Large-Ring and Cyclometalated Rhodium Complexes from Some Medium-Chain α,ω-Diphosphines

Christopher Crocker, R. John Errington, Richard Markham, Christopher J. Moulton, Kevin J. Odell, and Bernard L. Shaw*

Contribution from the School of Chemistry, The University, Leeds LS2 9JT, England.

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Abstract: $Bu^t_2P(CH_2)_5PBu^t_2$ reacts with $RhCl_3\cdot 3H_2O$ in ethanol to give a mixture of the binuclear 16-atom ring complex $[Rh_2H_2Cl_4\{Bu^t_2PCH_2CH_2CH_2CH_2CH_2PBu^t_2\}_2]$, which exists in solution as a mixture of two rotamers: a cyclometalated complex $[RhHCl\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$ of configuration **6** and another species, probably an olefin complex $[RhCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2PBu^t_2\}]$ (**8**). A similar reaction in refluxing tetrahydrofuran gave pure **6**. Treatment of the binuclear hydrido complex $[Rh_2H_2Cl_4\{Bu^t_2PCH_2CH_2CH_2CH_2CH_2PBu^t_2\}_2]$ with 2-methylpyridine promoted cyclometalation to give **6**. This cyclometalated hydride (**6**) is fluxional and at ambient temperature rapid C-H fission occurs, rendering Rh*H* and RhC*H* magnetically equivalent. An $^1H\{^{31}P,^{103}Rh\}$ INDOR experiment shows that the rhodium is equally coupled to both hydrogens. At −62 °C the fluxional process has effectively stopped. Treatment of $[RhHCl\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$ with CO and sodium methoxide gave the volatile $[Rh(CO)\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$. Treatment of $RhCl_3\cdot 3H_2O$ with $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ in ethanol or 2-propanol gives the 16-atom ring binuclear hydride $[Rh_2H_2Cl_4\{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2\}_2]$ (a mixture of six isomers or rotamers) together with a mixture of the cyclometalated hydride $[RhHCl\{Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2\}]$ (**12**) and the olefin complex $[RhCl\{Bu^t_2PCH_2CH_2C({=}CH_2)CH_2CH_2PBu^t_2\}]$ (**11**). The binuclear complex mixture with 2-methylpyridine gives the pure cyclometalated hydride **12**, which on heating in aqueous 2-propanol is quantitatively converted to the olefin complex **11**. **12** is not fluxional. Treatment of $RhCl_3\cdot 3H_2O$ with $Bu^t_2P(CH_2)_6PBu^t_2$ gives the olefin complex $[RhCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t_2\}]$ (trans C=C) (**10**) contaminated with what is probably the corresponding complex containing a cis C=C group (**13**). The new ligand *trans*-$Bu^t_2P(CH_2)_2CH{=}CH(CH_2)_2PBu^t_2$ was prepared. This with $RhCl_3\cdot 3H_2O$ gave predominantly **10** together with about 1% of **13**. *trans*-$[RhCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t_2\}]$ reacts with carbon monoxide in the presence of sodium tetraphenylboron or sodium perchlorate to give the salts $[Rh(CO)\{Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t_2\}]^+X^-$. *trans*-$Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$ (new ligand) reacts with $RhCl_3\cdot 3H_2O$ to give exclusively *trans*-$[RhCl\{Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2\}]$ (**9**). ^1H, ^{13}C, ^{31}P, and ^{103}Rh NMR data, including signs of coupling constants, and IR data are reported. Several of the complexes have had their crystal structures determined and these have been or will be reported separately.

We have shown that long-chain diphosphines of the type $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 5–10 or 12), containing the very bulky PBu^t_2 end groups, react with palladium or platinum halides to give very large chelate rings (12- to 45-membered) containing one, two, or three metal atoms.[1,2] The shorter chain diphosphines $Bu^t_2P(CH_2)_nPBu^t_2$, e.g., n = 5 or 6, and also $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ cannot span trans positions and only gave binuclear complexes but, additionally, they cyclometalated on the carbon chain; e.g., stable complexes of the type $[MCl\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$ (M = Pd or Pt) formed.[3,4] We have now investigated the action of these penta- and hexamethylene diphosphines on rhodium trichloride. Although less bulky tertiary phosphines (L) react with rhodium trichloride to give six-coordinate complexes, e.g., $[RhCl_3L_3]$, $[Rh_2Cl_6L_4]$, etc., we, and others, have shown that bulky phosphines, e.g., P(*o*-tolyl)$_3$ and PBu^t_2R (R = alkyl or aryl) (Q), react with rhodium trichloride to give a variety of products including coordinatively unsaturated rhodium(III) hydrides $[RhHCl_2Q_2]$, $[RhH_2ClQ_2]$, or rhodium(II) complexes *trans*-$[RhCl_2Q_2]$.[5-9] We therefore anticipated that the diphosphines $Bu^t_2P(CH_2)_nPBu^t_2$ (n = 5 or 6) might give binuclear large-ring coordinatively unsaturated hydrides and also might cyclometalate (as with platinum or palladium) to give a cyclometalated hydride. Compounds containing alkyl and hydrido groups attached to the same metal atom are rare but are believed to be involved as intermediates in many catalytic reactions, e.g., hydrogenation and olefin isomerization, etc.

We chose first to study the action of $Bu^t_2P(CH_2)_5PBu^t_2$ on rhodium trichloride. Addition of this diphosphine (1.5 mol per rhodium atom) to an ethanolic solution of rhodium trichloride rapidly gave a chocolate-brown precipitate. This proved to be very insoluble and intractable. However, on continued reflux over a period of 3 days the mixture gradually converted into a reddish-pink, crystalline precipitate and an orange solution. The crystalline product is formulated as a binuclear rhodium(III) hydride $[Rh_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$. Elemental analytical, molecular weight, and IR data are given in Table I and NMR (^1H and ^{31}P data) in Table II. In the IR spectrum the value of $\nu(RhCl_2)$, 345 cm^{-1}, is characteristic of a linear [Cl-Rh-Cl] unit,[7,10] and both this and the value of ν(RhH) (Table I) are close to those found for complexes of the type $[RhHCl_2(PBu^t_2R)_2]$ (R = Me, Et, or Pr^n) of configuration **1**.[7] Apart from the 345-cm^{-1} band, the IR spectrum strongly resembles that of *trans*-$[Pd_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$, the structure of which has been shown to be **2** by single-crystal X-ray diffraction.[3] The NMR spectra (^1H and ^{31}P) showed predominantly one species having equivalent rhodium atoms (data in Table II) and the hydride resonance, which did not change on cooling to −90 °C, has similar NMR parameters to those of $[RhHCl_2(PBu^t_2Pr^n)_2]$ (**1**). Of the possible rotamers (isomers) **3–5**, the last can be excluded since it contains two different ^1H, ^{31}P, and ^{103}Rh environments, leaving **3** and **4** as possible structures. The ^{31}P NMR spectrum showed a 1:1 doublet, δ(P) 48.1, ^1J(RhP) = 97 Hz, but additionally there was ca. 10% of a second species having δ(P) 44.6 ppm and ^1J(RhP) = 98 Hz, which in view of the similarity of NMR

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Table I. Melting Point, Elemental Analytical,[a] Molecular Weight, *M*,[a] and IR (cm^{-1}) Data (Nujol Mulls)

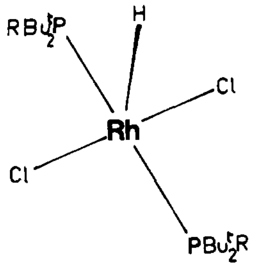
	mp, °C	C	H	halogen	M^b	ν(Rh-Cl)	ν(Rh-H)	ν(CO)
$[Rh_2H_2Cl_4\{Bu^t{}_2P(CH_2)_5PBu^t{}_2\}_2]$	200-209[d]	47.05 (47.2)	8.85 (8.65)	13.65 (13.25)	995 (1070)	345 s	1941 w,	
$[RhHCl\{Bu^t{}_2P(CH_2)_2CH(CH_2)_2PBu^t{}_2\}]$	209-215[c]	50.35 (50.75)	8.9 (8.95)	7.25 (7.15)	525 (499)	267 s	2205 w	
$[Rh(CO)\{Bu^t{}_2P(CH_2)_2CH(CH_2)_2PBu^t{}_2\}]$	173-216[c]	54.0 (54.0)	9.15 (9.05)		489 (489)			1900
$[Rh_2H_2Cl_4\{Bu^t{}_2P(CH_2)_2CHMe(CH_2)_2PBu^t{}_2\}_2]$	235-242[d]	47.6 (48.0)	8.8 (9.0)	13.0 (12.9)	1073 (1099)	343 s	1941 w, 1926 w	
$[RhHCl\{Bu^t{}_2P(CH_2)_2CMe(CH_2)_2PBu^t{}_2\}]$	221-225[c]	51.5 (51.5)	9.3 (9.4)	6.7 (6.7)	534 (512)	266	2230 w	
$[RhCl\{Bu^t{}_2P(CH_2)_2(C{=}CH_2)(CH_2)_2PBu^t{}_2\}]$	241-243[c]	51.5 (51.7)	9.15 (9.1)	7.1 (7.0)		286		
$[RhCl\{Bu^t{}_2P(CH_2)_2CH{=}CH(CH_2)_2PBu^t{}_2\}]$	230-235[c]	51.1 (51.7)	8.9 (9.1)	6.9 (7.0)	530 (511)	287 s		
$[Rh(CO)\{Bu^t{}_2P(CH_2)_2CH{=}CH(CH_2)_2PBu^t{}_2\}]ClO_4$	227-233[d]	45.75 (45.8)	7.7 (7.45)	5.9 (6.15)				1978
$[Rh(CO)\{Bu^t{}_2P(CH_2)_2CH{=}CH(CH_2)_2PBu^t{}_2\}]BPh_4$[e]	217-220	68.05 (68.6)	8.2 (8.1)					1989
$[RhCl\{Bu^t{}_2PCH_2CH{=}CHCH_2PBu^t{}_2\}]$	215-219[c,d]	49.85 (49.75)	8.7 (8.75)	7.25 (7.35)	482 (482)[f]	287 m		
$[Bu^t{}_2PHCH_2CH{=}CHCH_2PHBu^t{}_2]2Br^-$	265-268[c]	47.4 (47.45)	8.85 (8.75)	31.6 (31.6)				

[a] Calculated values in parentheses. [b] Measured osmometrically in chloroform solution, unless stated otherwise. [c] With sublimation. [d] With decomposition. [e] Conductivity in nitrobenzene at 22 °C 29 $cm^2\ \Omega^{-1}\ mol^{-1}$. [f] The most intense peak in the molecular ion, by mass spectrometry. This peak corresponds to the chlorine-35 isotope.

parameters is probably the other member of this pair (i.e., **3** or **4**). In the ^1H NMR spectrum a much weaker and broader resonance lay under the pattern associated with the major isomer and no doubt arises from this second species. Rotamers are common in $PBu^t{}_2R$-metal chemistry owing to restricted rotation around the metal-phosphorus bonds caused by strong nonbonding interactions between the Bu^t groups and other ligands attached to the metal, e.g., Cl or CO.[1,2,7]

From the orange solution obtained by refluxing $RhCl_3$ with $Bu^t{}_2P(CH_2)_5PBu^t{}_2$ in ethanol we obtained a highly crystalline, orange product. The composition of this product varied according to the reflux time (see below) but in one preparation was a single substance. On the basis of a single-crystal X-ray structural determination this material has been shown to be the cyclometalated hydride complex $[RhHCl\{Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2\}]$ of configuration **6**.[11,12] The behavior of this complex in solution is unusual and was discussed in our preliminary communication.[12] The ^1H NMR spectrum showed no hydride resonance at room temperature, but on cooling a broad resonance started to appear and at −62 °C it showed resolved coupling to ^{31}P and ^{103}Rh. The value of $^1J(RhH)$ (Table II) is higher than is usually found in rhodium(III) hydrides[13] but is close to the value of 52.8 Hz found in $[RhHCl\{Bu^t{}_2PCH_2C_6H_3CH_2PBu^t{}_2\}]$ (**7**).[4] We ascribe this temperature-dependent behavior to the occurrence of a rapid, reversible C-H/Rh-H fission as shown in Scheme I. In support of this interpretation the ^{103}Rh resonances, obtained by $^1H\{^{31}P,^{103}Rh\}$ INDOR experiments observing the outer lines of the *tert*-butyl "triplet", showed an equal coupling to two protons with an averaged coupling constant of 24 Hz. The ^{13}C NMR spectrum (data in Table III) was assigned with the aid of off-resonance proton decoupling. The equivalence of the *tert*-butyl groups arises from the rapid process shown in Scheme I.

As described above, treatment of rhodium trichloride with $Bu^t{}_2P(CH_2)_5PBu^t{}_2$ for 72 h gave the cyclometalated complex **6** but it was generally contaminated with ca. 5% of a second species (X) characterized by an AMX pattern in the ^{31}P NMR spectrum (A, M = ^{31}P; X = ^{103}Rh). We were unable to separate this minor component from the main species: the two co-



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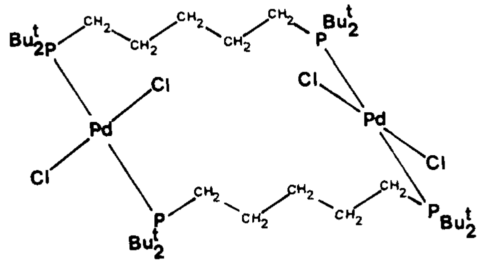

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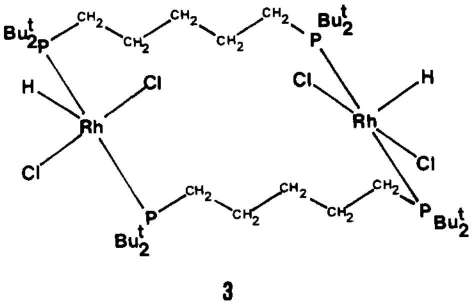

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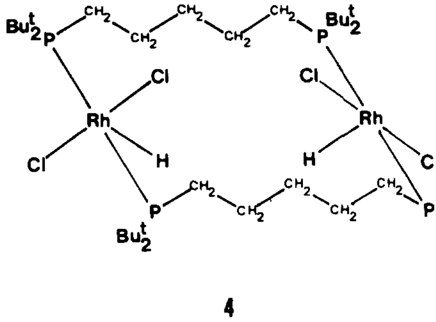

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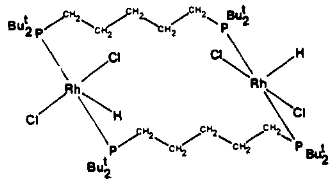
Table II. ^{1}H, ^{31}P, and ^{103}Rh NMR Parameters of the Complexes[a]

complex	*t*-Bu		hydride			other ^{1}H resonances	$\delta(^{31}P)$[c]	$^1J(RhP)$	$^2J(PP)$	$\delta(^{103}Rh)$[d]
	$\delta(^1H)$[b]	$[^3J(PH) + J(PH)]$	$\delta(^1H)$[b]	$^2J(PH)$	$^3J(Rh\text{-}H)$					
$[Rh_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$	$\{$1.50 1.44	+12 +12	−31.3	12	32		48.1	−97	+402	2736
$[RhHCl\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$	1.36	+12.9	−30.1[e]	19[e]	55[e]		84.8	−122	+357	1029
$[Rh(CO)\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$[f]	[f] $\{$1.27 1.24	12.5 12.7					103.7	156	*g*	*g*
$[RhCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2PBu^t_2\}]$[h]	1.44 1.33	+12.3[i] +11.9[i]				HC═CH δ 4.2	78.6	−136	+368	601
	1.58 1.25	+13.1[i] +13.0[i]					−35.9	−94		
$[RhHCl\{Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2\}]$	1.46 1.34	+13.1 +12.7	−27.3	−10.7	49.1	methyl δ 0.91	83.0	−125	+357	1011
$[RhCl\{Bu^t_2PCH_2CH_2(C{=}CH_2)CH_2CH_2PBu^t_2\}]$	1.41 1.38	+11.9 +12.5				C═C*H*$_2$ δ 2.32, *J*(PH) +4.1 *J*(RhH) 2.8	63.8	−131	+381	460
$[RhCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t_2\}]$	[j] $\{$1.48 1.37	+12.3 +12.3				C*H*═C*H* δ 3.14	74.4	−127	+362	243
	[k] $\{$1.49 1.38	+12.3 +12.3				C*H*═C*H* δ 3.23	73.8	−125	+360	194
$[Rh(CO)\{Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t_2\}][BPh_4]$	1.32 1.24	+13.8 +13.9				C*H*═C*H* δ 2.16	95.6	−106	+229	−736
$[RhCl\{Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2\}]$	1.57 1.19	+13.6 +13.7				C*H*═C*H* δ 3.13 CH$_2$ δ 2.8, 2.0	−42.5	−100	+351	983

[a] In CDCl$_3$ at ca. 298 K except where otherwise stated. [b] In parts per million to high frequency of SiMe$_4$. [c] In parts per million to high frequency of 85% H$_3$PO$_4$ taken as $\Xi(^{31}P)$ = 40 480 730 Hz, values ±0.1 ppm. [d] In parts per million to high frequency of $\Xi(^{103}Rh)$ = 3.16 MHz, values ±1 ppm. [e] At 211 K. [f] In C$_6$D$_6$. [g] Not measured. [h] Not isolated (see text). [i] ^3J(PH). [j] Major isomer, with trans arrangement of HC═CH. [k] Minor isomer, with cis arrangement (see text).



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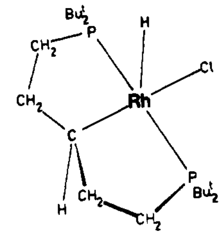

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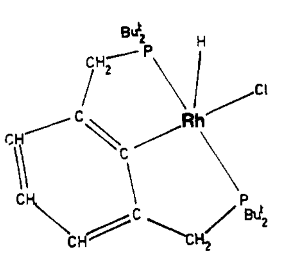

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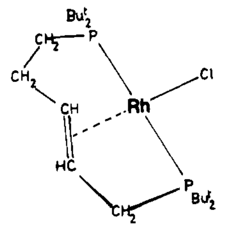

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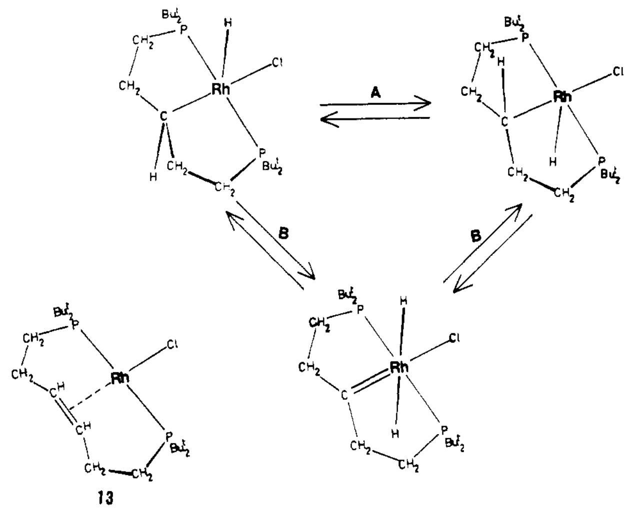
Scheme I. Possible Mechanisms to Explain the Fluxionality of **6**: (A) A Concerted Process Requiring a Transoid Arrangement of H–C–Rh–H and a Vacant Orbital on the Rhodium; (B) Stepwise, or Carbenoid (Ylide) Mechanism



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crystallized and appeared to be isomorphous and very similar. Thin layer chromatography on silica gel, fractional sublimation, or repeated fractional crystallizations were all unsuccessful. Detailed NMR studies on the mixture (see below) point to this second species (X) being a rhodium(I) olefin complex $[RhCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2PBu^t_2\}]$ (**8**). With a longer reflux time, e.g., 6 days, the insoluble binuclear complex $[Rh_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ is gradually broken down and the proportion of the second component (X) in solution increases to ca. 20%. A shorter reflux time led to pure **6** being formed, although the yield was low (a few percent). The formation of X also seems to be favored by high reflux temperatures; e.g., with 2-propanol as solvent the amount increased to ca. 50%, while in tetrahydrofuran very little was produced. In one preparation using 2-propanol, very small amounts of two additional species were produced (ca. 2–3% of each) whose ^{31}P NMR spectra were similar to those of **6** and X, respectively. The ^{31}P NMR parameters (in CDCl$_3$) for these two minor components were (A$_2$X species) $\delta(^{31}P)$ 84.6 ppm, $^1J(RhP)$ = 122 Hz; (AMX) $\delta(^{31}P)$ 79.2, $^1J(RhP)$ = 133 Hz, $\delta'(^{31}P)$ −40.7 ppm, $^1J(RhP)$ = 90, $^2J(PP')$ = 365 Hz. The reaction conditions are evidently critical but not well established since we have been unable to reproduce this result in spite of several attempts.

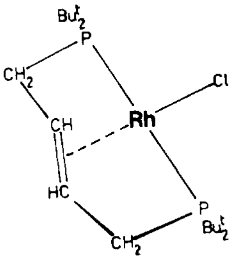
Although we were unable to obtain a pure sample of X by

Table III. ^{13}C NMR Data[a]

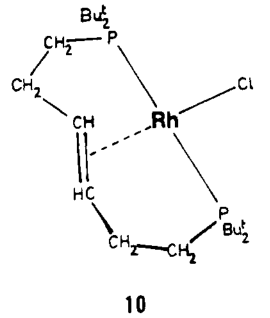
complex			$\delta(^{13}C)$[b]	$\lvert J(PC) + J'(PC)\rvert$	$J(RhC)$
$[\mathrm{RhHCl\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}}]$		$\mathit{C}\mathrm{CH_2CH_2P}$	49.8	<0.3	24.1
		$\mathit{C}\mathrm{H_2CH_2P}$	41.7	14.6	2.1
		$\mathit{C}\mathrm{H_2P}$	23.5	18.6	2.0
		$\mathit{C}\mathrm{(CH_3)_3}$	35.3	15.8	1.0
		$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	29.0	5.6	<0.5
$[\mathrm{RhCl\{Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t_2\}}]$	c	$\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{H}$	60.1	<0.3	16.2
		$\mathit{C}\mathrm{H_2CH_2P}$	31.1	14.9	1.2
		$\mathit{C}\mathrm{H_2P}$	14.0	13.8	1.5
		$\mathit{C}\mathrm{(CH_3)_3}$	35.8	12.8	0.5
			35.0	13.2	1.5
		$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	31.6	5.1	<0.5
			29.5	5.9	<0.5
	d	$\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{H}$	61.0	<0.3	16.4
		$\mathit{C}\mathrm{H_2CH_2P}$	30.9	14.7	1.2
		$\mathit{C}\mathrm{H_2P}$	14.3	14.4	1.5
		$\mathit{C}\mathrm{(CH_3)_3}$	36.0	13.4	0.8
			35.4	13.2	1.5
		$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	31.9	5.1	<0.5
			29.6	6.1	<0.5
$[\mathrm{RhCl\{Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2\}}]$		$\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{H}$	44.8	10.5	10.5
		$\mathit{C}\mathrm{H_2P}$	26.1	15.1	3.8
		$\mathit{C}\mathrm{(CH_3)_3}$	34.6	10.0	<0.3
			32.7	5.6	~0.4
		$\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$	29.6	6.7	<0.5
			29.2	7.2	<0.5

[a] In $CDCl_3$ at ca. 298 K; coupling constants ±0.3 Hz. [b] In parts per million to high frequency of $SiMe_4$. [c] Major isomer, with trans arrangement of HC=CH. [d] Minor isomer, with cis arrangement of HC=CH.

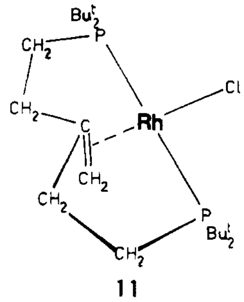
thin layer chromatography, fractions rich in it were obtained after repeated recrystallizations from light petroleum or methanol. As mentioned above, the ^{31}P nuclei of X are inequivalent and one of them has the very low shift of −35.9 ppm (Table II). Similar shifts to low frequency have been observed in strained four-membered rings; e.g., $\delta(P)$ is −40.4 ppm in $[PtMe_2(Ph_2PCH_2PPh_2)]$ compared to 54 ppm in $[PtMe_2(Ph_2PCH_2CH_2PPh_2]$,[15] and there is a concomitant decrease in $^1J(PtP)$ which parallels the behavior of $^1J(RhP)$ in our systems. The value of $^2J(PP)$ is typical of trans phosphorus atoms in neutral rhodium complexes of this type (cf. the other values in Table II). The ^1H NMR spectrum showed four separate *tert*-butyl doublets $[^3J(PH)]$, two associated with each phosphorus atom (from $^1H\{^{31}P\}$ selective decoupling experiments). There were also some resonances at higher frequency including a broad hump at δ 4.1. A $^1H\{^{103}Rh\}$ INDOR experiment observing this feature gave a ^{103}Rh resonance whose shift was within experimental error of that obtained by $^1H\{^{31}P,^{103}Rh\}$ INDOR observing the *tert*-butyl peaks. There was no hydride resonance, nor was there any evidence of coupling to ^1H in the ^{103}Rh INDOR spectrum. Thus an olefin complex is indicated containing one four- and one five-membered ring with a structure **8.** The "hump" at δ 4.2 in the ^1H NMR spectrum is thus due to the olefin protons. Perhaps the substance X and the second species showing an AMX ^{31}P NMR pattern are related by cis and trans isomerism about the coordinated C=C bond. The best evidence for formulating "X" as **8** lies in a comparison with the related complexes **9**, **10**, and **11**, all of which have been isolated and characterized (vide infra). In particular, we note that (i) **9** has a ^{31}P chemical shift of −42.5 ppm (i.e., at very low frequency because of the small rings); (ii) $\nu(Rh\text{-}Cl)$ is 286, 287, 287, and 286 cm^{-1} in X, **9**, **10**, and **11**, respectively (i.e., all are olefin-rhodium(I) complexes), some 20 cm^{-1} higher than with **6** or **12** (alkyl-rhodium(III) complexes); (iii) the ^{103}Rh chemical shift of **9** is at markedly higher frequency than that of **10** and $\delta(Rh)$ for X lies midway between the two (see Table II). An increase in $\delta(^{195}Pt)$ of comparable magnitude has been found for the four-membered ring complex $[PtMe_2(Ph_2PCH_2PPh_2)]$ relative to $[PtMe_2(Ph_2P[CH_2]_nPPh_2)]$[15] ($n$ = 2, 3, or 4) (>four-membered rings).



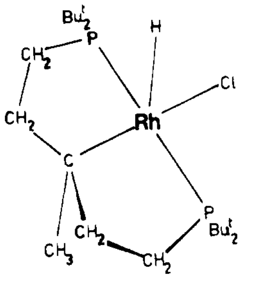
9



10



11



12

We have investigated the reactions of the binuclear complex $[Rh_2H_2Cl_4\{Bu^t_2P[CH_2]_5PBu^t_2\}_2]$ with base in attempts to promote cyclometalation. Treatment with 2-methylpyridine under mild conditions (50 °C, 3 min) gave the pure cyclometalated complex **6** and provides a good route to this compound (pyridine, a better ligand toward rhodium, gave undesirable pyridine-rhodium complexes as byproducts). We also attempted to remove a second mole of hydrogen chloride by treating **6** with the stronger base sodium methoxide in the presence of carbon monoxide (to take up the resulting coordination site). We found that conversion to the very volatile rhodium(I) carbonyl complex, $[\mathrm{Rh(CO)\{Bu^t{}_2PCH_2CH_2CHCH_2CH_2PBu^t{}_2\}}]$, occurred smoothly. Characterizing data are in the tables. A feature is the extremely low value for ν(C≡O), viz., 1900 cm^{-1}, presumably due to an unusually large rhodium → π^*(CO) back-donation promoted by the σ-bonded carbon in the trans position.

In view of the complexity of the behavior and number of products formed from $\mathrm{Bu^t{}_2P[CH_2]_5PBu^t{}_2}$ and $\mathrm{RhCl_3}$ we have explored the reaction of $\mathrm{Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2}$ with $\mathrm{RhCl_3}$. One effect of the methyl group would be to prevent the rapid process shown in Scheme I from occurring. We refluxed this mixture in 2-propanol for 40 h and obtained a red, crystalline precipitate and an orange solution. The red material on the basis of microanalytical and molecular-weight determinations (Table I) is formulated as $[\mathrm{Rh_2H_2Cl_4\{Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2\}_2}]$ with a 16-atom ring. ^{31}P NMR spectroscopy showed that this product was a mixture of six similar species in $\mathrm{CDCl_3}$ solution, having chemical shifts spanning the range 48.7-43.6 ppm and all with ^1J(RhP) = 97 ± 1 Hz. These species are probably analogues of the pentamethylene complexes **3** and **4** (or **5**), with the presence of the methyl group in the center of each chain increasing the number of isomers (rotamers). In the ^{1}H NMR spectrum, the hydride appeared as a complex overlapping multiplet centered at −31.2 ppm.

We found that this six-component mixture, when heated with 2-methylpyridine, gave a *single* cyclometalated hydrido complex $[\mathrm{RhHCl\{Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2\}}]$ in 75% yield. The structure of this complex has been determined as **12** by single-crystal X-ray crystallography (including location of the hydrogen atoms).[12,16] The ^{1}H NMR spectrum showed two *tert*-butyl triplets and as expected the hydride was not fluxional, showing an unchanging doublet of triplets pattern over the range 25 to −60 °C (NMR data in Table II). The stereochemistry of **12** is consistent with a concerted cis addition of C–H to rhodium.

When **12** was refluxed in 2-propanol over a period of days, it very slowly lost hydrogen to give the rhodium(I)-olefin complex **11.** We then discovered that water had a remarkable effect in promoting the reaction, quantitative conversion being attained by refluxing in 2-propanol containing 10% water for 3 days. The structure of this olefin complex has been established as **11** by single-crystal X-ray crystallography, and the ^{1}H NMR spectrum is consistent with this (data in Table II). We were unable to convert **6** to **8** by heating it in aqueous 2-propanol, the cyclometalated complex **6** being recovered unchanged.

The original orange solution obtained from the reaction product of $\mathrm{RhCl_3}$ with $\mathrm{Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2}$ in 2-propanol contained a mixture of **11** and **12.** We were unable to separate this mixture by fractional crystallization, sublimation, or thin layer chromatography (on silica gel).

The reaction of rhodium trichloride with the hexamethylene diphosphine $\mathrm{Bu^t{}_2P[CH_2]_6PBu^t{}_2}$ in ethanol or 2-propanol gives markedly different results from the reaction with the pentamethylene ligand. Some of this work has been reported in a preliminary note.[17] No binuclear or polynuclear complexes were isolated but a highly crystalline, orange complex was formed. ^{31}P and ^{1}H NMR spectroscopy showed this to be a two-component mixture, the major component being the olefin-rhodium(I) complex **10** (characterizing data in tables, crystal structure in ref 17 and 18). The ratio of these two components varied from 9:1 to 2.2:1 with different preparations but did not change after leaving in $\mathrm{CDCl_3}$ for 1 day. The major component has the trans C=C bond found in the solid state by X-ray diffraction and we suggest that the minor component is **13** with a cis C=C bond. The best evidence for this is the close similarity of NMR parameters between the two complexes, particularly the ^{13}C spectra (Table III). The difference in their ^{103}Rh chemical shifts, 49 ppm, is small compared to the total range of ^{103}Rh chemical shifts[19] and suggests a similar rhodium environment in the two species. When this isomeric mixture was treated with carbon monoxide in the presence of sodium tetraphenylboron in ethanol, we obtained $[\mathrm{Rh(CO)\{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2\}}][\mathrm{BPh_4}]$, which ^{31}P NMR showed to be a single species. (The analogous perchlorate salt was also obtained as one species.) (See tables for characterizing data.) $\mathrm{Ph_2P(CH_2)_6PPh_2}$ has been shown to react with $\mathrm{RhCl_3}$ to give an analogous olefin-rhodium(I) complex, viz., $[\mathrm{RhCl(Ph_2PCH_2CH_2CH{=}CHCH_2CH_2PPh_2)}]$.[20]

Since the hexamethylene diphosphine $\mathrm{Bu^t{}_2P(CH_2)_6PBu^t{}_2}$ was dehydrogenated on complexation to $\mathrm{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2}$, which was always a mixture of trans and cis isomers (mainly trans), we prepared pure *trans*-$\mathrm{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2}$ free from any of the cis isomer (see below). When reacted with rhodium trichloride in ethanol it gave no bi- or polynuclear species, but the mononuclear rhodium(I)-olefin complex **10.** However, even this complex was contaminated with a small (ca. 1%) amount of the corresponding cis complex **13** (^{31}P NMR evidence). Thus a small amount of olefin isomerization has occurred.

We have also synthesized and studied the new diphosphine *trans*-$\mathrm{Bu^t{}_2PCH_2CH{=}CHCH_2PBu^t{}_2}$. We were interested to see whether it could act as a tridentate ligand with effectively two four-membered rings. When this diphosphine was added to an aqueous 2-propanol solution of rhodium trichloride, a pinkish-brown precipitate formed. This suspension when heated gradually dissolved and the yellow, crystalline $[\mathrm{RhCl\{Bu^t{}_2PCH_2CH{=}CHCH_2PBu^t{}_2\}}]$ was isolated in excellent (>80%) yield. The structure **9** is based on the spectroscopic (IR, ^{1}H, ^{31}P, and ^{13}C NMR, and mass) evidence (tables). An X-ray diffraction study has confirmed the structure.[16] A full and unambiguous assignment of the ^{13}C NMR resonances (Table III) was possible by off-resonance decoupling. The low value of δ(P) and high value of δ(Rh) stem from the angle strain inherent in the four-membered rings and were helpful in the identification of the nature of complex "X", discussed above, for which structure **8** was assigned.

Preparation of the Diphosphines

$\mathrm{Bu^t{}_2P(CH_2)_\mathit{n}PBu^t{}_2}$ (n = 5 or 6) and $\mathrm{Bu^t{}_2PCH_2CH_2CHMeCH_2CH_2PBu^t{}_2}$ have been described previously.[3,4] The olefinic diphosphines were prepared as follows. The commercially available $\mathrm{HOOCCH_2CH_2CH{=}CHCH_2CH_2COOH}$ was converted to the trans dibromide $\mathrm{BrCH_2CH_2CH{=}CHCH_2CH_2Br}$ by literature methods.[21,22] We found that treatment of this dibromide with $\mathrm{PBu^t{}_2H}$ in methyl isobutyl ketone gave a sticky phosphonium dibromide in poor yield. However, similar treatment in the presence of sodium iodide gave the more tractable diiodide salt $[\mathrm{PBu^t{}_2HCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2H}]^{2+}2\mathrm{I}^-$ mixed with sodium bromide. This diphosphonium salt darkened on exposure to air or light and was not obtained pure. However, treatment of the mixture with sodium hydroxide readily gave the free diphosphine. This was characterized by its ^{1}H, ^{13}C, and ^{31}P NMR spectra (Table IV).

Treatment of *trans*-$\mathrm{BrCH_2CH{=}CHCH_2Br}$ with $\mathrm{PBu^t{}_2H}$ readily gave the diphosphonium salt $[\mathrm{Bu^t{}_2PHCH_2CH{=}CHCH_2PHBu^t{}_2}]2\mathrm{Br}^-$, which was obtained analytically pure (Table I). Treatment with sodium hydroxide gave the pure diphosphine $\mathrm{Bu^t{}_2PCH_2CH{=}CHCH_2PBu^t{}_2}$, as a white,

Table IV. NMR Data[a] for the Olefinic Diphosphines $Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t_2$ and $Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$

			$Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_3PBu^t_2$[b]					
^1H (C_6D_6)	δ 1.09 d	$^3J(PH) = 10.5$	δ 5.8 m $\{CH{=}CH\}$		^{31}P (C_6D_6)	δ 27.9 ppm		
^{13}C (C_6D_6) PCH_2	δ 21.2 d	$^1J(PC) = 22$	PCH_2CH_2	δ 31.7 d	$^2J(PC) = 25$	PCH_2CH_2CH	δ 130.8 d	$^3J(PC) = 15$
$PCMe_3$	δ 32.6 d	$^1J(PC) = 24$	$PC(CH_3)_3$	δ 30.0 d	$^2J(PC) = 15$			
			$Bu^t_2PCH_2CH{=}CHCH_2PBu^t_2$					
^1H (C_6D_6)	δ 1.10 d	$^3J(PH) = 10.5$		δ 5.75 m $\{CH{=}CH\}$, 2.25 m $\{PCH_2\}$				
^{31}P (C_6H_6/C_6D_6)	δ 27.5 ppm							

[a] s = singlet, d = doublet, m = multiplet. *J* values in hertz. [b] Recorded at 90 (^1H), 36.43 (^{31}P), and 22.62 MHz (^{13}C) on a Bruker Spectrospin HFX spectrometer at 27 °C.

crystalline solid. It was characterized by its ^1H and ^{31}P NMR spectra (Table IV).

Experimental Section

Unless stated otherwise ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded with a JEOL FX100 spectrometer using an internal deuterium lock. INDOR spectra were recorded with a modified Varian HA100 spectrometer as described elsewhere.[23] Values of $^2J(PP)$ in the complexes containing chemically equivalent phosphines were obtained by $^1H\{^{31}P\}$ INDOR observing the outside lines of the *tert*-butyl triplets (corresponding to the $\alpha\alpha$ and $\beta\beta$ ^{31}P spin states) as described in ref 24: values ±5 Hz. For most of the complexes, determination of ^{103}Rh chemical shifts by $^1H\{^{103}Rh\}$ double resonance was not possible because the ^1H *tert*-butyl resonances show no coupling to ^{103}Rh. However, satisfactory ^{103}Rh INDOR spectra could be obtained by $^1H\{^{31}P,^{103}Rh\}$ triple resonance since $^3J(PH)$ and $^1J(RhP)$ are substantial. Best results were obtained using very low powers of $\nu(^{31}P)$ such as to perturb the center of the monitored ^1H line by less than 0.1 Hz. For the complex $[RhHCl\{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2\}]$ the value of $\delta(^{103}Rh)$ obtained by this method was within 0.1 ppm of that determined by $^1H\{^{103}Rh\}$ INDOR observing the hydride resonances. INDOR also provided most of the signs of coupling constants given in Table II. The other spectroscopic measurements were carried out in the way described in recent papers from this laboratory.[25]

Melting points were determined on a Kofler hot-stage apparatus and are corrected. Analytical, melting point, molecular weight, and IR data are given in Table I.

Preparation of the Diphosphines. $Bu^t_2P(CH_2)_5PBu^t_2$[3] and $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$[4] were prepared as described previously; $Bu^t_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t_2$ was prepared from *trans*-$Br(CH_2)_2CH{=}CH(CH_2)_2Br$,[2] as described below.

***trans*-1,6-Bis(di-*tert*-butylphosphino)hex-3-ene.** Di-*tert*-butylphosphine (10.7 g, 0.072 mol) and sodium iodide (10.9 g, 0.072 mol) were added to a solution of *trans*-1,6-dibromohex-3-ene (8.83 g, 0.036 mol) in isobutyl methyl ketone (55 cm^3). The mixture was refluxed for 48 h and the precipitated phosphonium salt and sodium bromide were filtered off. This solid was dissolved in methanol (75 cm^3) and treated with a 2 M aqueous solution of sodium hydroxide (16 g, 0.4 mol). The methanol was evaporated under reduced pressure, water (100 cm^3) added, and the required product isolated with ether as a pale yellow oil, bp 110–120 °C (bath temperature) (0.05 mm), yield 4.7 g (0.026 mol, 38%).

1,4-Bis(di-*tert*-butylphosphonio)but-2-ene Dibromide. Di-*tert*-butylphosphine (12.2 g, 83.5 mmol) was added to a solution of *trans*-1,4-dibromobut-2-ene (8.9 g, 41.8 mmol) in dry acetone (80 cm^3). The mixture was heated under reflux for 4 h and then cooled and the product (19.1 g, 91%) isolated as prisms.

1,4-Bis(di-*tert*-butylphosphino)but-2-ene. A solution of 1,4-bis(di-*tert*-butylphosphonio)but-2-ene dibromide (10.0 g, 19.8 mmol) in degassed water (25 cm^3) was treated with a solution of sodium hydroxide (8.0 g, 200 mmol) in degassed water (30 cm^3). After extraction with ether (4 × 20 cm^3) the product was isolated as a white, crystalline solid by evaporation of the dried ether solution, yield 5.4 g (80%).

Action of 1,5-Bis(di-*tert*-butylphosphino)pentane on Rhodium Trichloride in Ethanol. A solution of rhodium trichloride trihydrate (2.46 g, 9.44 mmol) in ethanol (ca. 40 cm^3) was treated with the diphosphine (5.10 g, 14.2 mmol) and the mixture heated under reflux for 72 h. The mixture was then cooled and the precipitated crystalline solid filtered off. This was extracted exhaustively with hot light petroleum (bp 60–80 °C) to give an orange, highly crystalline (needles) extract of the cyclometalated product $[RhHCl\{Bu^t_2PCH_2CH_2CHCH_2CH_2PBu^t_2\}]$, which was sometimes pure but sometimes contaminated with up to 7% of other isomers which we were unable to remove (see text), yield 1.4 g (2.7 mol, 29%). A longer reflux time, e.g., 6 days, increased the proportion of these contaminating isomers to 20–30%. A shorter reflux time, e.g., 12 h, gave the pure cyclometalated complex **6** but only in poor yield (<5%). However, two reliable methods of preparing pure **6** are described below. The light petroleum insoluble residue was bis(dichlorohydrido)-μ-{1,5-di-*tert*-butylphosphinopentane}dirhodium(III), which was obtained as brick-red prisms (2.44 g, 2.28 mmol, 49%).

Action of $Bu^t_2P(CH_2)_5PBu^t_2$ on Rhodium Trichlorde in Tetrahydrofuran to Give Pure 6. A solution of rhodium trichloride trihydrate (0.87 g, 3.46 mmol) in tetrahydrofuran (25 cm^3) and water (1 cm^3) was treated with a solution of the diphosphine (1.50 g, 4.16 mmol) in tetrahydrofuran (15 cm^3) and the mixture heated under reflux for 6 days. The solvent was removed in vacuo and the residue recrystallized from benzene. This gave the pure cyclometalated complex **6** as orange prisms, yield 0.89 g (50%).

Conversion of $[Rh_2H_2Cl_4\{Bu^t_2P(CH_2)_5PBu^t_2\}_2]$ to $[RhHCl\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}]$. A mixture of the binuclear complex (0.72 g, 0.68 mmol) and 2-methylpyridine (10 cm^3) was warmed to 50 °C for 3 min. The resultant clear yellow solution was cooled to 20 °C and water added dropwise. This gave the required cyclometalated complex **6** (0.61 g, 1.24 mmol, 92%) as orange-yellow needles from light petroleum (bp 60–80 °C).

$[Rh(CO)\{Bu^t_2P(CH_2)_2CH(CH_2)_2PBu^t_2\}]$. Carbon monoxide was bubbled briskly through a solution of the cyclometalated complex **6** (64 mg, 0.128 mmol) in a solution of sodium methoxide in methanol (10 cm^3, 1.56 M) for 2 h. Addition of water (ca. 20 cm^3) and isolation with light petroleum (bp 60–80 °C) gave the required carbonyl complex, which was purified by sublimation (100 °C, 0.01 mm), yield 51 mg (0.102 mmol, 80%).

Action of $Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2$ on Rhodium Chloride. A suspension of finely ground rhodium trichloride trihydrate (1.82 g, 7.34 mmol) in 2-propanol (20 cm^3) was treated with the diphosphine (4.17 g, 11.11 mmol). The mixture was heated under reflux for 40 h and the solid was collected, washed with 2-propanol and then light petroleum (60–80 °C), and continuously extracted with dichloromethane. The dichloromethane solution was evaporated to give the binuclear complex $[Rh_2H_2Cl_4\{Bu^t_2PCH_2CH_2C(Me)CH_2CH_2PBu^t_2\}_2]$ as red prisms (2.40 g, 60%). The 2-propanol filtrate solution was evaporated to dryness to give a mixture of the two cyclometalated mononuclear complexes **11** and **12** (see Discussion).

Conversion of $[Rh_2H_2Cl_4\{Bu^t_2PCH_2CH_2CHMeCH_2CH_2PBu^t_2\}_2]$ to $[RhHCl\{Bu^t_2PCH_2CH_2CMeCH_2CH_2PBu^t_2\}]$. A solution of the binuclear complex (2.40 g, 2.18 mmol) in 2-methylpyridine (20 cm^3) was heated to 90 °C for 40 min. The mixture was filtered, the filtrate evaporated to low bulk, and the residue extracted with light petroleum (bp 60–80 °C). The required cyclometalated complex separated on cooling as large, orange prisms, yield 1.5 g (75%).

Dehydrogenation of 12 to 11. A solution of the hydridorhodium(III) complex (0.50 g, 0.46 mmol) in a 2-propanol (10 cm^3)-water (1 cm^3) mixture was heated under reflux for 6 days. The solvent was then removed by evaporation, the residue dissolved in dichloromethane, the solution filtered through Celite, and the product obtained by evaporation. It formed large, orange needles (0.47 g, 94%), mp 241–243 °C (with sublimation).

10 from $Bu^t_2P(CH_2)_6PBu^t_2$. A solution of rhodium trichloride trihydrate (0.47 g, 0.19 mmol) in 2-propanol (30 cm^3) was treated with $Bu^t{}_2P(CH_2)_6PBu^t{}_2$ (1.06 g, 2.34 mmol) and the mixture was heated under reflux for 20 h. The resultant orange solution when cooled gave the required product which formed orange needles from light petroleum (bp 60–80 °C), yield 0.45 g (0.088 mmol, 47%).

$[RhCl\{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2\}]$ from $Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2$. A solution of rhodium trichloride trihydrate (0.52 g, 2.09 mmol) in a mixture of water (2 cm^3) and 2-propanol (10 cm^3) was treated with a solution of $Bu^t{}_2P(CH_2)_2CH{=}CH(CH_2)_2PBu^t{}_2$ (1.17 g, 3.13 mmol) in benzene (3 cm^3). The mixture was refluxed for 7 days. The resultant yellow solution was evaporated to a glassy solid and then extracted with light petroleum (bp 60–80 °C). The required product (0.28 g, 27%) separated on cooling.

$[Rh(CO)\{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2\}]ClO_4$. Carbon monoxide was bubbled through a solution of the chloro complex (0.19 g, 0.38 mmol) in ethanol (ca. 20 cm^3) to which had been added a solution of sodium perchlorate monohydrate (0.25 g, 1.78 mmol) in water (0.5 cm^3). After 2 h water was slowly added to the resultant yellow solution to give the required perchlorate complex as yellow needles, yield 0.21 g (0.34 mmol, 92%).

$[Rh(CO)\{Bu^t{}_2PCH_2CH_2CH{=}CHCH_2CH_2PBu^t{}_2\}]BPh$. This was prepared similarly to the perchlorate (above) using an ethanol solution of sodium tetraphenylboron (fourfold excess). The product formed yellow microcrystals, yield 90%.

Action of $Bu^t{}_2PCH_2CH{=}CHCH_2PBu^t{}_2$ on Rhodium Trichloride. A solution of rhodium trichloride trihydrate (0.23 g, 0.89 mmol) in water (1 cm^3) and 2-propanol (25 cm^3) was treated with a solution of the diphosphine (0.68 g, 1.96 mmol) in 2-propanol (13 cm^3). A pinkish-brown precipitate was produced which had all dissolved after boiling the mixture for 3 h. The orange solution was filtered and the solvent removed at the pump to give an orange oil. Water (15 cm^3) was added and the precipitated yellow solid (0.35 g, 81%) filtered off. The product was recrystallized from dichloromethane-cyclohexane.

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Crystal Structures of Some Cyclic Phosphonium Salts and Their Relation to the Stereochemical Course of Base Hydrolysis

Judith C. Gallucci[1] and Robert R. Holmes*

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003. *Received October 9, 1979*

Abstract: Single-crystal X-ray analyses of 1-benzyl-1-phenylphosphorinanium bromide (I) and 1,1-diphenyl-4-methylphosphorinanium bromide (II) showed that their structures are very similar. Each contains the six-membered ring in the chair form and in the case of I the benzyl group is oriented equatorially at the tetrahedral phosphorus atom. I crystallizes in the monoclinic space group Cc with a = 16.666 (5) Å, b = 9.690 (4) Å, c = 11.806 (2) Å, β = 114.42 (2)°, and Z = 4. Full-matrix least-squares refinement gave R = 0.033 and R_w = 0.035 for the 1713 reflections having $I \geq \sigma(I)$. II crystallizes in the monoclinic space group $C2/c$ with a = 15.199 (4) Å, b = 10.986 (2) Å, c = 21.212 (8) Å, β = 99.71 (3)°, and Z = 8. Full-matrix least-squares refinement gave R = 0.40 and R_w = 0.042 for the 3100 reflections having $I \geq \sigma(I)$. The X-ray coordinates of I were used to initiate a molecular mechanics calculation designed to simulate base hydrolysis of the cis and trans isomers of 1-benzyl-1-phenyl-4-methylphosphorinanium bromide. The results support less inversion of configuration for the trans isomer compared to that for the cis isomer in accord with experimental results.

Introduction

The hydrolysis reactions of phosphonium salts represent widely studied systems.[2] In the absence of unusual steric effects[3] or departing groups of similar apicophilicity, chiral acyclic phosphonium salts hydrolyze with inversion of configuration.[4] For cyclic derivatives, ring size becomes an important determinant of reaction stereospecificity and reaction rate. For example, a comparison of the rates of alkaline de-

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