of these species. The UV and MCD spectra as indicated by the calculated *B* terms (Tables III and S1 and Figure 9) are characterized by prominent features that can function as markers. Strong $d_{xz} \rightarrow \pi^*$ transitions alone or coupled with nearly degenerate $d_{xy} \rightarrow \pi^*$ transitions produce negative *B* terms. $d_{xz} \rightarrow \pi^*$ transitions may be used to indicate which ligand (Cl^-, OH^-, H_2O) is present, particularly if only one type of Pt binding is found. $\pi_1 \rightarrow \pi^*$ and $\pi_2 \rightarrow \pi^*$ transitions are especially useful because their intensities in free acetamide and iminol are manifested in the Pt complexes. The signs of the MCD *B* terms are not a reliable means for establishing the ligand-related A or I transitions although in many cases the magnitudes are reproduced. One reason for this is the transitions of the complex that are close in energy to the chosen transition can mix into this transition and change the sign. Another reason may be the orientation of the A and I ligands relative to the molecular plane. $n \rightarrow \pi^*$ transitions might be expected to provide additional information, but they are weak.

Triplet transitions are anticipated for these spectral studies, as Pt possesses an appreciable spin-orbit coupling constant that allows the intermixing of singlet and triplet excited states. But it is beyond the scope of the MO methods employed to give satisfactory treatment to these conditions.

Summary

This work has indicated that there may be observed band shifts in a UV-visible and MCD spectral study of the hydrolysis of *cis*-DDP with acetamide. The energy shifts correlate well with expectations from the spectrochemical series and with orbital interaction diagrams for acetamide and its iminol tautomer. Although total and transition energies are likely to be overestimated as compared with experimental results, reasonable spectral assignments are made from the relative ordering and trends.

The Pt-O bonded acetamide complex is found to be the most stable species. Perpendicular arrangements of the acetamide moieties are more favorable than planar structures. The differences in the Pt-O- and P-N-bonding species are found particularly in their effects on ligand-ligand transitions and transitions involving $d \rightarrow \pi^*$, $d \rightarrow d$, and $d \rightarrow 6p_y$. The $\pi \rightarrow \pi^*$ transitions are of primary importance in distinguishing Pt-A and Pt-I species regardless of Pt-ligand coordination.

This preliminary examination of the acetamide system represents an essential step in the development of a reasonable picture at the molecular level for the interaction of platinum species with simple binding sites. This system appears to offer good prospects for experimental realization.

Acknowledgment. We thank Drs. Karsten Krogh-Jespersen and Seymour Hutner for numerous helpful discussions. Pace University Academic Computing Services are continuously thanked. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Table S1, showing theoretical absorption and MCD spectral results for *cis*-$Pt(NH_3)_2Cl_2$ hydrolysis products with both acetamide and its iminol (3 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie Moléculaire, Unité Associée au CNRS, Université de Nice, 06034 Nice, France, and Laboratoires de Chimie, Unité Associée au CNRS, Departement de Recherche Fondamentale, CENG, 38041 Grenoble, France

Improved Synthesis of Cyclamphosphine Oxide, a Potential Bidentate Asymmetric Ligand. Synthesis and Characterization of Some of Its Rhodium Complexes. Molecular and Crystal Structure of (Cyclamphosphine oxide)dicarbonylchlororhodium(I)

Frédéric Bouvier,[1a] Jean-Marc Dupart,[1a] André Grand,[1b] and Jean G. Riess*[1a]

Received September 25, 1986

Cyclamphosphorane, $C_{10}H_{21}N_4P$ (**1**), reacts with $ONMe_3$ to give cyclamphosphine oxide, $C_{10}H_{21}N_4PO$ (**2**), a potential bidentate asymmetric ligand, quantitatively. The action of **2** on $(Rh(CO)_2Cl)_2$ gives $(C_{10}H_{21}N_4PO)Rh(CO)_2Cl$ (**5**) and $(C_{10}H_{21}N_4PO)(Rh(CO)_2Cl)_2$ (**4**) wherein **2** behaves as a monodentate ligand and as a bridging ligand, respectively. An X-ray structure determination has been achieved on **5**, which crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.698$ (1) Å, $b = 9.777$ (1) Å, $c = 13.791$ (1) Å, $\beta = 93.93$ (1)°, and $Z = 4$. The structure of **5** shows that the NH site is coordinated to the rhodium atom whereas the phosphoryl site remains free. Only one diastereoisomer is formed. The P=O bond length (1.456 (2) Å) and the Rh-N bond length (2.118 (3) Å) are in the usual ranges. The six-membered ring adopts a slightly distorted boat conformation. The five-membered ring has a flattened envelope conformation. The interatomic (N)H-Cl distance of 2.306 (1) Å indicates a bent hydrogen bond. The dinuclear complex **4** can be converted into **5** by an additional 1 equiv of **2**, while **5** yields **4** in the presence of 0.5 equiv of $(Rh(CO)_2Cl)_2$.

Tricyclic tetraaminophosphine oxides were first reported in a patent by Richman in 1976.[2] They were obtained from the tetrasilylated cyclic tetraamines by reaction with PF_5 or OPF_3 and subsequent hydrolysis of the tetraaminofluorophosphorane that is formed. The same author more recently showed that these oxides, including cyclamphosphine oxide (**2**), could be obtained by hydrolyzing the corresponding ionic phosphonium chloride.[3] The first of these routes requires reagents that are neither readily available nor convenient to handle and are expensive, while neither yields nor experimental details were given for the second approach.

Moreover, the versatile ligand properties of cyclamphosphorane (**1**)[4,5] in its open tautomeric form **1b** raised the question of the coordination ability of its oxide **2**. We therefore wish to report a convenient, quantitative synthesis of **2**, in a single step from **1**, by using trimethylamine oxide as the oxidizing agent,[6,7] as well as the preparation and characterization of two rhodium complexes in which cyclamphosphine oxide behaves as a monodentate ligand through its NH site or as a bridging ligand through both its NH

---

(1) (a) Université de Nice. (b) CENG.

(2) Richman, J. E. U.S. Patent 3 987 128, 1976.

(3) Richman, J. E.; Flay, R. B.; Gupta, O. D. In *Phosphorus Chemistry*; ACS Symposium Series 171; American Chemical Society: Washington, DC, 1981; p 271.

(4) Dupart, J.-M.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 1167.

(5) Dupart, J.-M.; Grand, A.; Pace, S.; Riess, J. G. *Inorg. Chem.* **1984**, *23*, 3776.

(6) Vetter, H.-J.; Nöth, H. *Chem. Ber.* **1963**, *96*, 1308.

(7) Casabianca, F.; Pinkerton, A. A.; Riess, J. G. *Inorg. Chem.* **1977**, *16*, 864.

0020-1669/87/1326-2090$01.50/0

and PO sites. The X-ray structure determination of the former adduct is also reported.

Experimental Section

$C_{10}H_{21}N_4PO$ (2). Cyclamphosphorane was prepared according to Richman and Atkins;[8] $ONMe_3$ (Fluka) was sublimed in vacuo before use; toluene was distilled from Na/K alloy, and the reaction was carried out under dry nitrogen.

$ONMe_3$ (0.075 g, 1 mmol) is added to a solution of cyclamphosphorane (0.228 g, 1 mmol) in 30 mL of toluene. The mixture is stirred at room temperature; the reaction is considered to be complete when all the initially solid $ONMe_3$ (insoluble in toluene) has disappeared (ca. 6 h). The solvent and NMe_3 formed are pumped away. The residue is sublimed (100 °C (10^{-3} mmHg)) to give white hygroscopic needles of **2** (0.22 g; 90%), mp 145 °C. Anal. Calcd for $C_{10}H_{21}N_4PO$: C, 49.17; H, 8.67; N, 22.93. Found: C, 49.10; H, 8.99; N, 22.58. ^{31}P NMR (toluene; δ): +23.4. IR (KBr pellet; cm^{-1}): ν(N—H) 3320 (m); ν(P=O) 1220 (s). MS (chemical ionization with NH_3; *m/e*) MH^+ (100%).

$Rh(CO)_2Cl(C_{10}H_{21}N_4PO)$ (5). A 0.199-g (0.82-mmol) sample of **2** in 35 mL of toluene is added to a solution of $(Rh(CO)_2Cl)_2$ (0.157 g, 0.40 mmol) in 15 mL of toluene. The mixture is stirred at room temperature for 5 min. No gas evolvement is detected. After filtration, the filtrate is evaporated to yield 0.305 g of **5** as a yellow powder (85%), which is stable in dry air but rather instable in solution (toluene, CH_2Cl_2); mp 136 °C dec. Anal. Calcd for $C_{12}H_{21}N_4O_3PClRh$: C, 32.86; H, 4.82; N, 12.77; P, 7.06. Found: C, 32.98; H, 4.80; N, 12.37; P, 7.08. ^{31}P NMR (toluene; δ) +24.4 (s). IR (KBr pellet; cm^{-1}): ν(N—H) 3210 (m); ν(CO) 2095 (s), 2070 (shoulder), 2030 (s), 2000 (s), 1985 (shoulder), 1970 (shoulder); ν(P=O) 1235 (s); ν(RhCl) 324 (w), 309 (w). MS (chemical ionization with NH_3; *m/e*): $(M + 2)H^+$ (13.4%), MH^+ (39.4%), $(C_{10}H_{21}N_4PO)H^+$ (100.0%). Conductometric study (10^{-3} M in acetone; room temperature): $\Lambda = 0.07\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$.

$Rh_2(CO)_4Cl_2(C_{10}H_{21}N_4PO)$ (4). A 0.153-g (0.62-mmol) sample of **2** in 20 mL of toluene is added to a solution of $(Rh(CO)_2Cl)_2$ (0.234 g, 0.60 mmol) in 10 mL of toluene at −30 °C. The mixture is immediately filtered. The filtrate is concentrated, and pentane is slowly added at −30 °C to yield **4** as a yellow precipitate, which is filtered off (0.268 g, 70%). The air-sensitive yellow microcrystalline powder is rather unstable in solution. It crystallizes at −30 °C in toluene/heptane; mp 62–63 °C dec. Anal. Calcd for $C_{10}H_{21}N_4O_5Cl_2Rh_2\cdot 0.5C_7H_8$: C, 30.92; H, 3.68; N, 8.24; P, 4.56. Found: C, 30.90; H, 3.74; N, 8.39; P, 4.68. ^1H NMR (CD_2Cl_2; δ): 4.63 (broad, H(N); toluene of crystallization; 16%). ^{31}P NMR (toluene; δ): +29.6 (s). IR (KBr pellet; cm^{-1}): ν(N—H) 3200 (m); ν(CO) 2090 (s), 2000 (s); ν(P=O) 1170 (s); ν(RhCl) 315 (w). MS (chemical ionization with NH_3; *m/e*): $(Rh(CO)_2ClL + 2)H^+$ (20%), $(Rh(CO)_2ClL)H^+$ (71%), LH^+ (100%).

Synthesis of 5 from 4. A 0.067-g (0.27-mmol) sample of **2** in 15 mL of toluene is slowly added to a solution of 1.173 g (0.27 mmol) of **4** in 15 mL of toluene at −30 °C. The mixture is filtered. The dropwise addition of heptane to the filtrate led to the precipitation of **5** (0.182 g, 76%).

Synthesis of 4 from 5. A 0.243-g (0.55-mmol) sample of **5** in 20 mL of toluene is dropwise added to a solution of 0.107 g (0.27 mmol) of $(Rh(CO)_2Cl)_2$ in 10 mL of toluene at −30 °C. The mixture is immediately filtered. The dropwise addition of 150 mL of heptane to the filtrate at −30 °C gave **4** as a yellow precipitate (0.244 g, 70%).

Collection of X-ray Data for 5. Parallelepipedic yellow crystals were obtained by slow crystallization of **5** at −30 °C from a toluene/heptane solution. These crystals are monoclinic and belong to space group $P2_1/n$. Cell parameters have been refined by least squares from angular positions of 25 reflections in the range $18.8° < 2\theta < 28.8°$ by using an automatic Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation. The main crystal data are recorded in Table I. The intensities of 5253 reflections ($2° < \theta < 30°$) were collected and periodically checked. No decrease in the intensity of the standard reflections was observed during the data collection. The data were corrected for the Lorentz and polarization factors, but not for absorption or extinction. Among the independent reflections collected, 3840 ($F_o > 2.5\sigma(F_o)$) were used to refine the structure parameters. Scattering factors were those used for neutral atoms.[20]

Structure Solution and Refinement for 5. The Patterson function led to the position of the rhodium atom. The combination of the Patterson and direct methods and successive Fourier difference maps allowed the location of all the non-hydrogen atoms.

Table I. Crystallographic Data for $(CO)_2ClRh(C_{10}H_{21}N_4PO)$

formula	$C_{12}H_{21}N_4O_3PClRh$
temp, °C	20
space group	$P2_{1/n}$
M_r	438.6
a, Å	12.698 (1)
b, Å	9.777 (1)
c, Å	13.791 (1)
α deg	90
β deg	93.93 (1)
γ deg	90
V, Å^3	1708
Z	4
d_{calcd}, g/cm^3	1.71
d_{obsd}, g/cm^3	1.69 (flotation)
radiation	Mo Kα (0.71073 Å)
monochromator	graphite
cryst size, mm	0.2 × 0.2 × 0.2
abs coeff, cm^{-1}	12.36
data collcted	5253
no. of data used ($F_o > 2.5\sigma(F_o)$	3840
phasing technique	heavy atom and MULTAN solution
R^a	0.055
$R_w{}^b$	0.030
no. of variables	199
scan mode	ω
takeoff angle, deg	4
2θ max, deg	60
scan speed, deg·min^{-1}	2
check reflcns	116; $\bar{1}\bar{1}\bar{1}$; 530

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Atomic Coordinates

	x	y	z
Rh	0.20965 (2)	0.47499 (3)	0.62612 (2)
P	0.18389 (8)	0.16964 (10)	0.30240 (7)
Cl	0.11391 (9)	0.27481 (11)	0.64036 (7)
N1	0.22175 (20)	0.41989 (26)	0.47875 (19)
N2	0.26123 (22)	0.12832 (29)	0.39960 (21)
N3	0.11389 (22)	0.02838 (28)	0.30099 (19)
N4	0.09456 (20)	0.28447 (26)	0.32379 (19)
O1	0.24101 (19)	0.20998 (23)	0.21895 (16)
C1	0.32854 (28)	0.42127 (37)	0.43987 (27)
C2	0.38998 (28)	0.29871 (41)	0.47509 (29)
C3	0.37270 (30)	0.17280 (40)	0.40873 (30)
C4	0.24223 (32)	−0.01180 (39)	0.43159 (26)
C5	0.13163 (31)	−0.05096 (35)	0.38986 (25)
C6	0.00483 (31)	0.04075 (38)	0.26197 (26)
C7	−0.06299 (28)	0.13272 (40)	0.32240 (27)
C8	0.00507 (27)	0.24102 (36)	0.37771 (24)
C9	0.11639 (27)	0.43141 (34)	0.31872 (24)
C10	0.14171 (28)	0.49683 (32)	0.41679 (23)
C11	0.28447 (31)	0.63391 (42)	0.61173 (28)
C12	0.18590 (30)	0.51848 (40)	0.75195 (28)
O_2	0.32959 (26)	0.73129 (30)	0.60062 (21)
O_3	0.16393 (24)	0.54491 (31)	0.82808 (20)

The structure was refined with the XFLSN program,[9] with Rh, P, N, C, O, and Cl atoms anisotropic (anomalous scattering factor included for Rh). At this stage of refinement, a Fourier difference map showed significant electron densities in the position presumed for hydrogen atoms. They were introduced in the refinement ($B_{iso} = 6$ Å^2) but not refined (C–H = 1.09 Å; H–C–H and C–C–H = 109°). After the last refinement, a final Fourier difference map showed no peaks with more than 0.5 e Å^{-3}. The final R_w and R factors reached the values of 0.030 and 0.055 respectively.

The final atomic coordinates are reported in Table II, with esd's in parentheses. The numbering scheme is the same as in Figure 1, which shows an ORTEP view of the molecule. Interatomic distances and angles are given in Table III.

Results and Discussion

Synthesis of 2. Under the action of $ONMe_3$, the oxide of the open, initially minor tautomer of cyclamphosphorane is formed quantitatively indicating that equilibrium for compound **1** had been displaced toward **1b**. The formulation of **2** was confirmed by elemental analysis and mass spectroscopy. Its infrared spectrum exhibits a sharp vibration at 3320 cm^{-1} as expected for a free

---

(8) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149.

(9) Busing, W. R.; Martin, K. U.; Levy, H. A. *Oak Ridge Natl. Lab.,* [*Rep.*] *ORNL* (*U.S.*) **1971**, *ORNL-59-4-37.*

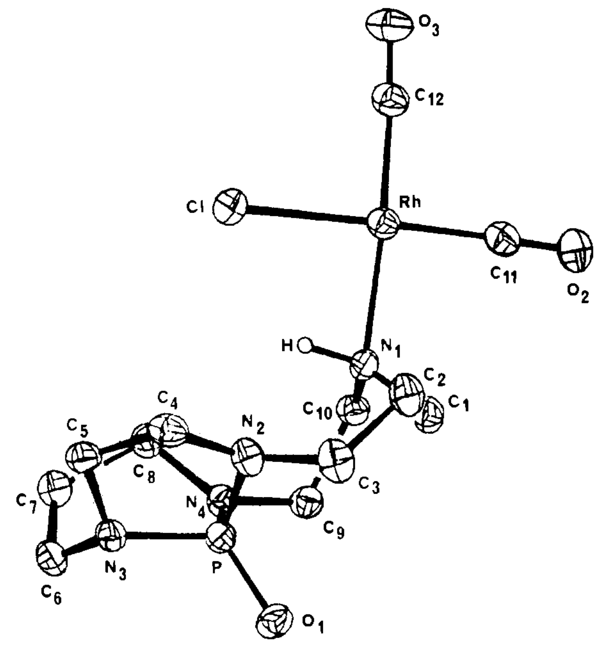
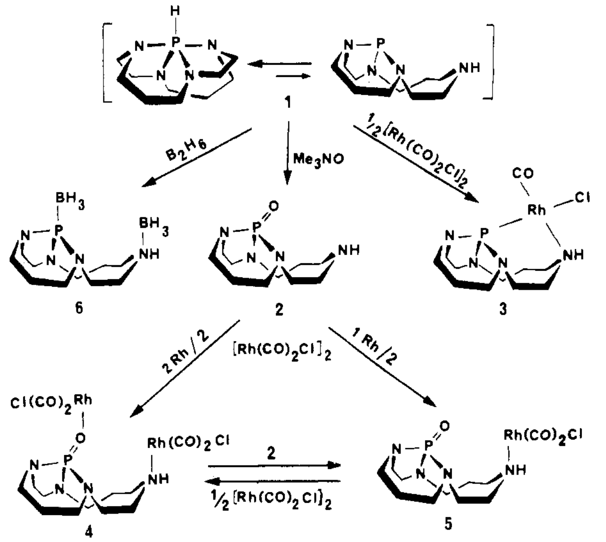


Figure 1. ORTEP drawing of **5** (probability for thermal ellipses: 20%).

Scheme I



N—H amino group, while the position of the strong $\nu(P{=}O)$ absorption at 1220 cm^{-1} is in agreement with the value (1218 cm^{-1}) calculated from the relation of Thomas and Chittenden for $OP(NR_2)_3$ compounds.[10] The chemical shift of the single sharp signal at 23.4 ppm in the ^{31}P NMR spectrum is very similar to that of HMPA.[11]

Coordination Ability of 2. In a recent paper,[4] cyclamphosphorane (**1**) was shown to act as a ligand when allowed to react with transition-metal derivatives such as $(Rh(CO)_2Cl)_2$, $Fe(CO)_2(NO)_2$, and $CpMo(CO)_3Cl$ to give adducts of the open phosphane tautomer, in which the latter behaves as a monodentate (through P) or a bidentate (through P and NH as in **3**; see Scheme I) ligand.

Its oxide, too, is a potential ligand, closely related to HMPA where its phosphorus donor site is concerned, and hence is expected to display a rather "hard", highly π-basic character through its phosphoryl group (the metal–phosphoryl bond is generally described as predominantly electrovalent, any π-back-donation from the metal being weak[12]). Several additional features are however built into the polycyclic structure of **2**: first, the free, flexible NH tentacle provides a second donor site capable of coordinating softer Lewis acids, which makes it a potential bidentate; second, the whole structure of the ligand is "enveloping" and asymmetric.

We have examined the coordination ability of **2** toward $(Rh(CO)_2Cl)_2$, which is known to react with amines[13] as well as with phosphoryl ligands[14] by splitting of its halogens bridges. When **2** is allowed to react with $(Rh(CO)_2Cl)_2$ in a Rh:ligand ratio of 1:1 in toluene at room temperature, no evolution of CO is observed and a yellow adduct that is readily soluble in toluene, is isolated. The analytical data are in good agreement with a mononuclear complex. The low $\nu(N{-}H)$ frequency of 3210 cm^{-1} in the IR spectrum indicates that the NH nitrogen is coordinated whereas the high $\nu(P{=}O)$ frequency of 1235 cm^{-1} (higher than that of **2**) points to a free PO group. In solution the product is further characterized by a ^{31}P resonance signal at +24.4 ppm, and the conductometric study is in agreement with a covalent structure. An X-ray structural investigation was performed on **5**, which definitively established the monodentate behavior of **2** through the NH amino group.

Table III. Selected Bond Lengths (Å) and Angles (deg) with Esd's

	Bond Distances		
P-O1	1.456 (2)	C1-C2	1.493 (5)
P-N2	1.657 (3)	C2-C3	1.541 (5)
P-N3	1.642 (3)	C4-C5	1.529 (5)
P-N4	1.637 (3)	C6-C7	1.531 (5)
		C7-C8	1.536 (5)
C1-N1	1.492 (4)	C9-C10	1.511 (4)
C10-N1	1.487 (4)		
C3-N2	1.478 (4)	N-H1	0.983 (3)
C4-N2	1.464 (4)	Rh-N1	2.118 (3)
C5-N3	1.455 (4)	Rh-Cl	2.319 (1)
C6-N3	1.456 (4)	Rh-C11	1.839 (4)
C8-N3	1.463 (4)	Rh-C12	1.832 (4)
C9-N4	1.466 (4)		
C11-O2	1.127 (4)	C12-O3	1.135 (4)
	Interatomic Distances		
H-Cl	2.306 (1)	H-P	3.154 (1)
H-N2	2.619 (3)	N-Cl	3.045 (3)
H-N4	2.692 (3)		
	Bond Angles		
N2-P-O1	113.9 (1)	C11-Rh-C12	91.5 (2)
N3-P-O1	121.1 (1)	C11-Rh-N1	92.3 (1)
N4-P-O1	110.2 (1)	N1-Rh-Cl	86.5 (1)
N2-P-N3	95.4 (1)	Cl-Rh-C12	89.7 (1)
N3-P-N4	101.4 (1)		
N4-P-N2	113.6 (1)	C12-Rh-N1	174.6 (1)
		C11-Rh-Cl	178.6 (1)
C6-N3-P	115.8 (2)		
C6-N3-C5	116.4 (3)	N1-C1-C2	110.1 (3)
P-N3-C5	112.7 (2)	C1-C2-C3	113.5 (3)
P-N2-C4	111.8 (2)	C2-C3-N2	112.5 (3)
P-N2-C3	120.6 (3)	N2-C4-C5	106.7 (3)
C4-N2-C3	115.2 (3)	C4-C5-N3	105.6 (3)
P-N4-C9	121.9 (2)	N3-C6-C7	113.8 (3)
P-N4-C8	117.7 (2)	C6-C7-C8	110.9 (3)
C9-N4-C8	117.7 (3)	C7-C8-N4	112.2 (3)
		N4-C9-C10	113.7 (3)
H-N1-Rh	83.1 (2)	C9-C10-N1	113.3 (3)
H-N1-C1	119.5 (3)		
H-N1-C10	110.3 (2)	Rh-C12-O3	175.2 (4)
Rh-N1-C10	109.3 (2)	Rh-C11-O2	178.4 (4)
C10-N1-C1	113.0 (3)		
Rh-N1-C1	118.0 (2)		
	Interatomic Angles		
N1-H-Cl	131.3 (2)	N1-H-P	99.8 (1)
N1-H-N2	110.7 (2)		
N1-H-N4	92.6 (2)	H-Cl-Rh	57.5 (0)

---

(10) Thomas, L. C. *The Identification of Functional Groups in Organophosphorus Compounds*; Academic: London, 1974; p 24.

(11) Scharzmann, E.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1960**, *82*, 6009.

(12) Joesten, M. D.; Hussain, M. S.; Lenhert, P. G. *Inorg. Chem.* **1970**, *9*, 151.

(13) Poilblanc, R.; Gallay, L. *J. Organomet. Chem.* **1971**, *27*, C53.

(14) Bandoli, G.; Clemente, D. A.; Deganello, G.; Carturan, G.; Uguagliati, P.; Belluco, U. *J. Organomet. Chem.* **1974**, *71*, 125.

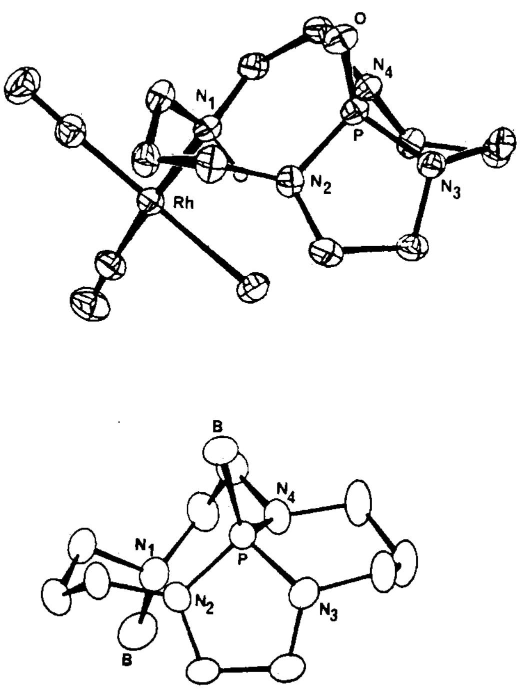


Figure 2. Conformations of the 6-membered ring in compounds **5** and **6** (bottom).

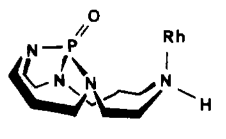
Molecular Structure of 5. In the solid state, the structure of **5** displays a NH site bound to the rhodium atom whereas the phosphoryl site remains free (Figure 1). The overall coordination geometry about Rh is close to square planar (the maximum deviation of the metal and ligand donor atoms from the coordination plane being only 0.04 Å) with two CO groups in cis positions.

The P═O bond length (1.456 (2) Å) is similar to that found in $OP(NMeCH_2)_3CMe$ (1.453 Å).[15] The Rh—N bond distance (2.118 (3) Å) is on the lower side of the range (2.07–2.25 Å)[16] usually observed for bonds between a Rh(I) and an aliphatic NH. The Rh–Cl bond length (2.319 (1) Å) is also comparable to those reported in similar complexes.[14]

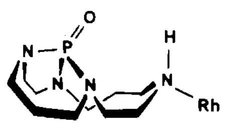
An interesting comparison can be drawn between **5** and cyclamphosphine–bis(borane) (**6**),[5] which both contain the same tricyclic tetraaminophosphine skeleton. Both also display a close-to-planar nitrogen atom, with a short P–N bond, and two rather pyramidal nitrogen atoms with longer P–N bonds. But in **5**, nitrogen N2, located in the bridgehead position between the 5- and 9-membered rings, is pyramidal (sum of bond angles around N2 ($\sum$N2) is 347.6 ± 2.4°) while it is planar in **6** ($\sum$N2 = 358.6 ± 3.0°), whereas nitrogen N4, in the bridgehead position between the 6- and 9-membered rings is planar in **5** ($\sum$N4 = 357.2 ± 2.1°) and pyramidal in **6** ($\sum$N4 = 348.8 ± 3.0°). This exchange of character between N2 and N4 is paralleled by changes in the P–N bond lengths: when one proceeds from **6** to **5**, P–N2 becomes longer (from 1.637 (4) to 1.657 (3) Å) while P–N4 becomes shorter (from 1.686 (3) to 1.637 (3) Å). The P–N3 bond length and the pyramidal character of N3 remain essentially the same in the two structures.

Some consequent effects appear in the conformation of the cycles: in **5** the 6-membered ring adopts a slightly distorted boat conformation in sharp contrast with the low-energy chair conformation found for this cycle in **6**. The 5-membered ring has a flattened envelope conformation whose tip is a carbon atom (C4) in **5** and the phosphorus atom in **6** (Figure 2).

Adduct **5** has two independent asymmetric centers (P and NH) and may, a priori, exist in two diastereoisomeric forms **5**′(*R*,*S*;*S*,*R*) and **5**″(*R*,*R*;*S*,*S*). Figure 1 shows that the diastereoisomer isolated is **5**′(*R*,*S*;*S*,*R*) as already observed with **6**. The single ^{31}P NMR signal observed for the crude reaction product indicates that it is the sole diastereoisomer (a pair of enantiomers) to form.



5'



5"

In this conformation the N1-bound hydrogen atom is located in the close neighborhood of the chlorine atom. The interatomic H–Cl distance of 2.306 (1) Å is shorter than the van der Waals approach, and probably indicates a bent hydrogen bond (a van der Waals radius of 1.0 Å for H and 1.8 Å for Cl are generally accepted[17,18]). The significant "squeezing" of the Rh–N1–H angle (83.1 (2)°) may be regarded as a consequence of the presence of such a hydrogen bond. Besides, the orthogonal orientation of the ligand's mean plane with respect to the square plane of the rhodium with the N-borne hydrogen located in the latter plane (Figure 1) may also be due to this hydrogen bond (H–N1–Rh–Cl torsion angle of −9.7 (1)°).

No intermolecular interactions were evidenced, the intermolecular contacts being not shorter than the van der Waals distances.

Cyclamphosphine Oxide as a Bridging Ligand. When the reaction of **2** with $(Rh(CO)_2Cl)_2$ is carried out in a two rhodium per ligand ratio and at low temperature (−30 °C) the binuclear complex **4** can be isolated in 70% yield as a microcrystalline powder. Adduct **4** is stable for several months when stored in an inert atmosphere at room temperature but decomposes in solution in toluene or CH_2Cl_2. The analytical and spectroscopical data indicates that **4** should be formulated as a binuclear complex (with toluene molecules as lattice molecules) and results from the displacement of both Rh–Cl–Rh bridges of $(Rh(CO)_2Cl)_2$ by cyclamphosphine oxide acting as a bidentate bridging ligand through both the phosphoryl oxygen and the secondary nitrogen donor sites. Characteristic infrared data are a ν(N–H) absorption at 3200 cm^{-1} typical of a metal-coordinated nitrogen atom and a strong band at 1170 cm^{-1} (no absorption at 1235 cm^{-1}), which also involves a coordinated PO group; two strong ν(CO) vibrations are found at 2090 and 2000 cm^{-1}. In the ^{31}P NMR spectrum the phosphoryl signal undergoes a downfield shift of 6 ppm with respect to **2** as expected from its coordination to a metal; no $^2J_{PRh}$ is observed, which is usual in such complexes.[19] No crystals appropriate for X-ray diffraction analysis could unfortunately be grown. Further evidence for this formulation is however brought by the fact that the reaction of **4** with 1 equiv of ligand **2** at low temperature gives adduct **5**, whereas the treatment of **5** with 0.5 equiv of $(Rh(CO)_2Cl)_2$ under the same conditions restores **4**. Thus, **4** is probably a stable intermediate in the reaction that leads to the mononuclear complex **5**.

These results show that both donor sites of cyclamphosphine oxide display a coordination ability toward rhodium(I); the coordination of the amino group appears however to be favored and is the sole product observed when the stoichiometry allows it. No mononuclear rhodium complex in which **2** behaves as a bidentate ligand has been observed to form, probably as a result of unfavorable steric arrangements, the smallest chelate cycle being a 7-membered one.

Supplementary Material Available: Tables SI and SII, listing thermal parameters and the derived hydrogen positions (2 pages); a table of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

---

(15) Clardy, J. C.; Kolpa, R. L.; Verkade, J. G. *Phosphorus* **1974**, *4*, 133.

(16) Bonnet, J.-J.; Jeannin, Y.; Maisonnat, A.; Kalck, P.; Poilblanc, R. *C. R. Seances Acad. Sci., Ser. C* **1975**, *281*, 15. Colquhoun, H. M.; Doughty, S. M.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 135. Bondoux, D.; Mentzen, B. F.; Tkatchenko, I. *Inorg. Chem.* **1981**, *20*, 839. Louie, B. M.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1985**, *63*, 3019.

(17) Olovsson, I.; Jonsson, P.-G. *The Hydrogen Bond*; Schuster P., Zundel, G., Sandorfy, C., Eds.; North-Holland: Amsterdam, 1976; Vol. 2, Chapter 8.

(18) Weast, R. C., Ed. *Handbook of Chemistry and Physics*; 60th ed.; CRC Press: Boca Raton, FL, 1979–1980; p D-194.

(19) Uson, R.; Oro, L. A.; Ciriano, M. A.; Lahoz, F. J.; Bello, M. C. *J. Organomet. Chem.* **1982**, *234*, 205.

(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.