closely related family of guanidinate anions,[3] further extending the chemistry of ligands containing this basic framework, and offering a degree of control over the donor properties of the ligand through the possible donation of the amide lone pair into the 'CN_3' core of the ligand.[4] Development of these classes of ligand to include the phospha(III)guanidinate anions (R′ = PR''_2) and the corresponding neutral phospha(III)guanidines has, to date, not received a comparable degree of study, although the synthesis,[5] and reactivity[6] of a related class of *N*-(*N′*,*N′*,*N″*,*N″*-tetramethyl)guanidine-substituted phosphines has been the subject of detailed studies by Schmutzler and co-workers.

The synthesis of neutral, silylated phospha(III)guanidines $(Me_3Si)RPC\{NR'\}\{N(SiMe_3)R''\}$ (**A**, Fig. 1) was first reported in 1980 from the insertion of a carbodiimide into one of the P–Si bonds of bis-silylated phosphines.[7] An NMR spectroscopic study determined that, depending on the nitrogen substituents, silyl-migration may occur to give the phosphaalkene derivative (**B**, Fig. 1). A related study of the reaction between heteroallenes and diphenylphosphine afforded the N*H* substituted derivative $Ph_2PC\{NAr\}\{NHAr\}$ (Ar = *p*-tolyl) in near quantitative yield.[8] Preliminary studies of the coordination chemistry of these compounds indicated P-donation to Mo and W centres for the neutral species (**C**, Fig. 1)[9] and a chelating P,N-coordination at rhodium and iridium for the phospha(III)guanidinate anion (*e.g.* **D**, Fig. 1).[10] An alternative method employed for the synthesis of phospha(III)guanidinates is the insertion of a carbodiimide into a metal–phosphide bond, used in the synthesis of the structurally characterised zirconocene derivative, $ZrCp'_2[(Me_3Si)_2PC\{NPh\}_2]Cl$ (**E**, Fig. 1).[11]

Previous work with both neutral and anionic amidines/guanidines has demonstrated a varied coordination behaviour at metal centres. The introduction of a phosphine moiety within the ligand framework increases the potential number of binding modes for the ligand (Fig. 2), and preliminary work in our group has demonstrated flexibility in the coordination of a phospha(III)guanidinate anion to lithium and aluminium, where either an N,N′- or N,P-coordination is observed (**IV** and **V**, respectively, Fig. 2), depending on the nature of the additional donor ligands in the coordination sphere of the metal.[12] We now report the synthesis of neutral phospha(III)guanidines, $Ph_2PC\{NR\}\{NHR\}$, *via* insertion of dialkylcarbodiimide into the Li–P bond of lithium diphenylphosphide and subsequent quenching of the phospha(III)guanidinate salt with $[HNEt_3][Cl]$. The coordination behaviour at group 6 metal carbonyl centres is described and a crystallographic study reveals formation of a 1-aza-3-phospha-4-metallacyclobut-1-ene ring rather than simple P-coordination of the ligand.

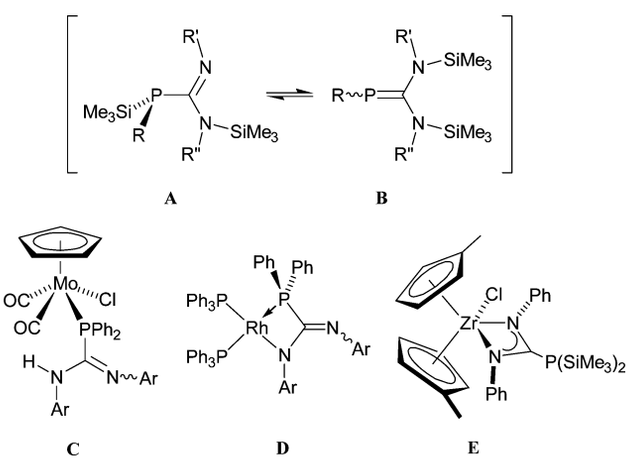

Fig. 1 Examples of phospha(III)guanidine and related metal complexes.

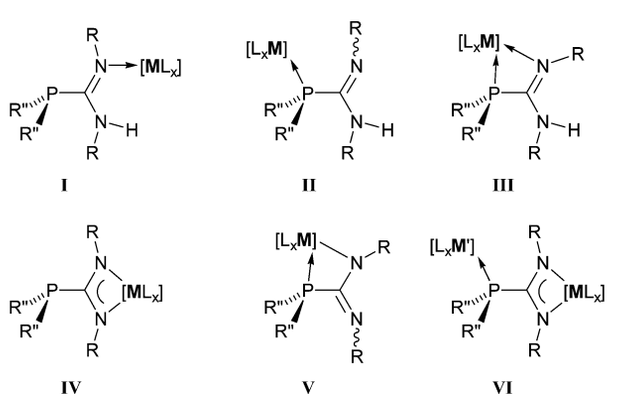

Fig. 2 Examples of potential bonding modes for neutral (**I–III**) and anionic (**IV–VI**) phospha(III)guanidine based compounds.

† Electronic supplementary information (ESI) available: an ORTEP representation and bond lengths and angles for **3a**; crystal structure and refinement data, bond lengths and angles and an ORTEP representation of the molecular structure of $Mo(CO)_4(pip)_2$. See http://www.rsc.org/suppdata/dt/b3/b302554c/

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2 Experimental

General experimental procedures

All manipulations were carried out under dry nitrogen using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agent and degassed prior to use. Diphenylphosphine, 1,3-diisopropylcarbodiimide and 1,3-dicyclohexylcarbodiimide were purchased from Aldrich and used as received. $Mo(CO)_4(pip)_2$ and $W(CO)_4(pip)_2$ were synthesised according to literature procedures.[13] Triethylamine hydrochloride was dried by recrystallisation from chloroform and heating *in vacuo* for 1 h.

Elemental analyses were performed by S. Boyer at London Metropolitan University. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300 (^{1}H), 75 (^{13}C{^{1}H}) and 121 (^{31}P{^{1}H}) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances; phosphorus chemical shifts were referenced to an external 85% aqueous solution of H_3PO_4. Coupling constants, *J*, are quoted in Hz.

$Ph_2PC\{NCy\}\{NHCy\}$ (1a). ^{n}BuLi (2.4 mL of a 2.5 M solution in hexanes, 6.00 mmol) was added dropwise to an ice-cooled solution of Ph_2PH (1.00 g, 5.37 mmol) in THF (50 mL). The resultant orange–red solution of lithium diphenylphosphide was stirred for 30 min at 0 °C after which time a solution of 1,3-dicyclohexylcarbodiimide (1.21 g, 5.86 mmol) in THF (20 mL) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight, resulting in the formation of a clear yellow solution. Dry $[HNEt_3][Cl]$ (0.81 g, 5.90 mmol) was added to the mixture as a THF slurry, and allowed to stir for 1 h affording a colourless solution. The volatile components were removed *in vacuo* and the product was extracted with hexane (2 × 50 mL) and the extracts were combined and concentrated. Storage at −30 °C resulted in the formation of pure **1a** as large colourless crystals. Yield 1.52 g (71%).

Anal. Calc. for $C_{25}H_{33}N_2P$: C, 76.50; H, 8.47; N, 7.14%. Found: C, 76.60; H, 8.59; N, 7.03%. ^{1}H NMR (C_6D_6, 298 K): δ 7.54–6.99 (m, 10H, C_6H_5), 4.16 (m, 2H, NCH), 3.83 (d, $^3J_{HH}$ = 6.9, 1H, N*H*Cy), 1.93–0.94 (m, 20H, Cy). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 152.3 (d, $^1J_{CP}$ = 32, PCN_2), 135.7 (d, $^1J_{CP}$ = 14, Ph-C_{ipso}), 134.2 (d, $^2J_{CP}$ = 20, Ph-C_{ortho}), 129.2 (d, $^3J_{CP}$ = 20, Ph-C_{meta}), 128.96 (Ph-C_{para}), 60.6 (Cy-C_1), 60.2 (Cy-C_1), 49.2 (Cy), 35.8 (Cy), 32.6 (Cy), 26.4 (Cy), 26.2 (Cy), 25.2 (Cy), 24.6 (Cy). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ −16.9. MS (EI$^+$, *m*/*z*): 392 $[M]^+$, 370 $[P_2Ph_4]$, 310 $[M - Cy]^+$, 207 $[M - PPh_2]^+$, 183 $[M - N(Cy)_2H]^+$. IR (Nujol mull, cm^{-1}): 3422s (N–H), 1583s (C=N), 1591s, 1463s, 1377m, 1344w.

$Ph_2PC\{N^iPr\}\{NH^iPr\}$ (1b). Compound **1b** was prepared using the procedure described for **1a**, using the following quantities: Ph_2PH (1.00 g, 5.37 mmol), ^{n}BuLi (2.4 mL, 6.00 mmol), 1,3-diisopropylcarbodiimide (0.92 mL, 5.90 mmol) and $[HNEt_3][Cl]$ (0.81 g, 5.90 mmol) resulting in the formation of colourless needles. Yield 1.19 g (71%).

Anal. Calc. for $C_{19}H_{25}N_2P$: C, 73.06; H, 8.07; N, 8.97%. Found: C, 73.16; H, 8.15; N, 8.95%. ^{1}H NMR (C_6D_6, 298 K): δ 7.49–7.00 (m, 10H, C_6H_5), 4.45 (m, 1H, =NC*H*Me$_2$), 4.35 (m, $^3J_{HH}$ = 6.2, 1H, –NC*H*Me$_2$), 3.66 (d, $^3J_{HH}$ = 6.2, NH), 1.28 (d, $^3J_{HH}$ = 6.1, 6H, CH*Me*$_2$), 0.96 (d, $^3J_{HH}$ = 6.4, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 152.3 (d, $^1J_{CP}$ = 32, P*C*N$_2$), 135.6 (d, $^1J_{CP}$ 14, Ph-C_{ipso}), 134.4 (d, $^2J_{CP}$ = 19, Ph-C_{ortho}), 129.4 (d, $^3J_{CP}$ = 21, Ph-C_{meta}), 129.1 (Ph-C_{para}) 52.4 (d, $^3J_{PC}$ 35, =N*C*H), 43.0 (–N*C*H), 25.4 (CH*Me*$_2$), 22.5 (CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ −17.4. MS (EI$^+$, *m*/*z*): 312 $[M]^+$, 183 $[M - N(^iPr)_2H]^+$, 127 $[M - PPh_2]^+$. IR (Nujol mull, cm^{-1}): 3432s (N–H), 1600s (C=N), 1219w, 1174w, 1027w, 969w, 800w, 743w, 695w.

$Mo[Ph_2PC\{NCy\}\{NHCy\}](CO)_4$ (2a). A solution of **1a** (0.39 g, 1.00 mmol) in CH_2Cl_2 (20 mL) was added to a slurry of $Mo(CO)_4(pip)_2$ (0.38 g, 1.00 mmol) in CH_2Cl_2 (20 mL). The resultant mixture was stirred at room temperature for 2 days to give a yellow solution. Filtration and cooling to −30 °C afforded pure **2a** as yellow crystals suitable for an X-ray study. Yield 0.22 g (37%).

Anal. Calc. for $C_{29}H_{33}MoN_2O_4P$: C, 58.00; H, 5.54; N, 4.66%. Found: C, 57.85; H, 5.39; N, 4.46%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.70–7.50 (m, 10H, C_6H_5), 4.61 (br t, 1H, N*H*Cy), 3.10 (m, 1H, NCH) 2.90 (m, 1H, NCH), 1.83–0.71 (m, 20H Cy). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 221.9 (d, $^2J_{CP}$ = 8, MoCO), 220.1 (d, $^2J_{CP}$ = 27, MoCO), 208.8 (d, $^2J_{CP}$ = 8, MoCO), 162.3 (d, $^1J_{CP}$ = 33, PCN_2), 132.1 (d, $^1J_{CP}$ = 14, Ph-C_{ipso}), 130.8 (d, $^2J_{CP}$ = 2, Ph-C_{meta}), 130.1 (d, $^3J_{CP}$ = 25, Ph-C_{ortho}), 129.2 (d, $^4J_{CP}$ = 10, Ph-C_{para}), 57.2 (d, $^3J_{CP}$ = 19, =NCy-C_1), 53.2 (–NCy-C_1), 34.6 (Cy), 32.8 (Cy), 25.2 (Cy), 25.1 (Cy), 24.9 (Cy), 24.7 (Cy). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 16.7. MS (EI$^+$, *m*/*z*): 600 $[M]^+$, 572 $[M - CO]^+$, 544 $[M - 2CO]^+$, 516 $[M - 3CO]^+$, 488 $[M - 4CO]^+$. IR (Nujol mull, cm^{-1}): 3359s (N–H), 2019s (CO), 1920s (CO), 1891s (CO), 1791s (CO), 1576s (C=N), 1147w, 1091w, 976w.

$W[Ph_2PC\{NCy\}\{NHCy\}](CO)_4$ (3a). Compound **3a** was prepared using the procedure described for **2a** using the following quantities: $W(CO)_4(pip)_2$ (0.23 g, 0.50 mmol) in CH_2Cl_2; a solution of **1a** (0.20 g, 0.50 mmol) in CH_2Cl_2 was added and stirred for 2 days. The resulting yellow solution was filtered, concentrated and cooled to −30 °C resulting in the formation of yellow crystals of **2**. Yield 0.19 g (55%).

Anal. Calc. for $C_{29}H_{33}N_2O_4PW$: C, 56.53; H, 6.64; N, 6.59%. Found: C, 56.60; H, 6.58; N, 6.55%. ^{1}H NMR ($CDCl_3$, 298 K): δ 7.70–7.51 (m, 10H, C_6H_5), 4.65 (t, 1H, NH), 3.07 (m, 1H, =NCH), 2.80 (m, 1H, NCH), 1.85–0.72 (m, 20H, NCy). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 212.0 (d, $^2J_{CP}$ = 45, WCO), 211.9 (d, $^2J_{CP}$ = 7, WCO), 204.5 (d, $^2J_{CP}$ = 7, WCO), 165.3 (d, $^1J_{CP}$ = 37, PCN_2), 134.5, 132.2 (d, $^1J_{CP}$ = 14, Ph-C_{ipso}), 131.2 (d, $^2J_{CP}$ = 2, Ph-C_{meta}), 130.2 (d, $^3J_{CP}$ = 8, Ph-C_{ortho}), 129.2 (d, $^4J_{CP}$ = 10, Ph-C_{para}), 128.8, 128.4, 57.7 (Cy-C_1), 57.6 (Cy-C_1), 53.2 (Cy), 34.6 (Cy), 32.9 (Cy), 25.1 (Cy), 24.9 (Cy), 24.8 (Cy), 24.7 (Cy). ^{31}P{^{1}H} NMR ($CDCl_3$, 298 K): δ 1.5 ($^1J_{WP}$ = 186). MS (EI$^+$, *m*/*z*): 688 $[M]^+$, 660 $[M - CO]^+$, 632 $[M - 2CO]^+$, 576 $[M - 4CO]^+$. IR (Nujol mull, cm^{-1}): 3350s (N–H), 2013s (CO), 1938s (CO), 1911s (CO), 1882s,sh (CO), 1577s (C=N), 1261w.

Crystallography

Details of the crystal data, intensity collection and refinement for ligands **1a** and **1b** and complexes **2a** and **3a** are listed in Table 1. Crystals were covered in oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.[14] Additional features are described below.

$Ph_2PC\{NCy\}\{NHCy\}$ (**1a**). H(1) was refined.

$Ph_2PC\{N^iPr\}\{NH^iPr\}$ (**1b**). The C(5)–C(7) isopropyl group is disordered with relative occupancies of 0.62 and 0.38. The major occupancy structure is illustrated in Fig. 4.

$W[Ph_2PC\{NCy\}\{NHCy\}](CO)_4$ (**3a**). The hydrogen atom on N(2) was refined; all others were riding.

CCDC reference numbers 201561–201565.

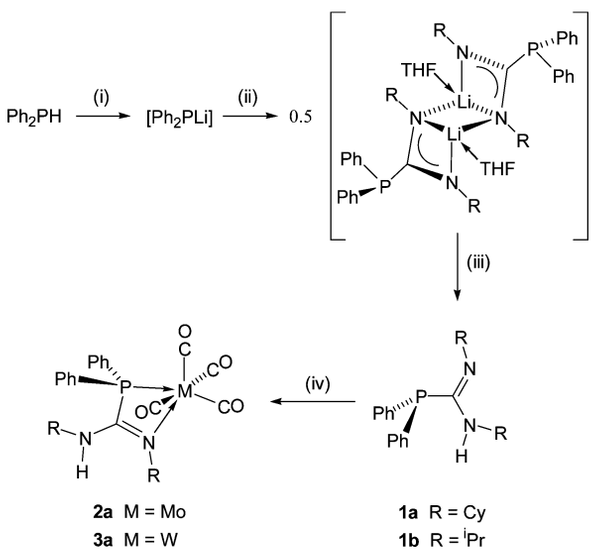
See http://www.rsc.org/suppdata/dt/b3/b302554c/ for crystallographic data in CIF or other electronic format, and an ORTEP representation and bond lengths and angles for **3a**.

3 Results and discussion

The neutral phospha(III)guanidine compounds $Ph_2PC\{NR\}\{NHR\}$ (**1a**, R = Cy; **1b** R = ^{i}Pr) were synthesised in good yields using the procedure outlined in Scheme 1. A THF solution of diphenylphosphine was lithiated with ^{n}BuLi at 0 °C followed by

Table 1 Crystal structure and refinement data for **1a**, **1b**, **2a** and **3a**

	1a	**1b**	**2a**	**3a**
Formula	$C_{25}H_{33}N_2P$	$C_{19}H_{25}N_2P$	$C_{29}H_{33}MoN_2O_4P$	$C_{29}H_{33}N_2O_4PW$
Formula weight	392.50	312.38	600.48	688.39
Temperature/K	173(2)	173(2)	173(2)	223(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal size/mm	0.30 × 0.30 × 0.15	0.30 × 0.30 × 0.20	0.30 × 0.20 × 0.20	0.30 × 0.15 × 0.05
Crystal system	Orthorhombic	Tetragonal	Monoclinic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P4_1$ (no. 76)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a/Å	9.0943(2)	12.1947(4)	32.0166(4)	32.0487(3)
b/Å	11.6147(2)	12.1947(4)	9.4980(2)	9.4740(1)
c/Å	21.0144(4)	12.6119(4)	21.3176(3)	21.3526(3)
β/°			118.448(1)	118.084(1)
V/Å^3	2219.70(8)	1875.52(11)	5699.8(2)	5719.92(11)
Z	4	4	8	8
D_c/Mg m^{-3}	1.18	1.11	1.40	1.60
Absorption coefficient/mm^{-1}	0.14	0.15	0.55	4.13
θ range for data collection/°	3.88–24.71	3.71–23.82	3.86–25.02	3.82–27.89
Reflections collected	11636	9328	14946	25963
Independent reflections (R_{int})	3593 (0.052)	2815 (0.057)	4577 (0.032)	6797 (0.042)
Reflections with $I > 2\sigma(I)$	3315	2695	4223	6127
Data/restraints/parameters	3593/0/257	2815/1/212	4577/0/338	6797/0/338
Goodness-of-fit on F^2	1.045	1.072	1.058	1.023
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.035$, $wR_2 = 0.075$	$R_1 = 0.039$, $wR_2 = 0.099$	$R_1 = 0.023$, $wR_2 = 0.055$	$R_1 = 0.022$, $wR_2 = 0.051$
R indices (all data)	$R_1 = 0.041$, $wR_2 = 0.078$	$R_1 = 0.042$, $wR_2 = 0.100$	$R_1 = 0.027$, $wR_2 = 0.057$	$R_1 = 0.027$, $wR_2 = 0.053$
Largest diff. peak and hole/e Å^{-3}	0.20 and −0.22	0.12 and −0.12	0.35 and −0.43	0.64 and −1.51



Scheme 1 Reagents and conditions: (i) ^{n}BuLi, THF, 0 °C; (ii) RN=C=NR, THF, 0 °C; (iii) [HNEt$_3$][Cl], THF, RT; (iv) M(CO)$_4$(pip)$_2$ (M = Mo, W), CH_2Cl_2, room temperature.

addition of a solution of 1 equivalent of carbodiimide, to produce a yellow solution of the lithium phospha(III)guanidinate.[12] Quenching the reaction with a slight excess of triethylamine hydrochloride afforded the neutral phospha(III)guanidines **1a** and **1b** that were purified by crystallisation from hexane at −30 °C.

The N*H* stretch is visible by infrared spectroscopy as a sharp peak (**1a**, 3422 cm^{-1}; **1b**, 3432 cm^{-1}) and a strong absorption assigned to the C=N stretching vibration is also present (**1a** 1583 cm^{-1}; **1b** 1600 cm^{-1}), comparable with the corresponding absorptions in previously synthesised amidines.[1] Proton NMR spectra of **1a** and **1b** showed N*H* resonances as a broad doublet, (**1a**, 3.83 ppm; **1b**, 3.66 ppm) with a three bond coupling to the α-hydrogen atom of the *N*-substituents (**1a**, 6.9 Hz; **1b**, 6.2 Hz). In **1b**, the C*H* resonances of the isopropyl substituent appear as two distinct multiplets at 4.45 and 4.35 ppm corresponding to the imino- and amino-nitrogen substituent respectively, the former showing a $^4J_{PH}$ coupling through the C=N double bond. In **1a**, the α-C*H* resonances for each cyclohexyl substituent are coincident at 4.16 ppm, present as a complex multiplet due to the overlap and the $^4J_{PH}$ coupling. The ^{31}P chemical shift in **1a** and **1b** (−16.9 and −17.4 ppm, respectively) is similar to the previously reported δ value of −14.7 for $Ph_2PC\{NAr\}\{NHAr\}$ (Ar = *p*-tolyl),[8] all of which resonate at a much higher frequency than the range of +116 to +170 ppm encountered in the phosphaalkene derivatives (**B**, Fig. 1),[7] suggesting little contribution from such a structure in solution.

Amidine compounds have been shown to exist in different isomeric and tautomeric forms in solution,[15] where the different tautomers are related by a hindered rotation about the C=N bond. Variable temperature NMR experiments of **1a** and **1b** however revealed the existence of only one isomer in solution, assigned as the E_{syn} isomer on the basis of a NOE between the α-CH of the nitrogen substituent and the *ortho*-protons of the phenyl group. Interconversion between tautomers and other possible isomeric forms was not detected in solution up to 333 K using NMR techniques, although evidence for a 1,3-hydrogen shift between the different nitrogen atoms begins to occur at this temperature. To further investigate the bonding within **1a** and **1b**, the molecular structures were solved using X-ray crystallography. ORTEP representations are illustrated in Figs. 3 and 4, crystal data are summarised in Table 1 and selected bond lengths and angles are collected in Table 2.

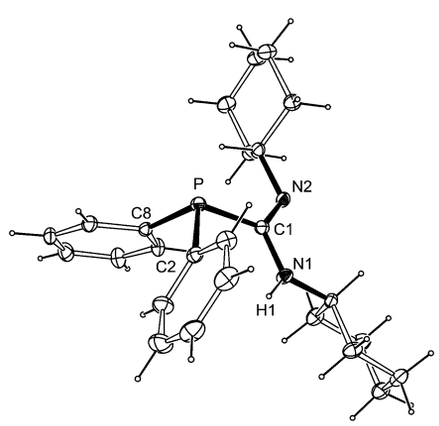


Fig. 3 Molecular structure of $Ph_2PC\{NCy\}\{NHCy\}$ (**1a**) with thermal ellipsoids drawn at the 30% probability level.

Despite crystallising in different crystal systems, the solid state structure of **1a** and **1b** exhibit similar gross structural features; both compounds are present in the monomeric form, with no evidence for formation of a hydrogen bonded dimer, as

Table 2 Selected bond lengths (Å), angles (°) and Δ_{CN} values (Å) for $Ph_2PC\{NCy\}\{NHCy\}$ (**1a**) and $Ph_2PC\{N^iPr\}\{NH^iPr\}$ (**1b**).

1a			
C(1)–N(1)	1.364(2)	P–C(1)	1.878(2)
C(1)–N(2)	1.286(2)	P–C(2)	1.833(2)
Δ_{CN}	0.078	P–C(8)	1.831(2)
N(1)–C(1)–N(2)	120.56(19)	C(1)–P–C(2)	102.05(9)
C(1)–P–C(8)	100.25(9)	C(2)–P–C(8)	103.44(9)
1b			
C(1)–N(1)	1.268(3)	P–C(1)	1.882(3)
C(1)–N(2)	1.372(3)	P–C(8)	1.835(3)
Δ_{CN}	0.104	P–C(14)	1.835(2)
N(1)–C(1)–N(2)	120.2(2)	C(1)–P–C(14)	101.80(11)
C(1)–P–C(8)	99.92(12)	C(8)–P–C(14)	101.81(11)

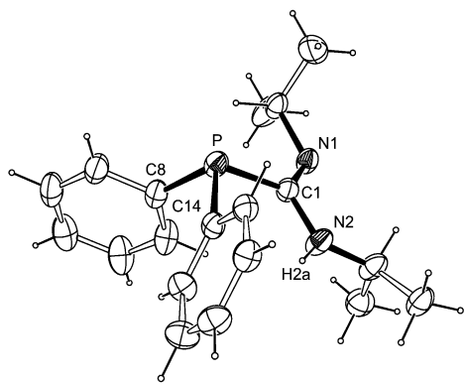


Fig. 4 Molecular structure of $Ph_2PC\{N^iPr\}\{NH^iPr\}$ (**1b**) with thermal ellipsoids drawn at the 30% probability level.

previously observed in several examples of structurally characterised amidines and guanidines.[16] In accordance with the solution state NMR data, only the E_{syn} isomer was found to be present in the solid state, presumably minimising interaction between the N_{amino}-substituent and the phenyl groups of the phosphine moiety. Relatively high Δ_{CN} values of 0.078 and 0.104 Å are observed for **1a** and **1b**, respectively [$\Delta_{CN} = d$(C–N) − d(C=N)],[17] in agreement with the NMR data, indicating little or no delocalisation is present over the amidine unit. Caution should be exercised when discussing such values however as a previous study of linked-bis(*N*,*N*′-dialkylamidinate) compounds has demonstrated that crystal packing effects can strongly influence this value.[18] The geometry of the phosphorous atom is pyramidal in each case (Σ_{angles} at phosphorus: **1a**, 305.7°; **1b**, 303.5°), with significantly smaller values than observed in both the lithium salt $[Ph_2PC\{N^iPr\}_2Li(THF)]_2$ (Σ_{angles} at phosphorus = 315.6°) and the aluminium complex $(Ph_2PC\{N^iPr\}_2)AlMe_2$ (Σ_{angles} at phosphorus = 309.6°),[12] where the ligand is present in its anionic form. Investigation of the distribution of substituents about phosphorus reveals that in each case, one of the P–C_{ipso} bonds is located approximately parallel to the 'CN_2' plane (torsion angles: **1a**, 4.16°; **1b**, 11.22°) projected towards the N_{amino} group. This may provide a small stabilising effect in the solid state *via* a weak interaction between the acidic N*H* proton and the π-cloud of the phenyl substituent [*e.g.* **1a**, H(1)–C(2) 2.42 Å; **1b**, H(2a)–C(14) 2.33 Å].

To explore the coordination potential of neutral phospha(III)guanidines at a metal centre, the reactivity of **1a** with group 6, carbonyl-containing species was investigated (Scheme 1). The reaction between $M(CO)_4(pip)_2$ [M = Mo, W; pip = piperidine] and 1 equivalent of **1a** proceeded smoothly at room temperature in CH_2Cl_2 to afford a crystalline yellow solid (**2a**, M = Mo; **3a**, M = W) in each case. The IR stretches for ν(N–H) and ν(C=N) [**2a**, 3359 and 1576 cm^{-1}; **3a**, 3350 and 1577 cm^{-1}, respectively] are shifted to lower energy, consistent with coordination at a metal centre reducing electron density over the phospha(III)guanidine ligand. The ν(CO) region of the IR spectra of **2a** and **3a** display absorbencies typical for an asymmetrically *cis*-substituted octahedral '$M(CO)_4$' fragment, indicating that the ligand may be interacting through both the phosphine and the amidine moieties. The frequency values are similar to those observed in related $[Mo(CO)_4(\kappa^2P,N)]$ complexes containing five-membered metallacyclic rings, suggesting a similar basicity for the phospha(III)guanidine ligand.[19] In contrast to the ^{1}H NMR data of the free ligand, the N*H* resonances [**2a**, 4.61 ppm; **3a**, 4.65 ppm] are observed as a pseudo-triplet coupling to the ^{31}P in addition to the α-C*H* of the nitrogen substituent, possibly due to an alteration in the torsion angle between the N*H* and P atoms or from a change in hybridisation of the phosphorus upon coordination.[20] The ^{31}P NMR data show a single peak shifted downfield [**2a**, 16.7; **3a**, 1.5 ppm] with respect to the free ligand, consistent with P-coordination at the metal, with a $^1J_{WP}$ of 186 Hz present in **3a**.

To determine the nature of the bonding of **1a** in complexes **2a** and **3a**, X-ray crystallographic studies were conducted. An ORTEP representation of **2a** is illustrated in Fig. 5, crystal data are summarised in Table 1 and selected bond lengths and angles are collected in Table 3.[21]

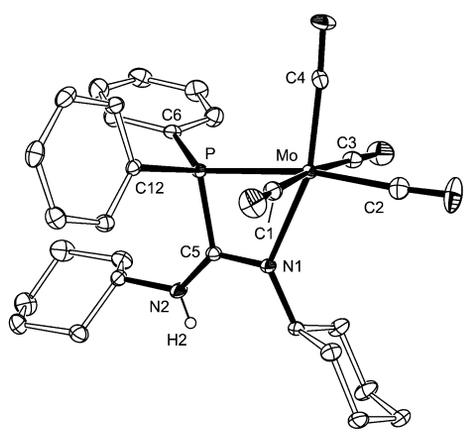


Fig. 5 Molecular structure of $Mo[Ph_2PC\{NCy\}\{NHCy\}](CO)_4$ (**2a**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, except H(2), omitted for clarity.

Complexes **2a** and **3a** are isostructural in the solid state, consisting of a monomeric metal centre with the neutral ligand chelating through both the phosphorus and the imino-nitrogen (see ESI† for an ORTEP representation and tables of bond lengths and angles for **3a**). This bonding mode differs from the P-coordination previously reported in the cyclopentadienyl molybdenum compounds (**C**, Fig. 1) and generates the first structurally characterised examples of 1-aza-3-phospha-4-metallacyclobut-1-ene rings.[22] The geometry at the metal centre is distorted octahedral, with the largest deviation from 90° being due to the formation of the chelate [P–M–N angles: **2a**, 62.78(4)°; **3a**, 62.84(5)°]. There is a significant decrease in the metal carbon distances for the CO ligands trans to both the imino nitrogen [**2a**, 1.9350(19) Å; **3a**, 1.936(3) Å] and phosphorus [**2a**, 1.986(2) Å; **3a**, 1.990(3) Å] in comparison with the remaining ligands [**2a**, 2.034 Å (ave); **3a**, 2.038 Å (ave)], also observed for the CO group *trans* to the piperidine ligand in the starting material [Mo–C(1) 1.945(3) Å; Mo–C(2) 2.035(2) Å].[21] The Mo–P distance in **2a** is slightly shorter than in the related complex *cis*-$Mo(CO)_4(PPh_3)_2$,[23] a likely consequence of the chelation of the N_{imino} group to the metal. The structure of the corresponding tungsten compound has not been reported, although a similar reduction in bond distance for **3a** is noted in comparison with the *trans*-$W(CO)_4(PPh_3)_2$.[24]

The framework of the ligand has undergone a significant structural rearrangement upon coordination (Fig. 6), trans-

Table 3 Selected bond lengths (Å), angles (°) and Δ_{CN} values (Å) for Mo[$Ph_2PC\{NCy\}\{NHCy\}$]$(CO)_4$ (**2a**) and W[$Ph_2PC\{NCy\}\{NHCy\}$]-$(CO)_4$ (**3a**)

2a			
Mo–P	2.4966(5)	Mo–N(1)	2.3129(15)
Mo–C(1)	2.054(3)	Mo–C(2)	1.986(2)
Mo–C(3)	2.024(3)	Mo–C(4)	1.9350(19)
C(5)–N(1)	1.304(2)	C(5)–N(2)	1.342(2)
Δ_{CN}	0.038	C(5)–P	1.8538(18)
N(1)–Mo–P	62.78(4)	N(1)–C(5)–N(2)	127.96(16)
N(1)–C(5)–P	103.93(12)	N(2)–C(5)–P	128.10(14)
C(6)–P–Mo	128.52(7)	C(12)–P–Mo	116.16(6)
C(6)–P–C(12)	105.74(9)		
3a			
W–P	2.4913(6)	W–N(1)	2.299(2)
W–C(1)	2.027(3)	W–C(2)	2.049(3)
W–C(3)	1.990(3)	W–C(4)	1.936(3)
C(5)–N(1)	1.301(3)	C(5)–N(2)	1.343(3)
Δ_{CN}	0.042	C(5)–P	1.853(2)
N(1)–W–P	62.84(5)	N(1)–C(5)–N(2)	128.2(2)
N(1)–C(5)–P	103.61(16)	N(2)–C(5)–P	128.22(18)
C(6)–P–W	116.13(7)	C(12)–P–W	128.00(8)
C(6)–P–C(12)	105.85(11)		

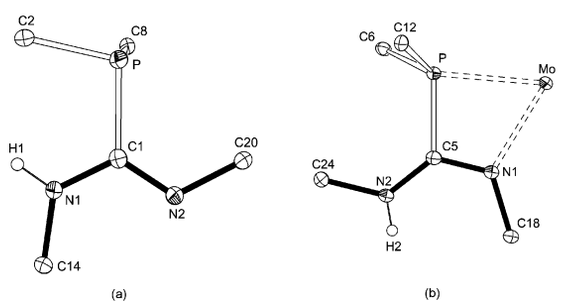


Fig. 6 Structural representation of the framework of the phospha(III)guanidine in (a) **1a** and (b) **2a**, highlighting the change from E_{syn} to Z_{anti}.

forming from the E_{syn} to the Z_{anti} tautomer as the imino-nitrogen interacts with the metal. The Δ_{CN} values [**2a**, 0.038 Å; **3a**, 0.042 Å] are smaller in comparison with the free ligand which, together with a shorter P–C bond [**2a**, 1.8538(18) Å; **3a**, 1.853(2) Å] suggests increased π-electron delocalisation throughout the core of the ligand. The geometry at the phosphorus atom approaches trigonal pyramidal, with the M and C_{ipso} groups forming the base (Σ_{angles} at phosphorus: **1a**, 350.4°; **1b**, 350.0°) and the P-atom displaced by 0.360 and 0.368 Å above this plane, in **2a** and **3a**, respectively.

To assess the importance of the piperidine ligands within the metal coordination sphere of the metal, the reactions between **1a** and Mo/W hexacarbonyls were attempted. Perhaps not surprisingly, the reactions did not proceed as rapidly as those where loss of a labile ligand is facile, and only a small amount of the chelate complexes were formed over a 3 day period (by ^{31}P NMR spectroscopy), with the major component being unreacted phospha(III)guanidine. The formation of the metallacyclic complexes **2a** and **3a** *via* loss of both equivalents of piperidine from the metal centre in the 1 : 1 reaction of **1a** with $M(CO)_4(pip)_2$ is not unexpected considering the lability of both N-donor ligands, and is likely to be driven by the chelate effect. Attempts to isolate complexes containing the monodentate ligand by the reaction of **1a** with the complexes $[M(CO)_5L]$ (M = Mo, W; L = THF, MeCN), containing a single labile ligand, also resulted isolation of **2a** and **3a**, again not too surprising considering the susceptibility of complexes of this type to undergo CO scrambling. This latter fact was further substantiated by the reaction between **1a** and $Mo(CO)_3(MeCN)_3$, which also gave the tetracarbonyl product **2a** as the only isolated product.

In conclusion, we have developed a high yielding route to neutral phospha(III)guanidine compounds of general formula $Ph_2PC\{NR\}\{NHR\}$. Structural analysis indicates a localised structure at the amidine moiety and retention of the lone-pair at phosphorus. Investigation of the bonding potential of these ligands at group 6 metal carbonyl centres has shown that rather than coordinating as a simple phosphine derivative, the imine nitrogen also binds to the metal, resulting in the formation of a previously unreported 1-aza-3-phospha-4-metallacyclobut-1-ene ring.

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