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Synthetic, Structural, and Catalytic Studies on Ethylene and Carbonyl Complexes of Rhodium(I) Containing 2-Alkoxy-1,3-dioxa-6,9-diaza-2-phosphacycloundecane Ligands

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The title compounds are produced by addition of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ or $[Rh(C_2H_4)_2(\mu\text{-}Cl)]_2$ to the appropriate, potentially tridentate, macrocyclic ligand. Crystallographic study of $[Rh(CO)(Cl)(6,9\text{-}Me_2\text{-}2\text{-}OMe\text{-}1,3,6,9,2\text{-}O_2N_2PC_6H_{12})]$ reveals that while all three donor atoms of the 11-membered macrocycle are formally associated with the rhodium center, one Rh–N bond is extremely long, 2.570 (5) Å, affording a geometry at the metal center that is intermediate between 4- and 5-coordinate. The origin of such distortion is traced to congestion within the macrocycle. It is suggested that the intermediacy of the structure between a planar 16e and trigonal-bipyramidal 18e configuration is related to the catalytic activity of these complexes. Crystals are orthorhombic, space group *Pbca*, with $a = 13.5964$ (15) Å, $b = 15.367$ (2) Å, $c = 14.621$ (2) Å, and $Z = 8$. With use of 2108 diffracted intensities recorded at 268 ± 1 K on an Enraf-Nonius CAD4 diffractometer the structure has been refined to $R = 0.0548$, $R_w = 0.0580$. The title complexes are shown to be good precursors for the catalytic hydroformylation of olefins. Catalytic asymmetric induction during styrene hydroformylation has given only 0.6% enantiomeric excess of hydratropaldehyde with the neomenthyl-substituted ligand in the presence of $[Rh(H)(Cl)(PPh_3)_3]$. However, these new ligands give complexes that are more effective than the classical 2,3-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ligand (DIOP) for aldehyde production under very mild conditions.

Introduction

Recently, we have been interested in the use of aminophosphine ligands to enhance regioselectivity in normal aldehydes during the catalytic hydroformylation of olefins on rhodium catalysts.[2-4]

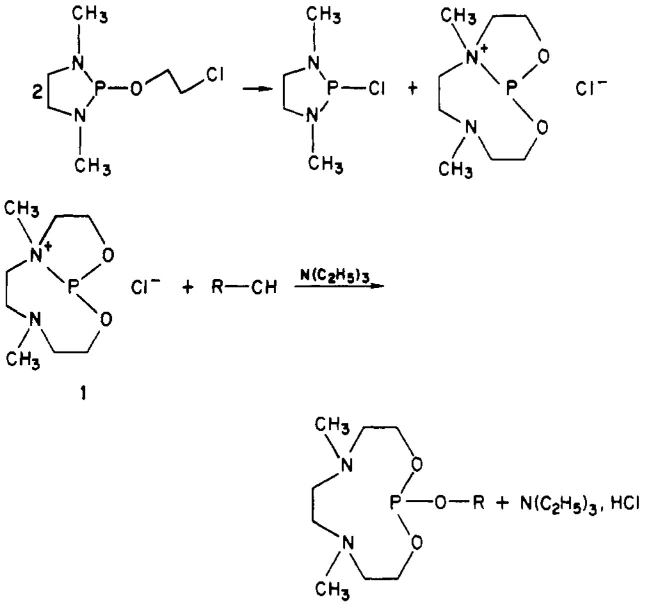
Such ligands, of general formula $(PPh_2)NR_1R_2$ (R_1, R_2 = alkyl, aryl), were chosen because of their very simple syntheses, by which the electron density on the metal could be easily changed upon variation of the nature of the substituents, and their ability to increase catalytic activity in codimerization reactions on nickel-based complexes[5] and to induce the best catalytic asymmetric induction during this carbon–carbon bond formation when chiral centers are introduced on the nitrogen substituents.[6] However, the failure to obtain good optical yields in styrene hydroformylation with chiral aminophosphine complexes[7] prompted us to look at new macrocyclic, potentially tridentate, ligands containing one phosphorus and two nitrogen atoms, in which chirality could be easily introduced.[8]

These latter compounds are of interest as ligands because of the differing affinities of nitrogen and phosphorus for metal centers, with the resultant possibility that the Rh–N bond might be more labile than Rh–P. During catalysis, this effect should be of particular utility under mild conditions, where one might suggest that only a Rh–N bond is broken; this specific dissociation could produce a coordinatively unsaturated species in which the Rh–P linkage is not dissociated, in order to hold the asymmetric center (when chiral substituents are linked to phosphorus) in close proximity to the metal. X-ray diffraction has been used to unambiguously characterize a suitably crystalline member of the family of complexes containing the macrocyclic ligand and to see if any clue to the mechanism of possible catalytic activity was discernible in the solid state. Subsequently, these complexes will be tested as potential catalytic precursors for classical and asymmetric hydroformylation according to the achiral or chiral nature of the macrocyclic ligand.

Experimental Section

All solvents were dried and degassed prior to use and all reactions carried out under an atmosphere of dinitrogen. The infrared spectra were recorded on an I.R. 12 Beckman spectrometer. Spectra of the rhodium complexes were done as CsI disks. The photoelectron spectra were obtained with an AEI ES 200 spectrometer, with either the C_{1s} (285 eV) or the Cl_{2p} (198.2 eV) binding energy taken as reference. NMR spectra were recorded on a Bruker WP 60 spectrometer.

Synthesis of Macrocyclic Ligands. The macrocyclic ligands were prepared according to the sequence[8]



The synthesis of the chloro compound 1 has already been described.[8]

6,9-Dimethyl-2-methoxy-1,3-dioxa-6,9-diaza-2-phosphacycloundecane (1a). All operations were carried out under nitrogen.

A solution of methanol (1.28 g, 40 mmol) in dried diethyl ether (100 mL) was added dropwise, with stirring, to a solution of the chloro compound (1) (9.6 g, 40 mmol) and triethylamine (40 mmol) in CH_2Cl_2 (40 mL).

After it stood for 2 h at ambient temperature, the triethylamine hydrochloride was filtered off and the solvents were removed by rotary evaporation. The residue was distilled at 70 °C (0.05 mm) as a

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(3) Grimblot, J.; Bonnelle, J. P.; Vaccher, C.; Mortreux, A.; Petit, F.; Peiffer, G. *J. Mol. Catal.* **1980**, *9*, 357.

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Table I. Synthesis and Analytical Data of 6,9-Dimethyl-2-alkoxy-1,3-dioxa-6,9-diaza-2-phosphacycloundecanes

starting alcohol (ligand)	bp, °C (p, mm)	yield, %	^{31}P NMR (H_3PO_4)		anal., % C	H	N
EtOH (**1b**)	80 (0.05)	80	142.3	calcd	48.04	9.27	11.20
				found	47.96	9.39	11.33
2-butanol (**1c**)	85 (0.05)	80	143	calcd	51.78	9.78	10.07
				found	51.25	9.98	10.06
(*S*)-(−)-2-methyl-1-butanol (**1d**)	80 (0.001)	75	143	calcd	53.41	10.00	9.58
				found	53.53	9.83	9.43
1-menthol (**1e**)	130 (0.001)	65	144.6	calcd	59.98	10.35	7.77
				found	59.93	10.53	7.44

Table II. NMR Spectroscopic Data for Compounds **1a**, **2a**, and **3a**[d]

	^{1}H,[a] δ		^{13}C,[b] δ		^{31}P,[c] δ		
	1a	**2a**	**1a**	**2a**	**1a**	**2a**	**3a**
OCH_3	3.4 d ($^3J = 10$)	3.6 d ($^3J = 11$)	48.9 d ($^2J = 9$)	50.9 d ($^2J = 9$)	139	96.8 ($J = 172$)	95.2 ($J = 171$)
NCH_2CH_2OP (*CH*$_2$OP)	3.6–4.3 m	4.1–4.5 m	61.5 d ($^2J = 11$)	63.5 d ($^2J = 22$)			
N*CH*$_2$*CH*$_2$N	2.5 s	2.82 s	56.3 s	54.4 s			
NCH_3	2.3 s	2.75 s	44.4 s	49.6 s			
N*CH*$_2$CH$_2$OP	2.4–2.9 m	2.4–2.9 m	58.7 d ($^3J = 3$)	59.45 d ($^2J = 8$)			
C=O				189.5 dd ($^1J = 42$, $^2J = 21$)			

[a] Solutions in $CDCl_3$, downfield shifts from Me_4Si. [b] Solutions in Me_2SO, downfield shifts from Me_4Si. [c] Solutions in $CDCl_3$, downfield shifts from H_3PO_4. [d] All J values in Hz.

Table III. Spectroscopic Data for Compounds **2** and **3**

	2a	2b	2c	2d	2e	3a	3b	3c	3d
$\nu_{C=O}$,[a] cm^{-1}	1969	1966	1971	1966	1961				
ν_{Rh-Cl}, cm^{-1}	300	292	300	285	291				
BE(N_{1s}),[b] eV	401.2 (398.9)	400.6 (398.9)	400.6 (398.9)	400.8 (399)		400.05	400.4	399.2	400.8
BE(P_{2p}), eV	133.7 (132.75)	133.65 (132.7)	133.55 (132.6)	133.9 (132.6)		133.3	133.5	132.3	133.3
BE($Rh_{3d_{5/2}}$), eV	309.1	308.75	309.7	309.9		308.8	308.6	307.7	308.9
BE(O_{1s}), eV	533.3 (532.1)	532.8 (532.1)	532.7 (532.2)	532.7 (532.1)		532.75	532.8	532.1	532.7
$I(Cl_{2p})/I(Rh_{3d_{5/2}})$[c]	0.23	0.213	0.19	0.34		0.26	0.237	0.217	0.34
$I(N_{1s})/I(Rh_{3d_{5/2}})$	0.288	0.251	0.23	0.266		0.238	0.248	0.226	0.17
$I(P_{2p})/I(Rh_{3d_{5/2}})$	0.154	0.142	0.157	0.162		0.10	0.123	0.133	0.10

[a] In CsI disks. [b] In parentheses are given the binding energies of the free ligands. [c] Intensity ratios of the photoelectronic signals. The binding energies are calculated by taking BE(Cl_{2p}) = 198.2 eV as reference in the complexes and BE(C_{1s}) = 285 eV in the free ligands.

Table IV. IR and ESCA Spectroscopic Data for Compounds **4**[a]

compd	$\nu_{C=O}$, cm^{-1}			BE(N_{1s}), eV	BE(P_{2p}), eV	BE($Rh_{3d_{5/2}}$), eV	BE(O_{1s}), eV	$I(Cl_{2p})/I(Rh_{3d_{5/2}})$	$I(N_{1s})/I(Rh_{3d_{5/2}})$	$I(P_{2p})/I(Rh_{3d_{5/2}})$
4a	1714	1986	2070	400.15	133.8	309.25	532.75	0.317	0.317	0.126
4b	1721	1992	2060	400.1	133.85	309.25	532.25	0.307	0.26	0.15
4c	1725	1987	2070	400.9	133.8	309.75	533.05	0.211	0.204	0.124
4d	1725	1986	2064							
4e	1730	1987	2069							

[a] The conditions are the same as in Table III.

colorless liquid (yield 75%). Anal. calcd for $C_9H_{21}H_2O_3P$: C, 45.76; H, 8.96; N, 11.86. Found: C, 45.78; H, 8.84; N, 11.80. For NMR data, see Table II (**1a**).

This general procedure was used to prepare and analyze the ligands depicted in Table I, where the R groups are ethyl (**1b**), *sec*-butyl (**1c**), (*S*)-(−)-2-methyl-1-butyl (**1d**), and menthyl (**1e**).

Synthesis of Rhodium Complexes of the Macrocyclic Ligands. Synthesis of the Carbonyl Complexes RhCl(CO)(PN$_2$) (2). To a yellow solution of $Rh_2Cl_2(CO)_4$ (0.507 g, 1.3 mmol) in 55 mL of benzene was added slowly 15 mL of a benzene solution of 0.616 g (2.61 mmol) of the macrocyclic methoxy ligand described above. The reaction was conducted under nitrogen in the dark. Stirring was continued for 30 min. Simultaneous to the carbon monoxide evolution, a purple compound **4a** precipitated from the solution. After filtration, yellow needles of **2a** crystallized from the mother liquor upon standing (yield 40%). Anal. Calcd for RhCl(CO)(PN$_2$) (**2a**), $C_{10}H_{21}N_2O_4PClRh$: C, 29.90; H, 5.22; N, 6.96; O, 15.90; P, 7.70; Cl, 8.81. Found: C, 30.26; H, 5.28; N, 7.02; O, 15.75; P, 7.43; Cl, 8.56. For NMR data, see Table II.

Similar complexes are prepared according to the same procedure from the rhodium carbonyl chloro dimer and ligands **1b–e** (Table III).

Synthesis of the Ethylenic Complex RhCl(C$_2$H$_4$)(PN$_2$) (3a). To an orange solution of 0.133 g (0.34 mmol) of $Rh_2(C_2H_4)_4Cl_2$ in 15 mL of benzene is added 5 mL of a benzene solution of 0.161 g (0.68 mmol) of ligand **1a**. The solution becomes yellow, and stirring is continued for 1 h. A yellow precipitate appears. It is purified by washing with benzene and petroleum ether; mp 210–215 °C dec. The solid is stable in air, but the solutions are air unstable. Anal. Calcd for RhCl(C_2H_4)(PN$_2$) (**3a**), $C_{11}H_{25}N_2O_3PClRh$: C, 32.80; H, 6.21; N, 6.96; O, 11.93; P, 7.70; Cl, 8.82. Found: C, 33.22; H, 6.19; N, 6.98; O, 12.03; P, 7.51; Cl, 9.08. IR: $\nu_{C=C}$ = 1473 cm^{-1}.

The same procedure is used to prepare complexes **3b–d** from ligands **1b–d** (Table III).

Synthesis of the Unknown Purple Complexes 4. In addition to the target complexes **2**, a purple complex **4** is always produced during reaction between $Rh_2Cl_2(CO)_4$ and the macrocyclic ligand. Complexes having the same characteristics can be obtained upon addition of carbon monoxide to either **2** or **3** in benzene. These purple compounds were purified by several washings with benzene; they exhibit identical patterns of $\nu_{C=O}$ vibrations in the 2100–1700-cm^{-1} range (Table IV). Although several attempts were made, with many solvents, it has been impossible to obtain crystals suitable for X-ray analysis, so that the structures of these new complexes are not known at present. Their solutions are air and light sensitive, and spectroscopic data indicate the following:

(1) The unusually low $\nu_{C=O}$ vibrations observed in these complexes ($1714 < \nu < 1730$ cm^{-1}) are consistent with a μ-C=O-bridged complex also bearing terminal CO groups ($\nu_{C=O} > 1986$ cm^{-1}, two bands).

(2) Preliminary experiments conducted with an electronic microprobe indicate that the P/Rh ratio is the same as in complexes **2** and **3**.

(3) From ESCA data (Table IV), it is also established that both nitrogen and phosphorus atoms are coordinated to the metal, as the binding energies of these atoms are higher (>1.2 eV) than in the free ligand and are similar to those observed for complexes **2** and **3** (Table IV). Furthermore, the symmetry of the N_{1s} signal observed in each case seems to indicate that the nitrogen atoms are equivalent. However, the product becomes orange in the electron beam, so that these data are not conclusive.

(4) Due to the instability of the methoxy complex **4a**, analytical data measured gave nonreproducible results. However, they are suitable for a dinuclear 18e complex for which the formula $[Rh_2Cl_2(PN_2)_2(\mu\text{-}CO)(CO)_2]$[22] can be tentatively assigned. In this complex, we assume that the tridentate ligand acts as bidentate, with a formal Rh–Rh bond. Further work needs to be done on these highly sensitive complexes in order to unambiguously establish their structure.

Molecular Structure Determination of 2a. A single crystal, ca. 0.04 × 0.03 × 0.02 cm, was sealed (epoxy-resin adhesive) inside a 0.05 cm diameter Lindemann tube under an atmosphere of dry, oxygen-free nitrogen. Preliminary Weissenberg and precession photographs (Cu Kα X radiation) yielded the space group and approximate cell dimensions. For accurate values and intensity data measurement the same crystal was set on an Enraf-Nonius CAD4 diffractrometer and cooled (cold air stream) to 268 ± 1 K. After an initial cell had been generated following the automatic centering of 25 relatively low-angle reflections ($9 < \theta < 12°$, Mo Kα X radiation, $\lambda = 0.71069$ Å), an asymmetric fraction of intensity data in the range $13.5 \leqslant \theta \leqslant 14°$ was rapidly recorded, from which 25 strong reflections were chosen and centered. The final cell dimensions and orientation matrix were generated by a least-squares fit. Crystal data: $RhC_{10}ClH_{21}N_2O_4P$; mol wt 402.5; space group *Pbca* (No. 61); $Z = 8$; $a = 13.5964$ (15), $b = 15.367$ (2), $c = 14.621$ (2) Å; $V = 3054.9$ (19) Å^3; μ(Mo Kα) = 12.75 cm^{-1}; $d_{calcd} = 1.750$ g cm^{-3}, $d_{obsd} = 1.75$ g cm^{-3}; $F(000) = 1632$.

Collection and Reduction of the Data. Three-dimensional intensity data ($h \geqslant 0$, $k \geqslant 0$, $l \geqslant 0$) were recorded, with use of a θ–2θ scan in 96 steps, in the range $1.5 < \theta < 27.0°$. Scan widths were given by $A + B \tan\theta$ with $A = 0.85$ and $B = 0.35$. After rapid prescan only those reflections considered significantly intense, $I \geqslant 1.0\sigma(I)$, were rescanned such that the final net intensity had $I > 33\sigma(I)$ subject to a maximum counting time of 60 s. Two standard reflections were remeasured once every 3600 s of X-ray exposure time, but subsequent analysis of their net counts as individual functions of time indicated no crystal decomposition or movement, or source variance, over the data collection period (ca. 49 h). Data were corrected for Lorentz and polarization effects but not for X-ray absorption. Of 3325 reflections measured, 2108 had $F_o \geqslant 2.0\sigma(F_o)$ and were retained for structure solution and refinement.

Solution and Refinement of the Structure. The position of the rhodium atom was deduced by analysis of the Patterson function and, together with the arbitrarily assigned thermal parameter[9] $U = 0.04$ Å^2, was refined to $R = 0.38$. An accompanying difference electron density synthesis yielded all remaining non-hydrogen atoms. With rhodium allowed anisotropic thermal vibration, further refinement of all located atoms reduced R to 0.083. Structure factors were weighted according to $w^{-1} = \sigma^2(F_o) + 0.00106(F_o^2)$, and all non-H atoms were assigned anisotropic thermal parameters. Methylene hydrogens were introduced into calculated positions (C–H = 1.08 Å, $U_H = 0.06$ Å^2) and allowed to ride on their respective carbon atoms, while methyl functions were treated as rigid groups (C–H = 1.08 Å, $U_H = 0.06$ Å^2). The 181 variables (including overall scale factor) were optimized by full-matrix least-squares refinement (data/variable ratio better than 11/1), which converged at $R = 0.0548$ and $R_w = 0.0580$, defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum_w(|F_o - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The estimated standard deviation of an observation of unit weight was 1.9. The maximum residue on a final difference map was less than 0.95 e Å^{-3}.

Table V. Fractional Coordinates of Refined Atoms in 2a

atom	*x*	*y*	*z*
Rh	0.22378 (4)	0.09669 (3)	−0.00667 (3)
Cl	0.33286 (15)	0.05233 (15)	0.11585 (12)
C(12)	0.1620 (6)	0.1634 (5)	0.0753 (5)
O(12)	0.1240 (5)	0.2046 (5)	0.1296 (4)
O(1)	0.0336 (3)	0.0710 (3)	−0.1308 (3)
C(11)	0.0562 (6)	−0.0153 (5)	−0.1634 (5)
C(10)	0.0945 (5)	−0.0770 (5)	−0.0908 (5)
N(9)	0.1940 (4)	−0.0614 (4)	−0.0570 (3)
C(8)	0.2704 (5)	−0.0824 (5)	−0.1250 (5)
C(7)	0.3619 (5)	−0.0293 (5)	−0.1098 (5)
N(6)	0.3438 (4)	0.0658 (4)	−0.1157 (3)
C(5)	0.3248 (5)	0.0905 (5)	−0.2125 (4)
C(4)	0.2644 (5)	0.1703 (5)	−0.2226 (5)
O(3)	0.1616 (4)	0.1543 (3)	−0.2082 (3)
P(2)	0.11995 (12)	0.13755 (12)	−0.10786 (10)
C(91)	0.2072 (6)	−0.1151 (5)	0.0262 (5)
C(61)	0.4348 (5)	0.1122 (6)	−0.0862 (5)
O(21)	0.0562 (3)	0.2207 (3)	−0.0853 (3)
C(21)	−0.0102 (5)	0.2597 (5)	−0.1501 (6)

Structure solution and refinement were carried out with the SHELX76 system,[10] implemented on the University of London Computer Centre CDC 7600 machine. Atomic scattering factors were calculated by using coefficients taken from ref 11a, appropriately corrected for anomalous dispersion by using published $\Delta f'$ and $\Delta f''$ values.[11b] Molecular geometry calculations were performed with the program XANADU[12] and plots constructed with ORTEP-II.[13]

Catalytic Reactions. For all reaction tests, a 300-mL stainless steel autoclave was used. The reactions were conducted in benzene (10 mL) at 80 °C with 1-hexene (5 mL) as substrate (olefin/Rh = 1000; $CO/H_2 = 1/1$; $P = 25$ atm; $t = 15$ h).

Olefin conversion and selectivities were determined by gas chromatography. For styrene hydroformylation, two different procedures have been retained: one the same as for 1-hexene, but with addition of 1 equiv of triethylamine ($Rh/NEt_3 = 1$), and a second series of experiments with an excess of ligand ($Rh/NEt_3 = 1$; L/Rh = 3).

Asymmetric catalysis at lower temperature with ligands **1d** and **1e** has been performed according to Pino's procedure,[14] by starting with $[Rh(H)(CO)(PPh_3)_3]$ as precursor, with an excess of chiral ligand: to 11.4 mL (0.1 mol) of styrene in 27.7 mL of benzene are added 230 mg (0.25 mmol) of $[Rh(H)(CO)(PPh_3)_3]$ and 1 mmol of the chiral ligand. The solution is stirred for 48 h at 40 °C under CO/H_2 (1/1, 1 atm) and analyzed by GPC for conversion and selectivity measurements, expressed by the normal/branched aldehyde ratio (hydrocinnamaldehyde/hydratropaldehyde).

The optical yields were determined on a Perkin-Elmer 141 differential polarimeter with neat hydratropaldehyde, purified by distillation of the catalytic solutions under vacuum.

Results and Discussion

From comparison of the spectroscopic properties of complexes **2a–e** and **3a–e** all appear to be isostructural, and their ESCA results are consistent with the macrocyclic ligand utilizing all three potential donor atoms in coordination to the Rh(I) center. The unequivocal structure of **2a**, at least in the solid state, has been established and will subsequently be discussed. Unfortunately, as indicated in the Experimental Section, single crystals suitable for a diffraction study could not be obtained from any of the series of purple compounds **4a–e**.

Molecular Structure of 2a. A perspective view of single molecule, demonstrating the atomic numbering scheme

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[9] The form of the isotropic thermal motion is given by $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

[10] G. M. Sheldrick, University Chemical Laboratory, Cambridge, England, 1976.

[11] "International Tables for X-ray crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) p 99; (b) p 149.

[12] G. M. Sheldrick, and P. Roberts, University Chemical Laboratory, Cambridge, England, 1976.

[13] Johnson, C. K. *Oak Ridge Natl. Lab.*, [*Rep.*] *ORNL* (*U.S.*) **1976**, *ORNL-5138*.

[14] Salomon, C.; Consiglio, G.; Botteghi, C.; Pino, P. *Chimia* **1973**, *27*, 215.

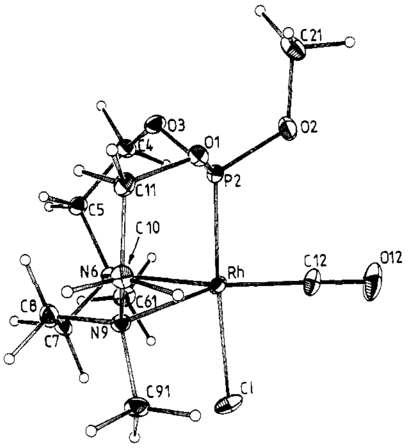

Figure 1. Perspective view of **2a** and atomic numbering scheme. Thermal ellipsoids are drawn at the 30% electron probability level, except for H atoms, which are given an artificial radius of 0.1 Å for clarity.

Table VI. Interatomic Distances (Å) in **2a**

Rh-Cl	2.423 (2)	C(8)-C(7)	1.504 (10)
Rh-C(12)	1.787 (7)	C(7)-N(6)	1.485 (8)
C(12)-O(12)	1.139 (8)	N(6)-C(61)	1.491 (8)
Rh-N(9)	2.570 (5)	N(6)-C(5)	1.488 (8)
Rh-N(6)	2.330 (5)	C(5)-C(4)	1.484 (10)
Rh-P(2)	2.1392 (16)	C(4)-O(3)	1.435 (8)
O(1)-C(11)	1.443 (8)	O(3)-P(2)	1.594 (4)
C(11)-C(10)	1.517 (10)	P(2)-O(1)	1.592 (5)
C(10)-N(9)	1.460 (8)	P(2)-O(2)	1.578 (5)
N(9)-C(91)	1.480 (8)	O(2)-C(21)	1.440 (9)
N(9)-C(8)	1.473 (8)		

Table VII. Interbond Angles (deg) in **2a**

P(2)-Rh-Cl	176.07 (7)	Rh-N(9)-C(10)	113.5 (4)
P(2)-Rh-C(12)	89.2 (2)	Rh-N(9)-C(8)	106.8 (4)
P(2)-Rh-N(9)	88.60 (13)	Rh-N(9)-C(91)	105.8 (4)
P(2)-Rh-N(6)	92.81 (13)	C(10)-N(9)-C(8)	112.9 (5)
Cl-Rh-C(12)	87.3 (2)	C(10)-N(9)-C(91)	107.4 (5)
Cl-Rh-N(9)	92.41 (13)	C(8)-N(9)-C(91)	110.3 (5)
Cl-Rh-N(6)	91.13 (13)	N(9)-C(8)-C(7)	111.4 (6)
C(12)-Rh-N(9)	131.3 (3)	C(8)-C(7)-N(6)	112.8 (5)
C(12)-Rh-N(6)	154.8 (3)	Rh-N(6)-C(7)	106.1 (4)
N(9)-Rh-N(6)	73.9 (2)	Rh-N(6)-C(5)	118.5 (4)
Rh-P(2)-O(1)	116.3 (2)	Rh-N(6)-C(61)	106.6 (4)
Rh-P(2)-O(3)	116.7 (2)	C(7)-N(6)-C(5)	109.6 (6)
Rh-P(2)-O(2)	117.1 (2)	C(7)-N(6)-C(6)	108.4 (5)
O(1)-P(2)-O(3)	99.9 (3)	C(5)-N(6)-C(61)	107.3 (5)
O(1)-P(2)-O(2)	99.1 (3)	N(6)-C(5)-C(4)	113.7 (5)
O(3)-P(2)-O(2)	104.9 (3)	C(5)-C(4)-O(3)	112.5 (6)
P(2)-O(1)-C(11)	120.2 (4)	C(4)-O(3)-P(2)	120.6 (4)
O(1)-C(11)-C(10)	114.6 (5)	P(2)-O(2)-C(21)	122.9 (5)
C(11)-C(10)-N(9)	116.9 (6)	Rh-C(12)-O(12)	178.0 (8)

adopted, is given in Figure 1. Table V lists final positional parameters of refined atoms. Anisotropic thermal parameters (Table XI), hydrogen positional parameters (Table XII), and a comparison of observed and calculated structure factors (Table XIII) have been deposited as supplementary material. In Table VI are listed the bond distances and in Table VII the interbond angles derived.

The coordination geometry of the metal atom in **2a** is perhaps best regarded as intermediate between formally 4- and 5-coordinate. Both Rh-N distances are long, but this is especially true of Rh-N(9) (2.570 (5) Å). We believe this to be a consequence of the geometrical requirements of the tridentate cyclic ligand (vide infra) and, as such, crucial to understanding the catalytic properties of this class of compound. If one ignores the Rh-N(9) linkage, **2a** is formally a 16e "planar" Rh(I) complex whose π-acceptor ligands (the carbonyl and phosphite functions) occupy their expected relative cis positions. Including N(9), the geometry at the (now 18e) center is perturbed toward trigonal bipyramidal (TBP), with P(2) and Cl occupying axial sites. Strong π-acceptor ligands of d^8 TBP complexes should, omnia paribus, occupy equatorial coordination positions since π-interaction is thereby maximized.[15-17] Clearly, both π-acceptor ligands cannot occupy positions that are cis in a formally square-planar geometry and, at the same time, both equatorial in a formally TBP one, and in terms of the latter formalism the phosphine moiety (the weaker π acceptor) stands axially to the metal. There is substantial evidence that the carbonyl ligand is strongly π bonded to the metal, as evidenced by the short[18] Rh-C(12) bond (1.787 (7) Å) and by the fact the C(12)-O(12) bond (1.139 (8) Å) is longer, although not significantly so, than that in free carbon monoxide.[19] Even though axial to the "5-coordinate" metal, however, π bonding to P(2) is by no means excluded since the (occupied) Rh $4d_{xz}$ and $4d_{yz}$ orbitals are of suitable symmetry for $d\pi$–$d\pi$ overlap, and certainly the Rh-P distance, 2.1392 (16) Å, is reasonably short.[16,20]

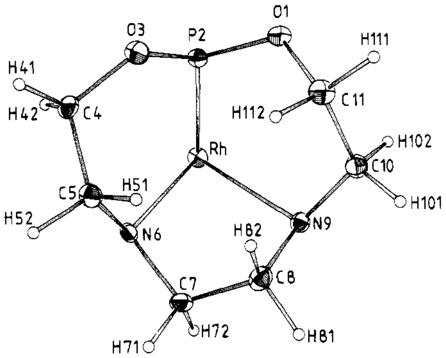

Figure 2. View through the 11-atom tridentate ligand for **2a**. The methoxy and methyl functions are omitted for clarity, as are the carbonyl and chloride ligands.

Table VIII. Catalytic Results for Hex-1-ene Hydroformylation at 80 °C[a]

complex	aldehyde, %	hex-2-ene, %	heptanal/ branched aldehydes
2a	38	56	2.43
2b	29	50	2.57
2c	50	48	1.7
2d	38	45	2
2e	40	39	2.2

[a] See Experimental Section for details: $CO/H_2 = 1/1$; solvent = benzene.

Interbond angles at Rh between axially and equatorially situated atoms lie in the fairly narrow range 87.3 (2)–92.81 (13)°, and that defined by P(2)-Rh-Cl is 176.07 (7)°. Angles between equatorial ligands alone are not so regular and reflect the intermediate nature of the metal coordination. Thus C(12)-Rh-N(6) is reduced from 180° for planar coordination toward 120° for a TBP geometry, the measured value, 154.8 (3)°, being not far from halfway between the two.

We have earlier suggested that the catalytic activity of compounds **2** and **3** might be linked to our observation of a long Rh-N(9) bond in **2a** and that this in turn is a consequence of intraligand crowding within the tridentate ligand. We now

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Table IX. Catalytic Results for Styrene Hydroformylation at 80 °C[a]

	2a		2b		2c		2d		DIOP	
	b	*c*	*b*	*c*	*b*	*c*	*b*	*c*	*b*	*c*
aldehydes, %	50	40	50	42	100	100	71	63	97	98
ethylbenzene, %	4	2	4	2	0	0	1	0	2	0
normal/branched aldehyde	0.91	0.32	0.9	0.3	0.41	0.13	0.73	0.23	0.34	0.63

[a] Conditions same as in Table VIII. [b] 1 equiv of NEt_3/equiv of rhodium added before catalysis. [c] With 1 equiv of NEt_3/equiv of rhodium and 3 equiv of ligand/equiv of rhodium.

Table X. Asymmetric Hydroformylation of Styrene at 40 °C[a]

ligand	aldehydes, %	normal/ branched aldehyde	ee	confign
DIOP (+)	20	0.59	12	*S*
1e (−)	96	0.25	0.6	*R*
1d (−)	50	0.17	0	

[a] See Experimental Section for details.

attempt to document our reasoning.

In Figure 2 the rhodium atom is viewed through the 11-membered ring, from which OMe and Me substituents have been removed for clarity. Table XIV (supplementary material) lists details of hydrogen-bonding and nonbonding contacts, and Table XV (supplementary material) contains information relating to best (least-squares) molecular planes. Of relevance to the present discussion is the observation that the coordinated ethylenediamine fragment adopts its usual[21] skew-ring conformation but that C(8) is only ca. 0.02 Å above the RhN_2 plane whereas C(7) is ca. 0.68 Å below it. H(82) stands axially to this 5-membered ring. The two saturated RhPOCCN rings are distinctly buckled, but the H atoms on their methylene carbons occupy positions that may be described as approximately axial or equatorial to the respective rings. Given the position of H(82), H(101) is clearly required to lie equatorially, and H(112) is consequently axial. It is likely that in turn the position of H(112) requires H(41) to lie equatorially and thus H(51) axially. This overall arrangement appears to be an inevitable consequence of the ligand's tridentate coordination but results in very short intraligand H(82)···H(112) and H(82)···H(51) contacts. As measured these are 2.03 and 1.91 Å, respectively. They would clearly be even more severe were not the ligand to distort in the most efficient manner possible, a concerted bend-back of $C(8)H_2$ and the dramatic lengthening of Rh–N(9). We suggest, very simply, that the already weakened Rh–N(9) bond is readily fractured to generate the coordinatively and electronically unsaturated center necessary for catalytic activity.

Figure 3 (supplementary material) presents a view of the crystal packing. There are two fairly weak unique H···Cl intermolecular contacts that might be indicative of some hydrogen bonding (Table XIV), although for the shorter of these, H(112) to Cl at $^1/_2 - x, -y, ^1/_2 + z$, the angle at Cl is far from tetrahedral. All H···H intramolecular contacts are >2.2 Å.

Catalytic Results. In Table VIII are reported the catalytic results obtained with $RhCl(CO)(PN_2)$[22] as catalytic precursors for hex-1-ene hydroformylation.

The above regioselectivities are consistent with most of the results generally obtained on aminophosphine complexes, but a particularly high extent of isomerization in hex-2-ene is observed for these new compounds, which explains the rather poor yield in aldehydes, as the hydroformylation rates for internal olefins are well-known to be much slower than for α-olefins.

Under similar conditions, in the presence of 1 equiv of triethylamine and with an excess of ligand, the regioselectivity in aldehydes during styrene hydroformylation favors in each case the production of hydratropaldehyde, more than does the classical DIOP complex (Table IX).

This beneficial effect for hydratropaldehyde production is confirmed upon working at lower temperature, under conditions that are suitable for asymmetric induction: the normal to branched aldehyde ratio is again lower for our new PN_2 complexes than with the DIOP system, as shown in Table X.

Unfortunately, in this last table, one can see that the enantiomeric excesses are very poor with these new ligands, as only a 0.6% ee is obtained with the neomenthyl (PN_2*) ligand. However, the chemical yields obtained are interesting in this respect: they show that these phosphite type complexes, in which chelating nitrogen moieties are introduced, could be useful in undergoing catalytic hydroformylation under very mild conditions as the activity is greatly increased. This last observation provides us with a promising opportunity for the enhancement of asymmetric induction upon working at lower temperature[23] or by the generation of catalytic species by electrochemical means at ambient temperature from RhCl(CO)(PN_2*) complexes.[24] Further work is in progress in this direction.

Registry No. 1, 64762-33-0; **1a**, 64762-31-8; **1b**, 64762-32-9; **1c**, 92014-37-4; **1d**, 92014-38-5; **1e**, 92014-39-6; **2a**, 92055-20-4; **2b**, 92055-21-5; **2c**, 92055-22-6; **2d**, 92055-23-7; **2e**, 92055-24-8; **3a**, 92078-15-4; **3b**, 92055-25-9; **3c**, 92055-26-0; **3d**, 92055-27-1; **4a**, 92055-28-2; $Rh_2Cl_2(CO)_4$, 14523-22-9; $Rh_2(C_2H_4)_4Cl_2$, 12081-16-2; $[Rh(H)(CO)(PPh_3)_3]$, 17185-29-4; methanol, 67-56-1; ethanol, 64-17-5; 2-butanol, 78-92-2; (*S*)-(−)-2-methyl-1-butanol, 1565-80-6; menthol, 1490-04-6; 1-hexene, 592-41-6; styrene, 100-42-5.

Supplementary Material Available: Anisotropic thermal parameters, hydrogen positional parameters, structure factor amplitudes, contact distances, and least-squares planes data (Tables XI–XV) and a packing diagram (Figure 3) (15 pages). Ordering information is given on any current masthead page.

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