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Ruthenium(II) Complexes of Benzylphosphines

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Reaction of the benzylphenylphosphines Bzl_nPPh_{3-n} (L) with "$Ru(CO)_2Cl_2$" produces the kinetically stable *trans*-$L_2Ru(CO)_2Cl_2$ (**1**), which thermally isomerize to the thermodynamically stable *cis*-$L_2Ru(CO)_2Cl_2$ (**2**). The kinetics, activation thermodynamics, and mechanisms of these processes were determined by ^{31}P NMR spectroscopy. The isomerization is a dissociative process (ΔS^{*} and ΔH^{*} are both positive) whose rate increases with an increase in the steric bulk of the phosphine and is retarded by excess carbon monoxide. A series of six complexes have been characterized by elemental analyses and infrared and ^1H, $^{13}C\{^1H\}$, and ^{31}P NMR spectroscopies. The crystal structures of *trans*-$(Bzl_3P)_2Ru(CO)_2Cl_2$ and *cis*-$(BzlPPh_2)_2Ru(CO)_2Cl_2$ have been determined from three-dimensional X-ray diffraction techniques. The structural data form a basis for discussion of the relative thermodynamic and kinetic stabilities of the isomers formed.

Introduction

There has been a great deal of interest recently in catalysts that are capable of performing selective homogeneous hydrogenations.[2] Tertiary phosphine complexes of transition metals have figured prominently in these reactions as excellent catalysts, in particular, complexes of ruthenium. Wilkinson[3] found that $RuCl_2(PPh_3)_4$ and $RuCl_2(PPh_3)_3$ were extremely efficient for the reduction of alkenes and alkynes at 25 °C and 1 atm. Fahey[4] found that $(PPh_3)_2Ru(CO)_2Cl_2$ was a very effective catalyst for the selective hydrogenation of cyclopolyolefins to cyclomonoolefins. The catalytic mechanism for both these catalysts involve ligand dissociation, a process which should be promoted by increasing the steric bulk of the ligands. In addition Mawby[5] suggested that the thermal and photochemical isomerization of $(R_3P)_2Ru(CO)_2Cl_2$ complexes is a dissociative process. The benzylphosphines, Bzl_nPPh_{3-n}, n = 1-3, are sterically more encumbering than PPh_3 and are also stronger bases. As a consequence ruthenium complexes of the benzylphosphines might be expected to display significant catalytic activity.

We have prepared and characterized a series of ruthenium complexes with the benzylphosphines and investigated their solution structure and reactivity. The results of those studies are reported herein.

Results and Discussion

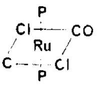
Numerous unsuccessful attempts were made to prepare L_4RuCl_2 or L_3RuCl_2 with the benzylphosphines. We were unable to isolate any crystalline ruthenium complexes from reactions of the benzylphosphines with "ruthenium blue solutions"[6] $(Ph_3P)_4RuCl_2$,[7] $[(norbornadiene)RuCl_2]_n$, $[(cyclooctadiene)RuCl_2]_n$, or $RuCl_3 \cdot 3H_2O$.

Having failed to obtain the L_nRuCl_2 complexes, we turned our attention to the carbonyl complexes. When solutions of $RuCl_3 \cdot 3H_2O$ in 2-methoxyethanol are refluxed under carbon monoxide and a benzylphosphine is added, complexes of the type $L_2Ru(CO)_2Cl_2$ are readily formed. These complexes potentially could have one of five different isomeric structures[8] (**1**-**5**). Only isomers **1** and **2** were isolated with the benzylphosphines. The initial kinetic product is the yellow, trans isomer (**1**) for Bzl_3P, Bzl_2PPh, and $BzlPPh_2$. Under vigorous reflux the thermodynamically stable, colorless cis isomer (**2**) is formed. The trans complexes (**1**) thermally isomerize in solution completely to the cis complexes (**2**) without decomposition. The benzylphosphines exhibit behavior similar to that of other bulky phosphines in that we were not able to prepare the $L_3Ru(CO)Cl_2$ complexes with the benzylphosphines.[9]

Table I. Infrared Spectral Data for $L_2Ru(CO)_2Cl_2$[a]

L	isomer	ν(C-O), cm^{-1}	ν(Ru-Cl), cm^{-1}	other vibrations
Bzl_3P	cis	1987, 2045	274, 298	349
	trans	2015	355	325
Bzl_2Ph	cis	1986, 2040	270, 299	375
	trans	2010	334	320
$BzlPPh_2$	cis	1995, 2058	285, 310	
	trans	2020	320	333

[a] Nujol mulls on CsBr plates.



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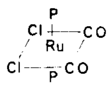

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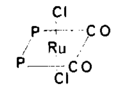

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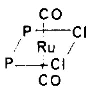

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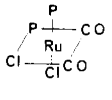

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The infrared and ^1H NMR data (Tables I and II, respectively) confirm the configuration of isomers **1** and **2**, the yellow trans and colorless cis isomers, respectively. The colorless complexes each show two strong vibrations at approximately 1980 and 2050 cm^{-1} due to mutually cis carbonyl groups, whereas the yellow complexes show only one strong vibration at approximately 2015 cm^{-1} due to mutually trans carbonyl groups. Both isomers show vibrations in the 270-355-cm^{-1} region due to ν_{RuCl}, one for the trans complexes and two for the cis.

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Table II. ^{1}H and ^{13}C{^{1}H} NMR Data of $CDCl_3$ Solutions of Benzylphosphine Complexes of $L_2Ru(CO)_2Cl_2$

L	$\delta[^1H(CH_2)]^a$	"J",^{b} Hz	line shape^c	isomer	$\delta[^{13}C(CH_2)]^a$	J_{PC}, Hz	line shape^c	$\delta[^{13}C(CO)]^a$	J_{PC}, Hz	line shape^c
Bzl_3P	3.57	7.08	t	cis	31.12	21.98	t	192.12	10.99	t
	3.53	6.35	t	trans	31.9	20.51	t			
Bzl_2Ph	3.93	8.06	t	cis	31.46	20.51	t			
	3.87	...	m	trans	55.87	51.20	t			
$BzlPPh_2$	4.47	8.06	t	cis						

^{a} Chemical shifts are relative to Me_4Si. ^{b} "J" = $|^nJ_{PH} + {}^{n+2}J_{PH}|$. ^{c} t = triplet, m = unresolved multiplet.

Table III. ^{31}P{^{1}H} NMR Data for the Complexes $L_2Ru(CO)_2Cl_2$ in $CDCl_3$ Solution

$\delta(^{31}P)^a$	L	isomer	$\delta(^{31}P)^b$	$\Delta\delta(^{31}P)_{obsd}{}^c$	$\Delta\delta(^{31}P)_{calcd}$	$\Delta\delta(^{31}P)_{obsd} - \Delta\delta(^{31}P)_{calcd}$
−12.9	Bzl_3P	cis	16.59	−29.49	-28.24^d	1.25
		trans	17.92	−30.82	-29.19^e	1.63
−12.1	Bzl_2PPh	cis	15.80	−27.90	-29.74^d	−1.84
		trans	16.47	−28.57	-30.98^e	−2.41
−10.4	$BzlPPh_2$	cis	23.12	−33.53	-32.94^d	0.59
		trans	25.19	−35.59	-34.82^e	0.77

^{a} Chemical shifts of the free phosphine. ^{b} Positive chemical shifts are downfield of 85% H_3PO_4. $^c\Delta\delta(^{31}P)_{obsd} = \delta(^{31}P\ \text{ligand}) - \delta(^{31}P\ \text{complex})$. ^{d} $\Delta\delta(^{31}P)_{calcd} = A[\delta(^{31}P\ \text{free ligand})] + B$ where $A = -1.88$, $B = -52.51$. ^{e} $A = -2.26$, $B = -58.28$.

It has been well established[10] that for transition-metal complexes containing two tertiary phosphine ligands with methylene groups attached to the phosphorus the appearance of the methylene resonance in the ^{1}H and ^{13}C{^{1}H} NMR is determined by the magnitude of $^2J_{pp}$. When the two phosphorus nuclei are mutually cis, $^2J_{pp}$ is generally less than 80 Hz and the methylene resonance appears as a doublet or "filled-in" doublet. If the two phosphorus nuclei are mutually trans, then $^2J_{pp}$ is generally 500 Hz or greater and the methylene resonance appears as a 1:2:1 triplet. Triplets were observed (Table II) for the methylene resonances of all complexes except *trans*-$(Bzl_2PPh)_2Ru(CO)_2Cl_2$, indicating mutually trans phosphine ligands. The methylene resonance of *trans*-$(Bzl_2PPh)_2Ru(CO)_2Cl_2$ was an unresolved quartet of triplets due to the unsymmetrical nature of this ligand.[10] Broad unresolved multiplets were observed for each complex centered at δ 7.2 with line shapes typical of trans phenylphosphines.[11] Due to limited solubility, satisfactory ^{1}H and ^{13}C NMR spectra of *trans*-$(BzlPPh_2)_2Ru(CO)_2Cl_2$ could not be obtained. The observation of mutually trans phosphines in all complexes is consistent with the phosphines' steric bulk, which seemingly precludes mutually cis phosphines.

The ^{13}C{^{1}H} NMR (Table II) show triplets for the methylene carbons except for *cis*- and *trans*-$(BzlPPh_2)_2Ru(CO)_2Cl_2$, which were too insoluble to show anything but the aromatic carbons. For all complexes the aromatic carbons were singlets, due to cancellation[10] of coupling constants, $|^nJ_{PC} + {}^{n+2}J_{PC}| = 0$, and therefore provide no structural information.

Each of the complexes showed a single resonance in their ^{31}P NMR (Table III), and the resonance of the trans isomer was downfield of that of the cis in each case. There has been very little success in correlating ^{31}P chemical shifts with other parameters[12,13] such as electronegativity or basicity of the groups attached to phosphorus. Greater success has been achieved in the correlation of the chemical shift of the free phosphine, $\delta(^{31}P)$, and the change in the chemical shift upon coordination, $\Delta\delta(^{31}P)$. The coordination chemical shift seems to be related to the bonding orbital structure of the phosphorus and indicates that the steric nature of the groups attached to phosphorus significantly affects the coordination chemical shift. Shaw[14,15] obtained linear relationships between $\delta(^{31}P)$ and $\Delta\delta(^{31}P)$ for both *cis*-$(R_3P)_2Ru(CO)_2Cl_2$ and *trans*-$(R_3P)_2Ru(CO)_2Cl_2$, and then later Shaw[16] showed that there was no linear relationship between these two parameters for the cis complexes. We have combined our data with Shaw's and find for the trans complexes that $\Delta\delta(^{31}P) = 0.330[\delta(^{31}P)] - 39.43$ ($R^2 = 0.434$), but there is no linear relationship for the cis complexes. Shaw[16] attributed the lack of this relationship to the unsymmetrical nature of the cis complexes allowing contributions from only a few configurations of the coordinated phosphine. We agree with this interpretation and suggest that for bulky phosphines where a specific configuration might be stabilized that there would not be a linear relationship. For the benzylphosphines alone the relationship between $\Delta\delta(^{31}P)$ and $\delta(^{31}P)$ is equally linear for the cis ($R^2 = 0.68$) and trans ($R^2 = 0.65$) isomers. We interpret this to mean that the bulky benzylphosphines are conformationally mobile in their complexes. This is supported[17] by the crystal structure data on *trans*-$(Bzl_3P)_2PdX_2$, X = CN, N_3, where both the cone angle and the conformation of the Bzl_3P are very different in the two complexes.

Table IV. Rate Constants and Activation Parameters for the Reaction *trans*-$L_2Ru(CO)_2Cl_2 \rightarrow$ *cis*-$L_2Ru(CO)_2Cl_2$ in $CDCl_3$ Solution

L	$10^{-4}k$, L mol^{-1} s^{-1}	T, °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
Bzl_3P	1.16	50	+15.70 ± 1	+5.8 ± 2
	0.97	43		
	0.48	38		
Bzl_2PPh	0.96	50	+17.52 ± 1	+9.5 ± 2
	1.32	43		
	0.23	34		

When they are heated in solution, these complexes thermally isomerize. The trans to cis isomerization was monitored by variable-temperature ^{31}P NMR as a function of time. The rate constants and activation parameters are listed in Table IV. The reliability of the data decreases with decreasing

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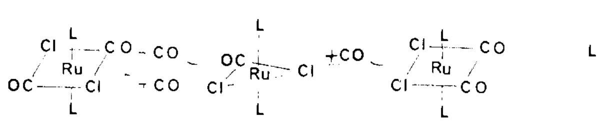
Table V. Final Positional[a] Parameters for $Ru(BzlPPh_2)_2(CO)_2Cl_2$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ru	1804 (1)[b]	3903 (1)	3225 (1)	Cl(3)	4644 (3)	3172 (2)	9641 (4)
Cl(1)	3177 (1)	3958 (1)	1928 (2)	Cl(4)	5197 (3)	4088 (2)	9162 (4)
Cl(2)	2692 (1)	3539 (1)	4915 (2)	Cl(5)	3794 (2)	3684 (1)	7661 (3)
C(1)	1172 (5)	4174 (2)	1858 (7)	Cl(6)	2178 (4)	7421 (1)	3153 (5)
O(1)	781 (4)	4325 (2)	1020 (5)	Cl(7)	1896 (3)	6495 (1)	3643 (4)
C(2)	740 (5)	3891 (2)	4194 (7)	Cl(8)	3571 (3)	6792 (3)	2579 (4)
O(2)	87 (4)	3903 (2)	4769 (6)	C(41)	4282 (7)	3717 (4)	9158 (9)
P(1)	2256 (1)	4632 (1)	4082 (2)	C(42)	2706 (8)	6918 (4)	3608 (10)
P(2)	1587 (1)	3154 (1)	2336 (2)	H(1)	389 (7)	392 (3)	975 (9)
C(3)	2004 (5)	5078 (2)	2920 (7)	H(2)	310 (7)	695 (3)	447 (9)
C(4)	1137 (6)	5276 (3)	2881 (8)	H(3)	67	520	356
C(5)	931 (6)	5588 (3)	1897 (9)	H(4)	31	574	187
C(6)	1556 (7)	5689 (3)	997 (9)	H(5)	140	591	29
C(7)	2398 (7)	5488 (3)	1010 (9)	H(6)	286	556	33
C(8)	2631 (6)	5183 (3)	1984 (8)	H(7)	325	504	201
C(9)	3498 (5)	4663 (2)	4448 (7)	H(8)	384	553	383
C(10)	3781 (5)	5061 (3)	5262 (8)	H(9)	430	616	516
C(11)	3929 (6)	5487 (3)	4767 (10)	H(10)	449	604	739
C(12)	4198 (7)	5854 (3)	5536 (13)	H(11)	425	532	830
C(13)	4301 (7)	5777 (4)	6821 (12)	H(12)	379	469	696
C(14)	4163 (8)	5366 (4)	7351 (11)	H(13)	157	548	524
C(15)	3900 (7)	4999 (3)	6579 (9)	H(14)	109	567	734
C(16)	1755 (5)	4802 (2)	5591 (7)	H(15)	102	511	895
C(17)	1541 (6)	5243 (2)	5915 (7)	H(16)	142	434	845
C(18)	1252 (7)	5352 (3)	7126 (8)	H(17)	181	415	632
C(19)	1217 (7)	5027 (3)	8058 (8)	H(18)	−26	310	130
C(20)	1454 (7)	4579 (3)	7769 (8)	H(19)	−92	320	−80
C(21)	1717 (6)	4467 (3)	6542 (7)	H(20)	5	332	−258
C(22)	1084 (5)	3174 (2)	732 (7)	H(21)	166	335	−230
C(23)	142 (6)	3155 (3)	547 (8)	H(22)	233	326	−19
C(24)	−238 (6)	3214 (3)	−674 (9)	H(23)	307	221	384
C(25)	321 (6)	3277 (3)	−1698 (8)	H(24)	296	139	359
C(26)	1257 (7)	3301 (3)	−1544 (8)	H(25)	252	108	162
C(27)	1652 (6)	3247 (3)	−319 (8)	H(26)	217	156	−15
C(28)	2708 (5)	2859 (2)	2175 (7)	H(27)	227	236	11
C(29)	2667 (5)	2355 (2)	1999 (7)	H(28)	57	233	168
C(30)	2880 (6)	2068 (3)	2997 (8)	H(29)	−31	179	288
C(31)	2815 (8)	1603 (3)	2852 (9)	H(30)	−51	189	511
C(32)	2560 (7)	1421 (3)	1726 (9)	H(31)	16	253	617
C(33)	2357 (7)	1698 (3)	690 (9)	H(32)	106	307	496
C(34)	2419 (6)	2156 (3)	843 (7)	H(33)	384	468	361
C(35)	880 (5)	2758 (2)	3220 (8)	H(34)	369	438	490
C(36)	481 (5)	2373 (2)	2622 (7)	H(35)	309	292	297
C(37)	−25 (6)	2062 (3)	3322 (9)	H(36)	304	299	141
C(38)	−145 (6)	2125 (3)	4608 (8)				
C(39)	244 (6)	2489 (3)	5226 (8)				
C(40)	722 (6)	2805 (3)	4525 (8)				

[a] The positional parameters are in fractional unit cell coordinates ×10^4 for the nonhydrogen atoms and ×10^3 for the hydrogen atoms. [b] In this and succeeding tables estimated standard deviations are given in parentheses for the least significant figures. Since H(3)–H(36) were not refined, no standard deviations are given.

solubility of the complexes, and quantitative data for $(BzlPPh_2)_2Ru(CO)_2Cl_2$ could not be obtained. For the isomerizations of both $(Bzl_3P)_2Ru(CO)_2Cl_2$ and $(Bzl_2PPh)_2Ru(CO)_2Cl_2$ both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are positive, indicative of a dissociative mechanism for the isomerization,[18] which would be expected for six-coordinate complexes.[19] Additional support for a dissociative mechanism is provided by the relative rates of the isomerization. It is anticipated that for a dissociative process an increase in the steric bulk of the complex should increase the rate of isomerization. Quantitatively, $(Bzl_3P)_2Ru(CO)_2Cl_2$ isomerizes faster than $(Bzl_2PPh)_2Ru(CO)_2Cl_2$, and this complex qualitatively isomerizes faster than $(BzlPPh_2)_2Ru(CO)_2Cl_2$. Furthermore, both the Bzl_3P and Bzl_2PPh complexes isomerize approximately 15 times faster than the analogous Me_2PPh complex.[20] In addition, the isomerizations are all slower in the presence of free carbon monoxide, indicating that the mechanism may involve the dissociation of one of the CO ligands as shown:



Because the cis complexes are all thermodynamically more stable than the trans complexes, cis to trans isomerization does not occur. For $(PPh_3)_2Ru(CO)_2Cl_2$ only the cis isomer may be isolated. This complex is an active hydrogenation catalyst[4] in the presence of excess PPh_3, which suggests that the catalytically active species may be $(PPh_3)_2Ru(CO)Cl_2$ and that PPh_3 in some way aids in the dissociation of carbon monoxide (perhaps through the intermediary of $(PPh_3)_3Ru(CO)Cl_2$, which we would expect to readily lose PPh_3).

The proposed structures for the benzylphosphine complexes based upon NMR and infrared data have been confirmed by single-crystal X-ray crystallography on *trans*-$(Bzl_3P)_2Ru(CO)_2Cl_2$ and *cis*-$(BzlPPh_2)_2Ru(CO)_2Cl_2$. ORTEP diagrams of the two complexes are shown in Figures 1 and 2, respec-

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[20] The trans to cis isomerization reaction was 50% complete in 3 h for L = Bzl_3P, 7 h for L = Bzl_2PPh, and 7 days for L = Me_2PPh at 50 °C in $CDCl_3$: Wilkes, L. W.; Nelson, J. H., unpublished results.

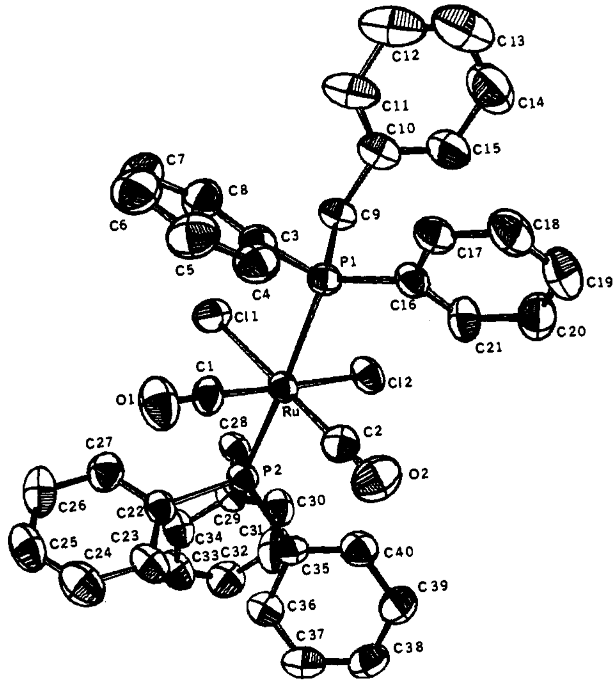

Figure 1. The $Ru(CO)_2(BzlPPh_2)Cl_2$ molecule. Ellipsoids of 50% probability are shown.[34]

Table VI. Selected Bond Lengths (Å) and Angles (Deg) for $Ru(BzlPPh_2)_2(CO)_2Cl_2$[a]

Ru-Cl(1)	2.430 (2)	Ru-P(1)	2.410 (2)
Ru-Cl(2)	2.428 (2)	Ru-P(2)	2.410 (2)
Ru-C(1)	1.869 (7)	C(1)-O(1)	1.131 (9)
Ru-C(2)	1.858 (7)	C(2)-O(2)	1.129 (10)

Cl(1)-Ru-Cl(2)	89.9 (1)	C(1)-Ru-P(1)	92.1 (2)
Cl(1)-Ru-C(1)	87.0 (2)	C(1)-Ru-P(2)	91.9 (2)
Cl(1)-Ru-C(2)	177.2 (2)	C(2)-Ru-P(1)	92.4 (2)
Cl(1)-Ru-P(1)	85.7 (1)	C(2)-Ru-P(2)	94.9 (2)
Cl(1)-Ru-P(2)	87.2 (1)	P(1)-Ru-P(2)	171.7 (1)
Cl(2)-Ru-C(1)	176.7 (2)	Ru-C(1)-O(1)	177.9 (6)
Cl(2)-Ru-C(2)	92.1 (2)	Ru-C(2)-O(2)	177.1 (6)
Cl(2)-Ru-P(1)	88.9 (1)	Ru-P(1)-C(3)	109.8 (2)
Cl(2)-Ru-P(2)	86.8 (1)	Ru-P(1)-C(9)	112.7 (2)
C(1)-Ru-C(2)	90.9 (3)	Ru-P(1)-C(16)	117.2 (2)

[a] The remaining bond lengths and angles of interest are given in the supplementary material.

tively. For *cis*-$(BzlPPh_2)_2Ru(CO)_2Cl_2$, the positional parameters are listed in Table V, and important bond lengths and bond angles are given in Table VI. For *trans*-$(Bzl_3P)_2Ru(CO)_2Cl_2$, fractional coordinates are listed in Table VII, and important bond distances and angles are listed in Table VIII. Both of these complexes are nearly regular octahedra with little distortion in bond angles. This could be attributed to the lack of large steric effects, which supports the conclusions derived from the ^{31}P NMR data. The Ru–P, Ru–Cl, Ru–C, and C–O bond lengths also all appear normal and are not significantly different from those observed for similar compounds as can be seen in Table IX. There are, however, significant differences in the Ru–C, Ru–Cl, and C–O bond lengths between the cis and trans complexes. The Ru–Cl and C–O bonds are longer and the Ru–C bonds shorter in *cis*-$(BzlPPh_2)_2Ru(CO)_2Cl_2$ than in *trans*-$(Bzl_3P)_2Ru(CO)_2Cl_2$, while the Ru–P bonds are essentially the same in the two compounds. These differences are a manifestation of the stronger trans influence[21] of CO than Cl. The infrared data (Table I) on these compounds also suggest that the Ru–C bonds are stronger and the Ru–Cl bonds weaker in the cis complexes than in the trans.

Collectively these data suggest the $(R_3P)_2Ru(CO)_2Cl_2$ complexes, which usually possess trans[8] R_3P (except for Et_2PPh) because of steric reasons. The greater thermodynamic stability of *cis*-$(R_3P)_2Ru(CO)_2Cl_2$ relative to *trans*-$(R_3P)_2Ru(CO)_2Cl_2$ results from electronic factors in maximizing the strength of the Ru–C bond at the expense of the Ru–Cl bond.

It is of interest to compare the structures of $(Bzl_3P)_2Ru(CO)_2Cl_2$, $(Bzl_3P)_2Pd(CN)_2$,[17] and $(Bzl_3P)_2Pd(N_3)_2$[17] for which the conformation of the Bzl_3P ligand changes in each case. For both the ruthenium chloride and palladium azide complexes the tribenzylphosphine configuration is such that ortho-metalation of the tribenzylphosphine could occur with minimum motion of the ligand and should therefore be reasonably facile. The ruthenium complexes do undergo base-promoted ortho-metalation reactions, which will be reported later. The nonbonded distances listed in Table X indicate significant interactions along what conceivably could be the ortho-metalation reaction coordinate.

Experimental Section

A. Reagents and Physical Measurements. The phosphines were prepared from commercial (Aldrich) PCl_3, $PhPCl_2$, and Ph_2PCl by standard Grignard reactions.[22] All chemicals were reagent grade and were used as received. Melting points were determined on a Meltemp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN 37921.

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer as Nujol mulls between CsBr plates.

The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 99.54, 25.00, and 40.26 MHz, respectively, on a JEOL FX-100 spectrometer in the Fourier-transform mode. The NM-3980 multinuclear probe was equipped with a JES-VT-3 variable-temperature controller. Temperatures were monitored with thermometers and/or thermocouples placed directly in the sample tubes and were found to be constant within ±1°. Proton and carbon-13 chemical shifts were measured relative to internal Me_4Si. Phosphorus-31 chemical shifts were measured relative to external PPh_3 and were corrected to 85% H_3PO_4 with downfield shifts being positive.

B. Preparation of the Complexes. The complexes were prepared by slight modifications of literature preparations for similar complexes.[16,23,24] An example of a typical preparation of each isomer is as follows.

***cis*-Dichlorodicarbonylbis(tribenzylphosphine)ruthenium(II).** A solution containing 0.17 g (0.65 mmol) of $RuCl_3{\cdot}3H_2O$ in 50 mL of 2-methoxyethanol was refluxed while carbon monoxide was bubbled through the solution for approximately 6 h. To the resultant yellow solution was added a solution of 0.49 g (1.62 mmol) of Bzl_3P in 10 mL of N_2-degassed CH_2Cl_2, and this solution was refluxed under carbon monoxide until a colorless solid or solution was obtained. A modified Dean–Stark trap was then inserted, and the solution volume was reduced with continued refluxing. The colorless crystals that volunteered were filtered and washed with anhydrous diethyl ether and vacuum-dried. The yield was 60% (based on ruthenium); mp 226–228 °C. Anal. Calcd for $C_{44}H_{42}Cl_2RuP_2O_2$: C, 63.15; H, 5.06. Found: C, 63.50; H, 5.10.

***trans*-Dichlorodicarbonylbis(tribenzylphosphine)ruthenium(II).** A solution containing 0.6032 g (2.3 mmol) of $RuCl_3{\cdot}3H_2O$ in 50 mL of absolute ethanol was refluxed under CO for approximately 6.5 h. To the resultant *cooled* solution was added a solution of 2.21 g (7.27 mmol) of $PBzl_3$ in 10 mL of degassed CH_2Cl_2, and the solution was allowed to sit at room temperature under CO. The yellow solid was

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Table VII. Fractional Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations[a] for $Ru(Bzl_3P)_2(CO)_2Cl_2$

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	0.0 (0)	0.0 (0)	0.0 (0)	51.6 (2)	33.9 (2)	35.0 (2)	24.9 (2)	9.6 (2)	15.6 (1)
Cl(2)	−1325 (1)	584 (1)	2001 (1)	58.9 (5)	50.3 (5)	41.5 (4)	26.5 (4)	13.9 (4)	14.9 (3)
C(3)	1253 (3)	−228 (3)	1268 (3)	69 (2)	35 (2)	46 (2)	26 (2)	4 (2)	14 (1)
O(4)	2010 (3)	−417 (2)	1877 (3)	109 (2)	57 (1)	70 (2)	44 (1)	−21 (1)	17 (1)
P(5)	1480 (1)	2377 (1)	1133 (1)	53.3 (5)	36.9 (4)	40.7 (4)	26.1 (4)	12.8 (4)	17.9 (3)
C(6)	2111 (3)	3309 (3)	3288 (3)	70 (2)	51 (2)	45 (2)	32 (2)	11 (2)	19 (1)
C(7)	2623 (4)	2623 (4)	4158 (3)	71 (2)	48 (2)	42 (2)	31 (2)	8 (2)	15 (1)
C(8)	4025 (4)	2933 (4)	4415 (4)	68 (2)	78 (2)	58 (2)	38 (2)	11 (2)	29 (2)
C(9)	4462 (4)	2407 (5)	5274 (4)	86 (3)	112 (3)	71 (3)	63 (3)	6 (2)	36 (2)
C(10)	3535 (5)	1676 (4)	5910 (4)	119 (4)	91 (3)	64 (2)	60 (3)	8 (2)	40 (2)
C(11)	2157 (5)	1450 (4)	5690 (4)	106 (3)	78 (3)	55 (2)	32 (2)	7 (2)	38 (2)
C(12)	1686 (4)	1956 (3)	4823 (4)	79 (2)	64 (2)	53 (2)	29 (2)	11 (2)	28 (2)
C(13)	462 (3)	3262 (3)	846 (3)	59 (2)	45 (2)	45 (2)	28 (2)	9 (1)	18 (1)
C(14)	1086 (3)	4781 (3)	1725 (3)	49 (2)	40 (2)	46 (2)	27 (1)	6 (1)	18 (1)
C(15)	840 (3)	5406 (3)	3184 (4)	64 (2)	52 (2)	59 (2)	33 (2)	16 (2)	25 (2)
C(16)	1385 (4)	6797 (4)	3985 (4)	94 (3)	62 (2)	56 (2)	50 (2)	2 (2)	7 (2)
C(17)	2182 (4)	7577 (3)	3319 (5)	92 (3)	42 (2)	97 (3)	31 (2)	−18 (2)	17 (2)
C(18)	2428 (4)	6981 (4)	1874 (5)	85 (3)	57 (2)	105 (3)	30 (2)	14 (2)	52 (2)
C(19)	1881 (4)	5596 (3)	1082 (4)	84 (2)	55 (2)	60 (2)	39 (2)	18 (2)	34 (2)
C(20)	3046 (3)	2983 (3)	298 (3)	67 (2)	51 (2)	54 (2)	29 (2)	22 (2)	27 (2)
C(21)	4386 (3)	3024 (3)	922 (3)	53 (2)	48 (2)	52 (2)	22 (2)	19 (2)	15 (2)
C(22)	4549 (3)	1866 (3)	658 (4)	55 (2)	50 (2)	70 (2)	25 (2)	7 (2)	7 (2)
C(23)	5766 (4)	1921 (4)	1301 (5)	64 (3)	73 (3)	91 (3)	41 (2)	10 (2)	16 (2)
C(24)	6870 (4)	3129 (5)	2197 (4)	58 (2)	94 (3)	72 (3)	35 (2)	8 (2)	10 (2)
C(25)	6776 (4)	4300 (4)	2417 (4)	58 (2)	73 (3)	66 (2)	6 (2)	11 (2)	3 (2)
C(26)	5544 (4)	4253 (3)	1798 (4)	77 (3)	58 (2)	68 (2)	29 (2)	30 (2)	21 (2)

atom	x	y	z	U_{iso}, Å^2	atom	x	y	z	U_{iso}, Å^2
H(6A)	2953 (34)	4294 (32)	3584 (36)	96 (11)	H(17)	2609 (32)	8503 (31)	3889 (35)	88 (10)
H(6B)	1192 (28)	3385 (26)	3658 (30)	64 (8)	H(18)	2940 (30)	7463 (30)	1424 (34)	82 (10)
H(8)	4837 (32)	3584 (30)	3981 (35)	91 (10)	H(19)	2031 (25)	5192 (24)	97 (27)	50 (7)
H(9)	5379 (34)	2542 (33)	5320 (38)	102 (12)	H(20A)	2697 (25)	2416 (25)	−714 (28)	50 (7)
H(10)	3970 (30)	1343 (28)	6457 (33)	77 (9)	H(20B)	3203 (29)	3863 (28)	465 (31)	69 (9)
H(11)	1391 (36)	1110 (35)	6160 (41)	118 (13)	H(22)	3809 (27)	1029 (26)	49 (29)	62 (8)
H(12)	683 (40)	1809 (38)	4809 (43)	128 (14)	H(23)	5787 (34)	1118 (33)	1216 (38)	101 (11)
H(13A)	316 (23)	2979 (22)	−188 (26)	40 (7)	H(24)	7739 (33)	3164 (32)	2639 (36)	96 (11)
H(13B)	−380 (25)	2886 (24)	1087 (28)	49 (7)	H(25)	7516 (33)	5141 (32)	2990 (37)	96 (11)
H(15)	311 (25)	4894 (24)	3639 (27)	50 (7)	H(26)	5434 (28)	4971 (27)	1904 (31)	69 (9)
H(16)	1236 (32)	7177 (31)	5026 (35)	92 (11)					

[a] Positional parameters are given $\times 10^4$ and thermal parameters $\times 10^3$ in Å^2. Numbers in parentheses are esd's in the units of the least significant digit given for the corresponding parameter. See Figures 1 or 2 for the identities of the atoms. The anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Table VIII. Selected Bond Lengths (Å) and Angles (Deg) for $(Bzl_3P)_2Ru(CO)_2Cl_2$[a]

Ru(1)–Cl(2)	2.418 (1)	P(5)–C(6)	1.875 (3)
Ru(1)–C(3)	1.948 (3)	P(5)–C(13)	1.855 (3)
Ru(1)–P(5)	2.398 (1)	P(5)–C(20)	1.856 (3)
C(3)–O(4)	1.122 (4)		
Cl(2)–Ru(1)–C(3)	93.71 (8)	Ru(1)–P(5)–C(6)	118.61 (10)
Cl(2)–Ru(1)–P(5)	85.04 (2)	Ru(1)–P(5)–C(13)	109.20 (9)
C(3)–Ru(1)–P(5)	90.03 (9)	Ru(1)–P(5)–C(20)	118.16 (10)
Ru(1)–C(3)–O(4)	173.66 (28)		

[a] The remaining bond lengths and angles of interest are given in the supplementary material.

filtered, washed with anhydrous diethyl ether, and vacuum-dried. The yield was 57% based on ruthenium; mp 225–227 °C. Anal. Calcd for $C_{44}H_{42}Cl_2RuP_2O_2$: C, 63.15; H, 5.06. Found: C, 63.00; H, 5.10.

In a similar manner the following complexes were prepared.

***cis*-Dichlorodicarbonylbis(dibenzylphenylphosphine)ruthenium(II).** The yield was 90%; mp 235–238 °C. Anal. Calcd for $C_{42}H_{38}Cl_2RuP_2O_2$: C, 62.37; H, 4.74. Found: C, 62.70; H, 4.10.

***trans*-Dichlorodicarbonylbis(dibenzylphenylphosphine)ruthenium(II).** The yield was 82%; mp 230–236 °C. Anal. Calcd for $C_{42}H_{38}Cl_2RuP_2O_2$: C, 62.37; H, 4.74. Found: C, 62.50; H, 4.60.

***cis*-Dichlorodicarbonylbis(benzyldiphenylphosphine)ruthenium(II).** The yield was 95%; mp 260–263 °C. Anal. Calcd for $C_{40}H_{34}Cl_2RuP_2O_2$: C, 61.54; H, 4.39. Found: C, 61.30; H, 4.70.

***trans*-Dichlorodicarbonylbis(benzyldiphenylphosphine)ruthenium(II).** The yield was 78%; mp 225–259 °C. Anal. Calcd for $C_{42}H_{38}Cl_2RuP_2O_2$: C, 61.51; H, 4.39. Found: C, 61.50; H, 4.40.

C. X-ray Data Collection. 1. *cis*-$(BzlPPh_2)_2Ru(CO)_2Cl_2$.[1b] Crystal Data. At 27 °C with Mo Kα (λ = 0.709 54 Å) radiation, a clear crystal of $(BzlPPh_2)_2Ru(CO)_2Cl_2$ yielded the following information: fw = 1019.37, a = 14.564 (2) Å, b = 29.391 (3) Å, c = 10.440 (2) Å, β = 90.48 (2)°, Z = 4, monoclinic, space group $P2_1/a$, D_{calcd} = 1.47 g cm^{-3}, μ = 9.01 cm^{-1} (no correction made).

Data were collected on an automated four-circle diffractometer described previously.[25] All data within a sphere of 45° (6885 reflections) in the hkl and $hk\bar{l}$ octants were measured with use of an ω-step scan technique.

As a general check on electronic and crystal stability, the intensities of 5 standard reflections were remeasured every 75 reflections. These standard reflections were not observed to vary significantly throughout the data collection period. Systematic extinctions of the type $h0l$, $h = 2n + 1$, and $0k0$, $k = 2n + 1$, uniquely indicate the space group as $P2_1/a$.

The intensity data were corrected for Lorentz and polarization effects. The variance in each intensity was calculated by

$$\sigma^2 = C_T + k_t C_B + (0.03C_T)^2 + (0.03C_B)^2$$

where C_T and C_B represent the total and background counts, k_t is a counting-time constant, and 0.03 is an estimate of nonstatistical error. The estimated deviations were calculated by a finite difference method.[26] Equivalent data were averaged, and 4688 reflections with $|F_o| > 3.0[\sigma(F_o)]$ were considered observed and retained for the structure analysis.

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(26) Lawton, S. L.; Jacobson, R. A. *Inorg. Chem.* **1968**, *7*, 2124.

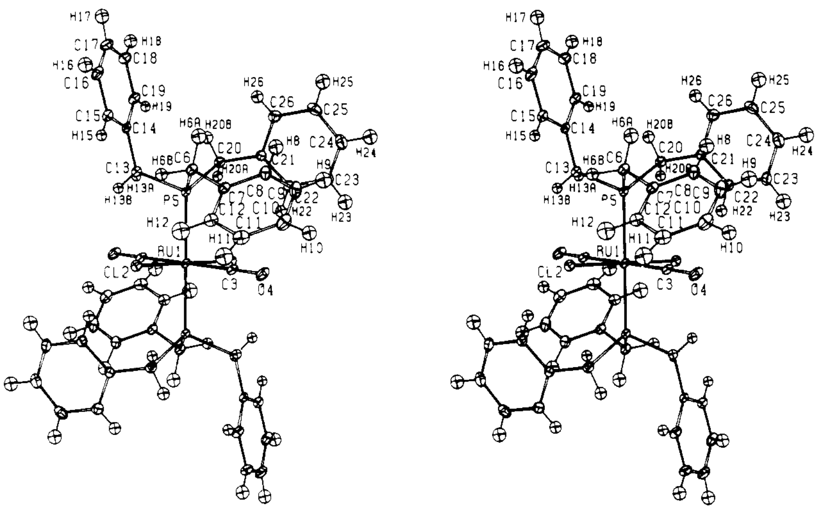

Figure 2. Stereoview of the $Ru(CO)_2(Bzl_3P)_2Cl_2$ molecule. Ellipsoids of 10% probability are shown.[34]

Table IX. Representative Structural Data for Ruthenium Complexes

complexes	d, Å Ru-P	Ru-Cl	Ru-CO	C-O	ref
trans-$(Bzl_3P)_2Ru(CO)_2Cl_2$	2.398	2.418	1.948	1.122	*a*
cis-$(BzlPPh_2)_2Ru(CO)_2Cl_2$	2.410	2.429	1.863	1.130	*a*
$(PPh_3)_3RuCl_2$	2.38	2.387	...	...	*b*
$Ru(Me_2SO)_4Cl_2$	...	2.435	...	...	*c*
$(PPh_3)_2Ru(CO)(SnCl_3)((CH_3)_2O)$	2.393	2.405	1.796	1.156	*d*
$(Me_2PPh)_2RuCl_2(CO)(C_2H_4)$	2.414	2.415 2.454	1.831	1.136	*e*
(π-allyl)$(NO)Ru(PPh_3)_2$	2.344 2.391	...	...	...	*f*
$(CSe)(PPh_3)_2Ru(CO)Cl_2$	...	2.428	...	...	*g*
$(RNC)(PPh_3)_2Ru(CO)(O_2C{-}C)$	2.373 2.386	...	1.81	1.14	*h*
$(CS)(PPh_3)_2RuCl_3Ru(PPh_3)_2Cl$	2.26-2.36	2.45-2.58	...	...	*i*
(*N,N'*-$Et_2Im)RuCl_2$		2.455 2.463			*j*
trans-$(CH_3C_6H_4N_3C_6H_4CH_3)Ru(CO)(PPh_3)_2$	2.343 2.354	...	1.866	...	*k*
$[(N_2HC_6H_5)(PPh_3)Ru(CO)_2Cl]\,ClO_4{\cdot}CH_2Cl_2$	2.439 2.415	2.424	1.911 1.912	1.055 1.122	*l*
$(Et_2NCS_2)_4Ru_3(CO)_3Cl_2$	...	2.55	1.68	1.22	*m*
$\{(SnMe_3)Ru(CO)_4\}_2$	...	...	1.932-1.947	1.129-1.140	*n*
(η-$C_6H_6)Ru(CO)(GeCl_3)_8$	...	...	1.87	1.14	*o*

[a] This work. [b] La Placa, S. J.; Ibers, J. A. *Inorg. Chem.* 1965, *4*, 778. [c] Mercer, A.; Troter, J. *J. Chem. Soc., Dalton Trans.* 1975, 2480. [d] Gould, R. O.; Sime, W. J.; Stephenson, T. A. *Ibid.* 1978, 76. [e] Brown, L. D.; Barnard, C. F. J.; Daniels, J. A.; Mawby, R. J.; Ibers, J. A. *Inorg. Chem.* 1978, *17*, 2932. [f] Schoonover, M. W.; Kubiak, C. P.; Eisenberg. R. *Ibid.* 1978, *17*, 3050. [g] Clark, G. R.; James, S. M. *J. Organomet. Chem.* 1977, *134*, 229. [h] Clark, G. R.; Waters, T. M.; Whittle, K. R. *J. Chem. Soc., Dalton Trans.* 1975, 2556. [i] Fraser, A. J. F.; Gould, R. O. *Ibid.* 1974, 1139. [j] Hitchcock, P. B.; Lappert, M. F.; Dye, P. L. *Ibid.* 1978, 826. [k] Brown, L. D.; Ibers, J. A. *Inorg. Chem.* 1976, *15*, 2788. [l] Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* 1975, *97*, 5369. [m] Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* 1975, 2422. [n] Howard, J. A. K.; Kellet, S. C.; Woodward, P. *Ibid.* 1975, 2332. [o] Chan, L. Y. Y.; Graham, W. A. G. *Inorg. Chem.* 1975, *14*, 1778.

Table X. Nonbonded Intramolecular Distances[a] (Å) for $(Bzl_3P)_2Ru(CO)_2Cl_2$

H(22)-C(3)	3.04 (3)	H(6B)-Cl(2)	3.09 (3)
H(22)-O(4)	3.11 (3)	H(13B)-Cl(2)	3.04 (3)
H(22)-Cl(2)	2.71 (3)	H(20A)-Cl(2)	2.98 (3)
H(12)-Cl(2)	2.86 (4)	C(3)-Cl(2)	3.006 (3), 3.202 (4)

[a] For comparison purposes the van der Waals radii are H 1.45, O 1.50, C 1.65, and Cl 1.80 Å: Bondi, A. *J. Phys. Chem.* 1964, *68*, 441. Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski I. J.; Van-Catledge, F. A. *J. Am. Chem. Soc.* 1968, *90*, 1199. As a consequence, several of these contacts are shorter than the sums of the appropriate van der Waals radii. In some cases, significant interactions between the nonbonded atoms are implied.

Solution and Refinement. The position of the ruthenium atom was obtained from analysis of a sharpened Patterson map. The positions of the remaining nonhydrogen atoms were found by subsequent structure factor and electron density map calculations.[27] The aromatic and methylene hydrogen positions were calculated and included in later structure factor calculations. The nonhydrogen positional and anisotropic thermal parameters were refined by block-diagonal matrix procedures[28] to a final conventional residual $R = 0.064$ and a weighted residual $R_w = 0.078$.

The molecular structure is illustrated in Figure 1. The atomic positional parameters and principal nonhydrogen bond lengths and angles are given in Tables V and VI (others are given in the supplementary material as Table VIA).

2. *trans*-$(Bzl_3P)_2Ru(CO)_2Cl_2$.[1c] Diffraction Section. A single crystal of $(Bzl_3P)_2Ru(CO)_2Cl_2$ with extreme dimensions of 0.28 ×

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(27) Hubbard, C. A.; Quicksall, C. O.; Jacobson, R. A. "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFPROJ, ALFFT, and FRIEDEL", U.S. Atomic Energy Commission Report IS-2625; Iowa State University and Institute for Atomic Research: Ames, Iowa, 1971.

(28) Lapp, R. L.; Jacobson, R. A. "ALLS, A Generalized Crystallographic Least Squares Program", U.S. Department of Energy Report IS-4708; Iowa State University: Ames, Iowa, 1979.

0.20 × 0.18 mm was mounted approximately along its longest dimension on a glass rod.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, λ 0.709 30 Å; $K\alpha_2$, λ 0.713 59 Å) was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations (see Crystal Data) were determined by least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 18.7°. The reflections were examined with use of the θ–2θ scan technique. Each reflection was scanned at a constant rate of 4.0° $\min^{-1}$ from 0.8° (in 2θ) below the calculated $K\alpha_1$ peak to 0.8° above the $K\alpha_2$ maximun. The background to scan time ratio was 0.7. Three check reflections, monitored after every 100 reflections during the course of data collection, showed no significant fluctuations.

Standard deviations were assigned according to the formula

$$\sigma(I) = [(\mathrm{CT} + B_1 + B_2)\omega^2 + (pI)^2]^{1/2}$$

where CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\mathrm{CT} - B_1 - B_2)$. A value of 0.02 was assigned to the empirical parameter p to account for instrumental inaccuracies. The weights (w) used in least-squares refinement of the structural parameters were the reciprocal squares of $\sigma(F_o)$. Of the 3550 unique reflections measured (those for which $2\theta < 50°$), 2830 had intensities such that $I > 3[\sigma(I)]$. All intensities were corrected for Lorentz and polarization effects.[29] The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction. A correction for the effect of absorption ($\mu = 6.32\ \mathrm{cm}^{-1}$) was not made. The atomic scattering factors for Ru^0, P^0, Cl^0, O^0, C^0,[30] and H(bonded)[31] were used; all but the last were modified to include the real part of the anomalous dispersion correction.[32]

Crystal Data: $(\mathrm{Bzl_3P})_2\mathrm{Ru(CO)_2Cl_2}$, triclinic, $P\bar{1}$, a = 10.478 (2) Å, b = 11.968 (3) Å, c = 9.623 (2) Å, α = 113.81 (2)°, β = 90.65 (2)°, γ = 112.63 (2)°, V = 998.9 (4) Å^3, mol wt 836.77, d_{obsd}(flotation) = 1.39 (1) g cm^{-3}, d_{calcd} = 1.39 g cm^{-3}, and Z = 1.

Structure Determination. Because there is only one molecule in this triclinic unit cell, the ruthenium atom could be placed at the origin, whether the space group is $P1$ or $P\bar{1}$. The resulting Fourier function, which was necessarily centrosymmetric, indicated reasonable positions for all of the nonhydrogen atoms in the unit cell with $R_1 = \sum(|F_o - |F_c||)/\sum F_o = 0.41$, so the space group $P\bar{1}$ was chosen. Of the 25 new atoms, 4 were designated Cl(2), C(3), O(4), and P(5) and the remaining as carbons. With use of the 1836 lowest angle reflections, 3 cycles of full-matrix least-squares refinement[33] with isotropic thermal parameters reduced R_1 to 0.083 and $R_2 = [\sum w(F_o - |F_c|)^2/wF_o^2]^{1/2}$ to 0.096. One cycle of isotropic (anisotropic for the Ru, Cl, and P atoms) refinement followed by two cycles of anistropic refinement led to R_1 = 0.043 and R_2 = 0.057. The 21 hydrogen positions were calculated with the assumption of a C–H distance of 0.95 Å, and a difference function showed a peak very near each of these calculated positions. One cycle of least-squares refinement with fixed calculated hydrogen positions led to R_1 = 0.036 and R_2 = 0.044, and another using all 2830 observed reflections resulted in R_1 = 0.048 and R_2 = 0.070. A difference Fourier function clearly revealed the positions of the 21 hydrogen atoms, which were then included in several more cycles of least-squares refinement with anisotropic thermal parameters for nonhydrogens and isotropic ones for hydrogens. At convergence, the error indices were R_1 = 0.029 and R_2 = 0.030. The "goodness-of-fit", $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$, is 1.44, where m (2830) is the total number of observations used in least-squares refinement, and s (316) is the total number of parameters. The overdetermination ratio (m/s) is 9.0.

In the final cycle of least-squares refinement, all shifts were less than 20% of their esd's. The two largest peaks on the final difference function (esd = 0.05 e Å^{-3}) were 0.29 e Å^{-3} in height and were less than 1.1 Å from Ru(1). The positional and thermal parameters of the atoms are listed in Table VII. Selected interatomic distances and angles are given in Table VIII (others are given in the supplementary material as Table VIIIA), and the least-square planes of interest are given in Table XI as supplementary material. Figure 2 shows a labeled stereoview of the molecule.

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Registry No. *cis*-$(\mathrm{Bzl_3P})_2\mathrm{Ru(CO)_2Cl_2}$, 80410-13-5; *trans*-$(\mathrm{Bzl_3P})_2\mathrm{Ru(CO)_2Cl_2}$, 80446-32-8; *cis*-$(\mathrm{Bzl_2PPh})_2\mathrm{Ru(CO)_2Cl_2}$, 80410-14-6; *trans*-$(\mathrm{Bzl_2PPh})_2\mathrm{Ru(CO)_2Cl_2}$, 80446-33-9; *cis*-$(\mathrm{BzlPPh_2})_2\mathrm{Ru(CO)_2Cl_2}$, 60661-10-1; *trans*-$(\mathrm{BzlPPh_2})_2\mathrm{Ru(CO)_2Cl_2}$, 60607-99-0.

Supplementary Material Available: Listings of observed and calculated structure factors, additional bond distances and angles for $(\mathrm{Bzl_3P})_2\mathrm{Ru(CO)_2Cl_2}$ (Table VIIIA) and $(\mathrm{BzlPPh_2})_2\mathrm{Ru(CO)_2Cl_2}$ (Table VIA), and least-squares planes of interest for $(\mathrm{Bzl_3P})_2\mathrm{Ru(CO)_2Cl_2}$ (Table XI) (40 pages). Ordering information is given on any current masthead page.

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(29) Ottersen, T. LP-76 Computer Program; University of Hawaii, 1976.

(30) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 71.

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