Synthesis, Structure, and Reactivity of Four-, Five-, and Six-Coordinate Ruthenium Carbyne Complexes

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Square-planar carbyne complexes of the form Ru(≡CR)(PCy_3)$_2$X (X = F, Cl, Br, I, O_3SCF_3) are prepared by net dehydrohalogenation of the Grubbs catalysts Ru(═CHR)(PCy_3)$_2Cl_2$ followed by substitution of the chloride ligand (when X ≠ Cl). The dehydrohalogenation can be effected in one step (R = *n*-Bu, Ph, *p*-C_6H_4Me) by Ge(CH[$SiMe_3$]$_2$)$_2$ or in two steps via treatment with excess aryloxide such as NaO-*p*-C_6H_4-*t*-Bu followed by $SnCl_2$. The latter route gives greater yields but is more restricted in scope. Addition of HCl (1 equiv) to Ru(≡CR)(PCy_3)$_2$X (X = Cl, Br, I) affords Ru(═CHR)(PCy_3)$_2$ClX; those with mixed halide ligand sets undergo rapid halide exchange in solution. Upon treatment with the appropriate oxidant, each Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2$X complex undergoes two-electron oxidation. Oxidation of Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2$X (X = F, Cl, Br, I) by XeF_2, C_2Cl_6, Br_2, and I_2, respectively, yields either six-coordinate bis-phosphine complexes Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2X_3$ (X = F, Cl) or square-pyramidal mono-phosphine complexes Ru(≡C-*p*-C_6H_4Me)(PCy_3)X_3 (X = Br, I) depending on the size of the halide ligands. Cationic square-pyramidal complexes of the form [Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2X_2$]$^+$ (X = Cl, I) can be prepared from Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2Cl_3$ by chloride abstraction using [Ph_3C]BF_4 and from Ru(≡C-*p*-C_6H_4-Me)(PCy_3)X_3 by addition of PCy_3. Hydride addition to Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2Cl_3$ yields the carbene complex Ru(═CHR)(PCy_3)$_2Cl_2$, whereas fluoride addition affords the carbyne complex Ru(≡C-*p*-C_6H_4-Me)(PCy_3)$_2Cl_2$F, results with important implications for metathesis of vinyl fluorides. X-ray structures of Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2X_2$F (X = F, Cl), [Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$]BF_4, and Ru(≡C-*p*-C_6H_4-Me)(PCy_3)I_3 reveal short Ru≡C bonds in the 1.670(5)−1.714(3) Å range; when two PCy_3 ligands are present, they are mutually *trans*. The benzylidyne ligands occupy the apical sites in the two square-pyramidal complexes. Of the five- and six-coordinate complexes, only the two fluoride-containing complexes Ru(≡C-*p*-C_6H_4Me)(PCy_3)$_2X_2$F (X = F, Cl) display reactivity toward alkynes, serving as alkyne dimerization catalysts.

Introduction

The number of ruthenium−carbene complexes available as a result of ongoing research into Ru-catalyzed olefin metathesis is large.[1] In spite of mechanistic homology between olefin metathesis and alkyne metathesis,[2−7] only a very few ruthenium−carbyne complexes have been reported,[8−14] and none of these are found to catalyze alkyne metathesis. Thus, homogeneous alkyne metathesis catalysis remains restricted to complexes of Mo, W, and Re.[1] The ruthenium−carbyne complexes that most closely resemble the Grubbs catalysts exemplified by Ru(CHPh)(L)(PCy_3)$_2Cl_2$ (Chart 1: L = PCy_3 [**1**], H_2IMes [**2**]; H_2IMes = 4,5-dihydro-1,3-bis(mesityl)imidazolin-2-ylidene) are the cationic square-pyramidal species such as [Ru(CCH_2R')(PR_3)$_2$-Cl_2]$^+$ (R = Cy [**3a**, **3b**], *i*-Pr [**4a**, **4b**]; R′ = Ph [**3a**, **4a**], *t*-Bu [**3b**, **4b**]), which Werner and co-workers prepared via protonation of the corresponding vinylidene complexes.[12] Similarly, protonation of allenylidene complexes can lead to alkenylcarbyne complexes.[15−19] Even these complexes, however, do not

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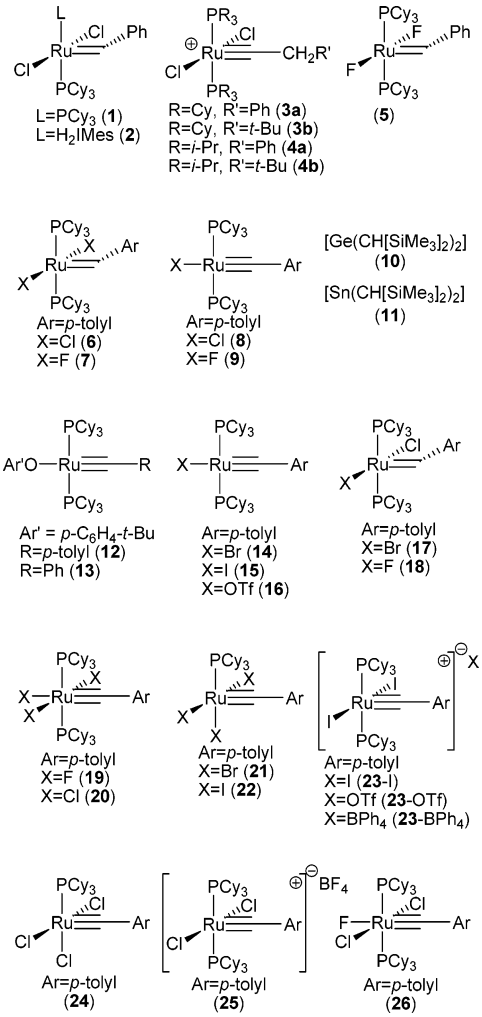
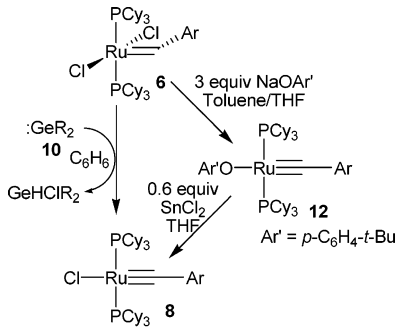
Chart 1. Numbered Compounds



catalyze alkyne metathesis, possibly because they are readily deprotonated to afford reactive 14-electron vinylidene complexes.[12]

Following Fischer's initial report in 1973, several synthetic routes to compounds that contain metal−carbon triple bonds have been developed.[8,20−22] Several years ago, Caulton disclosed the unexpected formation of square-planar Ru−carbyne complexes $Ru(CPh)(PR_3)_2(OPh)$ (R = *i*-Pr, Cy) by treatment of $Ru(CHPh)(PR_3)_2Cl_2$ with excess NaOPh.[9] Fogg similarly prepared $Ru(CPh)(PCy_3)_2(OC_6F_5)$ from **1** by reaction with $TlOC_6F_5$,[14] which led to the suggestion that product selectivity is driven by steric interactions at an intermediate stage and that phenoxide basicity was extraneous to the reaction,[14] given that similar treatment of **1** with $KOC(CX_3)_3$ (X = H, F) yields the four-coordinate carbene complexes $Ru(CHPh)(PCy_3)(OC(CX_3)_3)_2$ rather than the carbyne products of $HOC(CX_3)_3$ elimination.[9,10] Likewise, an admixture of 2 equiv of $TlOC_6F_5$ to a solution of $Ru(CHPh)(IMes)(py)_2Cl_2$ (py = pyridine; IMes = *N*,*N*′-bis(mesityl)imidazol-2-ylidene[23]) affords $Ru(CHPh)(IMes)(py)(OC_6F_5)_2$ cleanly.[14] We decided to harness the elimination route in order to prepare a number of ruthenium benzylidyne complexes for structural and reactivity studies, particularly in catalytic reactions involving alkyne substrates. Some of these results have been communicated.[24]

Scheme 1. Synthesis of Square-Planar Mono-chloride Benzylidyne Complex



Results and Discussion

It is tempting to suggest that the conspicuous absence of $Ru(CHPh)(PCy_3)_2F_2$ (**5**) from the family of "first-generation" Grubbs catalysts $Ru(CHPh)(PCy_3)_2X_2$ (X = Cl, Br, I) is due to instability of **5** with respect to HF elimination and formation of $Ru(CPh)(PCy_3)_2F$. Indeed, we find that reaction of $Ru(CH\text{-}p\text{-}C_6H_4Me)(PCy_3)_2Cl_2$ (**6**)[25] with CsF in an attempt to prepare $Ru(CH\text{-}p\text{-}C_6H_4Me)(PCy_3)_2F_2$ (**7**) affords a mixture of products that contains both $Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2Cl$ (**8**) and $Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2F$ (**9**). Here we have used the *p*-tolyl substituent for convenience of monitoring by ^1H NMR spectroscopy compared to **1** by virtue of a simplified aryl region and diagnostic Me resonance. Use of $[n\text{-}Bu_4N]F\cdot 3H_2O$ instead of CsF gives rise to a brown solution in which free PCy_3 is the only phosphorus-containing species observable by ^{31}P NMR spectroscopy. On the basis of these findings, we set out to examine the synthesis and reactivity of ruthenium−benzylidyne complexes, with special attention given to complexes that also contain one or more fluoride ligands.

Low-Valent Carbyne Complexes by Elimination from the Carbene Complexes. As previously communicated,[24] complex **8**, which is dark blue-green in the solid state and in solution, can be prepared rationally in 41.4% isolated yield via direct reaction of **6** with $Ge(CH[SiMe_3]_2)_2$[26] (**10**). In addition to benzylidyne complexes such as **8**, the germylene **10** also affords with equal facility carbyne complexes such as $Ru(C\text{-}n\text{-}Bu)(PCy_3)_2Cl$ by dehydrochlorination of $Ru(CH\text{-}n\text{-}Bu)(PCy_3)_2Cl_2$; however, $Ru(CH_2)(PCy_3)_2Cl_2$[25,27] does not react with **10** under the conditions attempted, but instead undergoes only the slow decomposition characteristic of $Ru(CH_2)(PCy_3)_2Cl_2$ in solution (Scheme 1). Unlike **10**, the amidogermylene $Ge(N[SiMe_3]_2)_2$[28] fails to convert **6** into **8** in appreciable yield. The dialkylstannylene $Sn(CH[SiMe_3]_2)_2$ (**11**)[26] does react with **6**, but several products are formed due to the fact that **8** itself reacts with **11**. Accordingly, when **6** is treated with 3 equiv of **11**, free PCy_3 is

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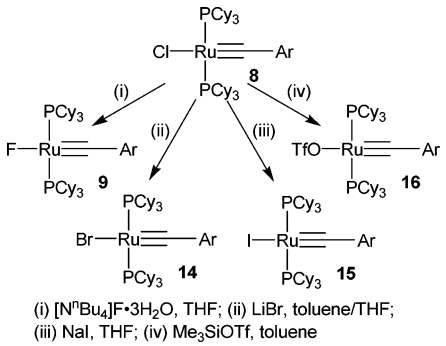
Scheme 2. Synthesis of Monohalide and Pseudohalide Complexes



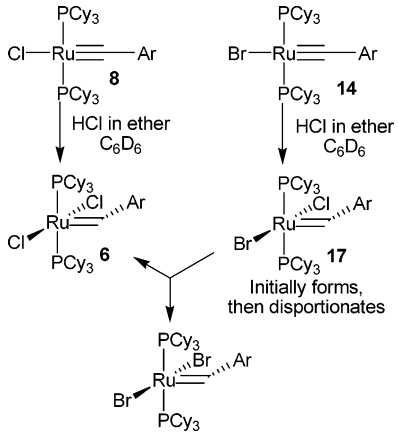
the only phosphorus-containing species observable by ^{31}P NMR spectroscopy after 40 min. Reaction of **6** with 1 equiv of **11** yields a mixture that contains **6**, **8**, and free PCy_3 in a 54:15:31 integration ratio after 16 h. Thus, **10** is the most convenient reagent we have found for single-step dehydrochlorination of **6** and its analogues.

Roper has reported six closely related ruthenium complexes that contain one additional ligand. In an unusual reaction, treatment of $Ru(=CCl_2)(CO)(PPh_3)_2Cl_2$ with 2 equiv of ArLi (Ar = Ph, 4-C_6H_4OMe, 1-naphthyl) at low temperature in tetrahydrofuran affords the neutral complexes $Ru(\equiv CAr)(CO)(PPh_3)_2Cl$ along with 1 equiv of ArCl. Upon reaction with CO, chloride is displaced, affording the cationic complexes $[Ru(\equiv CAr)(CO)_2(PPh_3)_2]^+$.[29,30] The osmium analogues behave similarly.[29,30]

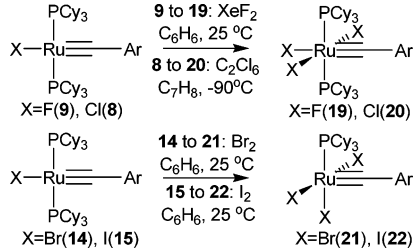
Convenient Two-Step Synthesis of 8. Although the reaction of **6** with **10** affords **8** rapidly and cleanly, for large-scale reactions we find that a two-step procedure yields **8** in greater overall yield more economically and without the need to synthesize and purify **10** (Scheme 1). Dissolution of a solid mixture of **6** and at least 3 equiv NaO-*p*-C_6H_4-*t*-Bu in a 4:1 (v/v) toluene−THF mixture affords a forest green analogue of Caulton's $Ru(CPh)(PCy_3)_2(OPh)$, $Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2(O\text{-}p\text{-}C_6H_4\text{-}t\text{-}Bu)$ (**12**), in 66% isolated yield on a multigram scale. A 4:1 solvent ratio by volume appears optimal. Some THF is required in order to obtain a reasonable reaction rate, but too much THF results in the formation of undesirable side products. We prefer to use NaO-*p*-C_6H_4-*t*-Bu instead of NaOPh for convenience of handling and simplification of ^{1}H NMR spectra. Additionally, as communicated previously, reaction of **1** with at least 3 equiv of NaO-*p*-C_6H_4-*t*-Bu affords square-planar $Ru(CPh)(PCy_3)_2(O\text{-}p\text{-}C_6H_4\text{-}t\text{-}Bu)$ (**13**), which, unlike $Ru(CPh)(P\text{-}i\text{-}Pr_3)_2(OPh)$ and $Ru(CPh)(PCy_3)_2(OC_6F_5)$, does not suffer from crystallographic disorder of the benzylidyne and aryloxide ligands, thus permitting precise determination of the Ru≡C bond length (1.7178(16) Å).[24] Addition of **12** dissolved in THF to a THF solution of 0.6 equiv of $SnCl_2$ affords **8** cleanly in 87% yield on a multigram scale; order of addition is important in order to avoid re-formation of **6**. In this way, we routinely obtain several grams of analytically pure **8** in 58% overall yield from **6** in two simple steps.

Substitution of the Chloride Ligand in 8. Complex **8** is an excellent precursor to a family of complexes of the form $Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2X$ (Scheme 2). Unsurprisingly, treatment of **8** with NaO-*p*-C_6H_4-*t*-Bu in 9:1 (v/v) toluene−THF regenerates **12** cleanly in 59% isolated yield. The bromo and iodo

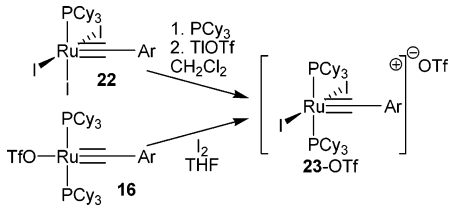
Scheme 3. Treatment of Planar Complexes with HCl



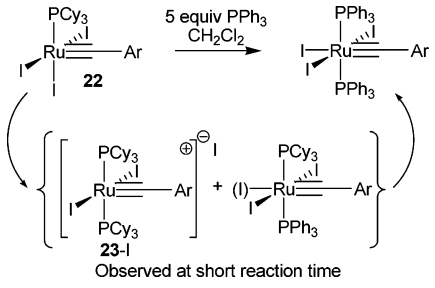
Scheme 4. Two-Electron Oxidation of Planar Monohalide Complexes



Scheme 5. Formation of a Cationic Bisphosphine Benzylidyne Complex



Scheme 6. Formation of a Triiodide Bisphosphine Benzylidyne



complexes $Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2X$ (X = Br [**14**], I [**15**]) are prepared from **8** by reaction with an excess of a suitable alkali halide. Treatment of **8** with 10 equiv of LiBr in 4:1 (v/v) toluene−THF affords blue-green **14** rapidly in 71% isolated yield; addition of 10 equiv of NaI to a THF solution of **8** results in its conversion to gray-green **15**, which can be isolated in 68% yield. The fluoro complex $Ru(C\text{-}p\text{-}C_6H_4Me)(PCy_3)_2F$ (**9**) can be prepared in several ways. Reaction of **8** with excess anhydrous CsF in THF is slow and proceeds only to approximately 50% conversion over 2 weeks at 22 °C. Similarly, SnF_2 converts **12** into **9** only slowly in THF. Much more rapid is the reaction of **8** with $[S(NMe_2)_3[SiF_2Me_3]$ (TAS-F). However, the expense of this reagent limits its utility. An excess of CsF reacts with **8** and 1.2 equiv of 18-crown-6 in 3:2 (v/v)

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Table 1. Crystallographic Data for Complexes 19, 22, 25, and 26

	19	22	25	26
formula	$C_{45}H_{74}Cl_2F_3P_2Ru$	$C_{26}H_{40}I_3PRu$	$C_{93}H_{156}B_2Cl_{14}F_8P_4Ru_2$	$C_{46}H_{73}Cl_6D_4FP_2Ru$
fw	905.95	865.32	2270.12	1028.81
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/m$	*Pbca*	$P2_1/c$	$P2_1/m$
a (Å)	9.5265(18)	17.267(2)	11.626(4)	13.721(3)
b (Å)	23.609(5)	17.974(2)	32.847(12)	17.724(4)
c (Å)	11.124(2)	18.631(3)	28.253(10)	20.827(5)
α (deg)	90	90	90	90
β (deg)	113.372(12)	90	99.152(6)	92.642(4)
γ (deg)	90	90	90	90
V (Å^3)	2296.6(8)	5782.3(14)	10652(7)	5059.6(19)
Z	2	8	4	4
radiation (Kα, Å)	0.71073	0.71073	0.71073	0.71073
T (K)	123(2)	123(2)	108(2)	123(2)
D_{calcd} (Mg m^{-3})	1.310	1.988	1.416	1.351
μ_{calcd} (mm^{-1})	0.569	3.814	0.751	0.724
F_{000}	958	3312	4728	2152
R1	0.0530	0.0271	0.0590	0.0402
wR2	0.0969	0.0807	0.1310	0.0816
GOF	1.030	1.288	1.160	1.010

DME−THF to effect quantitative formation of **9** over 48 h; **9** can then be isolated in 40% yield after two recrystallizations. However, **9** is most conveniently prepared by reaction of [*n*-Bu_4N]F·3H_2O with **8** over 3 h in THF; following this procedure **9** can be isolated in 81% yield. In THF, blue-green **9** gives rise to a doublet at δ 47.1 ($^2J_{FP}$ = 37 Hz) in the ^{31}P NMR spectrum due to coupling to one F nucleus, indicating that a single Ru−F bond persists on the NMR time scale. The ^{19}F NMR spectrum exhibits a triplet at δ −189.6 with the same coupling constant, thus establishing the presence of two equivalent ^{31}P nuclei. Additionally, the *p*-methylbenzylidyne α-C nucleus evinces coupling to a single ^{19}F nucleus and two equivalent ^{31}P nuclei (dt at δ 247.00 in the ^{13}C{^{1}H} NMR spectrum; $^2J_{CF}$ = 134.0 Hz, $^2J_{CP}$ = 18.9 Hz). We therefore propose that **9** adopts a square-planar geometry in solution, just as **13** does in the solid state,[24] a geometry that is consistent with a formal 16-electron count at Ru, ignoring any π-contribution from F.

Addition of 1 equiv of Me_3SiOTf (Tf = CF_3SO_2) to a solution of **8** in C_6D_6 causes precipitation of a blue-green powder that analyzes as Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$OTf (**16**). This compound is unstable in solution. However, upon dissolution in THF it forms a blue-green solution that exhibits single resonances at δ 44.0 and −77.5 in the ^{31}P and ^{19}F NMR spectra, respectively, prior to its decomposition into as-yet-uncharacterized products.

Reactions of Square-Planar Carbynes with HX. Formation of **8** from **6** is a net dehydrochlorination reaction. The reverse transformation is obtained rapidly and quantitatively by the simple expedient of treating **8** with ethereal HCl. Even at very low temperature, no intermediate in the protonation of **8** is observed. Similar treatment of **14** with 1 equiv of HCl initially affords the expected mixed dihalide complex Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$BrCl (**17**), but this complex rapidly undergoes halide exchange to give an equilibrium mixture that contains all three benzylidene complexes **17**, Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$$Br_2$, and **6** (Scheme 3). Rapid exchange of halide ligands between Ru(CHR)(PCy_3)$_2$$X_2$ (X = Cl, I) to yield statistical mixtures of these complexes with the corresponding mixed dihalide species Ru(CHR)(PCy_3)$_2$ClI has been noted.[31,32] Similarly rapid exchange of halide ligands in closely related catalysts was the subject of a recent report.[33] However, addition of HCl to **9** does not produce Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$ClF (**18**), but instead affords **6** and starting complex **9**. Likewise, treatment of **8** with Et_3N·3HF fails to yield **7** or **18**. Accordingly, we suggest that both **7** and **18** are unstable with respect to HF elimination under the conditions we have used and that this fact accounts for their conspicuous absence from the family of first-generation Grubbs catalysts.

Two-Electron Oxidation of Planar Carbynes. With the planar carbyne complexes Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$X (X = F, Cl, Br, I, OTf; **9**, **8**, **14**, **15**, **16**, respectively) in hand, we next examined their oxidation in order to obtain analogues of **3a** and **3b** that due to a lack of *β*-H atoms are not subject to conversion into vinylidene compounds by deprotonation. As shown in Scheme 4, all the halide complexes undergo clean two-electron oxidation to trihalide complexes. With the smaller halides, six-coordinate bis-phosphine complexes *trans,mer*-Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$$X_3$ (X = F, Cl: **19**, **20**, respectively) are formed preferentially. For oxidation of **9**, 1.35 equiv of XeF_2 in C_6H_6 is most effective, producing **19** in 45% isolated yield. AgF in THF is also effective, affording **19** in 16% yield. The NMR spectra of **19** are highly characteristic. The ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2 shows a doublet of triplets at δ 25.3 ppm ($^2J_{PF}$ = 34 Hz, $^2J_{PF}$ = 9.8 Hz) with coupling to two inequivalent fluorine environments, while the ^{19}F NMR provides two signals: a triplet of triplets at δ −190.96 ppm ($^2J_{FF}$ = 120 Hz, $^2J_{PF}$ = 32 Hz) for the fluoride *trans* to the carbyne unit and a broad doublet at δ −419.50 ppm ($^2J_{FF}$ = 120 Hz) for the mutually *trans* fluorides; coupling to the phosphine ligands was unresolved in this resonance. Complex **20** is isolated in 52% yield following reaction of **8** with C_2Cl_6. Although **19** is stable in solution for some time, **20** undergoes relatively rapid decomposition in solution. In contrast, five-coordinate square-pyramidal compounds Ru(C-*p*-C_6H_4Me)(PCy_3)X_3 (X = Br, I: **21**, **22**, respectively) are formed preferentially upon oxidation of Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$X with the corresponding halogen in hydrocarbon solution. Both **21** and **22** are stable for days in solution at 28 °C. In the syntheses of **21** and **22**, it was most convenient to use the appropriate halogen as the oxidant. Although **22** was isolated in 78% yield, **21** remains contaminated with [$BrPCy_3$]Br, which we have been unable to remove completely.

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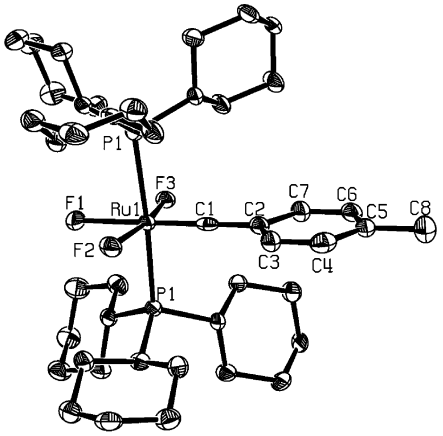

Figure 1. 50% thermal ellipsoid plot of **19**.

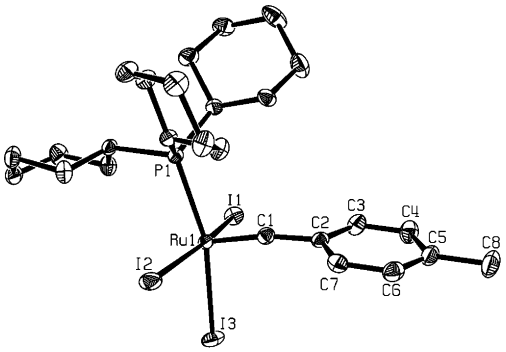

Figure 2. 50% thermal ellipsoid plot of **22**.

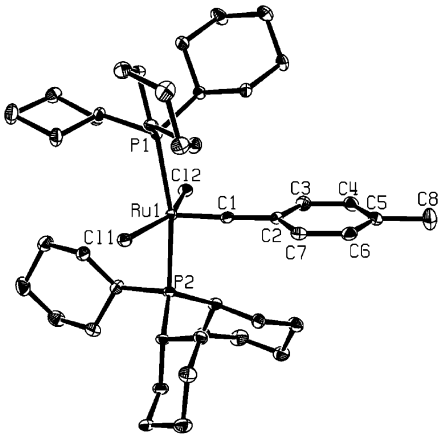

Figure 3. 50% thermal ellipsoid plot of the cation in **25**.

These oxidation reactions parallel the low-temperature oxidation of Ru(≡CPh)(CO)$(PPh_3)_2$Cl by I_2 to afford six-coordinate ionic [Ru(≡CPh)(CO)$(PPh_3)_2$ClI]I, a compound that upon heating in inert solvent loses CO and forms Ru(≡CPh)$(PPh_3)_2$-ClI_2.[29,34,35]

In the case of oxidation of **15** by I_2, only **22** is obtained; the putative six-coordinate bis-phosphine complex Ru(C-*p*-C_6H_4-Me)$(PCy_3)_2I_3$ is not observed. Nevertheless, addition of 1 equiv of PCy_3 to **22** in CD_2Cl_2 (in which **22** is quite soluble) gives rise to a new bis-phosphine complex. However, this complex is not Ru(C-*p*-C_6H_4Me)$(PCy_3)_2I_3$, even though addition of C_6D_6 followed by concentration under reduced pressure results in loss of PCy_3 and re-formation of solid **22**. Instead, we formulate this new compound as the ionic species [Ru(C-*p*-C_6H_4Me)-

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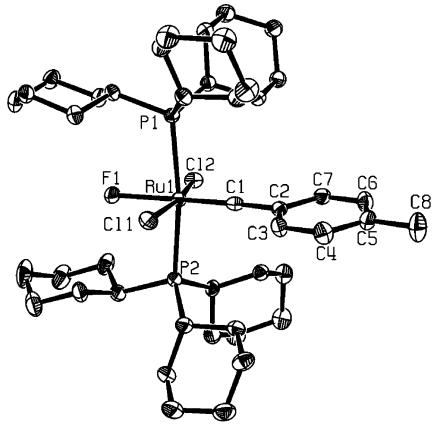

Figure 4. 50% thermal ellipsoid plot of **26**.

$(PCy_3)_2I_2$]I (**23**-I). Addition of PCy_3 followed by TlOTf (Tf = CF_3SO_2) to a solution of **22** yields soluble [Ru(C-*p*-C_6H_4Me)-$(PCy_3)_2I_2$]OTf (**23**-OTf) along with a precipitate of TlI. Compound **23**-OTf can also be prepared from **16** in 64% isolated yield by oxidation with I_2 (Scheme 5). Alternatively, reaction of **22** with PCy_3 followed by $NaBPh_4$ in CH_2Cl_2 affords [Ru-(C-*p*-C_6H_4Me)$(PCy_3)_2I_2$]BPh_4 (**23**-BPh_4) in 83% yield. Except for peaks due to BPh_4^- in the ^{1}H NMR spectrum of **23**-BPh_4, the ^{1}H and ^{31}P NMR spectra of **23**-I, **23**-OTf, and **23**-BPh_4 are identical, which establishes the presence of the discrete [Ru-(C-*p*-C_6H_4Me)$(PCy_3)_2I_2]^+$ unit in all three compounds. Accordingly, the preference for five-coordination in mono- and bis-tricyclohexylphosphine complexes when the halide ligands are bromide and iodide appears to be a steric effect. Werner has reported the formation of similar cationic five-coordinate carbyne complexes, including structurally characterized **4a** via protonation of vinylidene complexes.[11,12] Protonation of allenylidene complexes similarly affords alkenylcarbyne complexes.[15−19]

When **22** is subjected to excess PPh_3 in CH_2Cl_2, genuine six-coordinate Ru(C-*p*-C_6H_4Me)$(PPh_3)_2I_3$ is formed. An initial pair of doublets in the ^{31}P NMR spectrum is observed that is consistent with a mixed bis-phosphine complex such as Ru(C-*p*-C_6H_4Me)$(PCy_3)(PPh_3)I_3$ or [Ru(C-*p*-C_6H_4Me)$(PCy_3)(PPh_3)$-I_2]I, which can then disproportionate into Ru(C-*p*-C_6H_4Me)-$(PPh_3)_2I_3$ and **23**-I (Scheme 6). Compound **23**-I is also observed at short reaction times.

Although pseudo-octahedral **20** was the only Ru-containing product of oxidation of **8** by C_2Cl_6, the five-coordinate complex Ru(C-*p*-C_6H_4Me)$(PCy_3)Cl_3$ (**24**) can be isolated in 63% yield upon treatment of **20** with elemental sulfur, followed by extraction with toluene to remove the S=PCy_3 byproduct. Unlike **20**, **24** is stable for days in CD_2Cl_2 solution at 28 °C.

Treatment of **20** with $[Ph_3C][BF_4]$ in CH_2Cl_2 at 28 °C results in the abstraction of one chloride ligand to form a cationic five-coordinate complex, [Ru(C-*p*-C_6H_4Me)$(PCy_3)_2Cl_2$]BF_4 (**25**). The ^{1}H and ^{31}P NMR chemical shifts are consistent with those of **23**-I, **23**-OTf, and **23**-BPh_4, and those reported for [Ru(CCH_2-Ph)$(PCy_3)_2Cl_2$][B($C_6H_3(CF_3)_2$-3,5)$_4$] (**3a**).[12] The orange powder **25** can be isolated in 89.4% yield by concentration of the solvent and washing the remaining residue with pentane and ether.

Attempts to synthesize the five-coordinate complex Ru(C-*p*-C_6H_4Me)$(PCy_3)F_3$ through phosphine trapping of **19** with elemental sulfur, or ligand substitution of **24** or **22** with various fluoride sources, including AgF, [*n*-Bu_4N]F·$3H_2O$, TAS-F, and CsF, have thus far been unsuccessful. This apparent preference for six-coordination does not hinder intermetal halide exchange

Table 2. Selected Bond Lengths and Angles for Benzylidyne Complexes 19, 22, 25, and 26

	19	**22**	**25**	**26**
		Bond Distances (Å)		
Ru−C(1)	1.703(9)	1.670(5)	1.678(3)	1.714(3)
Ru−P(1)	2.4443(14)	2.4142(12)	2.4483(12)	2.4600(10)
Ru−P(2)	2.4444(14)		2.4321(12)	2.4658(11)
Ru−F(1) *trans* to carbyne	2.089(4)			2.0092(19)
Ru−X *cis* to carbyne	F(2): 1.985(4)	I(1): 2.6905(5)	Cl(1): 2.3527(11)	Cl(1): 2.4008(10)
Ru−X *cis* to carbyne	F(3): 1.989(4)	I(2): 2.6515(6)	Cl(2): 2.3359(11)	Cl(2): 2.3800(10)
Ru−I(3) *trans* to PCy_3		2.6992(6)		
		Bond Angles (deg)		
Ru−C(1)−C(2)	179.9(7)	168.8(4)	171.4(3)	169.9(3)
C(1)−Ru−P(1)	92.72(4)	97.01(16)	96.70(11)	93.96(11)
C(1)−Ru−P(2)	92.72(4)		95.77(11)	95.20(11)
C(1)−Ru−X *cis* halide	F(2): 94.9(3)	I(1): 93.23(16)	Cl(1): 105.28(11)	Cl(1): 89.09(12)
C(1)−Ru−X *cis* halide	F(3): 98.2(3)	I(2): 102.48(16)	Cl(2): 97.80(11)	Cl(2): 100.70(11)
C(1)−Ru−I(3)		97.95(16)		
F(1)−Ru−P(1)	87.27(4)			85.09(6)
F(1)−Ru−P(2)	87.27(4)			86.07(6)
I(3)−Ru−P(1)		164.88(3)		

of **19** and **20**, which occurs rapidly in dichloromethane. Attempted comproportionation of 2 equiv of **20** and 1 equiv of **19** led to a complex mixture rapidly at RT, the major product of which was determined to be the desired compound Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_2F$ (**26**) by independent synthesis (see below).

Structures of Oxidized Carbyne Complexes. No five- or six-coordinate ruthenium−benzylidyne complexes had been structurally characterized prior to this work, although the structures of several osmium benzylidyne complexes have been determined by X-ray diffraction.[30,36−40] Accordingly, we obtained the single-crystal X-ray structures of **19**, **22**, and Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_2F$ (**26**) for comparison to the few known ruthenium−carbyne structures. Pale brown **26** was prepared in 74% yield by reaction of **20** with [$S(NMe_2)_3$][$SiMe_3F_2$] (TAS-F). Crystallographic data for **19**, **22**, **25**, and **26** are listed in Table 1. Thermal ellipsoid plots of **19**, **22**, **25**, and **26** are shown in Figures 1−4.

The ^{1}H and ^{31}P NMR spectra and solubility properties of **19**, **20**, and **26** are indicative of six-coordination. As is seen in Figure 1, **19** adopts a pseudo-octahedral geometry in the solid state such that the two PCy_3 ligands are mutually *trans*, with a meridional arrangement of the three fluoride ligands. Structurally characterized complexes of ruthenium with three fluoride ligands are very rare.[41,42] Complex **19** is unique among these in that its fluoride ligands are all terminal rather than bridging. In general, fluoride complexes of ruthenium are uncommon but increasingly well known.[43,44] Complex **26** (Figure 4) adopts a similar geometry in which the unique fluoride ligand is *trans* to the carbyne moiety. This geometry parallels that seen in a closely related complex of osmium, Os(C-*p*-$C_6H_4NMe_2$)(PPh_3)$_2Cl_2$(NCS), in which the hardest ligand present, N-bonded thiocyanate, occupies the position *trans* to the carbyne ligand.[37] In square-pyramidal **22** and **25**, the *p*-methylbenzylidyne ligand occupies the apical position (Figures 2, 3). Important bond lengths and angles for **19**, **22**, **25**, and **26** are listed in Table 2.

The Ru≡C bond length of 1.670(5) Å in **22** is indicative of a triple bond. This is not significantly smaller than those found in six-coordinate carbyne complexes such as **19** (1.703(9) Å) and *trans,mer*-Ru(≡CCH=CMe_2)(PPh_3)$_2Cl_3$ (1.696(6) Å),[13] but is marginally less than that in **26**, which exhibits a rather long Ru≡C bond, 1.714(3) Å in length, comparable to that found in square-planar **13**.[24]

The slightly greater length of the Ru≡C bond in **22** than that in the cationic five-coordinate carbyne complex **4a**[$B(C_6H_3(CF_3)_2$-3,5)$_4$] (1.660(5) Å)[11,12] is not statistically significant, although it is worth noting that the Ru≡C internuclear separation in cationic **4a** is significantly shorter than those of all three six-coordinate carbyne complexes **19**, **26**, and Ru(≡CCH=CMe_2)(PPh_3)$_2Cl_3$. However, the Ru≡C bond in cationic **25** is indistinguishable from those of neutral **19** and **22**, and cationic **4a** by the 3σ criterion, and is significantly shorter only than the Ru≡C bond in **26**.

Formation of Carbene Complexes from Oxidized Carbynes. Addition of Schwartz's reagent to **20** results in quantitative formation of **6**[25] and Cp_2ZrCl_2[45] (Scheme 7). At present, the initial site of hydride attack is unclear, as **6** is the thermodynamic product. When the reaction is performed in a NMR spectrometer and monitored at low temperature, no hydride is observed at any point, but the carbene proton is seen immediately at −60 °C by ^{1}H NMR spectroscopy. The thermodynamic preference for the five-coordinate carbene complex as opposed to the isomeric six-coordinate carbyne−hydride complex is opposite of that found in related Os systems.[46−48] It is of note that addition of a hydride source to **20** results in formation of a carbene complex, whereas addition of a fluoride source to **20** results in formation of the carbyne complex **26**, which raises the question of the stability of α-halocarbene complexes of the type Ru(CXR)L_2X_2 and may have implications for metathesis of vinyl halides. We have recently noted that the new monofluoromethylidene complex Ru(CHF)(H_2IMes)(PCy_3)Cl_2[49] forms the corresponding terminal

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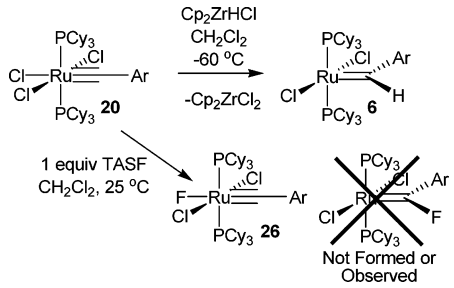
Scheme 7. Reactivity of 20 with Hydride and Fluoride Sources



carbide complex Ru(C)(H_2IMes)(PCy_3)Cl_2[50−53] cleanly and spontaneously under a number of conditions, thus accounting for the lack of successful olefin cross-metathesis reactions involving vinyl fluoride.[49] However, the formation of Ru(C)-(H_2IMes)(PCy_3)Cl_2 upon reaction of **2** with 1,1-disubstituted vinyl halides is unlikely, as C−C bond cleavage in an intermediate such as Ru(CXR)L_2X_2 would be required. Instead, formation of complexes akin to **20** and **26** is a likely possibility. We are currently studying reactions of **1** and **2** with appropriately substituted vinyl halides to address this point.

Alkyne Dimerization. Dimerization of terminal alkynes to form conjugated enynes[54−58] is of interest due to its atom-economy.[59] The enynes so formed are attractive building blocks in organic syntheses.[60] Many systems currently available employ a metal catalyst and a base to aid in the transformation. Single-component catalysts are known but are less common.[61] Complex **19** was found to effectively catalyze dimerization of terminal alkynes to give enynes. Catalytic reactions were carried out with 5 mol % **19** in C_6D_6 in a sealed J. Young NMR tube at 65 °C. After 28 h, dimerization of phenylacetylene gave at least 96% conversion to two enyne isomers, Z-1,4-diphenyl-1-buten-3-yne and 2,4-diphenyl-1-buten-3-yne in a 4:1 ratio, respectively. Throughout the course of the reaction, **19** showed decomposition by ^{1}H and ^{31}P NMR but retained some activity at the end of the reaction. The *Z*-isomer, the major product here, is the opposite isomer of that obtained by Ozerov and co-workers in recent Rh-catalyzed alkyne dimerizations.[61] Complex **19** similarly dimerized $Me_3SiC{\equiv}CH$. While the mechanism of the transformation mediated by **19** is not known, the fluoride ligand is essential to activity. This is shown by the fact that only **19** and the monofluoride complex **26** are active, though **26** is less efficient, under these conditions. The analogous trichloride complex **20** shows no activity. Metal−vinylidenes are often implicated in alkyne dimerization and cannot be ruled out at this point.

Conclusions

Dehydrochlorination of "first-generation" Grubbs catalysts can be accomplished in one step by reaction with the bulky dialkyl germylene Ge(CH[$SiMe_3$]$_2$)$_2$ (**10**) or in two steps via reaction with excess phenoxide ion followed by $SnCl_2$. Products of both processes are diamagnetic square-planar carbyne complexes of the form Ru(CR)(PCy_3)$_2$Cl. The one-step process works for both R = alkyl and R = aryl; in contrast, the two-step procedure fails at the first step when R = alkyl. The benzylidyne complex Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Cl (**8**) is a useful precursor to the corresponding monohalide and triflate complexes Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$X (X = F, Br, I, OTf). These benzylidyne complexes react rapidly and quantitatively with ethereal HCl to afford Grubbs catalysts Ru(CH-*p*-C_6H_4Me)-(PCy_3)$_2$XCl; when X ≠ Cl, halide exchange occurs rapidly in solution to generate a mixture of the three possible Grubbs catalysts Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$XCl, Ru(CH-*p*-C_6H_4Me)-(PCy_3)$_2$$Cl_2$ (**6**), and Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$$X_2$. The square-planar complexes undergo ready two-electron oxidation to the corresponding diamagnetic trihalide benzylidyne complexes, which are either square-pyramidal Ru(C-*p*-C_6H_4Me)(PCy_3)X_3 (X = Br, I) or pseudo-octahedral Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$$X_3$ (X = F, Cl). Steric effects appear to be responsible for this dichotomy, as attempts to generate six-coordinate Ru(C-*p*-C_6H_4-Me)(PCy_3)$_2$$I_3$ by addition of PCy_3 fail, instead affording cationic [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$$I_2$]I. However, six-coordinate Ru(C-*p*-C_6H_4Me)(PPh_3)$_2$$I_3$ can be synthesized by addition of excess PPh_3 to Ru(C-*p*-C_6H_4Me)(PCy_3)I_3. One PCy_3 ligand can be removed from Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$$X_3$ to yield Ru(C-*p*-C_6H_4Me)(PCy_3)X_3 upon reaction with elemental sulfur only for X = Cl. Four structurally characterized complexes, two neutral six-coordinate bis-phosphine complexes, one neutral five-coordinate monophosphine complex, and one cationic bis-phosphine complex, reveal Ru≡C bond lengths in the range 1.67−1.71 Å, consistent with ruthenium−carbon triple bonds. The five-coordinate complexes are best described as square pyramidal; the benzylidyne ligand occupies the apical position. Of the trihalide complexes, only the fluoride-containing complexes Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$$X_2$F (X = F, Cl) display reactivity toward alkynes, catalyzing the formation of conjugated enynes via dimerization of terminal alkynes. Hydride addition to Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$$Cl_3$ re-forms the Grubbs catalyst **6** cleanly.

Experimental Section

General Procedures. All reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen or in a nitrogen-filled MBraun Labmaster 130 glovebox, unless otherwise specified. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Varian Inova 300 MHz or 400 MHz NMR spectrometer. ^{1}H and ^{13}C spectra were referenced to solvent signals.[62] ^{19}F NMR spectra were referenced to external $CFCl_3$ in $CDCl_3$ ($\delta = 0$); ^{31}P NMR spectra were referenced to external 85% H_3PO_4 ($\delta = 0$).

Materials. [S(NMe_2)$_3$][SiF_2Me_3] (TAS-F), I_2, 1 M and 2 M HCl in ether, $Et_3N{\cdot}3HF$, and py(HF)$_n$ were purchased from Aldrich. Br_2, hexachloroethane, NaI, PPh_3, LiBr, triethylamine, [*n*-Bu_4N]F·3H_2O, 18-crown-6, trityl tetrafluoroborate, phenylacetylene, and 1,3,5-trimethoxybenzene were purchased from Acros. Trimethylsilylacetylene was purchased from GFS. $NaBPh_4$, TlOTf, XeF_2, CsF, AgF, Cp_2ZrHCl (Schwartz's reagent), and Cp_2ZrCl_2 were purchased

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from Strem. Elemental sulfur (S_8) was purchased from Mallinckrodt. All bulk solvents were obtained from VWR Scientific and dried by passage through solvent purification columns according to the method of Grubbs.[63] Deuterated solvents were purchased from CIL and dried over 4 Å molecular sieves. All liquid reagents were degassed and then dried over sieves or passed through activated alumina. Solid reagents were used as received. The starting compounds [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Cl] (**8**),[24] [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Br] (**14**),[24] [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$OTf] (**16**),[24] and [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$] (**6**)[25] were synthesized according to published procedures.

[Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$F] (9). Syntheses of this compound were reported previously.[24] An improved procedure is as follows. To a stirred blue-green solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Cl] (**8**) (1.001 g, 1.250 mmol) in THF (60 mL) was added [*n*-Bu_4N]F·$3H_2O$ (0.789 g, 2.50 mmol, 2.00 equiv) as a solid at once. The solid was washed in with THF (20 mL). The resulting green solution was stirred for 2.5 h, then concentrated to dryness. The remaining green solid was slurried in cold acetonitrile (10 mL) for 10 min, filtered, washed with cold acetonitrile (4 × 5 mL), and dried *in vacuo* for 2 h. Blue-green powder **9** (0.797 g, 1.02 mmol) was recovered pure in 81.3% yield.

[Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$I] (15). To a solid mixture of blue-green [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Cl] (**8**) (2.029 g, 2.53 mmol) and excess NaI (3.769 g, 25.1 mmol, 9.92 equiv) was added THF (240 mL). The heterogeneous mixture was stirred for 1.5 h, over which time the solution turned brown. The solution was then concentrated to dryness under vacuum. The brown material was extracted into toluene (240 mL) and stirred for 1 h. The solution was filtered through a bed of Celite to remove white sodium salts. The Celite was washed with toluene (3 × 50 mL) until all color was removed. The filtrate was concentrated to dryness. The brown residue was stirred in cold pentane (40 mL) for 1 h and then filtered. The precipitate was washed with cold pentane (2 × 10 mL) and dried *in vacuo* 4 h. Green-gray powder **15** (1.529 g, 1.71 mmol) was recovered pure in 67.7% yield. ^{1}H NMR (400 MHz, C_6D_6): δ 7.83 (d, $^3J_{HH}$ = 8.2 Hz, 2H C_6H_4Me), 6.59 (d, $^3J_{HH}$ = 7.6 Hz, 2H, C_6H_4Me), 1.64 (s, 3H, CH_3), 2.65, 2.36−2.33, 2.02−1.96, 1.78−1.76, 1.64−1.62, 1.27−1.17 (all m, 66H, PCy_3). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ 241.61 (t, J_{PC} = 17.5 Hz, Ru≡C−Ar), 141.15 and 140.58 (both s, *ipso*-C and *p*-C of C_6H_4Me), 129.99 and 127.82 (both s, C_6H_4Me), 38.79 (t, J_{PC} = 9.2 Hz, *ipso*-C of P(C_6H_{11})$_3$), 32.06 (br s, *m*-C of P(C_6H_{11})$_3$), 28.65 (t, J_{PC} = 5.3 Hz, *o*-C of P(C_6H_{11})$_3$), 27.77 (s, *p*-C of P(C_6H_{11})$_3$), 22.32 (s, CH_3). ^{31}P-{^{1}H} NMR (161.9 MHz, C_6D_6): δ 40.4 (s). Anal. Calcd for $C_{44}H_{73}IP_2Ru$: C, 59.25; H, 8.25. Found: C, 59.06; H, 8.51.

[Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Br_2$]. To a stirred solution of lithium bromide (2.070 g, 23.8 mmol, 20.0 equiv) in THF (20 mL) was added [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$] (**6**) (1.000 g, 1.20 mmol) as a solid. The solid was washed in with CH_2Cl_2 (40 mL). The solution was stirred for 3.5 h, then concentrated to dryness. The remaining purple material was extracted into toluene (40 mL) and stirred for 20 min. The mixture was filtered through a bed of wetted Celite and the purple color was washed through with toluene (2 × 30 mL). The filtrate was concentrated to dryness. The resulting purple solid was slurried in cold pentane (20 mL), filtered, washed with pentane (3 × 5 mL), and dried *in vacuo* for 5 h. Purple powder material (0.945 g) was recovered as ∼86% dibromide product by ^{1}H and ^{31}P NMR; 13% remained incompletely reacted. The purple powder was resubjected to the reaction conditions three times to provide the pure purple powder product (0.632 g, 0.682 mmol) in 57.1% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 19.83 (s, Ru=C*H*Ar), 8.33 (d, $^3J_{HH}$ = 6.9 Hz, 2H, C_6H_4Me), 7.12 (d, $^3J_{HH}$ = 7.6 Hz, 2H, C_6H_4Me), 2.85 (br s, 6H, PCH of PCy_3), 2.09 (s, 3H, CH_3), 1.80−1.70, 1.43−1.38, 1.25−1.15 (all m, 60H, PCy_3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 295.77 (t, J_{PC} = 8.8 Hz, Ru=CHAr), 151.35 (s, *p*-C of C_6H_4Me), 140.78 (*ipso*-C of C_6H_4Me), 131.71 and 129.61 (both s, C_6H_4Me), 33.41 (t, J_{PC} = 9.2 Hz, *ipso*-C of P(C_6H_{11})$_3$), 30.42 (br s, *m*-C of P(C_6H_{11})$_3$), 28.17 (t, J_{PC} = 5.4 Hz, *o*-C of P(C_6H_{11})$_3$), 26.94 (s, *p*-C of P(C_6H_{11})$_3$), 22.34 (s, CH_3). ^{31}P-{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 36.8 (s). Anal. Calcd for $C_{44}H_{74}Br_2P_2Ru$: C, 57.08; H, 8.06. Found: C, 57.11; H, 8.23.

[Ru(C-*p*-C_6H_4Me)(PCy_3)$_2F_3$] (19). Method A (XeF_2). To a stirred green solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$F] (**9**) (0.199 g, 0.254 mmol) in benzene (25 mL) was added XeF_2 (0.058 g, 0.34 mmol, 1.4 equiv) as a white crystalline solid at once. The reaction mixture was stirred for 45 min, over which time it turned from green to brown. The mixture was then concentrated to dryness. The remaining brown residue was slurried in cold hexanes (6 mL) for 15 min, filtered, and washed with hexanes (3 × 3 mL). The remaining solid was dried in vacuo 3 h. Pink-gray powder (0.148 g) was recovered containing a small amount of an unknown purple impurity, which is recognizable in the ^{1}H NMR spectrum as two broad peaks centered at δ 12.7 and 11.9 ppm in CD_2Cl_2. This impurity also tends to broaden the ^{19}F and ^{31}P NMR shifts of the product **19**, such that the coupling constants cannot be determined. To remove this impurity, the pink-gray powder was stirred in CH_2Cl_2 (10 mL). To the stirred brown solution was added triethylamine (25.0 μL, 0.180 mmol). The mixture was stirred for 30 min and then concentrated to dryness. The remaining residue was slurried in cold acetonitrile (6 mL) for 15 min, filtered, washed with acetonitrile (3 × 3 mL), and dried *in vacuo* 2 h. Pale pinkish-gray powder (0.111 g) was recovered with a minor amount of the above-mentioned impurity still present. The triethylamine treatment was repeated once. In this way, gray powder **19** (0.095 g, 0.12 mmol) was recovered in pure form in 45% overall yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.13 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 6.70 (d, $^3J_{HH}$ = 8.0 Hz, 2H, C_6H_4Me), 2.54 (br s, 6H, PCH of PCy_3), 1.67 (s, 3H, CH_3), 2.32−2.28, 1.89−1.53, 1.27−1.14 (all m, 60H, PCy_3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 147.25 (s, *p*-C of C_6H_4Me), 141.95 (d, J_{FC} = 11.6 Hz, *ipso*-C of C_6H_4Me), 132.34 and 130.27 (both s, C_6H_4Me), 34.48 (t, J_{PC} = 9.5 Hz, *ipso*-C of P(C_6H_{11})$_3$), 29.03 (br s, *m*-C of P(C_6H_{11})$_3$), 28.23 (t, J_{PC} = 5.5 Hz, *o*-C of P(C_6H_{11})$_3$), 26.99 (s, *p*-C of P(C_6H_{11})$_3$), 23.15 (s, CH_3). ^{19}F-{^{1}H} NMR (376.29 MHz, CD_2Cl_2): δ −190.96 (tt, $^2J_{FF}$ = 120 Hz, $^2J_{PF}$ = 32 Hz, RuF-*trans* to carbyne), −419.50 (br d, $^2J_{FF}$ = 120 Hz, RuF_2-*cis* to carbyne). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 25.3 (dt, $^2J_{PF}$ = 34 Hz, $^2J_{PF}$ = 10 Hz). Anal. Calcd for $C_{44}H_{73}F_3P_2Ru$: C, 64.29; H, 8.95. Found: C, 64.34; H, 9.84.

Method B (AgF). To a stirred green solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$F] (**9**) (0.069 g, 0.088 mmol) in THF (7 mL) was added silver(I) fluoride (0.028 g, 0.22 mmol, 2.5 equiv) as a solid at once. The reaction vial was wrapped in aluminum foil to protect the reaction from light. The heterogeneous mixture was stirred for 48 h, over which time the solution turned from green to brown. The reaction mixture was then filtered through a bed of wetted Celite and the brown color washed through with THF (2 × 3 mL). The filtrate was concentrated to dryness. The remaining solid was slurried in cold acetone (4 mL) for 10 min, filtered, washed with cold acetone (3 × 2 mL), and dried *in vacuo*. Gray powder **19** (0.011 g, 0.014 mmol) was recovered in 16% yield.

[Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_3$] (20). A blue-green solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Cl] (**8**) (0.253 g, 0.316 mmol) in toluene (20 mL) and a solution of hexachloroethane (0.078 g, 0.33 mmol, 1.0 equiv) in toluene (10 mL) were frozen with liquid N_2. The hexachloroethane solution was thawed until it was completely liquid and added all at once to the ruthenium solution as it just thawed enough to begin stirring. The reaction mixture was stirred and allowed to warm to glovebox temperature (30 °C) for 1 h, over which time the solution turned brown and a precipitate formed. The reaction mixture was concentrated under vacuum to dryness. The tan solid was slurried in cold pentane (10 mL) and stirred for

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10 min. The mixture was filtered. The solid was washed with cold acetonitrile (3 × 6 mL) and cold pentane (3 × 6 mL) and dried *in vacuo* 6 h. Tan powder **20** (0.145 g, 0.166 mmol) was recovered pure in 52.5% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.16 (d, $^3J_{HH}$ = 8.5 Hz, 2H, C_6H_4Me), 7.29 (d, $^3J_{HH}$ = 8.5 Hz, 2H, C_6H_4-Me), 2.68 (m, 6H, PCH of PCy_3), 2.42 (s, 3H, CH_3), 2.14−2.11, 1.87−1.62, 1.30−1.11 (all m, 60H, PCy_3). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 18.2 (s). Anal. Calcd for $C_{44}H_{73}Cl_3P_2Ru$: C, 60.64; H, 8.44. Found: C, 60.72; H, 8.31. Attempts to obtain a ^{13}C{^{1}H} NMR spectrum of this compound have failed due to low solubility and decomposition at elevated concentration.

[Ru(C-*p*-C$_6$H$_4$Me)(PCy$_3$)Br$_3$] (21). To a 20 mL scintillation vial was added a blue-green solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Br] (**14**) (0.102 g, 0.121 mmol) in dry benzene (10 mL) and a stirbar. The vial was sealed with a septum and secured with copper wire. The sealed solution was removed from the glovebox. To the stirred solution was added by syringe bromine (0.306 mL, 0.119 mmol, 0.986 equiv) in the form of a freshly prepared stock solution (0.389 M) in dry benzene. The reaction mixture was stirred for 1 h, over which time the solution turned brown and an orange-brown precipitate formed. The vial was returned to the glovebox. The reaction mixture was concentrated to ∼2 mL of solution and filtered. The remaining solid was dried *in vacuo* 4 h. The tan powder (0.095 g) was recovered. Integration of the ^{31}P NMR signals indicates 63% **21** and 37% [BrPCy$_3$]Br and, therefore, an 80% yield of **21**. [BrPCy$_3$]Br and **21** could not be separated due to similar solubilities. Note: By reaction with Br_2, trace water or use of toluene as solvent can each generate HBr in solution, which reacts rapidly with Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Br (**14**) to form Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$$Br_2$. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.03 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 7.30 (d, $^3J_{HH}$ = 7.9 Hz, 2H, C_6H_4Me), 3.07−2.98 (m resembles q, 3H, PCH of PCy_3), 2.41 (s, 3H, CH_3), 2.14−1.96, 1.84−1.48, 1.39−1.22 (all m, [BrPCy$_3$]Br and **21**-PCy_3). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 101.69 (s, [BrPCy$_3$]Br), 69.57 (s, **21**). NMR spectra for the mixture of **21** and [BrPCy$_3$]Br are reproduced in the Supporting Information.

[Ru(C-*p*-C$_6$H$_4$Me)(PCy$_3$)I$_3$] (22). To a stirred gray solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$I] (**15**) (0.200 g, 0.224 mmol) in 25 mL of benzene was added dropwise a solution of iodine (0.059 g, 0.23 mmol, 1.0 equiv) in 8 mL of benzene. The solution was stirred for 1 h, over which time the solution turned brown and a precipitate formed. The reaction mixture was concentrated under vacuum to one-quarter of the initial volume. The precipitate was filtered from the solution, washed with benzene (3 × 2 mL), and dried *in vacuo* 3 h. Brown powder **22** (0.152 g, 0.175 mmol) was recovered purely in 78.2% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.06 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 3.30 (m resembles q, 3H, PCH of PCy_3), 2.38 (s, 3H, CH_3), 2.04−1.92, 1.84−1.72, 1.61−1.52, 1.38−1.19 (all m, 30H, PCy_3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ 287.24 (d, J_{PC} = 10.7 Hz, Ru≡C−Ar), 149.80 (s, *ipso*-C of C_6H_4Me), 134.46 (s, *p*-C of C_6H_4-Me), 131.86 and 131.07 (both s, C_6H_4Me), 37.82 (d, J_{PC} = 21.9 Hz, *ipso*-C of P(C_6H_{11})$_3$), 31.47 (d, J_{PC} = 2.1 Hz, *m*-C of P(C_6H_{11})$_3$), 28.14 (d, J_{PC} = 11.2 Hz, *o*-C of P(C_6H_{11})$_3$), 26.58 (s, *p*-C of P(C_6H_{11})$_3$), 23.27 (s, CH_3). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 66.5 (s). Anal. Calcd for $C_{26}H_{40}I_3PRu$: C, 36.09; H, 4.66. Found: C, 36.10; H, 4.42.

Formation of [Ru(C-*p*-C$_6$H$_4$Me)(PCy$_3$)$_2$I$_2$]I (23-I). To a solid sample of PCy_3 (0.004 g, 0.01 mmol, 1 equiv) was added a red-brown solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)I_3] (**22**) (0.012 g, 0.013 mmol) in CD_2Cl_2 (ca. 0.75 mL). The solution was mixed well by pipet, and the solution darkened slightly. After 20 min the ^{1}H and ^{31}P NMR spectra were obtained, and the only observable species was identified as [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$$I_2$]I (**23-I**). Note: Attempts at isolation of **23-I** generally led to mixtures of **22** and **23-I**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.88 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_6H_4Me), 7.27 (d, $^3J_{HH}$ = 8.0 Hz, 2H, C_6H_4Me), 3.46 (br s, 6H, PCH of PCy_3), 2.48 (s, 3H, CH_3), 1.89−1.75, 1.47−1.17 (all m, 60H, PCy_3). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 51.1 (s). NMR spectra for the mixture of **23-I** are reproduced in the Supporting Information.

[Ru(C-*p*-C$_6$H$_4$Me)(PCy$_3$)$_2$I$_2$]OTf (23-OTf). Method A. To a stirred green-blue solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$OTf] (**16**) (0.063 g, 0.069 mmol) in 10 mL of THF was added rapidly a solution of iodine (0.018 g, 0.071 mmol, 1.0 equiv) in 2 mL of THF. The solution was stirred for 1 h, over which time the solution turned brown and a green precipitate formed. The reaction mixture was concentrated to dryness under vacuum. The remaining solid was slurried in pentane (8 mL) and stirred for 10 min. The mixture was filtered, washed with benzene (3 × 3 mL) and pentane (3 × 3 mL), and dried *in vacuo* 3 h. Bright green powder **23-OTf** (0.052 g, 0.044 mmol) was recovered in 64.2% yield.

Method B. To a stirred red-brown solution of [Ru(C-*p*-C_6H_4-Me)(PCy_3)I_3] (**22**) (0.152 g, 0.176 mmol) in 10 mL of CH_2Cl_2 was added a solution of PCy_3 (0.054 g, 0.19 mmol, 1.1 equiv) in 5 mL of CH_2Cl_2. The solution was stirred for 5 min, over which time the red-brown solution darkened slightly. Solid thallium(I) triflate (0.067 g, 0.19 mmol, 1.1 equiv) was added and washed in with CH_2Cl_2 (2 mL). A yellow precipitate formed immediately and the solution turned green-brown. The heterogeneous mixture was stirred for 1 h, filtered through a bed of wetted Celite, and washed through with CH_2Cl_2 (3 × 5 mL). The filtrate was concentrated to dryness under vacuum. The remaining solid was slurried in pentane (8 mL) and stirred for 10 min. The mixture was filtered, washed in with benzene (3 × 5 mL) and pentane (3 × 5 mL), and dried *in vacuo* 4 h. Bright green powder **23-OTf** (0.186 g, 0.159 mmol) was recovered pure in 90.4% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.88 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_6H_4Me), 7.25 (d, $^3J_{HH}$ = 8.0 Hz, 2H, C_6H_4Me), 3.45 (br s, 6H, PCH of PCy_3), 2.46 (s, 3H, CH_3), 1.92−1.75, 1.49−1.19 (all m, 60H, PCy_3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, −20 °C): δ 293.24 (br s, Ru≡C−Ar), 152.07 (s, *p*-C of C_6H_4Me), 131.94 (*ipso*-C of C_6H_4Me), 130.94 and 130.76 (both s, C_6H_4Me), 38.02 (br s, *ipso*-C of P(C_6H_{11})$_3$), 31.57 (br s, *m*-C of P(C_6H_{11})$_3$), 27.62 (t, J_{PC} = 5.0 Hz, *o*-C of P(C_6H_{11})$_3$), 26.16 (s, *p*-C of P(C_6H_{11})$_3$), 23.32 (s, CH_3). ^{19}F{^{1}H} NMR (376.3 MHz, CD_2Cl_2): δ −79.36 (s, OTf). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 51.1 (s). Anal. Calcd for $C_{45}H_{73}F_3I_2O_3P_2RuS$: C, 46.28; H, 6.30. Found: C, 46.31; H, 6.50.

[Ru(C-*p*-C$_6$H$_4$Me)I$_2$(PCy$_3$)$_2$]BPh$_4$ (23-BPh$_4$). To a stirred red-brown solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)I_3] (**22**) (0.142 g, 0.165 mmol) in 6 mL of CH_2Cl_2 was added a solution of PCy_3 (0.046 g, 0.16 mmol, 1.0 equiv) in 2 mL of CH_2Cl_2. The solution was stirred for 5 min, over which time the red-brown solution darkened slightly. Solid $NaBPh_4$ (0.084 g, 0.25 mmol, 1.5 equiv) was added and washed in with CH_2Cl_2 (2 mL). A white precipitate formed and the solution turned green-brown. The heterogeneous mixture was stirred for 1 h, filtered through a bed of CH_2Cl_2-wetted Celite, and washed through with CH_2Cl_2 (3 × 15 mL). The filtrate was concentrated to dryness under vacuum. The remaining solid was slurried in pentane (8 mL) and stirred for 30 min. The mixture was filtered, washed with pentane (3 × 5 mL), and dried *in vacuo* 6 h. Bright green powder **23-BPh$_4$** (0.183 g, 0.137 mmol) was recovered pure in 83.0% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.89 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 7.32 (br s, 8H, *o-H* of BPh_4), 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 7.03 (apparent t, 8H, *m-H* of BPh_4), 6.88 (t, $^3J_{HH}$ = 7.3 Hz, 4H, *p-H* of BPh_4) 3.47 (br s, 6H, PCH of PCy_3), 2.43 (s, 3H, CH_3), 1.93−1.75, 1.51−1.16 (all m, 60H, PCy_3). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 51.1 (s). Anal. Calcd for $C_{68}H_{93}BI_2P_2Ru$: C, 61.04; H, 7.01. Found: C, 61.50; H, 7.57.

[Ru(C-*p*-C$_6$H$_4$Me)(PPh$_3$)$_2$I$_3$]. To a solid mixture of brown [Ru(C-*p*-C_6H_4Me)(PCy_3)I_3] (**22**) (0.152 g, 0.176 mmol) and triphenylphosphine (0.235 g, 0.896 mmol, 5.10 equiv) was added CH_2Cl_2 (15 mL). The reaction mixture was stirred for 1 h. The solution was concentrated to dryness. The remaining brown residue was

slurried in cold pentane (8 mL) for 10 min, filtered, and washed with acetonitrile (3 × 5 mL) and pentane (3 × 3 mL). The remaining solid was dried *in vacuo* overnight. The impure orange powder (0.141 g) thus recovered was resubjected to the reaction conditions to eliminate some PCy_3-containing products. Orange powder product (0.071 g, 0.064 mmol) was then recovered pure in 36% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.09−8.02 (m, 12H, PPh_3), 7.44 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_6H_4Me), 7.49−7.35 (m, 18H, PPh_3), 6.58 (d, $^3J_{HH}$ = 8.0 Hz, 2H, C_6H_4Me), 2.25 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ −1.4 (s). Anal. Calcd for $C_{44}H_{37}I_3P_2Ru$: C, 47.63; H, 3.36. Found: C, 47.67; H, 3.52. Attempts to obtain a $^{13}C\{^1H\}$ NMR spectrum of this compound have failed due to low solubility and decomposition at elevated concentration.

[Ru(C-*p*-C_6H_4Me)(PCy_3)Cl_3] (24). To a stirred tan solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_3$] (**20**) (0.157 g, 0.180 mmol) in 10 mL of CH_2Cl_2 was added solid yellow S_8 (0.007 g, 0.03 mmol, 0.2 equiv). The sulfur was washed in with CH_2Cl_2 (2 mL). The solution was stirred for 30 min, over which time the solution turned red-brown. The reaction mixture was filtered and the filtrate concentrated to dryness under vacuum. The remaining residue was slurried in cold toluene (2 mL) and stirred for 10 min. The mixture was filtered, washed with cold toluene (2 × 2 mL) and cold pentane (3 × 3 mL), and dried *in vacuo* 6 h. Orange-brown powder **24** (0.067 g, 0.11 mmol) was recovered purely in 63% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.98 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 7.35 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 2.85 (m resembles q, 3H, PCH of PCy_3), 2.43 (s, 3H, CH_3), 2.00−1.57, 1.36−1.15 (all m, 30H, PCy_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 302.47 (d, J_{PC} = 13.8 Hz, Ru≡C−Ar), 150.32 (s, *ipso*-C of C_6H_4Me), 140.25 (s, *p*-C of C_6H_4Me), 131.56 and 130.94 (both s, C_6H_4Me), 34.98 (d, J_{PC} = 23.0 Hz, *ipso*-C of P(C_6H_{11})$_3$), 30.64 (d, J_{PC} = 1.5 Hz, *m*-C of P(C_6H_{11})$_3$), 28.02 (d, J_{PC} = 11.5 Hz, *o*-C of P(C_6H_{11})$_3$), 26.42 (s, *p*-C of P(C_6H_{11})$_3$), 23.34 (s, CH_3). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ 72.2 (s). Anal. Calcd for $C_{26}H_{40}Cl_3PRu$: C, 52.84; H, 6.82. Found: C, 53.13; H, 7.11.

[Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$]BF_4 (25). To a stirred golden solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_3$] (**20**) (0.101 g, 0.116 mmol) in CH_2Cl_2 (8 mL) was added a bright yellow solution of trityl tetrafluoroborate (0.040 g, 0.12 mmol, 1.1 equiv) in CH_2Cl_2 (4 mL). The trityl solution was washed in with CH_2Cl_2 (2 mL). The reaction mixture turned orange rapidly. The solution was stirred for 1.5 h, then concentrated to dryness under vacuum. The remaining solid was slurried in pentane (5 mL) and stirred for 10 min. The mixture was filtered, washed with pentane (3 × 3 mL) and ether (3 × 3 mL), and dried *in vacuo* 5 h. Orange powder **25** (0.096 g, 0.10 mmol) was recovered purely in 89% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.78 (d, $^3J_{HH}$ = 8.2 Hz, 2H, C_6H_4Me), 7.37 (d, $^3J_{HH}$ = 8.0 Hz, 2H, C_6H_4Me), 2.89 (br s, 6H, PCH of PCy_3), 2.47 (s, 3H, CH_3), 1.93−1.73, 1.52−1.15 (all m, 60H, PCy_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 299.69 (br s, Ru≡C−Ar), 152.70 (s, *p*-C of C_6H_4Me), 137.50 (*ipso*-C of C_6H_4Me), 131.89 and 131.34 (both s, C_6H_4Me), 34.98 (t, J_{PC} = 9.6 Hz, *ipso*-C of P(C_6H_{11})$_3$), 30.64 (br s, *m*-C of P(C_6H_{11})$_3$), 27.98 (t, J_{PC} = 5.6 Hz, *o*-C of P(C_6H_{11})$_3$), 26.50 (s, *p*-C of P(C_6H_{11})$_3$), 23.56 (s, CH_3). $^{19}F\{^1H\}$ NMR (376.3 MHz, CD_2Cl_2): δ −153.31 (s, BF_4). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ 49.9 (s). Anal. Calcd for $C_{44}H_{73}BCl_2F_4P_2Ru$: C, 57.27; H, 7.97. Found: C, 57.26; H, 8.16.

[Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$F] (26). To a solid mixture of tan [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_3$] (**20**) (0.075 g, 0.086 mmol) and tris-(dimethylamino)sulfonium difluorotrimethylsilicate (TAS-F) (0.026 g, 0.094 mmol, 1.1 equiv) was added CH_2Cl_2 (10 mL). The reaction mixture was stirred for 3 h, over which time it turned from tan to purple to brown. The solution was concentrated to dryness. The remaining brown residue was extracted into toluene (8 mL), filtered, and washed with toluene (3 × 3 mL). The filtrate was evaporated to dryness *in vacuo*. The remaining brown residue was slurried in cold pentane (8 mL) for 20 min, filtered, and washed with pentane (3 × 3 mL). The remaining solid was dried *in vacuo* 3 h. Tan powder **26** (0.055 g, 0.64 mmol) was recovered pure in 74% yield. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.96 (d, $^3J_{HH}$ = 8.4 Hz, 2H, C_6H_4Me), 7.19 (d, $^3J_{HH}$ = 8.0 Hz, 2H, C_6H_4Me), 2.67 (br s, 6H, PCH of PCy_3), 2.35 (s, 3H, CH_3), 2.08−2.02, 1.72−1.61, 1.40−1.07 (all m, 60H, PCy_3). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 293.93 (d, J_{FC} = 150.7 Hz, Ru≡C−Ar), 146.23 (s, *p*-C of C_6H_4Me), 143.85 (d, J_{FC} = 11.4 Hz, *ipso*-C of C_6H_4Me), 131.36 and 129.38 (both s, C_6H_4Me), 34.38 (t, J_{PC} = 8.9 Hz, *ipso*-C of P(C_6H_{11})$_3$), 29.25 (br s, *m*-C of P(C_6H_{11})$_3$), 28.17 (t, J_{PC} = 5.0 Hz, *o*-C of P(C_6H_{11})$_3$), 26.80 (s, *p*-C of P(C_6H_{11})$_3$), 22.77 (s, CH_3). $^{19}F\{^1H\}$ NMR (376.3 MHz, CD_2Cl_2): δ −219.4 (t, $^2J_{PF}$ = 41 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ 28.5 (d, $^2J_{PF}$ = 41 Hz). Anal. Calcd for $C_{44}H_{73}FCl_2P_2Ru$: C, 61.81; H, 8.61. Found: C, 62.11; H, 8.50.

Attempts to Synthesize [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2F_2$] (7) by Ligand Substitution. Method A. A purple solution of [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$] (**6**) (0.010 g, 0.012 mmol) and 18-crown-6 (0.005 g, 0.02 mmol, 1 equiv) in THF (ca. 0.5 mL) was added to white powder CsF (0.033 g, 0.22 mmol, 18 equiv). The heterogeneous mixture was transferred to an NMR tube by pipet and washed in with DME (ca. 0.5 mL). The reaction was monitored by ^{19}F and ^{31}P NMR spectroscopy. After 4 h, the ^{31}P NMR spectrum showed the following. $^{31}P\{^1H\}$ NMR (161.9 MHz, THF−DME): δ 36.6 (**6**, 83.3%) and 11.0 (free PCy_3, 16.7%). After 22 h, the solution was green-brown and the ^{31}P NMR spectrum showed the following. $^{31}P\{^1H\}$ NMR (161.9 MHz, THF−DME): δ 47.1 (d, $^2J_{FP}$ = 36 Hz, **9**, 25.4%), 42.6 (**8**, 3.5%), 36.6 (**6**, 30.3%), and 11.0 (40.8%). After 48 h, the ^{31}P NMR spectrum showed the following. $^{31}P\{^1H\}$ NMR (161.9 MHz, THF−DME): δ 47.1 (d, $^2J_{FP}$ = 36 Hz, **9**, 30.1%), 42.6 (**8**, 3.8%), 36.6 (**6**, 7.1%), and 11.0 (59.0%). The ^{19}F NMR was consistent with the formation of **9**.

Method B. A purple solution of [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$] (**6**) (0.010 g, 0.012 mmol) in C_6D_6 (ca. 0.75 mL) was added to white crystalline [*n*-Bu_4N]F·3H_2O (0.009 g, 0.03 mmol, 2.5 equiv). The sample was mixed well and transferred to an NMR tube by pipet. The solution turned brown rapidly. The reaction progress was monitored by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopies. After 25 min, the ^{31}P NMR spectrum showed the following. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 36.4 (**6**, (SM), 45.5%) and 10.5 (free PCy_3, 54.5%). After 24 h, the ^{31}P NMR spectrum showed the following. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 55.8 (10.4%), 54.5 (6.6%), 50.6 (10.4%), 36.4 (**6**, (SM), 34.4%), and 10.5 (free PCy_3, 59.0%). Similar results were obtained when the reaction was repeated with THF as the solvent.

Reaction of 14 with HCl in Ether. To a blue NMR solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$Br] (**14**) (0.009 g, 0.01 mmol) in C_6D_6 (ca. 0.75 mL) was added 2 M HCl in ether (5.1 μL, 0.010 mmol, 1.0 equiv). The NMR tube was then rapidly sealed and inverted three times to mix. Upon mixing, the solution immediately turned red-purple. The reaction progress was monitored by ^{1}H and ^{31}P NMR spectroscopy. After 15 min, the ^{31}P NMR spectrum showed the following. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 37.1 ([Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Br_2$], 21.1%), 36.8 ([Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$BrCl] (**17**), 55.1%), and 36.4 ([Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$-Cl_2] (**6**), 23.7%). The ^{1}H NMR spectrum showed three carbene peaks consistent with this mixture, two of which are associated with [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Br_2$] and **6**, and the third attributed to [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$BrCl] (**17**). ^{1}H NMR (400 MHz, C_6D_6): δ 20.50 (s). The reaction mixture remained unchanged overnight.

Reaction of 9 with HCl in Ether. To a green NMR solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$F] (**9**) (0.001 g, 0.01 mmol) in C_6D_6 (ca. 0.75 mL) was added 1 M HCl in ether (12.2 μL, 0.0122 mmol, 1.00 equiv). The NMR tube was then rapidly sealed and inverted three times to mix. The solution turned brown slowly. The reaction

progress was monitored by ^{1}H and ^{31}P NMR spectroscopies. After 30 min, the ^{31}P NMR spectrum showed the following. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 46.2 (br s, **9**, (SM), 23.4%) and 44.6 (br d, J = 26.9 Hz, 3.3%), and 36.4 ([Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$-Cl_2] (**6**), 73.3%). After 16 h, the ^{31}P NMR spectrum showed the following. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 46.2 (br s, **9** (SM), 20.5%), 36.4 ([Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$] (**6**), 72.8%), and 10.5 (free PCy_3, 6.7%). The ^{1}H NMR spectrum showed only one carbene peak associated with [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$] (**6**).

Reaction of 9 with Et$_3$N·3HF. To a green NMR solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$F] (**9**) (0.009 g, 0.01 mmol) in C_6D_6 (ca. 0.75 mL) was added Et$_3$N·3HF (2.0 μL, 0.012 mmol, 1.0 equiv). The NMR tube was then rapidly sealed and inverted three times to mix. The solution color remained unchanged. The reaction progress was monitored by ^{1}H and ^{31}P NMR spectroscopies. After 20 min, the ^{31}P NMR spectrum showed the following. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 46.2 (br s, **9**, (SM), 76.9%) and 44.6 (br d, J = 26.9 Hz, 23.1%). After 16 h, the ^{31}P NMR spectrum showed the following. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 46.0 (br s, **9** (SM)) and minor 10.3 (free PCy_3). No carbene peaks were ever visible in the ^{1}H NMR.

Reaction of 22 with PCy$_3$ and Reprecipitation with Benzene. To a solid sample of PCy_3 (0.004 g, 0.01 mmol, 1 equiv) was added a red-brown solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)I_3] (**22**) (0.010 g, 0.012 mmol) in CD_2Cl_2 (ca. 0.75 mL). The solution was mixed well by pipet and the solution darkened slightly. After 20 min the ^{1}H and ^{31}P NMR spectra were obtained. The ^{31}P NMR spectrum indicated the presence of only [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2I_2$]I (**23-I**) (^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 51.1 (s)). The sample was transferred to a small vial, and C_6D_6 (ca. 0.75 mL) was added. The sample was concentrated slowly under vacuum to remove approximately half the volume. A precipitate formed. The heterogeneous sample was transferred to an NMR tube. The ^{31}P NMR spectrum indicated the presence of only broadened PCy_3 (^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 11.5 (br s)). The sample was filtered through a pipet filter and washed with minimal C_6D_6. The brown solid precipitate was dissolved in CD_2Cl_2 (ca. 0.75 mL). The ^{31}P NMR spectrum indicated the presence of only **22** (^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 66.2 (br s)).

Halide Exchange between 19 and 20. To a tan solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_3$] (**20**) (0.011 g, 0.013 mmol) in CD_2Cl_2 (ca. 0.5 mL) was added a gray-brown solution of [Ru(C-*p*-C_6H_4-Me)(PCy_3)$_2F_3$] (**19**) (0.006 g, 0.007 mmol, 0.5 equiv) in CD_2Cl_2 (ca. 0.5 mL). The resulting orange-red solution was mixed well and transferred to an NMR tube by pipet. The reaction progress was monitored by ^{1}H, ^{19}F, and ^{31}P NMR spectroscopies. After 20 min, the ^{31}P NMR spectrum showed the following. ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 50.0 (s, 6.6%), 36.3 (s, **6**, 8.6%), 28.5 (d, J = 41 Hz, **26**, 41.7%), 24.6 (s, 26.5%), and 18.2 (s, **20**, 16.6%). After 16 h, the ^{31}P NMR spectrum was essentially unchanged.

Reaction of 20 with Schwartz's Reagent (Cp$_2$ZrHCl). To a solid sample of Schwartz's reagent, Cp_2ZrHCl (0.003 g, 0.01 mmol, 1 equiv), was added a tan solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2$-Cl_3] (**20**) (0.009 g, 0.01 mmol) in CD_2Cl_2 (ca. 0.75 mL). The solution was mixed well by pipet and turned from tan to red rapidly. After 20 min the ^{1}H and ^{31}P NMR spectra were obtained. Integration of the ^{31}P NMR spectrum indicated [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2$-Cl_2] (**6**) (91%) and minor free PCy_3 (9%). ^{1}H NMR spectroscopy indicated the presence of [Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$] (**6**) and Cp_2ZrCl_2 as the only Zr compound. The ^{1}H and ^{31}P NMR spectra were compared to literature values and independently synthesized samples ([Ru(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$], (**6**))[25] or commercial compounds (PCy_3 and Cp_2ZrCl_2).

Reaction of 20 with Schwartz's Reagent (Cp$_2$ZrHCl) at Low Temperature. To a J. Young NMR tube was added a golden solution of [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2Cl_3$] (**20**) (0.010 g, 0.012 mmol) in CD_2Cl_2 (ca. 0.50 mL). The solution was frozen with liquid N_2. A clear solution of Cp_2ZrHCl (0.004 g, 0.01 mmol, 1 equiv) in CD_2Cl_2 (ca. 0.5 mL) was added on top of the frozen Ru sample. The Zr solution was frozen with liquid N_2. The tube was sealed, and the overlying atmosphere was evacuated. The NMR probe was cooled to −60 °C. The NMR sample was allowed to thaw slightly outside the NMR to ensure the tube would not explode in the NMR probe. The tube was then inserted into the NMR probe and allowed to equilibrate for 3 min, and the reaction progress was monitored by ^{1}H NMR spectroscopy. The characteristic carbene peak of [Ru-(CH-*p*-C_6H_4Me)(PCy_3)$_2Cl_2$] (**6**) was observed immediately. No other carbene peaks or hydrides were ever observed by ^{1}H NMR spectroscopy.

Catalytic Alkyne Dimerization Reactions. To a 0.015 mM C_6D_6 solution of brown [Ru(C-*p*-C_6H_4Me)(PCy_3)$_2F_3$] (**19**) in a J. Young NMR tube was added a terminal alkyne (20 equiv) and an internal standard, 1,3,5-trimethoxybenzene (1 equiv). The tube was sealed and the solution frozen with liquid N_2. The overlying atmosphere was evacuated. The tube was heated in an oil bath at 65 °C. The reaction progress was monitored by NMR spectroscopy.

Dimerization of Phenylacetylene. After 28 h, integration of the ^{1}H NMR spectrum showed, relative to the internal standard, at least 96% conversion to two enyne isomers, (*Z*)-1,4-diphenyl-1-buten-3-yne and 2,4-diphenyl-1-buten-3-yne in a 4:1 ratio, respectively.

Dimerization of Trimethylsilylacetylene. After 28 h, integration of the ^{1}H NMR spectrum showed, relative to the internal standard, 64.0% conversion to two enyne isomers, (*Z*)-1,4-bis(trimethylsilyl)-1-buten-3-yne and 2,4-bis(trimethylsilyl)-1-buten-3-yne in a 2:1 ratio, respectively.

Crystal Structure Determinations. Complex 19. Gray plates of **19** were grown by vapor diffusion of pentane into a dichloromethane solution at −35 °C. A crystal of dimensions 0.10 × 0.06 × 0.06 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low-temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 123(2) K; the detector was placed at a distance 4.969 cm from the crystal. A total of 2480 frames were collected with a scan width of 0.5° in ω and ϕ with an exposure time of 60 s/frame. The integration of the data yielded a total of 28 679 reflections to a maximum 2θ value of 45.28° of which 3141 were independent and 2171 were greater than 2σ(I). The final cell constants were based on the *xyz* centroids of 3923 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group $P2(1)/m$ with Z = 2 for the formula $C_{44}H_{72}P_2F_3Ru\cdot(CH_2Cl_2)$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The complex lies on a crystallographic mirror plane. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0530 and wR2 = 0.0969 [based on $I > 2\sigma(I)$], R1 = 0.0953 and wR2 = 0.1109 for all data. Additional details are presented in the Supporting Information.

Complex 22. Brown needles of **22** were grown from a dichloromethane-d_2 solution at −35 °C. A crystal of dimensions 0.50 × 0.33 × 0.33 mm was cut from a larger crystal and mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low-temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 123(2) K; the detector was placed at a distance 4.980 cm from the crystal. A total of 3692 frames were collected with a scan width of 0.2° in ω and ϕ with an exposure time of 15 s/frame. The integration of the data yielded a total of 64 836 reflections to a maximum 2θ value of 56.58° of which 7155 were independent and 6344 were greater than 2σ(I). The final cell constants (Table 1) were based on the *xyz* centroids of 8129 reflections above 10σ(I). Analysis of

the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group *Pbca* with $Z = 8$ for the formula $C_{26}H_{40}PI_3Ru$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0271 and wR2 = 0.0807 [based on $I > 2\sigma(I)$], R1 = 0.0328 and wR2 = 0.0828 for all data. Additional details are presented in the Supporting Information.

Complex 25. Orange blocks of **25** were grown by vapor diffusion of pentane into a dichloromethane solution at −35 °C. A crystal of dimensions 0.44 × 0.40 × 0.28 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low-temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 108(2) K; the detector was placed at a distance 4.969 cm from the crystal. A total of 2645 frames were collected with a scan width of 0.5° in ω and ϕ with an exposure time of 25 s/frame. The integration of the data yielded a total of 229 661 reflections to a maximum 2θ value of 59.18° of which 29 746 were independent and 22 201 were greater than $2\sigma(I)$. The final cell constants were based on the *xyz* centroids of 2048 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group $P2(1)/c$ with $Z = 4$ for the formula $2(C_{44}H_{73}P_2Cl_2Ru)$, $5(CH_2Cl_2)$, $2(BF_4)$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0590 and wR2 = 0.1310 [based on $I > 2\sigma(I)$], R1 = 0.0853 and wR2 = 0.1431 for all data. Additional details are provided in the Supporting Information.

Complex 26. Orange needles of **26** were crystallized from a deuterated dichloromethane solution at −35 °C. A crystal of dimensions 0.40 × 0.22 × 0.10 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low-temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 123(2) K; the detector was placed at a distance 4.980 cm from the crystal. A total of 2635 frames were collected with a scan width of 0.5° in ω and ϕ with an exposure time of 30 s/frame. The integration of the data yielded a total of 87 016 reflections to a maximum 2θ value of 51.18° of which 9496 were independent and 6468 were greater than $2\sigma(I)$. The final cell constants were based on the *xyz* centroids of 5578 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group $P2(1)/c$ with $Z = 4$ for the formula $C_{44}H_{73}F_2P_2Cl_2Ru\cdot(CD_2Cl_2)_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0402 and wR2 = 0.0816 [based on $I > 2\sigma(I)$], R1 = 0.0828 and wR2 = 0.0950 for all data. Additional details are provided in the Supporting Information.

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Supporting Information Available: Spectral data for **21** and **23-I** and full crystallographic details for **19**, **22**, **25**, and **26** in pdf and cif formats. This material is available free of charge via the Internet at http://pubs.acs.org.

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