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Binuclear ruthenium complexes of fluorous phosphine ligands: Synthesis, properties, and biphasic catalytic activity. Crystal structure of $[Ru(\mu\text{-}O_2CMe)(CO)_2P(CH_2CH_2(CF_2)_5CF_3)_3]_2$

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ABSTRACT

The fluorocarbon soluble, binuclear ruthenium(I) complexes $[Ru(\mu\text{-}O_2CMe)(CO)_2L^F]_2$, where L^F is the perfluoroalkyl substituted tertiary phosphine, $P(C_6H_4\text{-}4\text{-}CH_2CH_2(CF_2)_7CF_3)_3$, or $P(CH_2CH_2(CF_2)_5CF_3)_3$, were synthesized and partition coefficients for the complexes in fluorocarbon/hydrocarbon biphases were determined. Catalytic hydrogenation of acetophenone to 1-phenylethanol in benzotrifluoride at 105 °C occured in the presence of either $[Ru(\mu\text{-}O_2CMe)(CO)_2P(C_6H_4\text{-}4\text{-}CH_2CH_2(CF_2)_7CF_3)_3]_2$ (**1**) or $[Ru(\mu\text{-}O_2CMe)(CO)_2P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**2**). The X-ray crystal structure of $[Ru(\mu\text{-}O_2CMe)(CO)_2P(CH_2CH_2\text{-}(CF_2)_5CF_3)_3]_2$ was determined. The compound exhibited discrete regions of fluorous and non-fluorous packing.

1. Introduction

Facile homogeneous catalyst/product separation has been demonstrated by Fluorous Biphasic Catalytic Systems, or FBS [1–4]. At the core of these catalytic systems is the miscibility of fluorocarbon compounds and solvents with hydrocarbon compounds and solvents at elevated temperatures, coupled with their immiscibility at ambient temperature [2]. In the seminal work, immobilization of a homogeneous transition metal catalyst in a fluorous phase was achieved by use of a perfluoroalkyl substituted trialkylphosphine compound (**A**, Fig. 1) as a unidentate ligand within the framework of alkene hydroformylation. Similar fluorous tagged derivatives of triphenylphosphine (**B**) and 1,2-bis(diphenylphosphino)ethane (**C**) have been used with rhodium complexes to promote solubility in supercritical carbon dioxide – $scCO_2$, another green solvent – for catalytic alkene hydroformylation [5]. Subsequent developments have generated numerous perfluoroalkyl substituted ligands, including fluorous phase labeled triarylphosphites (**D**) [6]. Fluorous tagged phosphine complexes have been employed to perform catalytic transformations in addition to hydroformylation, specifically, hydrogenation, hybroboration, hydrosilylation, and carbon–carbon coupling in both fluorous biphasic systems and $scCO_2$ [7–10].

As part of our studies of FBS through employment of fluorous ponytail substituted tertiary phosphine ligands, we have synthesized (Scheme 1) and characterized two dimeric $[Ru(\mu\text{-}O_2CMe)(CO)_2L^F]_2$ complexes, (**1**) where L^F = **B**, and (**2**) where L^F = **A**. Interest in di-μ-acetatotetracarbonyldiruthenium(I) compounds, $[Ru(\mu\text{-}O_2CMe)(CO)_2L]_2$, particularly where L is a tertiary phosphine such as PPh_3 or PBu_3, is due to their identification as catalysts or catalyst precursors for a variety of organic transformations. These transformations include the conversion of dimethyl oxalate to methyl glycolate and ethylene glycol [11], the conversion of acetic acid to ethyl acetate and methanol [12], the hydroformylation of alkenes [13], the benzylation of phenol [14], alkene isomerization [15], and the hydrogenation of alkenes and ketones [16]. Herein, we report the results of our investigations regarding the catalytic activity of diruthenium compounds **1** and **2** in fluorocarbon/hydrocarbon biphasic media.

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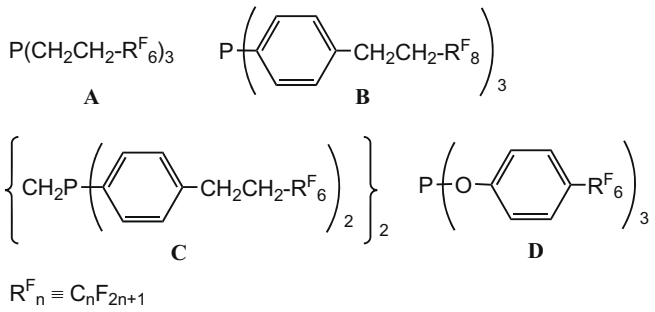
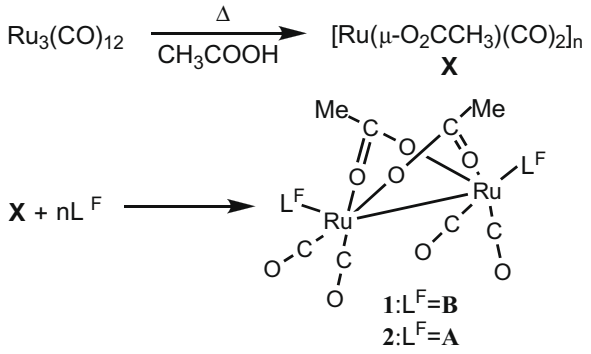


Fig. 1. Perfluoroalkyl substituted phosphines and phosphites.



Scheme 1.

2. Experimental

2.1. General information

Unless otherwise specified, all syntheses were performed under a nitrogen atmosphere with standard Schlenk techniques. The following solvents were distilled before use: benzotrifluoride from P_2O_5; perfluoromethylcyclohexane from P_2O_5; THF from sodium/benzophenone; toluene from sodium. The solvents 1,1,2-trichlorotrifluoroethane (CFC-113, Aldrich), perfluorodecalin (Lancaster), dichloromethane, diethyl ether, and *n*-pentane (all Fisher), and the deuterated solvents $CDCl_3$ and C_6D_6 (both CIL) were all used as received. $Ru_3(CO)_{12}$ (Strem, 99%), acetophenone, and 1-dodecene (both Aldrich) were used as received. Pre-coated F_{254} silica gel TLC plates, 20 cm × 20 cm × 250 μm (EMD Chemicals) were used as received. The compound, $[Ru(\mu\text{-}O_2CMe)(CO)_2]_n$, was prepared from ruthenium carbonyl and glacial acetic acid (Mallinkrodt, as received) by a literature method [17]. The perfluoroalkyl substituted phosphine compounds $P(CH_2CH_2(CF_2)_5CF_3)_3$ [18], and $P(C_6H_4\text{-}4\text{-}CH_2CH_2(CF_2)_7CF_3)_3$ [19], were prepared by literature methods.

Infrared spectra were obtained on a Perkin–Elmer Model 1600 FT-IR spectrometer using a liquid cell with KBr plates. A Varian Unity-500 MHz spectrometer was used to obtain ^1H, ^{19}F, and ^{31}P NMR spectra. The ^{19}F and ^{31}P chemical shifts are reported versus $CFCl_3$ and 85% H_3PO_4, respectively. The ^{19}F NMR assignments for **1** and **2** are consistent with the assigned ^{19}F NMR signals of the free ligands, Refs. [19,18], respectively. Field desorption mass spectra were obtained with a Micromass 70-VSE mass spectrometer by the staff of the Mass Spectrometry Center of the School of Chemical Sciences. Elemental analyses were conducted by the staff of the Microanalytical Laboratory of the School of Chemical Sciences.

2.2. Preparation of $[Ru(\mu\text{-}O_2CMe)(CO)_2P(C_6H_4\text{-}4\text{-}CH_2CH_2(CF_2)_7CF_3)_3]_2$ (**1**)

In a 75 mL Schlenk tube containing a magnetic stirbar, 25 mL of THF was added to 60 mg (0.28 mmol) of $[Ru(\mu\text{-}O_2CMe)(CO)_2]_n$ under N_2. To this orange suspension was added 484 mg (0.30 mmol) of $P(C_6H_4\text{-}4\text{-}CH_2CH_2(CF_2)_7CF_3)_3$. The Schlenk tube was heated in an oil bath for *circa* 1 h under N_2 with solvent reflux to form a clear yellow–orange solution; then the tube was cooled and the THF was removed under vacuum. The residue was dissolved in CFC-113 and subjected to TLC separation. Eluting with 3:1 *n*-pentane/dichloromethane provided a yellow product band which was extracted with dichloromethane. A second application of TLC, following the same procedure, provided compound **1** as a pale yellow solid (259 mg, 0.071 mmol, 51%). Anal. Calc. for $C_{104}H_{54}F_{102}O_8P_2Ru_2$: C, 34.38; H, 1.50. Found: C, 34.45; H, 1.47%. IR (CFC-113): ν(CO), 2029 (vs), 1986 (m), 1960 (vs), 1930 (w) cm^{-1}; $\nu(CO_2)$, 1578 (m), 1438 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.45 (2H, dd, *o*-H_A), 7.22 (2H, dd, *m*-H_B), 2.92 (2H, m, PC^1H_2), 2.37 (2H, m, $C^2H_2CF_2$), 1.67 (3H, s, $-CH_3$). ^{19}F NMR ($CDCl_3$): δ_F −81.2 (3F, t, J_{FF} 10 Hz, $C^{10}F_3$), −115.0 (2F, m, C^3F_2), −122.1 (2F, m, C^5F_2), −122.4 (4F, m, $C^6F_2C^7F_2$), −123.2 (2F, m, C^8F_2), −123.9 (2F, m, C^4F_2), −126.6 (2F, m, C^9F_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ_P 13.8 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ_P 14.3 (s). Mass Spec. (FD): *m/z* 3634 [M^+].

2.3. Preparation of $[Ru(\mu\text{-}O_2CMe)(CO)_2P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**2**)

In a 75 mL Schlenk tube containing a magnetic stirbar, 20 mL of THF was added to 50 mg (0.23 mmol) of $[Ru(\mu\text{-}O_2CMe)(CO)_2]_n$ under N_2. To this orange suspension 10 mL of a 0.026 M solution (0.26 mmol) of $P(CH_2CH_2(CF_2)_5CF_3)_3$ in THF was added by syringe. The Schlenk tube was heated in an oil bath for *circa* 1 h under N_2 with solvent reflux to form a clear yellow–orange solution; then the tube was cooled and the THF was removed under vacuum. The residue was washed with dichloromethane (3 × 3 mL), dissolved in CFC-113, and subjected to TLC separation. Eluting with 3:1 *n*-pentane/dichloromethane provided a yellow product band which was extracted with benzotrifluoride. A second application of TLC, eluting with 3:1 dichloromethane/diethyl ether and extracting with benzotrifluoride, provided compound **2** as a viscous, yellow–orange liquid (136 mg, 0.053 mmol, 46%). Anal. Calc. for $C_{56}H_{30}F_{78}O_8P_2Ru_2$: C, 26.10; H, 1.17. Found: C, 25.72; H, 1.11%. IR (CFC-113): ν(CO), 2032 (vs), 2002 (w), 1988 (m), 1964 (vs), 1936 (w) cm^{-1}; $\nu(CO_2)$, 1573 (m), 1442 (m) cm^{-1}. ^1H NMR (CFC-113/C_6D_6): δ 2.41 (2H, m, PC^1H_2), 1.93 (2H, m, $C^2H_2CF_2$), 1.87 (3H, s, $-CH_3$). ^{19}F NMR (CFC-113/C_6D_6): δ_F −81.9 (3F, t, J_{FF} 10 Hz, C^8F_3), −115.6 (2F, m, C^3F_2), −122.5 (2F, m, C^4F_2), −123.6 (2F, m, C^6F_2), −124.2 (2F, m, C^7F_2), −127.0 (2F, m, C^5F_2). $^{31}P\{^1H\}$ NMR (CFC-113/C_6D_6): δ_P 6.5 (s). Mass Spec. (FD): *m/z* 2578 [M^+].

2.4. Crystallographic analysis of **2**

Diffraction quality crystals of compound **2** were formed as a yellow saturated CFC-113 solution of **2** diffused into a layer of ethanol at −30 °C. The single crystal(s) of **2** exhibited non-merohedral twinning with an odd twin law between the domains. Relevant information is listed in Table 1. The systematic absences for 0*k*0, $k = 2n + 1$, and *h*0*l*, $h = 2n + 1$ were consistent with the monoclinic space group $P2_1/a$. A face-centered absorption correction was applied (absorption coefficient: $\mu = 0.669\ mm^{-1}$). Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield a unique dataset. The structure was solved by employing direct methods within the SHELXTL software package [20]. The correct positions for the ruthenium and phosphorus atoms were deduced from direct methods E-maps; subsequent least squares refinement and difference Fourier calcu-

Table 1
Crystal data, refinement parameters for **2**·$CFCl_2CF_2Cl$.

	Complex **2**·$CFCl_2CF_2Cl$
Empirical formula	$C_{58}H_{30}Cl_3F_{81}O_8P_2Ru_2$
Formula weight	2764.19
T (°C)	−80(2)
Space group	$P2_1/a$
a (Å)	10.76(1)
b (Å)	41.28(2)
c (Å)	20.66(1)
α (°)	90.0
β (°)	95.88(1)
γ (°)	90.0
V (Å^3)	9125(8)
Z	4
ρ_{calc} (g/cm^3)	2.012
μ (mm^{-1})	0.669
Total data	41 029
Unique data	40 886
Restraints/parameters	682/1463
R_1 (all data)[a]	0.2371
wR_2 (all data)[b]	0.2693
R_1 ($I > 2\sigma(I)$)[a]	0.0985
wR_2 ($I > 2\sigma(I)$)[b]	0.2200
Max, min (e Å^{-3})	1.424, −0.978

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_c|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^4]^{1/2}$.

lations established the positions of the remaining non-hydrogen atoms, which were refined with independent anisotropic displacement parameters. Hydrogen atoms were fixed in idealized positions and their displacement parameters were tied to those of the attached non-hydrogen atom. Successful convergences were indicated by maximum shift/error values that approached 0.000 for the last cycle(s) of the least squares refinements. The largest peak, 1.16 e Å^{-3}, in the final Fourier difference map was located 0.584 Å from the ruthenium atom Ru(2). Final analyses of variance between calculated and observed structure factors exhibited no perceptible errors. For every molecule of **2** there existed one molecule of solvate, 1,1,2-trichlorotrifluoroethane (CFC-113), possessing two disordered sites that have occupancy factors of 81% and 19%, respectively. Our model provides one solvate rotamer per disordered site. Selected bond lengths and bond angles for **2** are listed in Table 2.

Table 2
Average bond lengths (Å) and angles (°) for **2** and **4**.[a]

[Ru(μ-O$_2$CMe)(CO)$_2$P(CH$_2$CH$_2$(CF$_2$)$_5$CF$_3$)$_3$]$_2$·CFCl$_2$CF$_2$Cl ***2***			
Ru–Ru	2.725(1)	Ru–P–C	116.2(3)
Ru–C	1.84(1)	C–Ru–C	89.2(4)
Ru–O	2.129(5)	O–Ru–O	83.9(2)
Ru–P	2.398(2)	P–Ru–C	96.7(2)
C–O	1.157(9)	P–Ru–O	85.9(2)
P–C	1.828(8)	O–Ru–C(*cis*)	93.4(3)
Ru–Ru–C	93.8(2)	O–Ru–C(*trans*)	175.9(3)
Ru–Ru–O	83.3(2)	O–C–O	126.9(8)
Ru–Ru–P	165.33(7)	C–C–O	116.6(7)
[Ru(μ-O$_2$CMe)(CO)$_2$P(n-C$_4$H$_9$)$_3$]$_2$ ***4***			
Ru–Ru	2.718(5)	Ru–P–C	115.4(12)
Ru–C	1.76(5)	C–Ru–C	88.5(19)
Ru–O	2.10(3)	O–Ru–O	82.9(8)
Ru–P	2.39(1)	P–Ru–C	94.0(12)
C–O	1.20(4)	P–Ru–O	88.9(7)
P–C	1.83(3)	O–Ru–C(*cis*)	94.1(10)
Ru–Ru–C	94.8(12)	O–Ru–C(*trans*)	175.6(13)
Ru–Ru–O	82.0(4)	O–C–O	125.3(75)
Ru–Ru–P	167.7(4)	C–C–O	115.4(62)

[a] Ref. [16].

2.5. Measurement of partition coefficients

For each compound a 4 mL vial was tared and *circa* 10 mg of **1** or **2** was placed in the vial, perfluoromethylcyclohexane (1.00 mL) and toluene (1.00 mL) were then added. The vial was sealed, placed in an oil bath, and the bath temperature was slowly increased until a homogeneous solution (100–105 °C) resulted. This temperature was maintained for 30 min. The hydrocarbon phase from each vial was separated by syringe and was placed in a separate, tared vial, all solvents were removed under vacuum, and the amount of compound in each vial was determined gravimetrically. The average partitioning percentages (two measurements per compound), $C_6F_{11}CF_3/C_6H_5CH_3$, for compounds **1** and **2** were 92.7:7.3 and >99.5:<0.5, respectively.

2.6. Catalytic hydrogenation of acetophenone in the presence of *1* or *2*

In a stainless steel autoclave 20 mg of **1** (0.0055 mmol), or 20 mg of **2** (0.0078 mmol), were dissolved in 2.0 mL of benzotrifluoride, acetophenone 0.33 mL (2.8 mmol, **1**), or 0.46 mL (3.9 mmol, **2**), was added to the yellow solutions. The autoclave was pressurized to 735 psig with H_2 and heated to 105 °C for 25 h. After cooling and venting, the benzotrifluoride was removed from the contents under vacuum; pale yellow organic phases formed above viscous yellow–orange fluorous phases. These phases were separated via syringe.

The ^{1}H NMR spectra of the organic layers (**1** and **2**) exhibited the characteristic resonances of 1-phenylethanol [δ 4.89 (1H, q, J_{HH} = 6.5 Hz), 1.48 (3H, d, J_{HH} = 6.5 Hz)] and acetophenone [δ 2.59 (3H, s)]. Integration of signals determined a 3.2% conversion of acetophenone to 1-phenylethanol had occurred, a TON of 16 with **1** (8.8×10^{-2} mmol), and a 6.0% conversion, a TON of 30 with **2** (2.3×10^{-1} mmol). The organic phases were a pale yellow color, no resonances attributable to either acetate or the perfluoroalkyl substituted phosphine ligands of **1** or **2** or the free phosphines were detected in the ^{1}H NMR and ^{19}F NMR spectra of the organic layers. The fluorous phases (from **1** and **2**) were studied by infrared, ^{1}H NMR, ^{19}F NMR, and ^{31}P{^{1}H} NMR spectroscopies. The fluorous phase from **1** was composed of compound **1** along with other ruthenium carbonyl compounds, based on the both the infrared spectrum in CFC-113 which exhibited the carbonyl stretching peaks of **1** plus additional peaks and shoulders, and the ^{31}P{^{1}H} NMR spectrum in CFC-113/C_6D_6 which exhibited the resonance of **1** and an additional resonance. The fluorous phase from **2** was composed only of **2**, based on both the infrared spectrum in CFC-113 which contained only the carbonyl stretching peaks of **2**, and the ^{31}P{^{1}H} NMR spectrum in CFC-113/C_6D_6 which exhibited only the resonance of **2**.

2.7. Catalytic isomerization of 1-dodecene in the presence of *1*

In a stainless steel autoclave 15 mg (0.0041 mmol) of **1** was dissolved in 4.0 mL of perfluoromethylcyclohexane (PFMC), 1-dodecene, 1.0 mL (4.5 mmol) was added to the yellow solution. The autoclave was pressurized with 300 psig of both CO and H_2 (600 psig, 40.8 atm total) and heated to 150 °C for 25 h. After cooling and venting, a brown hydrocarbon phase and a yellow fluorous phase were separated by syringe, the PFMC was removed from the fluorous phase under vacuum.

The hydrocarbon phase was examined by both ^{1}H NMR and ^{19}F NMR spectroscopies which showed that isomerization to *cis*/*trans*-2-dodecene had occurred. The ^{1}H NMR spectrum of the hydrocarbon layer exhibited the characteristic vinylic proton resonances of both 1-dodecene [δ 5.79 (1H, m)] and *cis*/*trans*-2-dodecene [δ 5.39 (2H, m)]. Integration of the signals determined a 38.7% conversion of 1-dodecene to a mixture of *cis*/*trans*-2-dodecene had occurred, a

TON of 410 (1.7 mmol). The ^{1}H NMR and ^{19}F NMR spectra of the hydrocarbon phase did not contain any resonances attributable to either **1** or the free phosphine. The yellow fluorous phase was examined by infrared, ^{1}H NMR, ^{19}F NMR, and $^{31}P\{^{1}H\}$ NMR spectroscopies. The fluorous phase was composed of compound **1** along with other ruthenium carbonyl compounds, based on the both the infrared spectrum in CFC-113 which exhibited the carbonyl stretching peaks of **1** plus additional peaks and shoulders, and the $^{31}P\{^{1}H\}$ NMR spectrum in CFC-113/C_6D_6 which exhibited the resonance of **1** and two additional resonances.

3. Results and discussion

3.1. Preparation and properties

Following the general procedure of Crooks et al. [17], we found THF suspensions of the compound $[Ru(\mu\text{-}O_2CMe)(CO)_2]_n$ react with THF solutions of perfluoroalkyl substituted tertiary phosphines to generate the dimeric compounds $[Ru(\mu\text{-}O_2CMe)(CO)_2L^F]_2$, $L^F = P(C_6H_4\text{-}4\text{-}CH_2CH_2(CF_2)_7CF_3)_3$ (**1**), and $L^F = P(CH_2CH_2(CF_2)_5CF_3)_3$ (**2**). The reaction mixtures were maintained at reflux for *circa* 1 h, resulting in clear yellow–orange solutions. Preparative thin-layer chromatography of the reaction residues, using silica gel plates and mixtures of dichloromethane with either pentane or ether as eluents, provided both air-stable compounds **1** and **2** in good yields. To our knowledge, compounds **1** and **2** are the first reported dimeric transition metal compounds bearing fluorous substituted tertiary phosphine ligands.

Elemental analysis (C, H) and mass spectral molecular ions established the composition and purity for compounds **1** and **2**. Compound **1** is moderately soluble in typical hydrocarbon solvents such as pentane, hexane, and toluene, and is also soluble in dichloromethane and chloroform. Compound **2** is insoluble in pure hydrocarbon solvents but slightly soluble in dichloromethane and chloroform. Both **1** and **2** are soluble in ether, THF, and acetone. Compounds **1** and **2** are soluble in the universal solvents benzotrifluoride and 1,1,2-trichlorotrifluoroethane (CFC-113), and in the fluorous solvents perfluoromethylcyclohexane and perfluorodecalin. Note that effective separations of mixtures containing the target molecule along with excess fluorous tagged phosphine and fluorous tagged phosphine oxide were achieved with standard silica gel media and ordinary organic solvents [21].

3.2. Spectroscopic characterization of *1* and *2*

The infrared spectra of **1** and **2** exhibit a pattern of three (very strong–medium–very strong) carbonyl stretching bands, and zero to three additional weak bands or shoulders, in the 2200–1800 cm^{-1} region. Also, the infrared spectra of **1** and **2** feature another characteristic set of two prominent bands, due to the acetate ligands, in the 1600–1400 cm^{-1} region of the spectra. The major carbonyl stretching bands of **2** are all at higher frequencies than those of **1**. This phenomenon suggests the perfluoroalkyl substituted phosphine $P(CH_2CH_2(CF_2)_5CF_3)_3$ is a better π-acceptor than $P(C_6H_4\text{-}4\text{-}CH_2CH_2(CF_2)_7CF_3)_3$; providing a ranking of π-accepting ability that agrees with the results of our studies of compounds $W(CO)_5L^F$ [22]. The phosphorus-31 NMR spectra of **1** and **2** each consist of one singlet, and the proton NMR spectra of **1** and **2** also contain but one singlet assigned to the methyl groups of the bridging acetate moieties. Thus, the infrared and NMR data support a solution configuration for **1** and **2** in which both of the phosphine ligands and both of the bridging carboxylates are symmetrically equivalent. These equivalencies are achieved by the "sawhorse" configuration (C_{2v}) of $[Ru(\mu\text{-}O_2CMe)(CO)_2L]_2$ in which the *cis*-carbonyl groups are the four legs of the sawhorse. Thus, the solution configuration of **2** is consistent with the configuration of **2** in the solid state, as shown in Scheme 1 and Fig. 2.

3.3. Crystal structure of $[Ru(\mu\text{-}O_2CMe)(CO)_2P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (*2*)

The molecular structure of compound **2** is presented in Fig. 2, and a view of the crystal packing of **2** is shown in Fig. 3. Relevant crystallographic and structural data are provided in Tables 1 and 2. The ruthenium atoms reside in an irregular octahedral arrangement composed of five ligands and a ruthenium–ruthenium bond. For compound **2**, the ruthenium–ruthenium bond distance of 2.725(9) is comparable with other known Ru–Ru bond lengths of $[Ru(\mu\text{-}O_2CMe)(CO)_2L]_2$ compounds, specifically 2.736(5) and 2.718(1) Å where L = PPh_3 (**3**) [23], and PBu_3 (**4**) [16], respectively. Selected bond distances and bond angles for both **2** and **4** are presented in Table 2; many parameters are very similar between these two complexes. The structural congruity among $[Ru(\mu\text{-}O_2CMe)(CO)_2L]_2$ compounds is consistent with the observation that the perfluoroalkyl chains have little influence on the geometry of the first coordination sphere of the metal [24].

However, the solid state packing appears to be controlled by the perfluoroalkyl moieties. The molecules stack end-to-end, or ponytail-to-ponytail, thus constructing explicit fluorocarbon strata. Another interesting feature is the conformation of the individual perfluoroalkyl chains. None of the six fluorous tags can be described as fully *trans*-extended, as each chain displays some twisting and/or kinking. Also, the fluorine atom ellipsoids reveal considerable thermal motion that increases along the length of the chain. The twisting, flexing, or kinking of the perfluoroalkyl chains has been consistently observed in the few existing structures of transition metal compounds ligated by perfluoroalkyl substituted phosphines. The increasing thermal motion exhibited toward the ends of any given fluorocarbon chain is uniform trait of known structures [22,25]. In reported structures, the prevailing feature of the solid state packing is the "like-to-like" alignment, arrangement, or stacking of the perfluoroalkyl moieties so as to create extensive fluorous domains, as shown for **2** in Fig. 3.

3.4. Fluorocarbon–Hydrocarbon partitioning

Partitioning coefficients for compounds **1** and **2** were established with the original fluorous biphasic solvent system of $C_6F_{11}CF_3/C_6H_5CH_3$ [2]. Perfluoromethylcyclohexane (PFMC) and toluene have been frequently utilized to establish fluorocarbon/hydrocarbon partitioning; they are miscible at temperatures above 88.6 °C. The partitioning percentages, fluorocarbon/hydrocarbon, for compounds **1** and **2** are 92.7:7.3 and >99.5:<0.5, respectively. Comparable to, and equivalent with, the partitioning data of **2**, $C_6H_5CH_3/C_6F_{11}CF$ partitioning percentages of >99.7:<0.3 and 98.8:1.2 have been reported respectively for *trans*-$Ir(CO)(Cl)(L^F)_2$ [26], and *trans*-$NiCl_2(L^F)_2$ [27], where $L^F = P(CH_2CH_2(CF_2)_5CF_3)_3$. To our knowledge, no other reported partitioning data exist for transition metal complexes ligated by two $P(C_6H_4\text{-}4\text{-}CH_2CH_2\text{-}(CF_2)_7CF_3)_3$.

In their discussion of fluorous ponytail phosphine ligation to provide fluorous phase solubility, Horváth et al. [2b,c] originally discounted the viability of (substituted) triarylphosphine compounds, claiming that structural features such as arene rings could promote retention of the complex in the non-fluorous phase. Considering our measurements in the toluene/PFMC solvent system, the data support this claim as the fluorous phase retention of **1** is clearly less than that of **2**. However, regarding the *de jure* standard for fluorous biphasic solvent systems, toluene/PFMC, perhaps toluene is not an optimal choice for the hydrocarbon phase when triarylphosphines are utilized as ligands. Finally, in their review,

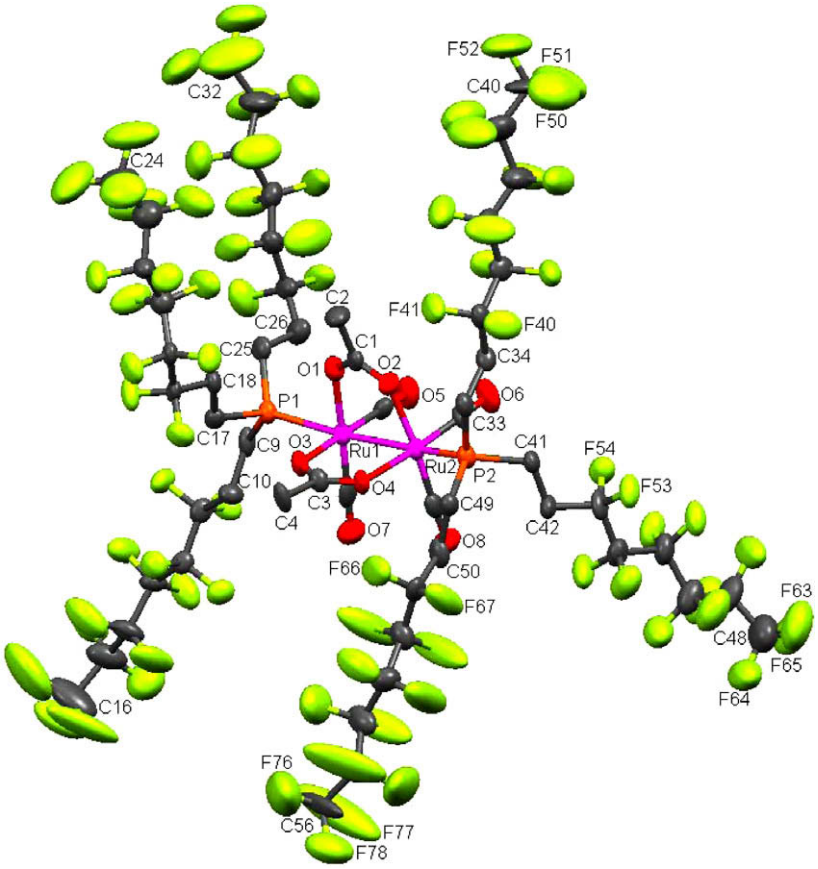


Fig. 2. ORTEP diagram (35%) of $[Ru(\mu\text{-}O_2CMe)(CO)_2P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**2**) with hydrogen and solvate atoms omitted.

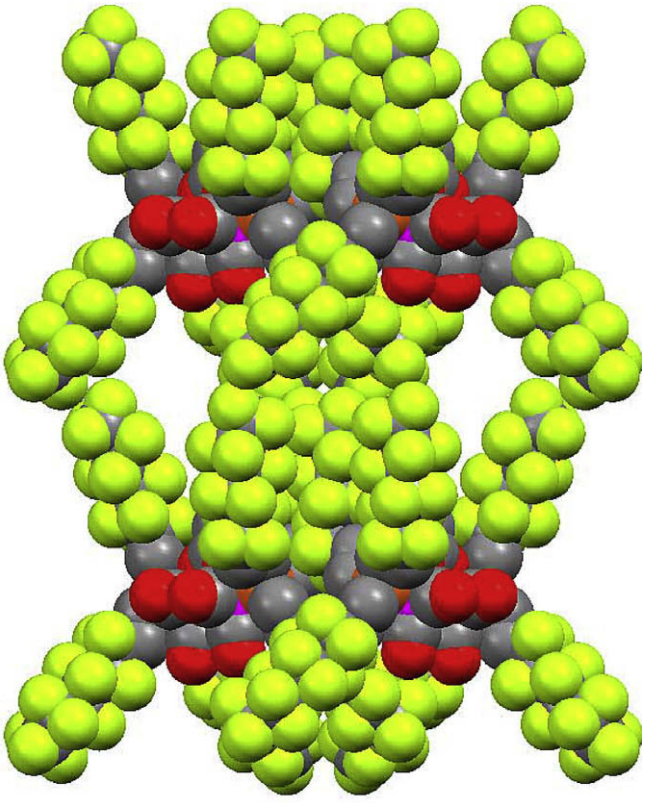


Fig. 3. Solid-state packing of complex (**2**) with carbonyls and ponytails visible.

Gladysz et al. [28] suggest a 90% fluorous phase partition as the minimum threshold for FBS compatibility.

3.5. Catalytic Hydrogenation of acetophenone in the presence of *1* or *2*

At H_2 pressures of 50 atm and at 105 °C (bath), the hydrogenation of acetophenone to 1-phenylethanol occurs in the presence of **1** or **2**. After 25 h under the above conditions, TON's for **1** and **2** were 16 and 30, respectively. Compound **1** or **2**, and the acetophenone were initially dissolved in benzotrifluoride, forming one phase. After catalysis, removal of the benzotrifluoride under oil pump vacuum caused a separation of fluorocarbon and organic phases. In both cases **1** or **2**, the organic phase exhibited a pale yellow color. No resonances attributable to either the acetate or phosphine ligands, and/or the free ligands, were detected in the ^1H NMR and ^{19}F NMR spectra of the organic layer. While the dimeric ruthenium complexes are yellow or yellow–orange in color, conjugated aromatic ketones and enones may result from aldol condensations involving acetophenone. The evidence obtained by spectroscopic characterization of both fluorous residues indicated the respective fluorous phases retained **1** or **2**. However, the fluorous residue containing **1** also contained observable amounts of free fluoroalkyl substituted triphenylphosphine oxide along with evidence of other ruthenium-carbonyl species. In contrast, the fluorous residue containing **2** proved to be composed exclusively of the starting dimer, **2**.

The catalytic hydrogenation of alkenes and ketones by **4**, as a catalyst or catalyst precursor, has been reported [12d,16]. In general, the conditions of these hydrogenations have been 120 °C $\leqslant T \leqslant$ 160 °C, and H_2 pressures of 130 atm. At temperatures greater than 80 °C, compounds **3** and **4** have each been exposed to

H_2 at pressures of at least 100 atm. At 80 °C and under 100 atm of H_2, **3** reacts with H_2 to form $Ru_4(\mu\text{-}H)_4(CO)_9(PPh_3)_3$ [29]. At higher temperatures, 100–140 °C, and H_2 at 100 atm, **3** reacts with H_2 to form predominantly $Ru_4(\mu\text{-}H)_4(CO)_7(\mu^4\text{-}PPh)(\mu\text{-}PPh_2)_2(PPh_3)$ and $Ru_3(\mu\text{-}H)(H)(CO)_7(\mu\text{-}PPh_2)_2(PPh_3)$. Compound **4** does not react with H_2 at $T \leqslant 120$ °C and H_2 at 170 atm [30]. At higher temperatures, 140 and 160 °C, and under 170 atm of H_2, **4** reacts with H_2 to form predominantly $Ru_4(\mu\text{-}H)_4(CO)_9(PBu_3)_3$ and $Ru_3(\mu\text{-}H)_2(CO)_7(\mu^3\text{-}PBu)(PBu_3)_2$.

3.6. Catalytic isomerization of 1-dodecene in the presence of *1*

Under 40.8 atm (total pressure) of CO and H_2 (1:1), 150 °C (bath), 1-dodecene was transformed to a mixture of *cis*- and *trans*-2-dodecene in the presence of **1**. In this example of FBS, the alkene(s) were not dissolved in a hydrocarbon solvent, substrate and products were the only hydrocarbon phase. Compound **1** was dissolved in perfluoromethylcyclohexane (PFMC) and was exposed, in the FBS, to an 1100-fold excess of 1-dodecene. After 25 h, 38.7% of the 1-dodecene, 1.7 mmol, was transformed to 2-dodecene, a TON of 410. The results of ^1H NMR and ^{19}F NMR on the hydrocarbon phase showed no traces of the characteristic resonances of compound **1**, nor of the free phosphine ligand. The results of the various spectroscopies, particularly infrared and ^{31}P NMR, on the fluorous residue reveal the presence of **1** along with two other compounds.

Under similar conditions, 29.6 atm (total pressure) of CO and H_2 (1:1), 85 °C, Kalck et al. determined that 1-octene was converted to 2-octene in the presence of $[Ru(\mu\text{-}O_2CMe)(CO)_2(PPh_3)]_2$, (**3**), and also in the presence of $[Ru(\mu\text{-}O_2CMe)(CO)_2(PR_3)]_2$, where R = OPh, and OMe [13b]. Under comparable conditions, 30.0 atm (total pressure) of CO and H_2 (1:1), 100–160 °C, Salvini et al. determined that isomerization of 1-hexene to *cis*- and *trans*-2-hexene occurred in the presence of $[Ru(\mu\text{-}O_2CMe)(CO)_2(PBu_3)]_2$, (**4**) [15].

4. Conclusions

The syntheses and reactivities of compounds **1** and **2** are comparable to the non-perfluoroalkyl substituted analogs, **3** and **4**. Under the conditions outlined above, catalytic isomerization and hydrogenation occur in the presence of **1** and **2**, similar to the catalytic activity of **3** and **4** in common organic solvents. Active FBS catalysis had occurred in the presence of **1** and **2**. All spectroscopic evidence points to the successful separation of fluorocarbon and the organic or hydrocarbon phases. Specifically, compounds **1** and **2** were not detected in the various organic or hydrocarbon phases and, the recovered fluorous phases were primarily composed of **1** and **2**. None of the recovered organic or hydrocarbon phases were completely colorless, indicating the possibility that trace amounts of some ruthenium species had leached into these phases. In some cases however, conjugated aromatic ketones and enones are potential by-products.

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Appendix A. Supplementary material

CCDC 703120 contains the supplementary crystallographic data for $[Ru(\mu\text{-}O_2CMe)(CO)_2P(CH_2CH_2(CF_2)_5CF_3)_3]_2$ (**2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.06.014.

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