Transfer-dehydrogenation of alkanes catalyzed by rhodium(I) phosphine complexes

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Abstract

Complexes of the form $Rh(PMe_3)_2ClL'$ ($L' = CO$ or trisubstituted phosphine) and $[Rh(PMe_3)_2Cl]_2$ have previously been reported to catalyze the transfer-dehydrogenation of alkanes, using olefinic hydrogen acceptors under a dihydrogen atmosphere. Such complexes are herein reported to effect transfer-dehydrogenation in the absence of H_2 but with much lower rates and total catalytic turnovers, even at much greater temperatures. Analogs with halides other than chloride (Br, I), or with pseudo-halides (OCN, N_3), are found to exhibit generally similar behavior: high catalytic activity under H_2 and measurable but much lower activity in the absence of H_2. Thermolysis (under argon) of complexes $[RhL_2Cl]_n$ ($n = 1$, 2; L is a phosphine bulkier than PMe_3) in cyclooctane in the absence of hydrogen acceptors yielded cyclooctene. However, transfer-dehydrogenation was plagued by ligand decomposition. Under a hydrogen atmosphere complexes containing ligands much bulkier than PMe_3 do not effect dehydrogenation. Complexes with tridentate ligands, $(\eta^3\text{-}PXP)RhL'$ ($PXP = (Me_2PCH_2Me_2Si)_2N$, $Me_2PCH_2(2,6\text{-}C_6H_3)CH_2PMe_2$; $L' = CO$, C_2H_4), were also found to catalyze thermal or photochemical dehydrogenation of cyclooctane with limited reactivity. The structure of $[Rh(PMe_3)_2Cl]_2$ was determined by single-crystal diffraction. The $Rh(\mu\text{-}Cl)_2Rh$ bridge of 1 is folded like that of $[Rh(CO)_2Cl]_2$, unlike that of the planar PPh_3 and P^iPr_3 analogs.

Keywords: Rhodium; Phosphines; Dehydrogenation; Catalysis; Alkanes

1. Introduction

The development of methods for the functionalization of alkanes remains one of the most important challenges in the field of catalysis. Dehydrogenation to give alkenes is a potential functionalization that is attractive in view of the versatility of alkenes as precursors for a wide range of useful and facile transformations, such as hydroformylation and polymerization. The ability of organometallic complexes to catalyze alkene hydrogenation with remarkable effectiveness [1] is promising in the context of dehydrogenation. Indeed, alkane transfer-dehydrogenation systems (i.e. systems using a sacrificial hydrogen acceptor), first developed by Crabtree and coworkers and Felkin and coworkers, have long stood as the foremost examples of organometallic-catalyzed alkane functionalization [2].

However, until recently there were no examples of such systems that yielded high catalytic turnover numbers (greater than ca. 70).

We recently reported that [3] under a dihydrogen atmosphere transfer-dehydrogenation of alkanes is catalyzed with remarkably high efficiency by complexes containing the $Rh(PMe_3)_2Cl$ fragment (Eq. (1)):

$$\text{alkane} + A \xrightarrow[\;Rh(PMe_3)_2ClL \text{ or } [Rh(PMe_3)_2Cl]_2\;]{\Delta H_2} \text{alkene} + AH_2$$

(1)
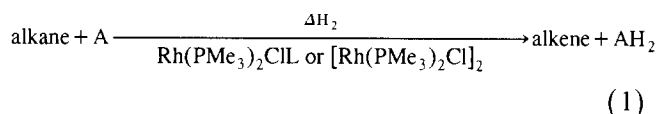
(A = sacrificial olefinic acceptor)

The reaction was found to be quite efficient for a wide range of alkanes and a moderately wide range of olefinic acceptors, including ethylene.

A substantial body of data supports the mechanism for the thermal reaction indicated in Scheme 1 [3].

Note that, according to Scheme 1, the catalytic activity of complexes $Rh(PMe_3)_2ClL'$ should increase with decreasing binding ability of L'; this is found to be the case, at least qualitatively [3]. However, the existence of complexes $Rh(PMe_3)_2ClL'$ depends upon the Rh–L'

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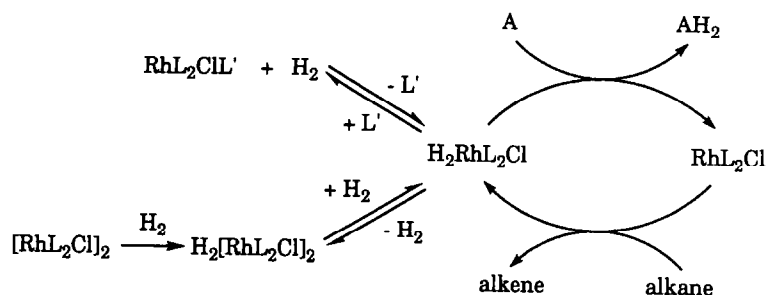
Scheme 1. Proposed mechanism of transfer-hydrogenation catalyzed by RhL_2ClL' or $[RhL_2Cl]_2$ under an H_2 atmosphere. A, olefinic acceptor; $L = PMe_3$; $L' = CO$ or a trisubstituted phosphine.

bonding being sufficiently strong to prevent dimerization of $Rh(PMe_3)_2Cl$ to give (Eq. (2))

$$2Rh(PMe_3)_2ClL' \rightleftharpoons [Rh(PMe_3)_2Cl]_2 + 2L' \qquad (2)$$
$$\mathbf{1}$$
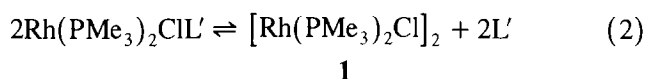
Thus the bridge strength of $[Rh(PMe_3)_2Cl]_2$ (1) is the limiting factor in the development of more effective

precursors of the $Rh(PMe_3)_2Cl$ fragment (and presumably more effective catalysts). Note that, like the monomers, 1 requires addition of H_2 to form $H_2Rh(PMe_3)_2Cl$ and thereby enter the same catalytic cycle (Scheme 1).

Although the reported $Rh(PMe_3)_2Cl$-based systems represent a significant step in the search for feasible catalysts for alkane dehydrogenation, they are not very

Table 1

Transfer-dehydrogenation catalyzed by $Rh(PMe_3)_2ClL'$ under Ar

| L'	Reaction vessel	T (°C)	t (h)	COE (mM)	NBA (mM)
PMe_3	sealed tube	150	69	23.0	27.8
PMe_3	sealed tube	150	165	37.8	47.1
P^iPr_3	septum-sealed	90	20	1.7	2.2
P^iPr_3	septum-sealed	120	19	19.8	12.8
P^iPr_3	septum-sealed	120	29	26.2	15.3
P^iPr_3	septum-sealed	120	39	30.0	16.2
P^iPr_3	sealed tube	120	28	5.2	6.3
P^iPr_3	sealed tube	120	41	23.3	22.4
PCy_3	septum-sealed	120	3	4.3	6.24
PCy_3	septum-sealed	120	21	17.6	18.3
PCy_3	septum-sealed	120	44	30.4	20.4
PCy_3	sealed tube	120	52	8.8	12.8
PCy_3	sealed tube	120	100	31.3	40.0
P^cPr_3	sealed tube	150	29	3.6	1.8
P^cPr_3	sealed tube	200	16	5.8	9.4
PPh_3	septum-sealed	120	20	1.6	0.9
PPh_3	sealed tube	150	25	5.8	6.2
PPh_3	sealed tube	150	50	9.7	12.0
$P(o\text{-tol})_3$	septum-sealed	90	17	1.9	0.6
$P(o\text{-tol})_3$	septum-sealed	120	23	2.4	4.1
$P(o\text{-tol})_3$	sealed tube	120	48	3.4	4.7
$P(o\text{-tol})_3$	sealed tube	120	96	4.7	5.9
$P(NMe_2)_3$	septum-sealed	120	12	2.5	5.1
$P(NMe_2)_3$	septum-sealed	120	24	6.0	9.6
$P(NMe_2)_3$	sealed tube	150	24	0.6	2.5

Reactions were carried out under 800 Torr argon; 10 mM catalyst solution in 4:1 (v/v) COA–NBE ([NBE] = 1.72 M). Septum-sealed cell: 0.5 ml solution in 5 ml cell. Sealed tube: 0.5 ml solution sealed in 10 ml Pyrex tube. Reactions were first conducted at 90°C; the temperature was then increased to 120°C, 150°C, and up to 200°C depending upon the apparent stability of the complex. Abbreviations: Cy = cyclohexyl; ^cPr = cyclopropyl; o-tol = o-tolyl.

suitable for most large scale applications. In particular, since a dihydrogen atmosphere is present, several moles of acceptor are consumed per mole alkene generated. Thus, in order to develop systems more suitable for practical applications, in particular systems effective in the absence of a dihydrogen atmosphere, we are investigating the effects of varying the catalytic conditions, the reaction components, and the effects of chemical modifications of these catalysts. Of particular interest would be precursors of species with catalytic properties similar to $Rh(PMe_3)_2Cl$, but with less tendency to undergo dimerization leading to inactivation.

2. Results and discussion

2.1. Transfer-dehydrogenation catalyzed by complexes $Rh(PMe_3)_2ClL'$ in the absence of H_2

A variety of $Rh(PMe_3)_2ClL'$ (L' = trisubstituted phosphine) complexes were synthesized by treating $[Rh(PMe_3)_2Cl]_2$ with L' in toluene. All isolated complexes were satisfactorily characterized by ^{1}H- and ^{31}P NMR. Most of these complexes exist as cis and trans isomers (except $L' = PPh_3$ or $P(NMe_2)_3$, which are exclusively trans). The complexes were assessed for their ability to catalyze transfer-dehydrogenation of cyclooctane (COA) using norbornene (NBE) as an acceptor under an argon atmosphere (Eq. (3)).

(3)
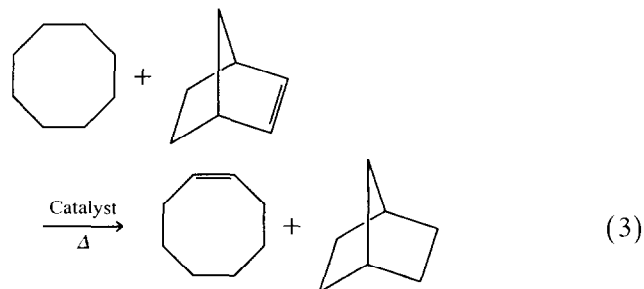
Reactions were carried out either in a 5 ml Pyrex reaction vessel sealed with an Ace Thread three-layered

septum, or in sealed tubes. Product yields were determined by gas chromatography (GC) calibrated with a series of solutions of authentic samples of known concentration. Results are given in Table 1.

At temperatures much greater than those previously found effective for catalysis under a hydrogen atmosphere, transfer-dehydrogenation of COA was indeed catalyzed by the $Rh(PMe_3)_2ClL'$ complexes in the absence of H_2. However, even at such temperatures the catalytic turnover rates are small and the catalysts undergo decomposition. The fact that more norbornane (NBA) than cyclooctene (COE) is observed in some cases, for example $Rh(PMe_3)_2Cl(PCy_3)$, is probably attributable to dehydrogenation of L' [4]. In other cases more COE than NBA is formed. This may be due to either the formation of free H_2 [5,6] (thermodynamically plausible in view of the high temperatures, small amounts of product, and large gas/solution volume ratios) and/or hydrogenated metal-containing species. However, since the amounts in question were so low, the fate of the hydrogen unaccounted for was left undetermined. Note that reactions carried out in the septum-sealed cell in some cases display greater turnover rates and acceptor-efficiency (defined as D/H, the ratio of dehydrogenation to hydrogenation) than those in sealed tubes. This may be attributable to the escape of H_2 through the septum (which is periodically pierced for GC analysis) and/or the inadvertent introduction of air to the septum-sealed cell. Introduction of air must be considered because the decomposition in those experiments occurred faster than in sealed tubes under similar conditions.

2.2. Transfer-dehydrogenation catalyzed by complexes $Rh(PMe_3)_3X$ and $[Rh(PMe_3)_2X]_2$ under H_2 atmosphere: the effect of varying X

The bonding of the $Rh(PMe_3)_2Cl$ units in dimeric 1 occurs mainly through a chloride bridge (see below) which must be cleaved to effect catalysis; thus, the

Table 2

Transfer-dehydrogenation of CoA catalyzed by $Rh(PMe_3)_3X$ or $[Rh(PMe_3)_2X]_2$ under H_2 atmosphere

Complex	Concentration (mM)	Product formation rates (mM h^{-1}) [a]		D/H [b]
		COE	NBA	
$Rh(PMe_3)_3Cl$	1.0	53.2	96.7	0.55
$Rh(PMe_3)_3Br$	1.0	29.8	67.7	0.44
$Rh(PMe_3)_3Br$	4.0	127	374	0.34
$Rh(PMe_3)_3(OCN)$	1.0	43.2	111	0.39
$Rh(PMe_3)_3(N_3)$	1.0	3.2	160	0.02
$[Rh(PMe_3)_2Cl]_2$	0.67	125	893	0.14
$[Rh(PMe_3)_2Br]_2$	0.67	108	293	0.37
$[Rh(PMe_3)_2I]_2$	0.67	7.8	261	0.03
$[Rh(PMe_3)_2(OCN)]_2$	0.67	100	773	0.13

[a] Conditions: P_{H_2} = 1600 Torr; 50°C; 300 ml ballast reaction cell described previously [3]. Solutions were 4:1 (v/v) COA–NBE ([NBE] = 1.72 M). All runs were of duration 2–3 h. [b] COE–NBA ratio (dehydrogenation: hydrogenation).

Table 3
CO stretching frequencies of complexes $RhL_2(CO)X$ (in benzene)

L	X	ν_{CO} (cm^{-1})
PMe_3	Cl	1956.7
PMe_3	Br	1957.7
PMe_3	I	1959.7
PMe_3	OCN	1960.5
PCy_3	Cl	1939.3
PMe^tBu_2	Cl	1940.3
P^iPr_3	Cl	1943.2
PMe_3	Cl	1956.7
$P(NMe_2)_3$	Cl	1958.6
P^cPr_3	Cl	1961.5
$P(p\text{-}C_6H_4NMe_2)_3$	Cl	1965.4
PPh_3	Cl	1983.0
$P(C_6F_5)_3$	Cl	2003.0

effect of substituting the chloride ligand is of particular interest. Substitutions of the chloride in $Rh(PMe_3)_3Cl$ and/or 1 were attempted by treatment of the chloro-complexes with a large excess (10 equivalents or greater) of MX (M = Li, Na or K; X is the substituting anion) in THF. Complexes of Br, I ($[Rh(PMe_3)_2I]_2$ only), OCN, and N_3 ($Rh(PMe_3)_3(N_3)$ only) were successfully prepared by this method. The isolated complexes were first assessed as transfer-dehydrogenation catalysts for Eq. (3) under H_2 atmosphere. Results of different catalytic runs under H_2 atmosphere are listed in Table 2.

All the RhL_3X complexes readily add H_2 at room temperature to form predominantly H_2RhL_3X (see Experimental section). Both catalytic reactivity and acceptor-efficiency (D/H) decrease as Cl in $Rh(PMe_3)_3Cl$ is substituted by other anions. Reactivity decreases in the order Cl > OCN > Br > N_3, and efficiency decreases in

the order Cl > Br > OCN > N_3. Perhaps the most notable result of varying the halide ligands of $Rh(PMe_3)_3X$ is the relatively small change in the degree of catalytic activity resulting from the substitutions. This observation seems generally most consistent with a mechanism in which the anion only plays the role of an ancillary ligand, such as that in Scheme 1. In particular, a mechanism based on anion loss (possibly as HX) would be expected to be more dependent on the nature of X. These results thus support previously reported data that argue against such mechanisms, for example the observation that the presence of added base does not promote catalysis [3].

For $[Rh(PMe_3)_2X]_2$, the trends in reactivity and acceptor-efficiency upon varying X are: Cl > Br > OCN > I, and Br > Cl ~ OCN > I respectively. As the complicated nature of the catalyst solutions under H_2 was not determined, we do not consider it reasonable to speculate on the reasons for this trend. An indication of the relative electron-richness of the respective $Rh(PMe_3)_2X$ moieties may be obtained from the CO stretching frequencies of the respective adducts $Rh(PMe_3)_2(CO)X$ (Table 3).

2.3. Catalysis by $[Rh(PMe_3)_2X]_2$ in the absence of H_2: the effect of varying X

The new anion-bridged derivatives were found to catalyze COA/NBE transfer-dehydrogenation in the absence of H_2 (see Table 4); however, like the $Rh(PMe_3)_2ClL'$ complexes, even at elevated temperatures these catalysts are orders of magnitude less active than under H_2. The dimeric precursors decomposed to

Table 4
Thermolysis of RhL_3X and $[RhL_2X]_2$ (L = PMe_3) in COA–NBE under Ar [a]

Complex	Concentration (mM)	T (°C)	t (h)	COE (mM)	NBA (mM)
RhL_3Cl	10.0	150	69	23.0	27.8
RhL_3Cl	10.0	150	165	37.8	47.1
$[RhL_2Cl]_2$	5.0	90	4	n.o.	n.o.
$[RhL_2Cl]_2$ [b]	5.0	120	28	3.6	3.3
$[RhL_2Cl]_2$ [b]	5.0	120	48	5.4	3.7
$[RhL_2Cl]_2$ [b]	5.0	120	74	10.2	5.0
$[RhL_2Br]_2$	4.0	90	4	0.96	n.o.
$[RhL_2Br]_2$ [c]	4.0	120	28	0.36	3.2
$[RhL_2I]_2$ [d]	5.0	90	6	n.o.	n.o.
$[RhL_2I]_2$ [d]	5.0	120	18	n.o.	n.o.
$[RhL_2(OCN)]_2$	4.0	90	3	n.o.	n.o.
$[RhL_2(OCN)]_2$	4.0	120	16	4.5	1.6
$[RhL_2(OCN)]_2$ [e]	4.0	120	39	6.1	2.5

[a] Conditions: P_{Ar} = 800 Torr; 0.5 ml solution in 5 ml septum-sealed cell for $[RhL_2X]_2$; 1.0 ml solution sealed in 10 ml Pyrex tube for RhL_3Cl. Solutions were in COA–NBE–benzene, (5:4:1 v:v; benzene was used to obtain the desired solubility); n.o. = not observed (less than ca. 0.2 mM). [b] Complex started to visibly decompose after 24 h at 120°C. [c] Complex started to visibly decompose after 3 h at 120°C. [d] Complex visibly decomposed at 90°C. [e] Complex started to visibly decompose after 24 h at 120°C.

various extents under high temperatures, as indicated by color changes of the solution and by the formation of precipitates. (No visible changes in solutions of $Rh(PMe_3)_3Cl$ were observed even after prolonged times at 150°C). For the parent complex 1, it was found that there was no significant change in reactivity even after some decomposition was visually observed. As was found with the $Rh(PMe_3)_2ClL'$ catalysts and discussed in the above section, in some cases more COE than NBA is formed.

2.4. Catalysis by $[RhL_2Cl]_n$ and RhL_3Cl: effects of varying L

In general, increased ligand bulk should severely inhibit the reactivity of a given fragment toward alkanes (or any given substrate of significant size). However, increased bulk should also result in a 'double' contribution to the repulsive forces involved in dimerization/ deactivation of the RhL_2Cl monomer. Accordingly, we recently found that $[Rh(P^iPr_3)_2Cl]_2$ (2) effects the simple dehydrogenation of cyclooctane to give $H_2Rh(P^iPr_3)_2Cl$ and $H_2[Rh(P^iPr_3)_2Cl]_2$ as the major products [7]; in this respect it is more reactive than the less crowded PMe_3 analog, 1. 2 also catalyzes COA transfer-dehydrogenation in the presence of a hydrogen-acceptor (NBE). However, the catalytic efficiency (ca. 4.0 turnovers at 90°C under argon) is severely limited by ligand decomposition pathways which appear

to involve dehydrogenation of the isopropyl groups [7]. Therefore, we considered analogs, of similar steric bulk, that would be expected to be more resistant to ligand dehydrogenation. PMe^tBu_2, which has no HCCH linkages, has a cone angle of 161°, essentially equal to that of P^iPr_3 (160°).

$[Rh(PMe^tBu_2)_2Cl]_n$ (3) was prepared analogously to the preparation of 2 [8]. Although the nature of 3 in solution is unclear, it is probably dimeric in view of the similarities in sterics between 3 and 2. 3 reacts with neat COA similarly to 2, resulting in the formation of COE and rhodium-containing species including H_2RhL_2Cl (L = PMe^tBu_2), RhL_2Cl_2H, $H_2[RhL_2Cl]_2$, and $H_2Rh_2L_3Cl_2(COE)$, (assigned by comparison of the ^1H and ^{31}P NMR spectra with those of the P^iPr_3 analogs, see Experimental section) but at a much slower rate than 2 (Table 5). When an acceptor is used (NBE) transfer-dehydrogenation does occur but the efficiency is extremely low; less than 1 turnover is observed.

Clearly this system is plagued by decomposition pathways other than dehydrogenation of an HCCH linkage which is not present in PMe^tBu_2. Ligand decomposition for 3 might occur by cyclometallation of the ^tBu group followed by P–C bond cleavage, which has been reported by Shaw [9] for PEt^tBu_2 and by Goel [10] for P^tBu_3, as well as other phosphine ligands [11].

For comparison, $[Rh(PCy_3)_2Cl]_n$ was also studied for the dehydrogenation of COA. Vrieze and coworkers have reported the dehydrogenative cyclometallations of

Table 5
Thermolysis of $[RhL_2Cl]_n$ in COA and COA–NBE under Ar

Substrate	COA			COA–NBE			
L	T (°C)	t (h)	COE (mM)	T (°C)	t (h)	COE (mM)	NBA (mM)
P^iPr_3 [a]	90	3	9.5	90	5	11.0	11.0
P^iPr_3 [a]	90	10	9.5	90	55	41.0	37.0
PMe^tBu_2	90	3	2.6	90	5	2.5	2.5
PMe^tBu_2	90	18	5.7	90	10	2.5	2.7
PMe^tBu_2	90	28	6.3				
PCy_3 [b]	90	2	6.5	90	3	3.4	7.3
PCy_3 [b]	90	6	6.7	90	9	6.0	12.1
PCy_3 [b]				90	90	15.0	14.3
P^cPr_3 [c]				150	56	4.1	1.0
$P(p-C_6H_4NMe_2)_3$ [d]				120	34	5.3	4.5
$P(p-C_6H_4NMe_2)_3$ [d]				120	72	5.6	4.9
PMe_3				90	4	n.o.	n.o.
PMe_3 [e]				120	28	3.6	3.3
PMe_3 [e]				120	48	5.4	3.7
PMe_3 [e]				120	74	10.1	5.0

Conditions: reactions were carried out using 0.5 ml solution in a 5-ml septum-sealed cell under 800 Torr Ar unlesss otherwise indicated. For reactions with COA, [Rh] = 20 mM; reactions with 4:1 COA–NBE ([NBE] = 1.72 M), [Rh] = 10 mM unless otherwise indicated.
[a] Ref. [11]. [b] 20 mM [Rh] suspension in COA; 10 mM [Rh] suspension in COA–NBE. [c] 0.5 ml of 5 mM ([Rh]$_2$) solution sealed in 10 ml Pyrex tube under 800 Torr Ar. [d] 0.5 ml of 3 mM ([Rh]$_2$) suspension in 4:1:5 (v/v/v) COA–NBE–benzene sealed in 10 ml Pyrex tube under 800 Torr Ar. [e] [Rh] = 5 mM.

this complex to form the four-coordinate product $[Cy_2P(\eta^2\text{-}3\text{-cyclohexenyl})]Rh(PCy_3)Cl$ [4]. Both a stoichiometric reaction with COA and catalytic transfer-dehydrogenation with COA/NBE were observed, with low yield and poor efficiency (Table 5). Saito and coworkers [12] recently reported a high-yield stoichiometric dehydrogenation of cyclohexane by this complex; the apparent contrast with our own results may be attributable, at least in part, to the much lower concentration of complex (0.1 mM) used in that work which should favor the monomeric forms of $Rh(PCy_3)_2Cl$ and any hydride-containing products.

As a ligand which should be resistant to cyclometallation, and therefore any subsequent decomposition steps, tricyclopropylphosphine (P^cPr_3) was investigated; although it is clearly less electron-rich than P^iPr_3 and much less bulky (cone angle = 128°) [13,14] [Rh-$(P^cPr_3)_2Cl]_2$ is apparently very robust as indicated by high temperature thermolysis. However, in the absence of H_2 it is not a particularly effective catalyst (see Table 6). As with the PMe_3 complexes, catalytic activity is greatly increased by the presence of H_2: for example, a solution of $[Rh(P^cPr_3)_2Cl]_2$ (0.5 mM) in COA/NBE under 1600 Torr H_2 at 50°C gave 70 and 2330 turnovers h^{-1} (mmol mmol^{-1}) for COE and NBA respectively. Note that the acceptor-efficiency (D/H) is much less than that found for the PMe_3 analog while under H_2. In the other extreme, $[Rh(P^iPr_3)_2Cl]_2$ gives only hydrogenation under H_2. This is presumably due to decreased reactivity of the more crowded RhL_2Cl fragments with alkane, relative to any of several possible deactivation pathways (including, for example, ligand addition, dimerization, oligomerization, addition to H_2).

Possible ligand decomposition pathways (including dehydrogenation and P–C bond cleavage) should be disfavored by substitution of the alkyl groups of the phosphine ligands by dialkylamino groups. Tris(dimethylamino)phosphine, $P(NMe_2)_3$ (cone angle 157° [15]), is almost as bulky as P^iPr_3. Accordingly, {Rh-$[P(NMe_2)_3]_2Cl\}_2$ was prepared; however, it was found

not to catalyze transfer-dehydrogenation in either the absence or the presence of H_2 (rapid hydrogenation of NBE occurs in the presence of H_2).

The carbonyl complexes of these bulky phosphines, $RhL_2(CO)Cl$, were independently synthesized by reacting CO with $[RhL_2Cl]_n$ in solution. CO stretching frequencies of the resulting complexes are listed in Table 3.

2.5. Catalysis by RhL_3Cl: effects of varying L

A number of phosphines can afford complexes of the type $Rh(PR_3)_3Cl$. Saito and coworkers have reported that dehydrogenation of COA could be achieved by refluxing Wilkinson's catalyst $Rh(PPh_3)_3Cl$ in COA [5,6]. The proposed mechanism involves thermolytic dissociation of the complex to form $[Rh(PPh_3)_2Cl]$. We considered that the isosteric $P(p\text{-}C_6H_4NMe_2)_3$ ligand might dissociate from $Rh[P(p\text{-}C_6H_4NMe_2)_3]_3Cl$ to a similar extent, and if so, its greater electron-donating ability might promote dehydrogenation. However, the complex was not found to be a highly effective catalyst (Table 6). Tri(phosphine) complexes where R = Me, Ph, and ^cPr were also investigated. In analogy with Wilkinson's catalyst [16] $Rh(P^cPr_3)_3Cl$ exists in equilibrium with $[Rh(P^cPr_3)_2Cl]_2$, as shown from both ^1H and ^{31}P NMR. Listed in Table 6 are the results of catalytic runs of these complexes. As noted above for the $[RhL_2Cl]_2$ dimers, increasing steric bulkiness seems to decrease the ratio of dehydrogenation:hydrogenation (cone angles for PR_3: Me, 118°; ^cPr, 128°; Ph, 145°).

2.6. Structure of $[Rh(PMe_3)_2Cl]_2$ (1)

As noted above, the catalytic ability of the $Rh(PMe_3)_2Cl$-based systems is in effect limited by the strength of the bridging interaction in 1. We were therefore interested in the structure of this complex, particularly the architecture of the bridge. At the outset of this work, $[Rh(PPh_3)_2Cl]_2$ was the closest analog of

Table 6
Transfer-dehydrogenation of COA catalyzed by $Rh(PR_3)_3Cl$

R	Concentration (mM)	Atmosphere	T (°C)	t (h)	COE (mM)	NBA (mM)	D/H
Me [a]	1.0	H_2	50	2	106	193	0.55
^cPr [a]	1.0	H_2	50	2	38	1580	0.024
Ph [a,b]	0.5	H_2	50	0.5	5.7	800	0.007
Me	10	Ar	150	69	23.0	27.8	—
Me	10	Ar	150	165	37.8	47.1	—
^cPr [c]	10	Ar	150	144	< 0.2	< 0.2	—
^cPr [c]	10	Ar	200	47	3.9	1.5	—
$p\text{-}C_6H_4(NMe_2)$ [d]	5	Ar	120	140	4.1	3.6	—

Conditions: [a] P_{H2} = 1600 Torr; 50°C; 300 ml ballast reaction cell. Solutions were made in 4:1 (v/v) COA–NBE except otherwise noted, [NBE] = 1.72 M. [b] 4:1:5 (v/v/v) COA–NBE–benzene, [NBE] = 0.85 M. [c] 4:1 (v/v) COA–NBE sealed in 10 ml Pyrex tube under 800 Torr Ar. [d] 0.5 ml of 5 mM suspension in 4:1 (v/v) COA–NBE sealed in 10 ml Pyrex tube under 800 Torr Ar.

1 to have been crystallographically characterized [17]. More recently, Binger et al. determined the structure of $[Rh(P^iPr_3)_2Cl]_2$ (**2**) [18]. These two reported structures are very similar. In both cases the core is a planar $Rh(\mu\text{-}Cl)_2Rh$ ring and the phosphorus atoms are located in the plane of the ring; each rhodium has an essentially square planar coordination geometry. This structure sharply contrasts with that of most other RhL_2Cl dimers. With the exceptions of $[(COD)RhCl]_2$ (COD = 1,5-cyclooctadiene) [19] and $(COE)_2\{PH[CH(SiMe_3)_2]_2\}_2Rh_2(\mu\text{-}Cl)_2$ [20], which also contain planar $Rh(\mu\text{-}Cl)_2Rh$ rings, in all other reported structures the $Rh(\mu\text{-}Cl)_2Rh$ ring has a pronounced folding (fold angles of 116–134°; 180° corresponds to a planar geometry; see Table 7).

On the basis of SCF-Xα-SW calculations, Norman has explained the folding [28] as arising from the "mixing of d_{z^2} character into the bonding d_{xz}–d_{xz} combination" (the locations of the Rh atoms define the x-axis). In the bent structure, this results in conversion of "a very weak, purely π bond into a stronger interaction, mainly of σ-type, between 'tilted d_{xz}' orbitals". Significantly, this refers to orbitals that are mainly centered on the bridging chloride ligands. Based on that theoretical work and on their determination of the planar geometry of $[Rh(PPh_3)_2Cl]_2$, Curtis and Butler suggested that the presence or absence of folding is determined by small changes in the metal–ligand bond orbitals [17].

This suggestion seemed to receive support from the recently determined planar structure of **2**; olefins, CO or perhaps other electron-withdrawing ligands, e.g. $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) [22], seemed to be required to give the bent structure. However, very recently Hofmann et al. have reported [21] that $[(dtbpm)RhCl]_2$ (dtbpm $= ^tBu_2PCH_2P^tBu_2$) possesses a structure that is folded (134°), although less so than previously reported examples. As the phosphine groups in this complex should be comparable in basicity with P^iPr_3, this observation would argue against the importance of electronic factors; however, the small bite
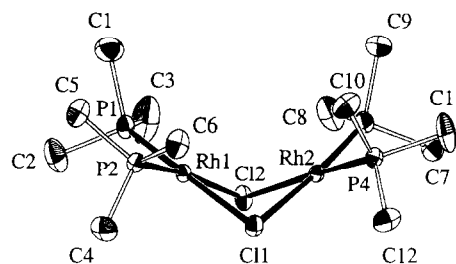

Fig. 1. Molecular structure of **1** (ORTEP; hydrogen atoms omitted for clarity).

angle of the dtbpm ligand may introduce additional changes in the metal–ligand bond orbitals. In particular, *EH* calculations by Hofmann et al. indicate that a small bite angle results in a significant weakening of the Rh–μ-Cl bonds [21].

Our structural determination of **1** (Fig. 1) reveals it to have the same folded $Rh(\mu\text{-}Cl)_2Rh$ structural motif as the olefin, carbonyl or dfepe complexes, in contrast with the other tetrakis(monophosphine) complexes, **2** and $[Rh(PPh_3)_2Cl]_2$. A $Rh(\mu\text{-}Cl)_2Rh$ folding angle of 119.1(1)° is found in **1**, lying within the narrow range (116–124°) reported for the olefin and carbonyl complexes. Thus, both planar and non-planar classes of dimer are now known to include complexes containing ligands that span wide (and overlapping) ranges of electronic properties (planar: PPh_3, P^iPr_3, COD, COE, $PH[CH(SiMe_3)_2]_2$; folded: CO, C_2H_4, η^2-2-methyl-2,4,-pentadiene, dfepe, $P(OPh)_3$, PMe_2Ph, dtbpm, PMe_3; see Table 7). In terms of their geometries, the ligands within each class also vary significantly; however, smaller ligands display a very distinct preference for the folded structure [29]. Therefore, we strongly favor an explanation for adoption of the planar structure based primarily on simple intramolecular ligand repulsion, rather than electronic properties or crystal-packing effects [30]. This explanation, by highlighting the crowding in the dimers of the very bulky ligands, is in accord with the greater reactivity of **2** vs. **1** with respect

Table 7

Various $Rh_2(\mu\text{-}Cl)_2$ complexes and fold angles (λ)

Complex	λ (deg)	Reference
$(PPh_3)_4Rh_2(\mu\text{-}Cl)_2$	180	[17]
$(P^iPr_3)_4Rh_2(\mu\text{-}Cl)_2$ (**2**)	180	[18]
$(COE)_2\{PH[CH(SiMe_3)_2]_2\}_2Rh_2(\mu\text{-}Cl)_2$	180	[20]
$(COD)_2Rh_2(\mu\text{-}Cl)_2$	180	[19]
$(dtbpm)_2Rh_2(\mu\text{-}Cl)_2$	134	[21]
$(dfepe)_2Rh_2(\mu\text{-}Cl)_2$	128	[22]
$(CO)_4Rh_2(\mu\text{-}Cl)_2$	124	[23]
$(COD)[P(OPh)_3]_2Rh_2(\mu\text{-}Cl)_2$	123	[24]
$(CO)_2(PMe_2Ph)_2Rh_2(\mu\text{-}Cl)_2$	123	[25]
$(PMe_3)_4Rh_2(\mu\text{-}Cl)_2$ (**1**)	119	this work
$(\eta^2$-2-methyl-2,4,-pentadiene$)_4Rh_2(\mu\text{-}Cl)_2$	116	[26]
$(C_4H_4)_4Rh_2(\mu\text{-}Cl)_2$	116	[27]

to alkane dehydrogenation (in the absence of H_2 atmosphere).

In all other respects the structure of **1** is as expected. Indeed, Rh–P bond distances (2.19–2.20 Å) and the P–Rh–P angles (96.54(7)°, 95.20(7)°) are virtually identical to the corresponding parameters of $[Rh(PPh_3)_2Cl]_2$. Crystallographic details and selected bond distances and angles are given in Tables 8 and 9.

2.7. Reactions of complexes of multidentate phosphine ligands

In a further effort to prepare analogs of $Rh(PMe_3)_2Cl$ that could not readily dimerize, we investigated tridentate anionic ligands that should enforce the geometry of the RhL_2Cl monomer [31]. As seen above, formation of **1** and other RhL_2Cl dimers involves the phosphines assuming a cis configuration. Thus, for example, in complexes of the tridentate ligand $(Me_2PCH_2SiMe_2)_2N$ (PNP) [32,33], the phosphino groups are held trans,

which should prevent dimerization. Furthermore, in this case, and probably with most other multidentate ligands as well, dimerization would not be expected because the central coordinating group (the amido in this case) is probably much too crowded to add to another metal center. Although $[(Ph_2PCH_2SiMe_2)_2N]Rh(COE)$ has been reported [34,35], the analog with dimethylphosphino groups could not be isolated. However, the uncharacterized species resulting from such attempts could be converted cleanly to $Rh(PNP)L'$ ($L' = CO$; C_2H_4) when stirred under CO or C_2H_4 atmosphere.

In analogy with $Rh(PMe_3)_2Cl(CO)$ [36,37], Rh(PNP)(CO) was found to catalyze the photodehydrogenation of COA, but only sluggishly. For example, 7 turnovers were achieved when a 2 mM solution of the complex in COA under 800 Torr CO was irradiated for 10 h (40°C) with a 500 W Hg-arc lamp. This compares with over 100 turnovers for $Rh(PMe_3)_2(CO)Cl$ [36,37]. Dehydrogenation was 70 times slower when 30 Torr CO was present. No dehydrogenation of COA was observed under thermal-transfer-dehydrogenation conditions, either under argon (90°C) or H_2 (1600 Torr, 50°C); only NBE hydrogenation was observed.

We considered the possibility that the lack of thermal catalytic reactivity of Rh(PNP)(CO) was due to a particularly strong Rh–CO bond, perhaps resulting from increased ligand-to-metal π-donation vis-a-vis Rh-$(PMe_3)_2Cl(CO)$ ($\nu_{CO} = 1956$ cm^{-1} vs. 1940 cm^{-1} for Rh(PNP)(CO)). Thus a derivative that was presumably more weakly ligated was prepared, $Rh(PNP)(C_2H_4)$, and evaluated for dehydrogenation. No reaction was found in the absence of H_2 under typical thermal reaction conditions. However, the complex catalyzes hydrogenation rapidly when 800 Torr H_2 is present; a 4 mM solution of $Rh(PNP)(C_2H_4)$ gave complete hydrogenation of NBE within 2 h at 50°C (ca. 430 turnovers) while only 2 turnovers COE were observed. 30 Torr of C_2H_4 completely suppressed hydrogenation under similar conditions. Presumably, the complex dissociates C_2H_4 to enter the hydrogenation catalytic cycle. Thus, the expected three-coordinate fragment can apparently be generated but it is much less reactive toward alkane compared with $Rh(PMe_3)_2Cl$.

Complexes **4** ($R = {}^tBu$; $L' = CO$, C_2H_4) have been synthesized according to Eq. (4) [38,39]. The analog with dimethylphosphino groups, $[\eta^3-Me_2PCH_2(2,6-C_6H_3)CH_2PMe_2]Rh(CO)$, (PCP)Rh(CO), was synthesized by a modified method.

Table 8
Crystal data and structure refinement for $[Rh(PMe_3)_2Cl]_2$ (1)

Empirical formula	$C_{12}H_{36}Cl_2P_4Rh_2$
Formula weight	581.01
Temperature (K)	153(5)
Radiation: type, wavelength (Å)	Mo K α, 0.71073
Diffractometer, monochromator type	CAD4, graphite
Standard reflections: no., interval (s)	3, 3600
Decay of standards (%)	0.6
Crystal system, space group	monoclinic, $P2_1/n$
No. refls, θ range for cell detection (deg)	25, 15.5 to 19.8
Unit cell dimensions	
a (Å)	12.187(4)
b (Å)	11.074(2)
c (Å)	17.469(2)
α (deg)	90.00(2)
β (deg)	107.85(2)
γ (deg)	90.00(2)
Volume (Å^3)	2244.2(9)
Z	4
Density (calculated) (Mg m^{-3})	1.718
Absorption coefficient (mm^{-1})	1.98
$F(000)$	1168
Crystal color, description	orange, lath
Crystal size (mm^3)	$0.05 \times 0.10 \times 0.15$
θ range for data collection (deg)	2 to 25
Index ranges	$0 \leqslant h \leqslant 14, 0 \leqslant k \leqslant 13,$ $-20 \leqslant l \leqslant 19$
Reflections collected	3800
Absorption correction	Numerical grid
Max. and min. transmission	0.902 and 0.755
Independent reflections	3620 ($R_{int} = 0.0218$)
Observed reflections	2985
Data/restraints/parameters	3620/0/206
Goodness-of-fit on F^2	1.028
Final $R(F)$, $wR(F^2)$ indices [$I > 2\sigma$]	0.038, 0.093
Final $R(F)$, $wR(F^2)$ (all data)	0.054, 0.099
Largest diff. peak and hole (e Å^{-3})	1.0 and -0.8

$$(4)$$

The CO stretching frequencies of $Rh(PMe_3)_2(CO)Ph$ [40] and $Rh(PMe_3)_2(CO)Cl$ are quite similar (1959 cm^{-1} and 1960 cm^{-1} respectively, pentane); this may indicate similar reactivity for their respective three-coordinate fragments (i.e. $Rh(PMe_3)_2Ph$ and $Rh(PMe_3)_2Cl$). However, ν_{CO} of (PCP)Rh(CO) was found to be 1944 cm^{-1} (C_6D_6). No photodehydrogenation was observed for Rh(PCP)(CO) either with or without the presence of CO at 50°C when irradiated by a 500 W lamp. Thus, the three-coordinate fragment (PCP)Rh is probably even less reactive than (PNP)Rh.

The fact that the (PNP)Rh and possibly (PCP)Rh fragments are much less effective dehydrogenation catalysts than $Rh(PMe_3)_2Cl$ might suggest that either loss of phosphine or rearrangement of the phosphine configuration from trans to cis is necessary at some point in the dehydrogenation cycle. The ability of RhL_2Cl fragments to add C–H bonds has been fairly well substantiated by flash photolysis [41] and photokinetic studies [36,37]. Supporting evidence is offered by calorimetry, which reveals that C–H addition to $Rh(P^iPr_3)_2Cl$ is unusually exothermic; the product has a trans-phosphine configuration which would suggest that such an arrangement is suitable for C–H addition [42]. However, phosphine loss or rearrangement may be required for β-elimination of the alkyl hydrides $RhL_2XH(R)$. Tanaka

and coworkers found that a cis-phosphine complex, $Rh(\eta^2\text{-}Me_2PCH_2CH_2PMe_2)(CO)Cl$, is catalytically inactive for photodehydrogenation [43]; possibly a trans-phosphine configuration is required for C–H oxidative addition while phosphine loss or rearrangement is required for β-elimination.

2.8. Conclusion

Several complexes of the form RhL_2XL' and $[RhL_2X]_2$ (L = PR_3; X = Cl, Br, I, OCN, N_3; L' = CO or PR_3) have been found to catalyze the thermochemical transfer-dehydrogenation of alkanes using NBE as a sacrificial hydrogen-acceptor. Under an inert atmosphere, catalysis is observed but turnover numbers and frequencies are rather low. Catalysis is much more efficient in the presence of H_2, in accord with previous reports of transfer-dehydrogenation efficiently catalyzed by $Rh(PMe_3)_2ClL'$ and $[Rh(PMe_3)_2Cl]_2$ under H_2. The proposed role of H_2 is to generate complexes RhL_2ClH_2 which then react with sacrificial olefin to give the 'active catalyst' RhL_2Cl. The ratio of D/H under H_2 atmosphere decreases with increasing ligand size; presumably this is due to decreased reactivity of the more crowded RhL_2Cl fragments with alkane, relative to their possible deactivation pathways (e.g. ligand addi-

Table 9
Bond lengths (Å) and angles (deg) for $[Rh(PMe_3)_2Cl]_2$ (1)

Rh(1)–P(1)	2.193(2)	Rh(1)–P(2)	2.203(2)	Rh(1)–Cl(2)	2.421(2)
Rh(1)–Cl(1)	2.439(2)	Rh(1)···Rh(2)	3.196(1)	Rh(2)–P(3)	2.187(2)
Rh(2)–P(4)	2.197(2)	Rh(2)–Cl(2)	2.412(2)	Rh(2)–Cl(1)	2.443(2)
P(1)–C(2)	1.802(7)	P(1)–C(3)	1.805(9)	P(1)–C(1)	1.844(9)
P(2)–C(5)	1.820(7)	P(2)–C(6)	1.824(7)	P(2)–C(4)	1.825(7)
P(3)–C(8)	1.812(7)	P(3)–C(7)	1.825(7)	P(3)–C(9)	1.831(8)
P(4)–C(10)	1.800(7)	P(4)–C(12)	1.820(7)	P(4)–C(11)	1.829(7)
P(1)–Rh(1)–P(2)	96.54(7)	P(1)–Rh(1)–Cl(2)	92.81(6)		
P(2)–Rh(1)–Cl(2)	170.04(6)	P(1)–Rh(1)–Cl(1)	173.55(6)		
P(2)–Rh(1)–Cl(1)	89.90(6)	Cl(2)–Rh(1)–Cl(1)	80.74(6)		
P(1)–Rh(1)–Rh(2)	125.84(5)	P(2)–Rh(1)–Rh(2)	126.35(5)		
Cl(2)–Rh(1)–Rh(2)	48.48(4)	Cl(1)–Rh(1)–Rh(2)	49.16(4)		
P(3)–Rh(2)–P(4)	95.20(7)	P(3)–Rh(2)–Cl(2)	94.15(6)		
P(4)–Rh(2)–Cl(2)	170.55(6)	P(3)–Rh(2)–Cl(1)	173.74(6)		
P(4)–Rh(2)–Cl(1)	89.74(6)	Cl(2)–Rh(2)–Cl(1)	80.84(6)		
P(3)–Rh(2)–Rh(1)	124.70(5)	P(4)–Rh(2)–Rh(1)	123.58(5)		
Cl(2)–Rh(2)–Rh(1)	48.73(4)	Cl(1)–Rh(2)–Rh(1)	49.06(4)		
Rh(1)–Cl(1)–Rh(2)	81.78(5)	Rh(2)–Cl(2)–Rh(1)	82.79(6)		
C(2)–P(1)–C(3)	100.6(4)	C(2)–P(1)–C(1)	100.3(4)		
C(3)–P(1)–C(1)	97.7(5)	C(2)–P(1)–Rh(1)	118.0(3)		
C(3)–P(1)–Rh(1)	116.3(3)	C(1)–P(1)–Rh(1)	120.2(3)		
C(5)–P(2)–C(6)	98.6(3)	C(5)–P(2)–C(4)	100.5(3)		
C(6)–P(2)–C(4)	100.8(4)	C(5)–P(2)–Rh(1)	126.3(2)		
C(6)–P(2)–Rh(1)	114.8(2)	C(4)–P(2)–Rh(1)	112.1(3)		
C(8)–P(3)–C(7)	99.7(4)	C(8)–P(3)–C(9)	100.2(4)		
C(7)–P(3)–C(9)	101.9(3)	C(8)–P(3)–Rh(2)	114.9(2)		
C(7)–P(3)–Rh(2)	118.9(2)	C(9)–P(3)–Rh(2)	118.1(3)		
C(10)–P(4)–C(12)	103.1(3)	C(10)–P(4)–C(11)	100.6(4)		
C(12)–P(4)–C(11)	97.7(4)	C(10)–P(4)–Rh(2)	112.4(2)		
C(12)–P(4)–Rh(2)	113.7(2)	C(11)–P(4)–Rh(2)	126.2(3)		

tion, dimerization, or addition of H_2). Complexes with tridentate ligands, $(Me_2PCH_2Me_2Si)_2N$ or Me_2PCH_2-$(2,6-C_6H_3)CH_2PMe_2$, displayed low catalytic activity, suggesting that phosphine loss or rearrangement may be required for β-elimination by the presumed alkyl hydride intermediate.

3. Experimental

3.1. General procedures

All manipulations involving organometallic species were conducted under inert atmosphere either in a Vacuum Atmospheres glovebox or by using Schlenk techniques. Nitrogen-sensitive complexes such as [Rh-$(PCy_3)_2Cl]_n$ and $[Rh(P^iPr_3)_2Cl]_2$ were stored and handled under argon. Catalytic reactions conducted under normal pressures were carried out in a fully anaerobic liquid-immersible cell constructed so as to hold a relatively large volume of gas over a small volume of solution in a thermostated oil bath. A detailed description of the cell can be found elsewhere [3]. For sealed tube experiments, a certain volume of solution was sealed in a 10 ml Pyrex tube and heated in a GC oven.

For COA photodehydrogenation, either a 200 W or a 500 W Hg-arc lamp was used. Irradiations were carried out in a photolysis apparatus which consisted of a 1 cm Pyrex cuvette fused to a 100 ml gas ballast tube fitted with a Kontes high-vacuum valve to allow the addition and removal of gases. Typically, 1.5 ml of a stock solution was added to the photolysis cell containing a Teflon stirbar. After several freeze–pump–thaw cycles, the desired atmosphere was introduced. During irradiation, all samples were maintained at required temperatures in thermostatically-controlled water baths.

Gas chromatographic analyses were performed with a temperature-programmed Varian 3400 GC using a 50 m HP-1 (cross-linked methyl silicone gum phase) capillary column with a flame ionization detector. Calibration curves were prepared using authentic samples. NMR spectra were recorded on either a Varian VXR-200 or XL-400-MHz spectrometer. ^1H NMR spectra were obtained in C_6D_6 unless otherwise noted and the chemical shift values were referenced to residual C_6D_5H which was set at δ 7.15; ^{31}P NMR spectra were either obtained in pure deutero solvents or in proteo solvents with a deutero solvent capillary. Chemical shift values were referenced to 85% H_3PO_4 which was set at δ 0. IR spectra were obtained on a Mattson Cygnus 100 FTIR spectrometer.

All chemicals were obtained commercially unless otherwise stated. All solvents were purified using accepted procedures [44,45] to remove unsaturated hydrocarbon impurities, dried over $CaCl_2$, and distilled from purple sodium–benzophenone ketyl solutions under argon. Hydrogen and CO were used as supplied by Math-

eson (99.999% grade for H_2 and 99.99% grade for CO). The same stock solution was used throughout each series of experiments to maximize self-consistency. Stock solutions were stored at $-35°C$ in a freezer built into the glovebox.

3.2. Synthesis of $Rh(PMe_3)_3X$ $(X = Cl, Br, OCN, N_3)$ complexes

$Rh(PMe_3)_3Cl$ was synthesized by the method of Wilkinson and coworkers. ^1H NMR: δ 1.04 (d, $J_{P-H} = 7.6$ Hz, 9 H), 1.26 (pseudo t, 18 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ -0.07 (dt, $J_{Rh-P} = 183.2$ Hz, $J_{P-P} = 45.6$ Hz, 1 P), -11.26 (dd, $J_{Rh-P} = 131.4$ Hz, 2 P).

The anion exchange reactions were performed similarly and represented by that of $Rh(PMe_3)_3Br$: a solution of $Rh(PMe_3)_3Cl$ (0.33 g, 0.905 mmol) in 20 ml dry THF was treated with 1.2 g (13.8 mmol) of LiBr. The mixture was stirred for 24 h and THF was removed in vacuo; the resulting solid was extracted with toluene and filtered through Celite. Recrystallization from toluene–hexanes gave 0.31 g product (85% yield). ^1H NMR: δ 1.03 (br d, 9 H), 1.30 (pseudo t, 18 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 0.94 (dt, $J_{Rh-P} = 182.0$ Hz, $J_{P-P} = 43.3$ Hz, 1 P), -13.0 (dd, $J_{Rh-P} = 130.0$ Hz, 2 P).

$Rh(PMe_3)_3(OCN)$. ^1H NMR: δ 0.93 (d, $J_{P-H} = 7.7$ Hz, 9 H), 1.07 (pseudo t, 18 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ -1.0 (dt, $J_{Rh-P} = 165.0$ Hz, $J_{P-P} = 47.9$ Hz, 1 P), -12.0 (dd, $J_{Rh-P} = 130.6$ Hz, 2 P).

$Rh(PMe_3)_3(N_3)$. ^1H NMR: δ 1.11 (br s); $^{31}P\{^1H\}$ NMR (C_6D_6): δ -1.0 (dt, $J_{Rh-P} = 160.0$ Hz, $J_{P-P} = 46.0$ Hz, 1 P), -11.0 (dd, $J_{Rh-P} = 150.0$ Hz, 2 P); $IR(C_6D_6)$: ν_{N_3} 2041.5 cm^{-1} (s).

All these complexes react with H_2 very rapidly in solution to formed adducts $cis,trans$-$H_2Rh(PMe_3)_3X$. A typical ^1H NMR spectrum of $cis,trans$-$H_2Rh(PMe_3)_3Cl$ is described elsewhere [3] and the dihydrides for all other anions exhibited similar patterns, which further confirms the identities of $Rh(PMe_3)_3X$.

3.3. Synthesis of $[Rh(PMe_3)_2X]_2$ $(X = Cl, Br, I, OCN)$ complexes

1 was synthesized by modification of the method of Werner and Weser [8]: 0.30 g (0.42 mmol) of $[Rh(COE)_2Cl]_2$ [47] was dissolved in 30 ml toluene and 0.15 ml of PMe_3 (1.67 mmol) dissolved in 5 ml of toluene was added dropwise with a gas-tight syringe over 30 min while maintaining vigorous stirring. The solution was stirred for 1 h after the phosphine was added and it turned yellow-orange. The solvent was removed in vacuo and the crude product was recrystallized from toluene giving 0.26 g (85% yield) product. ^1H NMR: δ 1.17 (pseudo t, $J_{P-H} = 4.2$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.36 (d, $J_{Rh-P} = 190.7$ Hz).

The anion exchange reactions were carried out similarly and represented by that of $[Rh(PMe_3)_2(OCN)]_2$: a solution of **1** (0.30 g, 0.52 mmol) in 30 ml dry THF was treated with 0.84 g (10.3 mmol) of KOCN. The mixture was stirred for 12 h and THF was removed in vacuo, the resulting solid was extracted with toluene and filtered through Celite. Recrystallization from toluene–hexanes gave 0.24 g product (80% yield). ^1H NMR: δ 1.10 (pseudo t, $J_{P-H} = 3.6$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 4.65 (d, $J_{Rh-P} = 187.6$ Hz); IR (toluene): $\nu_{(OCN)}$ 2177.5 cm^{-1} (s), 2159.2 cm^{-1} (s).

$[Rh(PMe_3)_2Br]_2$. ^1H NMR: δ 1.20 (pseudo t, $J_{P-H} = 3.7$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 3.75 (d, $J_{Rh-P} = 190.4$ Hz).

$[Rh(PMe_3)_2I]_2$. ^1H NMR: δ 1.25 (pseudo t); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 0.47 (d, $J_{Rh-P} = 186.1$ Hz).

The carbonyl complexes $Rh(PMe_3)_2(CO)X$ were obtained by reacting the respective dimers, $[Rh(PMe_3)_2X]_2$, with CO in solution.

$Rh(PMe_3)_2(CO)Cl$. ^1H NMR: δ 1.17 (t, $J_{P-H} = 3.0$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ −9.72 (d, $J_{Rh-P} = 114.1$ Hz); IR(C_6D_6): ν_{CO} 1956.7 cm^{-1}.

$Rh(PMe_3)_2(CO)Br$. ^1H NMR: δ 1.23 (t, $J_{P-H} = 3.2$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ −8.69 (d, $J_{Rh-P} = 104.4$ Hz); IR(C_6D_6): ν_{CO} 1957.6 cm^{-1}.

$Rh(PMe_3)_2(CO)I$. ^1H NMR: δ 1.35 (t, $J_{P-H} = 3.8$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ −6.66 (d, $J_{Rh-P} = 85.2$ Hz); IR(C_6D_6): ν_{CO} 1959.6 cm^{-1}.

$Rh(PMe_3)_2(CO)(OCN)$. ^1H NMR: δ 1.0 (t, $J_{P-H} = 3.0$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ −10.15 (d, $J_{Rh-P} = 115.1$ Hz); IR(C_6D_6): ν_{CO} 1960.5 cm^{-1}, $\nu_{(OCN)}$ 2219.9 cm^{-1}.

3.4. Synthesis of PMe^tBu_2

27 ml of 1.7 M ^tBuLi in pentane was added slowly with stirring to a solution of 2.0 ml (22.4 mmol) $PMeCl_2$ dissolved in 20 ml dry pentane in a 100 ml Schlenk flask cooled down to −78°C. The mixture was then allowed to warm up slowly after the addition had completed while maintaining vigorous stirring. The white precipitate was filtered off through Celite after 5 h, the solvent was removed in vacuo, and a light yellow oil was yielded. Trap-to-trap distillation gave the final product which as a colorless oil (2.3 g, $d = 0.87$, yield 65%). ^1H NMR: δ 0.83 (d, $J_{P-H} = 4.5$ Hz, 3 H), 1.04 (d, $J_{P-H} = 10.6$ Hz, 18 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 11.4 (s). The major impurity is $(PMe^tBu)_2$ (ca. 4% molar ratio). ^1H NMR: δ 0.88 (t, $J_{P-H} = 4.8$ Hz, 6 H), 1.13 (t, $J_{P-H} = 6.4$ Hz, 18 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ −31.04 (s)

3.5. Synthesis of P^cPr_3 (^cPr = Cyclopropyl)

^cPrLi was prepared by reacting ^cPrBr with excess Li in diethyl ether [48,49]; P^cPr_3 was made with 55% yield

($d = 0.93$) from the reaction of $P(OPh)_3$ and ^cPrLi in diethyl ether following the procedures of Denney and Gross [14]. ^1H NMR: δ 0.46 (m), 0.58 (m); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 17.6 (s). All spectroscopic data are consistent with reported values [50].

3.6. Synthesis of complexes with phosphines other than PMe_3

$[Rh(PCy_3)_2Cl]_n$ [51] and $[Rh(P^iPr_3)_2Cl]_2$ [52] were prepared by literature methods. Other complexes were made similarly, by treating $[Rh(COE)_2Cl]_2$ [47] with stoichiometric amounts of phosphines in toluene followed by removing solvent under vacuum and recrystallization from toluene–pentane. Only spectroscopic data are given below.

$[Rh(PMe^tBu_2)_2Cl]_2$. ^1H NMR: δ 0.65 (d, $J_{P-H} = 6.1$ Hz, 3 H), 1.26 (d, $J_{P-H} = 11.7$ Hz, 18 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 67.9 (d, $J_{Rh-P} = 217.6$ Hz).

$H_2Rh(PMe^tBu_2)_2Cl$. ^1H NMR: δ 1.17 (t, $J_{P-H} = 6.4$ Hz, 36 H, ^tBu), 1.43 (pseudo t, 6 H, Me), −22.37 (dt, $J_{Rh-P} = 26.1$ Hz, $J_{P-H} = 15.0$ Hz, 2 H, hydrides); $^{31}P\{selectively decoupled\}$ NMR (C_6D_6): δ 55.9 (dt, $J_{Rh-P} = 114.8$ Hz).

$Rh(PMe^tBu_2)_2(CO)Cl$. ^1H NMR: δ 1.15 (pseudo t, 6 H, Me), 1.28 (pseudo t, 36 H, ^tBu); $^{31}P\{^1H\}$ NMR (C_6D_6): only broad peaks were observed at room temperature owing to the free rotation of the alkyl groups around the P–C bond. IR (C_6D_6): ν_{CO} 1940.3 cm^{-1} [9].

$[Rh(P^cPr_3)_2Cl]_2$. ^1H NMR: δ 0.57 (m, 24 H), 0.65 (br m, 12 H), 1.15 (m, 24 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 43.2 (d, $J_{Rh-P} = 198.5$ Hz). The reaction of H_2 with $[Rh(P^cPr_3)_2Cl]_2$, like the reaction of H_2 with **1**, did not result in simple bridge cleavage. Instead, a complex mixture of products was formed, which included $H_2Rh(P^cPr_3)_2Cl$, $H_2[Rh(P^cPr_3)_2Cl]_2$, etc.

$Rh(P^cPr_3)_2(CO)Cl$. ^1H NMR: δ 0.52 (pseudo q, 12 H), 0.80 (m, 6 H), 0.97 (q, $J_{P-H} = 5.6$ Hz, 12 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 30.2 (d, $J_{Rh-P} = 121.4$ Hz). IR (C_6D_6): ν_{CO} 1961.5 cm^{-1}.

$Rh(P^cPr_3)_3Cl$. ^1H NMR: δ 0.57 (m, 18 H), 0.95 (m, 9 H), 1.16 (m, 18 H); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 16.3 (dd, $J_{Rh-P} = 142.0$ Hz, $J_{P-P} = 41.6$ Hz, 2 P), 45.01 (dt, $J_{Rh-P} = 190.0$ Hz, 1 P).

$cis,trans-H_2Rh(P^cPr_3)_3Cl$. ^1H NMR (hydride region only): δ −11.8 (dm, 1 H, $J_{Ptrans-H} = 157.6$ Hz, $J_{Rh-H} = 20.4$ Hz, $J_{Pcis-H} = 10.0$ Hz, $J_{H-H} = 3.8$ Hz), −20.74 (m, 1 H, $J_{Rh-H} = 21.0$ Hz, $J_{Ptrans-H} = 10.0$ Hz, $J_{Punique-H} = 10.0$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 18.5 (dt, $J_{Rh-P} = 97.3$ Hz, $J_{P-P} = 22.0$ Hz, 1 P), 42.7 (dd, $J_{Rh-P} = 113.6$ Hz, 2 P).

$[Rh(PPh_3)_2Cl]_2$. $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 49.4 (d, $J_{Rh-P} = 195.5$ Hz).

$\{Rh[P(NMe_2)_3]_2Cl\}_2$. ^1H NMR: δ 2.80 (pseudo t, $J_{P-H} = 4$ Hz); $^{31}P\{^1H\}$ NMR (C_6D_6) PMe_3).

{Rh[P(p-C$_6$H$_4$NMe$_2$)$_3$]$_2$Cl}$_2$. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ 47.5 (d, J_{Rh-P} = 197.4 Hz).

3.7. Synthesis of Rh(PMe$_3$)$_2$ClL' and RhL'$_2$ClL complexes (L' = bulky phosphine)

Rh(PMe$_3$)$_2$ClL' was prepared by slow addition of 2.0 equivalents of L' to a toluene solution of 1. The mixture was then stirred for 2 h at room temperature, followed by removing solvent under vacuum and recrystallization from toluene–hexanes. In most cases, mixture of cis and trans isomers were obtained, except for L' = PPh$_3$ and P(NMe$_2$)$_3$. Rh(PMe$_3$)$_2$Cl(PCy$_3$) and Rh(PMe$_3$)$_2$-Cl(P^{i}Pr$_3$) were reported earlier [3].

trans-Rh(PMe$_3$)$_2$Cl[P(NMe$_2$)$_3$]. Only the trans isomer was formed. ^{1}H NMR: δ 1.33 (pseudo t, J_{P-H} = 3.0 Hz, 18 H, P*Me$_3$*), 2.56 (d, J_{P-H} = 9.6 Hz, 18 H, P(N*Me$_2$*)$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −7.72 (dd, J_{Rh-P} = 136 Hz, J_{P-P} = 41 Hz, 2 P, *P*Me$_3$), 141.01 (dt, J_{Rh-P} = 265 Hz, 1 P, *P*(NMe$_2$)$_3$).

trans-Rh(PMe$_3$)$_2$Cl(PPh$_3$). Only the trans isomer was formed. ^{1}H NMR: δ 0.93 (psuedo t, 18 H, P*Me$_3$*), 7.41 (d, *Ph*), 8.08 (t, *Ph*); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −10.53 (dd, J_{Rh-P} = 128.2 Hz, J_{P-P} = 43.1 Hz, 2 P, *P*Me$_3$), 55.8 (dt, J_{Rh-P} = 198.4 Hz, 1 P, *P*Ph$_3$).

trans-Rh(PMe$_3$)$_2$Cl[P(*o*-Tol)$_3$]. A mixture of cis and trans isomers was obtained; only the trans isomer was characterized. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 45.5 (dt, J_{Rh-P} = 191.0 Hz, J_{P-P} = 51.4 Hz, 1 P, *P*(*o*-Tol)$_3$), 53.1 (dd, J_{Rh-P} = 208.9 Hz, 2 P, *P*Me$_3$).

trans-Rh(PMe$_3$)$_2$Cl(P^{c}Pr$_3$). A complex mixture of products including cis and trans isomers as well as [Rh(PMe$_3$)$_3$(P^{c}Pr$_3$)]Cl was obtained; only the trans isomer was characterized. ^{31}P{^{1}H} NMR (toluene-id$_8$, −80°C): δ −9.7 (dd, J_{Rh-P} = 128.4 Hz, J_{P-P} = 43.5 Hz, 2 P, *P*Me$_3$), 58.3 (dt, J_{Rh-P} = 190.3 Hz, 1 P, *P*^{c}Pr$_3$).

cis-Rh(PPh$_3$)$_2$Cl(PMe$_3$). This complex was synthesized from two different routes, i.e. (1) reaction of 1.0 equivalents of PMe$_3$ with Wilkinson's catalyst and (2) treatment of [Rh(PPh$_3$)$_2$Cl]$_2$ with 2.0 equivalents of PMe$_3$ in toluene. Only the cis isomer was isolated in both cases. ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$): δ −10.95 (ddd, J_{Rh-P} = 133.0 Hz, J_{P1-P} = 365.0 Hz, J_{P2-P} = 44.0 Hz, 1 P, *P*Me$_3$), 35.47 (ddd, J_{Rh-P1} = 137.0 Hz, J_{P2-P1} = 38.0 Hz, 1 P, *P$_1$*Ph$_3$ trans to PMe$_3$), 52.16 (ddd, J_{Rh-P2} = 195.0 Hz, 1 P, *P$_2$*Ph$_3$ cis to PMe$_3$ and Cl).

3.8 Synthesis of multidentate ligands (PNP, PCP) and their rhodium complexes

Synthesis of LiPMe$_2$. HPMe$_2$ has a strong stench and is extremely toxic and spontaneously flammable in air; the reaction should be carried out in a good fume hood with extreme caution exercised. It is highly volatile (b.p.: 20–22°C); therefore it was converted into LiPMe$_2$

immediately after being collected in order to avoid any possible hazard. HPMe$_2$ was made by the method of Parshall [53] and collected in a dry-ice–acetone trap; excess ^{n}BuLi in hexanes was then cannulated into the flask at −78°C and the mixture was allowed to warm up slowly and then stirred for 12 h. The resulting white precipitate was filtered off under nitrogen, generously washed with hexanes to remove the excess ^{n}BuLi, and dried under vacuum. ^{1}H NMR (acetone-d$_6$): δ 0.93 (d, J_{P-H} = 3 Hz).

Me$_2$PCH$_2$(2,6-C$_6$H$_4$)CH$_2$PMe$_2$. 0.5 g (7.4 mmol) of LiPMe$_2$ was dissolved in 15 ml THF and the resulting yellow solution cooled down to −10°C, whereupon a solution of 0.97 g (3.7 mmol) α,α'-dibromo-xylene dissolved in 10 ml THF was added dropwise with stirring. The end point was indicated by the initial yellow solution fading to colorless. The mixture was warmed up to room temperature slowly and stirred for 3 h. THF was removed under vacuum and the resulting white paste extracted with pentane and filtered through Celite. Pentane was removed under vacuum to yield a colorless oil. ^{1}H NMR: δ 0.84 (d, J_{P-H} = 2.7 Hz, 12 H, P*Me$_2$*), 2.56 (d, J_{P-H} = 6.0 Hz, 4 H, C*H$_2$*P), 6.91 (m, 3 H, *Ph*), 7.10 (t, J_{H-H} = 7.5 Hz, 1 H, *Ph*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −51 (s).

HRh[η^3-Me$_2$PCH$_2$(2,6-C$_6$H$_3$)CH$_2$PMe$_2$]Cl. The complex was generated and used in-situ. A slight excess of Me$_2$PCH$_2$(2,6-C$_6$H$_4$)CH$_2$PMe$_2$ was mixed with {Rh(COE)$_2$Cl}$_2$ in toluene and refluxed for 1 h yielding an orange solution. Some black precipitate formed in this process and was filtered off. Both ^{1}H- and ^{31}P NMR spectra were run for the solution. ^{1}H NMR (toluene, hydride region only): δ −17.8 (dt, J_{Rh-H} = 28 Hz, J_{P-H} = 14 Hz); ^{31}P{selectively decoupled} NMR (toluene): δ 27.3 (dd, J_{Rh-P} = 104 Hz).

Rh(η^3-Me$_2$PCH$_2$(2,6-C$_6$H$_3$)CH$_2$PMe$_2$)(CO). The solution of HRh(η^3-Me$_2$PCH$_2$(2,6-C$_6$H$_3$)CH$_2$PMe$_2$)Cl in toluene was treated with excess NaN(SiMe$_3$)$_2$ under 800 Torr CO. The initial orange solution turned to light yellow immediately upon exposure to CO. The solution was then put in a −30°C freezer to precipitate out excess NaN(SiMe$_3$)$_2$ and the resulting solution was pumped to dryness and recrystallized from toluene–pentane. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 54.8 (d, J_{Rh-P} = 146 Hz), IR (C$_6$D$_6$): ν_{CO} 1944 cm^{-1} (s).

LiN(Me$_2$SiCH$_2$PMe$_2$)$_2$ (LiPNP). The ligand was made according to the procedure of Fryzuk et al. [54]. ^{1}H NMR: δ 0.40 (s, 12 H, Si*Me$_2$*), 0.70 (br s, 4 H, PC*H$_2$*Si), 0.97 (s, 12 H, P*Me$_2$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): −56.2 (s).

Rh(η^3-N(Me$_2$SiCH$_2$PMe$_2$)$_2$)L' (L' = CO, C$_2$H$_4$). A solution of LiPNP (0.5 mmol) in toluene (5 ml) was added dropwise with stirring to a solution of [Rh(COE)$_2$Cl]$_2$ (0.25 mmol) in toluene (20 ml) at room temperature. The original orange solution darkened slightly during the addition. The solution was stirred for

1 h before exposed to 800 Torr of CO (or C_2H_4), and a bright yellow solution was obtained. The solvent was removed in vacuo. Recrystallization from toluene–pentane gave 80% yield of product.

$[\eta^3\text{-N}(Me_2SiCH_2PMe_2)_2]Rh(CO)$. ^{1}H NMR: δ 0.34 (s, 12 H, SiMe_2), 0.84 (t, $J_{P-H} = 5$ Hz, 4 H, PCH_2Si), 1.19 (t, $J_{P-H} = 3$ Hz, 12 H, PMe_2). IR (C_6D_6): ν_{CO} 1940 cm^{-1} (s).

$[\eta^3\text{-N}(Me_2SiCH_2PMe_2)_2]Rh(C_2H_4)$. ^{1}H NMR: δ 0.42 (s, 12 H, SiMe_2), 0.8 (t, $J_{P-H} = 2.4$ Hz, 4 H, PCH_2Si), 0.86 (pseudo q, 12 H, PMe_2), 2.29 (pseudo t, 4 H, C_2H_4).

3.9 Thermolysis of [Rh(PMe^{t}Bu$_2$)$_2$Cl]$_2$ in C_6D_{12} and in COA

$[Rh(PMe^tBu_2)_2Cl]_2$ (10 mM) in COA was heated at 90°C for 20 h in a J. Young NMR tube equipped with a valve allowing connection to a vacuum line. The solvent was removed under vacuum, the residual was redissolved in C_6D_6 and NMR spectra were taken. A mixture of products were found: $Rh(PMe^tBu_2)_2Cl_2$, $H_2Rh(PMe^tBu_2)_2Cl$, $Rh(PMe^tBu_2)_2Cl_2H(^{1}H$ NMR hydride region: δ -31.1 (dt, $J_{Rh-H} = 32.4$ Hz, $J_{P-H} = 13.0$ Hz)), and $H_2Rh_2(PMe^tBu_2)_3Cl(COE)$ (^{1}H NMR hydride region: δ -21.0 (dq, 1 H, $J_{Rh-H} = 23.6$ Hz, $J_{P-H} = J_{H-H} = 15.0$ Hz), -21.6 (dq, 1 H, $J_{Rh-H} = 24.5$ Hz, $J_{P-H} = J_{H-H} = 15.0$ Hz); ^{31}P$\{^1$H$\}$ NMR (C_6D_6): δ 53.9 (d, $J_{Rh-P} = 186$ Hz, 1 P), 58.9 (dt, $J_{Rh-P} = 114$ Hz, $J_{H-P} = 15$ Hz, 2 P)).

3.10. X-ray crystallography

A crystal of **1** was placed in oil in the glovebox and transferred to the chilled nitrogen stream (-120°C) of a CAD4 diffractometer (graphite-monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å). Three intensity standard reflections were checked every hour and showed less than 1% decay. The 3800 measured reflections were corrected for Lorentz effects, polarization, decay and absorption, the latter employing the numerical method found in SHELX76 [55]. The structure was solved by direct methods (SHELXS86) [56] and refined by least squares and Fourier techniques based upon F^2 (SHELXL93) [57]. All non-H atoms were refined with anisotropic displacement parameters. The H atoms were restrained to their calculated positions and given a common displacement parameter. There were no significant indications of extinction. The ORTEP [58] diagram in Fig. 1 was drawn with ellipsoids at the 50% probability level.

4. Supplementary material available

Tables of positional parameters, intramolecular distances and angles, torsion angles, least squares planes,

anisotropic displacement parameters and H atom parameters are available. Ordering information is given on any current masthead page.

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