Organometallics **1997,** *16,* 1841−1845 1841

Synthesis and Reactions of Dihydridobis[1,2-bis(bis(trifluoromethyl)phosphino)ethane]ruthenium(II), $RuH_2(dfmpe)_2$

Leslie D. Field* and Matthew P. Wilkinson

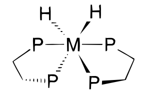
Department of Organic Chemistry, University of Sydney, Sydney, NSW 2006, Australia

Received April 24, 1996[⊗]

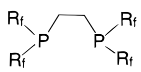
Two equivalents of dfmpe [dfmpe = 1,2-bis(bis(trifluoromethyl)phosphino)ethane] reacts with tris(triphenylphosphine)hydridochlororuthenium(II) to yield the ruthenium complex $RuHCl(dfmpe)_2$. Reduction of $RuHCl(dfmpe)_2$ using sodium borohydride affords the new complex $RuH_2(dfmpe)_2$ in high yield. Ultraviolet irradiation of $RuH_2(dfmpe)_2$ under 1 atm of deuterium gas results in the formation of $RuD_2(dfmpe)_2$; however, irradiation in the presence of organic substrates including arenes, alkanes, alkenes and alkynes fails to produce new organometallic species.

Introduction

Ethylene-bridged, bidentate bis(phosphines) $R_2PCH_2CH_2PR_2$ (R = alkyl, aryl) have proved to be a versatile and important class of compounds for the synthesis of organometallic complexes capable of activating C−H bonds in organic substrates.[1] Complexes such as $RuH_2(dmpe)_2$ (**1**) and $FeH_2(dmpe)_2$ (**2**) [dmpe = 1,2-bis(dimethylphosphino)ethane] react with C−H bonds to give complexes with metal−carbon bonds on irradiation with ultraviolet light.[2−6] Recently, fluorinated bis(phosphines) $(R_f)_2PCH_2CH_2P(R_f)_2$ (**5**) (R_f = perfluoroalkyl and perfluoroaryl) have emerged as new ligands,[7−10] and the electron-withdrawing nature of the fluorine atoms in close proximity to the phosphorus donors makes ligands of this type weak σ-donors and strong π-acceptors.[8,9] The electronic properties of the fluorinated ligand result in the formation of electron-poor transition metal complexes,[11] and the lack of C−H bonds close to the metal center makes the complexes less likely to degrade by internal C−H attack. The utility of organometallic complexes containing fluorinated bis(phosphines) in C−H activation reactions is only now beginning to be investigated, and the coordination properties of fluorinated bis(phosphines) $(CF_3CF_2)_2PCH_2CH_2P(CF_2CF_3)_2$ (**5b**) and $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (**5c**) have been investigated in some detail.



1 P−P = dmpe, M = Ru
2 P−P = dmpe, M = Fe
3 P−P = dfmpe, M = Ru
4 P−P = dfepe, M = Ru



5a $R_f = CF_3$ dfmpe
5b $R_f = CF_2CF_3$ dfepe
5c $R_f = C_6F_5$ dfppe

Complexes of these ligands with Cr,[8] Mo,[8,12,13] Fe,[14] Pt,[15] and Ru[11] have now been synthesized and characterized. The synthesis of $RuH_2(dfepe)_2$ (**4**) has been of particular interest since this was the first fluorinated analogue of $RuH_2(dmpe)_2$ (**1**) which has been well studied in the field of C−H activation.[11,16] The complex $RuH_2(dfepe)_2$ (**4**) was synthesized by the reaction of 2 equiv of dfepe with (η^4-cycloocta-1,5-diene)(η^6-cycloocta-1,3,5-triene)ruthenium(0), [Ru(COD)(COT)], under hydrogen gas, to give the complex in 41% yield.[11f] The complex **4** undergoes photochemical exchange of deuterium for hydrogen, but no room temperature C−H activation has been reported. The few reports of attempted reaction of fluorinated metal complexes with organic substrates indicate that incorporation of fluorinated bis(phosphines) into organometallic complexes imparts unique chemical and physical properties to the compounds.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(1) For early references, see, for example: (a) English, A. D.; Ittel, S. D; Jesson, J. P.; Tolman, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 4080−4089. (b) English, A. D.; Ittel, S. D.; Jesson, J. P.; Tolman, C. A. *J. Am. Chem. Soc.* **1979**, *101*, 7577−7585. (c) English, A. D.; Ittel, S. D; Jesson, J. P.; Tolman, C. A. *J. Am. Chem. Soc.* **1979**, *101*, 1742−1751. (d) Ittel, S. D.; Tolman, C. A.; Krusic, P. J.; English, A. D.; Jesson, J. P. *Inorg. Chem.* **1978**, *17*, 3432−3438.

(2) Baker, M. V.; Field, L. D. *Organometallics* **1986**, *5*, 821.

(3) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1987**, *109*, 2825−2826.

(4) Baker, M. V.; Field, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 7433−7434.

(5) Jones, W. D.; Kosar, W. P. *J. Am. Chem. Soc.* **1986**, *108,* 393−395.

(6) Yau, B. C. Y.; Field, L. D. Unpublished results, B.Sc. Honours Thesis, The University of Sydney, 1988.

(7) Cook, R. L.; Morse, J. G. *Inorg. Chem.* **1982**, *21*, 4103.

(8) See, for example: Schnabel, R. C.; Roddick, D. M. *ACS Symp. Ser.* **1994**, *55*, 421−437 and references therein.

(9) Ernst, M. F.; Roddick, D. M. *Inorg. Chem.* **1989**, *28*, 1624−1627.

(10) dfmpe was first made by L. R. Grant (Ph.D. Dissertation, University of Southern California Libraries, 1960, cited by A. B. Burg: Burg, A. B. *Acc. Chem. Res.* **1969**, *2*, 353).

(11) See, for example: (a) Schnabel, R. C; Carroll, P. S.; Roddick, D. M. *Organometallics* **1996**, *15*, 655−62. (b) Schnabel, R. C; Roddick, D. M. *Inorg. Chem.* **1993**, *32*, 1513−8. (c) Bennett, B. L; Birnbaum, J.; Roddick, D. M. *Polyhedron* **1995**, *14*, 187−195. (d) Schnabel, R. C; Roddick, D. M. *Organometallics* **1993**, *12*, 704−711. (e) Keady, M. S.; Koola, J. D.; Ontko, A. C.; Merwin, R. K.; Roddick, D. M. *Organometallics* **1992**, *11*, 3417−3421. (f) Koola, J. D.; Roddick, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 1450−1451.

(12) Ernst, M. F.; Roddick, D. M. *Organometallics* **1990**, *9*, 1586−1594.

(13) Ernst, M. F.; Roddick, D. M. *Inorg. Chem.* **1990**, *29*, 3627−3630.

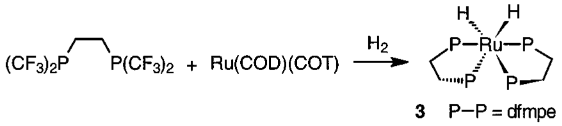
(14) Brookhart, M.; Chandler, W. A.; Pfister, A. C.; Santini, C. C.; White, P. S. *Organometallics* **1992**, *11*, 1263−1274.

(15) Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972−2978.

(16) (a) Cronin, L.; Nicasio, M. C.; Perutz, R. N.; Peters, R. G.; Roddick, D. M.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1995**, *117*, 10047−10054. (b) Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1992**, *114*, 7425. (c) Whittlesey, M. K.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Field, L. D.; Wilkinson, M. P.; George, M. W. *J. Am. Chem. Soc.* **1993**, *115*, 8627.

S0276-7333(96)00311-1 CCC: $14.00

Scheme 1



Perutz *et al.*[16] studied the photochemical generation of [Ru(drpe)$_2$] [drpe = dmpe, depe, dppe, and dfepe; depe = 1,2-bis(diethylphosphino)ethane; dppe = 1,2-bis(diphenylphosphino)ethane] from the corresponding dihydrides and was able to compare complexes with fluorinated and nonfluorinated ligands by flash photolysis and matrix isolation studies. The dihydride complexes all photochemically eliminate H_2, and spectroscopic evidence suggested that all complexes form four-coordinate [Ru(drpe)$_2$] species with structures which have close to square planar geometry. The [Ru(dfepe)$_2$] species is significantly less reactive than the nonfluorinated counterparts, and the study raised the possibility that the C_2F_5 group could interact with the Ru(0) center and restrict access of substrates to the metal.

Investigation of the coordination properties of $(CF_3)_2PCH_2CH_2P(CF_3)_2$ (**5a**) (dfmpe = 1,2-bis(bis(trifluoromethyl)phosphino)ethane)[10] has been impeded by the difficulty in synthesizing this ligand. To date, there are only few examples of metal complexes incorporating $(CF_3)_2PCH_2CH_2P(CF_3)_2$, and these include $Ni(CO)_2[(CF_3)_2PCH_2CH_2P(CF_3)_2]$,[17,18] $Ni(CO)[(CF_3)_2PCH_2CH_2P(CF_3)_2]_2$,[17,18] $Pt(Cl)_2[(CF_3)_2PCH_2CH_2P(CF_3)_2]$,[19] and $Mo(CO)_4[(CF_3)_2PCH_2CH_2P(CF_3)_2]$.[19] Our previous report of a new synthetic procedure for the synthesis of dfmpe[20] has made the compound more readily accessible and enabled its study as an ancillary ligand for organometallic complexes. We report here the synthesis and characterization of *cis*-RuH$_2$(dfmpe)$_2$ (**3**) via RuHCl(dfmpe)$_2$ (**6**) and examine some reaction chemistry of **3**.

Results and Discussion

Synthesis of *cis*-RuH$_2$(dfmpe)$_2$. The reaction of dfmpe with Ru(COD)(COT) under hydrogen gas in dichloromethane afforded *cis*-RuH$_2$(dfmpe)$_2$ (**3**) in yields of up to 25% (Scheme 1). The dihydride **3** was purified by flash chromatography and sublimation and was obtained as an air-stable, crystalline compound. High-field NMR spectra of **3** are shown in Figure 1. The ^{31}P NMR spectrum of RuH$_2$(dfmpe)$_2$ (**3**) shows two resonances (at δ 108.2 and 90.0 ppm) with complex multiplicity due to $^{31}P-^{31}P$ and $^{31}P-^{19}F$ coupling. The ^{19}F NMR spectrum exhibits four complex multiplets (at δ −56.9, −57.3, −58.0, and −60.0 ppm) also split by $^{31}P-^{19}F$ and $^{19}F-^{19}F$ coupling. The two resonances to low field in the ^{19}F NMR spectrum show a notable doublet splitting of about 70 Hz; however, extracting useful coupling information from any of the NMR spectra of **3** is complicated by the symmetry of the molecule and the magnetic nonequivalence that this imposes on various pairs of chemically equivalent nuclei. The ^1H NMR spectrum of **3** shows a symmetrical multiplet at δ −9.94 ppm (Figure 1b) which collapses to a singlet on phosphorus decoupling.

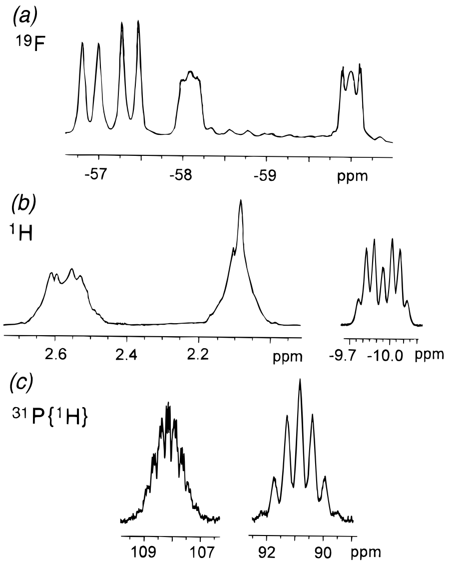


Figure 1. Sections of the ^{19}F, ^1H, and ^{31}P high-field NMR spectra of *cis*-RuH$_2$(dfmpe)$_2$ (**3**): (a) ^{19}F NMR spectrum ($CDCl_3$ solvent, 376 MHz, 300 K); (b) ^1H NMR spectrum ($CDCl_3$ solvent, 400 MHz, 300K); (c) $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$ solvent, 162 MHz, 300 K).

This synthesis via Ru(COD)(COT) affords **3** in variable and irreproducible yields, mainly due to the difficulty in reliably synthesizing Ru(COD)(COT). The synthesis of Ru(COD)(COT) is notoriously temperamental, and various attempts to increase the scale of Ru(COD)(COT) syntheses have been unsuccessful.[21] In addition, the cyclooctanes and cyclooctenes which are present as byproducts at the completion of the reaction make the purification of the complex **3** difficult.

Tris(triphenylphosphine)hydridochlororuthenium(II), RuHCl(PPh$_3$)$_3$, a compound which has been used recently as a precursor in the synthesis of RuHCl(dippe)$_2$ [dippe = 1,2-bis(diisopropylphosphino)ethane],[22] proved to be a more reliable precursor for the synthesis of **3**. Reaction of RuHCl(PPh$_3$)$_3$ with 2 equiv of dfmpe at room temperature afforded RuHCl(dfmpe)$_2$ (**6**) in 65% isolated yield. RuHCl(dfmpe)$_2$ is an air-stable, colorless solid which is soluble in organic solvents, but only sparingly soluble in light petroleum. The complex was readily recrystallized from hexane to form colorless prisms. Although crystals suitable for X-ray analysis were grown by slow solvent evaporation of a saturated solution, the complex crystallized (repeatedly) in the centrosymmetric space group $P2_1/n$, with the ruthenium atom lying on a crystallographic center of inversion and with half a molecule in the asymmetric unit. Consequently, the chloro and hydrido substituents are disordered in their (half-) occupancies of the axial sites in the octahedral coordination sphere. The hydride substituent could not be located from difference Fourier maps. The chloro substituent cleanly refines to half-occupancy, thereby confirming the molecular stoichiometry and the stereochemistry of the complex. The problem of structure refinement is further compounded

---

(17) Burg, A. B.; Street, G. B. *J. Am. Chem. Soc.* **1963**, *85*, 3522.

(18) Burg, A. B.; Street, G. B. *Inorg. Chem.* **1966**, *5*, 1532−1537.

(19) Phillips, I. G.; Ball, R. G.; Cavell, R. G. *Inorg. Chem.* **1988**, *27*, 4038−4045.

(20) Field, L. D.; Wilkinson, M. P. *Tetrahedron Lett.* **1992**, *33*, 7601−7604.

(21) See, for example: Bennett, M. A.; Neumann, H.; Thomas, M.; Wang, X. Q.; Pertici, P.; Salvadori, P.; Vitulli, G. *Organometallics* **1991**, *10*, 3237−3245.

(22) Jiminez-Tenerio, M.; Carmen Puerta, M.; Valerga, P. *Inorg. Chem.* **1994**, *33*, 3515−3520.

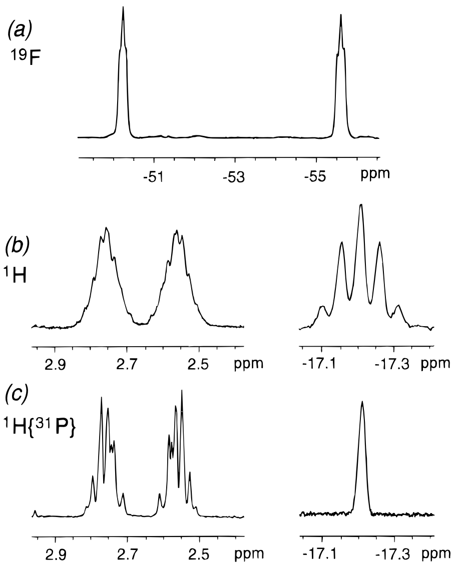


Figure 2. Sections of the ^{19}F and ^1H high-field NMR spectra of $RuHCl(dfmpe)_2$ (**6**): (a) ^{19}F NMR spectrum ($CDCl_3$ solvent, 376 MHz, 300 K); (b) ^1H NMR spectrum ($CDCl_3$ solvent, 400 MHz, 300 K); (c) $^1H\{^{31}P\}$ NMR spectrum ($CDCl_3$ solvent, 400 MHz, 300 K).

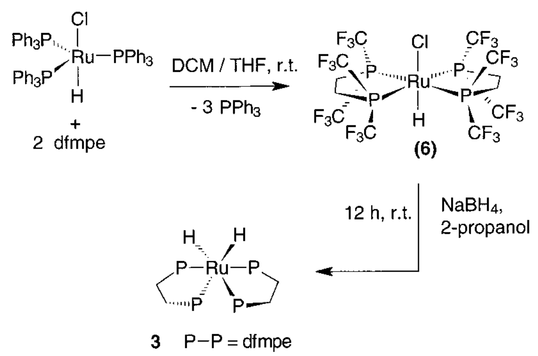
by extensive disorder in the orientations of the trifluoromethyl substituents.[23]

The ^{31}P NMR spectrum of $RuHCl(dfmpe)_2$ (**6**) shows one fluorine-coupled resonance at δ 96.2 ppm, indicating that all four phosphorus atoms are chemically equivalent. The ^{19}F NMR spectrum exhibits two resonances, due to the CF_3 groups on the upper and lower faces of the *trans* complex. Each of the ^{19}F resonances is complex due to the molecular symmetry and the magnetic inequivalence of the four phosphorus nuclei which couple to the CF_3 groups (Figure 2a). The ^1H NMR spectrum of **6** shows a quintet at δ −17.21 ppm, which collapses to a singlet on phosphorus decoupling (Figure 2b,c). The ^1H NMR spectrum of **6** also shows two phosphorus-coupled resonances at δ 2.75 and 2.56 ppm, which arise from the methylene protons on the dfmpe ligands.

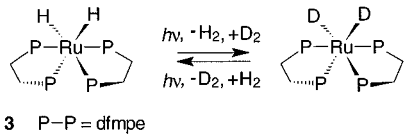
Reduction of $RuHCl(dfmpe)_2$ (**6**) using sodium borohydride in 2-propanol afforded $RuH_2(dfmpe)_2$ (**3**) in 67% yield (Scheme 2). This synthesis is a significant improvement on the synthesis of **3** using Ru(COD)(COT), both in yield and in ease of synthesis and purification.

In contrast to the precursor compound, $RuHCl(dfmpe)_2$ (**6**), the product $RuH_2(dfmpe)_2$ (**3**) is very soluble in perfluorohexane. The fluorocarbon solubility provides a relatively simple method for the separation of the desired fluorinated compound from most other organic and inorganic compounds in the reaction mixture. High solubility in perfluorinated solvents has been noted previously for the related complex $RuH_2(dfepe)_2$.[24]

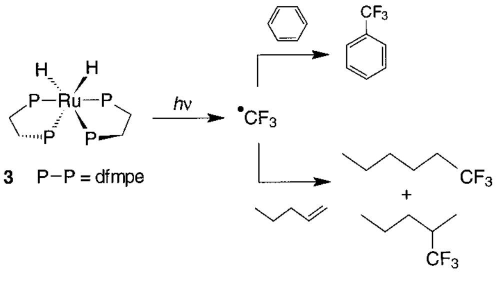
Scheme 2



Scheme 3



Scheme 4



Photochemical Reaction of $RuH_2(dfmpe)_2$ with D_2. A solution of $RuH_2(dfmpe)_2$ (**3**) in pentane was irradiated under an atmosphere of D_2 gas to assess the photochemical lability of the hydride ligands. Analysis of a sample of $RuH_2(dfmpe)_2$ (**3**) subjected to ultraviolet irradiation for an extended period (16 h) by ^2H NMR spectroscopy showed clean replacement of the metal-bound hydrides for deuterium (Scheme 3).

^2H NMR analysis of an identical sample of **3** in pentane under 1 atm of D_2 gas kept at room temperature in the dark for an extended period of time revealed no incorporation of deuterium into the hydride positions of $RuH_2(dfmpe)_2$ (**3**).

Photochemical Reaction of $RuH_2(dfmpe)_2$ with Organic Substrates. The complex $RuH_2(dfmpe)_2$ (**3**) is stable in the presence of benzene, CO, and alkenes at room temperature. The thermal reactivity of **3** at high temperature has not yet been studied; however, the dfepe analogue **4** is known to react with aromatic substrates at elevated temperatures.[11f] Ultraviolet irradiation of **3** in the presence of carbon monoxide, cyclopentene, toluene, benzene, 1-pentene, triethylsilane, and phenylacetylene showed the formation of no new organometallic products. ^{19}F NMR spectroscopic analysis of the reaction mixtures in all cases exhibited resonances only arising from $RuH_2(dfmpe)_2$ (**3**). Extended irradiation led only to the decomposition of $RuH_2(dfmpe)_2$ (**3**).

In reactions involving aromatic or unsaturated organic substrates, new organic products were observed in the ^{19}F NMR spectra. In the prolonged irradiation of $RuH_2(dfmpe)_2$ (**3**) in benzene, α,α,α-trifluorotoluene was identified by ^{19}F NMR and by GC/MS (Scheme 4). Similarly, trifluorohexanes were identified in the reaction mixture after extended irradiation of $RuH_2(dfmpe)_2$

---

[23] Data was refined to give an *R* factor of 4.8%; attempts to refine the data in a lower symmetry space group (*i.e.*, non-centrosymmetric space group) gave no improvement. $C_{12}H_9ClF_{24}P_4Ru$: M = 869.6, colorless, space group $P2_1/n$, a = 10.082(3) Å, b = 9.583(3) Å, c = 14.051(3) Å, β = 108.97(2)°, V = 1283.8(6) Å^3, D_c = 2.25 g cm^{-3}, Z = 2, $F(000)$ = 836.

[24] Brookhart, M.; Chandler, W.; Liu, Y.; Pienta, N. J.; Santini, C. C.; Hall, C.; Perutz, R. N.; Timney, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 3802.

(**3**) in the presence of 1-pentene. The formation of trifluoromethylated organic compounds in the reaction mixture is consistent with generation of CF_3 radicals, and this highlights one possible instability associated with the photochemistry of metal complexes containing coordinated dfmpe. Stable trifluoromethyl radicals can be formed (possibly with the involvement of the metal center), and these readily give rise to trifluoromethylated organic byproducts.

Reaction of $RuH_2(dfmpe)_2$ with Organic Acids. In contrast to the protonation of $RuH_2(dmpe)_2$ (**1**) in methanol solution to form the molecular hydrogen complex *trans*-$[RuH(H_2)(dmpe)_2]^+$,[25] the reaction of $RuH_2(dfmpe)_2$ (**3**) with neat methanol, trifluoroacetic acid, and triflic acid failed to form any new species. ^{19}F NMR spectra of solutions of **3** in neat methanol, trifluoroacetic acid, and triflic acid showed **3** as the only organometallic species present. A ^2H NMR spectrum of a sample of **3** which had been dissolved in d_4-methanol and recovered showed no detectable incorporation of deuterium even after four successive dissolutions.

Conclusion

A convenient and high-yielding synthesis of the new ruthenium dihydride $RuH_2(dfmpe)_2$ (**3**) has been developed from $RuHCl(PPh_3)_3$ via the intermediate $RuHCl(dfmpe)_2$ (**6**). This synthetic approach represents a significant improvement in the synthesis of this type of complex and may well prove to be a useful approach to other ruthenium chlorohydrido and dihydrido complexes containing fluorinated bis(phosphine) ligands.

The introduction of CF_3 groups to the phosphine ligand dramatically changes the physical and chemical properties of the complex, compared to the nonfluorinated analogue, $RuH_2(dmpe)_2$ (**1**). $RuH_2(dfmpe)_2$ (**3**) is remarkably stable and chemically robust: there are very few metal hydrides which could tolerate dissolution in neat triflic acid. Although $RuH_2(dfmpe)_2$ (**3**) photochemically exchanges hydride for deuteride in D_2 gas at room temperature, consistent with reductive elimination of H_2 to form $[Ru(dfmpe)_2]$, the complex shows no tendency to oxidatively add C−H bonds in organic substrates under continuous irradiation conditions. The lack of reactivity is not dissimilar to that noted for $[Ru(dfepe)_2]$.[16a]

Experimental Section

General Procedures. The preparation of (η^4-cycloocta-1,5-diene)(η^6-cycloocta-1,3,5-triene)ruthenium(0), Ru(COD)(COT), was based on the literature synthesis described by Pertici and co-workers.[26] $RuHCl(PPh_3)_3$ was synthesized following the method of Hallman, McGarvey, and Wilkinson.[27] 1,2-Bis(dichlorophosphino)ethane (dcpe) was purchased from Strem and used without further purification. Hexaethylphosphorus triamide (hepa) was synthesized following the literature procedure.[28] $RuCl_3{\cdot}3H_2O$ was obtained from Johnson-Matthey and used without further purification.

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Infrared spectra were acquired using a Perkin-Elmer 1600 series FTIR spectrometer. Samples for UV/visible spectrophotometric analysis were recorded on a Hitachi 150-20 spectrophotometer. NMR spectra were recorded on a Bruker AMX400 spectrometer, at resonant frequencies for ^1H, ^2H, ^{13}C, ^{31}P, and ^{19}F NMR of 400.13, 61.42, 100.62, 161.98, and 376.43 MHz, respectively. Chemical shifts (δ) are in parts per million, the downfield region being positive. ^1H and ^{13}C chemical shifts are referenced to solvent resonances. ^{31}P chemical shifts are referenced to external, neat trimethyl phosphite, taken as 140.85 ppm, and ^{19}F chemical shifts are referenced to external, neat hexafluorobenzene, taken as −163.0 ppm. Nitrogen (>99.5%), hydrogen (>99.9%), deuterium (>99.8%), and carbon monoxide (>99.0%) were purchased from BOC gases and used without further purification. Dichloromethane was distilled over P_2O_5 under a nitrogen atmosphere immediately prior to use. Pentane, THF, benzene, toluene, and hexane were stored over sodium benzophenone ketyl radical under a dry atmosphere and distilled under nitrogen prior to use. Ethanol and 2-propanol were distilled over magnesium alkoxide and stored under nitrogen prior to use. Deuterated solvents were purchased from Merck and used without further purification. Sodium borohydride was dried under vacuum overnight and then stored in a vacuum desiccator until required for use. 1,5-Cyclooctadiene was distilled and stored under nitrogen prior to use. Zinc powder was purchased from Aldrich and used without further purification. Flash silica used for chromatography was dried under vacuum overnight prior to use.

Photolysis experiments were carried out by suspending samples in a vacuum-jacketed Pyrex dewar containing ethanol cooled with a Lauda ETK 50 refrigeration coil. The apparatus was positioned approximately 10 cm from an Oriel 66033 high-pressure mercury lamp.

Compounds $RuH_2(dfmpe)_2$ (**3**) and $RuHCl(dfmpe)_2$ (**6**) failed to give acceptable C, H combustion microanalytical data (*i.e.*, within 0.4% for both C and H) despite repeated analysis, and this was attributed to the difficulty in analyzing highly fluorinated compounds using conventional combustion analysis (each >50% F by weight) and incomplete combustion.

Synthesis of dfmpe (5a). The ligand dfmpe (**5a**) was synthesized using a modification of the method previously reported,[20] and the procedure described here represents a significant improvement in the yield and method of isolation. In a typical reaction, trifluoromethyl bromide (36.0 g, 240 mmol) was condensed into a three-necked flask cooled to liquid nitrogen temperature and fitted with a dry-ice condenser. The flask was allowed to warm to −60 °C, and 1,2-bis(dichlorophosphino)ethane (4.0 g, 17 mmol) was added to the reaction mixture using an air-tight syringe. Dichloromethane (20 mL) was added, and a solution of hexaethylphosphorus triamide (34.0 g, 140 mmol) in dichloromethane (20 mL) was added over a period of 1 h while the temperature was maintained between −60 and −55 °C. The color of the reaction mixture was pale yellow after the addition of hepa was complete. Sulfur powder (2.0 g, 62 mmol) was added, and the reaction mixture was allowed to warm slowly to room temperature.[29] Dichloromethane and dfmpe were distilled from the reaction mixture under vacuum and collected at liquid nitrogen temperature. The dichloromethane solution obtained contained dfmpe (1.2 g, 3.3 mmol, 20%) as the sole component (>95%, 0.03 g/mL) and was used directly for most applications.[30] $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 0.2 (2P, m, $P(CF_3)_2$) ppm. ^1H NMR (CD_2Cl_2): δ 2.29 (4H, apparent triplet, PCH_2, splitting = 4 Hz) ppm. ^{19}F NMR (CD_2Cl_2): δ −51.5 (12F, m, $P(CF_3)_2$) ppm. $^{13}C\{^1H\}$ NMR

---

[25] Field, L. D.; Hambley, T. W.; Yau, B. C. K. *Inorg. Chem.* **1994**, *33*, 2009−2017.

[26] Pertici, P.; Vitulli, G. *Inorg. Synth.* **1983**, *22*, 178.

[27] Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143.

[28] Stuebe, C.; Lankelma, H. P. *J. Am. Chem. Soc.* **1956**, *78*, 976.

[29] Significant decomposition of dfmpe is observed if the reaction mixture is allowed to warm to room temperature in the presence of excess hepa. The reaction of hepa with elemental sulfur to form hexaethylphosphorus triamide sulfide is rapid (even at low temperature), and warming the reaction mixture to room temperature after the hepa has been sulfurized results in no decomposition of dfmpe.

[30] The yield of dfmpe can be increased (to *ca.* 30%) if the reaction mixture is extracted with perfluorohexanes (3 × 50 mL). No separation of dfmpe from perfluorohexane was attempted.

(CDCl$_3$): δ 14.9 (CH$_2$), 128.4 ppm (4C, m, CF3, $^1J_{C-F} = 325$ Hz) ppm. MS (EI) *m/e:* (M$^+$) 366 (0.5), 347 (5), 297 (100), 247 (27), 197 (23), 131 (5), 119 (10), 69 (90).

Synthesis of RuH$_2$(dfmpe)$_2$ (3) via Ru(COD)(COT). 1,5-Cyclooctadiene (8.8 g, 81 mmol) was added to a solution of ruthenium trichloride trihydrate (0.34 g, 1.3 mmol) in ethanol (10 mL). Zinc dust (3.5 g) was added, and the mixture was heated under reflux with magnetic stirring for 3 h. The solvent was removed under vacuum, and the residue was extracted into hexane (30 mL). The concentration of the solution was calibrated by ^{1}H NMR spectroscopy by integration of Ru(COD)(COT) resonances against an internal standard (trinitrotoluene) and found to contain 0.95 mmol of Ru(COD)(COT) (73%). This solution was used in subsequent reactions without further purification.

A solution of Ru(COD)(COT) (0.21 g, 0.65 mmol) in hexane (20 mL) was added to a reaction vessel and the solvent removed under vacuum. A solution of dfmpe (0.48 g, 1.3 mmol) in dichloromethane (15 mL) was added to this residue. The vessel was evacuated and filled with H$_2$ gas (at 1 atm pressure), and the reaction mixture was stirred for 16 h at room temperature. Flash silica (approximately 2 g) was added, and the solvent was removed under vacuum. The resulting dry powder was added to a column packed with flash silica and flushed with light petroleum. The crude product was recrystallized from hexane to give RuH$_2$(dfmpe)$_2$ (**3**) as white air-stable needles (0.15 g, 27%): mp 155−156 °C. The material is very volatile and sublimes easily at room temperature even under moderate vacuum. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 108.2 (2P, m), 90.0 (2P, m) ppm. ^{1}H NMR (CDCl$_3$): δ 2.58 (4H, m, PCH_2), 2.09 (4H, m, PCH_2), −9.94 (2H, m, RuH_2) ppm. ^{19}F NMR (CDCl$_3$): δ −56.9 (6F, d, P(CF_3)$_2$, dominant doublet splitting 70 Hz), −57.3 (6F, d, P(CF_3)$_2$, dominant doublet splitting 75 Hz), −58.0 (6F, m, P(CF_3)$_2$), −60.0 (6F, m, P(CF_3)$_2$) ppm. ^{13}C{^{1}H,^{31}P} NMR (CDCl$_3$): δ 127.1 (4C, m, P(CF$_3$)$_2$), 123.9 (4C, m, P(CF$_3$)$_2$), 23.5 (2C, s, CH$_2$P(CF$_3$)$_2$), 22.2 (2C, s, CH$_2$P(CF$_3$)$_2$) ppm. UV/vis (hexane): 254 nm ($\epsilon = 5.274 \times 10^3$, br shoulder), 222 nm ($\epsilon = 1.117 \times 10^4$, broad), and 191 nm ($\epsilon = 2.016 \times 10^4$). IR (KBr disk): 1931 cm^{-1} (weak) Ru−H. MS *m/e*: (M$^+$ − 1) 834 (50), 715 (40), 468 (53), 418 (30), 297 (37), 247 (10), 197 (20), 77 (28), 69 (100), 47 (32). High-resolution MS (M$^+$ − H$_2$): $C_{12}H_8F_{24}P_4Ru$ requires 833.82368 amu; found 833.822 amu.

Synthesis of RuHCl(dfmpe)$_2$ (6). A solution of dfmpe (0.84 g, 2.3 mmol) in dichloromethane (15 mL) was added to a solution of RuHCl(PPh$_3$)$_3$ (1.0 g, 1.1 mmol) in benzene (50 mL), and the mixture was stirred at room temperature for 1 h. The deep purple color of the reaction mixture changed to yellow as the reaction proceeded. The resulting solution was flushed through a small plug of flash silica with dichloromethane (50 mL) as eluent, and the solvent was removed under vacuum. The residue was washed with light petroleum (3 × 50 mL) and dried under vacuum. RuHCl(dfmpe)$_2$ (**6**) was obtained as an air-stable white powder (0.62 g, 65%): mp 217−218 °C dec. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 96.2 (4P, m) ppm. ^{1}H NMR (CDCl$_3$): δ 2.75 (4H, m, 2 × PCH_XH$_Y$CH_XH$_Y$P), 2.56 (4H, m, 2 × PCH$_X$$H_YCH_X$$H_Y$P), −17.21 (1H, quin, $^2J_{H-P} = 21$ Hz, RuH) ppm. ^{19}F NMR (CDCl$_3$): δ −50.3 (12F, m, 4 × F_3C$_X$PC$_Y$F$_3$), −55.6 (12F, m, 4 × F$_3$C$_X$PC$_Y$$F_3$) ppm. ^{13}C{^{1}H,^{31}P} NMR (CDCl$_3$): δ 126.0 (2 × 4C, q, 4 × F$_3$$\boldsymbol{C}_XPC_YF_3$, $^1J_{C-F} = 320$ Hz), 21.1 (4C, s, CH$_2$P) ppm. IR (Nujol mull): 1979 (w) cm^{-1}, Ru−H. MS (CI) *m/e*: (M$^+$ + 2) 871 (12), 835 (100), 803 (7).

Synthesis of RuH$_2$(dfmpe)$_2$ (3) via RuHCl(dfmpe)$_2$ (6). Sodium borohydride (20 mg, 0.5 mmol) was added to a solution of RuHCl(dfmpe)$_2$ (**6**) (100 mg, 0.1 mmol) in 2-propanol (20 mL), and the solution was stirred at room temperature for 16 h. The solvent was removed under vacuum, and the residue was extracted exhaustively with light petroleum. The combined extracts were stripped of solvent and the residue sublimed at 70 °C at 4 × 10^{-5} Torr onto a water-cooled cold finger to give RuH$_2$(dfmpe)$_2$ (**3**) (56 mg, 70 μmol, 67%) as a white air-stable solid. The compound was identical in all respects to that synthesized from Ru(COD)(COT).

Photochemical Reaction of RuH$_2$(dfmpe)$_2$ (3) with D$_2$ Gas. RuH$_2$(dfmpe)$_2$ (**3**) (5 mg, 6 μmol) was dissolved in pentane (0.3 mL) in an NMR tube equipped with a concentric Teflon valve, and the solution was degassed by three freeze−pump−thaw cycles on a high-vacuum line. The NMR tube was back-filled with D$_2$ gas (1 atm pressure), and the sample was irradiated with ultraviolet light at 0 °C for 16 h. A ^{2}H NMR spectrum of the sample showed a broad signal at −9.9 ppm, and a ^{1}H NMR spectrum showed no hydride present at −9.9 ppm.

In a blank experiment (no irradiation) RuH$_2$(dfmpe)$_2$ (**3**) (5 mg, 6 μmol) was dissolved in pentane (0.3 mL) in an NMR tube equipped with a concentric Teflon valve, and the solution was degassed by three freeze−pump−thaw cycles on a high-vacuum line. The NMR tube was back-filled with 1 atm of D$_2$ gas, and the sample was kept at room temperature in the dark for 43 h. A ^{2}H NMR spectrum of the sample showed no signal at −9.9 ppm, and a ^{1}H NMR spectrum showed a resonance present at −9.9 ppm.

Photochemical Reaction of RuH$_2$(dfmpe)$_2$ (3) with Organic Substrates. In a typical reaction, RuH$_2$(dfmpe)$_2$ (**3**) (5 mg, 6 μmol) was dissolved in the organic substrate (0.3 mL) in an NMR tube equipped with a concentric Teflon valve, and the solution was degassed by three freeze−pump−thaw cycles on a high-vacuum line and then back-filled with nitrogen. The sample was irradiated at room temperature for 16 h. The reaction was monitored in all cases by ^{19}F NMR spectroscopy.

Reaction of RuH$_2$(dfmpe)$_2$ (3) with Organic Acids. In a typical reaction, RuH$_2$(dfmpe)$_2$ (**3**) (5 mg, 6 μmol) was dissolved in the organic acid (0.3 mL) in an NMR tube, and the sample was kept at room temperature for 30 min. Analysis by ^{19}F NMR spectroscopy showed the presence of resonances due only to **3**, and in the case of triflic acid and trifluoroacetic acid, resonances due to these acids. No new resonances were observed.

RuH$_2$(dfmpe)$_2$ (**3**) (5 mg, 6 μmol) was dissolved in CD$_3$OD (0.5 mL), and the solvent was removed under vacuum. This procedure was repeated twice more, and the residue was dissolved in THF. Analysis of the sample by ^{2}H NMR spectroscopy showed no resonance in the hydride region of this spectrum.

Acknowledgment. We gratefully acknowledge financial support from the Australian Research Council and the Australian Government for an Australian Postgraduate Research Award (M.P.W.). We gratefully acknowledge Johnson-Matthey Pty. Ltd. for the generous loan of ruthenium salts. We thank Dr. P. Steel of the University of Canterbury (New Zealand) and Drs. T. W. Hambley and P. Turner of the University of Sydney for their efforts to analyze compound **6** by X-ray diffraction.

OM960311B