New Heterocyclic Compounds containing Niobium and Molybdenum; Crystal Structure of a Cyclomolybdaphosphazene†

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The linear phosphazene $[H_2NPPh_2NPPh_2NH_2]Cl$ (**1**) reacts with $MoCl_3N$ and $NbCl_5$ to form the new cyclometallaphosphazenes $\overline{NPPh_2NPPh_2NMoCl_3}$ (**3**) and $\overline{NPPh_2NPPh_2NNbCl_2}$ (**4**), respectively. The crystal structure of the acetonitrile adduct of the cyclomolybdaphosphazene (**3**) shows that the central six-membered ring is nearly planar.

The insertion of transition-metal atoms in SN ring systems[1] prompted us to explore the possibility of introducing such atoms into phosphazene ring systems. We recently reported[2] the discovery of the first cyclometallaphosphazene, $Cl_3WN_3P_2Ph_4$ (**2**), from (**1**) and tungsten hexachloride (Scheme 1). In this paper we report the synthesis of the corresponding molybdenum derivative (**3**) by a new route and also the synthesis of the niobium compound $\overline{NPPh_2NPPh_2NNbCl_2}$ (**4**).

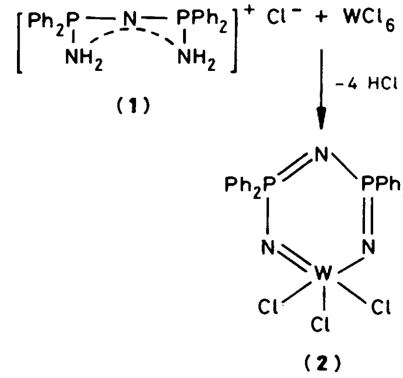
Results and Discussion

The linear phosphazene salt (**1**) reacts with nitridomolybdenum trichloride in refluxing chloroform to form the cyclometallaphosphazene (**3**) (Scheme 2) in up to 65% yield. Compound (**3**) is also formed in low yield (20%), together with unidentified metal halide-substituted phosphazene salts as evidenced by ^{31}P n.m.r. spectroscopy, when $MoCl_5$ is allowed to react with (**1**). This is probably a consequence of prior dissociation of $MoCl_5$ to $MoCl_4^+$ and $MoCl_6^-$ followed by substitution. The insertion of the $\geqslant Mo\equiv N$ unit of $MoCl_3N$ in the phosphazene skeleton probably proceeds through a 1,4-cycloaddition step with the phosphazene salt (**1**). Ammonium chloride is quantitatively formed in the reaction. This new synthetic route is a significant improvement in terms of both yield and purity of compound (**3**).

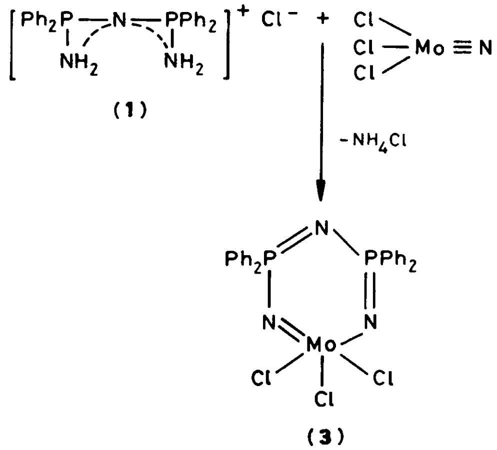
The interaction of salt (**1**) with $NbCl_5$ to form $\overline{NPPh_2NPPh_2NNbCl_2}$ (**4**) is much slower than the reactions with WCl_6 or $MoCl_5$, consistent with the lower reactivity of the former halide compared to the latter. Even after 48 h of refluxing in $CHCl_3$, the ^{31}P n.m.r. spectrum of the reaction mixture showed only 5% of (**4**) with more than 90% of unchanged (**1**). When this reaction is carried out in the presence of pyridine, compound (**4**) can be obtained in up to 30% yield.

Compounds (**3**) and (**4**) are pale yellow crystalline solids soluble in acetonitrile and moderately soluble in chloroform, tetrahydrofuran, or diethyl ether. Both are air stable in the crystalline state, but their solutions slowly decompose in the air.

Spectroscopic Characterization of Compounds (**3**) *and* (**4**).—The solid-state (KBr pellet) i.r. spectra showed absorptions between 1 180 and 1 250 cm^{-1} characteristic of P–N bonds. The high-resolution ^{31}P n.m.r. spectra (data in Table 1) indicate that all cyclometallaphosphazenes show a significant downfield chemical shift compared to the non-metallated cyclophosphazene analogues. This pronounced deshielding effect is probably a consequence of the electron-withdrawing property of the metal atom. The interpretation of such chemical shifts of cyclometallaphosphazenes containing different transition metals should become clearer when other derivatives are available.



Scheme 1.



Scheme 2.

Crystal Structure of $[\overline{NPPh_2NPPh_2NMoCl_3}\cdot 2CH_3CN]$.—The constitution of compound (**3**) was confirmed by the crystal-structure determination of the acetonitrile adduct (Figure). The central six-membered ring is nearly planar [root-mean-square (r.m.s.) deviation 0.04 Å], but may best be described as a shallow envelope with the Mo atom 0.13 Å above the plane formed by the P and N atoms. Its geometry is further characterized by pairwise similar bond lengths and angles (Table 2)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. ^{31}P N.m.r.[a] spectroscopic data for cyclometallaphosphazenes and their non-metallated analogues

Compound	δ/p.p.m.
$NPPh_2NPPh_2NWCl_3$[b] (**2**)	39.2
$NPPh_2NPPh_2NMoCl_3$ (**3**)	42.4
$NPPh_2NPPh_2NNbCl_2$ (**4**)	40.1
$N_3P_3Ph_4Cl_2$ (*gem*)[c]	17.2
$N_3P_3Ph_6$[c]	14.3

[a] All spectra are referenced to external 85% H_3PO_4. [b] From ref. 2. [c] From H. P. Latscha, *Z. Anorg. Allg. Chem.*, 1968, 7, 362.

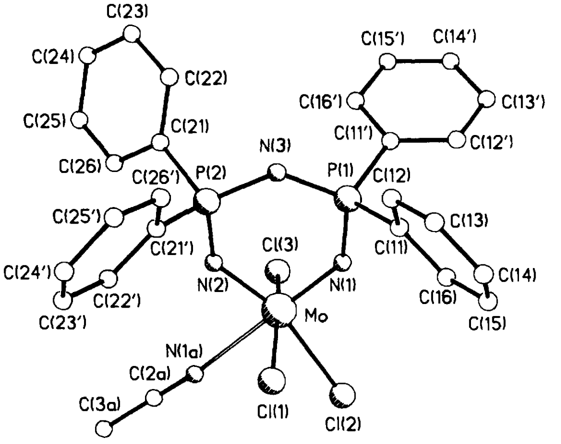

Figure. Perspective view of $NPPh_2NPPh_2NMoCl_3{\cdot}2CH_3CN$ with the atom numbering (hydrogen atoms omitted)

and differs from that of non-metallated analogues[3] mainly by the considerably larger angles at the N atoms adjacent to Mo, as a consequence of the increased size of the metal atom. The latter is co-ordinated octahedrally with one ligand position occupied by a weakly bonded acetonitrile molecule. The crystal structure, which is very similar to that of the corresponding tungsten compound,[2] contains a second, non-interacting acetonitrile within the asymmetric unit; this is probably the reason for obtaining suitable crystals only from this solvent.

Conclusions

Compounds (**2**)—(**4**) provide examples of metallaheterocycles which are of interest both from theoretical and practical points of view. There are prospects of synthesizing polymetallaphosphazenes through the ring-opening polymerization of (**2**)—(**4**). The presence of metal–halogen units allows further nucleophilic substitution reactions to be carried out, generating new organometallic as well as metal–metal bonded species. Experiments in these directions are under way.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen using solvents that had been dried and distilled under nitrogen. I.r. spectra were recorded on a Perkin-Elmer 180 spectrometer using Nujol mulls, mass spectra on a Varian CH5 instrument, and ^{31}P and ^{95}Mo n.m.r. spectra on a Bruker AM 250 instrument with 85% H_3PO_4 and $Na_2[MoO_4]$ as external standards, respectively. The salt $[H_2NPPh_2NPPh_2NH_2]Cl$ (**1**)[4] and $MoCl_3N$[5] were prepared as described in the literature; $MoCl_5$ and $NbCl_5$ were obtained from Fluka.

Table 2. Selected bond lengths (Å) and angles (°) for $NPPh_2NPPh_2NMoCl_3{\cdot}2CH_3CN$ with estimated standard deviations (e.s.d.s) in parentheses

Mo–Cl(1)	2.397(2)	Mo–Cl(2)	2.468(2)
Mo–Cl(3)	2.371(2)	Mo–N(1)	1.766(6)
Mo–N(2)	1.789(6)	Mo–N(1a)	2.390(6)
N(1)–P(1)	1.667(6)	P(1)–N(3)	1.581(7)
P(1)–C(11)	1.789(7)	P(1)–C(11')	1.785(9)
N(2)–P(2)	1.633(6)	P(2)–N(3)	1.585(6)
P(2)–C(21)	1.797(7)	P(2)–C(21')	1.804(9)
Cl(1)–Mo–Cl(2)	83.6(1)	Cl(1)–Mo–Cl(3)	164.1(1)
Cl(2)–Mo–Cl(3)	85.8(1)	Cl(1)–Mo–N(1)	94.7(2)
Cl(2)–Mo–N(1)	98.7(2)	Cl(3)–Mo–N(1)	98.6(2)
Cl(1)–Mo–N(2)	90.2(2)	Cl(2)–Mo–N(2)	163.9(2)
Cl(3)–Mo–N(2)	96.8(2)	N(1)–Mo–N(2)	96.7(3)
Cl(1)–Mo–N(1a)	83.2(2)	Cl(2)–Mo–N(1a)	81.7(3)
Cl(3)–Mo–N(1a)	83.6(2)	N(1)–Mo–N(1a)	177.8(3)
N(2)–Mo–N(1a)	82.7(2)	Mo–N(1)–P(1)	134.7(4)
N(1)–P(1)–N(3)	112.4(3)	N(1)–P(1)–C(11)	103.8(3)
N(3)–P(1)–C(11)	113.6(4)	N(1)–P(1)–C(11')	105.7(4)
N(3)–P(1)–C(11')	110.5(4)	C(11)–P(1)–C(11')	110.5(4)
Mo–N(2)–P(2)	134.3(4)	N(2)–P(2)–N(3)	113.2(4)
N(2)–P(2)–C(21)	106.5(3)	N(3)–P(2)–C(21)	110.7(4)
N(2)–P(2)–C(21')	106.7(4)	N(3)–P(2)–C(21')	111.8(3)
C(21)–P(2)–C(21')	107.6(4)	P(1)–N(3)–P(2)	127.9(4)

Preparation of $NPPh_2NPPh_2NMoCl_3$ (**3**).—(*a*) A dry sample of salt (**1**) (4.51 g, 10 mmol) was added to a suspension of $MoCl_3N$ (2.16 g, 10 mmol) in chloroform (150 cm^3) at room temperature. After 12 h of refluxing the brown precipitate was filtered off, washed with chloroform (100 cm^3), and dried *in vacuo*. The product was recrystallized twice from acetonitrile as yellow crystals, (yield 3.95 g, 64%), m.p. 170 °C (decomp.) (Found: C, 46.6; H, 3.4; N, 6.6; P, 9.8; $C_{24}H_{20}Cl_3MoN_3P_2$ requires C, 46.8; H, 3.2; N, 6.8; P, 10.0%). I.r. (KBr): 1 250s, 1 175s, 1 110m, 1 040s, 970s, and 340m cm^{-1}. Electron-impact (e.i.) mass spectrum: *m*/*z* 578 (*M* – Cl, 100%). N.m.r. spectra (CH_3CN, C_6D_6): ^{31}P, δ 42.2; ^{95}Mo, δ 1 105.7 p.p.m.

(*b*) A dry sample of salt (**1**) (4.50 g, 10 mmol) was added to a suspension of $MoCl_5$ (2.72 g, 10 mmol) in chloroform (150 cm^3) at room temperature. The reaction mixture was heated under reflux for 12 h. The light green precipitate was filtered off, washed with chloroform (100 cm^3), and dried *in vacuo*. The ^{31}P n.m.r. spectrum (CH_3CN, C_6D_6) of this crude product showed signals of comparable intensities at δ 35.0, 37.9, 42.5, and 52.9 p.p.m. Repeated recrystallization from acetonitrile yielded yellow crystals (yield 1.25 g, 20%), m.p. 170 °C (decomp.). The spectroscopic parameters were the same as listed in (*a*) for compound (**3**).

Preparation of $NPPh_2NPPh_2NNbCl_2$ (**4**).—A dry sample of salt (**1**) (5.0 g, 11 mmol) was added to a suspension of $NbCl_5$ (2.98 g, 11 mmol) in chloroform (150 cm^3) and pyridine (25 cm^3) at room temperature. After 24 h of refluxing, the reaction mixture was allowed to cool to ambient temperature and then filtered. The solvent was removed *in vacuo* to give a pale yellow solid of (**4**) which was recrystallized twice from acetonitrile (0.82 g). The pale yellow residue was evaporated to dryness *in vacuo* and recrystallized three times from acetonitrile to give the main crop of (**4**) (1.20 g, total yield 2.02 g, 31%), m.p. 185 °C (decomp.) (Found: C, 49.8; H, 3.2; Cl, 12.1; N, 7.2; P, 10.4; $C_{24}H_{20}Cl_2N_3NbP_2$ requires C, 50.0; H, 3.4; Cl, 12.3; N, 7.3; P, 10.7%). I.r. (KBr): 1 240s, 1 180vs, 1 110m, 1 040s, 970s, and 325m cm^{-1}. E.i. mass spectrum: *m*/*z* 575 (*M*, 100%). ^{31}P N.m.r. spectrum (CH_3CN, CD_3CN; external standard 85% H_3PO_4): δ 40.1 p.p.m. (s).

Table 3. Atomic fractional co-ordinates (× 10^4) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	2 316(1)	2 496(1)	1 419(1)	C(16′)	−1 598(9)	4 414(8)	2 527(6)
Cl(1)	4 451(2)	2 490(2)	2 333(2)	C(21)	−1 271(8)	821(7)	2 650(5)
Cl(2)	4 032(2)	3 375(2)	481(2)	C(22)	−2 373(8)	1 190(8)	3 161(5)
Cl(3)	572(2)	2 248(2)	182(2)	C(23)	−3 731(10)	489(9)	2 968(7)
N(1)	1 930(6)	3 862(5)	2 130(4)	C(24)	−3 975(9)	−552(9)	2 278(6)
P(1)	1 133(2)	4 222(2)	3 101(1)	C(25)	−2 856(10)	−922(8)	1 762(6)
N(2)	1 300(6)	1 491(5)	1 976(4)	C(26)	−1 503(9)	−239(8)	1 942(6)
P(2)	517(2)	1 680(2)	2 931(1)	C(21′)	1 473(7)	982(7)	3 659(5)
N(3)	465(7)	3 062(6)	3 413(4)	C(22′)	2 112(8)	−17(8)	3 234(6)
C(11)	2 527(8)	5 208(7)	3 897(5)	C(23′)	2 776(9)	−607(9)	3 782(6)
C(12)	2 493(10)	5 265(8)	4 824(6)	C(24′)	2 799(10)	−245(9)	4 701(7)
C(13)	3 607(12)	6 014(10)	5 453(7)	C(25′)	2 139(11)	733(9)	5 128(7)
C(14)	4 680(11)	6 684(9)	5 144(7)	C(26′)	1 491(10)	1 356(9)	4 601(6)
C(15)	4 692(10)	6 637(9)	4 235(7)	N(1a)	2 901(7)	642(6)	503(4)
C(16)	3 625(9)	5 908(8)	3 604(6)	C(2a)	3 040(8)	−275(7)	52(5)
C(11′)	−244(8)	5 040(7)	2 873(5)	C(3a)	3 226(9)	−1 431(7)	−528(6)
C(12′)	40(9)	6 263(8)	2 939(7)	N(1b)	7 049(15)	2 742(13)	8 301(8)
C(13′)	−998(11)	6 868(10)	2 686(9)	C(2b)	7 449(13)	3 473(11)	8 946(8)
C(14′)	−2 342(11)	6 243(10)	2 347(8)	C(3b)	7 956(14)	4 362(10)	9 765(9)
C(15′)	−2 646(11)	5 037(10)	2 281(7)				

X-*Ray Structure Analysis of* $\overline{\text{NPPh}_2\text{NPPh}_2\text{NMo}}\text{Cl}_3\cdot 2\text{CH}_3\text{CN}$.—*Crystal data.* $\text{C}_{24}\text{H}_{20}\text{Cl}_3\text{MoN}_3\text{P}_2\cdot 2\text{CH}_3\text{CN}$, $M = 696.8$, yellow crystals (0.4 × 0.3 × 0.1 mm) from acetonitrile sealed in a capillary, triclinic, space group $P\bar{1}$, $a = 9.433(1)$, $b = 11.524(1)$, $c = 15.141(2)$ Å, $\alpha = 104.60(1)$, $\beta = 92.42(1)$, $\gamma = 98.60(1)°$, $U = 1\ 569.4$ Å^3, $Z = 2$, $D_c = 1.474$ g cm^{-3}, μ(Mo-K_α) = 0.79 mm^{-1}, λ (Mo-K_α) = 0.7107Å, $F(000) = 704$.

Stoe-Siemens four-circle diffractometer, data collection (at room temperature) with profile-fitting method,[6] $2\theta_{\text{max.}} = 50°$; 5 507 unique reflections, 3 424 with $|F| > 4\sigma(F)$ treated as observed, empirical absorption correction ($R_{\text{int.}} = 0.033$ for 400 azimuthal scans).

Structure solved by Patterson and Fourier methods, blocked-cascade refinement (on F) of 355 parameters, all non-hydrogen atoms anisotropic. Riding model employed for H atoms with C–H 0.96 Å and $U(\text{H}) = 1.2\ U_{\text{eq.}}(\text{C})$, weighting scheme $w = [\sigma^2(F) + 0.0003F^2]^{-1}$; final $R = 0.067$ ($R' = 0.059$). All calculations performed with SHELXTL.[7] Atomic co-ordinates are shown in Table 3.

Acknowledgements

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