two-electron process of this compound.

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**Supplementary Material Available:** Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for 1, 2, and 3 (19 pages). Ordering information is given on any current masthead page.

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# Synthesis, Structure, and Reactivity Properties of $(\eta^5\text{-}C_5H_5)Ru[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2]X$ Complexes: New Electrophilic Analogues to $(\eta^5\text{-}C_5H_5)Ru(CO)_2X$ Systems

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The synthesis, structure, and reactivity properties of CpRu(dfepe)Cl (1, dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$) are reported. Thermolysis of $CpRu(Ph_3P)_2Cl$ in hydrocarbon solvent with excess dfepe at 140 °C gives 1 in good yield. In contrast to donor phosphine analogues, the chloride ligand in 1 is not labilized by halide-abstracting agents in the absence of trapping ligands. Crystallographic data for 1 confirm the presence of a short Ru–Cl bond (2.406 (1) Å). Sodium naphthylide reduction of 1 produces the thermally stable anion, $Na^+[CpRu(dfepe)]^-$, which upon treatment with $NH_4^+PF_6^-$ or $CH_3I$ affords the corresponding hydride and methyl derivatives CpRu(dfepe)H (3) and CpRu(dfepe)Me (4) in moderate yield. The hydride complex 3 is more conveniently prepared by the reaction of 1 with $AgBF_4$ under 1 atm of $H_2$, presumably via the incipient formation of a highly acidic dihydrogen or dihydride cationic complex. Crystal data for 1: monoclinic, $P2_1/n$, with $a$ = 7.7709 (15) Å, $b$ = 14.224 (2) Å, $c$ = 20.814 (4) Å, $\beta$ = 91.670 (15)°, $V$ = 2299.6 (7) Å$^3$, $Z$ = 4, $R_F$ = 5.21%, and $R_{wF}$ = 7.21%.

## Introduction

Piano-stool complexes $(\pi\text{-}C_nR_m)M(L)_x$ are an important class of organometallic compounds which continue to be the subject of numerous theoretical[1] and chemical investigations.[2,3] In the group VIII triad, ruthenium complexes of the general formulas $CpRu(L)_2X$ and $[CpRu(L)_3]^+$ (L = $R_3P$ or CO) have been studied extensively.[4] Electron-rich donor phosphine complexes $CpRu(R_3P)_2X$ are typified by $CpRu(Ph_3P)_2Cl$, which provides a versatile entry into a wide variety of substitutional derivatives derived from either phosphine or chloride displacement under mild conditions.[4-6] The chemistry of electron-poor dicarbonyls $CpRu(CO)_2X$ is likewise extensive yet often exhibits distinctly different reactivity patterns.[4]

We have reported the synthesis and properties of perfluoroalkylphosphine molybdenum $\pi$-arene complexes $(\eta^6\text{-}C_6H_5R)Mo(dfepe)(L)$ (dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$, L = $N_2$, CO, py, etc.) which serve as unique electron-poor analogues to unaccessed $(\pi\text{-arene})Mo(CO)_2(L)$ systems.[7] In light of the unusual steric and electronic properties of these Mo(0) arene piano stools, we have recently begun to examine the properties of potentially more electrophilic isoelectronic Mn(I)[8] and Ru(II) complexes. In this paper we present our initial studies of CpRu(dfepe)X systems and compare observed chemical properties with established $CpRu(L)_2X$ and $[CpRu(L)_3]^+$ systems.

## Results and Discussion

**Synthesis and Structure of CpRu(dfepe)Cl (1).** The ease of phosphine substitution previously demonstrated for $CpRu(Ph_3P)_2Cl$[5] suggested the straightforward synthesis of CpRu(dfepe)Cl (1) following eq 1. Although prior

$$CpRu(Ph_3P)_2Cl \xrightarrow[\Delta]{dfepe} \underset{1}{CpRu(dfepe)Cl} + 2Ph_3P \quad (1)$$

studies with dfepe have shown it to be a very weak donor ligand, the complete displacement of both triphenylphosphine ligands from $CpRu(Ph_3P)_2Cl$ can be achieved

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(7) Ernst, M. F.; Roddick, D. M. *Organometallics* **1990**, *9*, 1586.

(8) Merwin, R. K.; Roddick, D. M., unpublished results.

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**Table I. Summary of Crystallographic Data for ($\eta^5$-$C_5H_5$)Ru(dfepe)Cl (1)**

| | |
|---|---|
| formula | $C_{15}H_9ClF_{20}P_2Ru$ |
| cryst size (mm) | 0.36 × 0.42 × 0.80 |
| cryst syst | monoclinic |
| space group | $P2_1/n$ |
| temp (°C) | −100 |
| $a$ (Å) | 7.7709 (15) |
| $b$ (Å) | 14.224 (2) |
| $c$ (Å) | 20.814 (4) |
| $\beta$ (deg) | 91.670 (15) |
| $V$ (Å$^3$) | 2299.6 (7) |
| $Z$ | 4 |
| $\rho_{calc}$ (g/cm$^3$) | 2.217 |
| wavelength (Å) | 0.71073 |
| mol wt | 767.7 |
| $\mu$ (mm$^{-1}$) | 1.086 |
| $T_{max}/T_{min}$ | 0.2620/0.1788 |
| $2\theta$ range (deg) | 4.0–53.0 |
| scan type | $2\theta/\theta$ |
| scan range | 2.0 |
| reflns measd | 5327 |
| unique reflns | 4758 |
| no. of $F > 6.0\sigma(F)$ | 3893 |
| $R_F$ (%) | 5.21 |
| $R_{wF}$ (%) | 7.21 |
| goodness of fit | 2.31 |

at elevated temperatures due to relief of steric congestion in the starting material and the chelate effect. The reaction is solvent dependent. In toluene, the reaction of $CpRu(Ph_3P)_2Cl$ with excess dfepe yields 1 together with a significant amount (0.5–0.7 equiv) of a white solid which has been tentatively identified on the basis of $^1H$, $^{19}F$, and $^{31}P$ NMR spectroscopy and analytical data as primarily the monofluorinated triphenylphosphine, $(C_6H_4F)(C_6H_5)_2P$ (see Experimental Section). This side product appears to be derived from the reaction of free dfepe with the ortho-metalated species $CpRu(C_6H_4)PPh_2(Ph_3P)$.[9] When the reaction between $CpRu(Ph_3P)_2Cl$ and dfepe is carried out heterogeneously in a saturated hydrocarbon solvent, complex 1 is cleanly obtained in high yield. Addition of toluene in the latter stages of the thermolysis solubilizes the reaction mixture and does not lead to any significant formation of orthometallation products. The lack of C–F activation side reactions in saturated hydrocarbon solvents is likely due to the unfavorable elimination of HCl from $CpRu(Ph_3P)_2Cl$ to generate $CpRu(C_6H_4)PPh_2(Ph_3P)$ in nonpolar solvent media.

A general feature of $CpRu(R_3P)_2Cl$ chemistry when $R_3P$ is a triaryl- or trialkylphosphine is the facile displacement of chloride ligand in the presence of donor ligands or coordinating solvents such as acetonitrile or methanol.[5,10,11] For the series $CpRu(Ph_3P)_2Cl$, $CpRu(Ph_3P)((MeO)_3P)Cl$,[5g] and $CpRu((MeO)_3P)_2Cl$,[5c] the ease of chloride substitution qualitatively correlates with the increasing donor ability of the ancillary phosphine ligands. Consistent with this trend, the substitution of $Ph_3P$ ligands in complex 1 by the strong acceptor ligand dfepe results in greatly diminished chloride lability. Halide abstraction from 1 in THF by silver triflate, $TlBF_4$, or trimethylsilyltriflate to form cationic solvates does not occur to any appreciable extent. In the presence of carbon monoxide as a trapping ligand, however, treatment of 1 with $AgBF_4$ in $CH_2Cl_2$ gives the expected carbonyl complex $[CpRu(dfepe)(CO)]BF_4$ (2). Complex 2 exhibits a $\nu$(CO) band at 2075 cm$^{-1}$, considerably higher in energy than values reported for the more electron-rich complexes $CpRu(MeCN)_2(CO)^+$ (2000 cm$^{-1}$),[12] $CpRu(Ph_3P)_2(CO)^+$ (1980 cm$^{-1}$),[5a] and $CpRu(Me_3P)_2(CO)^+$ (1961 cm$^{-1}$).[10]

Structural studies for a series of $CpRu(L)_2Cl$ complexes have provided a useful correlation between Ru–P and Ru–Cl bond lengths and observed lability trends. Accordingly, the crystal structure of CpRu(dfepe)Cl has been determined in order to extend this series and also to compare Ru–P bonding trends with isoelectronic ($\eta^6$-arene)$Mo(R_3P)_2(L)$ systems. An ORTEP view of 1 is given in Figure 1. Crystal and data collection parameters are given in Table I; selected bond distances and angles and

**Table II. Selected Distances (Å) and Angles (deg) for ($\eta^5$-$C_5H_5$)Ru(dfepe)Cl (1)**

| Bond Distances | | | |
|---|---|---|---|
| Ru–Cl | 2.406 (1) | Ru–C(12) | 2.200 (6) |
| Ru–P(1) | 2.248 (2) | Ru–C(13) | 2.200 (7) |
| Ru–P(2) | 2.236 (2) | Ru–C(14) | 2.201 (7) |
| Ru–C(11) | 2.232 (8) | Ru–C(15) | 2.224 (7) |
| **Bond Angles** | | | |
| Cl–Ru–P(1) | 92.9 (1) | CNT–Ru–Cl[a] | 118.6 |
| Cl–Ru–P(2) | 90.6 (1) | CNT–Ru–P(1) | 130.8 |
| P(1)–Ru–P(2) | 83.1 (1) | CNT–Ru–P(2) | 129.0 |

[a] CNT: centroid of cyclopentadienyl ring.

**Table III. Atomic Coordinates (×10$^4$) and Isotropic Thermal Parameters (Å$^2$ × 10$^3$) for ($\eta^5$-$C_5H_5$)Ru(dfepe)Cl (1)**

| atom | $x$ | $y$ | $z$ | $U$[a] |
|---|---|---|---|---|
| Ru | 146 (1) | 75 (1) | 2261 (1) | 21 (1) |
| Cl | 3179 (2) | −268 (1) | 2305 (1) | 33 (1) |
| P(1) | 359 (2) | 1090 (1) | 3087 (1) | 26 (1) |
| P(2) | 619 (2) | 1363 (1) | 1676 (1) | 26 (1) |
| F(1) | 2061 (6) | 1800 (4) | 4122 (2) | 65 (2) |
| F(2) | 3624 (5) | 1218 (4) | 3381 (3) | 71 (2) |
| F(3) | 3842 (13) | 237 (7) | 4471 (5) | 166 (5) |
| F(4) | 1053 (14) | 60 (6) | 4487 (4) | 167 (5) |
| F(5) | 2453 (10) | −586 (4) | 3782 (3) | 92 (3) |
| F(6) | −2078 (7) | 386 (4) | 3823 (2) | 69 (2) |
| F(7) | −2891 (6) | 1473 (5) | 3162 (3) | 78 (2) |
| F(8) | −1167 (7) | 2758 (3) | 3998 (2) | 62 (2) |
| F(9) | −3399 (7) | 2039 (5) | 4291 (3) | 81 (2) |
| F(10) | −920 (7) | 1623 (3) | 4667 (2) | 59 (2) |
| F(11) | 3918 (5) | 1411 (4) | 1394 (2) | 63 (2) |
| F(12) | 2331 (6) | 2317 (3) | 779 (2) | 55 (2) |
| F(13) | 3722 (8) | 899 (5) | 141 (3) | 102 (3) |
| F(14) | 1014 (8) | 806 (5) | 170 (3) | 92 (3) |
| F(15) | 2579 (10) | −115 (4) | 745 (3) | 86 (3) |
| F(16) | −2501 (5) | 1968 (3) | 1697 (2) | 51 (1) |
| F(17) | −2066 (6) | 1098 (3) | 835 (2) | 55 (1) |
| F(18) | −801 (8) | 3408 (4) | 1111 (3) | 74 (2) |
| F(19) | −766 (7) | 2550 (5) | 241 (2) | 82 (2) |
| F(20) | −3159 (7) | 2877 (5) | 661 (3) | 86 (2) |
| C(1) | 561 (14) | 2327 (5) | 2805 (3) | 62 (3) |
| C(2) | 1325 (12) | 2353 (5) | 2175 (3) | 54 (3) |
| C(3) | 2152 (9) | 1063 (7) | 3712 (3) | 52 (3) |
| C(4) | 2378 (13) | 170 (8) | 4123 (4) | 74 (4) |
| C(5) | −1665 (9) | 1225 (5) | 3588 (3) | 41 (2) |
| C(6) | −1734 (10) | 1925 (6) | 4159 (3) | 47 (2) |
| C(7) | 2415 (8) | 1470 (5) | 1069 (3) | 42 (2) |
| C(8) | 2422 (12) | 734 (7) | 528 (4) | 62 (3) |
| C(9) | −1402 (9) | 1803 (5) | 1220 (3) | 41 (2) |
| C(10) | −1499 (11) | 2698 (7) | 799 (4) | 57 (3) |
| C(11) | −1236 (10) | −825 (5) | 1534 (4) | 49 (2) |
| C(12) | −2434 (8) | −356 (5) | 1909 (4) | 42 (2) |
| C(13) | −2217 (8) | −658 (5) | 2534 (4) | 48 (2) |
| C(14) | −840 (9) | −1301 (5) | 2565 (4) | 48 (2) |
| C(15) | −265 (9) | −1405 (5) | 1947 (5) | 54 (3) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

(9) Thermal ortho-metalation of $CpRu(R_3P)_2Cl$ complexes and activation of substrate C–F bonds has been reported: Bruce, M. I.; Gardner, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1976**, 81.

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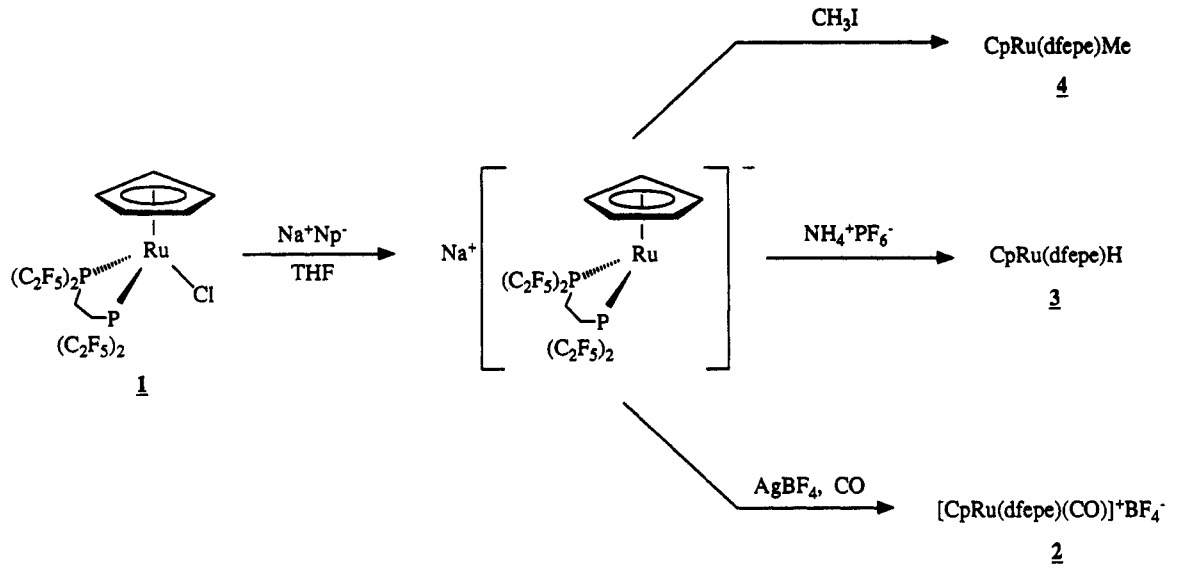
(11) Treichel, P. M.; Vincenti, P. J. *Inorg. Chem.* **1985**, *24*, 228.

(12) Crocker, M.; Green, M.; Morton, C. E.; Nagle, K. R.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1985**, 2145.

**Scheme I**



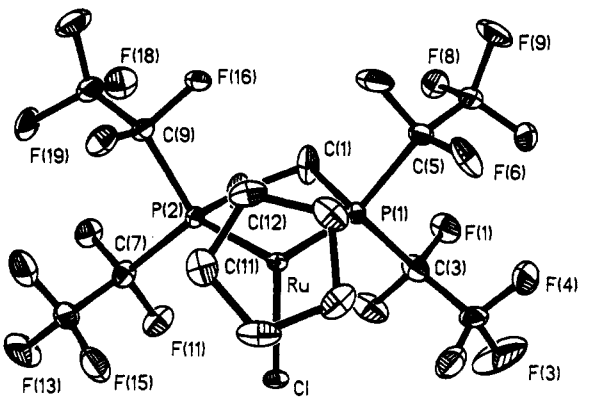




**Figure 1.** ORTEP view of $(\eta^5\text{-}C_5H_5)Ru(dfepe)Cl$ (1) with atom labeling scheme.

atomic coordinates are given in Tables II and III, respectively. As anticipated, the observed Ru–Cl bond length for 1, 2.406 (1) Å, is significantly shorter than that found for $CpRu(Ph_3P)_2Cl$ (2.453 (2) Å) and $CpRu(Me_3P)_2Cl$ (2.445 (6) Å average)[10] and is essentially identical to bond lengths reported for the more electron-poor complexes $CpRu((MeO)_3P)_2Cl$ (2.393 (3) Å)[5c] and $CpRu(Ph_3P)(CO)Cl$ (2.396 (6) Å).[13] Reported Ru–P bond distances for $CpRu(R_3P)_2Cl$ complexes appear to be sensitive to the sterics of the phosphorus ligand (Table IV). Thus, the Ru–P bond lengths for 1 (2.236 (2), 2.248 Å, $\theta$ = 129°) are intermediate between those of $CpRu(Ph_3P)_2Cl$ (2.337 (1) Å average, $\theta$ = 145°) and the phosphite complex $CpRu((MeO)_3P)_2Cl$ (2.217 (2) Å, $\theta$ = 107°), and are only slightly shorter than trimethylphosphine Ru–P values ($\theta$ = 118°). This steric trend largely obscures any decrease in Ru–P bond lengths ascribable to $d\pi$–$p\pi$ multiple bonding. Nevertheless, it is interesting to compare the degree of M–P bond shortening observed in comparable Ru(II) complexes to that seen in Mo(0) systems. For ($\eta^6$-arene)$Mo(R_3P)_2(L)$ complexes we previously noted a Mo–P bond contraction of 0.08 Å for dfepe as compared to the donor phosphine dmpe.[7] This difference is significantly larger than the 0.03 Å difference observed between 1 and $CpRu(Me_3P)_2Cl$ and is at least consistent with a lowered degree of metal–ligand backbonding for Ru(II) relative to Mo(0).

(13) Wilczewski, T.; Dauter, Z. *J. Organomet. Chem.* **1986**, *312*, 349.

**Table IV. Comparison of Metrical Data and Phosphine Cone Angles for $CpRu(R_3P)_2Cl$ Complexes**

| complex | Ru–Cl, Å | Ru–P (av), Å | $R_3P$ cone angle $\theta$,[a] deg |
|---|---|---|---|
| $CpRu(Ph_3P)_2Cl$[b] | 2.453 (2) | 2.337 (1) | 145 |
| $CpRu((MeO)_3P)(Ph_3P)Cl$[c] | 2.427 (1) | 2.331 (1) ($Ph_3P$) | |
| | | 2.224 (1) ($(MeO)_3P$) | 107 |
| $CpRu(Me_3P)_2Cl$[b] | 2.445 (6) | 2.275 (6) | 118 |
| $CpRu((MeO)_3P)_2Cl$[d] | 2.393 (3) | 2.217 (2) | |
| $CpRu(Ph_3P)(CO)Cl$[e] | 2.396 (6) | 2.311 (3) | |
| CpRu(dfepe)Cl | 2.406 (1) | 2.242 (2) | 129[f] |

[a] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. [b] Reference 10. [c] Reference 5g. [d] Reference 5c. [e] Reference 13. [f] Reference 7.

**Synthesis of CpRu(dfepe)H (3) and CpRu(dfepe)Me (4).** A wide range of $CpRu(R_3P)_2H$ complexes have been prepared from the corresponding chloride using hydride reagents[5a] or, more conveniently, by treatment with methoxide.[5e,14] These methods were not effective in the preparation of a hydride complex from 1. After prolonged refluxing of 1 with excess NaOMe in methanol, the starting material was recovered unchanged. In similar fashion, although the direct alkylation of $CpRu(R_3P)_2Cl$ complexes with Grignard or alkyllithium reagents is well-established, no clean alkylation of 1 was found with these reagents.

The general reluctance of 1 to undergo halide displacement reactions can be attributed to the unfavorable explicit or incipient formation of the electron-poor cation, $CpRu(dfepe)^+$. Since one of the hallmarks of $CpRu(CO)_2X$ substitution chemistry is access via the corresponding anion, we examined the utility of this approach for CpRu(dfepe)X systems. As shown in Scheme I, treatment of 1 with sodium naphthylide at −78 °C followed by addition of $NH_4PF_6$ or MeI afforded CpRu(dfepe)H (3) and CpRu(dfepe)Me (4), respectively, in moderate yield. A similar yield of 4 is obtained after allowing the reduced solution to warm to ambient temperature for 30 min prior to the addition of methyl iodide, indicating that $Na^+[CpRu(dfepe)]^-$ has significant thermal stability. The stability of this anion suggested that a direct deprotonation of 3 would be feasible. Surprisingly, no reaction between 3 and excess KH in tetrahydrofuran-$d_8$ after 48 h at 130

(14) (a) Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

°C was observed by $^1H$ NMR.

Spectroscopic and analytical data are consistent with the formulations of **3** and **4**. The hydride ligand of **3** exhibits a characteristic triplet at $\delta$ −13.60 ($^2J_{PH}$ = 34 Hz) and has an associated weak infrared band at 2003 cm$^{-1}$. An unusual feature of the $^1H$ NMR spectrum for **4** is that the methyl resonance appears at $\delta$ −0.20 as an apparent *pentet* ($J$ = 5 Hz), not a triplet as expected for a simple $^3J_{PH}$ coupling. This resonance collapses into a triplet ($J$ = 5 Hz) with phosphorus decoupling, indicative of additional coupling to two equivalent fluorines. $^{19}F$ NMR of **4** confirms that this coupling is due to only *one* of the four sets of diastereotopic $CF_2$ resonances. It is likely that the observed coupling is not a $^5J_{FH}$ through-bond interaction but rather a through-space coupling with a proximal set of chemically equivalent fluorines analogous to F(2) and F(11) in Figure 1.

A route to **3** more convenient than that detailed in Scheme I is given in eq 2. Stirring a solution of **1** with

$$\underset{\mathbf{1}}{\text{CpRu(dfepe)Cl}} + AgBF_4 \xrightarrow[CH_2Cl_2]{H_2} \xrightarrow{-HBF_4} \underset{\mathbf{3}\ (83\%)}{\text{CpRu(dfepe)H}} \quad (2)$$

$AgBF_4$ in $CH_2Cl_2$ under 1 atm of hydrogen for several hours followed by the addition of $Et_3N$ gave CpRu(dfepe)H in 83% isolated yield. Although this reaction undoubtedly proceeds via either a dihydride or dihydrogen cationic complex,[15] initial efforts to characterize this intermediate have not been successful. It is notable that attempts to isolate a protonated intermediate by precipitation from $CH_2Cl_2$ solution with diethyl ether resulted in the isolation of the neutral hydride, indicating that the basicity of **3** is extremely low and protonation of ether is favored.[16]

## Summary

Our preliminary survey of the spectroscopic, structural, and reactivity properties of CpRu(dfepe)Cl and its derivatives confirm our initial expectation that such complexes should be quite electron-poor. Of particular interest is the ready accessibility of $Na^+[CpRu(dfepe)]^-$, a rare example of a stable organometallic anion that does not have carbonyl ancillary ligands.[17] Efforts are currently underway to isolate and characterize this intermediate. In a complementary sense, the facile deprotonation of either $CpRu(dfepe)(H)_2^+$ or $CpRu(dfepe)(\eta^2\text{-}H_2)^+$ implied by eq 2 similarly suggests that dfepe induces highly electron-deficient behavior relative to conventional $CpRu(R_3P)_2H$ complexes.[14,18] Further work elucidating the reactivity of CpRu(dfepe)H toward protonic acids and the heterolytic activation of dihydrogen by $CpRu(dfepe)^+$ will be presented in a forthcoming paper.

## Experimental Section

**General Procedures.** All manipulations were conducted under an atmosphere of purified nitrogen using Schlenk, high vacuum line, and/or glovebox techniques. Dry oxygen-free solvents were vacuum distilled prior to use. Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded on a Mattson Cygnus 100 or Perkin-Elmer 1600 FTIR instrument as Nujol mulls, unless otherwise noted. NMR spectra were obtained with a JEOL JNM-FX270 or GSX-400 instrument. $^{31}P$ NMR spectra were referenced to an 85% $H_3PO_4$ external standard. $^{19}F$ NMR were referenced to a $CF_3CO_2Et$ external standard (−75.32 ppm vs $CFCl_3$, with upfield shifts taken to be negative). $CpRu(Ph_3P)_2Cl$ was prepared following a literature procedure.[19] $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (dfepe) was prepared as described previously.[20]

**CpRu(dfepe)Cl (1).** A medium-walled Carius tube fitted with a 4-mm Kontes Teflon high-vacuum valve was charged with 1.01 g (1.39 mmol) of $CpRu(Ph_3P)_2Cl$, 1.64 g (2.90 mmol) dfepe and 15 mL of octane and heated to 140 °C. After 1 day, 5 mL of toluene was added to solubilize the heterogeneous mixture and the thermolysis was continued at 140 °C for an additional day. After cooling, 0.4 mL (6.4 mmol) of methyl iodide was added and the solution was warmed to 80 °C for 6 h. The contents of the reaction tube were rinsed into a swivel filter frit assembly with a few milliliters of toluene, and the volatiles were removed under vacuum. The residue was taken up in 20 mL of diethyl ether and filtered to remove $Ph_3PMe^+I^-$. After extracting the phosphonium residue several times with ether, the filtrate was concentrated until orange crystals began forming. Cold filtration at −78 °C and drying under vacuum yielded 0.875 g (82%) of pure **1**. Anal. Calcd for $C_{15}H_9ClF_{20}P_2Ru$: C, 23.47; H, 1.18. Found: C, 23.60; H, 1.14. $^1H$ NMR ($CDCl_3$, 400 MHz, 20 °C): $\delta$ 5.20 (s, 5 H; $\eta^5\text{-}C_5H_5$), 2.57 (m, 4 H; $PCH_2CH_2P$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161.7 MHz, 20 °C): $\delta$ 116.4 (m). $^{19}F$ NMR ($CD_2Cl_2$, 376.05 MHz, 20 °C): $\delta$ −75.28 (d, $^3J_{PP}$ = 12 Hz; $PCF_2CF_3$), −73.37 (d, $^3J_{PP}$ = 24 Hz; $PCF_2CF_3$), −99 to −104.2 (m, overlapping $PCF_2CF_3$ ABX multiplets).

**Characterization of Fluorinated $Ph_3P$ Side Product.** The synthesis of **1** was carried out as described above, using toluene as the thermolysis solvent. $^1H$ NMR of the crude isolated product showed **1** as the sole metal-containing species, together with aromatic resonances (ca. 10 protons relative to the dfepe backbone) due to an aromatic side product. Slow crystallization of **1** from toluene/heptane followed by sublimation of the soluble residue at 100 °C ($10^{-4}$ Torr) gave a small amount of white solid, tentatively identified on the basis of spectroscopic and analytical data as a mixture of mono- and difluorinated triphenylphosphine. Anal. Calcd for $C_{18}H_{14}FP$: C, 77.14; H, 5.04. Anal. Calcd for $C_{18}H_{13}F_2P$: C, 72.48; H, 4.39. Found: C, 74.42; H, 5.05. $^1H$ NMR ($CDCl_3$, 400 MHz, 20 °C): $\delta$ 8.02 (dd, $J$ = 14, 6 Hz), 7.67 (dd, $J$ = 10, 6 Hz), 7.54 (m), 7.46 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.7 MHz, 20 °C): $\delta$ 30.1 (br s). $^{19}F$ NMR ($CDCl_3$, 376.05 MHz, 20 °C): $\delta$ −191.3 (d, $J$ = 7 Hz; 30% of −191.4 resonance), −191.4 (d, $J$ = 7 Hz).

**[CpRu(dfepe)(CO)]$BF_4$ (2).** A 25-mL round-bottom flask was charged with 370 mg (0.482 mmol) of **1** and 170 mg (0.873 mmol) of $AgBF_4$ and placed under vacuum. $CH_2Cl_2$ (10 mL) was condensed in at −78 °C, and the reaction mixture was placed under 1 atm of CO and allowed to warm to ambient temperature with stirring. Initially yellow, after warming the solution became colorless and a white precipitate formed. After 4 h the solid was filtered off and washed briefly with a minimal amount of $CH_2Cl_2$ to remove traces of starting material. The remaining solid was taken up in 15 mL of acetone and filtered to remove the silver salts; concentration of the filtrate and cooling to −78 °C afforded 180 mg (44%) of **2** after cold filtration and drying. Anal. Calcd for $C_{16}H_9BF_{24}OP_2Ru$: C, 22.69; H, 1.07. Found: C, 22.68; H, 0.95. IR (cm$^{-1}$): 2075 (s), 2062 (sh). $^1H$ NMR (acetone-$d_6$, 270 MHz, 20 °C): $\delta$ 6.37 (s, 5 H; $\eta^5\text{-}C_5H_5$), 3.37 (m, 4 H; $PCH_2CH_2P$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161.7 MHz, 20 °C): $\delta$ 119.8 (m). $^{19}F$ NMR ($CD_2Cl_2$, 376.05 MHz, 20 °C): $\delta$ −77.0 (s; $PCF_2CF_3$), −77.4 (d, $^3J_{PP}$ = 15 Hz; $PCF_2CF_3$), −104.3 (ABX (AB component), $\nu_A$ = −103.9 ppm, $\nu_B$ = −104.6 ppm, $^2J_{FF}$ = 335 Hz, $^2J_{FP}(A)$ = 113 Hz, $^2J_{FP}(B)$ = 77 Hz; $PCF_2CF_3$), −109.4 (ABM$_3$X (AB component), $\nu_A$ = −108.6 ppm, $\nu_B$ = −110.2 ppm, $^2J_{FF}$ = 310 Hz, $^2J_{FP}(A)$ = 42 Hz, $^2J_{FP}(B)$ = 92 Hz, $^3J_{FP}(A)$ = 15 Hz, $^3J_{FP}(B) \approx 0$ Hz; $PCF_2CF_3$), −150.6 (s; $BF_4^-$).

**CpRu(dfepe)H (3). Method A.** To a solution of 0.500 g (0.65 mmol) of **1** in 5 mL of THF at −78 °C was added a THF solution of sodium naphthylide (prepared from 30 mg (1.3 mmol) of Na and 260 mg (2.03 mmol) of naphthylene in 3 mL of THF) dropwise by syringe until the dark green naphthylide color persisted. At this point 0.21 g (1.3 mmol) of $NH_4PF_6$ in 3 mL of THF was added

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and the reaction mixture was stirred at −78 °C for 15 min before warming to ambient temperature. The volatiles were removed under dynamic vacuum and the residue was taken up in petroleum ether and filtered. Concentration of the filtrate and cooling to −78 °C precipitated an off-white solid; the crude yield after drying was 0.215 g (45%). At 20 °C the solid obtained from this method becomes gummy unless all traces of naphthylene have been completely removed by sublimation.

**Method B.** A mixture of 518 mg (0.675 mmol) 1 and 210 mg (1.08 mmol) $AgBF_4$ in 10 mL of $CH_2Cl_2$ at −78 °C was placed under 1 atm of $H_2$. The reaction vessel was sealed off and allowed to warm to ambient temperature with stirring. After 12 h, the initially yellow solution of 1 became colorless and a precipitate of AgCl was observed. At this point the solution was cooled to −78 °C, the $H_2$ was removed, and 0.25 mL (1.8 mmol) $Et_3N$ was added by vacuum transfer. After warming and stirring for 30 min the volatiles were removed and the residue was extracted repeatedly with petroleum ether. Concentration of the filtrate to 2 mL and cooling to −78 °C yielded after cold filtration and drying 412 mg (83%) of analytically pure ruthenium hydride 3. 3 is air stable and highly soluble in nonpolar solvents and sublimes readily at 80 °C ($10^{-4}$ Torr). Anal. Calcd for $C_{15}H_{10}F_{20}P_2Ru$: C, 24.57; H, 1.37. Found: C, 24.89; H, 1.38. IR ($cm^{-1}$): 2003 (m), 1302 (s), 1226 (vs), 1120 (s), 961 (s), 867 (m), 814 (m), 744 (s). $^1H$ NMR (benzene-$d_6$, 270 MHz, 20 °C): $\delta$ 4.79 (s, 5 H; $\eta^5\text{-}C_5H_5$), 1.70 (m, 4 H; $PCH_2CH_2P$), −13.60 (t, $^2J_{PH}$ = 34 Hz, 1 H; RuH). $^{31}P\{^1H\}$ NMR (benzene-$d_6$, 161.7 MHz, 20 °C): $\delta$ 122.0 (m). $^{19}F$ NMR (benzene-$d_6$, 376.05 MHz, 20 °C): $\delta$ −73.9 (s; $PCF_2CF_3$), −75.2 (s; $PCF_2CF_3$), −109.7 (ABX (AB component), $\nu_A$ = −109.3 ppm, $\nu_B$ = −110.0 ppm, $^2J_{FF}$ = 317 Hz, $^2J_{FP}(A)$ = 61, $^2J_{FP}$ = 80 Hz; $PCF_2CF_3$), −112.0 (ABX (AB component), $\nu_A$ = −110.7 ppm, $\nu_B$ = −113.3 ppm, $^2J_{FF}$ = 305 Hz, $^2J_{FP}(A)$ = 59, $^2J_{FP}(B)$ = 34 Hz; $PCF_2CF_3$).

**CpRu(dfepe)Me (4).** Using the procedure described for 3, a solution of $Na^+[CpRu(dfepe)]^-$ in 5 mL of THF at −78 °C was prepared from 1.008 g (1.31 mmol) 1 and sodium napthylide. After 30 min, 0.2 mL (3.2 mmol) of methyl iodide was added via syringe and the solution was warmed to ambient temperature. THF and naphthylene were removed under vacuum and the remaining residue was sublimed at 60 °C ($10^{-4}$ Torr). The isolated yield was 0.478 g (49%). Anal. Calcd for $C_{16}H_{12}F_{20}P_2Ru$: C, 25.71; H, 1.62. Found: C, 25.73; H, 1.65. $^1H$ NMR (acetone-$d_6$, 270 MHz, 20 °C): $\delta$ 5.21 (s, 5 H; $\eta^5\text{-}C_5H_5$), 2.60 (m, 4 H; $PCH_2CH_2P$), −0.20 (tt, $^2J_{PH} \approx J_{FH} \approx 5$ Hz, 3 H; $Ru(CH_3)$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161.7 MHz, 20 °C): $\delta$ 122.8 (m). $^{19}F$ NMR (benzene-$d_6$, 376.05 MHz, 20 °C): $\delta$ −77.2 (d, $^3J_{FF}$ = 21 Hz; $PCF_2CF_3$), −77.7 (s; $PCF_2CF_3$), −104.0 (ABX (AB component), $\nu_A$ = −102.0 ppm, $\nu_B$ = −106.0 ppm, $^2J_{FF}$ = 322 Hz, $^2J_{FP}(A)$ < 5 Hz, $^2J_{FP}(B)$ = 85 Hz; $PCF_2CF_3$), −105.0 (ABX (AB component), $\nu_A$ = −104.3 ppm, $\nu_B$ = −105.6 ppm, $^2J_{FF}$ = 320 Hz, $^2J_{FP}(A)$ = 99 Hz, $^2J_{FP}(B)$ = 72 Hz; $PCF_2CF_3$).

**Crystal Structure of CpRu(dfepe)Cl (1).** X-ray data were collected on a Siemens R3m/V automated diffractometer system with a dedicated Microvax II computer system and fitted with an LT-2 low temperature device. The radiation used was Mo K$\alpha$ monochromatized by a highly ordered graphite crystal. The parameters used during the data collection are summarized in Table I. All computations used the SHELTXTL PLUS (Version 3.4) program library (Siemens Corp., Madison, WI).

A suitable crystal of 1 was grown by diffusing methanol into a solution of 1 in THF. Unit cell dimensions were derived from a least-squares fit of 50 random reflections ($22° \le 2\theta \le 30°$). The Laue symmetry was determined to be $2/m$. Data were collected using the $2\theta/\theta$ scan technique with a variable scan rate of 5.0 to 30.0 deg/min. Analysis of systematic absences for the total data set indicated that the space group was $P2_1/n$. Three standard reflections monitored after every 100 data collected showed no systematic variation; the $R$ for averaging 350 redundant data was 0.026. Data were corrected for absorption using an empirical ellipsoidal model based on $\varphi$ scans for 12 reflections with $8° \le 2\theta \le 50°$.

The structure of 1 was solved using the SHELXTL PLUS Patterson interpretation program; all non-hydrogen atoms were located on a series of difference Fourier maps and were refined anisotropically. Hydrogen atom positions were added in ideal calculated positions with $d$(C–H) = 0.96 Å and with fixed isotropic thermal parameters for the cyclopentadienyl and ligand backbone hydrogens set at 1.2–1.3 times the isotropic equivalent of the attached carbon atom. Full-matrix least-squares refinement gave an $R$ value of 0.052 ($R_W$ = 0.072) for 3893 data with $I > 3\sigma(I)$. The final difference Fourier map showed a maximum residual peak of 1.2 e/Å$^3$ associated with the C(4) trifluoromethyl group, which exhibited anomalously large thermal coefficients indicative of a mild positional disorder. No other significant residual peaks were observed in the rest of the molecule.

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**Supplementary Material Available:** Tables of complete X-ray data collection parameters (Table S1), atomic coordinates (Table S2), bond distances (Table S3), bond angles (Table S4), anisotropic thermal parameters (Table S5), and hydrogen atom coordinates and isotropic thermal parameters (Table S6) for 1 (7 pages). Ordering information is given on any current masthead page.

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