Generation and Reactivity of {(Ethane-1,2-diyl)-bis[diisopropylphosphine-κ*P*]}-{[2,4,6-tri(*tert*-butyl)phenyl]phosphino-κ*P*}rhodium ([Rh{PH(^{t}Bu$_3$C$_6$H$_2$)}(^{i}Pr$_2$PCH$_2$CH$_2$P^{i}Pr$_2$)]): Catalytic C–P Bond Formation *via* Intramolecular C–H/P–H Dehydrogenative Cross-Coupling

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Dedicated to the memory of Professor *Luigi M. Venanzi*, an exceptional scholar, gentleman, mentor, and friend

The complex [Rh(η^3-benzyl)(dippe)] (**1**; dippe = bis(diisopropylphosphino)ethane = (ethane-1,2-diyl)bis-[diisopropylphosphine]) reacted cleanly with Mes*PH$_2$ (**2**; Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) to provide a new Rh species [Rh(H)(dippe)(L)] (**3**), L being the 2,3-dihydro-3,3-dimethyl-1*H*-phosphindole ligand **4** (= ^{t}Bu$_2$C$_6$H$_2$(CMe$_2$CH$_2$PH)) (*Scheme 1*). Complex **3** was converted to the corresponding chloride [Rh(Cl)(dippe)(L)] (**6**) when treated with CH$_2$Cl$_2$, whereas the dimeric species [Rh$_2${μ-^{t}Bu$_2$C$_6$H$_2$(CMe$_2$CH$_2$P)}(μ-H)(dippe)$_2$] (**7**) was formed upon thermolysis in toluene (*Scheme 2*). The structures of **6** and **7**·C$_7$H$_8$ were determined by X-ray crystallography. Complexes **1** and **3** served as catalyst precursors for the dehydrogenative coupling of C–H and P–H bonds in the conversion of **2** to **4** (*Scheme 3*). Deuteration studies with Mes*PD$_2$ exposed a complex series of bond-activation pathways that appear to involve C–H activation of the dippe ligand by the Rh-atom (*Schemes 4* and *5*)

Introduction. – The activation of element-hydrogen bonds by transition-metal fragments represents a fundamental step in a number of metal-catalyzed transformations [1]. Studies that further our understanding of the way in which main-group species are transformed within the coordination sphere of metal complexes are, therefore, of particular relevance since these investigations may uncover novel reaction pathways, and ultimately lead to new catalytic processes. In this context, activations of *multiple* element-hydrogen bonds in a single substrate have attracted considerable interest, leading to the genesis of dehydrocoupling methods [2].

Recently, we reported the first direct observation of 1,2-shifts (α-eliminations [3]) that convert silyl(transition metal) complexes [M(SiHR$_2$)(L)$_n$] into base-free (silanylidene)hydridometals [M(H)(=SiR$_2$)L$_n$]. This intriguing intramolecular process was initially observed for a cationic, three-coordinate silanylplatinum compound, in which a 1,2-hydride migration led to the formation of a more stable, four-coordinate square-planar complex [4]. Cationic and zwitterionic (silylene)hydridoiridium complexes possessing either octahedral [5] or three-legged piano-stool [6] geometries have also been prepared *via* α-hydride elimination routes. It is noteworthy that in two cases,

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transition-metal complexes with a silanylidene ligand resulted directly from the sequential activation of two Si–H fragments on a single R_2SiH_2 substrate [5][6].

In attempting to assess the generality of this 1,2-shift process as a route to multiple bonds between main-group and transition-metal fragments $L_nM{=}ER_m$, neutral, three-coordinate Group 9 metal complexes bearing reactive main-group substituents represent important synthetic targets. Particularly appealing are phosphido derivatives of the type [M(PHR)L_2] (L = 2-electron donor; M = Group 9 metal), since α-hydride elimination from the P-atom could lead to the formation of terminal phosphinidine complexes [M(H)(=PR)L_n], a hitherto elusive class of molecules[2]). Herein we report on the reactivity of [Rh(PHMes*)(dippe)] (Mes* = 2,4,6-tri(*tert*-butyl)phenyl; dippe = bis(diisopropylphosphino)ethane = (ethane-1,2-diyl)bis[diisopropylphosphine]) which is generated *in situ* by P–H bond activation. This intermediate does not lead to the late metal phosphinidine [Rh(H)(=PMes*)-dippe)], but instead undergoes intramolecular C–H bond activation, leading to the formation of a new P–C bond. This stoichiometric process can be incorporated into a dehydrogenative catalytic cycle.

Results and Discussion. – For generation of a three-coordinate phosphidorhodium complex of the type [Rh(PHR)L_2], the reaction of [Rh(η^3-benzyl)(dippe)] (**1**) [8] with [2,4,6-tri(*tert*-butyl)phenyl]phosphine (Mes*PH_2; **2**) [9] was examined. It was thought that this reaction might proceed *via* P–H oxidative addition to the Rh-atom, followed by reductive elimination of toluene. This combination of main-group and transition-metal precursors seemed promising, since the dippe ligand is known to support square-planar silylene complexes [4], while the Mes* fragment has proven efficient in kinetically stabilizing metal-phosphorus multiple bonds in early metal phosphinidine complexes [7].

Treatment of **1** with 1 equiv. of **2** rapidly resulted in the liberation of toluene and clean formation of a new Rh complex **3** (*Scheme 1*), which was observed to contain three nonequivalent P-centers and a Rh–H fragment by ^{31}P- and ^{1}H-NMR spectroscopy. The complexity of the ^{t}Bu signals, the appearance of new CH_2 and PH resonances in the ^{1}H-NMR spectrum, as well as a low field ^{31}P-NMR shift [7] attributed to an aryl-substituted phosphine (–23.9 ppm) suggested that **3** is a complex of the known fused-ring-system phosphine 5,7-di(*tert*-butyl)-2,3-dihydro-3,3-dimethyl-1*H*-phosphindole (**4**) [10], and not the desired (phosphinidine)rhodium complex **5**. Metal complexes ligated by **4** and its derivatives are known [11]; for example, *Champion* and *Cowley* [11] reported that treatment of Mes*P=C=O with [$Fe_2(CO)_9$] leads to the formation of [$Fe(CO)_4$(**4**)]. These workers propose that [$Fe(CO)_4$(**4**)] is generated from the terminal-phosphinidine ligand of [$Fe(CO)_4$(=PMes*)]. Indeed, it is known that 'Mes*P' itself rearranges to **4** *via* insertion of the P-atom into one of the C–H bonds of the *ortho*-positioned ^{t}Bu group [10][12]. While it is plausible that **3** is similarly derived from **5**, an alternative mechanistic pathway leading from the intermediate [Rh(PHMes*)(dippe)] to **3**, involving C–H oxidative addition and P–C reductive elimination steps, is equally viable. No intermediates were observed when the reac-

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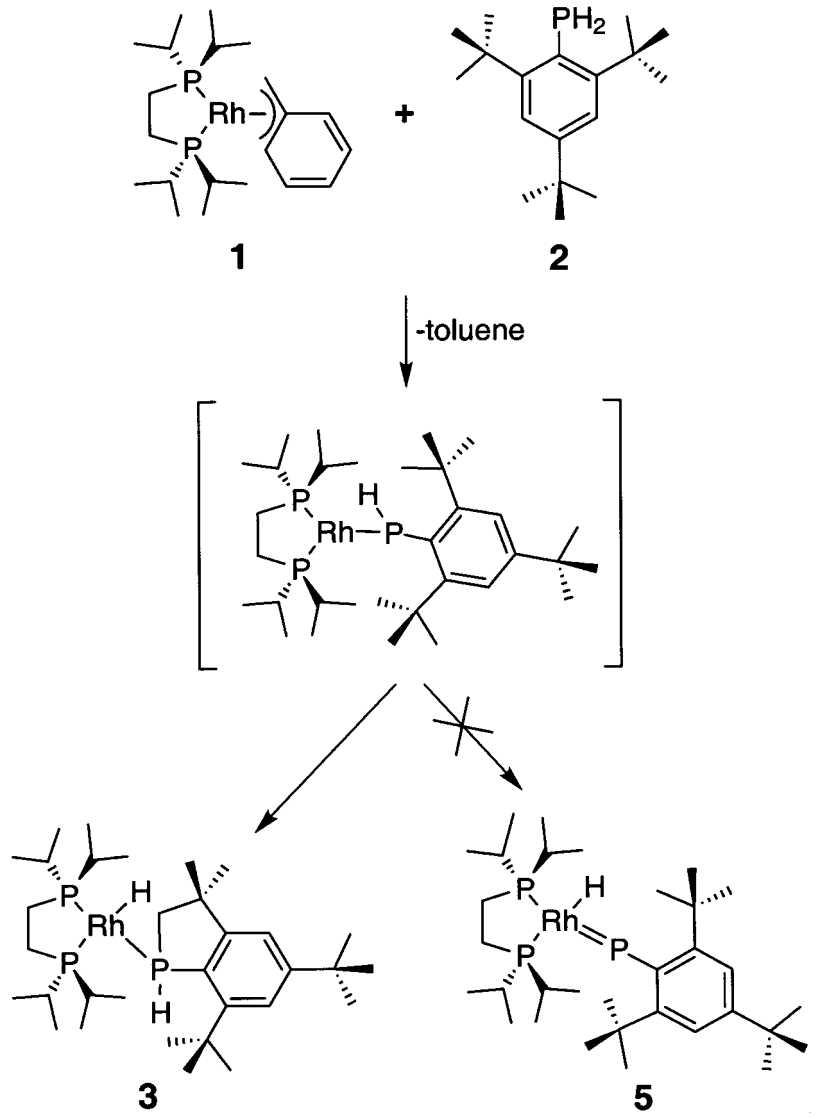
[2]) While isolable, terminal-phosphinidine complexes of the early metals have been prepared, late-metal derivatives have been generated only transiently, see [7].

Scheme 1



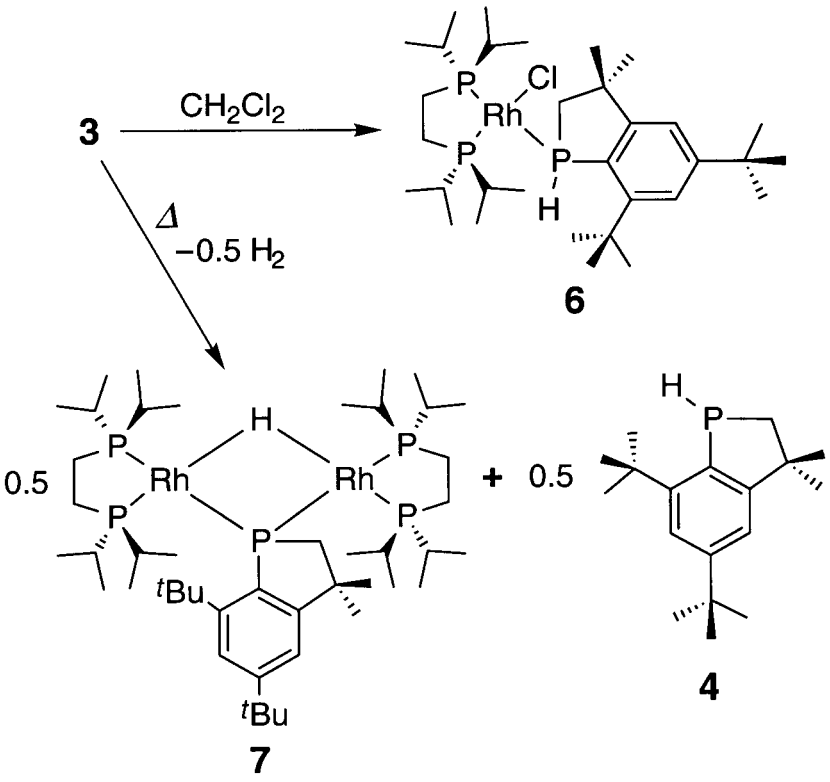
tion of **1** and **2** was monitored by NMR spectroscopy at $-80°$. Similarly, attempts to trap transient low-valent species with but-2-yne and diphenylacetylene were unsuccessful.

The hydride **3** reacts with CH_2Cl_2 within 8 h, producing the corresponding monomeric chlororhodium complex **6** (*Scheme 2*) in 89% yield, along with small amounts of the known complex $[RhCl(dippe)]_2$ [13]. Analogous reactions employing either CCl_4 or $CHCl_3$ also led to **6**, along with larger amounts of $[RhCl(dippe)]_2$. The structure of **6** was determined by X-ray-diffraction techniques (see *Fig. 1*), which

indirectly confirmed the connectivity proposed for **3**. Crystallographic data and selected structural parameters are collected in *Tables 1* and *2*, respectively. The Rh^I center in **6** exhibits a distorted square-planar geometry, with coordination sites occupied by the dippe, chloro, and cyclic phosphine **4** ligands. Although a statistically significant progression of Rh–P bond lengths (Rh–P(1) > Rh–P(3) > Rh–P(2)) is observed, these distances fall within the previously observed range for Rh–P bonds in related systems[3]). The Rh–Cl distance in **6** is also identical to those observed in analogous '[$RhClP_3$]' complexes[4]). The structural attributes of the phosphindole moiety in **6** mirror those found in related crystallographically characterized species [11]. The P(1) center is distorted considerably from ideal tetrahedral geometry. Geometric distortions are also apparent at the aromatic C(18), which possesses angles ranging from *ca.* 110 to 131°.

It was recently observed in the reaction of SiH_2Mes_2 (Mes = 2,4,6-trimethylphenyl) with [Ir(Cp*)(Me)(PMe_3)](OSO_2CF_3) (Cp* = pentamethylcyclopentadienyl) that a cyclometallated species is formed as the kinetic product, which in turn isomerizes to the

Scheme 2



[3]) For a selection of crystallographically characterized [Rh(dippe)] complexes, see [14].

[4]) For a recent selection of crystallographically characterized '[$RhClP_3$]' complexes, see [15].

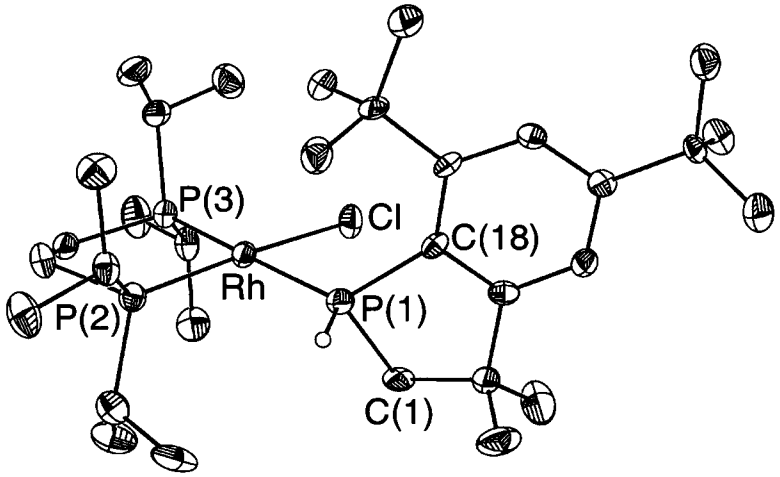


Fig. 1. *Crystallographically determined structure of* **6**. Depicted with 50% thermal ellipsoids. Selected H-atoms are omitted for clarity.

Table 1. *Summary of Crystallographic Data*

	6	**7**·C_7H_8
Empirical formula	$C_{32}H_{61}ClP_3Rh$	$C_{53}H_{101}P_5Rh_2$
Formula weight	677.08	1099.01
Temperature	−108(2)°	−124(2)°
Crystal system	monoclinic	monoclinic
Lattice parameters	a = 14.2475(5) Å	a = 11.9099(7) Å
	b = 13.6514(6) Å	b = 20.105(1) Å
	c = 19.0902(4) Å	c = 12.0247(5) Å
	β = 109.247(2)°	β = 90.746(2)°
Volume	3505.5(2) Å^3	2879.0(3) Å^3
Space group	$P2_1/n$	$P2_1$
Z	4	2
D_{calc}	1.283 g/cm^3	1.268 g/cm^3
μ(MoK_α)	0.719 mm^{-1}	0.743 mm^{-1}
F_{000}	1440	1168
θ-range for data collection [°]	1.87 to 25.60	1.69 to 25.60
Reflections collected	15355	12951
Independent reflections	5880	7308
R(int)	0.0764	0.0545
Data/restraints/parameters	5735/0/337	7200/1/551
Goodness-of-fit on F^2	0.702	0.967
R_1 ($I > 2.00\sigma$)	0.0379	0.0558
wR_2 ($I > 2.00\sigma$)	0.0461	0.1162
R_1 (all data)	0.1130	0.1063
wR_2 (all data)	0.0556	0.1297
T_{min}, T_{max}	0.847, 0.962	0.862, 0.939
Max peak in final diff. map	0.479 e$^-$/Å^3	0.735 e$^-$/Å^3
Min peak in final diff. map	−0.437 e$^-$/Å^3	−0.743 e$^-$/Å^3

Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *for* **6** *and* **7** · C_7H_8

6		**7** · C_7H_8	
Bond distances:			
Rh–P(1)	2.323(1)	Rh–Rh	3.157(1)
Rh–P(2)	2.191(1)	Rh(1)–P(1)	2.338(3)
Rh–P(3)	2.261(1)	Rh(1)–P(2)	2.209(3)
Rh–Cl	2.405(1)	Rh(1)–P(3)	2.252(3)
P(1)–C(1)	1.839(4)	Rh(2)–P(1)	2.342(3)
P(1)–C(18)	1.840(4)	Rh(2)–P(4)	2.182(3)
C(1)–C(4)	1.522(5)	Rh(2)–P(5)	2.262(3)
C(5)–C(18)	1.400(5)	P(1)–C(1)	1.89(1)
C(13)–C(18)	1.420(5)	P(1)–C(18)	1.92(1)
Bond angles:			
P(1)–Rh–Cl	85.96(4)	P(1)–Rh(1)–P(2)	105.1(1)
P(2)–Rh–Cl	172.53(4)	P(2)–Rh(1)–P(3)	84.5(1)
P(3)–Rh–Cl	89.54(4)	P(1)–Rh(1)–P(3)	169.2(1)
P(1)–Rh–P(2)	97.87(5)	P(1)–Rh(2)–P(4)	104.5(1)
P(1)–Rh–P(3)	175.15(5)	P(1)–Rh(2)–P(5)	168.8(1)
P(2)–Rh–P(3)	86.41(4)	P(4)–Rh(2)–P(5)	85.8(1)
Rh–P(1)–C(1)	110.4(2)	C(1)–P(1)–Rh(1)	118.1(4)
Rh–P(1)–C(18)	125.6(2)	C(1)–P(1)–Rh(2)	119.8(4)
C(1)–P(1)–C(18)	91.8(2)	C(1)–P(1)–C(18)	89.9(5)
P(1)–C(18)–C(5)	109.9(3)	C(18)–P(1)–Rh(1)	123.8(3)
P(1)–C(18)–C(13)	131.0(3)	C(18)–P(1)–Rh(2)	124.1(3)
C(5)–C(18)–C(13)	119.1(4)	Rh(1)–P(1)–Rh(2)	84.8(1)

thermodynamic (silylene)iridium complex [6]. In an attempt to effect a similar conversion of **3** to **5**, a sample of the former was taken up in (D_8)toluene and monitored by NMR spectroscopy. Within 96 h at room temperature, slow decomposition of **3** to a complex mixture of products was observed. However, heating solutions of **3** at 80° for 72 h resulted in the clean production of 0.5 equiv. each of the binuclear complex **7** and the free phosphindole **4**, along with varying amounts of H_2. Consistent with the structural formulation given in *Scheme 2*, compound **7** exhibits two ^{31}P-NMR resonances (85.8 and 90.1 ppm) attributed to the dippe ligand and a third resonance (113.3 ppm) due to the bridging phosphido moiety. Features of the ^{1}H-NMR spectrum of **7** (including a rather complex *m* at −7.80 ppm) are also consistent with the proposed structure. The solid-state structure of **7** (crystallized as the toluene solvate) was determined by X-ray-diffraction techniques (see *Fig. 2*). Crystallographic data and selected structural parameters are collected in *Tables 1* and *2*, respectively. Compound **7** is comprised of two edge-sharing distorted square planes bridged by phosphido and hydrido ligands, and hinged at an angle of *ca.* 31° (least-squares planes defined by Rh(1), P(1), P(2), P(3), H(1) and Rh(2), P(1), P(4), P(5), H(1)). The metal-metal separation in **7** (3.157(1) Å) nears the limit commonly accepted for appreciable metal-metal bonding (< 3.2 Å) [16], but the relatively low-field ^{31}P-NMR chemical shift of the phosphido ligand suggests no significant Rh–Rh interaction [17]. The structure of **7** can be compared with the only other crystallographically characterized binuclear rhodium complex bridged exclusively by phosphido and hydrido ligands, [Rh_2(μ-^{t}Bu_2P)(μ-H)(^{t}Bu_2PH)$_2$(CO)$_2$], which is formulated as having a Rh–Rh bond

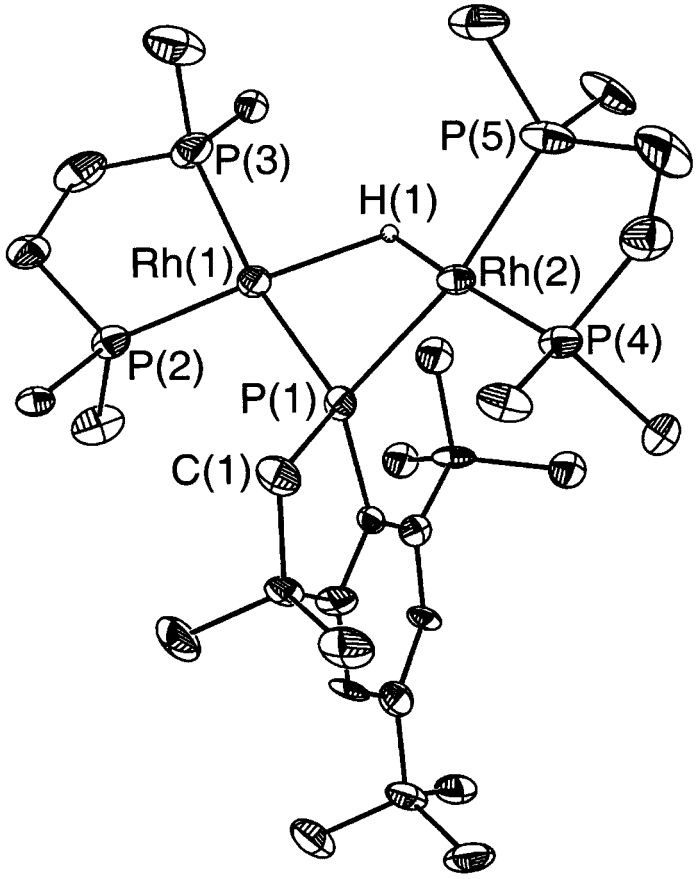
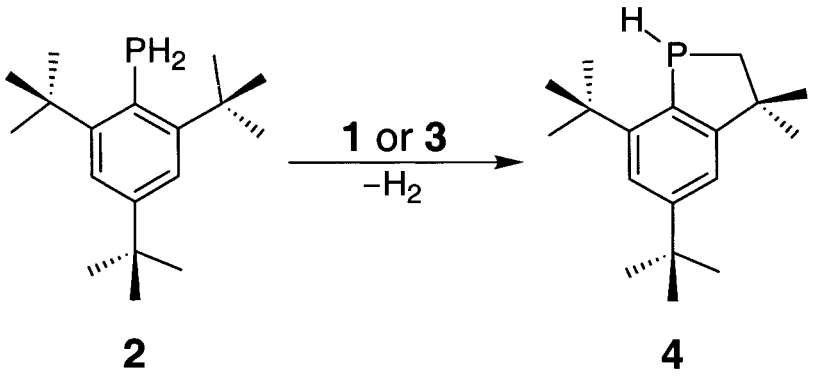


Fig. 2. *Crystallographically determined structure of* **7**·C_7H_8. Depicted with 30% thermal ellipsoids. The toluene solvate, isopropyl Me groups, and selected H-atoms are omitted for clarity. Only the major components of the disordered Rh_2 and *tert*-butyl fragments are shown.

(2.906(2) Å) order of approximately one [18]. The Rh–P bridging distances in this latter complex (2.272(4) and 2.278(4) Å) are significantly shorter than those found in **7** (2.338(3) and 2.342(3) Å). As in **6**, the P-center in the bridging phosphido moiety of **7** resides in a severely distorted tetrahedral environment.

Liberation of the cyclic phosphine **4** in the transformation **3** → **7** suggested the possibility that Mes*PH_2 (**2**) may be catalytically cyclized to **4** in the presence of a Rh^I compound. Indeed, complexes **1** and **3** function equally well as catalyst precursors for the conversion of **2** to **4**, which overall corresponds to the catalytic didehydro coupling of alkyl C–H and P–H bonds to yield a new P–C linkage (*Scheme 3*). In preliminary experiments, *ca.* 10 mol-% of the Rh-catalyst precursor was employed for the conversion of 60 mg of **2** in C_6D_6 (*ca.* 0.1M), and the progress of the reaction was monitored by NMR spectroscopy. Although *ca.* 2 h were required to attain only three turnover cycles under ambient conditions, the catalysis was found to proceed with

Scheme 3

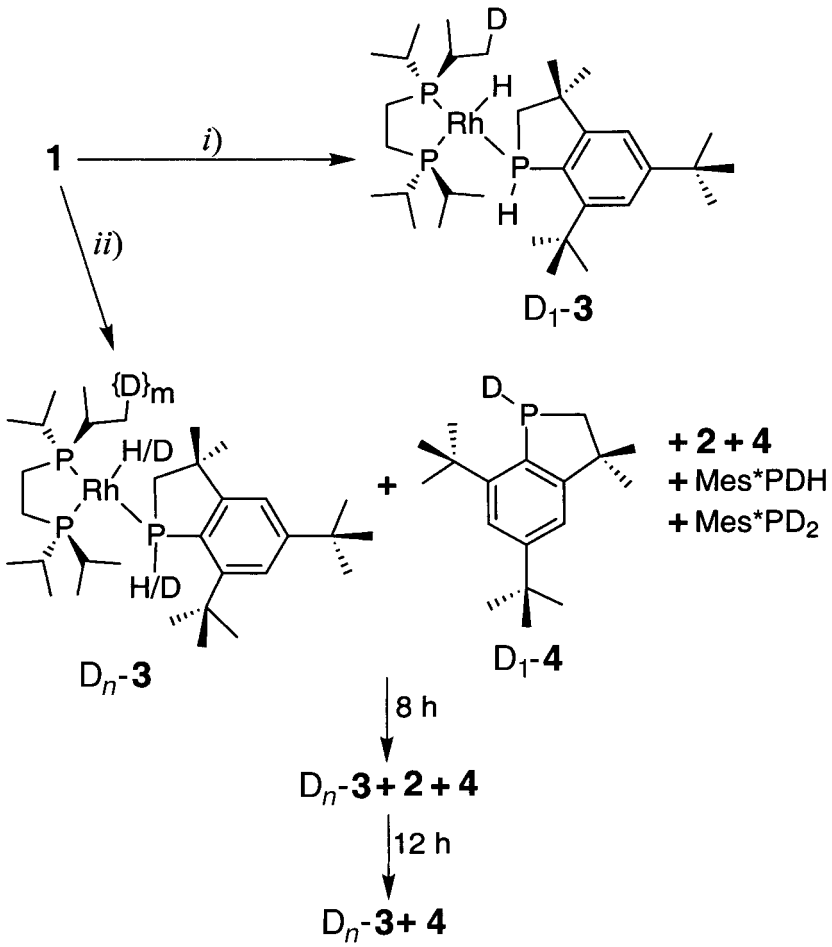


extremely high efficiency; only **2** and **4** were observed throughout, and after 72 h, *ca.* 90% conversion was attained. Upon completion of a catalytic run, the introduction of additional substrate **2** led to continued catalysis, albeit with reduced activity. The crucial role of the Rh-atom in this catalytic transformation was verified by the complete lack of reactivity found when solutions of **2** were treated with dippe alone. *Glueck* and co-workers [19] have examined related transformations in the Rh-catalyzed isomerization of phosphacumulenes. Currently, there is considerable interest in the development of new methods for the formation of P–C bonds (for examples, see [20]), and routes based on the dehydrocoupling of C–H and P–H bonds could be highly useful.

In an attempt to gain mechanistic insight into the aforementioned stoichiometric and catalytic transformations, the reaction of **1** with Mes*PD_2 in C_6D_6 was monitored by NMR spectroscopy. Surprisingly, the stoichiometric reaction between **1** and Mes*PD_2 led to the formation of a product D_1-**3** that exhibited slightly broadened isopropyl Me resonances in the ^{1}H-NMR spectrum, and no detectable amount of D incorporated at either P or Rh (*Scheme 4*). Deuteration of the dippe ligand was even more prominent in the reaction of **1** with 5.0 equiv. of Mes*Pd_2. ^{1}H-NMR Data acquired after 30 min indicated that substantial D-incorporation into the isopropyl Me groups, along with partial deuteration of P and Rh, had occurred to give the Rh complex D_n-**3**. The ^{1}H- and ^{31}P-NMR spectra of the reaction mixture also revealed the presence of Mes*PD_2, Mes*PDH, Mes*PH_2 (**2**), the phosphindole **4**, its deuterated analogue D_1-**4**, and small amounts of an unidentified species (δ (^{31}P) = –24.3). After an additional 8 h at room temperature, the D-containing free phosphines Mes*PD_2, Mes*PDH, and D_1-**4** were consumed. Finally, after a total reaction time of *ca.* 21 h, only D_n-**3**, **4**, and the unidentified impurity were detected, in keeping with the catalytic dehydrogenation process depicted in *Scheme 3*. Throughout, neither deuteration of the ^{t}Bu groups nor productive activation of C_6D_6 was detected. The nearly exclusive inclusion of D into the isopropyl Me groups of the dippe ligand was confirmed by the ^{2}H-NMR data acquired upon completion of the reaction.

The facile Rh-mediated H/D exchange of D from Mes*PD_2 at the C–H units of the isopropyl Me groups of the dippe ligand reveals the operation of a complex series of reaction equilibria in this system. One simplified mechanistic rationale for the observed

Scheme 4



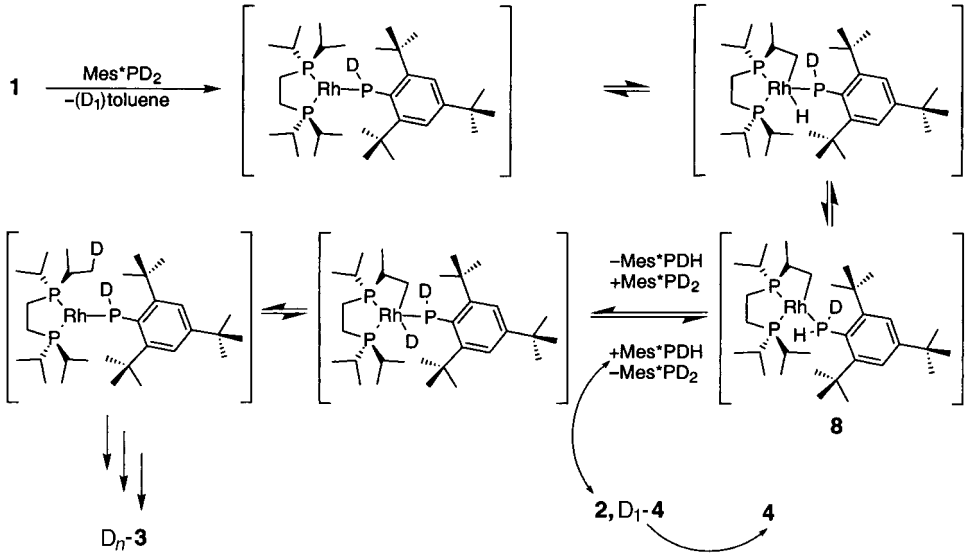
i) 1.0 Mes*PD_2, 10 min. *ii*) 5.0 Mes*PD_2, 30 min.

D-scrambling is presented in *Scheme 5*. Treatment of **1** with Mes*PD_2 presumably leads to the deuterated intermediate [Rh(PDMes*)(dippe)], along with 1 equiv. of (D_1)toluene. Subsequent insertion into an isopropyl Me C–H bond[5]), followed by reductive elimination of P–H could lead to the strained intermediate **8**[6]). Reaction of this Rh-complex with the coordinated Mes*PDH fragment *via* P–D oxidative addition, followed by C–D reductive elimination, Rh-insertion into a new isopropyl C–H bond, and P–H reductive elimination would generate Mes*PH_2 (**2**) and a more highly deuterated version of **8**. The observed formation of Mes*PH_2 from Mes*PD_2 by NMR spectroscopy (*vide supra*) suggests that such a P–D/C–H exchange process is somewhat fast relative to the Rh-catalyzed P–C bond-formation process depicted in

[5]) A related metallation process involving a PCP 'pincer' complex of Rh has been observed [21].

[6]) A neutral three-coordinate alkylrhodium(I) complex has recently been reported [22].

Scheme 5



Scheme 3. Dehydrogenative cyclization could then convert mixtures of Mes*PD_2, Mes*PDH, and Mes*PH_2 (**2**), into the phosphindole **4** and its deuterated analogue D_1-**4**. Subsequent P–D bond activation chemistry transforms D_1-**4** into **4**. Alternatively, **8** could take up 1 equiv. of Mes*PD_2, ultimately leading to deuteration of the P–H and Rh–H groups in D_n-**3**. Whereas bond-activation pathways leading to D-incorporation at the C–H bonds of the *ortho*-positioned ^{t}Bu group are also readily envisioned, the ^{1}H- and ^{2}H-NMR spectroscopic data suggest that such processes are not important.

In summary, the reactive intermediate [Rh(PHMes*)(dippe)], does not lead to an isolable phosphinidine complex, but instead undergoes intramolecular C–H bond activation to afford the new hydridorhodium complex **3**. This hydrido complex in turn reacts with chlorinated solvents to yield **6** and, upon thermolysis, is converted to the binuclear species **7**. Complex **3** also serves as a catalyst precursor for the intramolecular dehydrogenative coupling of P–H and alkyl C–H bonds in **2**, leading to the phosphindole **4**. This latter transformation is of interest, as it corresponds to the activation and coupling of two simple element-hydrogen bonds in a dehydrogenative cross-coupling. Deuteration studies with Mes*PD_2 revealed a complex series of interconnected reaction manifolds that likely involve a dippe-metallated intermediate. Future investigations will focus on exploring the generality and utility of Rh-catalyzed C–H/P–H dehydrogenative coupling, and on the synthesis of phosphinidine complexes *via* α-migration processes.

Experimental Part

General. All manipulations were performed under N_2 by means of *Schlenk* techniques or in a glove box. Dry, O_2-free solvents were employed throughout. Toluene was distilled from Na, and pentane from Na benzophenone. (D_6)Benzene and (D_8)toluene were distilled from Na/K alloy, and CH_2Cl_2 and CD_2Cl_2 were

dried over CaH_2 and distilled prior to use. The compounds [Rh(η^3-benzyl)(dippe)] [8] and Mes*PH_2 (**2**) [9] were prepared according to the literature, while $LiAlD_4$ (*Aldrich*) was used as received. IR Spectra: *Mattson Infinity-60-MI-FTIR* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra: at 500 (^1H), 125 ($^{13}C\{^1H\}$), or 202 MHz ($^{31}P\{^1H\}$) and r.t., unless otherwise noted; *Bruker DRX-500* spectrometer; chemical shifts δ in ppm downfield of $SiMe_4$ (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P); *J* in Hz. Elemental analyses were performed by the Micro-Mass Facility in the College of Chemistry at the University of California, Berkeley.

*[5,7-Di(*tert*-butyl)-2,3-dihydro-3,3-dimethyl-1*H*-phosphindole-κ*P*]{(ethane-1,2-diyl)bis[diisopropylphosphine-κ*P*]}hydrorhodium* (**3**). To a soln. of [Rh(η^3-benzyl)(dippe)] (0.138 g, 0.303 mmol) in pentane (5 ml) was added a soln. of Mes*PH_2 (0.084 g, 0.303 mmol) in pentane (3 ml). After stirring the resulting deep red soln. at r.t. for 30 min, the mixture was filtered through *Celite* ® and stored at $-30°$ for 24 h, producing **3** (0.169 g, 87%). Anal. pure yellow powder. IR: 2226*s* (PH), 1767*s* (RhH). ^1H-NMR ((D_6)benzene, 25°): 7.51 (*m*, 1 arom. H); 7.18 (*m*, 1 arom. H); 6.23 (*dm*, $^1J(H,P) = 272.5$, PH); 2.48 (*m*, $PHCH_2CMe_2$); 2.02 (*m*, 2 H, Me_2CHP); 1.88 (*m*, 2 H, Me_2CHP); 1.80 (*s*, 1 ^{t}Bu); 1.46 (*s*, 3 H, $PHCH_2CMe_2$); 1.29 (*s*, 1 ^{t}Bu); 1.27 (*s*, 3 H, $PHCH_2CMe_2$); 1.23–0.93 (*m*, 28 H, Me_2CHP, PCH_2CH_2P); −4.61 (*d*, *d't'*, $^1J(H,Rh) = 112.3$, $^2J(H,P_{trans}) = 31.4$, $^2J(H,P_{cis}) = 19.5$, RhH). $^{13}C\{^1H\}$-NMR ((D_6)benzene, 25°): 156.8 (*d*, $^2J(C,P) = 9.7$, arom. C); 152.8 (*d*, $^2J(C,P) = 9.7$, arom. C); 152.3 (*d*, $^4J(C,P) = 1.3$, arom. C); 134.8 (*d*, $^1J(C,P) = 32.1$, arom. C); 122.7 (*d*, $^3J(C,P) = 7.5$, arom. CH); 118.6 (*d*, $^3J(C,P) = 7.5$, arom. CH); 45.3 (*m*, $PHCH_2CMe_2$); 42.7 (*d*, $^1J(C,P) = 27.9$, $PHCH_2CMe_2$); 37.5 (*s*, Me_3C); 35.4 (*s*, Me_3C); 33.3 (*d*, $^4J(C,P) = 5.1$, $Me_3C-C(7)$); 32.0 (*s*, $Me_3C-C(5)$); 30.8 (*d*, $^4J(C,P) = 5.3$, $PHCH_2CMe_2$); 30.2 (*s*, $PHCH_2CMe_2$); 28.4–26.6 (*m*, Me_2CHP); 24.0–23.6 (*m*, PCH_2CH_2P); 21.2 (*m*, Me_2CHP); 20.9 (*m*, Me_2CHP); 20.6 (*m*, Me_2CHP); 20.4 (*m*, Me_2CHP); 19.8 (*m*, Me_2CHP); 19.7 (*m*, Me_2CHP); 19.5 (*m*, Me_2CHP); 19.1 (*m*, Me_2CHP). $^{31}P\{^1H\}$-NMR ((D_6)benzene, 25°): 102.9 (*ddd*, $^2J(P,P_{trans}) = 318.7$, $^1J(P,Rh) = 159.4$, $^2J(P,P_{cis}) = 21.2$, PCH_2CH_2P *cis* to H); 83.6 (*ddd*, $^1J(P,Rh) = 130.6$, $^2J(P,P_{cis}) = 28.0$, $^2J(P,P_{cis}) = 21.2$, PCH_2CH_2P trans to H); −23.9 (*ddd*, $^2J(P,P_{trans}) = 318.7$, $^1J(P,Rh) = 149.2$, $^2J(P,P_{cis}) = 28.0$, PH). Anal. calc. for $C_{32}H_{62}P_3Rh$: C 59.81, H 9.72; found: C 60.06, H 9.83.

*Chloro[5,7-di(*tert*-butyl)-2,3-dihydro-3,3-dimethyl-1*H*-phosphindole-κ*P*]{(ethane-1,2-diyl)bis[diisopropylphosphine-κ*P*]}rhodium* (**6**). To **3** (0.079 g, 0.123 mmol) was added CH_2Cl_2 (5 ml), followed by stirring for 8 h. Subsequently, the mixture was evaporated and the remaining yellow residue extracted with pentane (2 × 4 ml). The extracts were then concentrated to *ca*. 3 ml and cooled to −30°, producing **6** (0.074 g, 89%). Yellow prisms. IR: 2282*s* (PH). ^1H-NMR ((D_6)benzene, 25°) 7.54 (*m*, 1 arom. H); 7.18 (*m*, 1 arom. H); 5.76 (*dm*, $^1J(H,P) = 283.0$, PH); 3.14 (*m*, 1 H, Me_2CHP); 2.65 (*m*, 1 H, Me_2CHP); 2.22 (*m*, 1 H, Me_2CHP); 1.92 (*m*, 3 H, Me_2CHP); 1.85 (*s*, 1 ^{t}Bu); 1.58 (*s*, 3 H, $PHCH_2CMe_2$); 1.38 (*m*, 6 H, Me_2CHP); 1.23 (*s*, 1 ^{t}Bu); 1.20 (*s*, 3 H, $PHCH_2CMe_2$); 1.19–0.81 (*m*, 22 H, Me_2CHP, PCH_2CH_2P). $^{13}C\{^1H\}$-NMR ((D_6)benzene, 25°); 158.9 (*m*, arom. C); 152.6 (*m*, arom. C); 152.5 (*m*, arom. C); 127.9 (*m*, arom. C); 122.6 (*d*, $^3J(C,P) = 8.3$, arom. CH); 117.9 (*d*, $^3J(C,P) = 7.4$, arom. CH); 45.0 (*m*, $PHCH_2CMe_2$); 39.1 (*d*, $^1J(C,P) = 26.8$, Hz, $PHCH_2CMe_2$); 37.3 (*s*, Me_3C); 35.0 (*s*, Me_3C); 33.2 (*d*, $^4J(C,P) = 3.8$, $Me_3C-C(7)$); 32.1 (*s*, $Me_3C-C(5)$); 31.1 (*s*, $PHCH_2CMe_2$); 30.9 (*d*, $^4J(C,P) = 6.7$, $PHCH_2CMe_2$); 29.2 (*m*, Me_2CHP); 27.1–26.6 (*m*, Me_2CHP); 25.2–24.7 (*m*, PCH_2CH_2P); 24.2–17.5 (*m*, Me_2CHP). $^{31}P\{^1H\}$-NMR ((D_6)benzene, 25°): 92.3 (*ddd*, $^1J(P,Rh) = 180.8$, $^2J(P,P_{cis}) = 33.6$, $^2J(P,P_{cis}) = 27.0$, PCH_2CH_2P *trans* to Cl); 90.6 (*ddd*, $^2J(P,P_{trans}) = 363.0$, $^1J(P,Rh) = 147.1$, $^2J(P,P_{cis}) = 27.0$, PCH_2CH_2P *cis* to Cl); −25.0 (*ddd*, $^2J(P,P_{trans}) = 363.0$, $^1J(P,Rh) = 126.8$, $^2J(P,P_{cis}) = 33.6$, PH). Anal. calc. for $C_{32}H_{61}ClP_3Rh$: C 56.76, H 9.08; found: C 56.61, H 9.26.

A crystalline sample (0.14 × 0.14 × 0.09 mm) of **6** generated by this methodology proved suitable for single-crystal X-ray diffraction analysis.

*{μ-[5,7-Di(*tert*-butyl)-2,3-dihydro-3,3-dimethyl-1*H*-phosphindole-κ²*P*]}bis{(ethane-1,2-diyl)bis[diisopropylphosphine-κ*P*]}(μ-hydro)dirhodium* (**7**). A reaction vessel equipped with a PTFE valve was charged with a soln. of **3** (0.116 g, 0.180 mmol) in toluene (5 ml) and stored at 80° for 72 h. Upon cooling to r.t., the mixture was concentrated to *ca*. 3 ml, filtered through *Celite*®, and stored at −30° for 48 h, producing orange-red crystals of **7**·C_7H_8 (0.088 g, 89%). Anal. pure samples of **7** were obtained free of solvent by recrystallization of **7**·C_7H_8 from pentane. ^1H-NMR ((D_6)benzene, 25°): 7.41 (*m*, 1 arom. H); 7.18 (*m*, 1 arom. H); 2.70 (*m*, PCH_2CMe_2); 2.44 (*m*, 4 H, Me_2CHP); 2.17 (*m*, 2 H, Me_2CHP); 1.91 (*m*, 2 H, Me_2CHP); 1.70 (*s*, 6 H, PCH_2CMe_2); 1.55 (*s*, 1 ^{t}Bu); 1.43 (*m*, 9 H, Me_2CHP); 1.35 (*s*, 1 ^{t}Bu); 1.16–1.12 (*m*, 29 H, Me_2CHP, PCH_2CH_2P); 1.03 (*m*, 6 H, Me_2CHP); 0.92 (*m*, 6 H, Me_2CHP); 0.74 (*m*, 6 H, Me_2CHP); −7.80 (*m*, RhH). $^{13}C\{^1H\}$-NMR ((D_6)benzene, 25°): 154.5 (*m*, arom. C); 150.9 (*d*, $^2J(C,P) = 7.5$, arom. C); 148.6 (*m*, arom. C); 144.2 (*m*, arom. C); 122.9 (*d*, $^3J(C,P) = 7.0$, arom. CH); 117.7 (*d*, $^3J(C,P) = 6.8$, arom. CH); 44.4 (*d*, $^2J(C,P) = 4.9$, Hz, PCH_2CMe_2); 41.5 (*m*, PCH_2CMe_2); 36.0 (*s*, Me_3C); 34.9 (*s*, PCH_2CMe_2); 34.8 (*s*, Me_3C); 34.6 (*d*, $^4J(C,P) = 4.2$, $Me_3C-C(7)$); 31.6 (*s*, $Me_3C-C(5)$); 29.4 (*m*, Me_2CHP); 29.1 (*m*, Me_2CHP); 28.3 (*m*, Me_2CHP); 25.3 (*m*, Me_2CHP); 23.8 (*m*, PCH_2CH_2P); 23.2 (*m*, Me_2CHP); 22.4 (*m*, Me_2CHP); 22.0 (*m*, Me_2CHP); 20.9 (*m*, Me_2CHP); 20.0

(*m*, *Me*$_2$CHP); 19.7 (*m*, PCH$_2$*C*H$_2$P); 19.0 (*m*, *Me*$_2$CHP); 18.0 (*m*, *Me*$_2$CHP); 17.0 (*m*, *Me*$_2$CHP). ^{31}P{^{1}H}-NMR ((D$_6$)benzene, 25°): 113.3 (*m*, RhPRh); 90.1 (*m*, PCH$_2$CH$_2$*P cis* to H); 85.8 (*m*, *P*CH$_2$CH$_2$P *trans* to H). Anal. calc. for $C_{46}H_{93}P_5Rh_2$: C 54.87, H 9.31; found: C 54.68, H 9.40.

A crystalline sample (0.15 × 0.13 × 0.12 mm) of **7** · C_7H_8 proved suitable for single-crystal X-ray diffraction analysis.

*[2,4,6-Tri(*tert*-butyl)phenyl](D$_2$)phosphine* Mes*PD$_2$. This compound was prepared as described for Mes*PH$_2$ (**2**) [9], with the exception that LiAlD$_4$ (98 atom-%) was employed, and quenching of the reaction was carried out with D$_2$O in place of a 20% HCl soln. The resulting product was isolated as a *ca.* 85 : 15 mixture of Mes*PHD and Mes*PD$_2$. ^{31}P{^{1}H}-NMR ((D$_6$)benzene, 25°): −131.5 (*t*, ^1J(P,D) = 32.4, Mes*PHD); −132.6 (*quint.*, ^1J(P,D) = 32.4, Mes*PD$_2$).

X-Ray Crystallography[7]). Single-crystal X-ray-diffraction data for **6** and **7** · C_7H_8 were collected from samples mounted on a quartz fiber with *Paratone N* hydrocarbon oil. Data collection was carried out by means of graphite-monochromated MoK_α (λ 0.71069 Å) radiation with a *Siemens SMART* diffractometer, equipped with a *CCD* area detector. The preliminary orientation matrix and unit-cell parameters were determined by collecting 60 10-s frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected with ω scans of 0.3°, counted for a total of 20 s per frame. Frame data were integrated (*XY* spot spread = 1.60°; *Z* spot spread = 0.60°) and corrected for *Lorentz* and polarization effects with the program SAINT [23]. The program SADABS [24] was utilized for the scaling of diffraction data and the application of an empirical absorption correction based on redundant reflections. The structures were solved by direct methods procedure in the *Siemens* SHELXTL [25] program library, and refinement was carried out by the full-matrix least-squares method on F^2. Apart from the exceptions noted below, anisotropic thermal parameters were used for the non-H-atoms, and all C-bonded H-atoms were added at calculated positions and refined by means of a riding model with isotropic displacement parameters equal to 1.2 (1.5 for Me groups) times the equivalent isotropic displacement parameter of the attached C-atom. The H-atom bound to the P-atom in **6** was located in the difference map and refined with a thermal parameter equal to 1.2 times the equivalent isotropic displacement parameter of the attached P-atom. During the refinement of **7** · C_7H_8, alternative Rh-positions (Rh(1A) and Rh(2A), offset along the Rh(1)–Rh(2) vector) were identified and refined isotropically with a fixed thermal parameter. The occupancy of the two Rh_2 pairs was refined as a free variable (*ca.* 94 : 6). No other atomic positions associated with this minor disorder component were located. Although the heavy-atom core in **7** · C_7H_8 refined cleanly, significant disorder in the some of the ^{i}Pr and ^{t}Bu groups was encountered, and, thus, C(16), C(15A), C(16A), C(17A), C(27), C(27A), C(28), C(28A), C(30), and C(30A) were refined isotropically. The occupancy of two orientations of the ^{t}Bu Me groups (C(15), C(16), C(17); C(15A), C(16A), C(17A)) was refined as a free variable (*ca.* 67 : 33), whereas the disordered ^{i}Pr C-atom positions (C(27), C(27A); C(28), C(28A); C(30), C(30A)) were each fixed at 50% occupancy. H-Atoms were not added at calculated positions for C(15A), C(16A), C(17A), C(27A), C(28A), and C(30A). During the refinement of **7** · C_7H_8, an electron-density peak located in a reasonable position between Rh(1) and Rh(2) was assigned as the hydro ligand (H(1)) and not refined. No unusually close intermolecular contacts between the target molecule **7** and the toluene solvate were present. The final refined value of the absolute structure parameter (−0.02(5)) confirmed the configuration chosen.

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7) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-162112 (**6**) and CCDC-162113 (**7** · C_7H_8). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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