Base-Promoted Hydroalkylation Reactions of the η^5-C_5Me_5 Ligand Coordinated to Rhodium: Probing a Mechanism. New Compounds with the η^5-$C_5Me_4CF_3$ Ligand

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Dichloro(pentamethylcyclopentadienyl)rhodium(III) dimer, [{(η^5-C_5Me_5)$RhCl_2$}$_2$] (**1**), reacts with diphenylvinylphosphine to produce [(η^5-C_5Me_5)Rh{$CH_2CHP(C_6H_5)_2$}Cl_2] (**2**) and [(η^5-C_5Me_5)Rh{$CH_2CHP(C_6H_5)_2$}$_2$Cl]X (**3**, X = Cl^- (**a**), PF_6^- (**b**)). In acetonitrile, compound **1** undergoes a base-promoted hydroalkylation reaction with potassium *tert*-butoxide and diphenylvinylphosphine to produce [{η^5-C_5Me_3-1,3-[$CH_2CH_2CH_2P(C_6H_5)_2$]$_2$}RhCl]X (**4**, X = Cl^- (**a**), PF_6^- (**b**), BPh_4^- (**c**)) and [{η^5−C_5Me_3-1,2-[$CH_2CH_2CH_2P(C_6H_5)_2$]$_2$}RhCl]X (**5**, X = Cl^- (**a**), PF_6^- (**b**), BPh_4^- (**c**)). Compounds **4a**−**c** and **5a**−**c** contain chelating 1,3- and 1,2- bis-((diphenylphosphino)propyl)trimethylcyclopentadienide ligands. Compounds **2** and **3** are precursors on the pathway toward formation of **4a** and **5a**. Compound **1** reacts with allyldiphenylphosphine to produce [(η^5-C_5Me_5)Rh{$CH_2CHCH_2P(C_6H_5)_2$}Cl_2] (**6**) and [(η^5-C_5Me_5)Rh{$CH_2CHCH_2P(C_6H_5)_2$}$_2$Cl]X (**7**, X = Cl^- (**a**), PF_6^- (**b**)). In acetonitrile, compound **1** reacts with allyldiphenylphosphine in the presence of potassium *tert*-butoxide to produce a complex mixture of products that may contain hydroalkylation adducts. Dichloro-{(trifluoromethyl)tetramethylcyclopentadienyl}rhodium(III) dimer, [{(η^5-$C_5Me_4CF_3$)$RhCl_2$}$_2$] (**8**), reacts with diphenylvinylphosphine to produce [(η^5-$C_5Me_4CF_3$)Rh{$CH_2CHP(C_6H_5)_2$}Cl_2] (**9**), however the bis(phosphine) analog cannot be isolated or characterized. In refluxing ethanol, compound **8** reacts with diphenylvinylphosphine in the absence of potassium *tert*-butoxide to undergo hydroalkylation accompanied by conversion of the CF_3 group into a carboethoxy functionality producing [{η^5-$C_5(CO_2Et)Me_3$-2-[$CH_2CH_2CH_2P(C_6H_5)_2$]}$RhCl_2$] (**10**). Complexes **3b**, **7b**, and **10** were characterized by single-crystal X-ray crystallography.

Introduction

Cyclopentadienyl (η^5-C_5H_5) and substituted cyclopentadienyl ligands, especially pentamethylcyclopentadienyl (η^5-C_5Me_5), are ubiquitous in organometallic chemistry as stabilizing ligands for transition metals. Recent synthetic endeavors[1−6] have been directed at functionalizing η^5-C_5Me_5 ligands to make η^5-C_5Me_4R, where the R groups are pendant arms that may also serve as donors toward a metal. The impetus is to design "hybrid" ligands[7] that may enhance selectivity in catalytic systems[2,7] or stabilize reactive intermediates.[3,4b] η^5-C_5Me_5 ligands may be functionalized before or after their coordination to a transition metal,[1a] but the latter method is sometimes more desirable. Examples of both methods have been published[1−6] that culminate in a wide variety of pendant R groups including amines (achiral[1a,b,3] and chiral[2]), alkanes,[6] alkenes,[1e,g,4a−c] arenes,[1d,e,g,j] ethers,[1a,5] halides,[1a−c,f] and many others.[1a−i] Research dating back to the early seventies established that methyl groups of a metal-coordinated η^5-C_5Me_5 ligand can be activated thermally[8g] or by the action of strong bases.[1i] Since that time, a great deal of work demonstrates that a variety of transition metals including Rh,[1d,h,i] Ir,[1c,e,g,i,10] Ru,[1a,b,f,j] Fe,[9] Pd,[11] Ti,[8a,e,f] Zr,[8b,d] W,[12] and other metals[8c] activate η^5-C_5Me_5 ligands. In spite of the aforementioned work, there are only a few

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(1) (a) Fan, L.; Turner, M. L.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *Organometallics* **1995**, *14*, 676. (b) Fan, L.; Turner, M. L.; Hursthouse, M. B.; Abdul Malik, K. M.; Gusev, O. V.; Maitlis, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 385. (c) Miguel-Garcia, J. A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1992**, 131. (d) Gusev, O. V.; Rubezhov, A. Z.; Miguel-Garcia, J. A.; Miatlis, P. M. *Mendeleev Commun.* **1991**, 21. (e) Miguel-Garcia, J. A.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Organomet. Chem.* **1991**, *413*, 427. (f) Wei, C.; Aigbirhio, F.; Adams, H.; Bailey, N. A.; Hempstead, P. D.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1991**, 883. (g) Miguel-Garcia, J. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1990**, 1472. (h) Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2335. (i) Kang, J. W.; Maitlis, P. M. *J. Organomet. Chem.* **1971**, 30, 127. (j) O'Leary, S. R.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1995**, 2019.

(2) Adams, H.; Bailey, N. A.; Colley, M.; Schofield, P. A.; White, C. *J. Chem. Soc., Dalton Trans.* **1994**, 1445.

(3) Jutzi, P.; Kristen, M. O.; Dahlhaus, J.; Neumann, B.; Stammler, H.-G. *Organometallics* **1993**, *12*, 2980.

(4) (a) Zimmermann, K. H.; Pilato, R. S.; Horváth, I. T.; Okuda, J. *Organometallics* **1992**, *11*, 3935. (b) Okuda, J.; Zimmermann, K. H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 430. (c) Okuda, J.; Zimmermann, K. H. *J. Organomet. Chem.* **1988**, *344*, C1.

(5) Siemeling, U. *J. Chem. Soc., Chem. Commun.* **1992**, 1335.

(6) Gloaguen, B.; Astruc, D. *J. Am. Chem. Soc.* **1990**, *112*, 4607.

(7) (a) Lindner, E.; Bader, A. *Coord. Chem. Rev.* **1991**, *108*, 27. (b) Podlahová, J.; Kratochvíl, B.; Langer, V. *Inorg. Chem.* **1981**, *20*, 2160.

(8) (a) Luinstra, G. A.; Teuben, J. H. *J. Am. Chem. Soc.* **1992**, *114*, 3361. (b) Horton, A. D. *Organometallics* **1992**, *11*, 3271. (c) Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3246. (d) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (e) Pattiasina, J. W.; Hissink, C. E.; de Boer, J. L.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 7758. (f) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (g) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(9) Weber, L.; Kaminski, O.; Boese, R.; Bläser, D. *Organometallics* **1995**, *14*, 820.

(10) Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862.

(11) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H.-J.; Krüger, C. *Organometallics* **1983**, *2*, 1369.

(12) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* **1985**, 945.

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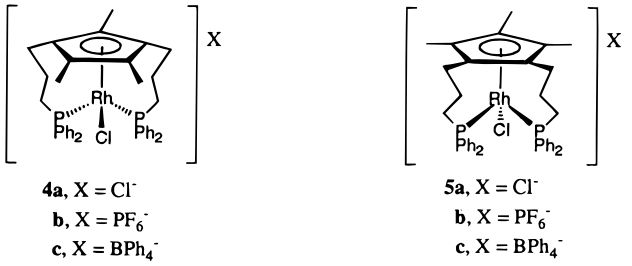
Chart 1. Compounds 4a−c and 5a−c



4a, X = Cl^-
b, X = PF_6^-
c, X = BPh_4^-

5a, X = Cl^-
b, X = PF_6^-
c, X = BPh_4^-

examples of η^5-C_5Me_4R ligands containing pendant phosphines[1a,1e,9,13,14] and a small number of difunctionalized (η^5-$C_5Me_3R_2$) ligands.[13,14] In this paper we describe the synthesis and characterization of novel rhodium complexes containing chelating (phosphinopropyl)cyclopentadienide ligands of the type η^5-$C_5Me_3R_2$, which are formed by base-promoted intramolecular hydroalkyl addition,[15] and the intermediates that precede their formation. Such ligands may be useful in the same applications described above. A preliminary account of this work has appeared.[13]

First, the syntheses of two intermediates that precede hydroalkylation are described. Next, the conditions that promote hydroalkylation between diphenylvinylphosphine and [{(η^5-C_5Me_5)$RhCl_2$}$_2$] (**1**) to form the chelating (phosphinopropyl)cyclopentadienide ligands are described. Following that are attempts to produce new chelating ligands with allyldiphenylphosphine. Finally, the reactions of the compound [{(η^5-$C_5Me_4CF_3$)$RhCl_2$}$_2$] (**8**), (an analog of compound **1**) with diphenylvinylphosphine were investigated to probe the effects of an electron-withdrawing group on hydroalkylation.

Results and Discussion

We recently reported[13] that refluxing a mixture of [{(η^5-C_5Me_5)$RhCl_2$}$_2$] (**1**) and diphenylvinylphosphine (DPVP) in benzene in the presence of azobis(isobutyronitrile) (AIBN) led to the formation of two novel rhodium complexes, [{η^5-C_5Me_3-1,3-[$CH_2CH_2CH_2P(C_6H_5)_2$]$_2$}-RhCl]X (**4**, X = Cl^- (**a**), PF_6^- (**b**), BPh_4^- (**c**)) and [{η^5−C_5Me_3-1,2-[$CH_2CH_2CH_2P(C_6H_5)_2$]$_2$}RhCl]X (**5**, X = Cl^- (**a**), PF_6^- (**b**), BPh_4^- (**c**)). Schematic representations of **4a**−**c** and **5a**−**c** are shown in Chart 1. The novelty of this reaction is the unusual reaction between the vinyl moiety on the coordinated phosphorus atom and the methyl groups of the η^5-C_5Me_5 ligand. The terminal vinylic carbon atom forms a new C−C bond to a methyl group with concomitant C−H bond cleavage and formation of a new C−H bond on the carbon α to the phosphorus atom. Formally, the methyl groups of the η^5-C_5Me_5 have undergone a hydroalkyl addition (or hydroalkylation) to the vinylphosphine ligands.[15] To the best of our knowledge, this is the only example of such an addition in these types of systems.

X-ray crystallographic analyses established the structures of **4b** and **5c**.[13] Figures 1 and 2 show the structural drawings of the cations of **4b** and **5c**, respectively. For each compound, the analysis revealed a distorted octahedral geometry at rhodium with a coordinated methyl-substituted cyclopentadienyl ring, two diphenylphosphine moieties, and one chloride. Each rhodium-bound diphenyl phosphine group is connected to the cyclopentadienyl ring *via* three methylene carbons. A similar linkage is observed for an analogous phosphine in the reported[17] ruthenium complex [{η^5-$C_5H_4CH_2CH_2PPh_2$}-$Ru(PPh_3)Cl$]. The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data for **4b** and **5c** are in accord with both structures (see Experimental Section).

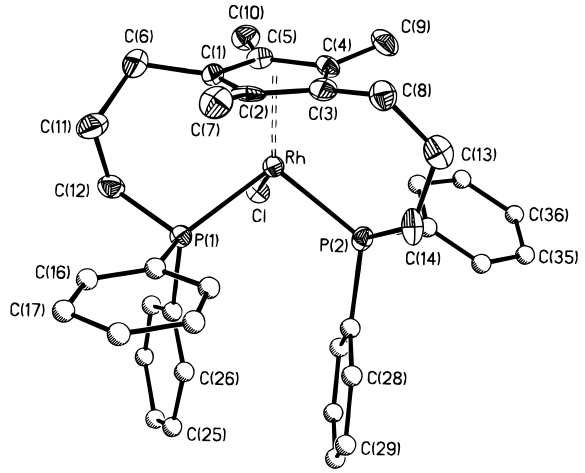


Figure 1. Structural drawing of the cation of [{η^5-C_5Me_3-1,3-[$CH_2CH_2CH_2P(C_6H_5)_2$]$_2$}RhCl]PF_6 (**4b**), showing the atom-numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.[13]

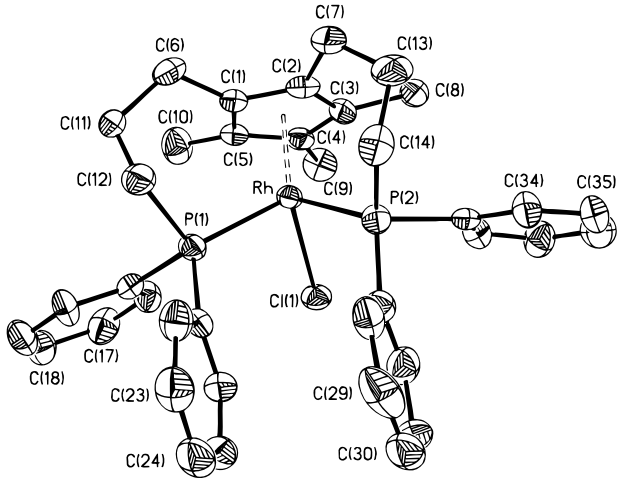
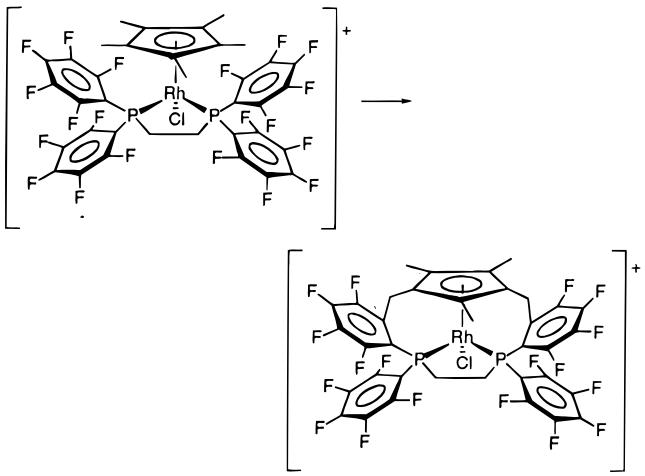


Figure 2. Structural drawing of the cation of [{η^5-C_5Me_3-1,2-[$CH_2CH_2CH_2P(C_6H_5)_2$]$_2$}RhCl]BPh_4 (**5c**), showing the atom-numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.[13]

The structure of a similar molecule, [{η^5-C_5Me_3-[$CH_2C_6F_4P(C_6F_5)CH_2$]$_2$-1,3}RhCl]BF_4, has been reported[14] recently; however in that system the 1,3 methyl groups formed new C−C bonds with a bis(bis(pentaflourophenyl)phosphino)ethane (dfppe) ligand (Scheme 1). The authors suggest the mechanism of its formation involves C−F bond cleavage and elimination of HF to make a chelating aryldiphosphine. The geometric constraints of the dfppe ligand probably prevent the 1,2 isomer from forming in this system.

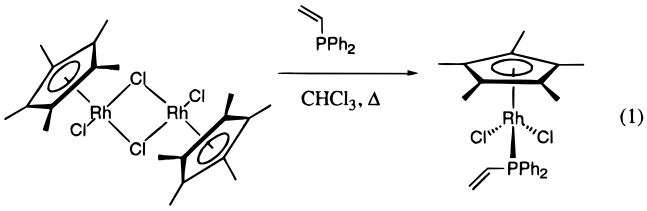
(13) Barthel-Rosa, L. P.; Catalano, V. J.; Nelson, J. H. *J. Chem. Soc., Chem. Commun.* **1995**, 1629.
(14) Atherton, M. J.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karaçar, A.; Russell, D. R.; Saunders, G. C. *J. Chem. Soc., Chem. Commun.* **1995**, 191.
(15) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1992; p 790 ff.
(16) Hoard, D. W.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 612.
(17) Slawin, A. M. Z.; Williams, D. J.; Crosby, J.; Ramsden, J. A.; White, C. *J. Chem. Soc., Dalton Trans.* **1988**, 2491.

Scheme 1



After compounds **4b** and **5c** were reported, we discovered that these compounds are also formed in the presence of potassium *tert*-butoxide (in acetonitrile) and all subsequent investigations were run under these conditions. In all investigations regardless of conditions, two compounds were observed (**2**, **3**; *vide infra*) in the reaction mixtures before addition of potassium *tert*-butoxide. These precursors were independently synthesized and characterized to better understand the mechanism leading to the formation of compounds **4** and **5**.

1.0. Reactions of [{(η^5-C_5Me_5)$RhCl_2$}$_2$] (1) with Diphenylvinylphosphine (DPVP). When **1** was refluxed in chloroform with 2 equiv of DPVP, the monosubstituted rhodium complex [(η^5-C_5Me_5)Rh{$CH_2CHP(C_6H_5)_2$}Cl_2] (**2**) formed (eq 1). In chloroform-*d*, the

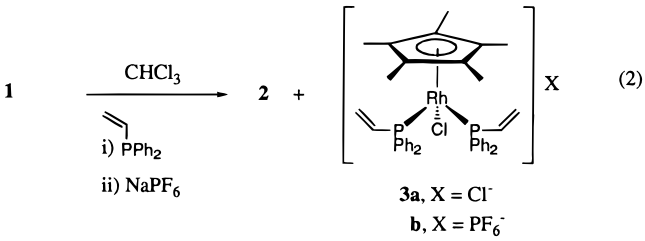


(1)

1 **2**

$^{31}P\{^1H\}$ NMR spectrum for **2** shows a doublet at δ = 27.4 (J_{Rh-P} = 140.7 Hz) corresponding to the coordinated DPVP. The ^1H NMR spectrum (see Experimental Section for complete assignments) shows three multiplets in the olefinic region consisting of a doublet of double doublets at δ = 6.9 (J_{P-H} = 25, J_{H-H} = 18.7, J_{H-H} = 11 Hz), a doublet of doublets at δ = 5.9 (J_{P-H} = 39, J_{H-H} = 11 Hz), and an apparent triplet at δ = 5.4 ppm (J_{P-H} = J_{H-H} = 18.7 Hz) for the vinyl protons. The aliphatic region shows a doublet at δ = 1.41 (J_{P-H} = 3.4 Hz) for the η^5-C_5Me_5 ligand. The integrated peak ratio between the vinyl protons and the η^5-C_5Me_5 ligand is 1:5. The spectroscopic data confirm two points: (1) One DPVP had coordinated to rhodium. (2) The vinyl group had not undergone a hydroalkylation with the η^5-C_5Me_5 ligand.

When **1** was stirred at room temperature with 4.5 equiv of DPVP in chloroform, the disubstituted rhodium complex [(η^5-C_5Me_5)Rh{$CH_2CHP(C_6H_5)_2$}$_2$Cl]Cl (**3a**) formed along with compound **2**. The ratio of **2** to **3a** typically is 5:1. The ratio of **2** to **3a** changes as a function of solvent polarity; less polar solvents favor the formation of **2**, while polar solvents increase the concentration of **3a**. Following a mixing period of 1 to 2 h, a halide scavenger is necessary to drive the substitution to completion (eq 2). For example, a methanolic solution



(2)

3a, X = Cl^-
b, X = PF_6^-

of $NaPF_6$ was used to make the salt **3b**. In chloroform, the $^{31}P\{^1H\}$ NMR spectrum of **3a** shows a doublet at δ = 22.0 (J_{Rh-P} = 139Hz), while the spectrum of **3b** shows a doublet at δ = 21.9 (J_{Rh-P} = 134 Hz). The resonance for **3b** is shifted upfield from that of **2**, which is consistent with **3b** having an overall positive charge. The ^1H NMR spectrum for **3b** in the olefinic region is more complicated compared to the spectrum of **2** because of second-order effects arising from coupling to both phosphorus nuclei. Three broad resonances are apparent at δ = 6.0, 5.7, and 5.3 ppm for the vinyl protons. The aliphatic region shows a triplet at δ = 1.4 (J_{P-H} = 3.5 Hz) for the η^5-C_5Me_5 ligand. The integrated peak ratio between the vinyl protons and the η^5-C_5Me_5 ligand is 1:2.5. An X-ray diffraction study also confirmed the structure of **3b**.

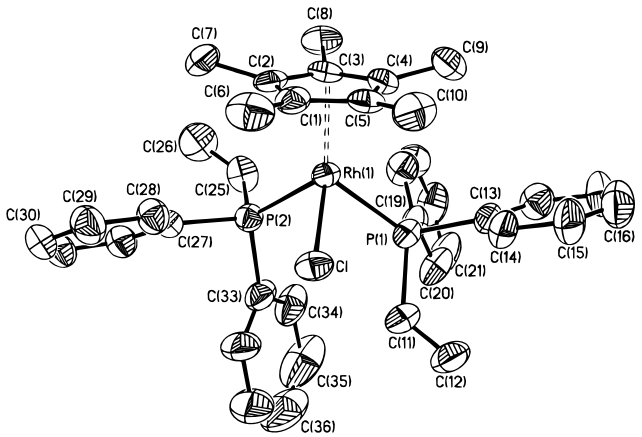


Figure 3. Structural drawing of the cation of [(η^5-C_5Me_5)Rh{$CH_2CHP(C_6H_5)_2$}$_2$Cl]PF_6 (**3b**), showing the atom-numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Figure 3 shows the structural drawing of the cation of **3b**. Selective bond distances and angles are listed in Table 1. Crystallographic data and details of structure determination and refinement are given in Table 4. The analysis revealed a distorted octahedral coordination geometry at rhodium with one η^5-C_5Me_5 ligand, two DPVP ligands bound through phosphorus, and one chloride. There are no unusual interionic contacts. The average Rh−P bond distance in **3b** is 2.345(2) Å. The calculated distance between rhodium and the centroid of the of η^5-C_5Me_5 ligand is 1.887 Å, which is longer than the distances of 1.875 Å in **4b**, 1.856 Å in **5c**,[13] and 1.837 Å in the dfppe[14] compound. The average P−C(vinyl) bond distance is 1.808(8) Å, and the average C−C(vinyl)

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for $[(\eta^5\text{-}C_5Me_5)Rh\{CH_2CHP(C_6H_5)_2\}_2Cl]PF_6$ (3b)

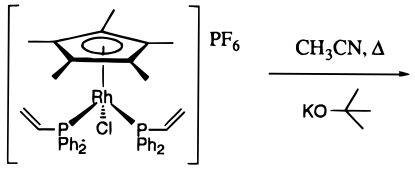
Bond Distances			
Rh−P(1)	2.349(2)	P(1)−C(11)	1.803(8)
Rh−P(2)	2.340(2)	P(2)−C(25)	1.812(8)
Rh−Cl	2.376(2)	C(11)−C(12)	1.304(10)
Rh−C(1−5)[a]	1.887	C(25)−C(26)	1.306(10)
Bond Angles			
P(1)−Rh−P(2)	93.96(8)	Rh−P(2)−C(25)	112.0(3)
Cl−Rh−P(1)	86.05(8)	P(1)−C(11)−C(12)	125.8(8)
Cl−Rh−P(2)	90.33(8)	P(2)−C(25)−C(26)	128.4(8)
Rh−P(1)−C(11)	115.7(3)		

[a] C(1−5) denotes the centroid of the cyclopentadienyl ring.

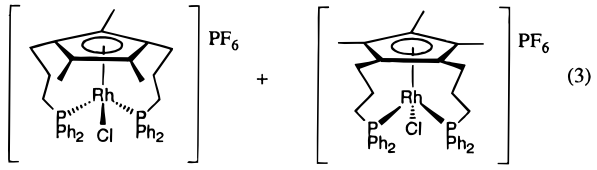
distance is 1.305(10) Å, which is typical for a C−C double bond distance of 1.3 Å. The crystallographic and spectroscopic data for **3b** confirmed that the vinyl groups had not undergone hydroalkylation and two DPVP ligands were coordinated to rhodium.

1.1. Conversion of 3b into 4b and 5b. The reaction of **3b** in the absence of potassium *tert*-butoxide was investigated. Compound **3b** was refluxed in acetonitrile for a total time of 18 h. The course of the reaction was monitored at regular intervals using ^{1}H NMR spectroscopy. Throughout the duration of the reaction, the vinyl peaks *did not* transform into peaks in the aliphatic region, which would indicate hydroalkylation. After 18 h, the $^{31}P\{^1H\}$ NMR spectrum of the mixture was measured. The spectrum showed **3b**, a small amount of **2**, diphenylvinylphosphine oxide, unidentified singlets at δ = 51.3 and 13.6 ppm, and a broad, featureless hump around 30 ppm. These results indicate that compound **3b** is not converted into **4b** and/or **5b** in the absence of potassium *tert*-butoxide, but some decomposition of **3b** occurs.

The reaction of **3b** in the presence of potassium *tert*-butoxide was investigated. In acetonitrile, compound **3b** was refluxed in the presence of 1 equiv (per mole of rhodium) of potassium *tert*-butoxide. After 30 min, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction solution showed doublets at δ = 17.9 (J_{Rh-P} = 133 Hz) and δ = 21.9 (J_{Rh-P} = 132 Hz) and singlets at δ = 51.3, 23.4, and 13.5 ppm. In addition, two multiplets which appeared to be doublets of doublets were present at δ = 31.8 (J_{P-P} = 36.3, J_{Rh-P} = 166.8 Hz) and δ = −6.7 ppm (J_{P-P} = 36.3, J_{Rh-P} = 101.0 Hz). These two multiplets are not present when the reaction is complete and may represent an intermediate compound where one of the two DPVP ligands has undergone hydroalkylation (*vide infra*). Also present in the spectrum were broad featureless bumps in the baseline around 30 ppm. The doublet at δ = 17.9 ppm indicates the presence of compound **5b**, the 1,2 hydroalkylation product. Compound **3b** cannot be distinguished from **4b** (the 1,3 hydroalkylation product) using $^{31}P\{^1H\}$ NMR spectroscopy because their chemical shifts are virtually identical. Compound **3b** shows a doublet at δ = 21.9 (J_{Rh-P} = 134 Hz), while that of **4b** is a doublet at δ = 22.0 (J_{Rh-P} = 135 Hz). However, **3b** and **4b** are easily distinguished by ^{1}H NMR spectroscopy. The reaction mixture was refluxed for 48 h. Following workup and isolation of the products by column chromatography and fractional crystallization, ^{1}H and $^{31}P\{^1H\}$ NMR analyses revealed that compounds **4b** and **5b** formed in an approximate 1:1 ratio (eq 3). These results, coupled with our previous results,[13] establish that a base or a radical initiator is necessary to facilitate hydroalkylation.



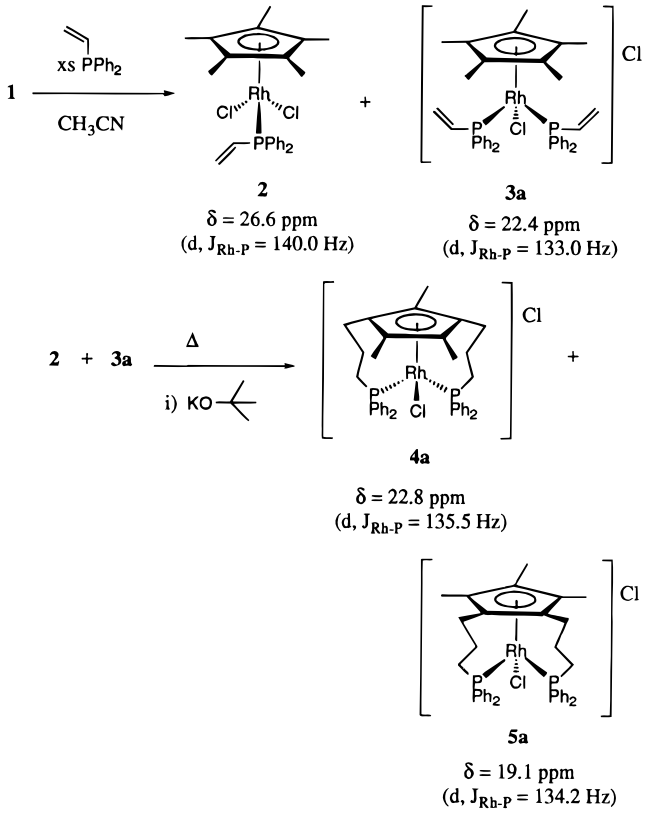
3b



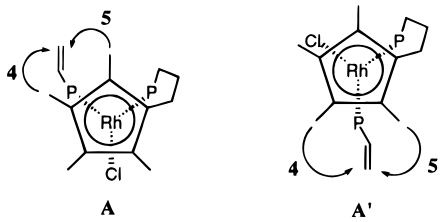
4b **5b** (3)

1.2. Conversion of 1 into 4 and 5. The reaction of **1** with DPVP and potassium *tert*-butoxide was investigated. When **1** was mixed with 4.5 equiv of DPVP in acetonitrile (before addition of the base), compounds **2** and **3a** formed in approximately a 1:1 ratio (by $^{31}P\{^1H\}$ NMR spectroscopy). One equiv of potassium *tert*-butoxide (per mole of dimer) was added to the mixture, which was then refluxed for 48 h. The use of excess base has been avoided since it may promote excessive decomposition of **3a**. The reaction mixture turned from a clear red to opaque brown upon addition of the base, and then gradually back to dark red. The workup included addition of $NaPF_6$, column chromatography and fractional crystallization to give **4b** and **5b**. The results discussed above suggest a stepwise mechanism for the formation of **4a** and **5a** (Scheme 2). Compound **1** first reacts with DPVP to form a mixture of **2** and **3a**. Upon addition of the base, compound **3a** is converted

Scheme 2. Proposed Mechanism



Scheme 3. Schematic Representation of the Proposed Diastereomeric Intermediates (A/A′) for the Formation of Compounds 4 and 5 with Phenyl Groups Omitted for Clarity



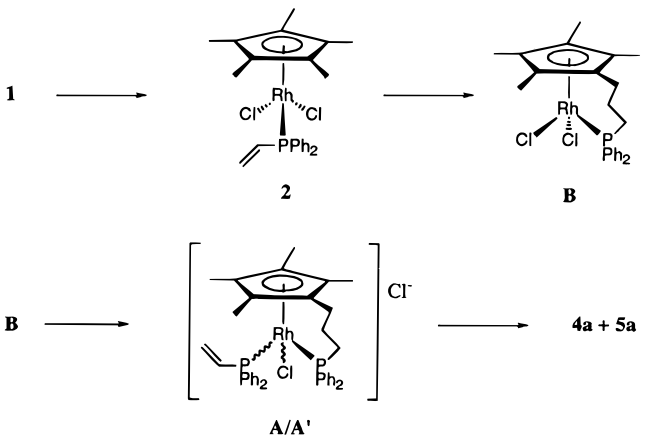
A **A'**

into a mixture of **4a** and **5a**. As compound **3a** gets consumed, compound **2** is converted into **3a**.

As mentioned in section 1.1, two resonances were spectroscopically observed that may have represented an intermediate species between **3a**, **4a**, and **5a**. Scheme 3 shows a schematic representation of a pair of diastereomeric intermediates (**A**/**A′**) that may be immediate precursors to compounds **4a** and **5a.** It is unlikely that both DPVP ligands would simultaneously undergo hydroalkylation since that would require a tertiary event. Therefore, it is reasonable to propose that one DPVP ligand undergoes hydroalkylation, followed by a second addition. If this occurs, the first hydroalkylation would produce structures **A** and **A′**. Compounds **4a** and **5a** are obtainable from both intermediates. Theoretically, compounds **4a** and **5a** should be produced in a statistical 1:1 ratio, which is not altered by the addition of a halide scavenger. Experimentally, the ratio of **4b**,**c** to **5b**,**c** is determined after chromatography and fractional crystallization; therefore mechanical losses may influence the ratios. The intermediates proposed in Scheme 3 have not been isolated but may have been observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture described in section 1.1.

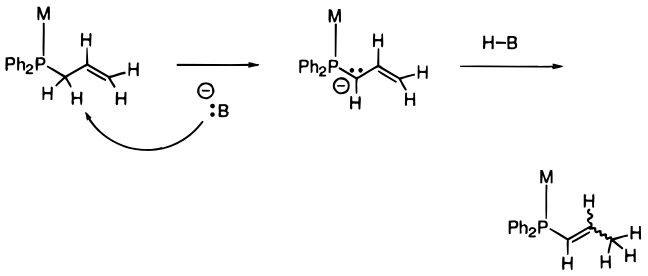
Besides the conversion of **3a** into **A**/**A′**, there is another reasonable pathway for the formation of **A**/**A′** that must be considered. An alternative mechanism toward the formation of **4a** and **5a** is shown in Scheme 4. Compound **2** could be hydroalkylated into structure **B**, followed by coordination of a second DPVP to give the intermediates **A**/**A′**, which then proceed onto **4a** and **5a**. It is entirely possible that both mechanisms are operating simultaneously; however, the observed data suggest that proceeding through compound **3a** is the more likely pathway. At present, compounds **A**/**A′** and **B** have not been isolated; however, the possibility of this alternative mechanism warrants further investigations.

Scheme 4. Alternative Mechanism



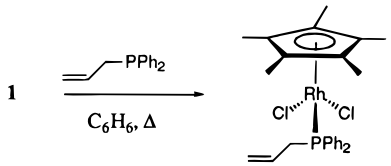
2 **B** **A/A'**

Scheme 5. Possible Rearrangement of ADPP



2.0. Reactions of [{(η^5-C_5Me_5)$RhCl_2$}$_2$] (1) with Allyldiphenylphosphine (ADPP). Another phosphine ligand that had the potential to react with **1** by way of hydroalkylation was allyldiphenylphosphine (ADPP); therefore the reaction between **1** and ADPP was investigated. This system is complicated by the possibility of base-promoted rearrangement of the allyl[18] moiety to a propenyl-phosphine moiety, which may then undergo hydroalkylation (Scheme 5). As a result, a multitude of potential products may form in this system.

When **1** was refluxed in benzene with 2 equiv of ADPP, the monosubstituted rhodium complex [(η^5-C_5Me_5)$Rh\{CH_2CHCH_2P(C_6H_5)_2\}Cl_2$] (**6**) formed (eq 4). The

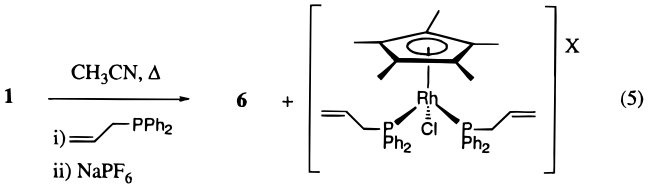


(4)

6

$^{31}P\{^1H\}$ NMR spectrum for **6** shows a doublet at δ = 31.0 ppm (J_{Rh-P} = 142.8 Hz) corresponding to the coordinated ADPP. The ^1H NMR spectrum shows three multiplets at δ = 5.43, 4.83, and 4.66 ppm for the olefinic protons and one at δ = 3.61 ppm for the methylene protons of the ADPP ligand. The η^5-C_5Me_5 resonance occurs as a doublet at δ = 1.35 ppm (J_{P-H} = 3.5 Hz). As with compound **2**, the spectroscopic data for **6** confirms monocoordination without hydroalkylation.

When **1** was reacted with excess ADPP in refluxing acetonitrile for 2 h, the disubstituted rhodium complex [(η^5-C_5Me_5)$Rh\{CH_2CHCH_2P(C_6H_5)_2\}_2Cl$]Cl (**7a**) formed along with compound **6**. A methanolic solution of $NaPF_6$ was added to drive the reaction to completion and form the salt **7b** (eq 5). The $^{31}P\{^1H\}$ NMR spectrum of **7a** in



(5)

7a, X = Cl^-
b, X = PF_6^-

acetonitrile shows a doublet at δ = 21.8 ppm (J_{Rh-P} = 136.4 Hz), while the spectrum of **7b** in chloroform-*d*

(18) Horner, L.; Ertel, I.; Ruprecht, H. D.; Belovsky, O. *Chem. Ber.* **1970**, *103*, 1582.
(19) Rigby, W.; McCleverty, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 382.

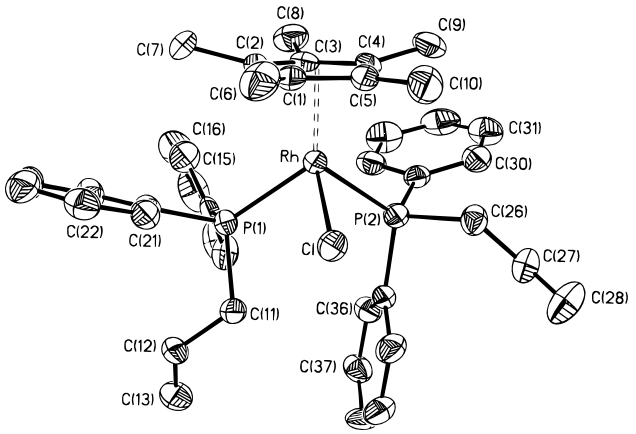


Figure 4. Structural drawing of the cation of $[(\eta^5\text{-}C_5Me_5)Rh\{CH_2CHCH_2P(C_6H_5)_2\}_2Cl]PF_6$ (**7b**), showing the atom-numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[(\eta^5\text{-}C_5Me_5)Rh\{CH_2CHCH_2P(C_6H_5)_2\}_2Cl]PF_6$ (7b)

	Bond Distances		
Rh−P(1)	2.363(2)	P(2)−C(26)	1.838(7)
Rh−P(2)	2.351(2)	C(11)−C(12)	1.497(9)
Rh−Cl	2.402(2)	C(26)−C(27)	1.516(10)
Rh−C(1−5)[a]	1.874	C(12)−C(13)	1.294(10)
P(1)−C(11)	1.838(7)	C(27)−C(28)	1.256(10)
	Bond Angles		
P(1)−Rh−P(2)	97.60(8)	P(1)−C(11)−C(12)	117.3(5)
Cl−Rh−P(1)	90.52(7)	P(2)−C(26)−C(27)	117.8(6)
Cl−Rh−P(2)	86.98(7)	C(11)−C(12)−C(13)	125.1(8)
Rh−P(1)−C(11)	113.5(2)	C(26)−C(27)−C(28)	125.6(8)
Rh−P(2)−C(26)	109.0(2)		

[a] C(1−5) denotes the centroid of the cyclopentadienyl ring.

shows a doublet at $\delta = 20.9$ ppm ($J_{Rh-P} = 135.2$ Hz). The upfield shift of the resonance for **7b** compared to that of **6** is consistent with **7b** having an overall positive charge. The ^1H NMR spectrum shows significant line broadening for the allyl protons but the aliphatic region shows a triplet at $\delta = 1.27$ ppm ($J_{P-H} = 3.7$ Hz) for the η^5-C_5Me_5 ligand. The integrated peak ratio between the vinyl and methylene ADPP resonances and the η^5-C_5Me_5 methyl resonance is 1:1.5. An X-ray diffraction study of **7b** also confirmed its structure.

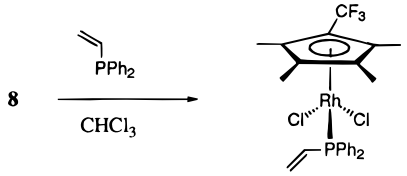
Figure 4 shows the structural drawing of the cation of **7b**. Selected bond distances and angles are listed in Table 2. Crystallographic data and details of structure determination and refinement are given in Table 4. The analysis revealed a distorted octahedral coordination at rhodium with one η^5-C_5Me_5 ligand, two ADPP ligands bound through phosphorus, and one chloride. There are no unusual interionic contacts. The average Rh−P bond distance in **7b**, 2.357(2) Å, is not significantly different from the average Rh−P bond distance of 2.345(2) Å in **3b**. The calculated distance of 1.874 Å from rhodium to the centroid of the η^5-C_5Me_5 ligand is similar to the distance of 1.887 Å in **3b**. The C−C double bonds in **7b**, C(12)−C(13) and C(27)−C(28), have distances of 1.294(10) and 1.256(10) Å, respectively, which are typical for a C−C double-bond distance of about 1.3 Å. As with **3b**, the spectroscopic and crystallographic data for **7b** confirmed disubstitution of ADPP without hydroalkylation.

2.1. Reactions of 1 and 7b. The reaction of **7b** in the presence and absence of potassium *tert*-butoxide was investigated. Using $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, the experiments showed that **7b** decomposed to **6**, ADPP oxide, and other unidentified compounds depending on the conditions. The other unidentified compounds may be rearranged ADPP on rhodium or hydroalkylation products, but the evidence remains inconclusive. The experiments show that **7b** is susceptible to rearrangements and decomposition in both the presence and absence of base.

The reaction of **1** with ADPP and potassium *tert*-butoxide was investigated and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. When **1** was mixed with excess ADPP in acetonitrile, compounds **6** and **7a** formed in a 1.7:1 ratio before any base was added. One mole equiv of potassium *tert*-butoxide (per mole of dimer) was added to the mixture, which was then refluxed for 48 h. The $^{31}P\{^1H\}$ NMR spectrum showed a complex mixture of compounds exhibited by resonances at $\delta = 70.0$, 63.9, 43.8, 25.2, 21.3 (d, $J_{Rh-P} = 134$Hz), and 16.6 ppm. The resonances at $\delta = 70.0$ and 43.8 ppm appear to be doublets, while those at $\delta = 63.9$, 25.2, and $\delta = 16.6$ ppm appear to be doublets of doublets (but may also be groups of doublets). Also visible were the characteristic resonances for **6** and ADPP oxide. The doublet at $\delta = 21.3$ ppm may represent the disubstituted hydroalkylation product or compound **7a**. As stated earlier, the chemical shift difference between **3b** and **4b** is approximately 0.2−0.4 ppm; therefore, it is reasonable to suggest that the same may be true for **7a** and its hydroalkylated isomer. Identical results were obtained when *tert*-butyl alcohol was used as the solvent. Unfortunately, chromatography and fractional crystallization have failed to produce any pure products from these mixtures. The reaction of **1** with ADPP in the presence of base is clearly more complicated than those with the DPVP ligand, and the results are inconclusive toward hydroalkylation.

3.0. Reactions of $[\{(\eta^5\text{-}C_5Me_4CF_3)RhCl_2\}_2]$ (8) with DPVP. The recently synthesized[20ab] (trifluoromethyl)tetramethylcyclopentadienyl ligand (η^5-$C_5Me_4CF_3$) exhibits electronic properties equivalent to those of η^5-C_5H_5 but retains the steric equivalence of η^5-C_5Me_5.[20b] Derivatives of η^5-$C_5Me_4CF_3$ containing pendant arms would be interesting analogs of compounds **4** and **5**. The reaction between **8** and DPVP was investigated in order to probe the effects of the electronic withdrawing properties on hydroalkylation. The CF_3 group has the potential to increase the selectivity of the "1,3-isomer" over the "1,2-isomer" because of the increased acidity of the methyl hydrogens.

When **8** was stirred with 2 equiv of DPVP in chloroform, the monosubstituted rhodium complex $[(\eta^5\text{-}C_5Me_4CF_3)Rh\{CH_2CHP(C_6H_5)_2\}Cl_2]$ (**9**) formed (eq 6). The



(6)

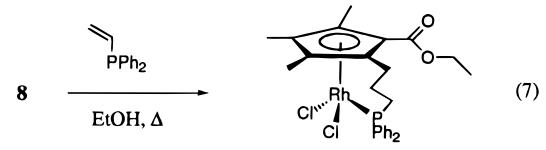
9

(20) (a) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R., Jr. *Inorg. Synth.* in press. (b) Gassman, P. G.; Mickelson, J. W.; Sowa, J. R., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6942.

$^{31}P\{^1H\}$ NMR spectrum in chloroform-*d* for **9** shows a doublet at $\delta = 28.4$ ppm ($J_{Rh-P} = 134.5$ Hz) corresponding to the coordinated DPVP. The ^1H NMR spectrum of **9** in the olefinic region shows multiplets at $\delta = 6.92$, 5.99, and 5.41 ppm corresponding to the vinyl protons. The aliphatic region shows two doublets at $\delta = 1.64$ ($J_{P-H} = 3.9$ Hz) and $\delta = 1.53$ ppm ($J_{P-H} = 2.9$ Hz) corresponding to the two sets of methyl groups on the η^5-$C_5Me_4CF_3$ ligand. The integrated ratio between the vinyl proton and the η^5-$C_5Me_4CF_3$ methyl resonances is 1:2:2. The spectroscopic data confirm monocoordination of DPVP without hydroalkylation.

In an attempt to synthesize a bis(phosphine) complex with the η^5-$C_5Me_4CF_3$ ligand, compound **8** was reacted with 4 equiv (or greater) of DPVP under a variety of conditions. In the $^{31}P\{^1H\}$ NMR spectra of all mixtures, small amounts of a compound were observed at $\delta_{av} = 21$ ppm ($J_{Rh-P} = 132$ Hz), which may have represented a bis(phosphine) compound. Unfortunately, this compound remains inseparable from the crude reaction mixtures. Several different solvents were used including methylene chloride, acetone, acetonitrile, and chloroform. A number of different halide scavengers were also used including $AgBF_4$, $NaPF_6$, NH_4PF_6, and $AgNO_3$. Inseparable mixtures of products typically formed after the addition of a halide scavenger.

3.1. Reaction of 8 with DPVP in Ethanol. In refluxing ethanol, compound **8** was allowed to react with 2 equiv of DPVP in the absence of potassium *tert*-butoxide resulting in the formation of the monosubstituted hydroalkylated product [{η^5-$C_5(CO_2Et)Me_3$-2-[$CH_2CH_2CH_2P(C_6H_5)_2$]}$RhCl_2$] (**10**) (eq 7). Presumably, the



(7)

10

enhanced acidity of the methyl hydrogens adjacent to the CF_3 group allows hydroalkylation to occur in the absence of potassium *tert*-butoxide. In addition to hydroalkylation of DPVP, the CF_3 group was defluorinated and converted to an ethyl ester.[21] In chloroform-*d*, the $^{31}P\{^1H\}$ NMR spectrum shows a doublet at $\delta = 30.3$ ppm ($J_{Rh-P} = 135.9$ Hz) corresponding to the hydroalkylated diphenylphosphine moiety. The ^{19}F NMR spectrum is silent. The ^1H NMR spectrum shows broad resonances in the aliphatic region at $\delta = 2.71$ and 2.57 ppm corresponding to the methylene linkage. The methyl groups attached to the cyclopentadienyl ring occur as doublets at $\delta = 2.21$ ($J_{P-H} = 3.5$ Hz) and 2.01 ($J_{P-H} = 7.5$ Hz) and a singlet at 1.61 ppm. The ethyl ester group contains diastereotopic methylene protons and shows a second-order, ABX_3, multiplet centered at $\delta = 3.96$ ppm, while the methyl resonance appears as an apparent triplet at $\delta = 1.18$ ppm ($J_{H-H} = 7.0$ Hz). An X-ray diffraction study of **10** also confirmed its structure.

Figure 5 shows the structural drawing of **10**. Selected bond distances and angles are listed in Table 3, and

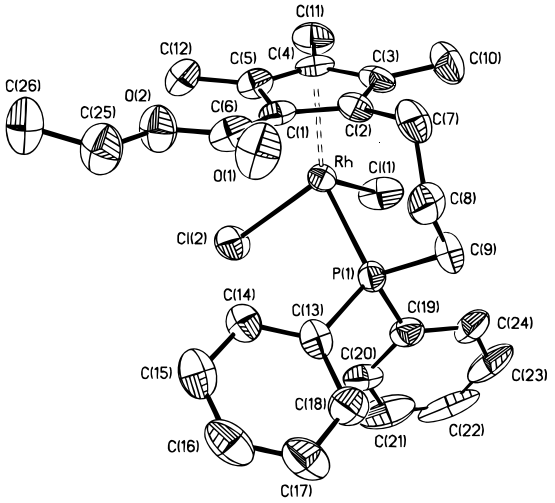


Figure 5. Structural drawing of [{η^5-$C_5(CO_2Et)Me_3$-2-[$CH_2CH_2CH_2P(C_6H_5)_2$]}$RhCl_2$] (**10**), showing the atom-numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for [η^5-$C_5(CO_2Et)Me_3$-2-{$CH_2CH_2CH_2P(C_6H_5)_2$}$RhCl_2$] (10)

Bond Distances			
Rh−P(1)	2.284(3)	C(2)−C(7)	1.535(12)
Rh−Cl(1)	2.359(3)	C(1)−C(6)	1.464(14)
Rh−Cl(2)	2.370(3)	O(1)−C(6)	1.199(11)
Rh−C(1−5)[a]	1.824	O(2)−C(6)	1.333(12)
P(1)−C(9)	1.815(9)	O(2)−C(25)	1.483(12)
C(8)−C(9)	1.526(13)	C(25)−C(26)	1.454(13)
C(7)−C(8)	1.515(14)		

Bond Angles			
P(1)−Rh−Cl(1)	90.84(10)	C(7)−C(8)−C(9)	115.2(10)
P(1)−Rh−Cl(2)	90.63(10)	C(8)−C(7)−C(2)	117.9(9)
Cl(1)−Rh−Cl(2)	89.96(11)	O(1)−C(6)−O(2)	123.8(10)
C(9)−P(1)−Rh	109.2(4)	C(6)−O(2)−C(25)	115.8(8)
C(8)−C(9)−P(1)	111.6(7)	C(26)−C(25)−O(2)	108.1(10)

[a] C(1−5) denotes the centroid of the cyclopentadienyl ring.

crystallographic data are listed in Table 4. The analysis revealed a distorted octahedral coordination geometry consisting of the following moieties bound to rhodium: a substituted cyclopentadienyl ligand containing three methyl groups and an ethyl ester, one diphenylphosphine, and two chloride ions. The remaining position on the cyclopentadienyl ring is connected *via* three methylene carbons to the diphenylphosphine group. The Rh−P bond distance in **10**, 2.284(3) Å, is shorter than the average Rh−P distances of 2.317(3) Å in **4b** and 2.324 Å in **5c**[13] but longer than the average distance of 2.273 Å in the dfppe compound.[14] The calculated distance between rhodium and the centroid of the cyclopentadienyl ligand is 1.824 Å for compound **10**, which is shorter than the calculated distances[13] of 1.875 Å in **4b**, 1.856 Å in **5c**, and 1.837 Å in the dfppe[14] compound.

The defluorination of the CF_3 group to the ester was surprising, but such reactions are known. Kobayashi[21] discussed the base-promoted esterification (and other reactions) of CF_3-substituted quinolines, and Olsson[22] discovered the defluorination of CF_3-substituted cyclo-

(21) Kobayashi, Y.; Kumadaki, I. *Acc. Chem. Res.* **1978**, *11*, 197−204.

(22) Olsson, T.; Wennerstrom, O. *Acta Chem. Scand.* **1978**, *B32*, 293.

Table 4. Crystallographic Data for Compounds 3b, 7b, and 10

	3b	7b	10
chem formula	$C_{38}H_{41}ClF_6P_3Rh$	$C_{40}H_{45}ClF_6P_3Rh$	$C_{26}H_{30}Cl_2O_2PRh$
fw	842.98	871.03	579.28
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	10.748(11)	10.541(1)	10.586(2)
b (Å)	16.838(2)	14.833(1)	13.903(2)
c (Å)	21.360(3)	25.362(2)	17.808(2)
β (deg)	98.12(2)	99.90(1)	105.914(10)
V (Å^3)	3827.1(8)	3906.4(5)	2520.6(5)
Z	4	4	4
T (K)	298	293	298
ρ_{calcd} (g/cm^3)	1.463	1.481	1.526
cryst size (mm)	0.2 × 0.3 × 0.4	0.39 × 0.32 × 0.34	0.18 × 0.19 × 0.38
μ (cm^{-1})	6.97	6.86	9.74
transm min/max	0.79/0.77	0.45/0.50	0.77/0.83
2θ range (deg)	3.5−45	3.5−45	3.5−45
F(000)	1720	1784	1184
reflcns collcd	6449	6656	4319
indepdt reflcns	5013	5103	3298
$R_1(F)^a$	0.054	0.056	0.063
w$R_2(F^2)^b$	0.127	0.094	0.132
GOF^c	1.017	1.008	1.030

^{a} $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} w$R_2(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{0.5}$. ^{c} GOF $= S = [\Sigma[w(F_o^2 - Fc^2)^2]/(n - p)]^{0.5}$.

pentadiene. Sowa, Gassman, and co-workers have found that a CF_3 group is generally quite stable when attached to five-membered rings that are bound to transition metals in an η^5-fashion.[23] Despite this observation, defluorination is observed[24] in the preparation of $[(\eta^5\text{-}C_5Me_4CF_3)Fe(CO)_2]_2$ since small amounts of $[(\eta^5\text{-}C_5Me_5)(CO)Fe(\mu\text{-}CO)_2Fe(CO)(\eta^5\text{-}C_5Me_4CF_3)]$ are detectable (see Experimental Section of ref 24). Apparently, the action of refluxing ethanol (without any added base) was enough to promote the defluorination of **10** (eq 7).

Compound **10** extends the series of chelating (phosphinopropyl)cyclopentadienide ligands and increases the potential derivitization at rhodium compared to **4** and **5** since two chloride ions are available for replacement at rhodium. In addition, the ester functionality has the potential to participate in a neighboring group effect and may enhance the reactivity of a rhodium-coordinated substrate.

Summary

The hydroalkylation reaction may proceed[15] by three different pathways: thermally *via* free radical intermediates, under base catalysis *via* carbanion intermediates, and/or under acid catalysis *via* carbocation intermediates. In this contribution, the novel chelating (phosphinopropyl)cyclopentadienide ligands of compounds **4a** and **5a** have been shown to form in a stepwise manner from **1** by a base-promoted reaction. Compound **1** reacts with DPVP to form **2** and **3a**, whereupon the base transforms **3a** into **4a** and **5a**. It is proposed that **4a** and **5a** are produced from a diastereomeric pair of intermediates **A** and **A′**. Similarly, compound **1** reacts with ADPP to produce **6** and **7a**; however, simple conversion of **7a** into hydroalkylation products remains to be discovered. The ADPP system is complicated by side reactions and decomposition. Compound **8** reacts with DPVP in the absence of base to produce **10**, a new compound in the series of hydroalkylated DPVP groups on rhodium.

The transformations described in the work may not be limited to just rhodium and DPVP. The hydroalkylation of η^5-C_5Me_5 ligands coordinated to ruthenium, iron, and manganese with substrates such as DPVP, phenyl vinyl sulfoxide, 2-vinylpyridine, and N,N-dimethylacrylamide are currently under investigation.

Experimental Section

A. Reagents and Physical Measurements. All chemicals were reagent grade and were used as received from commercial sources (Aldrich or Fisher Scientific) or synthesized as described below. Solvents were dried by standard procedures and stored over Linde type 4 Å molecular sieves. All syntheses were conducted in Schlenk glassware under a nitrogen atmosphere. C_5Me_5H,[25a] $HC_5Me_4CF_3$,[20a] $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$,[25b] and $[\{(\eta^5\text{-}C_5Me_4CF_3)RhCl_2\}_2]$[20a] were synthesized by literature procedures. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded at 500, 500, 125, and 202.4 MHz, respectively, on a Varian Unity Plus 500 FT-NMR spectrometer. Proton and carbon chemical shifts are relative to internal Me_4Si, while phosphorus chemical shifts are relative to external 85% H_3PO_4(aq) with positive values being downfield of the respective reference.

B. Syntheses. General Conditions. The syntheses of compounds **4b** and **5b** are described in detail, but one can obtain **4c** and **5c** by using $NaBPh_4$ in place of $NaPF_6$ and by following the same isolation procedure. Unless otherwise stated, all chromatography was performed using the following general procedure: A 60 mL sintered glass fritted funnel was used as the column and attached to a 1000 mL Erlenmeyer flask equipped with a side arm. A layer of silica gel (grade 12, 28−300 mesh, Aldrich, 2.5 cm layer) was covered with Celite (Aldrich, 0.5 cm layer) and firmly packed with a spatula and suction. The crude reaction product was dissolved in a minimal amount of a volatile solvent (usually CH_2Cl_2) and loaded onto the column, and the solvent was removed with suction. All subsequent solvents were eluted with suction.

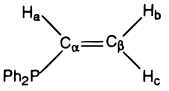
Preparation of $[(\eta^5\text{-}C_5Me_5)Rh\{CH_2CHP(C_6H_5)_2\}Cl_2]$ (2). A suspension of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ (0.15 g, 0.24 mmol) in

(23) John R. Sowa, Jr. Personal communication.

(24) Gassman, P. G.; Sowa, J. R., Jr.; Hill, M. G.; Mann, K. R. *Organometallics* **1995**, *14*, 4879.

(25) (a) Threlkel, R. S.; Bercaw, J. E.; Seidler, P. E.; Stryker, J. M.; Bergman, R. G. *Org. Synth.* **1987**, *65*, 42. (b) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228.

25 mL of $CHCl_3$ was purged with nitrogen for 15 min, after which diphenylvinylphosphine (0.15 mL, 0.51 mmol) was added *via* syringe and the mixture was stirred at room temperature until dissolution of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ was complete. The clear red solution was refluxed for 6 h, after which the solvent was removed *in vacuo*. Excess phosphine was removed by allowing the oily residue to stand in 200 mL of hexanes for at least 8 h. The hexanes were decanted through filter paper and discarded. The product was then purified by chromatography. The following solvents were eluted sequentially to collect six fractions: (1) 600 mL of hexanes, (2) 500 mL of 10% Et_2O in hexanes, (3) 750 mL of 40% Et_2O in hexanes, (4) 750 mL of Et_2O, (5) 450 mL of CH_2Cl_2, and (6) 400 mL of MeOH. The first three fractions contained diphenylvinylphosphine and its oxide and were discarded. The fourth and fifth fractions primarily contained the product, **2**, and were evaporated to dryness, combined, and kept separate from the sixth fraction which contained compounds **3a** and diphenylvinylphosphine oxide. The combined fourth and fifth fractions were rechromatographed on the same type of column with 750 mL of 30% Et_2O in hexanes followed by 500 mL of CH_2Cl_2. The CH_2Cl_2 fraction contained pure **2** and was evaporated to dryness to give 0.12 g (0.23 mmol) in 47% yield based on $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$. Complex **2** is air stable in solution and the solid state. Mp: 212−216 °C. Anal. Calcd for $C_{24}H_{28}Cl_2PRh$: C, 55.32; H, 5.37; Cl, 13.61. Found: C, 55.15; H, 5.22; Cl, 13.47.



^{1}H NMR ($CDCl_3$): δ 7.90−7.38 (m, 10H, Ph), 6.92 (ddd, ^2J(PH) = 24.9 Hz, $^3J(H_aH_c)$ = 18.7 Hz, $^3J(H_aH_b)$ = 11.7 Hz, 1H, H_a), 5.94 (dd, ^3J(PH) = 39.1 Hz, $^3J(H_aH_b)$ = 11.7 Hz, 1H, H_b), 5.43 (apparent t, ^3J(PH) = $^3J(H_aH_c)$ = 18.7 Hz, 1H, H_c), 1.41 (d, ^4J(PH) = 3.4 Hz, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.49 (d, ^2J(PC) = 9.4 Hz, C_o), 132.47 (d, ^1J(PC) = 49.0 Hz, C_α), 130.77 (s, C_β), 130.75 (s, C_p), 129.61 (d, ^1J(PC) = 44.2 Hz, C_i), 128.12 (d, ^3J(PC) = 10.1 Hz, C_m), 98.73 (dd, ^1J(RhC) = 6.9 Hz, ^2J(PC) = 3.1 Hz, C_5Me_5), 8.82 (d, ^3J(PC) = 1.5 Hz, C_5Me_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.4 (d, ^1J(RhP) = 140.7 Hz).

Preparation of $[(\eta^5\text{-}C_5Me_5)Rh\{CH_2CHP(C_6H_5)_2\}_2Cl]PF_6$ (3b). A suspension of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ (0.20 g, 0.32 mmol) in 20 mL of $CHCl_3$ was purged with nitrogen for 15 min, after which diphenylvinylphosphine (0.28 mL, 1.41 mmol) was added *via* syringe, and the mixture was stirred at room temperature for 3 h. A 5 mL volume of MeOH was added to the reaction solution followed by a methanolic solution of $NaPF_6$ (0.15g, 0.87 mmol), and the mixture was stirred for 15 min. All solvents were removed *in vacuo*, and the crude product was extracted into CH_2Cl_2 (150 mL) and filtered to remove inorganic salts. The product was then purified by chromatography. The following fractions were collected: (1) 500 mL, 4:1 hexanes/Et_2O; (2) 500 mL, 1.5:1 hexanes/Et_2O; (3) 500 mL, 1:1.5 hexanes/Et_2O; (4) 500 mL, 1:4 hexanes/Et_2O; (5) 750 mL of Et_2O; (6) 500 mL of CH_2Cl_2; (7) 250 mL of $CHCl_3$; (8) 250 mL of MeOH. Fractions 1−4 were combined and discarded. Fraction 5 contained product **3b** with impurities and was kept separate. Fractions 6 and 7 contained pure **3b** and were combined. Fraction 8 was discarded. Fraction 5 was rechromatographed using the same column setup as described above. The following fractions were collected: (1′) 1750 mL, 1:1 hexanes/Et_2O; (2′) 500 mL of CH_2Cl_2; (3′) 250 mL of $CHCl_3$. Fractions 2′ and 3′ contained pure **3b** and were combined with fractions 6 and 7 and dried under high vacuum to give 0.50 g of **3b** in 90% yield. Crystals of **3b** may be obtained by slow diffusion of a 1:1 Et_2O/hexanes solution into a saturated CH_2Cl_2 solution of **3b.** Compound **3b** is air stable in solution and the solid state. Mp: 185−189 °C. Anal. Calcd for $C_{38}H_{41}ClF_6P_3Rh$: C, 54.16; H, 4.87; Cl, 4.21. Found: C, 54.02; H, 5.01, Cl, 4.13. ^{1}H NMR ($CDCl_3$): δ 7.86−7.00 (m, 20H, Ph), 5.98 (broad m, 2H, vinyl-CH), 5.68 (broad m, 2H, vinyl-CH), 5.32 (broad m, 2H, vinyl-CH), 1.37 (t, ^4J(PH) = 3.5 Hz, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.67 (broad m, C_o), 133.51 (broad m, C_o), 132.62 (s, C_p), 132.35 (s, C_p), 131.46 (broad m, C_β), 129.55 (d, ^1J(PC) = 48.8 Hz, C_i), 128.89 (broad m, C_m), 128.33 (T, $|^3J(PC) + {}^5J(PC)|$ = 10.8 Hz, C_m), 127.60 (d, ^1J(PC) = 46.6 Hz, C_α), 127.42 (d, ^1J(PC) = 49.5 Hz, C_i), 105.48 (dt, ^1J(RhC) = 5.2, ^2J(PC) = 2.2 Hz, C_5Me_5), 9.14 (t, ^3J(PC) = 1.4 Hz, C_5Me_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.9 (d, ^1J(RhP) = 134.1 Hz), −143.6 (septet, ^1J(PF) = 712.8 Hz, PF_6^-).

Preparation of $[\{\eta^5\text{-}C_5Me_3\text{-}1,3\text{-}[CH_2CH_2CH_2P(C_6H_5)_2]_2\}RhCl]PF_6$ (4b) and $[\{\eta^5\text{-}C_5Me_3\text{-}1,2\text{-}[CH_2CH_2CH_2P(C_6H_5)_2]_2\}RhCl]PF_6$ (5b). A suspension of $[\{(\eta^5\text{-}C_5Me_5)RhCl_2\}_2]$ (0.21 g, 0.34 mmol) in 25 mL CH_3CN was purged with nitrogen for 15 min, after which diphenylvinylphosphine (0.30 mL, 1.41 mmol) was added *via* syringe, and the clear red mixture was stirred at room temperature for 15 min. To this solution was added $KOC(CH_3)_3$ (0.03 g, 0.31 mmol) with 5 mL of CH_3CN. The clear red reaction solution turned dark brown immediately after addition of the base. The solution was refluxed for 48 h and gradually turned back to red. A solution of $NaPF_6$ (0.14g, 0.86 mmol) in 8 mL of MeOH was added to the reaction mixture, which was then stirred for 15 min at room temperature. All solvents were removed *in vacuo*, and the crude product was extracted into CH_2Cl_2 (150 mL) and filtered to remove inorganic salts. The product was then purified by gravity column chromatography using a 2 × 18 cm column packed with Al_2O_3. The following fractions were collected: (1) 2500 mL of CH_2Cl_2; (2) 250 mL of 1% MeOH/CH_2Cl_2; (3) 250 mL of MeOH. Fractions 1 and 2 contained **4b** and **5c** and some impurities and were combined. Compounds **4b** and **5b** are then separated from each other by fractional crystallization by allowing Et_2O to slowly diffuse into a saturated CH_2Cl_2 solution of the combined fractions. Compound **5b** precipitates out of the solution as orange needles. Repeated fractional crystallizations may be necessary to quantitatively remove **5b** from **4b**. If necessary, compound **4b** can be chromatographed using the flash technique described in the general Conditions Section with Al_2O_3 and 1000 mL of CH_2Cl_2 or recrystallized from CH_2Cl_2/*n*-butyl ether solutions as red crystals. Typical yields for **4b** are 0.10 g (35%) and for **5b** are 0.12 g (42%) based on **1**. Both **4b** and **5b** are air stable in solution and the solid state. Data for **5c** are also provided.

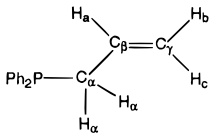
Data for $[\{\eta^5\text{-}C_5Me_3\text{-}1,3\text{-}[CH_2CH_2CH_2P(C_6H_5)_2]_2\}RhCl]PF_6$ (4b). Mp: 250 °C dec. Anal. Calcd for $C_{38}H_{41}ClF_6P_3Rh\cdot 0.5\,CH_2Cl_2$: C, 52.24; H, 4.74; Cl, 8.01. Found: C, 51.98; H, 4.87; Cl, 7.92. ^{1}H NMR ($CDCl_3$): δ 7.36−7.00 (m, 20H, Ph), 5.30 (s, 1H, 0.5 CH_2Cl_2), 2.46 (broad m, 8H, CH_2), 2.20 (broad m, 2H, CH_2), 1.86 (T, $|^4J(PH) + {}^4J(P'H)|$ = 6.50 Hz, 6H, CH_3), 1.80 (broad m, 2H, CH_2), 1.07 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.97 (T, $|^2J(PC) + {}^4J(PC)|$ = 8.42 Hz, C_o), 132.84 (T, $|^2J(PC) + {}^4J(PC)|$ = 9.30 Hz, C_o), C_i not observed, 131.46 (s, C_p), 130.06 (s, C_p), 129.06 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.80 Hz, C_m), 127.87 (T, $|^3J(PC) + {}^5J(PC)|$ = 10.06 Hz, C_m), 98.4 (broad m, ring-C), 23.76 (complex m, C_α), 20.68 (broad s, C_γ), 20.38 (T, $|^2J(PC) + {}^4J(PC)|$ = 6.41 Hz, C_β), 11.27 (broad s, CH_3), 11.00 (T, $|^3J(PC) + {}^3J(P'C)|$ = 2.77 Hz, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.0 (d, ^1J(RhP) = 134.9 Hz), −143.6 (septet, ^1J(PF) = 712.8 Hz, PF_6^-).

Data for $[\{\eta^5\text{-}C_5Me_3\text{-}1,2\text{-}[CH_2CH_2CH_2P(C_6H_5)_2]_2\}RhCl]PF_6$ (5b). ^{1}H NMR ($CDCl_3$): δ 7.82−6.71 (m, 20H, Ph), 3.16 (broad m, 2H, CH_2), 2.90 (broad m, 2H, CH_2), 2.57 (broad m, 4H, CH_2), 2.16 (broad m, 2H, CH_2), 1.86 (s, 3H, CH_3), 1.58 (broad m, 2H, CH_2), 1.45 (T, $|^4J(PH) + {}^4J(P'H)|$ = 10.0 Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.52 (broad m, C_o), 132.69 (broad m, C_o), 131.83 (T, $|^1J(PC) + {}^3J(PC)|$ = 48.0 Hz, C_i), 131.44 (T, $|^1J(PC) + {}^3J(PC)|$ = 50.8 Hz, C_i), 130.74 (s, C_p), 129.65 (s, C_p), 128.47 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.30Hz, C_m), 128.40 (T, $|^3J(PC) + {}^5J(PC)|$ = 9.6 Hz, C_m), 121.45 (d, ^1J(RhC) = 3.1 Hz, ring-C), 103.06 (m, ring-C), 94.10 (dT, ^1J(RhC) = 6.9 Hz, $|^2J(PC) + {}^2J(P'C)|$ = 2.9 Hz, ring-C), 20.54 (complex

m, CH_2), 20.19 (broad s, CH_2), 19.41 (broad s, CH_2), 11.24 (T, $|^3J(PC) + {}^3J(P'C)| = 4.3$ Hz, CH_3), 10.07 (T, $|^3J(PC) + {}^3J(P'C)| = 2.4$ Hz, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.2 (d, $^1J(RhP) = 134.0$ Hz), −143.5 (septet, $^1J(PF) = 712.6$ Hz, PF_6^-).

Data for [{η^5-C_5Me_3-1,2-[$CH_2CH_2CH_2P(C_6H_5)_2$]$_2$}RhCl]-BPh_4 (5c). Mp: 220 °C dec. Anal. Calcd for $C_{62}H_{61}BClP_2Rh \cdot 0.5\ CH_2Cl_2$: C, 70.87; H, 5.85; Cl, 6.69. Found: C, 70.63; H, 5.91; Cl, 6.47. ^1H NMR ($CDCl_3$): δ 7.84−6.68 (m, 40H, Ph), 5.30 (s, 1H, 0.5 CH_2Cl_2), 2.43 (broad m, 2H, CH_2), 2.16 (broad m, 2H, CH_2), 1.94 (broad m, 6H, CH_2), 1.82 (T, $|^4J(PH) + {}^4J(P'H)| = 3.0$ Hz, 3H, CH_3), 1.46 (broad m, 2H, CH_2), 1.34 (T, $|^4J(PH) + {}^4J(P'H)| = 10.50$ Hz, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.71−127.15 (complex m, P-C_6H_5, B-C_6H_5), 121.51 (d, $^1J(RhC) = 3.14$ Hz, ring-C), 103.09 (complex m, ring-C), 94.07 (d, $^1J(RhC) = 6.03$ Hz, ring-C), 20.67 (complex m, CH_2), 20.27 (broad s, CH_2), 19.39 (T, $|^3J(PC) + {}^5J(PC)| = 3.39$ Hz, CH_2), 11.23 (T, $|^3J(PC) + {}^3J(P'C)| = 3.64$ Hz, CH_3), 10.07 (T, $|^3J(PC) + {}^3J(P'C)| = 1.89$ Hz, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.3 (d, $^1J(RhP) = 133.8$ Hz).

Preparation of [(η^5-C_5Me_5)Rh{$CH_2CHCH_2P(C_6H_5)_2$}Cl_2] (6). A suspension of [{(η^5-C_5Me_5)$RhCl_2$}$_2$] (0.20 g, 0.33 mmol) in 25 mL of benzene was purged with nitrogen for 15 min, after which allyldiphenylphosphine (0.15 mL, 0.695 mmol) was added *via* syringe, and the dark red reaction mixture was refluxed for 24 h. All solvents were removed *in vacuo*, and 250 mL of hexanes was added to the residue. After standing for 15 h, the hexane was decanted through a paper filter and all solvents were removed *in vacuo*. The hexane extract contained unreacted phosphine which oxidized. The hexane-insoluble residue, after drying *in vacuo*, gave 0.33 g of pure product **6** in 95% yield based on [{(η^5-C_5Me_5)$RhCl_2$}$_2$]. Mp: 220−223 °C. Anal. Calcd for $C_{25}H_{30}Cl_2PRh$: C, 56.21; H, 5.62; Cl, 13.27. Found: C, 56.13; H, 5.34; Cl, 13.15.

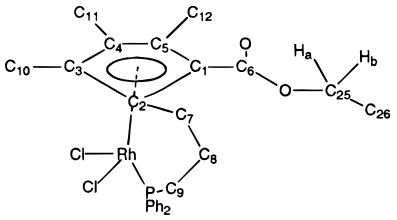


^1H NMR ($CDCl_3$): δ 8.1−7.4 (m, 10H, Ph), 5.43 (ddtd, $^3J(H_aH_b) = 10.2$ Hz, $^3J(H_aH_c) = 17.0$ Hz, $^3J(H_aH_\alpha) = 8.0$ Hz, $^3J(PH_a) = 3.9$ Hz, 1H, H_a), 4.83 (dddt, $^3J(H_aH_b) = 10.2$ Hz, $^2J(H_bH_c) = 1.8$ Hz, $^4J(H_\alpha H_b) = 1.0$ Hz, $^4J(PH_b) = 3.8$ Hz, 1H, H_b), 4.66 (ddtd, $^3J(H_aH_c) = 17.0$ Hz, $^2J(H_bH_c) = 1.8$ Hz, $^4J(H_\alpha H_c) = 2.0$ Hz, $^4J(PH_c) = 4.4$ Hz, 1H, H_c), 3.61 (dddd, $^3J(H_aH_\alpha) = 8.0$ Hz, $^4J(H_bH_\alpha) = 1.0$ Hz, $^4J(H_cH_\alpha) = 2.0$ Hz, $^2J(PH_\alpha) = 9.5$ Hz, 2H, H_α), 1.35 (d, $^4J(PH) = 3.5$ Hz, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.1 (d, $^2J(PC) = 8.8$ Hz, C_o), 130.8 (d, $^4J(PC) = 2.6$ Hz, C_p), 130.2 (d, $^3J(PC) = 13.2$ Hz, C_γ), 128.4 (d, $^1J(PC) = 41.5$ Hz, C_i), 127.9 (d, $^3J(PC) = 9.8$ Hz, C_m), 119.6 (d, $^2J(PC) = 9.4$ Hz, C_β), 98.5 (dd, $^1J(RhC) = 6.9$ Hz, $^2J(PC) = 2.9$ Hz, C_5Me_5), 33.0 (d, $^1J(PC) = 26.5$ Hz, C_α), 8.6 (d, $^3J(PC) = 1.4$ Hz, C_5Me_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.0 (d, $^1J(RhP) = 142.8$ Hz).

Preparation of [(η^5-C_5Me_5)Rh{$CH_2CHCH_2P(C_6H_5)_2$}$_2$Cl]-PF_6 (7b). A suspension of [{(η^5-C_5Me_5)$RhCl_2$}$_2$] (0.12 g, 0.19 mmol) in 20 mL of CH_3CN was purged with nitrogen for 15 min, after which allyldiphenylphosphine (0.23 mL, 1.1 mmol) was added *via* syringe. Upon addition of the phosphine all of the [{(η^5-C_5Me_5)$RhCl_2$}$_2$] dissolved, resulting in a clear red solution. The reaction mixture was refluxed for 2 h and then cooled to room temperature. A methanolic solution of $NaPF_6$ (0.098 g, 0.58 mmol) was added to the reaction mixture, and it was stirred for 15 min. All solvents were removed *in vacuo* resulting in a yellow/red viscous residue. The crude product was extracted into CH_2Cl_2 (75 mL) and filtered to remove NaCl. The CH_2Cl_2 was removed *in vacuo*, and the product was chromatographed. The fractions collected were as follows: (1) 500 mL, 4:1 hexanes/Et_2O; (2) 500 mL, 1.5:1 hexanes/Et_2O; (3) 500 mL, 1:1.5 hexanes/Et_2O; (4) 1500 mL, 1:1.5 hexanes/Et_2O; (5) 250 mL, 1:4 hexanes/Et_2O; (6) 750 mL of CH_2Cl_2; (7) 500 mL, 1:1 CH_2Cl_2/$CHCl_3$; (8) 250 mL of CH_2Cl_2; (9) 250 mL of MeOH. Fractions 1−3 contained phosphine oxide and were discarded. Fractions 6 and 7 contained 80% pure (by $^{31}P\{^1H\}$ NMR) product and were combined. All other fractions were discarded. All solvents were removed *in vacuo*, and the orange solid was dried under high vacuum for 15 h. The dried product was further purified by washing with 3 × 75 mL portions of Et_2O and decanting through filter paper. The insoluble residue was dried under high vacuum to give 0.13 g of **7b** in 40% yield. The product may be recrystallized by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution. Compound **7b** is air stable in solution and the solid state. Mp: 142−150 °C. Anal. Calcd for $C_{40}H_{45}ClF_6P_3Rh$: C, 55.18; H, 5.17; Cl, 4.07. Found: C, 54.92; H, 5.23; Cl, 3.94. ^1H NMR ($CDCl_3$): δ 7.64−7.27 (m, 20H, Ph), 5.09−4.88 (broad m, 6H, *CH*=*CH*$_2$), 3.19 (broad m, 4H, H_α), 1.27 (t, $^4J(PH) = 3.7$ Hz, 15H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.40−133.26 (broad m, C_o), 131.86 (s, C_p), 131.82 (s, C_p), 129.92 (broad m, C_i), 129.11 (T, $|^3J(PC) + {}^5J(PC)| = 10.06$ Hz, C_γ), 128.67 (T, $|^3J(PC) + {}^5J(PC)| = 10.56$ Hz, C_m), 120.46 (T, $|^2J(PC) + {}^4J(PC)| = 10.18$ Hz, C_β), 105.91 (dt, $^1J(RhC) = 5.41$ Hz, $^2J(PC) = 1.89$ Hz, C_5Me_5), 30.7 (broad m, C_α), 9.22 (t, $^3J(PC) = 1.51$ Hz, C_5Me_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.9 (d, $^1J(RhP) = 134.8$ Hz), −143.6 (septet, $^1J(PF) = 712.8$ Hz, PF_6^-).

Preparation of [(η^5-$C_5Me_4CF_3$)Rh{$CH_2CHP(C_6H_5)_2$}Cl_2] (9). A suspension of [{(η^5-$C_5Me_4CF_3$)$RhCl_2$}$_2$] (0.15 g, 0.21 mmol) in 15 mL of $CHCl_3$ was purged with nitrogen for 15 min, after which diphenylvinylphosphine (0.18 mL, 0.91 mmol) was added *via* syringe, and the clear red solution was stirred at room temperature for 2.5 h. All solvents were removed *in vacuo*, and the residue was washed with 4 × 100 mL of hexanes to remove excess phosphine. The hexane-insoluble portion was chromatographed by eluting with the following: (1) 1000 mL hexanes; (2) 400 mL, Et_2O; (3) 500 mL, CH_2Cl_2. The first fraction was discarded, and the second and third were combined as they contain mostly compound **9** and some phosphine oxide. The oxide can be removed by washing with Et_2O although this also extracts compound **9**. Crystals of **9** can be grown by slow diffusion of 1:1 Et_2O/hexanes into a CH_2Cl_2 solution to give 0.22 g of **9** in 89.8% yield. Complex **9** is air stable in solution and the solid state. Mp: 209−212 °C. Anal. Calcd for $C_{24}H_{25}Cl_2F_3PRh$: C, 50.13; H, 4.35; Cl, 12.33. Found: C, 49.97; H, 4.19; Cl, 12.21. ^1H NMR ($CDCl_3$): δ 7.84−7.42 (m, 10H, Ph), 6.92 (ddd, $^2J(PH) = 25.5$ Hz, $^3J(H_aH_c) = 18.2$ Hz, $^3J(H_aH_b) = 12.1$ Hz, 1H, H_a), 5.99 (dd, $^3J(PH) = 40.5$ Hz, $^3J(H_aH_b) = 12.1$ Hz, 1H, H_b), 5.41 (dd, $^3J(PH) = 20.3$ Hz, $^3J(H_aH_c) = 18.8$ Hz, 1H, H_c), 1.64 (d, $^4J(PH) = 3.9$ Hz, 6H, 2,5-CH_3), 1.53 (d, $^4J(PH) = 2.9$ Hz, 6H, 3,4-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 134.6 (d, $^2J(PC) = 9.2$ Hz, C_o), 131.8 (d, $^1J(PC) = 51.2$ Hz, C_α), 131.1 (d, $^4J(PC) = 2.6$ Hz, C_p), 130.2 (br s, C_β), 128.7 (d, $^1J(PC) = 49.4$ Hz, C_i), 128.1 (d, $^3J(PC) = 10.3$ Hz, C_m), 124.2 (q, $^1J(CF) = 273.4$ Hz, CF_3), 105.3 (s, 2,5-*C*−*C*H_3), 101.6 (s, 3,4-*C*−*C*H_3), 80.3 (qd, $^2J(CF) = 35$ Hz, $^1J(RhC) = 9.0$ Hz, *C*−*C*F_3), 9.48 (qd, $^4J(CF) = 2.0$ Hz, $^3J(PC) = 1.8$ Hz, 2,5-CH_3), 8.60 (d, $^3J(PC) = 1.6$ Hz, 3,4-CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.4 (d, $^1J(RhP) = 134.5$ Hz).

Preparation of [{η^5-$C_5(CO_2Et)Me_3$-2-[$CH_2CH_2CH_2P(C_6H_5)_2$]}$RhCl_2$] (10). A suspension of [{(η^5-$C_5Me_4CF_3$)$RhCl_2$}$_2$] (0.30 g, 0.41 mmol) in 25 mL of EtOH was purged with nitrogen for 15 min, after which diphenylvinylphosphine (0.35 mL, 1.8 mmol) was added *via* syringe, and the clear red solution was stirred at room temperature for approximately 15 min. The dark red solution was then refluxed for 4 h after which the solvent was removed *in vacuo*. The residue was chromatographed by eluting with the following solvents: (1) 700 mL of 1:1 CH_2Cl_2/Et_2O, (2) 600 mL of MeOH. The MeOH fraction was discarded. The first fraction was further purified by recrystallization from acetone at room temperature to give 0.14 g of compound **10** in 29.2% yield. Compound **10** is air stable in solution and in the solid state. Mp: 123−126 °C. Anal. Calcd for $C_{26}H_{30}Cl_2O_2PRh$: C, 53.93; H, 5.18; Cl, 12.24. Found: C, 53.78; H, 5.02; Cl, 12.31.



^{1}H NMR ($CDCl_3$): δ 7.78−7.27 (m, 10H, Ph), 3.99 (m, A part of ABX_3, $^2J(H_aH_b) = 10.50$ Hz, $^3J(H_aCH_3) = 7.0$ Hz, 1H, H_a), 3.94 (m, B part of ABX_3, $^2J(H_bH_a) = 10.50$ Hz, $^3J(H_bCH_3) = 7.0$ Hz, 1H, H_b), 2.74−2.53 (broad m, 2H, C_7-CH_2), 2.23−1.89 (broad m, 4H, CH_2CH_2P), 2.21 (d, $^4J(PH) = 3.5$ Hz, 3H, CH_3), 2.01 (d, $^4J(PH) = 7.5$ Hz, 3H, CH_3), 1.61 (s, 3H, CH_3), 1.18 (apparent t, $^3J(H_aCH_3) = {}^3J(H_bCH_3) = 7.0$ Hz, 3H, C_{26}-H_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 166.46 (d, $^3J(PC) = 0.75$ Hz, CO_2), 134.33 (d, $^3J(PC) = 10.06$ Hz, C_m), 132.72 (d, $^3J(PC) = 8.17$ Hz, C_m), 132.04 (d, $^1J(PC) = 53.80$ Hz, C_i), 131.12 (d, $^1J(PC) = 49.28$ Hz, C_i), 130.80 (d, $^4J(PC) = 2.64$ Hz, C_p), 130.09 (d, $^4J(PC) = 3.14$ Hz, C_p), 128.21 (d, $^2J(PC) = 10.56$ Hz, C_o), 127.64 (d, $^2J(PC) = 10.94$ Hz, C_o), 118.72 (dd, $^1J(RhC) = 3.96$ Hz, $^2J(PC) = 3.33$ Hz, ring-C), 106.88 (dd, $^1J(RhC) = 13.58$ Hz, $^2J(PC) = 3.52$ Hz, ring-C), 105.12 (dd, $^1J(RhC) = 6.66$ Hz, $^2J(PC) = 2.39$ Hz, ring-C), 92.75 (d, $^1J(RhC) = 7.17$ Hz, ring-C), 72.53 (broad d, $^1J(RhC) = 9.68$ Hz, ring-C), 61.36 (s, C_{25}), 21.75 (dd, $^3J(PC) = 8.8$ Hz, $^2J(RhC) = 1.25$ Hz, C_7), 21.50 (s, C_8), 21.23 (d, $^1J(PC) = 31.43$ Hz, C_9), 13.80 (s, CH_3), 11.92 (d, $^3J(PC) = 2.14$ Hz, CH_3), 10.44 (s, CH_3), 8.84 (d, $^3J(PC) = 3.90$ Hz, CH_3). ^{31}P {^{1}H} NMR ($CDCl_3$): δ 30.3 (d, $^1J(RhP) = 135.9$ Hz).

C. X-ray Data Collection and Processing for 3b, 7b, and 10. Orange crystals of **3b** and **7b** were grown by slow diffusion of ether into a saturated CH_2Cl_2 solution, and deep red crystals of **10** were grown by slow evaporation of an acetone solution. Crystal data and details of data collection are given in Table 4. The crystals were coated with epoxy, mounted on glass fibers, and placed on a Siemens P4 diffractometer. Data were collected in the ω-mode with Mo K_α graphite-monochromated radiation ($\lambda = 0.710\,73$ Å). Two check reflections monitored every 100 reflections showed random (<2%) variation during the data collection. Unit cell parameters were determined by least-squares refinement of 24 reflections for **3b**, **7b**, and **10**. The data were corrected for Lorentz, polarization, and absorption (using an empirical model derived from azimuthal data collections). Scattering factors and corrections for anomalous dispersion were taken from a standard source.[26] Calculations were performed with the Siemens SHELXTL Plus version 5.0 software package on a personal computer. The structures were solved by direct methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C−H vector was fixed at 0.96 Å.

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Supporting Information Available: For the compounds **3b**, **7b**, and **10**, listings of crystal and refinement data, atomic coordinates and *U* values, bond lengths and angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters (16 pages). Ordering information is given on any current masthead page.

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(26) *International Tables for X-Ray Crystallography*; D. Reidel Publishing Co.: Boston, MA, 1992, Vol. C.