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Facile syntheses of new multidentate (phosphino)amines: X-ray structure of 1,4-$\{(OC)_4Mo(Ph_2P)_2NCH_2\}_2C_6H_4$

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Abstract

The rigid backbone tetradentate (phosphino)amines 1,4-$\{(Ph_2P)_2N\}_2C_6H_4$, 1,4-$\{(Ph_2P)_2NCH_2\}_2C_6H_4$ and the unprecedented octadentate ligand 1,2,4,5-$\{(Ph_2P)_2NCH_2CH_2SCH_2\}_4C_6H_2$ were readily prepared, in one-step, by full phosphinylation of the appropriate primary amine with Ph_2PCl in Et_2O with NEt_3 as auxiliary base. Reaction with stoichiometric amounts of $[Mo(CO)_4(\eta^4\text{-nbd})]$ (nbd = norbornadiene) afforded either binuclear or tetranuclear *P*,*P*′-chelate complexes; the X-ray structure of one example is presented.

Keywords: Amines; Carbonyl complexes; Crystal structure; Molybdenum; NMR spectroscopy; Phosphorus ligands

1. Introduction

The co-ordination and organometallic chemistry of phosphorus bearing ligands possessing one (or more) P–N bond(s) has received some attention especially of late [1]. Potentially this ligand family is extremely attractive since preparative routes enable access to various structural modifications via simple P–N bond formation. Although poorly exploited in catalysis, with respect to tertiary phosphines and phosphites, phosphorus(V) derivatives [2] or complexes (generated in situ or performed) stabilised by such ligands are effective in several catalytic reactions [1b,c,f,3]. Asymmetric catalysis with chiral variants incorporating an amino–phosphine functionality have also been described [4]. Our interest in this unique class of ligand stems from the systematic control of stereoelectronic factors by subtle manipulation of the R group(s) either on the phosphorus or nitrogen precursors. Recently we reported the synthesis of two new keto-functionalised (phosphino)amines and demonstrated that these co-ordinated ligands undergo remarkably clean $\sigma(C_{sp}2\text{-H})$ bond activation affording novel five-membered metallacycles [5].

One fascinating class of tertiary polyphosphine ligand that has attracted considerable recognition of late are dendrimers terminally coated with $-\{PR_2\}_n$ groups, since they constitute excellent scaffolds for metallodendrimer construction [6]. We are interested in developing synthetic routes to (phosphino)amine coated dendrimers given the useful catalytic properties of P–N containing ligands. However, prior to this work, surprisingly few studies of simple model compounds such as bi- or polydentate (phosphino)amines have been documented [7]. Accordingly we describe here convenient, high yielding syntheses of new tetradentate and octadentate (phosphino)amines by multiple phosphinylations. Stoichiometric reaction of these ligands with $[Mo(CO)_4(\eta^4\text{-nbd})]$ affords either binuclear $[1,4\text{-}\{(OC)_4Mo(Ph_2P)_2N\}_2C_6H_4]$, $[1,4\text{-}\{(OC)_4Mo(Ph_2P)_2NCH_2\}_2C_6H_4]$ or tetranuclear $[1,2,4,5\text{-}\{(OC)_4Mo(Ph_2P)_2NCH_2CH_2SCH_2\}_4C_6H_2]$ molybdenum(0) complexes, respectively. Spectroscopic and single-crystal X-ray diffraction studies are reported.

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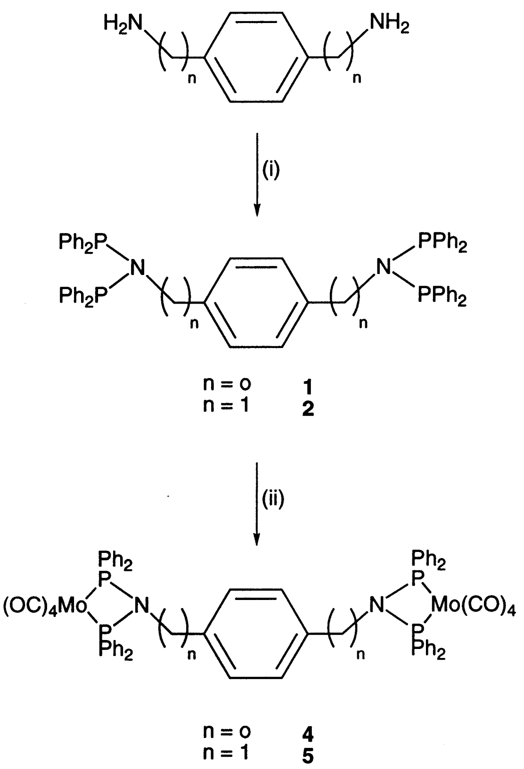
2. Results and discussion

The synthesis of the rigid backbone (phosphino)amines **1** and **2** was based on reaction of commercially available 1,4-$(H_2N)_2C_6H_4$ or 1,4-$(H_2NCH_2)_2C_6H_4$ and four equivalents of Ph_2PCl in Et_2O with NEt_3 (Scheme 1). This synthetic procedure circumvents the use of 1,4-$\{(Cl_2P)_2N\}_2C_6H_4$ as starting material which reportedly involves prolonged reflux and proceeds in low (13%) yield [8]. Compounds **1** and **2** were isolated, after workup, in excellent yields (77 and 96%, respectively) as white or off-white solids and were characterised by $^{31}P\{^1H\}$- and ^1H-NMR spectroscopy.[2] The $^{31}P\{^1H\}$-NMR spectra both display single P resonances at δ(P) 70.2 (for **1**) and δ(P) 60.6 ppm (for **2**) and, in the case of **1**, similar to that found for the closely related system $(Ph_2P)_2NPh$ [δ(P) 68.8 ppm]. The ^1H-NMR spectra exhibit no NH resonances and in full accord with complete N–H substitution. Using the same procedure we also synthesised (in 95% yield) the novel octapodal ligand 1,2,4,5-$\{(Ph_2P)_2NCH_2CH_2SCH_2\}_4C_6H_2$ (**3**) (Scheme 2) from the known tetraamine precursor 1,2,4,5-$\{H_2NCH_2CH_2SCH_2\}_4C_6H_2$ [9]. The $^{31}P\{^1H\}$-NMR spectrum (at 101.3 MHz) showed a single, sharp resonance at δ(P) 61.5 ppm indicating a remarkably clean eightfold N–H to N–PPh_2 transformation. No evidence for any partially substituted products was observed. The simplicity of the ^1H-NMR spectrum of **3**, coupled with the absence of any NH resonances, provides further testimony for a highly symmetrical structure and no defect species present. Ligand **3** is unique and may be viewed as a prototype of a much broader family of (phosphino)amine surface-functionalised dendrimers. This procedure should bode well for the rapid construction of new dendrimeric materials.



Scheme 1. (i) 4 Ph_2PCl, NEt_3, Et_2O; (ii) 2 $[Mo(CO)_4(\eta^4\text{-nbd})]$.

In order to probe the ligating behaviour of the ligands **1**–**3** we chose to prepare the organic soluble molybdenum(0) tetracarbonyl complexes **4**–**6** (Schemes 1 and 2). Hence treatment of $[Mo(CO)_4(\eta^4\text{-nbd})]$ with either 0.5 equivalents (for **1** and **2**) or 0.25 equivalents (for **3**) of (phosphino)amine in dichloromethane gave the corre-

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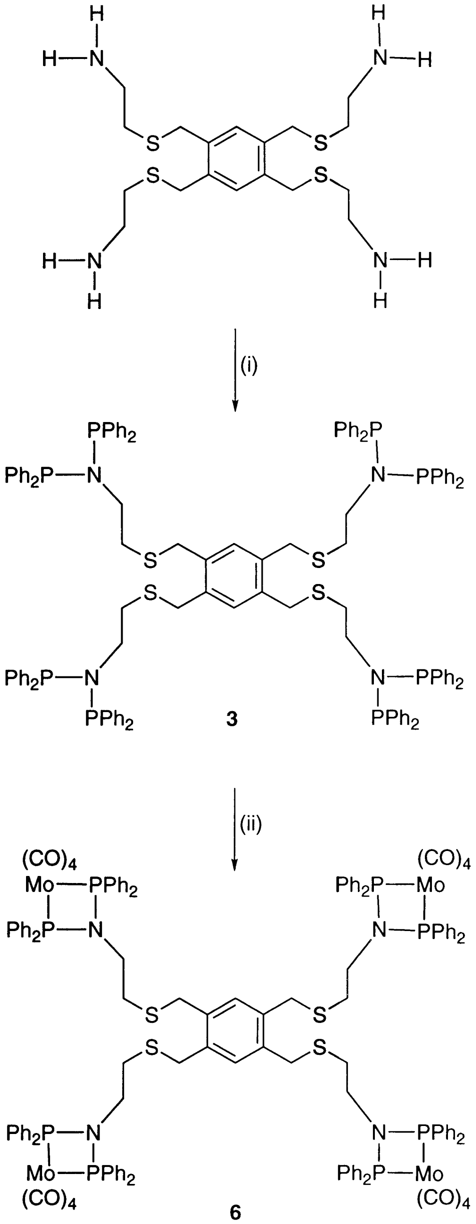
[2] A typical synthesis is illustrated here for compound **2**. To a stirred suspension of 1,4-$(H_2NCH_2)_2C_6H_4$ (1.25 g, 9.18 mmol) in NEt_3 (3.67 g, 36.27 mmol) and Et_2O (100 ml), Ph_2PCl (8.70 g, 39.43 mmol) in Et_2O (30 ml) was added dropwise over 30 min whilst the temperature was maintained at ca. 0 °C. After the addition of further Et_2O (40 ml) the mixture was stirred for ca. 3 days. The solvent was evaporated to dryness under reduced pressure and degassed distilled water (50 ml) added. The solid was filtered by suction filtration, washed with distilled water (50 ml), hexane (2 × 50 ml) and absolute EtOH (75 ml). Yield: 7.68 g, 96%. Anal. Calcd. (Found) for $C_{56}H_{48}N_2P_40.5H_2O$: C, 76.26 (76.26); H, 5.61 (5.50); N, 3.18 (3.24)%. Selected sprectroscopic data: ^1H-NMR (250 MHz, $CDCl_3$): δ 7.31–7.20 [–$P(C_6H_5)_2$], 6.45 [C_6H_4], 4.36 [^3J(PH) 21.0 Hz, CH_2]. $^{31}P\{^1H\}$-NMR (36.2 MHz, $CDCl_3$): δ 60.6. IR (KBr): ν 2852 (alkyl CH), 863 (PN) cm^{-1}. FAB MS: m/z 873 $[M^+]$ in addition to 889 [M+1O], 905 [M+2O], 921 [M+3O] and 937 [M+4O]. For **1**: Anal. Calc. (Found) for $C_{54}H_{44}N_2P_40.5H_2O$: C, 75.95 (75.58); H, 5.32 (5.14); N, 3.28 (3.25)%. ^1H-NMR (250 MHz, $CDCl_3$): δ 7.26–7.13 [–$P(C_6H_5)_2$], 5.99 [C_6H_4]. $^{31}P\{^1H\}$-NMR (36.2 MHz, $CDCl_3$): δ 70.2. IR (KBr): ν 929 (PN) cm^{-1}. FAB MS: m/z 844 $[M^+]$. For **3**: Anal. Calc. (Found) for $C_{114}H_{106}N_4P_8S_4\cdot 3H_2O$: C, 69.78 (69.75); H, 5.77 (5.48); N, 2.86 (2.98)%. ^1H-NMR (250 MHz, $CDCl_3$): δ 7.35–7.24 [–$P(C_6H_5)_2$], 6.79 [C_6H_2], 3.46, 3.29, 2.00 [CH_2]. $^{31}P\{^1H\}$-NMR (100.6 MHz, $CDCl_3$): δ 61.5. IR (KBr): ν 844 (PN) cm^{-1}. FABMS: m/z 1909 $[M^+]$.

[3] A typical synthesis is illustrated here for compound **4**. 1,4-$\{(Ph_2P)_2N\}_2C_6H_4$ (0.070 g, 0.0828 mmol) was added to a solution of CH_2Cl_2 (20 ml) and $[Mo(CO)_4(\eta^4\text{-nbd})]$ (0.050 g, 0.167 mmol). The solution was stirred for 30 min and the volume reduced in vacuo to ca. 1–2 ml. The addition of Et_2O (20 ml) and petroleum ether (b.p. 60–80 °C, 10 ml) gave a solid which was collected by suction filtration, washed with petroleum ether (b.p. 60–80 °C, 5 ml) and dried in vacuo. Yield: 0.090 g, 86%. Anal. Calc. (Found) for $C_{62}H_{44}N_2P_4O_8Mo_2$: C, 59.06 (59.56); H, 3.52 (3.63); N, 2.22 (2.14)%. Selected spectroscopic data: ^1H-NMR (250 MHz, $CDCl_3$): δ 7.43–7.21 [–$P(C_6H_5)_2$], 6.02 [C_6H_4]. $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): δ 95.2 ppm. IR (KBr): ν 2019, 1929, 1902, 1880 (CO), 936, 911 (PN) cm^{-1}. FABMS: m/z 1261 $[M^+]$. For **5**: Anal. Calc. (Found) for $C_{64}H_{48}N_2O_8P_4Mo_2\cdot 0.25CH_2Cl_2$: C, 58.90 (58.50); H, 3.74 (3.67); N, 2.14 (2.15)%. ^1H-NMR (250 MHz, $CDCl_3$): δ 7.44–7.28 [–$P(C_6H_5)_2$], 5.82 [C_6H_4], 3.92 [^3J(PH) 20 Hz CH_2]. $^{31}P\{^1H\}$-NMR (36.2 MHz, $CDCl_3$): δ 95.8 ppm. IR (KBr): ν 2850 (alkyl CH), 2016, 1921, 1894, 1878 (CO), 840 (PN) cm^{-1}. FABMS: m/z 1289 $[M^+]$. For **6**: Anal. Calc. (Found) for $C_{130}H_{106}N_4O_{16}P_8S_4Mo_4$: C, 56.98 (57.13); H, 3.90 (4.25); N, 2.04 (1.84)%. ^1H-NMR (250 MHz, $CDCl_3$): δ 7.49–7.35 [–$P(C_6H_5)_2$], 6.28 [C_6H_2], 3.07, 1.89, 1.60 [CH_2]. $^{31}P\{^1H\}$-NMR (36.2 MHz, $CDCl_3$): δ 91.2 ppm. IR (KBr): ν 2020, 1926, 1899, 1882 (CO), 844 (PN) cm^{-1}. FABMS: m/z 2740 $[M^+]$.

sponding molybdenum complexes **4**–**6** in good yields.[3] In all cases a single downfield resonance at ca. δ(P) 95 ppm was observed and in a region similar to that of the mononuclear complex [Mo(CO)$_4${(P,P'-Ph$_2$P)$_2$NPh}] (**7**) [δ(P) 94.4 ppm]. The infrared spectra of **4**–**6** show four intense ν(CO) bands, typically in the region 2020–1878 cm^{-1}, consistent with a *cis* tetracarbonylmolybdenum fragment [7]. The FAB mass spectral data for **4**–**6** each showed a molecular ion peak at m/z 1261 (for **4**), 1289 (for **5**) and 2740 (for **6**).

Crystals of **5** suitable for a single crystal X-ray diffraction study[4] were obtained by slow diffusion of Et$_2$O + petroleum ether (b.p. 60–80 °C) into a CDCl$_3$ + CH$_2$Cl$_2$ over several days. The structure (Fig. 1) confirms the binuclear arrangement with two *cis* ‘Mo(CO)$_4$’ metal fragments P,P'-ligated by the tetradentate ligand **2**. The molecule is situated across an inversion centre. The four-membered Mo–P–N–P ring is non planar [the dihedral angle between the Mo(1)–P(1)–P(2) and P(1)–N(1)–P(2) planes is 15.7°] and roughly symmetrical. Within the metalloring the Mo–P and P–N distances are comparable to those previously reported [7]. Furthermore, the Mo–C bond lengths *trans* to **2** [both 2.000(2) Å] are marginally shorter than those of Mo(1)–C(3) [2.047(2) Å] and Mo(1)–C(4) [2.037(2) Å]. The axial CO ligands are slightly distorted [C(3)–Mo(1)–C(4) 172.02(9)°] and as expected if there exists substantial intragroup repulsions between C(3)–O(3)/C(4)–O(4) and two phenyl groups of the co-ordinated ligand **2**. Crystals of **4** have also been isolated but the poor crystal quality precluded an accurate structure determination. Nevertheless the refinement again clearly indicates that the gross structure comprises a binuclear structure with two ‘Mo(CO)$_4$’ moieties linked via a bridging 1,4-{(Ph$_2$P)$_2$N}$_2$C$_6$H$_4$ ligand [10].



Scheme 2. (i) 8 Ph$_2$PCl, NEt$_3$, Et$_2$O; (ii) 4 [Mo(CO)$_4$(η^4-nbd)].

3. Conclusions

The proficient syntheses of three new di- and poly(phosphino)amines and their complexation to a zerovalent molybdenum precursor has been demonstrated for the first time. It is envisaged that this procedure for ligand construction and subsequent metal co-ordination be extended to the synthesis of cascade molecules bearing greater numbers of peripheral coated –N(PR$_2$)$_2$ [or –N(H)PR$_2$] functionalities. Further ligand and complexation studies towards catalytically beneficial metals (e.g. Ru, Rh, Pd) are in progress and will be reported in due course.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

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[4] Crystal data for complex **5**: C$_{64}$H$_{48}$Mo$_2$N$_2$O$_8$P$_4$, $M = 1288.80$, monoclinic, space group $C2/c$, $a = 18.4183(6)$, $b = 17.1998(4)$, $c = 18.5880(6)$ Å, $\beta = 99.3450(10)°$, $U = 5810.4(3)$ Å^3, $Z = 4$, $\mu = 0.559$ mm^{-1}, $T = 100(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 18890 reflections collected, 6639 were independent ($R_{int} = 0.0507$). $R_1 = 0.0323$ [$I > 2\sigma(I)$], $wR_2 = 0.0711$. The structure was solved using SHELXS-97 [11] and developed via alternating least square cycles and difference Fourier synthesis (SHELXL-97) [11] with the aid of the program XSEED [12]. All non-hydrogen atoms were modelled anisotropically, while hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride. All calculations were carried out with either a Silicon Graphics Indy workstation or an IBM compatible PC.

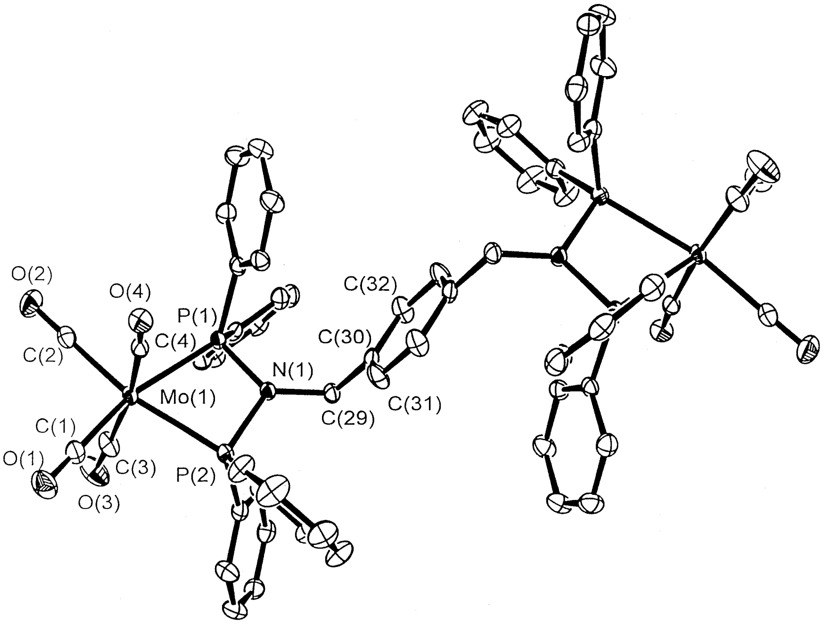

Fig. 1. The X-ray structure of **5**. Selected bond distances (Å) and angles (°): Mo(1)–P(1) 2.5185(6), Mo(1)–P(2) 2.4940(6), Mo(1)–C(1) 2.000(2), Mo(1)–C(2) 2.000(2), Mo(1)–C(3) 2.047(2), Mo(1)–C(4) 2.037(2), P(1)–N(1) 1.718(1), N(1)–P(2) 1.708(1). P(1)–Mo(1)–P(2) 65.14(1), P(1)–Mo(1)–C(3) 99.70(7), P(1)–Mo(1)–C(4) 87.87(6), P(1)–Mo(1)–C(1) 162.74(7), P(1)–Mo(1)–C(2) 100.18(7), P(2)–Mo(1)–C(3) 90.34(7), P(2)–Mo(1)–C(4) 95.19(6), P(2)–Mo(1)–C(1) 100.61(7), P(2)–Mo(1)–C(2) 164.62(7), C(3)–Mo(1)–C(4) 172.02(9), C–Mo(1)–C range 83.68(9)–94.63(9), Mo(1)–P(1)–N(1) 93.81(6), Mo(1)–P(2)–N(1) 94.91(6), P(1)–N(1)–P(2) 103.93(9).

Data Centre, CCDC no. 191805. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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