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# Synthesis and structural studies of molybdenum and palladium complexes of 1,5-diaza-3,7-diphosphacyclooctane ligands

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## Abstract

1,5-Diaza-3,7-diphosphacyclooctanes form 1:1 complexes with the metal fragments $Mo(CO)_4$ and $PdCl_2$. Two of these products along with a parent heterocycle have been structurally characterized. The $[P(Ph)CH_2N(2\text{-pyridyl})CH_2]_2$ ring is found in a crown conformation while its *cis*-$Mo(CO)_4$ complex adopts a *chair–boat* ligand conformation. On the other hand, the *cis*-$PdCl_2$ complex of $[P(Ph)CH_2N(Bz)CH_2]_2$ is found to retain a highly flattened crown ligand conformation. Unlike the related eight-membered heterocycle 1,3,5,7-tetraoxa-2,4,6,8-tetraphosphacyclooctane which behaves as a tetradentate ligand chelating homo- or hetero-bimetallics, coordination to a second metal by these complexes was not realized. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Molybdenum; Palladium; Phosphorus; Heterocycles; Metal complexes

## 1. Introduction

Eight-membered rings containing two or more donor atoms have a coordination chemistry between multidentate macrocycles and smaller heterocycles that have limited chelating ability [1–4]. If these donor atoms are in the 1,5 positions, chelation of a metal can potentially result in one of several possible *ligand* conformations including *chair–chair, boat–boat* and *chair–boat* (Fig. 1). The most common of these found in solid-state structures appears to be the *chair–boat,* although the *boat–boat* form has been observed in a number of six-coordinate complexes [1–9]. Our interest in tetraphosphorus heterocyclic ligands, especially the 1,3,5,7-tetraoxa-2,4,6,8-tetraphosphacyclooctane rings (or cyclotetraphosphoxane $[RP{-}O]_4$) which can adopt one of eight coordination modes [10], led us to reexamine the potentially tetradentate 1,5-diaza-3,7-diphosphacyclooctanes which were first prepared by Markl et al. in 1980 [11]. Monometallic metal complexes featuring 1:1 and 1:2 metal/ligand ratios have been synthesized and structural studies of two Pt(II) and one Cu(I) as well as a single parent heterocycle, $[P(Ph)CH_2N(Ph)CH_2]_2$, have appeared [12–15]. We report herein the structure of the $[P(Ph)CH_2N(2\text{-pyridyl})CH_2]_2$ heterocycle (ligand **1**) and syntheses and structures of its $Mo(CO)_4$ complex as well as the $PdCl_2$ complex of $[P(Ph)CH_2N(Bz)CH_2]_2$ (ligand **2**).

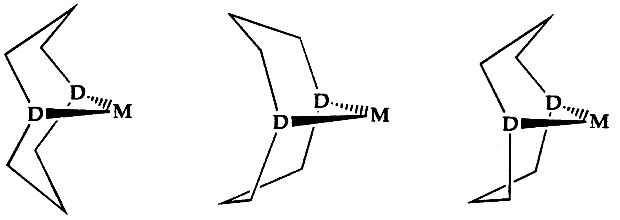

Fig. 1. Eight-membered ligand ring chelating conformations.

## 2. Experimental

### 2.1. General considerations

The ligands $[P(Ph)CH_2N(2\text{-pyridyl})CH_2]_2$, **1**, and $[P(Ph)CH_2N(Bz)CH_2]_2$, **2**, were prepared according to the literature method [11]. $Mo(CO)_4(\eta^2\text{-norbornadiene})$, $PdCl_2{-}2PhCN$, and $NiCl_2$–(dimethoxyethane) were obtained using the literature procedures [16–18]. All complexes were prepared and handled under a nitrogen atmosphere using standard Schlenk techniques. Solvents were reagent grade and dried and distilled under nitrogen immediately before use. Elemental analyses were per-

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formed on a Perkin-Elmer 2400 Elemental Analyzer. Proton, $^{13}$C, and $^{31}$P NMR spectra were recorded on JEOL-FX-90Q spectrometer and a Bruker AM 360 spectrometer. IR spectra of products were obtained as KBr pellets using a Nicolet MX-1 FT-spectrophotometer.

### 2.2. Syntheses

#### 2.2.1. $Mo(CO)_4[P(Ph)CH_2N(2\text{-pyridyl})CH_2]_2$, $Mo(CO)_4$–1

To a flask containing 0.37 g (0.86 mmol) of ligand **1** and 0.30 g (0.99 mmol) of $Mo(CO)_4(\eta^2$-norbornadiene) was added 30 ml of methylene chloride. After stirring at room temperature for 20 h, the yellow solution was concentrated to 15 ml and 20 ml of hexane was added to precipitate a small amount of brown material. This was filtered off and to the filtrate was added a further 25 ml hexane. The yellow precipitate formed was filtered off, washed with hexane, and dried to give 0.35 (64%) of the complex $Mo(CO)_4$–**1**. X-ray crystals were obtained from toluene and hexane. IR (cm$^{-1}$, CO): 2014, 1919, 1389, 1877. $^1$H NMR ($CDCl_3$, $\delta$) 7.24–8.15 (m, Ph), 6.59–6.65 (m, Py), 4.55 (d, NC*H*HP, $^2J_{HH}=14.3$ Hz)) and 4.35 (d, NCH*H*P, $^2J_{HH}=14.3$ Hz). $^{13}$C NMR ($CDCl_3$, $\delta$) CO's: 216.2 (t, $^2J_{PC}=7.0$ Hz), 209.8 (t, $^2J_{PC}=9.0$ Hz); 158.5, 148.0, 138.1, 129.3, 113.7, 106.3, 134.8 (t, $J_{PC}=13.9$ Hz), 131.3 (t, $J_{PC}=6.7$ Hz), 129.3 (t, $J_{PC}=4.7$ Hz), 49.4 (t, $J_{PC}=13.2$ Hz). $^{31}$P NMR ($CDCl_3$, $\delta$) 23.2 (s). Analysis from calculation for $C_{30}H_{28}MoN_4O_4P_2$: C, 54.07%; H, 4.23%; N, 8.41%. Found: C, 54.23%; H, 4.02%; N, 8.30%.

#### 2.2.2. $PdCl_2[P(Ph)CH_2N(Bz)CH_2]_2$, $PdCl_2$–2

To a flask containing 0.30 g (0.62 mmol) of ligand **2** and 0.21 g (0.62 mmol) of $PdCl_2$–2PhCN was added 20 ml of methylene chloride. All the solids dissolved immediately to give a brown solution. After 30 min of stirring, a thick yellow suspension formed. This was filtered and the residue washed with cold hexane and dried to give 0.27 g (65%) of the tan-brown complex $PdCl_2$–**2**. X-ray crystals were obtained from $CH_2Cl_2$/toluene. $^1$H NMR ($CDCl_3$, $\delta$) 7.34–7.50 (m, Ph), 4.37 (s, NC*H*$_2$Ph), 3.66 (d, NC*H*HP, $^2J_{HH}=13.6$ Hz), 3.60 (dd, NCH*H*P, $^2J_{HH}=13.6$ Hz and $^2J_{PH}=6.1$ Hz). $^{13}$C NMR data ($CDCl_3$, $\delta$) 136.2, 131.7, 130.1, 129.3, 128.7, 132.4 ($J_{PC}=3.8$ Hz), 129.0 (t, $J_{PC}=5.5$ Hz), 125.44 (dd, $J_{PC}=52.9$ and 2.7 Hz), 63.8 (s, N*C*H$_2$Ph), 51.4 (m, N*C*H$_2$P). $^{31}$P NMR ($CDCl_3$, $\delta$) −9.2 (s). Analysis from calculation for $C_{30}H_{32}Cl_2N_2P_2Pd$: C, 54.61%; H, 4.89%; N, 4.29%. Found: C, 54.54%; H, 5.02%; N, 4.24%.

#### 2.2.3. $NiCl_2[P(Ph)CH_2N(Bz)CH_2]_2$, $NiCl_2$–2

To a flask containing 0.20 g (0.42 mmol) of ligand **2** and 0.090 g (0.42 mmol) of $NiCl_2$–dme was added 20 ml of toluene. After 5 min, the reaction mixture turned into a purple suspension. After 1 h, this was filtered and the residue washed with cold toluene to give 0.13 g (49%) of the product $NiCl_2$–**2**. Small, branched purple crystals were obtained from $CH_2Cl_2$/hexane. Analysis from calculation for $C_{30}H_{32}Cl_2N_2NiP_2$: C, 58.86%; H, 5.27%; N, 4.58% Found: C, 59.05%; H, 5.62%; N, 4.53%.

### 2.3. Attempts at synthesis of bimetallic complexes

Use of excess metal reagents ($Mo(CO)_4$–nbd, $PdCl_2$–2PhCN or $NiCl_2$–dme) in the above preparations failed to yield any isolable bimetallic products. Further attempts at coordination of a second metal ($NiCl_2$, $CoCl_2$, $ZnCl_2$, etc.) at the open nitrogen donor sites in the monometallic complexes $Mo(CO)_4$–**1**, $PdCl_2$–**2** and $NiCl_2$–**2** were also unsuccessful.

### 2.4. X-ray crystallography

Crystal, data collection, and refinement parameters are given in Table 1. The systematic absences in the diffraction data were consistent with monoclinic space group $C2/c$ for both **1** and $PdCl_2$–**2**, and uniquely consistent for the orthorhombic space group *Pbca* for $Mo(CO)_4$–**1**. Structures of **1** and $PdCl_2$–**2** were refined in the centrosymmetric space group which yielded chemically reasonable and computationally stable results. Semi-empirical absorption correction was applied to the latter set of $PdCl_2$–**2** and ignored in the others. All three structures were solved by direct methods, completed by subsequent Fourier syntheses and refined by full-matrix least-squares procedures. The compound was found on a two-fold axis in $PdCl_2$–**2**. The phenyl carbons in **1** were refined isotropically. All other nonhydrogen atoms were refined anisotropically with hydrogen atoms treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL PLUS (4.2) Library (G. Sheldrick, Siemens XRD, Madison, WI).

## 3. Results and discussion

The two parent 1,5-diaza-3,7-diphosphacyclooctanes, $[P(Ph)CH_2N(2\text{-pyridyl})CH_2]_2$ (ligand **1**) and $[P(Ph)CH_2N(Bz)CH_2]_2$ (ligand **2**), were prepared using the literature methods in moderate yields [11]. Complexes of these were readily obtained using the respective metal precursors $Mo(CO)_4(\eta^2$-norbornadiene), $PdCl_2$–2PhCN, and $NiCl_2$–(dimethoxyethane). Isolated products included yellow $Mo(CO)_4$–**1**, orange $PdCl_2$–**2**, and purple $NiCl_2$–**2**. All three products were found to be 1:1 complexes by elemental analyses even when excess metal reagents were used in their preparations, confirming earlier reports of monometallic coordination [12–14]. The crystal structures of ligand **1**, $Mo(CO)_4$–**1**, and $PdCl_2$–**2** have been determined. We were not able to grow X-ray quality crystals of the $NiCl_2$ complex of ligand **2**. Its paramagnetic nature,

Table 1
Crystallographic data for **1**, $Mo(CO)_4$–**1** and $PdCl_2$–**2**

| | **1** | $PdCl_2$–**2** | $Mo(CO)_4$–**1** |
|---|---|---|---|
| Formula | $C_{26}H_{28}N_4P_2$ | $C_{30}H_{32}Cl_2N_2P_2Pd$ | $C_{30}H_{28}MoN_4O_4P_2$ |
| Formula weight | 458.5 | 659.8 | 666.4 |
| Space group | *C*2/*c* | *C*2/*c* | *Pbca* |
| *a* (Å) | 26.831(6) | 22.526(6) | 14.983(4) |
| *b* (Å) | 10.535(2) | 7.972(2) | 19.995(7) |
| *c* (Å) | 19.576(2) | 15.839(5) | 19.583(9) |
| $\beta$ (°) | 121.74(2) | 98.52(2) | – |
| *V* ($Å^3$) | 4706(2) | 2813(1) | 5867(4) |
| *Z* | 8 | 4 | 8 |
| *D* (calc) (g $cm^{-3}$) | 1.294 | 1.558 | 1.509 |
| $\mu$ (MoK$\alpha$) ($cm^{-1}$) | 2.07 | 9.87 | 5.99 |
| Temp (K) | 298 | 238 | 298 |
| Radiation | MoK$\alpha$ ($\lambda$=0.71073 Å) | | |
| *R*(*F*) (%) | 5.59 | 3.67 | 6.18 |
| *R*(*wF*) (%) | 6.51 | 4.89 | 8.06 |

[a] Quantity minimized=$\Sigma w\Delta^2$; $R=\Sigma\Delta/\Sigma(F_o)$; $R(w)=\Sigma\Delta^{1/2}/\Sigma(F_o-w^{1/2})$, $\Delta=|(F_o-F_c)|$.

however, suggested a non-planar geometry at the metal center, consistent with the observed pseudo-tetrahedral geometry around the nickel vertex of the previously reported Mo(CO)4[$^i$Pr$_2$NPO]$_4$NiBr$_2$ [19].

### 3.1. *Crystal structure of* $[CH_2P(Ph)CH_2N(2\text{-}pyridyl)]_2$, *ligand* ***1***

The heterocycle was found to adopt the familiar *crown* conformation with essentially planar ring nitrogen environments (Fig. 2). The sum of the bond angles around either N(1) or N(2) totalled 359°. The two phosphorus lone pairs are oriented *syn* to each other, suitable for metal chelation. Average ring P–C distances and N–C bond lengths were 1.87 Å and 1.45 Å, respectively. Selected bond distances and angles are presented in Table 2. For comparison, the previously reported structure of $[P(Ph)CH_2N(Ph)CH_2]_2$ has endocyclic angles within 2° of those in **1** [15]. Near planarity of the ring nitrogen bonding geometry is also observed. Its average ring P–C bond length of 1.88 Å and N–C length of 1.45 Å are essentially analogous. Both heterocyclic conformations are close to an idealized crown.

### 3.2. *Crystal structure of* $Mo(CO)_4[P(Ph)CH_2N(2\text{-}pyridyl)CH_2]_2$, $Mo(CO)_4$–***1***

Unlike several six-coordinate metal complexes of 1,5-dithiacyclooctane and many 1,5-diazacyclooctane derivatives [8,9], a *chair–boat* ligand conformation was observed in this complex (Fig. 3). The distorted octahedral coordination environment around Mo features a compressed P(1)–Mo–P(2) angle of only 74.9(1)° and *cis*-P–Mo–C angles greater than orthogonality ranging from 91.0(3)° to 101.7(3)° for P(1)–Mo–C(3). This significant expansion of the P(1)–Mo–C(3) angle is a direct consequence of the proximity of the P(1)–phenyl group. The

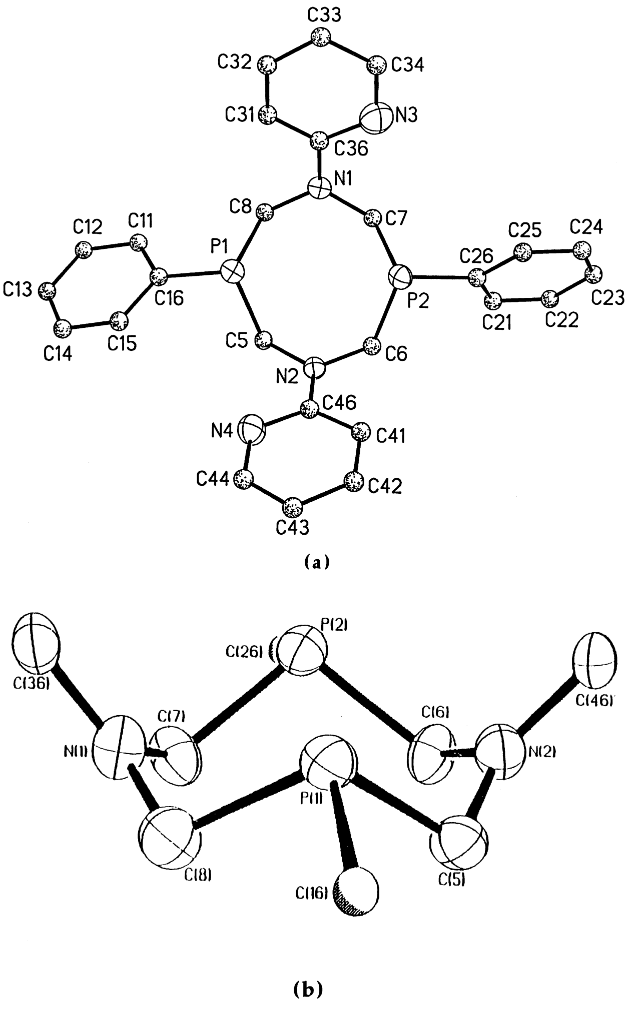

Fig. 2. (a)Molecular structure of $[P(Ph)CH_2N(2\text{-}Py)CH_2]_2$, **1**; (b) *Crown* conformation of ligand **1**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**

| | | | |
|---|---|---|---|
| P(1)–C(5) | 1.876(7) | P(1)–C(8) | 1.862(6) |
| P(1)–C(16) | 1.826(4) | P(2)–C(6) | 1.856(6) |
| P(2)–C(7) | 1.884(7) | P(2)–C(26) | 1.820(4) |
| N(1)–C(7) | 1.444(7) | N(1)–C(8) | 1.459(6) |
| N(1)–C(36) | 1.385(9) | N(2)–C(5) | 1.451(7) |
| N(1)–C(6) | 1.449(5) | N(2)–C(46) | 1.374(8) |
| C(5)–P(1)–C(8) | 101.0(3) | C(5)–P(1)–C(16) | 97.2(2) |
| C(8)–P(1)–C(16) | 101.5(3) | C(6)–P(2)–C(7) | 100.4(3) |
| C(6)–P(2)–C(26) | 101.0(3) | C(7)–P(2)–C(26) | 98.7(3) |
| C(7)–N(1)–C(8) | 118.9(5) | C(7)–N(1)–C(36) | 121.1(4) |
| C(8)–N(1)–C(36) | 118.7(4) | C(5)–N(2)–C(6) | 118.4(5) |
| C(5)–N(2)–C(46) | 120.9(4) | C(6)–N(2)–C(46) | 120.1(4) |
| P(1)–C(5)–N(2) | 114.6(4) | P(2)–C(6)–N(2) | 113.6(4) |
| P(2)–C(7)–N(1) | 114.3(4) | P(1)–C(8)–N(1) | 113.2(4) |

average Mo–P bond length of 2.49 Å is almost identical to that found in the structure of $Mo(CO)_4[{}^iPr_2NPO]_4$ [20]. Both ring nitrogens are near planarity with bond angle sums totalling 360° and 357° at N(1) and N(2), respectively. Average ring P–C and N–C distances are 1.86 Å and 1.45 Å, essentially unchanged from the free ligand values. The observed shorter *cis*-Mo–C(carbonyl) bond lengths of 1.98 Å (average) compared to *trans*-Mo–C distances of 2.03 Å (average) is well established in metal carbonyl phosphine structures. Selected bond distances and angles are listed Table 3.

Chelation of the $Mo(CO)_4$ moiety led to a closing of the two phosphorus ring atoms from the free ligand value of 3.750(2) Å to only 3.023(3) Å. The other notable change, of course, is the flipping of N(1) from the *crown* into the *chair–boat* conformation as manifested in changes of its ring torsional angles from 85.70° and −91.0° to −70.0° and 67.8°, respectively (Table 4).

In solution at ambient temperature, this complex appeared to be either conformationally mobile or in a structure of higher symmetry with ring methylenes appearing as a single AB system in its $^1H$ NMR spectrum. Interestingly, no discernable $^2J_{PH}$ coupling was observed. Its $^{13}C\{^1H\}$ NMR spectrum contained a single virtual triplet at 49.4 ppm assignable to four equivalent methylene ring carbons.

The same *chair–boat* coordination ring conformation was also found in the solid-state structures of Cu(I) and Pt(II) complexes of related 1,5-diaza-3,7-diphosphacyclooctanes [12–14]. In $CuI(pyridine)[P(Ph)CH_2N(p\text{-}tolyl)CH_2]_2$, however, one of the ring nitrogens is more pyramidal with bond angles totalling only 344°. The other ring nitrogen bond angles do add up to a near-planar value of 354°. The P–Cu–P angle is 86.78(6)°, far short of the ideal tetrahedral angle, but still considerably larger than the P–Mo–P angle in $Mo(CO)_4$–**1**. The shorter Cu–P distance of 2.26 Å compared to the average Mo–P bond length of 2.49 Å is consistent with the discrepancy in P–M–P angles.

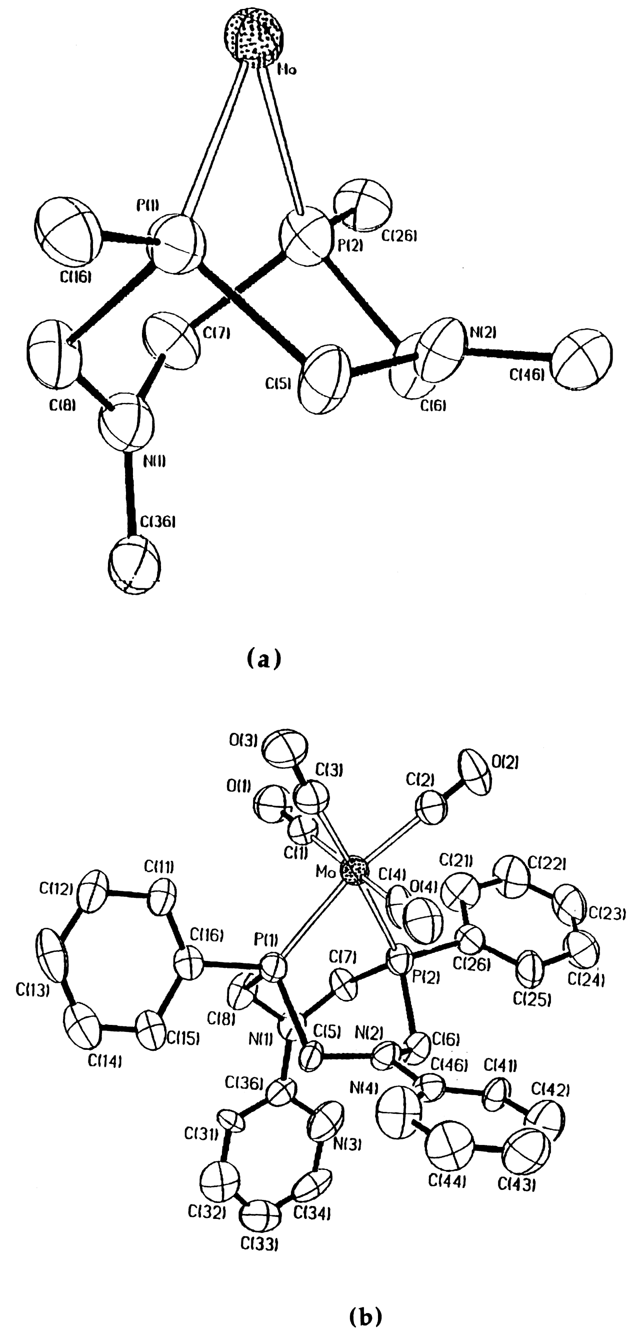

Fig. 3. (a) Core structure of $Mo(CO)_4–[P(Ph)CH_2N(2\text{-}Py)CH_2]_2$, $Mo(CO)_4$–**1**; (b) molecular structure of $Mo(CO)_4$–**1**.

### *3.3. Crystal structure of $PdCl_2[P(Ph)CH_2N(Bz)CH_2]_2$, $PdCl_2$–2*

The heterocyclic ligand was found in a highly distorted crown conformation with both nitrogens flattened towards the four ring-carbon plane. These ring nitrogens are only 0.223 Å from the least-squares plane of these ring-carbons, whereas the phosphorus atoms are a full 1.123 Å out of this plane (Fig. 4). Although not previously observed in

Table 3
Selected bond lengths (Å) and bond angles (°) for $Mo(CO)_4$–**1**

| | | | |
|---|---|---|---|
| Mo–P(1) | 2.480(3) | Mo–P(2) | 2.492(3) |
| Mo–C(1) | 2.013(13) | Mo–C(2) | 1.988(11) |
| Mo–C(3) | 1.978(12) | Mo–C(4) | 2.041(13) |
| N(1)–C(7) | 1.451(12) | N(1)–C(8) | 1.439(12) |
| N(1)–C(36) | 1.392(13) | N(2)–C(5) | 1.455(11) |
| N(2)–C(6) | 1.446(12) | N(2)–C(46) | 1.392(14) |
| P(1)–C(5) | 1.863(10) | P(1)–C(8) | 1.861(10) |
| P(1)–C(16) | 1.802(10) | P(2)–C(6) | 1.850(10) |
| P(2)–C(7) | 1.868(10) | P(2)–C(26) | 1.823(11) |
| P(1)–Mo–P(2) | 74.9(1) | P(1)–Mo–C(1) | 91.0(3) |
| P(2)–Mo–C(1) | 93.1(3) | P(1)–Mo–C(2) | 167.1(2) |
| P(2)–Mo–C(2) | 92.3(3) | C(1)–Mo–C(2) | 90.6(5) |
| P(1)–Mo–C(3) | 101.7(3) | P(2)–Mo–C(3) | 176.6(3) |
| C(1)–Mo–C(3) | 86.6(5) | C(2)–Mo–C(3) | 91.1(5) |
| P(1)–Mo–C(4) | 87.7(3) | P(2)–Mo–C(4) | 95.6(3) |
| C(1)–Mo–C(4) | 170.5(5) | C(2)–Mo–C(4) | 92.8(4) |
| C(3)–Mo–C(4) | 84.5(5) | C(7)–N(1)–C(8) | 116.6(8) |
| C(7)–N(1)–C(36) | 125.1(8) | C(8)–N(1)–C(36) | 118.3(8) |
| C(5)–N(2)–C(6) | 118.4(7) | C(5)–N(2)–C(46) | 120.9(8) |
| C(6)–N(2)–C(46) | 117.3(8) | Mo–P(1)–C(5) | 112.5(3) |
| Mo–P(1)–C(8) | 113.4(3) | C(5)–P(1)–C(8) | 102.3(4) |
| Mo–P(1)–C(16) | 122.6(3) | C(5)–P(1)–C(16) | 103.7(4) |
| C(8)–P(1)–C(16) | 99.9(4) | Mo–P(2)–C(6) | 113.9(3) |
| Mo–P(2)–C(7) | 115.0(3) | C(6)–P(2)–C(7) | 99.6(4) |
| Mo–P(2)–C(26) | 118.6(3) | C(6)–P(2)–C(26) | 106.6(5) |
| C(7)–P(2)–C(26) | 100.8(5) | N(2)–C(5)–P(1) | 113.7(6) |
| N(2)–C(6)–P(2) | 113.0(7) | N(1)–C(7)–P(2) | 111.6(7) |
| N(1)–C(8)–P(1) | 113.4(6) | | |

1,5-diaza-3,7-diphosphacyclooctane complexes [12–14], this coordinating ring conformation was found in the related tetraphosphoxane complex $PdCl_2[^iPr_2NPO]_4$ which had all six non-coordinating atoms of the $P_4O_4$ ring within 0.01 Å of planarity [21]. Upon metal chelation, the ligand **2** phosphorus atoms are brought together to a separation of only 2.963 Å. Ring torsional angles reflect this chelating conformation compared to the two other structures described in this study (Table 4). At both ring N's, the torsional angles are substantially smaller in magnitude with values of −64.0° and 60.8° than those for ligand **1**.

The near square-planar palladium coordination sphere contains a distorted P–Pd–P angle of 82.5(1)° and Cl–Pd–Cl angle of 91.9(1)°. The average Pd–Cl and Pd–P bond lengths of 2.362(1) Å and 2.247(1) Å are unexceptional. Again, average ring P–C and N–C distances of 1.89 Å and 1.45 Å, respectively, are very similar to those of related heterocycles and complexes. Interestingly, both ring nitrogens have bonding environments almost midway between

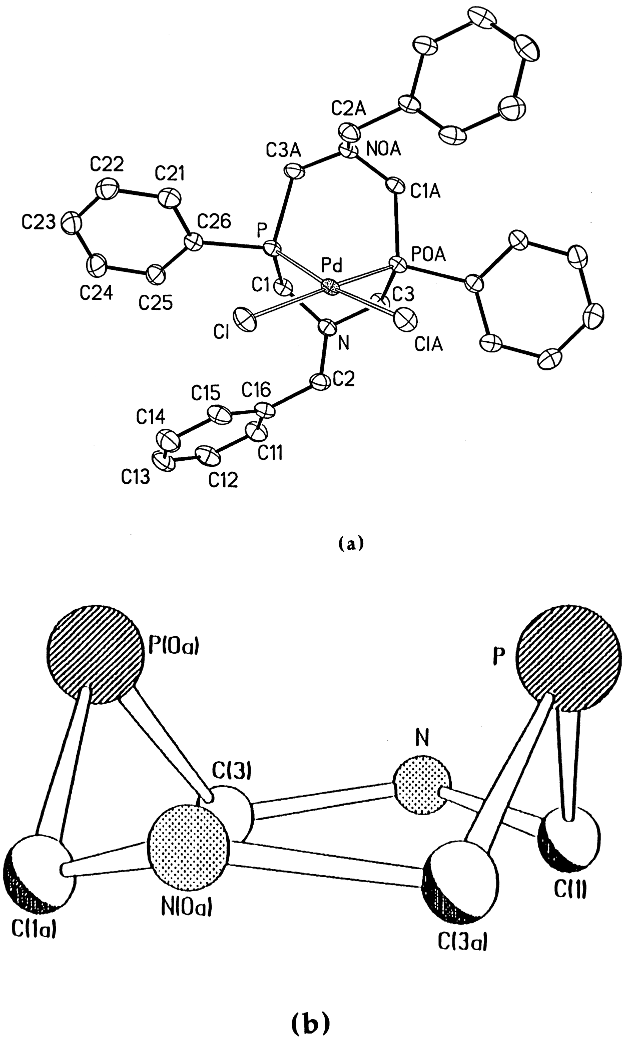

Fig. 4. (a) Molecular structure of $PdCl_2$–$[P(Ph)CH_2N(Bz)CH_2]_2$, $PdCl_2$–**2**; (b) ligand conformation in $PdCl_2$–**2**.

Table 4
Comparison of ring torsional angles (°) for **1**, $Mo(CO)_4$–**1** and $PdCl_2$–**2**

| **1** | | $Mo(CO)_4$–**1** | | $PdCl_2$–**2** | |
|---|---|---|---|---|---|
| C(8)–P(1)–C(5)–N(2) | 100.5 | C(8)–P(1)–C(5)–N(2) | 103.9 | C(3A)–P–C(1)–N | 111.0 |
| C(5)–P(1)–C(8)–N(1) | −93.7 | C(5)–P(1)–C(8)–N(1) | −48.5 | C(1)–P–C(3A)–N(0A) | −106.3 |
| C(7)–N(1)–C(8)–P(1) | 85.7 | C(7)–N(1)–C(8)–P(1) | −70.0 | C(1A)–N(0A)–C(3A)–P | 60.8 |
| C(8)–N(1)–C(7)–P(2) | −91.0 | C(8)–N(1)–C(7)–P(2) | 67.8 | C(3A)–N(0A)–C(1A)–P(0A) | −64.0 |
| C(6)–P(2)–C(7)–N(1) | 100.5 | C(6)–P(2)–C(7)–N(1) | 51.5 | C(3)–P(0A)–C(1A)–N(0A) | 111.0 |
| C(7)–P(2)–C(6)–N(2) | −94.7 | C(7)–P(2)–C(6)–N(2) | −110.8 | N–C(3)–P(0A)–C(1A) | −106.3 |
| C(5)–N(2)–C(6)–P(2) | 86.2 | C(5)–N(2)–C(6)–P(2) | 66.6 | C(1)–N–C(3)–P(0A) | 60.8 |
| C(6)–N(2)–C(5)–P(1) | −90.5 | C(6)–N(2)–C(5)–P(1) | −63.3 | C(3)–N–C(1)–P(0A) | −64.0 |

Table 5
Selected bond lengths (Å) and bond angles (°) for PdCl$_2$–**2**

| | | | |
|---|---|---|---|
| Pd–Cl | 2.362(1) | Pd–P | 2.247(1) |
| Pd–ClA | 2.362(1) | Pd–PA | 2.247(1) |
| P–C(1) | 1.878(3) | P–C(26) | 1.810(3) |
| P–C(3A) | 1.894(3) | N–C(1) | 1.456(4) |
| N–C(2) | 1.469(4) | N–C(3) | 1.439(4) |
| Cl–Pd–P | 93.1(1) | Cl–Pd–ClA | 91.9(1) |
| P–Pd–ClA | 172.9(1) | Cl–Pd–PA | 172.9(1) |
| P–Pd–PA | 82.5(1) | ClA–Pd–PA | 93.1(1) |
| Pd–P–C(1) | 111.4(1) | Pd–P–C(26) | 119.8(1) |
| C(1)–P–C(26) | 107.4(1) | Pd–P–C(3A) | 109.8(1) |
| C(1)–P–C(3A) | 104.4(1) | C(26)–P–C(3A) | 102.7(1) |
| C(1)–N–C(2) | 116.6(2) | C(1)–N–C(3) | 113.1(2) |
| C(2)–N–C(3) | 113.6(2) | P–C(1)–N | 116.0(2) |
| N–C(2)–C(16) | 112.6(3) | N–C(3)–PA | 117.1(2) |

planar and pyramidal with bond angles summing to 343°. Other selected bond lengths and angles are listed in Table 5.

At ambient temperature, the solution $^1$H NMR spectrum of this complex exhibited an ABX$_2$ pattern with geminal $^2J_{AB}=13.6$ Hz and $^2J_{PB}=6.1$ Hz. This is not inconsistent with retention of the symmetrical solid-state structure, though alternative ring conformations as well as dynamical behavior can also produce this pattern.

### *3.4. Attempts at coordination of a second metal*

Attempts to use the ring nitrogens in these complexes as donors towards a second metal center (e.g. Zn$^{2+}$, Co$^{2+}$, Ni$^{2+}$) and form heterobimetallics were uniformly unsuccessful. Karasik et al. have previously observed similar behavior at the nitrogen sites of related 1,5-diaza-3,7-diphosphacyclooctanes [12–14]. The near-planarity at the ring nitrogens found in these structures as well as their divergent orientations clearly disfavor chelation of a second metal center. By contrast, the related 1,3,5,7-tetraoxa-2,4,6,8-tetraphosphacyclooctane molybdenum complex, Mo(CO)$_4$[$^i$Pr$_2$NPO]$_4$, has a *boat–boat* conformation [10,19]. As a result, the two convergent phosphorus lone pairs are predisposed for chelation of a second metal to complete the adamantanoid bimetallic cage structure.

## Supplementary data

Tables of X-ray experimental details and crystallographic data, all atomic coordinates, anisotropic thermal parameters, and bond distances and angles for the structures of ligand **1** (Deposition No. 103281), Mo(CO)$_4$–**1** (Deposition No. 103282), and PdCl$_2$–**2** (Deposition No. 103295) have been deposited at the Crystallographic Data Center (CCDC, Cambridge, UK).

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