# **Reactions of** $(PMe_3)_4Ru(C_2H_4)$ and $(DMPE)_2Ru(C_2H_4)$ with Weak Proton-Donating Electrophiles HX (X = OAr, SAr, NHPh, PHPh). Synthesis of Complexes with Metal-Heteroatom Single Bonds

Melinda J. Burn,<sup>†</sup> Michael G. Fickes,<sup>‡</sup> Frederick J. Hollander, and Robert G. Bergman<sup>\*</sup>

Department of Chemistry, University of California, Berkeley, California 94720

Received June 21, 1994<sup>®</sup>

Reactions of the ruthenium ethylene complexes  $(PMe_3)_4Ru(C_2H_4)$  and  $(DMPE)_2Ru(C_2H_4)$ with a variety of HX compounds (X = SAr, OAr, PPhH, NHPh and Ph) have been explored. In all cases, the tetrakis(trimethylphosphine) complex reacted to form ethylene and the hydrido species,  $(PMe_3)_4Ru(H)(X)$ . However, parallel studies with the related material  $(DMPE)_2Ru(C_2H_4)$  suggest that these complexes react as strained metallacycles toward HX. Thus, the bis(DMPE) analog gave the ethyl species  $(DMPE)_2Ru(X)(CH_2CH_3)$  in its reactions with HSAr and PH<sub>2</sub>Ph, and thermolysis of these ethyl complexes led to the formation of the hydrides and free ethylene. The reaction of the DMPE ethylene complex with p-cresol allowed isolation of an intermediate cationic ethylene hydride species, but this was converted rapidly to the corresponding aryloxy hydride complex, even at room temperature. With  $NH_2Ph$  the bis(DMPE) complex formed only the corresponding hydride species. In an attempt to generate an acetylene complex that similarly might react as a strained metallacyclopropene, (PMe<sub>3</sub>)<sub>4</sub>Ru(CH=CH<sub>2</sub>)<sub>2</sub> was generated from the reaction of CH=CH<sub>2</sub>MgBr with (PMe<sub>3</sub>)<sub>4</sub>RuCl<sub>2</sub>. However, thermolysis of the divinyl species led only to the formation of the butadiene complex,  $(PMe_3)_3Ru(C_4H_6)$ .

## Introduction

Oxidative addition and reductive elimination reactions are critical processes in the catalytic and stoichiometric applications of transition-metal reagents in organic synthesis.<sup>1</sup> Two-electron oxidative addition reactions can be described as shown:

$$M^{(n)} + A - B = B - M^{(n+2)}$$

The addition of C-H bonds across a metal center has been well studied, but much less is known about the addition of X-H bonds, where X is a heteroatom (O, S, N, P). Recent syntheses of late transition metalheteroatom compounds have resulted in the formation of new metal alkoxides, arylamides, thiolates and phosphides, formed primarily by the metathesis reaction of a metal halide and an alkali alkoxide, amide, thiolate or phosphide, rather than by an oxidative addition reaction. Recent examples include  $Cp*Ir(PPh_3)(Y)(H)$ where  $Y = OEt^2$  and NHPh,<sup>3</sup> trans-(PR<sub>3</sub>)<sub>2</sub>Pt(H)(YAr)

where Y = O and NH,<sup>4,5</sup> [(PMe\_3)<sub>4</sub>Ir(H)(Y)]PF<sub>6</sub> where Y = OMe and SH,<sup>6</sup> (PMe<sub>3</sub>)<sub>4</sub>Ru(YPh)(H) where Y = O and NH,<sup>7</sup> and Os(PHPh)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.<sup>8</sup>

We have discovered a versatile route into metalheteroatom compounds using ruthenium ethylene complexes. In this study, we have found that (PMe<sub>3</sub>)<sub>4</sub>Ru- $(C_2H_4)$  (1) is a useful precursor to a variety of complexes containing metal-heteroatom bonds. Complex 1 is conveniently prepared by treatment of  $(PMe_3)_4RuCl_2(2)$ with two equivalents of EtMgCl.<sup>9</sup> As shown previously,  $(PMe_3)_4Ru(C_2H_4)$  (1) reacts with *p*-cresol and aniline.<sup>7</sup> The reaction of 1 and p-cresol occurred at room temperature to form the cresolate hydride, (PMe<sub>3</sub>)<sub>4</sub>Ru(H)- $(OC_6H_4-p-CH_3)$  (3, Scheme 1). Neither phosphine dissociation nor ethylene dissociation occurs in 1 at an appreciable rate at room temperature.<sup>10</sup> Although with late transition metals like Ru such species are often regarded as alkene complexes, the Ru-ethylene moiety reacts (at least in an overall sense) as a strained metallacyclopropane. It was proposed that the *p*-cresol reaction proceeded by initial protonation of the electronrich ruthenium center, followed by olefin insertion into the metal-hydride bond and reaction with aryloxide to form the unobserved ruthenium ethyl cresolate, (PMe<sub>3</sub>)<sub>4</sub>- $Ru(Et)(OC_6H_4$ -*p*-CH<sub>3</sub>).<sup>7</sup> Ionization of the aryloxide to

<sup>&</sup>lt;sup>†</sup> Present address: Central Research and Development Dept., Experimental Station, E. I. duPont de Nemours and Co., Wilmington, DE 19880-0328. <sup>‡</sup> Present address: Department of Chemistry, Massachusetts Insti-

tute of Technology, Cambridge, MA 02139. \* Abstract published in Advance ACS Abstracts, November 1, 1994.

Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. Principles and Applications of Organotransition Metal Chemistry; University Science Books: Mill Valley, CA, 1987.
 Newman, L. J.; Bergman, R. G. J. Am. Chem. Soc. 1985, 107,

<sup>5314.</sup> (3) Glueck, D. S.; Winslow, L. N.; Bergman, R. G. Organometallics

<sup>1991, 10, 1462.
(4)</sup> Fornies, T.; Green, M.; Spencer, J. L.; Stone, F. G. A. J. Chem. Soc., Dalton Trans. 1977, 1006.

<sup>(5)</sup> Cowan, R. L.; Trogler, W. C. J. Am. Chem. Soc. 1989, 111, 475.
(6) Milstein, D.; Calabrese, J. C.; Williams, I. D. J. Am. Chem. Soc.

<sup>1986, 108(20), 6387.</sup> (7) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. Organometallics 1991, 10, 1875.

<sup>(8)</sup> Bohle, D. S.; Jones, T. C.; Rickard, C. E. F.; Roper, W. R. J. Chem.

Soc., Chem. Commun. 1984, 865.
 (9) Wong, W.-K.; Chiu, K. W.; Statler, J. A.; Wilkinson, G.; Motavelli,

M.; Hursthouse, M. B. Polyhedron 1984, 3, 1255. (10) Hartwig, J. F. Ph. D. Thesis 1991, University of California, Berkeley.



form an ion pair,  $[(PMe_3)_4Ru(Et)]^+[OAr]^-$ , to facilitate  $\beta$ -hydride elimination, followed by loss of ethylene and ion pair collapse would form the observed product **3**. The reaction of the complex **1** with aniline required heating to form the analogous product,  $(PMe_3)_4Ru(NHPh)(H)$  (**4**).<sup>7</sup>

Studies of the reactivity of the related  $(DMPE)_2Ru$ system began in 1965<sup>11</sup> when the dihydride complex,  $(DMPE)_2RuH_2$  (5), was first reported.<sup>12</sup>  $(DMPE)_2RuH_2$ has received recent attention as a source of the coordinately unsaturated species,  $(DMPE)_2Ru.^{13,14}$  The 16electron species has been generated by photo-induced loss of H<sub>2</sub> from  $(DMPE)_2RuH_2.^{13,15}$  The ethylene complex,  $(DMPE)_2Ru(C_2H_4)$  (6), was briefly mentioned in the literature but no preparative details were given.<sup>13,16</sup> Complex 6 offers a potential route to rutheniumheteroatom complexes with a bidentate ligand system.

In this paper we report further investigations of the reactions of ruthenium ethylene complexes,  $(PMe_3)_4Ru$ - $(C_2H_4)$  (1) and  $(DMPE)_2Ru(C_2H_4)$  (6), with a variety of HX compounds, where X = SAr, OAr, NHAr, and PPhH. We have observed that, in the tetrakis(trimethylphosphine) system, the hydrido products  $(PMe_3)_4Ru(H)(X)$  are formed. In contrast, in the bis(DMPE) system the ethyl products  $(DMPE)_2Ru(Et)(X)$  and an ethylene hydride cationic intermediate  $(DMPE)_2Ru(C_2H_4)H^+X^-$  were isolated. Thermolysis of the ethyl and ethylene hydride complexes led to the formation of the hydrido analogues,  $(DMPE)_2Ru(H)(X)$ .

In an attempt to generate a strained metallacyclopropene, dichloride **2** was treated with vinyl Grignard reagent to form the divinyl species,  $(PMe_3)_4Ru(CH=CH_2)_2$ (7). However,  $\beta$ -hydrogen elimination to form a metallacycle did not occur. Thermolysis of complex 7 led to the formation of a butadiene complex,  $(PMe_3)_3Ru(\eta^4-C_4H_6)$  (8).

#### Burn et al.

## Results

Synthesis of Trimethylphosphine Complexes. The electron donating, monodentate trimethylphosphine ligand facilitated the addition of a variety of HX complexes to  $(PMe_3)_4Ru(C_2H_4)$  (1) to form  $(PMe_3)_4Ru$ -(H)(X) complexes. Reaction of  $(PMe_3)_4Ru(C_2H_4)$  (1)<sup>9</sup> with one equivalent of *p*-thiocresol in a pentane solution at ambient temperature resulted in the formation of the *p*-thiocresolate hydride complex,  $cis-(PMe_3)_4Ru(H)$ - $(SC_6H_4CH_3)$  (9) in 49% yield as shown in Scheme 1. The reaction occurred rapidly and the yellow product immediately precipitated out of the pentane solution. The presence of the hydride ligand is confirmed by a doublet of doublet of triplets in the <sup>1</sup>H NMR spectrum at  $\delta$  -8.95 (J(triplet) = 28.1 Hz, J(doublet) = 28.1 Hz and 85.1 Hz),the result of coupling to the three types of phosphine ligands. The A<sub>2</sub>MX pattern in the  ${}^{31}P{}^{1}H$  NMR spectrum confirms the cis geometry of complex 9. The phosphine, P<sub>X</sub>, trans to the strongest trans-influence ligand, the hydride, resonates furthest upfield.

In an analogous manner aryloxide complexes *cis*-(PMe<sub>3</sub>)<sub>4</sub>Ru(H)(OC<sub>6</sub>H<sub>4</sub>-*p*-Y) (Y = Cl (10), NO<sub>2</sub> (11)) were prepared by treatment of (PMe<sub>3</sub>)<sub>4</sub>Ru(C<sub>2</sub>H<sub>4</sub>) (1) with the corresponding para-substituted phenol at room temperature in pentane in 45% and 78% isolated yield, respectively. Both complexes display an A<sub>2</sub>MX-type splitting pattern in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and diagnostic hydride resonances in the <sup>1</sup>H NMR spectrum at  $\delta$  -7.8 for 10 and  $\delta$  -8.1 for 11.

Unlike the weakly acidic HXAr complexes, phenyl phosphine reacted with ethylene complex 1 to form fac-(PMe<sub>3</sub>)<sub>3</sub>(PPhH<sub>2</sub>)Ru(H)(PPhH) (**12**) (50% yield), the result of the addition of the P-H bond to the ruthenium center and the exchange of one  $\sigma$ -bound trimethylphosphine for a  $\sigma$ -bound phenylphosphine. The reaction was accompanied by a color change from pale yellow to deep yellow. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a pattern indicating that all of the phosphine groups are magnetically and chemically inequivalent. The phosphide ligand appears furthest upfield as a broad multiplet at  $\delta$  -47.3. The presence of a hydride is confirmed in the <sup>1</sup>H NMR spectrum by a multiplet at  $\delta$  -9.42.

In an attempt to investigate ligand lability in ethylene complex 1, a benzene solution of  $(PMe_3)_4Ru(C_2H_4)$  (1) was heated in the presence of 1 equivalent of  $C_2D_4$  at 45 °C. After 6h  $(PMe_3)_3Ru(C_2H_4)(C_2D_4)$  (13) and free  $PMe_3$  were formed. Identification of 13 is based on comparison to the known complex  $(PMe_3)_3Ru(C_2H_4)_2$ (14).<sup>17</sup> An A<sub>2</sub>B pattern in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum indicates three  $\sigma$ -bound phosphine groups on the ruthenium center and the <sup>1</sup>H NMR spectrum confirms the presence of bound ethylene groups. Free ethylene was not observed. As alluded to previously, thermolysis of a benzene solution of ethylene complex 1 at 90 °C resulted in the initial formation of a mixture of cis- $(PMe_3)_4Ru(Ph)(H)$  (15) and  $(PMe_3)_3Ru(C_2H_4)_2$  (14), which was transformed to pure 15 after 12 h.7 Identification of phenyl hydride 15 was based on a comparison of its

<sup>(11)</sup> Chatt, J.; Davidson, J. M. J. Chem. Soc. 1965, 843.

<sup>(12)</sup> The dihydride was more thoroughly characterized in: Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. J. Am. Chem. Soc. **1976**, 98, 6073.

<sup>(13)</sup> Bergamini, P.; Sostero, S.; Traverso, O. J. Organomet. Chem. 1986, 299, C11.

<sup>(14)</sup> Jones, W. D.; Kosar, W. P. J. Am. Chem. Soc. 1986, 108, 5640.
(15) Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Perutz, R. N.;
Whittlesey, M. K. J. Am. Chem. Soc. 1992, 114, 7425.

<sup>(16)</sup> Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. J. Am. Chem. Soc. 1978, 100, 4080.

<sup>(17)</sup> Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. J. Am. Chem. Soc. **1991**, 113, 3404. We did not determine whether the compound isolated in this reaction is one pure isotopomer or whether it is a statistical mixture of 50% **13** and 25% each of the corresponding bisethylene and bis-tetradeuterioethylene complexes.

 <sup>(18)</sup> Werner, H.; Werner, R. J. Organomet. Chem. 1981, 209, C60.
 (19) Chatt, J.; Hayter, R. G. J. Chem. Soc. 1961, 896.



NMR spectral data to literature data for cis-(PMe<sub>3</sub>)<sub>4</sub>-Ru(Ph)(H).<sup>17</sup>

Attempts to obtain a simple addition product of t-butyl alcohol to 1 were not successful. Instead, formation of cis-(PMe<sub>3</sub>)<sub>4</sub>Ru(C<sub>6</sub>D<sub>5</sub>)(D) (**d**<sub>6</sub>-15), (PMe<sub>3</sub>)<sub>3</sub>Ru(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (14)<sup>17</sup> and free PMe<sub>3</sub> was observed when a d<sub>6</sub>-benzene solution of ethylene complex 1 and t-BuOH was heated to 80 °C led to (Scheme 2). No reaction occurred at room temperature. When the same reactants were heated in  $d_8$ -THF, the products formed were the cyclometalated hydride (PMe<sub>3</sub>)<sub>3</sub>Ru(H)(Me<sub>2</sub>PCH<sub>2</sub>) (16),<sup>18</sup> the bis-ethylene complex 14, and free PMe<sub>3</sub>.

Synthesis of DMPE Complexes. In order to study the effect of the phosphine ligands on the reactivity of ruthenium ethylene complexes, a room temperature synthesis of  $(DMPE)_2Ru(C_2H_4)$  (6) was developed. The reaction of *trans*- $(DMPE)_2RuCl_2$  (17),<sup>19</sup> excess ethylene and sodium in THF afforded complex 6 in 90% isolated yield (Scheme 3). Complex 6 has been reported previously<sup>13,16</sup> although no preparative data were given. Ethylene complex 6 exhibits an AA'XX' splitting pattern in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum but due to similar coupling constants, two pseudo triplets are observed at  $\delta$  43.9 and 37.2.

In contrast to the tetrakis(trimethylphosphine) ruthenium ethylene complex 1, bis(DMPE)ethylene com-

Table 2. Selected Intramolecular Distances (Å) for cis-(DMPE)<sub>2</sub>Ru(CH<sub>2</sub>CH<sub>3</sub>)(SC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>) (18)

	/= : -		<b>-</b>
Ru-S	2.522(3)	$P_1 - C_{10}$	1.869(13)
$Ru-P_1$	2.346(3)	$P_1 - C_{11}$	1.847(13)
Ru-P <sub>2</sub>	2.342(3)	$P_1 - C_{12}$	1.874(13)
Ru-P <sub>3</sub>	2.270(3)	$P_2 - C_{13}$	1.848(14)
Ru-P <sub>4</sub>	2.302(3)	$P_2 - C_{14}$	1.829(12)
$Ru-C_1$	2.230(10)	$P_2 - C_{15}$	1.820(13)
$C_1 - C_2$	1.548(16)	$C_{12} - C_{13}$	1.561(17)
S-C <sub>3</sub>	1.791(11)	$P_3 - C_{16}$	1.834(12)
$C_3 - C_4$	1.398(15)	$P_3 - C_{17}$	1.852(13)
$C_3 - C_8$	1.402(15)	$P_3 - C_{18}$	1.859(11)
$C_4 - C_5$	1.435(15)	$P_4 - C_{19}$	1.843(12)
$C_5 - C_6$	1.404(15)	$P_4 - C_{20}$	1.838(13)
$C_6 - C_7$	1.410(15)	$P_4 - C_{21}$	1.821(12)
$C_7 - C_8$	1.395(15)	$C_{18} - C_{19}$	1.561(16)
$C_6 - C_9$	1.523(16)		

plex **6** reacted with HSC<sub>6</sub>H<sub>4</sub>-*p*-Me in benzene at room temperature (Scheme 4) to afford *cis*-(DMPE)<sub>2</sub>Ru(SC<sub>6</sub>H<sub>4</sub>*p*-Me)(CH<sub>2</sub>CH<sub>3</sub>) (**18**) in 75% yield. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **18** exhibits a six line pattern of multiplets due to the unsymmetrical cis orientation of the phosphorus ligands. Thermolysis of a benzene solution of ethyl thiocresolate **18** at 85 °C for 14 h resulted in the formation of *trans*-(DMPE)<sub>2</sub>Ru(SC<sub>6</sub>H<sub>4</sub>Me)(H) (**19**) (48% yield). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows the characteristic singlet for a trans complex, and the ruthenium hydride signal appears at  $\delta$  –18.01 in the <sup>1</sup>H NMR spectrum.

A suitable crystal of the DMPE ethyl thiolate complex 18 was obtained by crystallization from a benzene/ pentane (1:10) solution at -30 °C, and an X-ray diffraction study of its structure was carried out. Crystal and data collection parameters are provided in Table 1, intramolecular bond distances are tabulated in Table 2, and intramolecular angles are provided in Table 3. An ORTEP drawing of complex 18 is shown in Figure 1. The structure of 18 is approximately octahedral with a Ru-S bond length of 2.552(3) Å and a ruthenium ethyl (Ru-C1) bond length of 2.230(10) Å. The C-C bond length in the ethyl fragment is 1.548(16) Å. The aryl ring is twisted out of the Ru-C1-X plane with a torsion angle between S-Ru-C1-C2 of 106.85(0.77)°.

Addition of one equivalent of aniline to  $(DMPE)_2Ru$ -(C<sub>2</sub>H<sub>4</sub>) (**6**) followed by heating to 120 °C for eight days afforded *cis*-(DMPE)<sub>2</sub>Ru(NHPh)(H) (**20a**), small amounts of the trans isomer **20b** and *cis*-(DMPE)<sub>2</sub>RuH<sub>2</sub>. Complex **20a** was isolated in 45% yield by recrystallization

	C <sub>21</sub> H <sub>44</sub> P <sub>4</sub> RuS (18)	C <sub>18</sub> H <sub>39</sub> NP <sub>4</sub> Ru (20a)	$C_{20}H_{43}P_5Ru(21)$	C <sub>19</sub> H <sub>40</sub> OP <sub>4</sub> Ru (23)	C35H60O3P4Ru <sup>c</sup> (24)
FW	553.6	494.5	539.5	509.5	753.8
cryst system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	P212121	$P2_1/n$	C2/c	$P2_1/n$	$P2_1/n$
a, Å	9.3977(9)	9.496(2)	33.628(7)	12.6944(19)	12.528(8)
b, Å	15.2531(20)	16.714(3)	9.1956(13)	10.5119(16)	18.202(5)
<i>c</i> , Å	18.6320(20)	15.191(5)	18.440(3)	19.456(3)	16.592(5)
a, deg	90.0	90.0	90.0	90.0	90.0
$\beta$ , deg	90.0	99.07(2)	114.910(16)	107.377(13)	98.27(4)
$\gamma$ , deg	90.0	90.0	90.0	90.0	90.0
V, Å <sup>3</sup>	2670.8(8)	2380.9(18)	5172.3(33)	2477.6(14)	3744.4(49)
Z	4	4	8	4	4
size, mm	$0.28 \times 0.28 \times 0.33$	$0.12 \times 0.28 \times 0.35$	$0.25 \times 0.50 \times 0.50$	$0.20 \times 0.27 \times 0.32$	$0.22 \times 0.26 \times 0.38$
color	yellow	brown	yellow	pale yellow	colorless
$d(\text{calc}), \text{g cm}^{-3}$	1.38	1.38	1.39	1.37	1.34
$\mu$ (calc), cm <sup>-1</sup>	8.9	9.1	9.0	8.8	5.8
$2\theta$ between	24° and 28°	24° and 26°	24° and 32°	$24^{\circ}$ and $34^{\circ}$	26° and 32°

Table 1. Crystal Parameters<sup>a,b</sup> for Compounds 18, 20a, 21, 23 and 24

<sup>*a*</sup> Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo K $\alpha$  components of 24 reflections with 2 $\theta$  between the angles listed in the last row of the Table. <sup>*b*</sup> In this and all subsequent tables the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) of the reported value. <sup>*c*</sup> Formula, density and absorption coefficient are all calculated for the pure compound as hydride. The particular crystal studied apparently had 15% chloride impurity.



**Figure 1.** ORTEP diagram of *cis*-(DMPE)<sub>2</sub>Ru(CH<sub>2</sub>CH<sub>3</sub>)-(SC<sub>6</sub>H<sub>4</sub>-*p*-Me) (**18**).

Table 3.	Selected	Intramolecular	Angles	(deg)	for
cis-(DI	MPE)2Ru	(CH <sub>2</sub> CH <sub>3</sub> )(SC <sub>6</sub> H	4-p-CH	) ( <b>1</b> 8)	

S-Ru-P <sub>1</sub>	85.68(10)	$Ru - P_1 - C_{11}$	120.9(4)
S-Ru-P <sub>2</sub>	89.90(10)	$Ru - P_1 - C_{12}$	108.3(4)
S-Ru-P <sub>3</sub>	170.16(10)	$C_{10} - P_1 - C_{11}$	98.9(6)
S-Ru-P <sub>4</sub>	86.17(9)	$C_{10} - P_1 - C_{12}$	100.7(6)
$S-Ru-C_1$	92.3(3)	$C_{11} - P_1 - C_{12}$	100.9(6)
$P_1 - Ru - P_2$	83.51(11)	$Ru - P_2 - C_{13}$	109.2(5)
$P_1 - Ru - P_3$	93.47(11)	$Ru - P_2 - C_{14}$	121.9(4)
$P_1 - Ru - P_4$	96.23(10)	$Ru - P_2 - C_{15}$	122.3(4)
$P_1 - Ru - C_1$	177.8(3)	$C_{13} - P_2 - C_{14}$	98.2(6)
$P_2 - Ru - P_3$	99.75(10)	$C_{13} - P_2 - C_{15}$	100.8(6)
$P_2 - Ru - P_4$	176.08(11)	$C_{14} - P_2 - C_{15}$	100.2(6)
$P_2$ -Ru- $C_1$	95.8(3)	$P_1 - C_{12} - C_{13}$	107.2(9)
$P_3 - Ru - P_4$	84.18(10)	$P_2 - C_{13} - C_{12}$	108.8(9)
$P_3 - Ru - C_1$	88.7(3)	$Ru - P_3 - C_{16}$	123.7(4)
$P_4 - Ru - C_1$	84.3(3)	Ru-P <sub>3</sub> -C <sub>17</sub>	121.1(4)
$Ru-C_1-C_2$	120.1(7)	$Ru - P_3 - C_{18}$	109.7(4)
Ru-S-C <sub>3</sub>	116.6(4)	$C_{16} - P_3 - C_{17}$	97.1(6)
$S-C_3-C_4$	122.4(8)	$C_{16} - P_3 - C_{18}$	101.2(5)
S-C3-C8	117.8(8)	$C_{17} - P_3 - C_{18}$	100.1(5)
$C_4 - C_3 - C_8$	119.7(10)	$Ru - P_4 - C_{19}$	110.4(4)
$C_3 - C_4 - C_5$	119.4(10)	$Ru-P_4-C_{20}$	118.5(4)
$C_4 - C_5 - C_6$	120.7(10)	$Ru-P_4-C_{21}$	121.0(4)
$C_5 - C_6 - C_7$	118.4(10)	$C_{19} - P_4 - C_{20}$	98.9(6)
$C_5 - C_6 - C_9$	120.2(11)	$C_{19} - P_4 - C_{21}$	103.1(6)
$C_7 - C_6 - C_9$	121.3(10)	$C_{20} - P_4 - C_{21}$	101.7(6)
$C_6 - C_7 - C_8$	121.0(11)	$P_3 - C_{18} - C_{19}$	108.9(8)
$C_3 - C_8 - C_7$	120.8(11)	$P_4 - C_{19} - C_{18}$	108.0(8)
$\mathbf{R}_{11} - \mathbf{P}_{1} - \mathbf{C}_{10}$	123 3(4)		

from a benzene/pentane (1/10) mixture. The cis configuration was determined by the ABMX pattern in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The hydride appears as a pseudo doublet of quartets at  $\delta$  -7.26 in the <sup>1</sup>H NMR spectrum. Heating a solution of (DMPE)<sub>2</sub>Ru(C<sub>2</sub>H<sub>4</sub>) and one equivalent of aniline at lower temperature (90 °C) for 5.5 days allowed selective formation of *trans*-(DMPE)<sub>2</sub>Ru(NPhH)(H) (**20b**) in 15% yield (Scheme 4). Under these milder conditions complex **6** was not fully converted to **20b** but the 2:1 mixture of ethylene complex **6** and **20b** was easily separated by recrystallization. Complex **20b** exhibits a singlet in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at  $\delta$  44.5. The hydride appears as a quintet at  $\delta$  -19.13 in the <sup>1</sup>H NMR spectrum.

An X-ray quality crystal of the DMPE anilido hydride **20a** was obtained from a concentrated toluene solution, and its structure was solved by Patterson methods. Crystal and data parameters are provided in Table 1, intramolecular bond distances are tabulated in Table 4 and intramolecular angles are provided in Table 5. An ORTEP drawing of complex **20a** is shown in Figure 2. The structure is approximately octahedral, with a Ru-N bond length of 2.168(9) Å and a Ru-N-C13 bond angle of 132.8(7)°. The hydride was not located.



 Table 4.
 Selected Intramolecular Distances (Å) for

 cis-(DMPE)<sub>2</sub>Ru(H)(NHPh) (20a)

	× ,	<u> </u>	,
$Ru-P_1$	2.298(3)	P3-P8	1.860(13)
Ru-P <sub>2</sub>	2.335(3)	$P_3 - P_9$	1.868(13)
Ru-P <sub>3</sub>	2.244(3)	$P_4 - P_{10}$	1.840(13)
Ru-P <sub>4</sub>	2.274(3)	$P_4 - C_{11}$	1.850(14)
Ru-N	2.168(9)	$P_4 - C_{12}$	1.831(13)
$P_1 - C_1$	1.861(13)	$C_9 - C_{10}$	1.537(16)
$P_1 - C_2$	1.827(15)	$N-C_{13}$	1.345(13)
$P_1 - C_3$	1.848(13)	$C_{13} - C_{14}$	1.419(15)
$P_2 - C_4$	1.872(13)	C13-C18	1.429(15)
$P_2 - C_5$	1.833(13)	$C_{14} - C_{15}$	1.394(16)
$P_2 - C_6$	1.835(13)	C15-C16	1.400(16)
$C_3 - C_4$	1.542(18)	$C_{16} - C_{17}$	1.418(15)
$P_3 - C_7$	1.844(12)	$C_{17} - C_{18}$	1.393(15)

In a manner similar to that used in the reaction with *p*-thiocresol, treatment of  $(DMPE)_2Ru(C_2H_4)$  (6) with PPhH<sub>2</sub> at room temperature led to the formation of  $(DMPE)_2Ru(PPhH)(CH_2CH_3)$  (21) after 30 h. The <sup>31</sup>P-{<sup>1</sup>H} NMR spectrum of this material shows eight complicated multiplets due to the unsymmetrical cis orientation of the phosphorus ligands. The phosphide phosphorus atom resonates far upfield ( $\delta$  -62.5) as a very broad multiplet. The signal due to the hydrogen atom attached to the phosphide ligand appears as a doublet at  $\delta$  2.82 (J = 198 Hz).

A crystal suitable for X-ray determination of the DMPE ethyl phosphide 21 was obtained at -30 °C. Complex 21 crystallized in space group C2/c. An ORTEP drawing of compound 21 is shown in Figure 3. Crystal and data parameters are tabulated in Table 1; intramolecular bond distances and angles are shown in Tables 6 and 7, respectively. As in the case of the ethyl thiocresolate 18, complex 21 is approximately octahedral. The metal phosphide (Ru-P5) bond length in 21 is 2.453(2) Å and the ruthenium ethyl (Ru-C1) distance is 2.225(7) Å. The C-C bond length in the ethyl fragment is 1.556(9) Å. Thermolysis of a THF solution of the ethyl phosphido complex 21 at 90 °C for six days



**Figure 2.** ORTEP diagram of *cis*-(DMPE)<sub>2</sub>Ru(H)(NHPh) (20a).



**Figure 3.** ORTEP diagram of *cis*-(DMPE)<sub>2</sub>Ru(CH<sub>2</sub>CH<sub>3</sub>)-(PPhH) (**21**).

Table 5.	Selected Intramolecular Angles (deg) for
	cis-(DMPE) <sub>2</sub> Ru(H)(NHPh) (20a)

	···· (- · ···/•		
$P_1 - Ru - P_2$	84.56(11)	$Ru-P_3-C_7$	125.9(4)
$P_1 - Ru - P_3$	99.45(12)	$Ru-P_3-C_8$	117.9(4)
$P_1 - Ru - P_4$	173.76(12)	$Ru-P_3-C_9$	109.4(4)
P <sub>1</sub> -Ru-N	89.7(2)	$C_7 - P_3 - C_8$	98.6(5)
$P_2 - Ru - P_3$	96.35(11)	$C_7 - P_3 - C_9$	99.9(6)
$P_2 - Ru - P_4$	100.13(11)	$C_8 - P_3 - C_9$	101.4(6)
P <sub>2</sub> -Ru-N	89.0(3)	$Ru - P_4 - C_{10}$	111.6(4)
$P_3 - Ru - P_4$	84.20(12)	$Ru-P_4-C_{11}$	119.4(4)
P <sub>3</sub> -Ru-N	169.8(2)	$Ru - P_4 - C_{12}$	118.7(5)
P <sub>4</sub> -Ru-N	86.3(2)	$C_{10} - P_4 - C_{11}$	104.2(6)
$Ru-P_1-C_1$	121.7(4)	$C_{10} - P_4 - C_{12}$	101.4(6)
$Ru-P_1-C_2$	117.2(5)	$C_{11} - P_4 - C_{12}$	99.1(6)
$Ru-P_1-C_3$	109.9(4)	$P_3 - C_9 - C_{10}$	108.8(9)
$C_1 - P_1 - C_2$	100.4(6)	$P_4 - C_{10} - C_9$	109.4(9)
$C_1 - P_1 - C_3$	102.4(6)	$Ru-N-C_{13}$	132.8(7)
$C_2 - P_1 - C_3$	102.8(7)	$N-C_{13}-C_{14}$	122.9(10)
$Ru-P_2-C_4$	107.5(4)	$N-C_{13}-C_{18}$	121.5(10)
$Ru-P_2-C_5$	125.0(4)	$C_{14} - C_{13} - C_{18}$	115.6(10)
$Ru-P_2-C_6$	118.9(4)	$C_{13} - C_{14} - C_{15}$	122.2(11)
$C_4 - P_2 - C_5$	101.1(6)	$C_{14} - C_{15} - C_{16}$	121.6(11)
$C_4 - P_2 - C_6$	100.0(6)	$C_{15} - C_{16} - C_1^7$	117.5(11)
$C_5 - P_2 - C_6$	100.4(6)	$C_{16} - C_{17} - C_{18}$	121.0(10)
$P_1 - C_3 - C_4$	110.6(9)	$C_{13} - C_{18} - C_{17}$	122.1(10)
$P_2 - C_4 - C_3$	108.5(9)		

afforded an equilibrium mixture of two products, **22a** and **22b**, in a 2:1 ratio. Although we were not able to separate and fully characterize these materials, the NMR and IR data for this mixture are consistent with the formation of the cis and trans isomers of the corresponding hydrido phosphido complexes  $(DMPE)_2Ru-(PPhH)(H)$ , respectively.

Unlike the reactions of HSAr,  $H_2NPh$ , and  $H_2PPh$ , *p*-cresol reacted with  $(DMPE)_2Ru(C_2H_4)$  to form *trans*- $(DMPE)_2Ru(OC_6H_4-p-CH_3)(H)$  (23) directly. Heating 6

Table 6. Selected Intramolecular Distances (Å) for cis-(DMPE)<sub>2</sub>Ru(CH<sub>2</sub>CH<sub>3</sub>)(PHPh) (21)

			<u> </u>
Ru-P <sub>1</sub>	2.312(2)	P <sub>3</sub> -C <sub>9</sub>	1.858(7)
Ru-P <sub>2</sub>	2.289(2)	$P_3 - C_{10}$	1.839(8)
Ru-P <sub>3</sub>	2.337(2)	$P_3 - C_{11}$	1.845(8)
Ru-P <sub>4</sub>	2.334(2)	$C_{11} - C_{12}$	1.584(12)
Ru-P5	2.453(2)	P4-C12	1.843(9)
$Ru-C_1$	2.225(7)	$P_4 - C_{13}$	1.869(8)
$C_1 - C_2$	1.556(9)	$P_4 - C_{14}$	1.864(8)
$P_1 - C_3$	1.834(8)	$P_5 - C_{15}$	1.835(7)
$P_1 - C_4$	1.847(7)	$C_{15} - C_{16}$	1.402(9)
$P_1 - C_5$	1.866(7)	$C_{15} - C_{20}$	1.399(9)
$C_5 - C_6$	1.555(11)	$C_{16} - C_{17}$	1.408(10)
$P_2 - C_6$	1.849(7)	$C_{17} - C_{18}$	1.378(11)
$P_2 - C_7$	1.840(7)	$C_{18} - C_{19}$	1.416(12)
$P_2 - C_8$	1.836(8)	$C_{19} - C_{20}$	1.399(11)

Table 7. Selected Intramolecular Angles (deg) for cis-(DMPE)<sub>2</sub>Ru(CH<sub>2</sub>CH<sub>3</sub>)(PHPh) (21)

P <sub>5</sub> -Ru-P <sub>4</sub>	87.25(7)	$Ru-P_4-C_{13}$	120.2(3)
$P_5 - Ru - P_3$	86.27(7)	$Ru-P_4-C_{12}$	109.0(3)
$P_5 - Ru - P_1$	174.82(7)	$C_{13} - P_4 - C_{14}$	97.9(4)
$P_5 - Ru - P_2$	90.28(6)	$C_{14} - P_4 - C_{12}$	100.3(4)
$P_5 - Ru - C_1$	92.12(19)	$C_{13} - P_4 - C_{12}$	101.2(4)
$P_3 - Ru - P_4$	83.71(7)	$Ru-P_3-C_{11}$	109.2(3)
$P_1 - Ru - P_4$	93.64(7)	Ru-P <sub>3</sub> -C <sub>9</sub>	122.5(3)
$P_2 - Ru - P_4$	96.51(7)	$Ru - P_3 - C_{10}$	121.3(3)
$P_4 - Ru - C_1$	179.36(19)	$C_9 - P_3 - C_{11}$	99.0(4)
$P_1 - Ru - P_2$	84.55(7)	$C_{10} - P_3 - C_{11}$	101.2(4)
$P_1 - Ru - C_1$	86.99(19)	$C_9 - P_3 - C_{10}$	99.8(4)
$P_1 - Ru - P_3$	98.90(7)	$P_4 - C_{12} - C_{11}$	108.1(6)
$P_2 - Ru - P_3$	176.53(7)	$P_3 - C_{11} - C_{12}$	108.1(5)
$P_3 - Ru - C_1$	96.12(18)	$Ru-P_1-C_3$	125.2(3)
$P_2 - Ru - C_1$	83.63(18)	$Ru-P_1-C_4$	122.0(3)
$Ru-C_1-C_2$	118.7(5)	$Ru-P_1-C_5$	107.8(2)
$Ru-P_5-C_{15}$	117.7(2)	$C_3 - P_1 - C_4$	96.9(4)
$P_5 - C_{15} - C_{16}$	120.2(5)	$C_3 - P_1 - C_5$	101.0(4)
$P_5 - C_{15} - C_{20}$	121.4(5)	$C_4 - P_1 - C_5$	99.6(4)
$C_{16} - C_{15} - C_{20}$	118.1(6)	$Ru-P_2-C_6$	109.1(2)
$C_{15} - C_{16} - C_{17}$	120.5(7)	$Ru-P_2-C_8$	121.2(3)
$C_{16} - C_{17} - C_{18}$	121.6(7)	$Ru - P_2 - C_7$	121.3(3)
$C_{17} - C_{18} - C_{19}$	118.2(7)	$C_6 - P_2 - C_8$	101.0(4)
$C_{18} - C_{19} - C_{20}$	120.3(7)	$C_6 - P_2 - C_7$	101.8(4)
$C_{15} - C_{20} - C_{19}$	121.3(7)	$C_7 - P_2 - C_8$	99.1(4)
$Ru-P_4-C_{14}$	124.5(3)	$P_1 - C_5 - C_6$	107.0(5)
		$P_2 - C_6 - C_5$	108.2(5)

with 1 equivalent of *p*-cresol at 75 °C for 3 h led to the formation of **23** in 71% yield (Scheme 4). An X-ray diffraction study was carried out on a crystal of the hydrido *p*-cresolato complex **23** obtained from a toluene/ pentane (1:10) solution at -30 °C. An ORTEP drawing of **23** is shown in Figure 4, crystal and data parameters are listed in Table 1, and intramolecular bond distances and angles are tabulated in Tables 8 and 9, respectively. The Ru-O bond length is 2.239(2) Å and the Ru-H bond length is 1.63(3) Å. The hydride was located; it lies below the DMPE phosphorus plane and the cresolate oxygen is located above the plane, tilted out of the normal by approximately 15°.

When  $(DMPE)_2Ru(C_2H_4)$  was treated with excess p-cresol at -30 °C rapid precipitation of the salt [trans- $(DMPE)_2Ru(C_2H_4)(H)$ ]<sup>+</sup>[OC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>•2HOC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>]<sup>-</sup> (**24**) (Scheme 4) was observed. Two equivalents of unreacted p-cresol remain hydrogen-bonded to the cresolate counterion of **24** even after recrystallization. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **24** at 25 °C shows a broad singlet at  $\delta$  41.5; the <sup>1</sup>H NMR spectrum displays a singlet at  $\delta$  14.32 for the hydrogen-bonded protons, one broadened multiplet for the ethylene protons at  $\delta$ 1.92 and the hydride multiplet at  $\delta$  -9.88.

An X-ray crystal structure study was carried out on the ethylene hydrido complex 24. Approximately 15%



Figure 4. ORTEP diagram of  $trans-(DMPE)_2Ru(H)(OC_6H_4-p-Me)$  (23).



Figure 5. ORTEP diagram of the cation in [trans- $(DMPE)_2Ru(C_2H_4)(H)^+[OC_6H_4-pMe^2HOC_6H_4-pMe]$  (24).

Table 8.	Selected	Intramolecu	ılar Distanc	ces (A) fo	r
tran	s-(DMPE)	$_{2}Ru(H)(OC)$	$(H_4-p-CH_3)$	(23)	

	<u>, , , , , , , , , , , , , , , , , , , </u>	<u>, , i</u>	<u> </u>
Ru-P <sub>1</sub>	2.289(1)	$P_1 - C_8$	1.832(3)
Ru-P <sub>2</sub>	2.296(1)	$P_1 - C_9$	1.822(3)
Ru-P <sub>3</sub>	2.299(1)	$P_1 - C_{10}$	1.840(3)
Ru–P <sub>4</sub>	2.295(1)	$P_2 - C_{11}$	1.844(3)
Ru-O	2.239(2)	$P_2 - C_{12}$	1.830(3)
Ru-H(Ru)	1.63(3)	$P_2 - C_{13}$	1.829(3)
$O-C_1$	1.302(3)	$C_{10}-C_{11}$	1.518(4)
$C_1 - C_2$	1.404(4)	$P_3 - P_{14}$	1.822(3)
$C_1 - C_6$	1.414(3)	P <sub>3</sub> -C <sub>15</sub>	1.819(3)
$C_2 - C_3$	1.386(4)	$P_3 - P_{16}$	1.846(3)
$C_3 - C_4$	1.381(4)	$P_4 - C_{17}$	1.848(3)
$C_4 - C_5$	1.389(4)	P4-C18	1.822(3)
$C_4 - C_7$	1.508(4)	P4C19	1.821(3)
$C_5 - C_6$	1.373(4)	$C_{16} - C_{17}$	1.514(4)

of the hydride sites in the crystal examined contained chloride presumably derived from the  $CH_2Cl_2$  used in crystallization. Although we were not able to obtain NMR evidence for the chloride contaminant, mass spectral analysis registered the chloride impurity. An ORTEP drawing of the organometallic portion of **24** is shown in Figure 5, and an ORTEP diagram of the hydrogen-bonded *p*-cresolate anion is provided in Figure 6. The crystal and data collection parameters are given in Table 1; the intramolecular bond distances are tabulated in Tables 10 and 12 and the intramolecular



**Figure 6.** ORTEP diagram of the anion  $[p-Me-C_6H_4O\cdot 2HOC_6H_4-p-Me]^-$  in **24**.

Table 9. Selected Intramolecular Angles (deg) for trans-(DMPE)<sub>2</sub>Ru(H)(OC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>) (23)

$P_1 - Ru - P_2$	84.16(2)	$Ru-P_1-C_9$	119.85(11)
$P_1 - Ru - P_3$	94.45(2)	$Ru-P_1-C_{10}$	108.84(9)
$P_1 - Ru - P_4$	175.68(2)	$C_8 - P_1 - C_9$	100.64(15)
P <sub>1</sub> -Ru-O	100.80(5)	$C_8 - P_1 - C_{10}$	102.07(14)
$P_1-Ru-H$	85.7(10)	$C_9 - P_1 - C_{10}$	102.38(14)
$P_2 - Ru - P_3$	173.78(2)	$Ru - P_2 - C_{11}$	109.69(8)
$P_2 - Ru - P_4$	96.28(2)	$Ru-P_2-C_{12}$	116.69(10)
P <sub>2</sub> -Ru-O	106.43(5)	$Ru - P_2 - C_{13}$	123.94(11)
$P_2$ -Ru-H	85.6(10)	$C_{11} - P_2 - C_{12}$	100.56(14)
$P_3 - Ru - P_4$	84.66(2)	$C_{11} - P_2 - C_{13}$	102.39(13)
P3-Ru-O	79.79(5)	$C_{12} - P_2 - C_{13}$	100.38(14)
P <sub>3</sub> -Ru-H	88.2(10)	$P_1 - C_{10} - C_{11}$	110.16(18)
P4-Ru-O	83.21(5)	$C_{10} - C_{11} - P_2$	108.82(18)
P <sub>4</sub> -Ru-H	90.0(10)	$Ru - P_3 - C_{14}$	119.64(13)
O-Ru-H	166.7(10)	$Ru - P_3 - C_{15}$	120.41(12)
$Ru-O-C_1$	137.58(16)	$Ru - P_3 - C_{16}$	107.83(11)
$O - C_1 - C_2$	124.5(2)	$C_{14} - P_3 - C_{15}$	102.24(19)
$O - C_1 - C_6$	120.4(2)	$C_{14} - P_3 - C_{16}$	101.69(16)
$C_2 - C_1 - C_6$	115.1(2)	$C_{15} - P_3 - C_{16}$	102.26(18)
$C_1 - C_2 - C_3$	121.8(2)	$Ru - P_4 - C_{17}$	108.87(10)
$C_2 - C_3 - C_4$	122.3(3)	$Ru-P_4-C_{18}$	117.14(13)
$C_3 - C_4 - C_5$	116.6(2)	$Ru-P_4-C_{19}$	122.77(12)
$C_3 - C_4 - C_7$	121.7(3)	$C_{17} - P_4 - C_{18}$	102.52(19)
$C_5 - C_4 - C_7$	121.7(3)	$C_{17} - P_4 - C_{19}$	101.33(16)
$C_4 - C_5 - C_6$	122.0(3)	$C_{18} - P_4 - C_{19}$	101.44(19)
$C_1 - C_6 - C_5$	122.2(3)	$P_3 - C_{16} - C_{17}$	109.16(21)
$Ru-P_1-C_8$	120.37(11)	$C_{16} - C_{17} - P_4$	109.80(20)

 Table 10.
 Selected Intramolecular Distances (Å) for

 [trans-(DMPE)<sub>2</sub>Ru(C<sub>2</sub>H<sub>4</sub>)(H)]<sup>+</sup> (24)

Ru-P <sub>1</sub>	2.328(3)	$P_2 - C_6$	1.834(9)
Ru-P <sub>2</sub>	2.324(2)	$P_2 - C_7$	1.827(10)
Ru-P <sub>3</sub>	2.314(3)	$P_2 - C_8$	1.842(10)
Ru-P <sub>4</sub>	2.317(2)	$C_5 - C_6$	1.550(12)
$Ru-C_1$	2.265(10)	$P_3 - C_9$	1.844(10)
$Ru-C_2$	2.269(10)	$P_3 - C_{10}$	1.843(10)
Ru-Cl**	2.425(15)	$P_3 - C_{11}$	1.862(10)
$C_1 - C_2$	1.430(12)	$P_4 - C_{12}$	1.847(10)
$P_1 - C_3$	1.826(11)	P4-C13	1.842(12)
$P_1 - C_4$	1.840(10)	$P_4 - C_{14}$	1.852(11)
$P_1 - C_5$	1.847(9)	$C_{11} - C_{12}$	1.540(13)

angles in Tables 11 and 13. The structure of 24 is pseudo-octahedral, with the ethylene ligand occupying an axial position and exhibiting nearly identical Ru-C distances of 2.26 and 2.27 Å. The ethylene C-C bond distance is 1.43 Å. These values should be interpreted with caution because of the 15% chloride impurity in the crystal.

Table 11. Selected Intramolecular Angles (deg) for [trans-(DMPE)<sub>2</sub>Ru(C<sub>2</sub>H<sub>4</sub>)(H)]<sup>+</sup> (24)

$P_1$ -Ru- $P_2$	83.69(8)	$C_4 - P_1 - C_5$	100.1(4)
$P_1 - Ru - P_3$	171.28(10)	$Ru-P_2-C_6$	109.3(3)
$P_1 - Ru - P_4$	95.90(9)	$Ru-P_2-C_7$	116.9(3)
$P_1 - Ru - C_1$	93.7(3)	$Ru-P_2-C_8$	122.4(3)
$P_1-Ru-C_2$	93.3(3)	$C_6 - P_2 - C_7$	102.0(4)
$P_2 - Ru - P_3$	94.73(9)	$C_6 - P_2 - C_8$	102.4(4)
$P_2 - Ru - P_4$	164.35(9)	$C_7 - P_2 - C_8$	101.2(4)
$P_2 - Ru - C_1$	116.16(24)	$P_1 - C_5 - C_6$	111.0(6)
$P_2 - Ru - C_2$	79.54(24)	$P_2 - C_6 - C_5$	108.7(6)
$P_3 - Ru - P_4$	83.30(9)	$Ru-P_3-C_9$	119.1(3)
$P_3 - Ru - C_1$	94.64(25)	$Ru - P_3 - C_1^0$	120.0(3)
$P_3 - Ru - C_2$	94.85(25)	$Ru - P_3 - C_{11}$	110.4(3)
$P_4 - Ru - C_1$	79.49(24)	$C_9 - P_3 - C_{10}$	101.6(4)
$P_4 - Ru - C_2$	116.07(24)	$C_9 - P_3 - C_{11}$	100.2(4)
$C_1 - Ru - C_2$	36.8(3)	$C_{10} - P_3 - C_{11}$	102.6(4)
**Cl-Ru-P1	81.8(4)	$Ru - P_4 - C_{12}$	109.0(3)
**Cl-Ru-P2	85.2(3)	Ru-P4-C13	115.8(4)
**Cl-Ru-P3	89.5(4)	$Ru-P_4-C_{14}$	123.0(4)
**Cl-Ru-P4	79.3(3)	$C_{12} - P_4 - C_{13}$	101.5(5)
$Ru-P_1-C_3$	120.0(3)	$C_{12} - P_4 - C_{14}$	102.1(5)
$Ru - P_1 - C_4$	119.5(3)	$C_{13} - P_4 - C_{14}$	102.7(5)
$Ru-P_1-C_5$	109.5(3)	$P_3 - C_{11} - C_{12}$	109.4(7)
$C_3 - P_1 - C_4$	101.6(5)	$P_4 - C_{12} - C_{11}$	108.5(6)
$C_3 - P_1 - C_5$	103.4(5)		/

Table 12. Selected Intramolecular Distances (Å) for  $[(p-CH_3-C_6H_4O)-2HOC_6H_4-p-CH_3]^-$  (24)

C <sub>101</sub> -O <sub>1</sub>	1.365(10)	C <sub>203</sub> -C <sub>204</sub>	1.411(12)
$C_{101} - C_{102}$	1.413(12)	$C_{204} - C_{205}$	1.393(12)
$C_{101} - C_{106}$	1.385(12)	$C_{204} - C_{207}$	1.554(13)
$C_{102} - C_{103}$	1.411(12)	$C_{205} - C_{206}$	1.403(12)
$C_{103} - C_{104}$	1.379(12)	C <sub>301</sub> -O <sub>3</sub>	1.360(10)
$C_{104} - C_{105}$	1.406(12)	$C_{301} - C_{302}$	1.386(12)
$C_{104} - C_1^{07}$	1.533(12)	$C_{301} - C_{306}$	1.406(12)
$C_{105} - C_{106}$	1.401(12)	$C_{302}-C_{303}$	1.419(12)
$C_{201} - O_2$	1.342(10)	C303-C304	1.393(13)
$C_{201} - C_{202}$	1.396(12)	C304-C305	1.391(12)
$C_{201} - C_{206}$	1.406(12)	$C_{304} - C_{307}$	1.519(13)
$C_{202} - C_{203}$	1.422(12)	C305-C306	1.420(12)
		O <sub>1</sub> •••O <sub>2</sub>	2.479(8)
		O <sub>2</sub> ···O <sub>3</sub>	2.543(9)

Table 13. Selected Intramolecular Angles (deg) for  $[p-CH_3-C_6H_4O-2HOC_6H_4-p-CH_3]^-$  (24)

$C_{101} - O_1 - O_2$	113.1(5)	$C_{201} - C_{202} - C_{203}$	119.8(8)
$C_{201} - O_2 - O_1$	121.1(5)	$C_{202} - C_{203} - C_{204}$	120.7(8)
$C_{201} - O_2 - O_3$	122.2(5)	$C_{203} - C_{204} - C_{205}$	118.6(8)
$C_{301} - O_3 - O_2$	113.1(5)	$C_{203} - C_{204} - C_{207}$	120.8(8)
$O_1 - C_{101} - C_{102}$	118.3(8)	$C_{205} - C_{204} - C_{207}$	120.5(8)
$O_1 - C_{101} - C_{106}$	121.6(8)	$C_{204} - C_{205} - C_{206}$	121.1(8)
$C_{102} - C_{101} - C_{106}$	120.1(8)	$C_{201} - C_{206} - C_{205}$	120.5(8)
$C_{101} - C_{102} - C_{103}$	118.7(8)	$O_3 - C_{301} - C_{302}$	118.5(8)
$C_{102} - C_{103} - C_{104}$	122.0(8)	$O_3 - C_{301} - C_{306}$	120.9(8)
$C_{103} - C_{104} - C_{105}$	118.0(8)	C302-C301-C306	120.5(8)
$C_{103} - C_{104} - C_{107}$	121.5(8)	$C_{301} - C_{302} - C_{303}$	119.9(8)
$C_{105} - C_{104} - C_{107}$	120.5(8)	C302-C303-C304	120.8(9)
$C_{104} - C_{105} - C_{106}$	121.4(9)	$C_{303} - C_{304} - C_{305}$	118.5(9)
$C_{101} - C_{106} - C_{105}$	119.7(8)	$C_{303} - C_{304} - C_{307}$	120.7(8)
$O_2 - C_{201} - C_{202}$	120.1(8)	$C_{305} - C_{304} - C_{307}$	120.7(9)
$O_2 - C_{201} - C_{206}$	120.5(8)	C <sub>304</sub> -C <sub>305</sub> -C <sub>306</sub>	121.9(9)
$C_{202} - C_{201} - C_{206}$	119.4(8)	$C_{301} - C_{306} - C_{305}$	118.3(8)

Synthesis of Divinyl Complex (PMe<sub>3</sub>)<sub>4</sub>Ru(CH= CH<sub>2</sub>)<sub>2</sub> (7) and Its Conversion to Butadiene Complex (PMe<sub>3</sub>)<sub>3</sub>Ru( $\eta^4$ -C<sub>4</sub>H<sub>6</sub>) (8). Treatment of (PMe<sub>3</sub>)<sub>4</sub>-RuCl<sub>2</sub> (2) with two equivalents of CH<sub>2</sub>CHMgCl at room temperature afforded *cis*-(PMe<sub>3</sub>)<sub>4</sub>Ru(CH=CH<sub>2</sub>)<sub>2</sub> in 50% yield (Scheme 5). The cis orientation of 7 was confirmed by the A<sub>2</sub>X<sub>2</sub> splitting pattern in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum.

Thermolysis of a benzene solution of divinyl complex 7 for two days at 80 °C yielded an orange solution that exhibited an  $A_2B$  pattern in the  ${}^{31}P{}^{1}H$  NMR spectrum. The presence of free PMe<sub>3</sub> in both the  ${}^{31}P{}^{1}H$  and  ${}^{1}H$ 

Scheme 5



NMR spectra indicated the dissociation of a phosphine group. Cooling a hexane solution of the product of this reaction afforded pure butadiene complex 8a in 48% isolated yield. The <sup>1</sup>H NMR spectrum shows a doublet at  $\delta$  1.37, corresponding to the unique PMe<sub>3</sub> group trans to the butadiene ligand, and a virtual triplet at  $\delta$  1.01 for the methyl groups on the mutually trans phosphine ligands. The <sup>1</sup>H and <sup>13</sup>C $\{$ <sup>1</sup>H $\}$  NMR spectra are consistent with the formation of a butadiene complex (8a, Scheme 5). The assignment of peaks in the <sup>1</sup>H NMR spectrum was made in analogy to the known Ru(CO)3-(butadiene),<sup>20</sup> formed from the reaction of  $Ru_3(CO)_{12}$  and 1,3-butadiene.<sup>20</sup> The difference in the  ${}^{13}C{}^{1}H$  NMR chemical shifts of the butadiene carbons ( $\delta$  79.1 (CH) and  $\delta$  28.9 (CH<sub>2</sub>)) and the lack of coupling in the <sup>1</sup>H NMR spectrum suggest that the structure is that of a chelating butadiene with substantial metallacyclopentene character (8a and 8b, Scheme 5).

## Discussion

**Trimethylphosphine Complexes.** The reactions of  $(PMe_3)_4Ru(C_2H_4)$  (1) can be divided into two groups: those that occur at 25 °C and those that occur at higher temperatures. We consider the room temperature reactions first.

Previous studies on the reactivity of  $(PMe_3)_4Ru(C_2H_4)$ (1) showed that the ethylene complex readily reacts with *p*-cresol at room temperature to form the cresolate hydride by a protonation mechanism.<sup>7</sup> We find that treatment of ethylene complex 1 with *p*-thiocresol, *p*-chlorophenol, or *p*-nitrophenol at room temperature resulted in the immediate conversion of 1 to the hydrides  $(PMe_3)_4Ru(H)(ZC_6H_4-p-Y)$  (9, Z = S, Y = CH<sub>3</sub>; 10, Z = O, Y = Cl; 11, Z = O, Y = NO<sub>2</sub>). Similarities between the reaction conditions and the presence of an acidic hydrogen in the organic reagent support a mechanism analogous to that in the *p*-cresol reaction<sup>7</sup> despite

<sup>(20)</sup> Zobl-Ruh, S.; vonPhilipsborn, W. Helv. Chim. Acta 1980, 63, 773.

the large differences in  $pK_a$ 's of the acidic hydrogens. The mechanism proposed for the reaction of *p*-cresol involves initial protonation of the electron-rich ruthenium center by HXAr, followed by ethylene insertion to form a possible ruthenium ethyl cresolate intermediate, *cis*-(PMe<sub>3</sub>)<sub>4</sub>Ru(Et)(OC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>). This is supported by the studies done on the bis(DMPE) complexes discussed in the next section. Ionization of the aryloxide to form an ion pair [(PMe<sub>3</sub>)<sub>4</sub>Ru(Et)]<sup>+</sup>[OAr]<sup>-</sup> would facilitate  $\beta$ -hydride elimination to form the observed product **3** (Scheme 6).

Addition of *p*-thiocresol to the *p*-cresolate complex **3** resulted in the complete conversion to the *p*-thiolato complex **9** and *p*-cresol (eq 1) at room temperature. The facility of this process is a consequence of the formation of (a) a stronger O-H bond relative to an S-H bond and (b) a stronger Ru-S bond compared to a Ru-O bond.<sup>21</sup>



Studies performed on the related metal-hydroxy and metal-thiol systems suggest that the stronger interaction between the soft sulfur atom and the soft metal center is a result of more covalent character in the metal sulfur bond. $^{6,22-24}$ 

The reaction of ethylene complex 1 with one equivalent of phenylphosphine also occurs readily at room temperature. Neither dissociation of trimethylphosphine nor dissociation of ethylene from 1 occurs at this temperature. However, the fact that the phosphinesubstituted complex (PMe<sub>3</sub>)<sub>3</sub>(PPhH<sub>2</sub>)Ru(H)(PPhH) (12) is the final product suggests that the mechanism is more complicated than a simple protonation reaction. No mechanistic studies were performed as hydrido phosphido 12 is relatively unstable at room temperature and decomposes in solution to a complex mixture of products after 15 min. Support for the formation of an intermediate ethyl phosphide species was obtained, however, by reactivity studies in the bis(DMPE) system discussed in the next section.  $\beta$ -Hydride elimination to form the phosphido hydride followed by phosphine exchange of one PMe<sub>3</sub> by PhPH<sub>2</sub> is one possible pathway to the final product 12 (Scheme 7). Electron donation from the phosphido phosphorus atom may make the ruthenium center in (PMe<sub>3</sub>)<sub>4</sub>Ru(H)(PPhH) more substitutionally labile than that in 1.

At temperatures above 25 °C, the ethylene complex 1 can react by a number of pathways as seen from the product distributions in the following reactions. Deuterated ethylene displaces one phosphine ligand to form the bis(ethylene) complex 13 (Scheme 1) at 45 °C. At temperatures above 90 °C in benzene, ethylene complex 1 leads to phenyl hydride 15.7 Complex 15 has been previously prepared from the reaction of the tetrakis-(trimethylphosphine) ruthenium benzyne complex with *n*-propanol.<sup>17</sup> Detailed studies of the reductive elimina-



tion reaction of the phenyl hydride 15 to form benzene and the cyclometalated hydride 16 (eq 2) were reported



previously.<sup>25</sup> We propose that at 90 °C, dissociation of free ethylene forms an L<sub>4</sub>Ru intermediate that can activate the benzene solvent to form the phenyl hydride. The free ethylene liberated reacts with  $(PMe_3)_4Ru(C_2H_4)$  to form the bis(ethylene) complex,  $(PMe_3)_3Ru(C_2H_4)_2$ , and free PMe<sub>3</sub>.

**DMPE Complexes.** The behavior of bis(DMPE) system provides a useful comparison with that of the tetrakis(trimethylphosphine) system. The enhanced stability of the DMPE complexes, attributed to the chelate effect of the bidentate ligand, makes phosphine dissociation pathways less feasible and facilitates the isolation of intermediates, such as the cationic ethylene hydrido and ethyl complexes, not observed in the trimethylphosphine system.

Although  $(DMPE)_2Ru(C_2H_4)$  (6) has been mentioned previously in the literature,<sup>13,16</sup> we have found a new route to complex 6 (Scheme 3) and have explored its reactivity with various HX complexes (Scheme 4). Complex 6 readily reacts with *p*-thiocresol at room temperature to form  $(DMPE)_2Ru(SC_6H_4-p-CH_3)(Et)$  (18). Thermolysis of complex 18 at 85 °C for 14 h results in the loss of ethylene and the formation of *trans*- $(DMPE)_2RuH(SAr)$  (19) (Ar = C<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>, Scheme 4). By contrast, we have not observed the ethyl species in the reaction of the tetrakis(trimethylphosphine) ethylene complex 1 and HSC<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub>, where the reaction occurred rapidly at room temperature to form only the corresponding hydride complex (Scheme 1).

PPhH<sub>2</sub> reacted with bis(DMPE) ethylene complex **6** in a manner analogous to *p*-thiocresol, leading at room temperature to the ethyl phosphido complex **21**. Complex **21** is stable at room temperature and only undergoes  $\beta$ -hydride elimination at temperatures above 60 °C to form a mixture of *trans* and *cis*-(DMPE)<sub>2</sub>Ru(H)-(PHPh) (**22a** and **22b**). Unlike the trimethylphosphine

<sup>(21)</sup> Huheey, J. E.; Keiter, E. A.; Keiter, R. L. Inorganic Chemistry: Principles of Structure and Reactivity; 4th ed.; Harper and Row: New York, 1993, Ch. 9.

<sup>(22)</sup> Pearson, R. G. J. Chem. Ed. 1968, 45, 581.

<sup>(23)</sup> Pearson, R. G. J. Chem. Ed. 1968, 45, 643.

<sup>(24)</sup> Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. J. Am. Chem. Soc. 1993, 115, 5875.

<sup>(25)</sup> Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. J. Am. Chem. Soc. 1991, 113, 6492.



system, phosphine substitution of the DMPE ligands by PPhH<sub>2</sub> was not observed.

In contrast to the reactions of *p*-thiocresol and PPhH<sub>2</sub>, aniline does not react with ethylene complex **6** at room temperature. However, at 90 °C formation of the anilido hydride (DMPE)<sub>2</sub>Ru(NPhH)(H) (**20b**) is observed. Monitoring the reaction by <sup>1</sup>H NMR spectrometry showed that the trans isomer **20b** is formed initially and subsequently rearranges to the cis form **20a**, suggesting that trans **20b** is the kinetic product of the reaction of **6** and aniline. This indicates that the reaction does not proceed by direct oxidative addition as is presumed in the case of the (PMe<sub>3</sub>)<sub>4</sub> analogue.<sup>7</sup>

The reaction of  $HOC_6H_4$ -*p*-CH<sub>3</sub> with bis(DMPE) ethylene complex **6** at room temperature slowly forms the *p*-cresolate hydride **23** with no observable rutheniumethyl species. However, at low temperature only the protonated ethylene hydride cation **24** is formed, presumably due to stabilization of the cresolate counterion by unreacted *p*-cresol. At room temperature, the reaction proceeded slowly to afford the *p*-cresolate hydride **23** with no observable ruthenium ethyl species as a second intermediate.

The isolation of the ethyl thiocresolate 18, ethyl phosphide 21, and ethylene hydride cation 24 provides some insight regarding the mechanism of reactions of weakly acidic reagents with 6 (Scheme 8). As previously mentioned, we propose that  $(PMe_3)_4Ru(C_2H_4)$  (1) reacts by initial protonation of the metal center to form an ethylene-hydrido cationic complex (25, Scheme 6), which may undergo reversible ethylene insertion to form the corresponding ruthenium ethyl species. Loss of ethylene from the ethylene-hydride cation leads to the neutral hydride product 27. However, these proposed intermediates were not observed in the tetrakis(trimethylphosphine) system. The increased stability of the bis(DMPE) complexes allows for the isolation of the intermediate ethyl species, (DMPE)<sub>2</sub>Ru(Et)(X), and ethylene species  $[(DMPE)_2Ru(H)(C_2H_4)]^+[OC_6H_4-p-CH_3]^+$ 2HOC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>]<sup>-</sup> and provides support for the mechanistic hypothesis.

A number of complexes similar to the protonated ethylene species 24 are known, and the reversible migratory insertion process of metal-complexed alkene into an M-H bond has been studied extensively.<sup>26-32</sup> Whether the Ru ethyl or the Ru ethylene hydride cationic complex is isolated must in part be controlled by the ability of the counteranion to coordinate to the protonated metal center. Soft-soft interactions, such as Ru-S and Ru-P, favor the ethyl species. By comparison, the soft-hard Ru-O interaction that would be present with *p*-cresolate as the counterion provides less driving force for insertion, and the ionic intermediate is isolated.

X-ray Structures of 18, 21, 20a, 23, and 24. X-ray structural analyses of the ethyl thiolate 18 and the ethyl phosphide 21 reveal that these complexes are very similar. Although a slightly shorter Ru-S distance might be expected, based on the smaller atomic radius of sulfur compared to phosphorus,<sup>21</sup> the Ru-P bond is significantly shorter than the Ru-S bond (Ru-P = 2.453-(2) compared to Ru-S = 2.522(3) Å) suggesting the presence of some multiple bond character in the Ru-P bond (see discussion below). The Ru-ethyl bond lengths in complexes 18 (2.230(10) Å) and 21 (2.225(7) Å) are not statistically different despite the change in environment at the metal center. These bond lengths are slightly longer than the metal-ethyl bond distances in other ruthenium-ethyl compounds such as  $Ru(Et)_2(t Bu_2bipy_2$  where the Ru-Et distances are 2.138(7) and 2.142(8) Å.33

The Ru-P distances in the structures of both 18 and 21 reflect the relative trans influence properties of the various ligands. Comparison of the tabulated data of the Ru-P bond distances trans to the ethyl groups, or to another phosphine ligand, reveal the increasing trans influence trend SAr < phosphine  $\approx$  phosphide  $\approx$  ethyl.<sup>1</sup> The Ru-S-C angle in 18 is 116.6 (4)° and the Ru-P-C angle in 21 is 117.7 (2)°, indicating that this angle is not particularly sensitive to the difference in  $\pi$ -donating abilities of the thiolate and phosphide ligands.

There are only a few examples in the literature of structurally characterized terminal phosphidometal complexes.<sup>8,34-37</sup> A terminal phosphido-ligand in an  $L_nM$ -PR<sub>2</sub> complex can be either planar or pyramidal at phosphorus. A planar phosphorus center (A) should

$$LnM = P \overset{R}{\underset{(A)}{\leftarrow}} LnM \overset{P}{\underset{(A)}{\leftarrow}} LnM \overset{P}{\underset{(A)}{\leftarrow}} R$$

have a short M-P bond length and a large (approx. 130°) M-P-R bond angle. In contrast, a longer M-P bond length and a smaller (<114°) M-P-R angle would be consistent with a pyramidal phosphorus center (B). The Ru-P5 (phosphide) bond length in **21** is 2.453(2) Å, longer than the Ru-P (phosphine) distances in the literature that range from 2.289–2.337 Å, and the Ru-P5-Ar(C15) angle is 117.7(2)°. Although the phosphorusbound hydrogen was not located, the structure appears

- (28) Benfield, R. E.; Cragg, H. R.; Jones, R. G.; Swain, A. C. Nature **1991**, 353, 340.
- (29) Werner, H.; Feser, R. Angew. Chem. Int. Ed. (Engl.) 1979, 18, 157.
  - (30) Werner, H.; Werner, R. J. Organomet. Chem. **1979**, 174, C63. (31) Werner, H.; Feser, R. J. Organomet. Chem. **1982**, 232, 351.
  - (31) Werner, H.; Feser, R. J. Organomet. Chem. **1982**, 232, 351. (32) Doherty, N. M.; Bercaw, J. E. J. Am. Chem. Soc. **1985**, 107.
- 2670.
- (33) Black, S. I.; Skapski, A. C.; Young, G. B. J. Chem. Soc., Chem. Commun. 1989, 911.
- (34) Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. J. Am. Chem. Soc. 1985, 107, 4670.
  - (35) Stephen, D. W.; Ho, J. Organometallics 1992, 11, 1014.

<sup>(26)</sup> Byrne, J. W.; Kress, J. R. M.; Osborn, J. A.; Ricard, L.; Weiss, R. E. J. Chem. Soc., Chem. Comm. 1977, 662.

<sup>(27)</sup> Brookhart, M.; Lincoln, M. J. Am. Chem. Soc. 1988, 110, 8719.

<sup>(36)</sup> Weber, L.; Meine, G.; Boese, R.; Augart, N. Organometallics 1987, 6(12), 2484.

<sup>(37)</sup> Vaughan, G. A.; Hillhouse, G. L.; Rheingold, A. L. Organomet. 1989, 8, 1760.

to be consistent with a phosphorus center that has a pyramidal geometry (B). However, the short Ru-P (phosphide) bond length suggests some double bond character may be present in the metal-phosphide bond.

In contrast the metal-nitrogen bond distance in 20a is very similar to that of the previously reported tetrakis(trimethylphosphine) analogue (Ru-N 2.160(6) Å).<sup>7</sup> The Ru-P3 (trans to the amido ligand) distance of 2.244(3) Å in 20a is similar to Ru-P3 (trans to the thiocresolate group) in 18 (2.270(3) Å) and consistent with a comparable trans influence. A Ru-P2 distance of 2.335(3) Å (trans to the hydride ligand, which was not located in the structural study) is slightly longer than the Ru-P distances in 18 and 21 trans to the ethyl ligand, also in accord with the expectedly stronger trans influence of H relative to  $C^{1}$ 

In comparison to  $(PMe_3)_4Ru(H)(OC_6H_4-p-CH_3)^7$ , the structure of  $trans-(DMPE)_2Ru(H)(OC_6H_4-p-CH_3)$  (23) shows the Ru-O bond length of 2.239(2) Å to be slightly longer and the Ru-O-Cipso bond angle of 137.9(4)° slightly larger than that in the cis tetrakis(trimethylphosphine) analog. The increased bond length could be attributed to the trans influence of the hydride ligand. One unusual feature of the structure is the 15.4° tilt of the Ru-O vector from the normal to the phosphorus plane in the direction between P3 and P4. This detail is ascribed in part to steric interaction between the *p*-cresolate phenyl ring and the DMPE methyl groups. The Ru-H distance of 1.63(3) Å is slightly smaller than that for the related PMe<sub>3</sub> complex.<sup>7</sup>

The most unique structure described in this paper<sup>38</sup> is the cationic complex,  $[trans-(DMPE)_2Ru(C_2H_4)(H)]^+$ - $[OC_6H_4-p-CH_3+2HOC_6H_4-p-CH_3]^-$  (24). Analysis of the X-ray data for this structure detected approximately 15% chloride presence in the hydride position. The source of chloride is undoubtedly the  $CH_2Cl_2$  used as a recrystallization solvent as no halogenated solvents were used in the synthesis of the complex. The hydridechloride exchange suggests a fairly reactive hydride. The Ru-C1 and Ru-C2 bond lengths are 2.265(10) Å and 2.269(10) Å, respectively, and the ethylene C1-C2 bond distance is 1.430(12) Å. The  $[OC_6H_4-p-CH_3\cdot 2HOC_6H_4$ p-CH<sub>3</sub>]<sup>-</sup> counter-ion is propeller shaped; the O1-O2 and O2-O3 distances of 2.479(8) Å and 2.543(9) Å, respectively, constitute examples of very strong hydrogen bonding.<sup>39</sup>

Behavior of Divinyl Complex 7. It was initially hoped that, in a manner similar to the reaction with EtMgCl, reaction of dichloride 2 with vinylmagnesium bromide would yield a metallacyclopropene. However, the product isolated was the divinyl species, (PMe<sub>3</sub>)<sub>4</sub>- $Ru(CH=CH_2)_2$  (7). Thermolysis of 7 could result in either coupling of the vinylic groups to give a butadiene ligand or loss of one of the vinyl groups as ethylene to give a metallacyclopropene, analogous to preparation of the benzyne complex (23) from  $(PMe_3)_4Ru(Ph)_2$   $(24).^{17}$ In the event, thermolysis of 7 in benzene led to the formation of butadiene complex 8. Spectroscopic details indicate that the chelating butadiene ligand has substantial metallacyclopentene character.<sup>20</sup>

The most plausible mechanism for the formation of butadiene 8 would be a direct concerted C-C reductive elimination of the two vinyl ligands to form the butadiene species. Although C-C reductive elimination is not as well known as C-H reductive elimination for ruthenium complexes it has been invoked in a number of other systems such as the thermolysis of (alkyl)(acyl)rhenium complexes to form ketones.40 Butadiene complexes of transition metals are well known and are typically prepared by the reaction of butadiene with a coordinatively unsaturated metal species.<sup>20,41-44</sup> However, there is literature precedent for butadiene species formed from C-C coupling reactions. For example, addition of diphenylacetylene to Cp(PPh<sub>3</sub>)Co(Me)<sub>2</sub> forms  $Cp(PPh_3)Co(C_4Ph_4)^{45,46}$  and  $Cp_2MCl_2$  (M = Zr or Hf) reacts with CH<sub>2</sub>CHLi to form Cp<sub>2</sub>M(C<sub>4</sub>H<sub>6</sub>).<sup>47</sup> Interestingly, in direct contrast to the formation and relative stability of divinyl complex 7, intermediate divinyl species are not observed in the Co, Zr or Hf cases.

#### Summary

The reactivity of two strained phosphine-substituted ruthenium metallacyclopropanes (or ruthenium ethylene species) has been explored. The reactivity depends dramatically upon whether four PMe<sub>3</sub> ligands or two bis-dimethylphosphinoethane (DMPE) ligands are bound to ruthenium. For example, stable intermediate ethyl complexes could be isolated from the reaction of a variety of HX compounds (X = SAr, OAr, PPhH) with  $(DMPE)_2Ru(C_2H_4)$  (6). Thermolysis of  $(DMPE)_2Ru(Et)$ - $(SC_6H_4-p-Me)$  resulted in the formation of the hydride,  $trans-(DMPE)_2Ru(H)(SC_6H_4-p-Me)$ . In contrast, reactions of  $(PMe_3)_4Ru(C_2H_4)$  (1) with HX immediately resulted in the formation of the hydride species, and no ethyl intermediates could be observed.

A possible mechanism for these reactions involves initial protonation of the metal center by HX. This was initially proposed by Hartwig et al. for the reaction of  $(PMe_3)_4 Ru(C_2H_4)$  with cresol.  $^7\,$  Due to the reactivity of the PMe<sub>3</sub> complexes no intermediates were observed. We have observed similar behavior in the reactions of  $(PMe_3)_4Ru(C_2H_4)$  with HX (X = SC<sub>6</sub>H<sub>4</sub>-p-Me, OC<sub>6</sub>H<sub>4</sub>-p-Me, PPhH). Once again the presence of bidentate phosphine ligands provided additional stability to the intermediate ethyl species. The ethyl species have been isolated and shown to undergo conversion to the hydride products, and a unique ethylene hydride species,  $[(DMPE)_2Ru(C_2H_4)(H)]^+[OAr 2HOAr]^-$  has been isolated and characterized by X-ray crystallography. This species rapidly rearranges to form  $(DMPE)_2Ru(H)(OAr)$  in solution at room temperature.

Attempts to extend the metallacyclopropane-like behavior of ethylene complex 6 to the corresponding metallacyclopropene analog were not successful. Treatment of dichloride 2 with vinyl Grignard reagent resulted in the formation of a divinyl species,  $(PMe_3)_4$ -

<sup>(38)</sup> Benfield, F. W. S.; Green, M. L. H. J. Chem. Soc. Dalton Trans. 1974. 1324.

<sup>(39)</sup> Emsley, J. Chem. Soc. Rev. 1980, 91.

<sup>(40)</sup> Goldberg, K. I.; Bergman, R. G. J. Am. Chem. Soc. 1989, 111, 1285

<sup>(41)</sup> Ruh, S.; vonPhilipsborn, W. J. Organomet. Chem. 1977, 127, C59.

<sup>(42)</sup> Chang, J.; Bergman, R. G. J. Am. Chem. Soc. 1987, 109, 4298.

 <sup>(43)</sup> Wreford, S. S.; Whithey, J. F. Inorg. Chem. 1981, 20, 3918.
 (44) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. Organometallics 1989, 8, 105.

<sup>(45)</sup> Evitt, E. R.; Bergman, R. G. J. Am. Chem. Soc. 1978, 100, 3237. (46) Yamazaki, H.; Hagihara, N. J. Organomet. Chem. 1970, 21, 431.

<sup>(47)</sup> Beckhaus, R.; Thiele, K.-H. J. Organomet. Chem. 1986, 317, 23.

 $Ru(CH=CH_2)_2$  which led upon thermolysis to the butadiene complex 8.

#### **Experimental Section**

General Considerations. Unless otherwise noted, all reactions and manipulations were carried out under a nitrogen atmosphere in a Vacuum Atmospheres 553-2 Dri-Lab inert atmosphere box with attached M6-40-1H Dri-Train or under argon using standard Schlenk and vacuum techniques. Glassware was dried in an oven at 150 °C.

Reactions involving gaseous reagents were handled on a vacuum line equipped with a MKS Baratron gauge. A known pressure of volatile gaseous reagents, calculated from the ideal gas law, was expanded into a bulb of known volume and then condensed at -196 °C into a high pressure vessel consisting of a thick-walled glass bomb attached to a Kontes vacuum stopcock.

Infrared spectra were taken on a Mattson Galaxy 3000 -Fourier Transform Infrared spectrometer (FTIR). All <sup>1</sup>H, <sup>31</sup>P-{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained at room temperature on a superconducting FT spectrometer incorporating Nicolet computers and cryomagnets assembled in the UC Berkeley NMR laboratory by Mr. Rudi Nunlist. The <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>13</sup>C{<sup>1</sup>H} spectra were determined at 300 MHz, 121 MHz and 75 MHz, respectively. Elemental analyses were conducted by the U.C. Berkeley Microanalysis Facility. FAB-MS was carried out on a VG-70SE instrument in the U.C. Berkeley Mass Spectrometry Facility.

To prepare sealed NMR tubes, the sample tube was attached by Cajon adapters directly to Kontes vacuum stopcocks. Known volume bulb vacuum transfers were accomplished with an MKS Baratron gauge attached to a high vacuum line.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Trimethylphosphine (Aldrich) was dried over Na and vacuum transferred prior to use. *p*-Thiocresol was recrystallized from pentane and *p*-nitrophenol and *p*-chlorophenol were purified by sublimation. Aniline was heated to reflux in benzene using a Dean-Stark trap and then vacuum distilled. (PMe<sub>3</sub>)<sub>4</sub>Ru(C<sub>2</sub>H<sub>4</sub>) (1),<sup>9</sup> (PMe<sub>3</sub>)<sub>4</sub>RuCl<sub>2</sub> (2),<sup>48</sup> (PMe<sub>3</sub>)<sub>3</sub>Ru(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> (14)<sup>17</sup> and *trans*-(DMPE)<sub>2</sub>RuCl<sub>2</sub><sup>19</sup> were prepared by literature methods.

Pentane and hexane (UV grade) were distilled from  $LiAlH_4$ under nitrogen. Benzene and toluene were distilled from sodium benzophenone ketyl under nitrogen. Ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl. Deuterated solvents for use in NMR experiments were dried as their protiated analogues and vacuum transferred from the drying agent.

 $(PMe_3)_4Ru(H)(SC_6H_4CH_3)$  (9). One equivalent of p-thiocresol (15.9 mg, 0.128 mmol) dissolved in 5 mL of pentane was slowly added to a pentane solution of  $(PMe_3)_4Ru(C_2H_4)(1)(53.6)$ mg, 0.124 mmol) at room temperature. A yellow precipitate formed immediately. The mixture was stirred at room temperature for 3 h to insure complete reaction. The solution was filtered and the remaining solvent was removed from the yellow precipitate in vacuo. The product was recrystallized at -30 °C from a CH2Cl2/ether mixture obtained by room temperature diffusion of ether into  $CH_2Cl_2$  solution of 9 (32.1 mg, 49% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.58 (d, J = 7.9 Hz), 6.74 (d, J = 7.9 Hz), 2.16 (s), 1.42 (d, J = 7.1 Hz), 1.34 (t, J = 2.6Hz), 1.32 (d, J = 5.5 Hz), -8.95 (dq, J = 28.1 Hz, J = 85.1Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  20.6 (m, J = 17.9 Hz, J = 31.0Hz), 9.8 (dd, J = 31.0 Hz, J = 26.7 Hz), -0.74 (m);  ${}^{13}C{}^{1}H{}$ NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  131.84 (s), 131.43 (d, J = 2.7 Hz), 130.28 (s), 127.83 (t, J = 12.8 Hz), 27.95 (d, J = 23.6 Hz), 23.76 (dt, J = 23.63.7 Hz, J = 13.0 Hz), 22.64 (d, J = 17.5 Hz), 20.60 (s). IR  $(CD_2Cl_2)\;\nu_{Ru-H}\;1860\;cm^{-1}.$  Anal. Calcd for  $C_{19}H_{44}P_4RuS:\;C,$ 43.09; H, 8.37. Found: C, 42.91; H, 8.27.

(48) Sellman, D.; Bohlen, E. Z. Naturforsch. 1982, 37B, 1026.

(PMe<sub>3</sub>)<sub>4</sub>Ru(H)(OC<sub>6</sub>H<sub>4</sub>-p-Cl) (10). Treatment of (PMe<sub>3</sub>)<sub>4</sub>-Ru(C<sub>2</sub>H<sub>4</sub>) (1) (74.2 mg, 0.171 mmol) dissolved in 5 mL of pentane with HOC<sub>6</sub>H<sub>4</sub>-p-Cl (25.5 mg, 0.199 mmol) resulted in a change in color of the solution from yellow to white and the formation of a white precipitate over 15 min at room temperature. The mixture was allowed to stir an additional 15 min to ensure complete reaction before the pentane solvent was removed in vacuo. The white residue was dissolved in a minimum amount of ether (0.5 mL) and 5 mL of pentane was diffused into the solution at room temperature. The ether/ pentane mixture was cooled to -30 °C. After 2 days, 40.8 mg (48%) of pure white solid 10 was collected by filtration. <sup>1</sup>H NMR (d<sub>8</sub>-THF)  $\delta$  6.70 (d, J = 8.9 Hz), 6.60 (d, J = 8.9 Hz), 1.38 (d, J = 5.71 Hz), 1.33 (d, J = 7.8 Hz), 1.30 (t, J = 2.8 Hz), -7.93 (ddt, J = 26.5 Hz(triplet), J = 26.5 Hz, J = 101.2 Hz, 1H); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  A<sub>2</sub>MX 16.2 (dt, P<sub>M</sub>), 1.76 (dd, P<sub>A</sub>),  $-12.50 (dt, P_X) J_{AM} = 33.0 Hz, J_{AX} = 26.7 Hz, J_{MX} = 16.5 Hz;$ <sup>13</sup>C{<sup>1</sup>H} NMR ( $d_8$ -THF)  $\delta$  170.7 (d, J = 4.4 Hz), 128.4 (s), 121.6 (s), 113.8 (s), 27.4 (dm, J = 26.5 Hz), 23.2 (dt, J (triplet) = 12.9 Hz, J (doublet) = 3.8 Hz), 20.8 (dm, J = 15.9 Hz); IR (d<sup>8</sup>-THF) 2814 (w), 2908 (m), 2978 (m), 2225 (w), 1873 (m), 1483 (s), 1319 (s), 1423 (m). Anal. Calcd for C<sub>18</sub>H<sub>41</sub>ClOP<sub>4</sub>Ru: C, 40.49; H, 7.74. Found: C, 40.04; H, 7.52.

(PMe<sub>3</sub>)<sub>4</sub>Ru(H)(OC<sub>6</sub>H<sub>4</sub>-p-NO<sub>2</sub>) (11). A benzene solution of p-nitrophenol (37.9 mg, 0.272 mmol) was added dropwise to a solution of (PMe<sub>3</sub>)<sub>4</sub>Ru(C<sub>2</sub>H<sub>4</sub>) (1) (95.4 mg, 0.220 mmol) over 15 min at room temperature. The solution color turned from yellow to orange immediately upon addition of *p*-nitrophenol. The solution was stirred at room temperature for an additional 8 h to insure complete reaction. The solution was filtered through Celite and the solvent was removed under vacuum. Recrystallization from a 10:1 mixture of pentane:benzene at -30 °C gave 89.4 mg (78%) of orange solid 11. <sup>1</sup>H NMR (d<sub>8</sub>-THF)  $\delta$  7.82 (d, J = 9.4 Hz, 2H), 6.63 (d J = 9.0 Hz, 2H), 1.41 (d, J = 5.7 Hz), 1.36 (d, J = 8.0 Hz), 1.30 (t, J = 2.7 Hz), -8.03(ddt, J = 25.7 Hz, J = 101.2 Hz, 1H); <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ A<sub>2</sub>MX 19.4 (dt, P<sub>M</sub>), 2.48 (dd, P<sub>A</sub>), -0.74 (dt, P<sub>X</sub>)  $J_{AM} = 33.8$ Hz,  $J_{AX} = 25.9$  Hz,  $J_{MX} = 16.9$  Hz; <sup>31</sup>P{<sup>1</sup>H} NMR (d<sub>8</sub>-THF)  $\delta$ A<sub>2</sub>MX 17.8 (dt, P<sub>M</sub>), 17.1 (dd, P<sub>A</sub>), -12.9 (dt, P<sub>X</sub>)  $J_{AM} = 34.2$  Hz,  $J_{AX} = 25.9$  Hz,  $J_{MX} = 17.1$  Hz. <sup>13</sup>C{<sup>1</sup>H} NMR (d<sub>8</sub>-THF)  $\delta$ 179.8 (d, J = 3.9 Hz), 133.7 (s), 126.6 (s), 120.0 (s), 27.1 (dd, J= 1.5 Hz, J = 31.9 Hz), 23.2 (dt, J = 3.5 Hz, J = 13.1 Hz), 20.8 (d, J = 16.8 Hz); IR (C<sub>6</sub>H<sub>6</sub>)  $\nu_{\text{Ru-H}}$  2003 cm<sup>-1</sup>. Anal. Calcd for C<sub>18</sub>H<sub>41</sub>P<sub>4</sub>NO<sub>3</sub>Ru: C, 39.71; H, 7.59. Found: C, 39.53; H, 7.36

(PMe<sub>3</sub>)<sub>3</sub>(PPhH<sub>2</sub>)Ru(H)(PHPh) (12). To a benzene solution (10 mL) of  $(PMe_3)_4Ru(C_2H_4)$  (1) (56.7 mg, 0.131 mmol) was added one equivalent of phenylphosphine (15.0 mg, 0.136 mmol) dissolved in 1 mL of benzene. The solution became vivid yellow immediately. The solution was allowed to stir at room temperature for 5 min before the solvent was removed in vacuo. The yellow residue was dissolved in 1 mL of pentane and cooled to -30 °C. After 24 h, 36.8 mg (51%) of yellow crystalline product was isolated. <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$  6.47 (m), 6.05 (m), 6.26 (d, J = 125.3 Hz), 5.32 (d, J = 75.5 Hz), 5.11(m), 3.02 (m), 2.72 (d, J = 180.7 Hz), 1.42 (d, J = 5.97 Hz), 1.32 (m), 1.03 (d, J = 5.7 Hz), 0.99 (d, J = 6.4 Hz), -9.42 (m).<sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  -6.0 (m), -7.8 (M), -10.1 (m), -12.9 (m), -14.8 (m), -19.8 (m), -47.3 (m).  $^{13}C\{^{1}H\}$  NMR (C\_6D\_6)  $\delta$ 134.2 (d, J = 10.4 Hz), 132.8 (d, J = 12.9 Hz), 128.7 (s), 126.9(s), 122.5 (s), 65.4 (s), 63.5 (s), 25.3 (d, J = 19.0 Hz), 21.3 (d, J= 19.5 Hz), 23.8 (dd, J = 11.3 Hz, J = 19.2 Hz). Anal. Calcd for C21H4P5Ru: C, 45.90; H, 7.52. Found C, 45.65; H, 7.84.

 $(PMe_3)_3Ru(C_2H_4)(C_2D_4)$  (13). A degassed benzene solution (0.7 mL) of  $(PMe_3)_4Ru(C_2H_4)$  (8.3 mg, 0.019 mmol) in an NMR tube was pressurized with  $C_2D_4$  (0.019 mmol) and the tube was sealed under vacuum. The tube was placed in a 45 °C oil bath and heated at 45 °C for 6 h. Comparison of the NMR spectra of the single product formed to literature data for  $(PMe_3)_3Ru(C_2H_4)_2^{17}$  confirmed its assignment as complex 13.

 $(DMPE)_2Ru(C_2H_4)$  (6). trans- $(DMPE)_2RuCl_2$  (17) (3.619 g, 7.68 mmol) was dissolved in 60 mL of THF in a glass vessel

 Table 14.
 Data Collection Parameters<sup>a</sup>

		<u></u>			
	18	20a	21	23	24
temp, K	-89 °C	−114 °C	−100 °C	−95 °C	-112 °C
$2\theta$ range	3-50°	3-45°	3–45°	3-50°	3-45°
scan width $(\Delta \theta)$	$0.70 + 0.35 \tan \theta$	$0.90 + 0.35 \tan \theta$	$0.85 + 0.35 \tan \theta$	$0.80 \pm 0.35 \tan \theta$	$1.00 \pm 0.35 \tan \theta$
scan type	$\theta - 2\theta$	$\theta - 2\theta$	$\theta - 2\theta$	$\theta - 2\theta$	ω
scan speed ( $\theta$ , deg/min)	5.49	8.24	5.49	5.49	8.24
vert aperture (mm)	4.0	4.0	4.0	6.0	6.0
horiz aperture (mm)	$2.0 \pm 1.0 \tan \theta$	$2.2 \pm 1.0 \tan \theta$	$2.0 \pm 1.0 \tan \theta$	$2.0 \pm 1.0 \tan \theta$	$2.3 + 1.0 \tan \theta$
reflections measured	+h,+k,+l	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. rflns collected	2687	3243	3671	4694	5080
no. unique rflns	2663	3107	3359	4244	4885
min/max transmission	0.931/0.984	0.810/0.999	0.833/0.998	0.94	0.925/1.000
no. params refined	139	122	235	387	203
R(F), %	4.6	6.4	4.6	2.20	6.1
$R_{\rm w}(F), \%$	6.0	7.8	7.2	2.77	7.7
$R_{\rm all}, \%$	7.1	8.4	5.2	2.93	8.3
goodness of fit	2.30	2.95	3.44	1.319	2.99
p factor	0.03	0.03	0.03	0.03	0.03

<sup>*a*</sup> General information: Diffractometer: ENRAF-Nonius CAD-4. Background: measured over  $0.25(\Delta\theta)$  (in the case of 24, measured over  $0.25(\Delta\omega)$ ) added to each of the scan. Monochromator: highly oriented graphite, ( $2\theta = 12.2^{\circ}$ ). Radiation: Mo Ka ( $\lambda = 0.71073$  Å). Absorption correction: empirical.

containing finely cut Na (1.60 g, 69.6 mmol). The vessel was degassed with three freeze-pump-thaw cycles on a vacuum line and excess ethylene (54.1 mmol, 1.7 atm) was transferred from a known-volume bulb. The reaction mixture was stirred vigorously at room temperature for 8 d, during which time purple (presumably NaCl and colloidal Na<sup>28</sup>) solid was formed. The excess ethylene and the THF solvent were removed under vacuum, and product 6 was extracted with pentane  $(6 \times 8 \text{ mL})$ to yield 2.97 g (90%) pure product. <sup>1</sup>H NMR ( $C_6D_6$ )  $\delta$  1.48 (d, J = 4.2Hz), 1.35 (m), 1.22 (m), 1.17 (vt, J = 42.2Hz), 1.06 (s), 1.02 (m), 0.85 (m), 0.79 (t, J = 2.3 Hz); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  A<sub>2</sub>B<sub>2</sub> 43.9 (t, J = 28.6 Hz), 37.2 (t, J = 28.5 Hz), <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  33.0 (m), 25.8 (t, J = 11.5 Hz), 21.0 (m), 8.5 (m), 7.9 (m); IR 2967 (s), 2898 (vs), 2803 (w), 1427 (m), 1270 (w), 1100 (m), 923 (vs), 880 (m), 684 (m), 630 (m) cm<sup>-1</sup>. Anal. Calcd for  $C_{14}$ -H<sub>36</sub>P<sub>4</sub>Ru: C, 39.16; H, 8.45. Found C, 39.34; H, 8.41.

 $cis-(DMPE)_2Ru(SC_6H_4Me)(CH_2CH_3)$  (18). A solution of p-thiocresol (29.2 mg, 0.235 mmol) in 3.0 mL of benzene was added slowly to a benzene solution of  $(DMPE)_2Ru(C_2H_4)$  (6) (100 mg, 0.234 mmol) dissolved in 10 mL of benzene. After two hours, the solvent was removed under vacuum and the product was recrystallized from a pentane/benzene solution (10/1)at -30 °C to yield 99.5 mg (75%) of yellow crystals. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.86 (d, J = 7.9 Hz, 2H), 6.99 (d, J = 7.8 Hz, 2H), 2.18 (s), 1.82 (dq, J = 2.7 Hz, 7.1 Hz), 1.74 (dd, J = 1.4Hz, J = 7.4 Hz), 1.44 (d, J = 6.6 Hz), 1.30 (d, J = 7.2 Hz), 1.09 (d, J = 7.6 Hz), 1.02 (d, J = 5.7 Hz), 0.92 (dd, J = 1.3 Hz, 8.1Hz), 0.82 (d, J = 5.0 Hz), 0.74 (d, J = 6.6 Hz), 0.46 (br s); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  48.3 (ddd, J = 11.6 Hz, J = 20.0 Hz, J = 28.7Hz), 43.8 (t, J = 21.8 Hz, J = 20.8 Hz), 41.0 (t, J = 21.6 Hz, J = 21.0 Hz), 29.9 (dd, J = 7.7 Hz, J = 28.6 Hz), 27.1 (dd, J= 7.7 Hz, J = 28.6 Hz), 21.3 (seven line multiplet, J = 8.1 Hz, J = 11.6 Hz, J = 22.2 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  45.6 (d, J =8.2 Hz), 137.2 (s), 130.8 (s), 32.8 (m), 32.1 (m), 31.1 (dd, J =21.9 Hz, J = 27.2 Hz), 29.4 (dd, J = 16.7 Hz, J = 25.1 Hz), 24.4 (dd, J = 6.6 Hz, J = 12.1 Hz), 22.1 (dd, J = 3.0 Hz, J =19.3 Hz), 21.3 (s), 20.5 (d, J = 14.1 Hz), 18.5 (m), 15.7 (dd, J= 2.5 Hz, J = 23.1 Hz), 15.2 (d, J = 17.2 Hz), 14.3 (dd, J = 3.1Hz, J = 20.3 Hz), 9.2 (d, J = 20.9 Hz), 5.1 (d, J = 60.0 Hz); IR 2966 (m), 2906 (s), 2013 (m), 1953 (m), 1481 (m), 1402 (m), 1257 (m), 1085 (w), 966 (s), 890 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>21</sub>H<sub>44</sub>P<sub>4</sub>RuS: C, 45.56; H, 8.01. Found C, 45.37; H, 7.90.

X-ray Crystal Structure Determination of 18. Yellow crystals of 18 were obtained by vapor diffusion of pentane into a benzene solution of 18 followed by cooling to -30 °C for 2 days. A single crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. The crystal used for data collection was then transferred to an Enraf-Nonius CAD-4 diffractometer, centered in the beam, and cooled to -89 °C by a nitrogen flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. Automatic peak search and indexing procedures yielded an orthorhombic reduced primitive cell for 18. Inspection of the Niggli values revealed no conventional cell of higher symmetry.

The 2687 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background and Lorentz and polarization effects. No correction for crystal decomposition was necessary. Inspection of the azimuthal scan data showed a variation Imin/Imax = 0.95 for the average curve. An empirical correction based on the observed variation was applied to the data. Inspection of the systematic absences indicated uniquely space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. Removal of systematically absent and redundant data left 2663 unique data in the final data set.

The structure was solved by Patterson methods and refined by standard least-squares and Fourier techniques, and all nonhydrogen atoms were refined with anisotropic thermal parameters.

The final residuals for 139 variables refined against the 2239 accepted data for which  $F^{2>}3\sigma(F^{2})$  were R = 4.6%,  $R_{\rm w} = 6.0\%$  and G.O.F. = 2.30. The *R* value for all 2663 data was 7.1%.

The quantity minimized by the least-squares program was  $\sum w(|F_o| - |F_c|)^2$ , where w is the weight of a given observation. The p-factor, used to reduce the weight of the intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of  $\sin\theta/\lambda$ ,  $|F_o|$ , and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.87 e<sup>-</sup>/Å, and the lowest excursion -0.22 e<sup>-</sup>/Å.

Crystal parameters for 18 are listed in Table 1. The bond distances and bond angles are given in Tables 2 and 3, and the data collection parameters are listed in Table 14. The positional, thermal and anisotropic parameters of the nonhydrogen atoms and their estimated standard deviations are available as supplementary material.

trans-(DMPE)<sub>2</sub>Ru(SC<sub>6</sub>H<sub>4</sub>Me)(H) (19). In an NMR tube cis-(DMPE)<sub>2</sub>Ru(Et)(p-thiocresolate) (46.5 mg, 0.084 mmol) was dissolved in 0.7 mL of benzene. The solution was degassed with one freeze-pump-thaw cycle and the NMR tube was sealed under vacuum. The solution was heated to 85 °C for 24 h. The tube was cracked open under an N<sub>2</sub> atmosphere and the solvent removed by lyophilization. Complex 19 was recrystallized at -30 °C from a benzene/pentane solution obtained by room temperature vapor diffusion of pentane into a concentrated benzene solution of 19. Pale yellow crystals of 19 were obtained (21.3 mg, 48% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$ 

## Complexes with Metal-Heteroatom Single Bonds

7.65 (d, J = 7.9 Hz), 6.88 (d, J = 7.7 Hz), 2.19 (s), 1.67 (m), 1.44 (s), 1.23 (m), 1.12 (s), -18.01 (quintet, J = 22.0 Hz); <sup>31</sup>P-{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  43.2 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN)  $\delta$  149.5 (s), 136.0 (s), 130.1 (s), 128.4 (s), 31.6 (quintet, J = 13.5 Hz), 24.6 (quintet, J = 6.5 Hz), 20.8 (s), 15.3 (quintet, J = 5.6 Hz); IR 2962 (m), 2910 (m), 2896 (s), 1856 (m,  $\nu_{Ru-H}$ ), 1478 (m), 1425 (m), 1296 and 1276 (w), 1074 (m), 935 (s), 890 (m), 725 and 705 (m), 637 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>40</sub>P<sub>4</sub>RuS: C, 43.42; H, 7.67. Found C, 43.65; H, 7.52.

 $cis-(DMPE)_2Ru(NHPh)(H)$  (20a).  $(DMPE)_2Ru(C_2H_4)$  (6) (0.208 g, 0.485 mmol) was dissolved in 20 mL of THF in a high pressure vessel. Aniline (45  $\mu$ L, 0.48 mmol) was syringed directly into the solution in one portion and the resulting mixture was degassed once by a freeze-pump-thaw cycle. The solution was heated at 120 °C for eight days, interrupted once to be degassed a by freeze-pump-thaw cycle to remove free ethylene. The solvent was removed in vacuo and the product recrystallized by vapor diffusion of pentane into a concentrated benzene solution at room temperature and cooling the resulting pentane/benzene solution to -30 °C to induce crystallization. This single crystallization gave clean product as golden crystalline clusters (107.3 mg, 45% yield). <sup>1</sup>H NMR (d<sub>8</sub>-THF)  $\delta$  6.47 (br, 4H), 5.57 (t, J = 7.1 Hz, 1H), 1.65 (m), 1.42 (d, J = 6.1 Hz), 1.39 (d, J = 5.3 Hz), 1.34 (d, J = 8.2 Hz), 1.30 (d, J =6.3 Hz), 1.25 (s), 1.23 (m), 1.19 (s), 1.16 (d, J = 6.8 Hz), -7.53  $(dq, J = 28.1 Hz, 96.0 Hz); {}^{31}P{}^{1}H MR (d_8-THF) \delta 49.4 (t, J)$ = 21.8 Hz), 47.5 (br. m), 46.6 (t, J = 21.8 Hz), 44.3 (dd, J = 17.0, 26.1 Hz), 41.6 (dd, J = 16.2, 26.6 Hz), 31.6 (br. m); <sup>13</sup>C-{<sup>1</sup>H} NMR ( $d_8$ -THF)  $\delta$  163.8 (s), 128.0 (br), 117.1 (br), 105.9 (s), 36.1 (m), 33.4 (m), 31.0 (t, J = 21.8 Hz), 30.2 (dd, J = 16.1, 25.6 Hz), 28.0 (dd, J = 7.1, 28.4 Hz), 21.6 (d, J = 16.6 Hz), 20.9 (d, J = 15.7 Hz), 20.5 (m), 19.0 (m), 16.0 (d, J = 20.4 Hz),12.8 (d, J = 9.6 Hz); IR 3353 (vw), 2962 (m), 2896 (s), 2803 (w), 1829 (m,  $\nu_{Ru-H}$ ), 1591 (s), 1492 (vs), 1419 (m), 1313 (m), 922 (s), 889 (m), 696 (m) cm<sup>-1</sup>. Anal. Calcd for  $C_{18}H_{39}NP_4$ -Ru: C, 43.72; H, 7.95; N, 2.83. Found C, 43.50; H, 8.03; N, 2.87.

X-ray Crystal Structure Determination of 20a. Brownish-red crystals of 20a were obtained from a concentrated toluene solution cooled to -30 °C. A single crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. Data were collected and refined as described for 18. Crystal parameters for 20a are listed in Table 1. The bond distances and bond angles are given in Tables 4 and 5, and the data collection parameters are listed in Table 14. The positional, thermal and anisotropic parameters of the non-hydrogen atoms and their estimated standard deviations are available as supplementary material.

 $trans-(DMPE)_2Ru(NHPh)(H)$  (20b).  $(DMPE)_2Ru(C_2H_4)$ (99.5 mg, 0.23 mmol) was dissolved in 20 mL of THF and aniline (22.0  $\mu$ L, 0.24 mmol) was syringed into the solution. The bomb was degassed once by a freeze-pump-thaw cycle and the mixture heated at 90 °C for 5.5 days. The solvent was removed in vacuo, and the product was isolated from the remaining starting material by recrystallization under N2. The solid was dissolved in a minimum amount of benzene and pentane vapor was slowly diffused into the benzene solution at room temperature. The resulting benzene/pentane solution was cooled to -30 °C to induce crystallization. Reddish crystals were obtained (17.6 mg, 15% yield).  $\,^1H\,(C_6D_6)\,\delta$  7.22 (t, J = 7.4), 6.38 (m), 6.24 (d, J = 7.8 Hz), 1.42 (m), 1.27 (s),1.16 (m), 1.10 (s), -19.13 (quin, J = 22.9 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR  $(C_6D_6) \delta 44.5 (s); {}^{13}C{}^{1}H NMR (d_8-THF) \delta 128.2 (s), 115.8 (s),$ 104.7 (s), 32.3 (quintet, J = 13.6 Hz), 24.7 (m), 16.3 (br s). Anal. Calcd for C<sub>18</sub>H<sub>39</sub>NP<sub>4</sub>Ru: C, 43.72; H, 7.95; N, 2.83. Found C, 43.92; H, 7.74; N, 2.68.

cis-(DMPE)<sub>2</sub>Ru(PPhH)(CH<sub>2</sub>CH<sub>3</sub>) (21). Phenylphosphine (66.5  $\mu$ L, 0.605 mmol) was syringed into a THF solution of (DMPE)<sub>2</sub>Ru(C<sub>2</sub>H<sub>4</sub>) (6, 252.8 mg, 0.589 mmol, dissolved in 10 mL THF). After stirring for 29 h at room temperature, the solvent was removed *in vacuo* and the product was recrystallized from a pentane/benzene (10:1) solution at -30 °C. The

recrystallization procedure was repeated once to yield 269 mg (89.4%) of yellow crystals. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.84 (dd, J = 5.2, 6.7), 7.17 (t, J = 7.7 Hz), 7.06 (t, J = 6.8 Hz), 2.82 (d, J = 198.2Hz), 1.76 (dq, J = 2.5, 6.7 Hz), 1.62 (d, J = 6.0 Hz), 1.40 (m), 1.30 (d, J = 3.0 Hz), 1.10 (m), 1.01 (d, J = 5.7 Hz), 0.86 (m), 0.80 (m), 0.69 (d, J = 7.7 Hz), 0.14 (m); <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ 43.0 (m), 40.4 (m), 40.0 (m), 39.0 (m), 30.1 (7 line m), 27.5 (m), 22.0 (broad s), -62.5 (very broad m, 1820 Hz);  $^1\mathrm{H}$  (d\_8-THF)  $\delta$  7.33 (m), 6.81 (t, J = 7.3 Hz), 6.74 (t, J = 6.9 Hz), 2.36 (d, J = 189.1 Hz), 1.60 (m), 1.55 (d, J = 6.8 Hz), 1.47 (m), 1.33 -1.31 (complicated m), 1.25 (d, J = 5.1 Hz), 0.58 (d, J = 7.4Hz), 0.15 (d, J = 131.8 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (d<sub>8</sub>-THF)  $\delta$  154.5 (d, J = 34.3 Hz), 134.0 (d, J = 12.9 Hz), 126.9 (d, J = 3.3 Hz),122.5 (s), 33.1 (m), 32.1 (m), 23.9 (t, J = 10.8 Hz), 22.5 (d, J =15.5 Hz), 21.8 (d, J = 14.2 Hz), 20.4 (m), 19.2 (dd, J = 7.6, 22.8 Hz), 16.7 (t, J = 17.8 Hz), 15.2 (dd, J = 3.5, 19.1 Hz), 12.7 (m), 9.0 (d, J = 21.9 Hz), 2.5 (dq, J = 9.7, 56.6 Hz); IR 3055 (w), 2967 (m), 2905 (s), 2830 (m), 1576 (w), 1465 (w) 1427 (w), 1290 (w), 1257 (w), 1205 and 1188 (w), 1099 and 1070 (m), 1018 (m), 930 (s), 896 (m), 691 (m) cm<sup>-1</sup>. Anal. Calcd for C<sub>20</sub>H<sub>43</sub>P<sub>5</sub>Ru: C, 44.53; H, 8.03. Found C, 44.60; H, 7.99.

X-ray Crystal Structure Determination of 21. Bright yellow crystals of air-sensitive 21 were obtained from a benzene/pentane solution at -30 °C. A single crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. Data were collected and refined as described for 18. Crystal parameters for 21 are listed in Table 1. The bond distances and bond angles are given in Tables 6 and 7, and the data collection parameters are listed in Table 14. The positional, thermal and anisotropic parameters of the non-hydrogen atoms and their estimated standard deviations are available as supplementary material.

Thermolysis of cis-(DMPE)<sub>2</sub>Ru(Et)(PHPh). A THF solution (6 mL) of cis-Ru(Et)(PHPh)(DMPE)<sub>2</sub> (21) (0.284 g, 0.526 mmol) was transferred to a 100 mL high pressure vessel and heated at 90 °C for 6 d. The solvent was removed in vacuo, and the yellow solid was triturated with  $2 \times 3$  mL of pentane and dried in vacuo to yield 0.2667 g (99%) of crude product. NMR analysis of this material indicated it to be a 2:1 mixture of (hydrido)(phosphido)ruthenium complexes 22a and 22b (see text). <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  8.26 (m, *cis*), 7.64 (m, *trans*), 7.18 (t, J = 7.3 Hz, cis), 7.04 (m, trans), 6.99 (m, cis), 3.00 (br, cis P-H), 2.8 (br, trans P-H), 2.40 (br, cis P-H), 2.2 (br, trans P-H) 1.62 (m), 1.58 (d, J = 6.9 Hz, *cis*), 1.32 (s, *trans* DMPE Me), 1.27(d, J = 8.0 Hz, cis), 1.22 (d, J = 5.9 Hz, cis), 1.13 (s, trans DMPE Me), 1.10 (m, cis), 1.05 (m, cis), 0.85 (d, J = 5.6 Hz, cis), 0.82 (m), -9.33 (m, cis Ru-H), -13.55 (m, trans Ru-H); <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  47.3 (br, *cis*), 44.8 (br, *cis*), 43.6 (s, trans), 40.9 (br, cis), 40.3 (br, cis), 28.5 (br, cis), -63.0 (dd, J = 13.0, 87.2 Hz, *cis* Ru-PHPh), -78.0 (s, *trans* Ru-PHPh); <sup>13</sup>C-{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  133.1 ((d, J = 14.3 Hz, trans C<sub>ortho</sub>), 132.9  $(d, J = 11.4 \text{ Hz}, cis C_{ortho}), 127.3 (d, J = 4.2 \text{ Hz}, trans C_{meta}),$ 126.9 (d, J = 1.8 Hz, cis C<sub>meta</sub>), 122.0 (s, cis), 121.7 (s, trans), 33.9 (m), 33.0 (m), 31.5 (m), 31.2 (m), 30.2 (m), 28.0 (m), 26.6 (m), 21.8 (m), 18.4 (m), 16.4 (m), 15.9 (m), 15.1 (m); IR (C<sub>6</sub>H<sub>6</sub>) 3055 (w), 2962 (s), 2896 (s), 1829 (m,  $\nu_{Ru-H}$ ), 1776 (m,  $\nu_{Ru-H}$ ), 1571 (m), 1419 (m), 1260 (s), 1087 (vs), 1021 (s), 928 (s), 703 (s)  $cm^{-1}$ .

trans-(DMPE)<sub>2</sub>Ru(H)(OC<sub>6</sub>H<sub>4</sub>-p-CH<sub>3</sub>) (23). A benzene solution (6 mL) of p-cresol (61.3 mg, 0.567 mmol) was added slowly to a stirred benzene solution of (DMPE)<sub>2</sub>Ru(C<sub>2</sub>H<sub>4</sub>) (221.0 mg, 0.515 mmol, dissolved in 2 mL of C<sub>6</sub>H<sub>6</sub>) in a 100 ml high pressure vessel. The mixture was heated for 4 h at 75 °C and then the warm solution was degassed *in vacuo*. The reaction mixture was lyophilized, and the product was extracted with 3 mL toluene leaving behind a white insoluble solid. After removing the toluene in *vacuo*, the product was recrystallized from a pentane/toluene (10:1) solution at -30 °C to yield 187 mg (71%) of light yellow crystals. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.11 (d, J = 8.1), 6.38 (d, J = 7.7 Hz), 2.40 (s), 1.66 (m), 1.32 (s), 1.26 (m), 1.00 (s), -23.20 (quintet, J = 21.8 Hz); <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  45.5 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  171.4 (s), 129.5 (s), 119.9 (s),

116.8 (s), 31.1 (quintet, J = 13.4 Hz), 22.8 (quintet, J = 7.5 Hz), 21.1 (s), 15.4 (quintet, J = 5.3 Hz); IR (C<sub>6</sub>H<sub>6</sub>) 2969 (w), 2903 (m), 1929 (m,  $\nu_{\text{Ru-H}}$ ), 1604 (m), 1489 (vs), 1419 (w), 1313 (m), 928 (s), 889 (m), 730 (w), 710 (w) cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>40</sub>OP<sub>4</sub>Ru: C, 44.79; H, 7.91. Found C, 44.60; H, 7.99.

X-ray Crystal Structure Determination of 23. Large, pale yellow crystals of 23 were collected by vapor diffusing pentane (10 mL) into a toluene solution of 23 (1 mL) and cooling the resulting pentane/toluene solution to -30 °C for 24 h. A single crystal was mounted on a glass fiber using Paratone N hydrocarbon oil and data taken and analyzed as described for complex 18 (see Table 1).

In a difference Fourier map calculated following the refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks were found corresponding to the positions of all the hydrogen atoms. Hydrogen atoms were included in structure factor calculations and refined with isotropic thermal parameters. In the final cycles of least-squares, 51 data in two regions of the h0/ plane were given zero weight because they had abnormally large weighted difference values.

The final residuals for 387 variables refined against the 3563 accepted data for which  $F^{2}>3\sigma(F^{2})$  were R=2.20%,  $R_{\rm w}=2.77\%$  and GOF = 1.319. The *R* value for all 4244 data was 2.93\%. In the final cycles of refinement a secondary extinction parameter was included (maximum correction: 11% on *F*).

Inspection of the residuals ordered in ranges of  $\sin\theta/\lambda$ ,  $|F_o|$ , and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.43 e<sup>-</sup>/Å, and the lowest excursion  $-0.10 \text{ e}^{-}/\text{Å}$ .

Crystal data parameters for 23 are listed in Table 1. The bond distances and bond angles are given in Tables 8 and 9, and the data collection parameters are listed in Table 14. The positional, thermal and anisotropic parameters of the nonhydrogen atoms and their estimated standard deviations are available as supplementary material.

 $[trans-(DMPE)_2Ru(C_2H_4)(H)]^+[OC_6H_4-p-CH_3-2HOC_6H_4$ p-CH<sub>3</sub>]<sup>-</sup> (24). A toluene solution (3.0 mL) of *p*-cresol (30 mg, 0.276 mmol) was cooled to -30 °C and added rapidly to a cold (-30 °C) toluene solution of (DMPE)<sub>2</sub>Ru(C<sub>2</sub>H<sub>4</sub>) (55 mg, 0.139 mmol dissolved in 0.5 mL of toluene), instantly generating a white precipitate. The temperature of the reaction solution was maintained at -30 °C for 10 min, at which point the supernatant was decanted off and the white solid washed with  $2 \times 1 \text{ mL cold} (-30 \text{ °C})$  pentane. The solid was dried in *vacuo* to yield 63.2 mg (91.1%) of the crude product. The crude product (50.0 mg) was dissolved in  $CH_2Cl_2$ , and pentane (10:1 pentane to  $CH_2Cl_2$ ) was slowly diffused into the solution at -30 °C. Clear, colorless crystals of the pure product were obtained (30.3 mg, 55%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) & 14.32 (s, 2H), 6.84 (d, J = 8.1 Hz, 6H), 6.71 (d, J = 8.1Hz, 6H), 2.18 (s, 9H),1.89 (m, 4H), 1.64 (m, 8H), 1.43 (s, 12H), 1.20 (s, 12H), -9.91 (quintet, J = 22.6 Hz, 1H); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  41.5 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>) δ 160.3 (s), 129.7 (s), 124.2 (s), 117.0 (s), 46.3 (s), 30.5 (quintet, J = 13.2 Hz), 22.8 (quintet, J = 8.8Hz), 20.5 (s), 13.0 (quintet, J = 6.7 Hz); MS-FAB [sulfolane] m/z = 431.089 [M<sup>+</sup>]. The spectrum also contained a small pattern centered around m/z = 465 with relative intensities

that match exactly those predicted for the corresponding chloride; a 15% contamination by this material was noted in the X-ray study summarized below.

X-ray Crystal Structure Determination of 24. Clear, colorless crystals of 24 formed from vapor diffusion of pentane into  $CH_2Cl_2$  carried out at -30 °C. A single crystal was mounted on a glass fiber using Paratone N hydrocarbon oil. Data were collected and refined as described for 18. The specific crystal parameters for 24 are listed in Table 1. The positional, thermal and anisotropic parameters of the non-hydrogen atoms and their estimated standard deviations are available as supplementary material. The bond distances and bond angles are given in Tables 10 and 12 and Tables 11 and 13, respectively, and the data collection parameters are listed in Table 14.

**Ru**(**CH=CH**<sub>2</sub>)<sub>2</sub>(**PMe**<sub>3</sub>)<sub>4</sub> (7). Vinylmagnesium bromide (5.0 mL of a 1.0 M ether solution, 0.50 mmol) was added by syringe to an ether (10 mL) slurry of Ru(PMe<sub>3</sub>)<sub>4</sub>(Cl)<sub>2</sub> (2) (111 mg, 0.234 mmol) at room temperature. After stirring for 6 h the orange solution turned white. The ether was removed *in vacuo* and the product was extracted with pentane (8 × 10 mL). The pentane was removed in *vacuo* and 7 was crystallized from hexane at -30 °C. After 2 d, 55.0 mg of white product 7 (50%) was obtained. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  8.2 (m, 2H), 6.6 (m, 2H), 5.7 (m, 2H), 1.18 (t, J = 27 Hz, 18H), 1.13 (d, J = 4.7 Hz, 18H); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  121.6 (t, J = 4.7 Hz), 69.52 (s), 24.03 (m), 20.19 (t, J = 13.2); <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  -6.44 (t, J = 25.8 Hz), -12.43 (t, J = 25.8 Hz). Anal. Calcd for C<sub>16</sub>H<sub>42</sub>P<sub>4</sub>-Ru: C, 41.83; H, 9.21. Found: C, 41.78; H, 9.01.

**Ru**( $\eta^4$ -C<sub>4</sub>H<sub>6</sub>)(**PMe**<sub>8</sub>)<sub>3</sub> (8). A degassed benzene (10 mL) solution of 7 (72.5 mg, 0.158 mmol) was heated to 55 °C for 48 h during which time the colorless starting solution turned orange. The solvent was removed in *vacuo* and the product was crystallized from hexanes at -30 °C yielding 29.0 mg (48%) of orange crystals: mp 165-170 °C; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  4.3 (br. s, 2H), 1.33 (d, J = 6.8 Hz), 1.01 (t, J = 5.5 Hz), -0.42 (m); <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  2.81 (t, J = 6.8 Hz), -1.79 (d, J = 6.7 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  79.1 (m), 28.9(m), 25.8(m), 24.1-(m); MS-FAB [sulfolane] m/z = 384 [M<sup>+</sup>].

Acknowledgment. We are grateful for financial support of this work from the National Institutes of Health (Grant no. R37 GM25459). The authors would like to express their gratitude to Dr. Robert D. Simpson for his suggestion of the synthesis of  $(DMPE)_2Ru(C_2H_4)$ -(6).

Supplementary Material Available: Tables of crystal and data collection parameters, positional and thermal parameters, bond distances and angles, and torsion angles for 18, 20a, 21, 23, and 24 (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; ordering information is given on any current masthead page.

OM940486Q