Se···F and S···F interactions both form As–F bonds (As(1)–F(11) = 1.742 (8) Å, As(2)–F(21) = 1.761 (8) Å) that are somewhat longer than the other As–F bonds and also longer than the As–F bond of 1.719 (3) Å in potassium hexafluoroarsenate.[31] It is clear from Figure 2 that these weak anion–cation bonding interactions also have a significant effect on the thermal motion of the hexafluoroarsenate anions. For example, the librations in anion 1 are limited principally to rotations about the F(11)–As(1)–F(14) axis as is shown by the thermal ellipsoids for the "equatorial" fluorines, which are significantly elongated along axes in the equatorial plane and approximately tangential to the As–F bonds. This evidence is probably more conclusive than the bond-length differences, which are notably reduced on applying thermal corrections to the bond lengths since the riding correction for the "equatorial" fluorines is larger than that for the "axial" fluorines. The distortion in the octahedral geometry of the two hexafluoroarsenate anions due to the lengthening of these As–F bonds is slight (1–2° in some cases).

In the hexafluoroantimonate salt, the average Sb–F bond length is 1.86 (1) Å and no individual value(s) appears to be significantly longer than the remaining values. This is consistent with the slightly weaker Se···F and S···F interactions involving these anions. However, it may still be observed that those atoms that are involved in the shortest interionic interactions also have the smallest anisotropic thermal parameters (for example, atoms F(12), F(14), and F(21)). The observed average Sb–F bond length is slightly longer than that for $K^+SbF_6^-$ of 1.844 (7) Å.[32]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. $Se_4S_2N_4(AsF_6)_2$, 79135-72-1; $Se_4S_2N_4(SbF_6)_2$, 79135-73-2; S_4N_4, 28950-34-7; $Se_8(AsF_6)_2$, 79152-63-9; $Se_4(AsF_6)_2$, 53513-64-7; $Se_4(Sb_2F_{11})_2$, 53513-63-6.

Supplementary Material Available: Tables A–G, giving final positional and anisotropic thermal parameters, structure factor amplitudes at room and low temperature, equations of least-squares planes, and geometry of the anion–cation interactions in compounds (59 pages). Ordering information is given on any current masthead page.

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Chelating 2-(Diphenylphosphino)pyridine. Synthesis and Structure of Dichlorodicarbonyl(2-(diphenylphosphino)pyridine)ruthenium(II)

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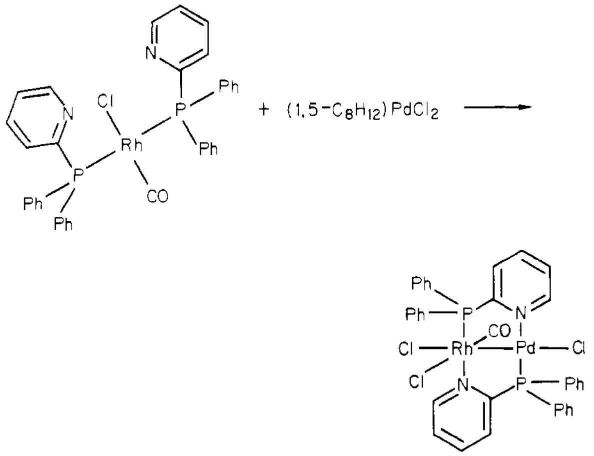
The white complex $Ru(Ph_2Ppy)(CO)_2Cl_2$ (Ph_2Ppy = 2-(diphenylphosphino)pyridine) has been synthesized by the addition of chlorine to $[Ru(CO)_3Ph_2Ppy]_3$ and has been characterized by a single-crystal X-ray structural analysis. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 8.375 (3) Å, b = 15.034 (4) Å, and c = 15.559 (3) Å at 140 K. The structure was refined by full-matrix least-squares methods to a final R of 0.030 for the 1367 reflections that had $I > 3\sigma(I)$. The complex is six-coordinate with a four-membered chelate ring involving Ru–P and Ru–N bonding to the 2-(diphenylphosphino)pyridine ring. The following trans ligand pairs are present: PRuCl, NRuCO, and ClRuCO. The conversion of $Ru(Ph_2Ppy)(CO)_2Cl_2$ into $Ru(Ph_2Ppy)_2(CO)_2Cl_2$ is described.

Introduction

We have recently described the use of 2-(diphenylphosphino)pyridine (Ph_2Ppy) in the stepwise construction of binuclear transition-metal complexes.[1-4] Two coordination modes for this ligand have been encountered previously. In a number of complexes (e.g., $Rh(Ph_2Ppy)_2(CO)Cl$[1,2] and $Ru(CO)_3(Ph_2Ppy)_2$[4]) this ligand acts as a phosphorus-bound monodentate ligand. In these cases it closely resembles triphenylphosphine. The presence of the uncoordinated nitrogen however allows such complexes to bind a second metal ion. An example is shown in reaction 1.[1,2] In the product, 2-(diphenylphosphino)pyridine acts as a bridging ligand. Other coordination modes for Ph_2Ppy that are readily anticipated include monodentate coordination through nitrogen and chelation of a single metal ion. In the latter case this ligand should structurally resemble ortho-metalated[5] triphenylphosphine.



(1)

One of the five products resulting from the reaction between $Ru(CO)_3(Ph_2Ppy)_2$ and $(1,5\text{-}C_8H_{12})PdCl_2$ is a white crystalline material with the composition $Ru(Ph_2Ppy)(CO)_2Cl_2$.[4] Here we report on an independent synthesis of this material, the first

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we have found with a chelating 2-(diphenylphosphino)pyridine ligand, and its structural characterization by X-ray crystallography.

Experimental Section

Synthesis of Compounds. 2-(Diphenylphosphino)pyridine[4,5] and $[Ru(Ph_2Ppy)(CO)_3]_3$[4,7] were obtained by routes described elsewhere.

$Ru(Ph_2Ppy)(CO)_2Cl_2$. A saturated solution of chlorine in dichloromethane was added dropwise to a violet solution of 0.294 g (0.129 mmol) of $[Ru(Ph_2Ppy)(CO)_3]_3$ in 10 mL of dichloromethane. The addition of the chlorine-containing solution was stopped after the mixture became yellow. Ethyl ether was added dropwise to precipitate the product as grayish white crystals. The product was collected by filtration, washed with dichloromethane and vacuum dried; yield 0.176 g, 50%.

$Ru(Ph_2Ppy)_2(CO)_2Cl_2$. A solution of 43 mg (160 mmol) of 2-(diphenylphosphino)pyridine and 40 mg (80 mmol) of $Ru(Ph_2Ppy)(CO)_2Cl_2$ in 20 mL of dichloromethane was heated under reflux for 1.5 h. After the solution was cooled, ethyl ether was added dropwise to it. The white crystalline solid that formed was collected by filtration, washed with ethyl ether, and vacuum dried; yield 53 mg, 86%. Anal. Calcd for $C_{36}H_{28}N_2O_2Cl_2P_2Ru$: C, 57.30; H, 3.75; N, 3.71; Cl, 9.40. Found: C, 57.06; H, 3.82; N, 3.63; Cl, 9.71.

Physical Measurements. Infrared spectra were recorded from dichloromethane solutions on a Perkin-Elmer 180 infrared spectrometer. Proton-decoupled ^{31}P NMR spectra were recorded on a Nicolet NT-200 Fourier transform spectrometer at 81 MHz. An external 85% phosphoric acid reference was used for ^{31}P NMR spectra, and the high-frequency-positive convention, recommended by IUPAC, has been used in reporting chemical shifts.

X-ray Data Collection. Crystals suitable for X-ray data collection were obtained by diffusion of diethyl ether into a dichloromethane solution of **1**. A colorless needle of 0.10 × 0.17 mm thickness was cut to a length of 0.25 mm and mounted along the needle axis on the goniometer head of a Syntex $P2_1$ automated diffractometer. The collection of X-ray data was carried out at 140 K with use of graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation. Reflections were initially located by using a rotation photograph. A typical reflection had a width at half-height of 0.30° on an ω scan. With use of 10 centered reflections and the $P2_1$ automatic indexing program, the lattice was assigned as orthorhombic P. This was confirmed by a series of axial photographs. Quick scans of the important reflections for space group determination yielded the following conditions: $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$; $hk0$, $h0l$, $0kl$, no conditions. Thus, the space group was $P2_12_12_1$ (No. 19). A density of 1.62 g cm^{-3} was measured by flotation in tetrabromomethane/CCl_4 at room temperature, which agrees with that calculated for $Z = 4$, if a 2–3% increase in density at 140 K is assumed. A least-squares fit of fourteen reflections with $30° < 2\theta < 40°$ yielded cell dimensions $a = 8.375$ (3), $b = 15.034$ (4), and $c = 15.559$ (3) Å.

Data were collected with use of an ω scan of 1° range and speed ranging from 3 to 60°/min. Stationary background counts were collected with a 1° offset from the center of the peak. Two check reflections were monitored throughout and showed only a random fluctuation. Reflections were collected to $2\theta = 45°$, yielding 1491 data. The data were corrected for Lorentz and polarization effects but not for absorption (μ(Mo Kα) = 19.6 cm^{-1}); for a crystal of the dimensions given, the absorption correction factors range from 1.38 to 1.73. Reduction of the data to F_o and $\sigma(F_o)$ were as previously described.[8]

Solution and Refinement of the Structure. Neutral-atom scattering factors[9] and corrections for anomalous dispersion for Ru, Cl, and P[10] were from common sources. The structure was solved by locating the ruthenium atom on a Patterson map and refining its position together with the positions of one phosphorus and two chlorine atoms that were found on a first Fourier map. This brought R ($\sum||F_o| - |F_c||/\sum|F_o|$) to 0.23. A second Fourier map revealed the remaining nonhydrogen atoms; three more cycles of full-matrix least-squares refinement of all 26 atoms using isotropic thermal parameters and the 1367 reflections for which $I > 3\sigma(I)$ brought R to 0.038. The quantity minimized during refinement was $\sum w(kF_o - |F_c|)^2$ where k is a scale factor and w is given the Hughes weighting scheme. At this stage the determination of the handedness of the crystal was carried out. This determination was based upon the identification of enantiomer-sensitive reflections[11] as computed from the function

$$D = (\Delta F_B)^2/\sigma^2(F_o)$$

where ΔF_B refers to the Bijvoet difference $|F(hkl) - F(\bar{h}\bar{k}\bar{l})|$. For the 45 reflections with $D > 4.0$, we obtained $R = 0.040$ for the original hand and $R = 0.055$ for its enantiomorph. This is a clear indication that the original choice of hand was correct. Three additional cycles of full-matrix least-squares refinement with anisotropic thermal parameters for all nonhydrogen atoms brought R to 0.030. In the final cycle of refinement, the last shift in any parameter was less than 0.07 of its esd. A structure factor calculation that included the hydrogen atoms at calculated positions yielded an R of 0.027. No feature corresponding to atoms larger than hydrogen atoms were found on a final difference map. Final positional and anisotropic thermal parameters are given in Table II. Tables of structure factor amplitudes are available as supplementary material. Calculations were peformed on a Data General Eclipse Computer with use of local crystallographic programs developed by Professor H. Hope.

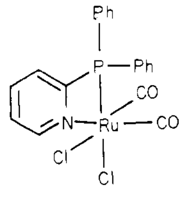
Table I. Spectroscopic Data for Ruthenium Complexes

compd	$^{31}P\{H\}$ NMR, ppm^a	ν(CO), cm^{-1} ^{a}
$Ru(Ph_2Ppy)(CO)_2Cl_2$	−6.84	2067, 2007
$Ru(Ph_2Ppy)(CO)_2Br_2$	−8.87	2066, 2007
$Ru(Ph_2Ppy)_2(CO)_2Cl_2$	21.49	2062, 2002
$Ru(Ph_3P)_2(CO)_2Cl_2$	17.78	2058, 1996
Ph_2Ppy	−3.36	
Ph_3P	−4.94	

^{a} In dichloromethane solution.

Results

Synthetic Studies. $Ru(Ph_2Ppy)(CO)_2Cl_2$ (**1**) is conveniently synthesized by the addition of chlorine to $[Ru(Ph_2Ppy)(CO)_3]_3$ followed by precipitation of the product with ether. Spectroscopic data characterizing this and other new compounds is reported in Table I. The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of a single resonance shifted to a lower frequency than the free ligand. Although shifts in this direction are uncharacteristic of coordinated phosphines, similar shifts are exhibited by ortho-metalated triphenylphosphine complexes of ruthenium and other metals.[12,13] Thus, low-frequency shifts may be indicative of the existence of strained, four-membered chelate ring formation by this group of ligands. The appearance of only one ^{31}P resonance in the NMR spectrum of $Ru(Ph_2Ppy)(CO)_2Cl_2$ indicates that the sample is obtained as a single isomer, although four geometrical isomers, each with a chelating 2-(diphenylphosphino)pyridine ligand, are possible. Further definition of the geometry of $Ru(Ph_2Ppy)(CO)_2Cl_2$ comes from the infrared spectrum, which



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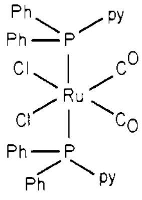
shows two carbonyl stretching absorptions. Consequently the carbonyl groups must occupy mutually cis positions. The structure of Ru(Ph$_2$Ppy)(CO)$_2$Cl$_2$ has been further delineated by the X-ray crystal structure, which establishes structure **1** as correct.

Examination of the ^{31}P{^{1}H} NMR spectrum of a solution of [Ru(Ph$_2$Ppy)(CO)$_3$]$_3$ after treatment with chlorine reveals the presence of **1** along with three other resonances at 20.88, 32.97, and 43.17 ppm with relative intensities 2.4:2.1:1:3.88. Thus the formation of **1** is accompanied by preparation of other species, which we have not identified. However, from the chemical shifts it does not appear that any of these involve a chelating 2-(diphenylphosphino)pyridine. Oxidation of [Ru(Ph$_2$Ppy)(CO)$_3$]$_3$ with bromine produces Ru(Ph$_2$Ppy)(CO)$_2$Br$_2$ (^{31}P{^{1}H} NMR -8.87 ppm) along with additional species giving phosphorus resonances at 30.53 (doublet, J = 9.5 Hz) 30.98, 43.18, and 48.43 (doublet, J = 9.5 Hz) ppm. Oxidation of [Ru(Ph$_2$Ppy)(CO)$_3$]$_3$ with iodine is more complex and yields at least 11 groups of resonances in the ^{31}P NMR spectrum. Further work on identifying these species is in progress.

The chelating 2-(diphenylphosphino)pyridine ligand falls into the class of hemilabile ligands of Jeffrey and Rauchfuss.[14] The pyridine nitrogen is expected to be more readily displaced from a low-valent metal than is the phosphorus end of the bidentate ligand. The ring strain (vide infra) within the four-membered chelate should facilitate ring opening. Other examples of facile ring opening of the amine end of amine/phosphine ligands have been established.[14-17] In the present case Ru(Ph$_2$Ppy)(CO)$_2$Cl$_2$ reacts with additional 2-(diphenylphosphino)pyridine under mild conditions to form Ru(Ph$_2$Ppy)$_2$(CO)$_2$Cl$_2$ (**2**). Spectroscopic data for **2** are presented in Table I along with the analogous data for Ru(Ph$_3$P)$_2$(CO)$_2$Cl$_2$.[18] Comparison of the physical properties in these two complexes suggests that **2** has the geometry shown with monodentate, P-bound 2-(diphenylphosphino)pyridine ligands. The observation of a single ^{31}P{^{1}H} NMR resonance for **2** indicates that both phosphine ligands occupy chemically equivalent sites. Consequently replacement of the pyridine nitrogen by the phosphine ligand has been accompanied by rearrangement of the other ligands.



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Ru(Ph$_2$Ppy)(CO)$_2$Cl$_2$ does not react with carbon monoxide to give the hypothetical tricarbonyl Ru(Ph$_2$Ppy)(CO)$_3$Cl$_2$ that would form if the carbon monoxide were to replace the pyridine nitrogen. The nonoccurrence of this tricarbonyl is not unexpected, however, and probably is related to the inability of Ru(II) to accommodate the necessary back-bonding of three carbonyl ligands and a phosphine. For comparison, treatment of [Ru(Ph$_3$P)(CO)$_3$]$_3$ with halogens produces the halo-bridged dimers [Ru(CO)$_2$(PPh$_3$)X]$_2$(μ-X)$_2$.[19]

Molecular Structure of Ru(Ph$_2$Ppy)(CO)$_2$Cl$_2$. Ru(Ph$_2$Ppy)(CO)$_2$Cl$_2$ crystallizes with one molecule in the asymmetric unit and no unusual intermolecular contacts. There is no crystallographically imposed symmetry on the molecule. A perspective drawing of the molecule, which shows the atom labeling scheme, is shown in Figure 1. Final atomic coordinates and temperature factors are given in Table II. Selected interatomic distances and angles are presented in Tables III and IV, respectively.

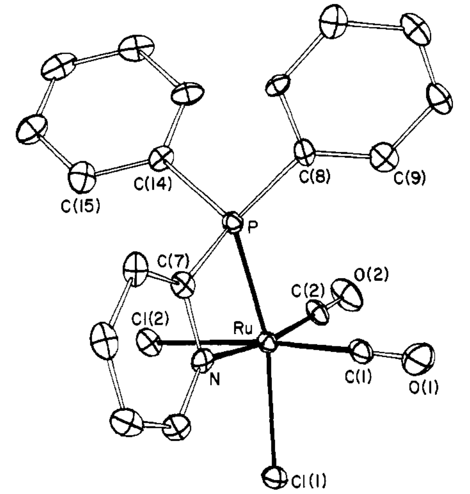

Figure 1. Perspective view of Ru(Ph$_2$Ppy)(CO)$_2$Cl$_2$.

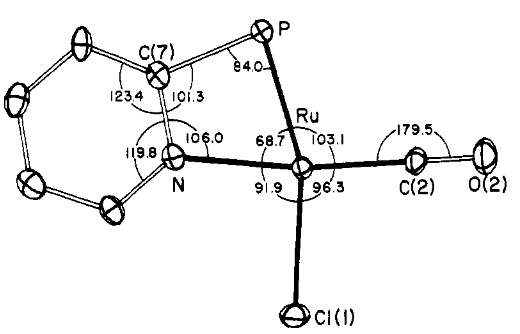

Figure 2. Bond angles in the plane of the chelate ring of Ru(Ph$_2$Ppy)(CO)$_2$Cl$_2$.

The coordination sphere of the ruthenium atoms consists of two mutually cis carbonyl ligands, two mutually cis chloride ligands, and the chelating phosphinopyridine ligand, which is coordinated through both the phosphorus and the nitrogen atoms. The observed arrangement of the ligands places the three π-acceptor ligands in nearly orthogonal positions so that none are trans to one another.

The geometry about the ruthenium is pseudooctahedral. The bond angles between cis ligands, except for the NRuP and PRuC(2) angles, are all close to the ideal value of 90°. As expected, the donor atoms are arranged in three nearly orthogonal planes (planes 1–3 of Table V). Due to the presence of the four-membered chelate ring, however, the phosphorus atom does not occupy the expected coordination site. Rather it is pulled off-axis toward the pyridine nitrogen. Thus the P–Ru–N angle is compressed to 68.7 (2)° and the P–Ru–C(2) angle has opened to 103.1 (2)°. Further evidence of the displacement of the phosphorus atom from a normal coordination site comes from the displacement of the phosphorus atom from plane 3 shown in Table V and from consideration of the bond angles between trans ligands. The P–Ru–Cl(1) angle of 160.4 (1)° shows the largest deviation from the ideal value of 180°; the other two angles are 171.7 (3)° for N–Ru–C(2) and 173.8 (3)° for C(1)–Ru–Cl(2).

Within the four-membered chelating ring all of the bond angles have suffered compression. A drawing of this portion of the molecule is shown in Figure 2. As noted previously

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Table II. Positional and Anisotropic Thermal Parameters for $Ru(Ph_2Ppy)(CO)_2Cl_2$[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	0.10263 (7)	0.10518 (4)	0.22395 (4)	0.99 (3)	1.06 (3)	1.14 (3)	0.15 (2)	0.02 (2)	−0.04 (3)
Cl(1)	0.1610 (2)	0.1105 (1)	0.0725 (1)	2.49 (9)	1.73 (8)	1.16 (7)	0.54 (8)	0.20 (6)	0.00 (7)
Cl(2)	−0.0022 (2)	−0.0427 (1)	0.2012 (1)	1.26 (7)	1.63 (8)	2.01 (8)	−0.04 (7)	−0.05 (7)	−0.45 (7)
P	0.1266 (2)	0.0725 (1)	0.3692 (1)	1.01 (9)	1.05 (7)	1.11 (7)	0.04 (7)	0.06 (7)	−0.04 (6)
O(1)	0.2683 (8)	0.2822 (4)	0.2399 (4)	3.2 (3)	2.5 (3)	2.9 (3)	−1.1 (3)	0.8 (3)	−0.1 (2)
O(2)	−0.2242 (7)	0.1886 (4)	0.2124 (4)	2.2 (3)	2.9 (3)	2.7 (3)	1.4 (2)	−0.4 (3)	−0.6 (2)
N	0.3245 (8)	0.0436 (4)	0.2513 (4)	0.9 (3)	1.1 (3)	1.5 (3)	−0.3 (2)	0.1 (2)	0.0 (2)
C(1)	0.2033 (10)	0.2162 (5)	0.2347 (5)	2.0 (3)	1.4 (4)	1.1 (3)	0.7 (3)	−0.1 (3)	−0.1 (3)
C(2)	−0.1006 (10)	0.1567 (5)	0.2165 (5)	1.4 (4)	1.5 (3)	1.4 (3)	0.6 (3)	−0.4 (4)	−0.4 (3)
C(3)	0.4495 (9)	0.0204 (5)	0.2041 (5)	1.0 (4)	1.7 (4)	1.9 (4)	−0.3 (3)	0.2 (3)	−0.0 (3)
C(4)	0.5815 (10)	−0.0218 (5)	0.2411 (5)	1.2 (4)	2.0 (4)	1.9 (4)	−0.6 (3)	0.2 (3)	−0.6 (3)
C(5)	0.5774 (11)	−0.0403 (5)	0.3293 (5)	1.5 (4)	1.5 (3)	2.4 (4)	0.1 (3)	−0.6 (3)	−0.3 (3)
C(6)	0.4461 (9)	−0.0142 (5)	0.3789 (6)	0.9 (4)	1.2 (3)	2.4 (4)	−0.1 (3)	−0.3 (3)	0.1 (3)
C(7)	0.3236 (10)	0.0263 (5)	0.3372 (5)	0.8 (3)	1.1 (3)	1.6 (3)	−0.6 (3)	−0.1 (3)	−0.3 (3)
C(8)	0.1485 (9)	0.1572 (5)	0.4512 (5)	1.0 (3)	0.9 (3)	1.8 (3)	−0.0 (3)	0.2 (3)	−0.2 (3)
C(9)	0.0942 (10)	0.2440 (5)	0.4353 (5)	0.9 (3)	1.9 (3)	2.0 (3)	−0.3 (3)	0.0 (3)	−0.2 (3)
C(10)	0.0991 (11)	0.3068 (5)	0.5010 (5)	1.6 (3)	1.6 (3)	2.4 (4)	0.2 (3)	0.3 (4)	−0.7 (3)
C(11)	0.1471 (10)	0.2828 (6)	0.5830 (6)	1.6 (4)	1.9 (4)	2.1 (4)	0.4 (3)	−0.1 (3)	−0.8 (3)
C(12)	0.2016 (10)	0.1955 (5)	0.5998 (5)	1.1 (3)	1.7 (3)	2.2 (4)	−0.3 (3)	−0.1 (3)	0.1 (3)
C(13)	0.2032 (9)	0.1330 (5)	0.5336 (5)	0.8 (3)	1.4 (3)	1.0 (3)	0.2 (3)	0.0 (3)	0.5 (3)
C(14)	0.0143 (9)	−0.0138 (5)	0.4238 (5)	0.6 (3)	1.4 (3)	1.2 (3)	−0.6 (3)	−0.5 (3)	0.1 (3)
C(15)	0.0467 (10)	−0.1041 (6)	0.4081 (5)	1.9 (4)	1.7 (3)	2.1 (3)	−0.3 (3)	−0.5 (3)	−0.1 (3)
C(16)	−0.0442 (11)	−0.1684 (6)	0.4493 (6)	1.7 (4)	2.3 (4)	2.1 (4)	−0.6 (3)	−0.2 (3)	0.5 (3)
C(17)	−0.1692 (11)	−0.1438 (6)	0.5037 (6)	2.1 (4)	2.9 (4)	1.6 (4)	−1.5 (3)	−0.6 (3)	0.5 (3)
C(18)	−0.2035 (1)	−0.0530 (6)	0.5190 (5)	0.8 (3)	3.0 (4)	1.5 (4)	−1.1 (3)	−0.5 (3)	−0.1 (3)
C(19)	−0.1109 (10)	0.0112 (5)	0.4780 (5)	1.3 (3)	2.6 (4)	1.2 (3)	−0.3 (3)	−0.1 (3)	0.2 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*)]$.

Table III. Bond Distances (Å) for $Ru(Ph_2Ppy)(CO)_2Cl_2$

Ru–Cl(1)	2.408 (2)	C(7)–N	1.36 (1)
Ru–Cl(2)	2.417 (2)	N–C(3)	1.32 (1)
Ru–P	2.322 (2)	C(3)–C(4)	1.40 (1)
Ru–N	2.119 (6)	C(4)–C(5)	1.40 (1)
Ru–C(1)	1.877 (8)	C(5)–C(6)	1.40 (1)
Ru–C(2)	1.874 (8)	C(6)–C(7)	1.36 (1)
C(1)–O(1)	1.14 (1)	P–C(8)	1.812 (8)
C(2)–O(2)	1.14 (1)	P–C(14)	1.813 (8)
P–C(7)	1.859 (8)	P···N	2.511 (7)

Table IV. Bond Angles (Deg) for $Ru(Ph_2Ppy)(CO)_2Cl_2$

P–Ru–N	68.7 (2)	Ru–P–C(14)	124.2 (3)
P–Ru–Cl(1)	160.4 (1)	C(7)–P–C(8)	111.2 (4)
P–Ru–Cl(2)	88.8 (1)	C(7)–P–C(14)	108.6 (3)
P–Ru–C(1)	93.6 (3)	C(8)–P–C(14)	103.1 (4)
P–Ru–C(2)	103.1 (2)	Ru–N–C(3)	134.2 (5)
N–Ru–Cl(1)	91.8 (2)	Ru–N–C(7)	106.0 (5)
N–Ru–Cl(2)	86.9 (2)	Ru–C(1)–O(1)	177.8 (8)
N–Ru–C(1)	88.7 (3)	Ru–C(2)–O(2)	179.5 (7)
N–Ru–C(2)	171.7 (3)	P–C(7)–N	101.3 (5)
Cl(1)–Ru–Cl(2)	87.8 (1)	P–C(7)–C(6)	135.2 (6)
Cl(1)–Ru–C(1)	87.8 (3)	N–C(3)–C(4)	121.1 (7)
Cl(1)–Ru–C(2)	96.3 (2)	C(3)–C(4)–C(5)	118.3 (8)
Cl(2)–Ru–C(1)	173.8 (3)	C(4)–C(5)–C(6)	120.3 (8)
Cl(2)–Ru–C(2)	92.4 (3)	C(5)–C(6)–C(7)	117.1 (8)
C(1)–Ru–C(2)	92.6 (3)	C(6)–C(7)–N	123.4 (7)
Ru–P–C(7)	84.0 (3)	C(7)–N–C(1)	119.8 (7)
Ru–P–C(8)	123.0 (3)		

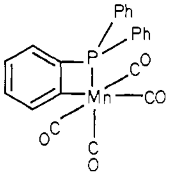
the P–Ru–N angle of 68.7 (2)° is considerably distorted from the ideal value of 90°. A similar reduction has occurred in the Ru–P–C(7) angle, which is reduced from the ideal value of 109.5 to 84.0 (3)°. The compression of the angles external to the pyridine ring, N–C(7)–P and Ru–N–C(7), is much less. Otherwise the dimensions of the pyridine ring are within normal limits. The intrachelate P–C(7) distance is significantly longer than the two extrachelate P–C distances. This lengthening of the P–C(7) bond in part compensates for angular strain within the chelate ring. Because of the high degree of angular distortion within this chelate ring, it is not surprising that 2-(diphenylphosphino)pyridine has been found to act as a monodentate or bridging ligand more frequently than as a chelating ligand.

Table V. Selected Least-Squares Planes for $Ru(Ph_2Ppy)(CO)_2Cl_2$[a]

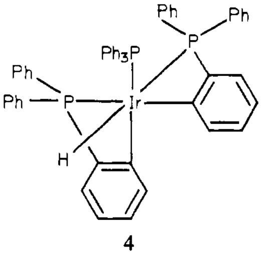
atom	dev from plane, Å	atom	dev from plane, Å
Plane 1: $3.449x + 13.5448y + 2.1244z = 2.2287$			
Ru	0.026	C(2)	−0.005
P	−0.026	Cl(1)	−0.021
N	0.015		
Plane 2: $-1.4965x - 0.8796y + 15.2815z = 3.2041$			
Ru	−0.028	C(2)	0.117
Cl(2)	−0.089	N	0.112
C(1)	−0.112		
Plane 3: $7.5169x - 6.2389y + 2.3180z = 0.6906$			
Ru	−0.056	Cl(1)	−0.002
P	0.025	P	0.664
C(1)	0.033		
Plane 4: $3.5157x + 13.4009y + 2.6600z = 2.3860$			
Ru	−0.020	C(4)	0.007
P	0.013	C(5)	−0.020
N	0.008	C(6)	0.000
C(3)	0.011	C(7)	0.001

[a] All atoms listed were used to define the planes except the P of plane 3.

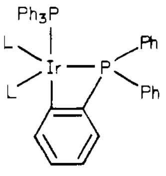
The geometry of the chelate ring in $Ru(Ph_2Ppy)(CO)_2Cl_2$ may be compared with that of complexes containing orthometalated triphenylphosphine. Relevant complexes of established structure include **3**,[20] **4**[21] and **5** (L = CO, C_2H_4).[22]



3



4



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Each of these possesses a planar MC_2P ring, which displays significant angular compression. The C–P–Ru angle in Ru(Ph_2Ppy)$(CO)_2Cl_2$ may be compared to the C–P–Mn angle of 85.2 (3)° in **3**,[19] the C–P–Ir angles of 83.8 (3) and 84.1 (2)° in **4**,[20] and the C–P–Ir angles of 83.7 (L = C_2H_4) and 85.7° (L = CO) in **5**.[21] The compression of the P–Ru–N angle is similar to that found for the C–Mn–P angle of 67.5 (3)° in **3**[19] and the two C–Ir–P angles of 67.1 (3) and 67.8 (2°) in **4**.[20] The largest angular displacement of a ligating atom from a normal coordination site involves the phosphorus atom of **3**, just as noted with Ru(Ph_2Ppy)$(CO)_2Cl_2$ above. Thus while the PMnC(phenyl) angle is compressed, the PMC(CO) angle has opened to 101.2 (4)°. The trans P–M–C angle of 159.9 (5)° is considerably less than the other two trans angles, C(phenyl)–Mn–C(CO) 168.7 (5)° and C(CO)–Mn–C(CO) 172.9°. In considering the similarity between ortho-metalated triphenylphosphine and 2-(diphenylphosphino)pyridine it should also be noted that ortho-metalated triphenylphosphine not only acts as a chelating ligand but can also function as a bridging ligand as shown for the complex $HOs_3(CO)_9PPh_3(PPh_2C_6H_4)$.[23]

The bond lengths from ruthenium to its neighboring atoms all appear normal. Ruthenium(II)–phosphorus distances span the range 2.21–2.44 Å depending on the trans ligand.[14,24] The Ru–P distance of 2.322 (2) Å with trans chloride may be compared with the 2.318 (7) Å Ru–P distance in *fac*-$Ru_2Cl_3(PEt_2Ph)_6^{3+}$.[25] The Ru–N distance of 2.119 (6) Å falls between the Ru–N(pyridine) distances found in (tetraphenylporphyrinato)carbonyl(pyridine)ruthenium(II) (2.193 (4) Å trans to carbon monoxide)[26] and in $[(py)_4RuO_2C_2O_2Ru(py)_4][BF_4]_2$ (2.067 (7) Å trans to oxalate and 2.092 (7) Å trans to pyridine).[27] The two Ru–C distances (1.877 (8) and 1.874 (8) Å) are equivalent within experimental error and reflect no difference in trans effect between the pyridine and chloride ligands. Related Ru(II)–C(carbonyl) distances are 1.838 (9) Å (trans to pyridine) in (tetraphenylporphyrinato)carbonyl(pyridine)ruthenium(II),[26] 1.831 (10) Å (trans to Cl) in $Ru(CO)Cl_2(C_2H_4)(PPh_3)_2$,[28] and 1.911 (8) (trans to Cl) and 1.912 (7) Å (trans to phenyldiazene) in $[RuCl(CO)_2(HN_2C_6H_5)(PPh_3)_2][ClO_4]$.[29] Both carbonyl groups are linearly coordinated, and the C–O bond distances are normal. The two Ru–Cl distances of 2.417 (2) and 2.408 (2) Å are very similar despite the fact that different trans ligands are involved (carbonyl and phosphine, respectively). These distances are appreciably shorter than the Ru–Cl distance of 2.513 Å in *mer*-$[RuCl_3(PEt_3Ph)_3]^-$ where chloride is trans to phosphorus,[25] of 2.454 (3) Å in $RuCl_2(CO)(C_2H_4)(PMe_2Ph)_2$ where chloride is trans to carbonyl,[28] and of 2.428 (6) Å in $RuCl_2(CO)(CSe)(PPh_3)_2$ where chloride also is trans to carbonyl.[30] But the Ru–Cl distances in Ru(Ph_2Ppy)$(CO)_2Cl_2$ are comparable to the Ru–Cl distances (2.391–2.446 Å) in compounds where the Ru–Cl unit is trans to another chloride ligand. It was previously noted[23] that the Ru–Cl distances increase with changes in the trans ligand in the order $Cl^- < CO < PR_3$. This paralleled the observations on the Ru–Cl stretching frequency, which showed that the Ru–Cl frequency decreases as the trans ligand changes in the order $Cl^- > CO > PR_3$.[31] The observations on Ru(Ph_2Ppy)$(CO)_2Cl_2$ do not follow these trends.

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Registry No. Ru(Ph_2Ppy)$(CO)_2Cl_2$, 78790-90-6; Ru$(Ph_2Ppy)_2(CO)_2Cl_2$, 78790-91-7; $[Ru(Ph_2Ppy)(CO)_3]_3$, 78803-80-2; Ru(Ph_2Ppy)$(CO)_2Br_2$, 78790-92-8.

Supplementary Material Available: Structure factor tables for Ru(Ph_2Ppy)$(CO)_2Cl_2$ (9 pages). Ordering information is given on any current masthead page.

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