The Synthesis, Characterisation, and Reactivity of Some Polydentate Phosphinoamine Ligands with Benzene-1,3-diyl and Pyridine-2,6-diyl Backbones

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The polydentate phosphinoamines $1,3\text{-}\{(Ph_2P)_2N\}_2C_6H_4$ and $2,6\text{-}\{(Ph_2P)_2N\}_2C_5H_3N$ have been prepared in a single step from the reaction of the amines $1,3\text{-}(NH_2)_2C_6H_4$ or $2,6\text{-}(NH_2)_2C_5H_3N$ with Ph_2PCl in presence of Et_3N ($1:4:4$ molar ratio) in CH_2Cl_2. Reaction of $1,3\text{-}\{(Ph_2P)_2N\}_2C_6H_4$ or $2,6\text{-}\{(Ph_2P)_2N\}_2C_5H_3N$ with elemental sulfur or selenium in CH_2Cl_2 affords the corresponding tetrasulfide or tetraselenide, respectively, in good yield. The complexes $[1,3\text{-}\{Mo(CO)_4(Ph_2P)_2N\}_2(C_6H_4)]$ and $[2,6\text{-}\{Mo(CO)_4(Ph_2P)_2N\}_2(C_5H_3N)]$ were prepared from the reaction of these phosphinoamines with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) in toluene, and the structure of the latter complex has been determined by single-crystal X-ray diffraction analysis.

Introduction. – The coordination chemistry of bis(phosphino) amines, $RN(PR'_2)_2$, has attracted considerable interest in recent years, due, in part, to their chemical and structural proximity to the widely used bis(diphenylphosphino)methane, $H_2C(PPh_2)_2$ (dppm) [1]. Compared to diphosphines with the P–C–P linkage, bis(phosphino)-amines with P–N–P skeletons have proved to be much more versatile ligands, and varying the substituents on both the P- and N-centres gives rise to changes in the P–N–P angle and the conformation around the P-centres [2][3]. Small variations in these ligands can cause significant changes in their coordination behaviour and the structural features of the resulting complexes [4]. A structural characteristic of most of these ligands is that the lone pair of electron at the P-centres point towards each other, indicating that these ligands prefer to adopt a bidentate-chelating bonding mode as opposed to adopting bridging coordination geometries [5]. This feature enables the synthesis of a wide range of four-membered ring systems containing transition metals such as Pd, Pt, Mo, Cu, Ni and Ru, which have potential uses in catalysis [6]. By careful control of the reaction conditions, certain bis(phosphino)amines can also coordinate to the transition metals in a mono-dentate mode, giving rise to mononuclear complexes as well as dinuclear complexes in which the ligand bridges two metal centres [1a]. The oxidised forms of the bis(phosphino)amine $RN(P(:X)R'_2)_2$ (where X = O, S or Se) are also interesting ligands, especially in the synthesis of small-membered ring systems [7–9]. The coordination chemistry of bis(phosphino)amines has been reviewed [10], and further possibilities are highlighted in a very recent review that describes, more generally, the chemistry of diphosphines with inorganic backbone [11].

Among the bis(phosphino)amines, (diphenylphosphino)aniline derivatives are the most frequently used precursors in investigations, because of their facile synthesis and high stability [12][13]. Starting from the commercially available anilines and its

derivatives, a large number of (diphenylphosphino)anilines have been prepared and characterised, and their reactivities have been investigated. However, despite the availability of diamines, there are surprisingly few studies of polydentate phosphino-amines with more than one $N(PR_2)_2$ unit have been reported. Such polydentate ligands may provide interesting coordination properties based on a larger numbers of coordination centres, with, for example, dinuclear transition metal complexes being obtained from N,N,N',N'-tetrakis(diphenylphosphino)benzene-1,4-diamine, based on two chelating P−N−P units [14]. Furthermore, it is also possible to use such ligands to prepare heteronuclear transition complexes and macrocyclic ring systems [15].

Extending our program in the design and study of multifunctional P−N-based ligands [5][16], we report herein the synthesis, characterisation, and reactivity of two new tetradentate ligands based on benzene-1,3-diyl and pyridine-2,6-diyl backbones.

Results and Discussion. – Several methods have been developed for the synthesis of phosphinoamines and diphosphinoamines, and aminolysis seems to be the most commonly used [17]. Two new tetradentate phosphinoamines with rigid backbones were prepared from the commercially available starting materials $2,6\text{-}(H_2N)_2C_5H_3N$ and $1,3\text{-}(H_2N)_2C_6H_4$ by the aminolysis method in CH_2Cl_2. It has been found that the solvent has a significant influence on the reaction rate and on the reaction product [5]. Et_2O or toluene is a very good solvent, but the reaction is very slow, especially for anilines and related compounds. In many cases, bis(phosphino)imines are also formed, and these are poorly soluble and might easily be discarded as $Et_3N \cdot HCl$, which also precipitates from the reaction. CH_2Cl_2 is a more-appropriate solvent for aminolysis reactions because all the components formed in the reaction are soluble in the reaction media, also allowing the reaction to be monitored by ^{31}P-NMR spectroscopy. In a typical reaction, 4 equiv. of Ph_2PCl were added slowly to a CH_2Cl_2 solution of $2,6\text{-}(H_2N)_2C_5H_3N$ or $1,3\text{-}(H_2N)_2C_6H_4$ containing Et_3N to afford the tetradentate amino-phosphines $1,3\text{-}\{(Ph_2P)_2N\}_2C_6H_4$ **1** and $2,6\text{-}\{(Ph_2P)_2N\}_2C_5H_3N$ **2**, respectively (*Scheme*). The related ligand $1,4\text{-}\{(Ph_2P)_2N\}_2C_6H_4$ has recently been prepared by the same aminolysis method, but with Et_2O as the solvent [14]. This synthesis route requires several days stirring at room temperature. With CH_2Cl_2 as the solvent for the synthesis of **1** and **2**, the reaction is complete within 2–4 h at room temperature.

The $^{31}P\{^1H\}$-NMR spectra of the reaction solutions after 2 h show a *singlet* resonance at 68.1 ppm for **1** and at 59.5 ppm for **2**, indicating that all of the four P-atoms are equivalent in solution, and that formation of the products is essentially quantitative. The formation of bis(phosphino)imines is not observed.

After removal of the solvent, the $Et_3N \cdot HCl$ is removed by washing the resulting solid with H_2O, and compounds **1** and **2** are isolated in excellent yields, 97% for **1** and 98% for **2**.

To probe the reactivity of the new ligands, reactions with elemental S and Se as well as the transition metal complex $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) were carried out. Unlike phosphinoamines, which usually react smoothly with elemental S or Se at room temperature, the reaction of **1** and **2** with elemental S and Se requires elevated temperatures. Only after reflux in toluene for 24 h could **1** and **2** be converted completely to the tetrasulfides $1,3\text{-}\{(SPh_2P)_2N\}_2C_6H_4$ (**3**) and $2,6\text{-}\{(SPh_2P)_2N\}_2C_5H_3N$ (**4**), respectively. Compounds **3** and **4** were initially analysed by $^{31}P\{^1H\}$-NMR

Scheme. *Synthetic Routes to Compounds* **1–8**

1 X = CH, **2** X = N

7 X = CH
8 X = N

3 X = CH, Y = S
4 X = N, Y = S
5 X = CH, Y = Se
6 X = N, Y = Se
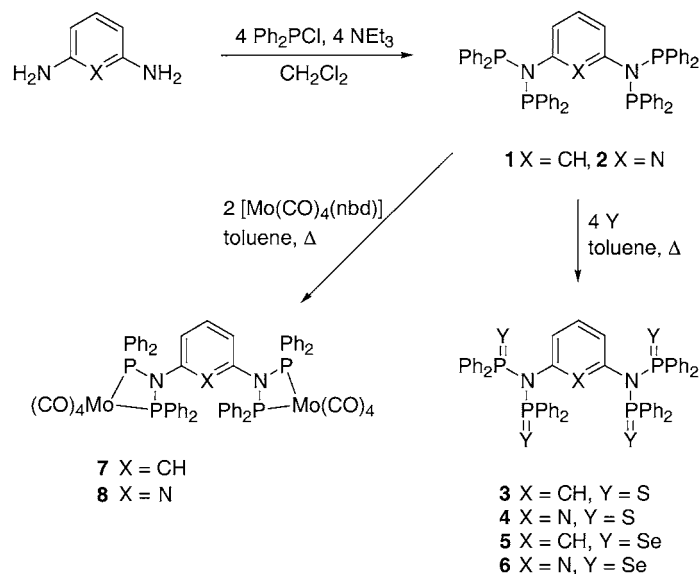
spectroscopy, which exhibited *singlet* resonances at 70.4 and 69.3 ppm, respectively. Compounds **1** and **2** were reacted with Se in a similar fashion, with the formation of the tetraselenide derivatives 1,3-{(SePh$_2$P)$_2$N}$_2$C$_6$H$_4$ (**5**) and 2,6-{(SePh$_2$P)$_2$N}$_2$C$_5$H$_3$N (**6**), respectively. The ^{31}P{^{1}H}-NMR spectra of **5** and **6** exhibited *singlet* resonances at 71.2 and 69.3 ppm, with ^1J(P,Se) coupling constants of 799 and 805 Hz, for **5** and **6**, respectively, as would be expected for these compounds. Compounds **3–6** were fully characterised by other methods (see *Exper. Part*).

Compounds **1** and **2** were also reacted with 2 equiv. of [Mo(CO)$_4$(nbd)] in toluene under reflux to afford the dinuclear complexes [1,3-{Mo(CO)$_4$(Ph$_2$P)$_2$N}$_2$(C$_6$H$_4$)] (**7**) and [2,6-{Mo(CO)$_4$(Ph$_2$P)$_2$N}$_2$(C$_5$H$_3$N)] (**8**) in high yield. Both P−N−P units selectively chelate the Mo-atom to form two four-membered P−N−P−Mo hetero-cycles. The ^{31}P{^{1}H}-NMR spectra of **7** and **8** exhibit *singlet*s at 97.0 and 95.0 ppm, respectively. No other signals could be detected in the ^{31}P-NMR spectrum, suggesting that there are no dimers, higher oligomers or other species formed despite the four P coordination centres. In complex **8**, the N-atom in the pyridine ring is uncoordinated. The chemical shifts of the complexes **7** and **8** are in agreement with structurally similar compounds [13][14], and there does not appear to be any significant influence of the N-atom in the pyridine ring.

Compounds **7** and **8** were analysed by electrospray ionisation mass spectrometry. Since both compounds are neutral and not readily protonated (despite containing basic groups), they were derivatised by reaction with methoxide. Hence, **7** and **8** were each dissolved in a MeONa/MeOH solution and injected directly into the instrument. Two strong peaks were observed, the one of highest relative intensity corresponding to the doubly methoxylated anion [M+(OMe)$_2$]$^-$ and the less-intense peak to the singly methoxylated anion [M+(OMe)]$^-$. This derivatisation technique has been widely

used to determine the molecular weights of transition metal carbonyl compounds [18], and benefits from methoxylation taking place only once, even when the reagent is present in large excess, and even for polynuclear compounds. In the case of **7** and **8**, the two Mo-centres are essentially independent, which allows the double methoxylation process, presumably once at each metal centre. What is surprising, perhaps, is that the $[M + (OMe)_2]^-$ is only singly charged and is not a 2 – anion. The mass does not correspond to an additional proton being present, and attempts to determine the molecular weight of **7** and **8** by protonation (dissolution in a HCOOH/MeOH solution) were unsuccessful. No peaks were observed in **7**, and **8** showed a high mass peak centred at m/z 1284 of low relative intensity, poor peak shape, and not assignable to anything sensible. It is possible that the pyridine N-atom in **8** is protected from protonation by the bulky groups surrounding it (see below). The IR spectra of **7** and **8** show characteristic vibrations in the ν_{CO} region between 1935 – 1872 cm^{-1}.

Crystals of **7** and **8** were grown from a solution of toluene at room temperature, and while the former were not of suitable quality for X-ray analysis, the latter were analysed by single-crystal X-ray diffraction. The molecular structure of **8** is shown in the *Figure*, and key bond parameters are listed in the caption.
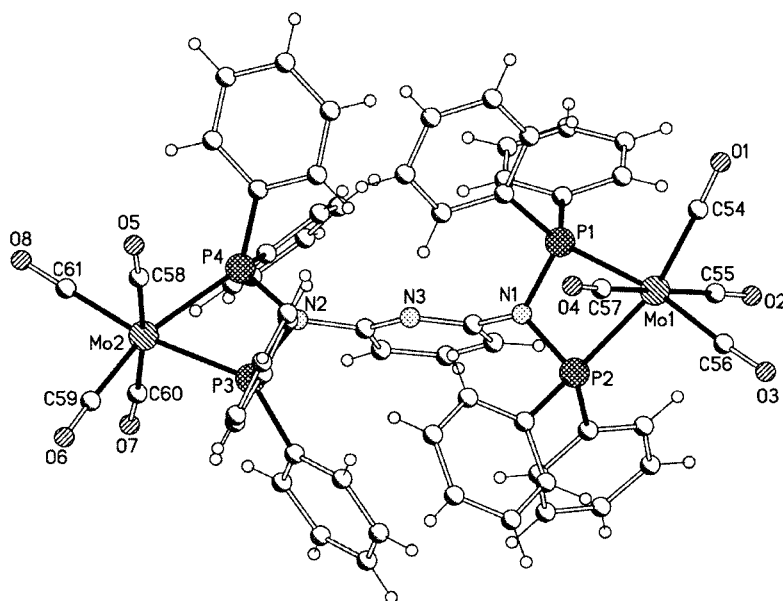

Figure. *Molecular structure of* **8** *in the solid state.* Key bond lengths [Å] and angles [°] include: Mo(1)−C(54), 1.985(7); Mo(1)−C(56), 1.997(7); Mo(1)−C(55), 2.041(6), Mo(1)−C(57), 2.043(6); Mo(1)−P(1), 2.4729(14); Mo(1)−P(2), 2.5085(2), Mo(2)−C(61), 1.996(8); Mo(2)−C(59), 2.008(7); Mo(2)−C(58), 2.021(6); Mo(2)−C(60), 2.051(7); Mo(2)−P(3), 2.4637(18); Mo(2)−P(4), 2.5091(16); P(1)−N(1), 1.715(4); P(2)−N(1), 1.735(4); P(3)−N(2), 1.721(5); P(4)−N(2), 1.734(5), C(54)−Mo(1)−P(2), 163.8(2); C(56)−Mo(1)−P(2), 105.15(19); P(1)−Mo(1)−P(2), 65.97(5); C(61)−Mo(2)−P(4), 104.1(2); C(59)−Mo(2)−P(4), 159.5(2); P(3)−Mo(2)−P(4), 66.09(5); P(1)−N(1)−P(2), 103.6(2); P(3)−N(2)−P(4), 103.4(2).

The structure of **8** shows that the central pyridine-2,6-diyl unit is somewhat strained by virtue of the bulky substituents groups. All distances concerning N and P refer to single bonds, whereas a closer look at the Mo−CO bond lengths reveals the *trans*-influence of the phosphinoamine ligand [13][19] (Mo−C(*trans*)$_{average}$ = 1.997(7) Å *vs.* Mo−C(non-*trans*)$_{average}$ = 2.039(6) Å). The Mo−P distances range between 2.464(2) and 2.509(2) Å, and are in good agreement with previously reported structures [13][14]. The steric hindrance of such bulky substituents, along with the very short P ··· P bite distance of 2.712(2) Å, illustrates why the geometry around the metal centres is distorted. The ligand is twisted around the central pyridine ring, being the plane between the planes N(1), P(1), P(2) and N(2), P(3), P(4) of 40.8°, and such disposition is then amplified by the coordination of the Mo(CO)$_4$ moieties.

Both complexes **7** and **8** are very stable in organic solvents and in H$_2$O. Complex **8** failed to undergo methylation with MeI at room temperature, indicating that the N-atom is effectively protected by the bulky N(PPh$_2$)$_2$Mo(CO)$_4$ groups. Even in the presence of HCl, the N-atom in **8** does not show any nucleophilicity. Quenching a sample of **8** in CDCl$_3$ with HCl (37 wt-% in H$_2$O) at room temperature does not result in any changes to the ^{1}H- or ^{31}P{^{1}H}-NMR spectra, and the complex could be recovered after removal of the solvent. The lack of reactivity of the pyridine ring N-atom is not completely unexpected based on the X-ray structure. First, there are several weak–medium interactions between the pyridine N-atom (N3) with the H-atoms from the Ph rings bonded to P-centres, typically 2.534−3.061 Å, possibly indicating a delocalisation of electron density. Second, the distance between the H-atoms on the Ph ring bonded to the two side-arm P-atoms are very short, typically 2.312−2.607 Å, further indicating that the N(3) atom is closely protected.

In summary, the facile synthesis of two polydentate ligands and their reactivities towards elemental S and Se, as well as their complexation towards a zero-valent Mo precursor, has been demonstrated. Both the ligands and their S/Se derivatives represent potential precursors to polycyclic rings with inorganic backbones and P-containing macrocyclic systems. Further studies in this direction are in progress and will be reported in due course.

Experimental Part

General. All manipulations were performed under an inert atmosphere of dry N$_2$ by standard *Schlenk* techniques. All the starting materials are commercially available and were used as received. Solvents were dried using the appropriate reagents and distilled prior to use. NMR Spectra were recorded in CDCl$_3$ at 20° with a *Bruker DMX-200* instrument with Me$_4$Si for ^{1}H and 85% H$_3$PO$_4$ for ^{31}P as external standards. IR Spectra were recorded on a *Perkin-Elmer 2000* FT-IR spectrometer. ESI Mass spectra were recorded on a *ThermoFinnigan LCQ*™ *Deca XP Plus* quadrupole ion-trap instrument. Samples were infused directly into the source at 5 μl min^{-1} using a syringe pump. The spray voltage was set at 5 kV and the cap. temp. at 50°. The MS detector was tuned automatically on the base peak, which optimised the remaining parameters. Elemental analysis was carried out at the Institute of Molecular and Biological Chemistry (EPFL).

Synthesis of N,N,N′,N′-*Tetrakis(diphenylphosphino)benzene-1,3-diamine* (**1**). The Ph$_2$PCl (8.826 g, 40.0 mmol) was added slowly to a soln. of 1,3-(H$_2$N)$_2$C$_6$H$_4$ (1.081 g, 10.0 mmol) and Et$_3$N (4.048 g, 40.0 mmol) in CH$_2$Cl$_2$ (50 ml) at 0°. The resulting white suspension was stirred for 2 h, and the solvent was removed under reduced pressure. The solid was washed with degassed H$_2$O (3 × 15 ml) and the solid was dried in air. Yield: 8.195 g (97%). M.p. 171°. ^{1}H-NMR 6.30−7.30 (*m*, arom. H). ^{31}P-NMR: 68.10 (*s*). Anal. calc. for C$_{54}$H$_{44}$N$_2$P$_4$: H 5.25, C 76.77, N 3.32; found H 5.45, C 76.56, N 3.18.

Synthesis of N,N,N′,N′-*Tetrakis(diphenylphosphino)pyridine-2,5-diamine* (**2**). The Ph$_2$PCl (8.826 g, 40.0 mmol) was added slowly to a soln. of 1,3-(H$_2$N)$_2$C$_5$H$_3$N (1.091 g, 10.0 mmol) and Et$_3$N (4.048 g, 40.0 mmol)

in CH_2Cl_2 (50 ml) at 0°. The resulting white suspension was stirred for 4 h, and the solvent was removed under reduced pressure. The solid was washed with degassed H_2O (3 × 15 ml), and the solid was dried in air. Yield: 8.291 g (98%). M.p. 191°. IR: 3069, 1558, 1478, 1427, 1217, 1090, 1041, 897, 868, 850. ^{1}H-NMR 6.20 – 7.39 (*m*, arom. H). ^{31}P-NMR: 59.50 (*s*). Anal. calc. for $C_{53}H_{43}N_3P_4$: H 5.12, C 75.26, N 4.97; found H 5.36, C 75.20, N 4.96.

Synthesis of (**3**). Elemental S (0.151 g, 4.72 mmol) was added to a soln. of **1** (0.996 g, 1.180 mmol) in toluene (10 ml), and the mixture was refluxed for 24 h. After allowing the mixture to cool to r.t., the white solid was collected by filtration, washed with Et_2O (2 × 15 ml) and dried *in vacuo*. Yield: 1.011 g (88%). M.p. 245° (dec.). ^{1}H-NMR: 6.70 – 8.70 (*m*, arom. H). ^{31}P-NMR: 70.4 (*s*). Anal. calc. for $C_{54}H_{44}N_2P_4S_4$: H 4.56, C 66.65, N 2.88; found H 4.58, C 67.04, N 2.75.

Synthesis of N,N,N′,N′-*Tetrakis(diphenylthiophosphinoyl)pyridine-2,6-diamine* (**4**). Elemental S (0.151 g, 4.72 mmol) was added to a soln. of **1** (1.000 g, 1.180 mmol) in toluene (10 ml), and the mixture was refluxed for 24 h. After allowing the reaction mixture to cool to r.t., the white solid was collected by filtration, washed with Et_2O (2 × 15 ml) and dried *in vacuo*. Yield: 1.023 g (89%). M.p. 285°. ^{1}H-NMR: 6.70 – 8.20 (*m*, arom. H). ^{31}P-NMR: 69.3 (*s*). Anal. calc. for $C_{53}H_{43}N_3P_4S_4$: H 4.45, C 65.35, N 4.31; found H 4.45, C 65.48, N 4.28%.

Synthesis of N,N,N′,N′-*Tetrakis(diphenylselenophosphinoyl)benzene-1,3-diamine* (**5**). Elemental Se (0.135 g, 1.71 mmol) was added to a soln. of **1** (0.360 g, 0.427 mmol) in toluene (10 ml), and the mixture was refluxed for 24 h. After allowing the mixture to cool to r.t., the white solid was collected by filtration, washed with Et_2O (2 × 15 ml) and dried *in vacuo*. Yield: 0.421 g (85%). M.p. 290° (dec.). $C_{54}H_{44}N_2P_4Se_4$: ^{1}H-NMR: 6.80 – 8.17 (*m*, arom. H). ^{31}P-NMR: 71.2 (*s*, ^1J(P,Se) = 799 Hz). Anal. calc. for $C_{54}H_{44}N_2P_4Se_4$: H 3.82, C 55.88, N 2.41; found H 3.88, C 55.80, N 2.39.

Synthesis of N,N,N′,N′-*Tetrakis(diphenylselenophosphinoyl)pyridine-2,6-diamine* (**6**). Elemental Se (0.192 g, 2.432 mmol) was added to a soln. of **2** (0.514 g, 0.608 mmol) in toluene (10 ml), and the mixture was refluxed for 24 h. After allowing the mixture to cool to r.t., the white solid was collected by suction filtration, washed with Et_2O (2 × 15 ml) and dried *in vacuo*. Yield: 0.607 g (86%). M.p. 236°. ^{1}H-NMR: 6.70 – 8.30 (*m*, arom. H). ^{31}P-NMR: 69.3 (*s*, ^1J(P,Se) = 805). Anal. calc. for $C_{53}H_{43}N_3P_4Se_4$: H 3.73, C 54.80, N 3.62; found H 3.73, C 55.05, N 3.57.

Synthesis of [1,3-{Mo(CO)$_4$(Ph$_2$P)$_2$N}$_2$(C$_6$H$_4$)] (**7**). [Mo(CO)$_4$(nbd)] (0.107 g, 0.354 mmol) was added to a soln. of **1** (0.152 g, 0.18 mmol) in toluene (10 ml), and the mixture was refluxed for 2 h. After cooling to r.t., the mixture was stored at r.t. overnight, during which time crystals formed and were collected by filtration. Yield: 0.218 g (96%). M.p. 270° (dec.). IR (ν_{CO}): 1935*w*, 1895*s*, 1876*vs*. ^{1}H-NMR: 6.20 – 7.50 (*m*, arom. H). ^{31}P-NMR: 97.0 (*s*). ESI-MS (neg. mode): 1323 $[M + (OMe)_2]^-$, 1292 $[M + (OMe)]^-$. Anal. calc. for $C_{62}H_{44}Mo_2N_2O_8P_4$: H 3.52, C 59.06, N 2.22; found H 3.72, C 59.19, N 2.12.

Synthesis of [2,6-{Mo(CO)$_4$(Ph$_2$P)$_2$N}$_2$(C$_5$H$_3$N)] (**8**). [Mo(CO)$_4$(nbd)] (0.107 g, 0.354 mmol) was added to a soln. of **1** (0.152 g, 0.18 mmol) in toluene (10 ml), and the mixture was refluxed for 2 h. After cooling to r.t., the mixture was stored at r.t. overnight, during which time crystals formed and were collected by filtration. Yield: 0.216 g (95%). M.p. 230° (dec.). IR (ν_{CO}: 1925*w*, 1888*s*, 1872*vs*. ^{1}H-NMR 6.10 – 7.80 (*m*, arom. H). ^{31}P-NMR: 95.0 (*s*). ESI-MS (neg. mode): 1324 $[M + (OMe)_2]^-$, 1293 $[M + (OMe)]^-$. Anal. calc. for $C_{61}H_{43}Mo_2N_2O_8P_4$: H 3.43, C 58.07, N 3.33; found H 3.44, C 58.17, N 3.26.

Crystal Data of **8**. $C_{61}H_{43}Mo_2N_3O_8P_4$, M_r 1261.74, monoclinic, space group $P2_1/n$, $a = 11.650(3)$, $b = 18.0556(17)$, $c = 27.236(5)$ Å, $\beta = 94.675(17)°$, $V = 5710.0(18)$ Å^3, $T = 140(2)$ K, $Z = 4$, $\mu = 0.609$ mm^{-1}, $\lambda = 0.71070$ Å, 34163 measured reflections, 10069 independent reflections, $R_{int} = 0.0606$, R_1 $[I > 2\sigma(I)] = 0.0569$, wR_2 (all data) = 0.1802. Additional material, consisting of fractional atomic coordinates, displacement parameters, observed and calculated structure factors, and a complete list of bond distances and bond angles are available from CCDC, Deposition No. 210921. Copies of the data can be obtained, free of charge on application to *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.ac.uk).

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