termined that the Os–H–Os bond energy is 17 kJ/mol greater than the Ru–H–Ru bond energy[22] in the pair $(\mu\text{-H})_3M_3(\mu_3\text{-COMe})(CO)_9$. Furthermore, the free energy of activation for hydrogen elimination from $H(\mu\text{-H})M_3(CO)_{11}$ is 36 kJ/mol lower than the value for the corresponding $(\mu\text{-H})_3M_3(\mu_3\text{-COMe})(CO)_9$ for both Ru and Os pairs. Since the M–H–M bond has been estimated to be ca. 45 kJ/mol more stable than the combination of M–H and M–M bonds,[22] the lower free energies of activation for reductive elimination from $H(\mu\text{-H})M_3(CO)_{11}$, compared with the corresponding values for $(\mu\text{-H})_3M_3(\mu_3\text{-COMe})(CO)_9$, may be largely attributed to the relative ground-state energies (Figure 6). Terminal hydride ligands are kinetically and thermodynamically more reactive than are bridging hydrides.

There still is no detailed understanding of the kinetics and thermodynamics of hydride reactivity in cluster systems. Clearly, bridging hydrides are not always energetically more favorable than terminal hydrides, otherwise $H_2Ru_3(CO)_{11}$ should have a different structure than it does. The accumulation of additional quantitative data on hydride reactivity in clusters having a variety of hydride coordination modes is necessary to determine the relationships between structure and reactivity.

Acknowledgment. We thank Professor Jim Atwood for the loan of the variable-temperature infrared accessory and for helpful discussions. We also thank Dr. John Pazik and Professor O. T. Beachley for assistance with vacuum line measurements. We thank Dr. S. A. R. Knox for the gift of $Ru_3(CO)_{12}$ and for facilities provided to conduct the work at Bristol. This work was funded in part by the National Science Foundation (Grants CHE8900921 and CHE8520276 to J.B.K.). J.B.K. also acknowledges support from the Alfred P. Sloan Foundation. FT-IR spectra and stopped-flow kinetics were measured at the University of Bristol.

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Tetrafluoroethyl Complexes Derived from Insertion of the Tetrafluoroethylene Ligand into an Iridium–Hydride Bond

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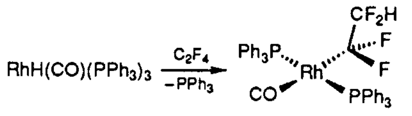
The reaction of $IrH(CO)(PPh_3)_3$ with tetrafluoroethylene gives the hydride olefin complex $IrH(C_2F_4)(CO)(PPh_3)_2$. Further reactions of $IrH(C_2F_4)(CO)(PPh_3)_2$ with a coordinating ligand L (L = C_2F_4, CO, C_2H_4) result in the insertion of the coordinated olefin into the iridium–hydrogen bond and formation of tetrafluoroethyl complexes, $Ir(CF_2CF_2H)(L)(CO)(PPh_3)_2$. Thermal displacement of the ethylene ligand in $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ gives the four-coordinate complex $Ir(CF_2CF_2H)(CO)(PPh_3)_2$. The X-ray crystal structure of the dicarbonyl complex $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ is described. $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ crystallizes in the triclinic space group $P\bar{1}$ with a = 9.868 (5) Å, b = 11.5727 (5) Å, c = 17.083 (9) Å, α = 103.9 (4)°, β = 94.14 (4)°, γ = 113.09 (3)°, and Z = 2 with d(calcd) = 1.699 g cm^{-3} for a molecular weight of 873.83. The structure was refined to give R = 0.0400 and R_w = 0.0407, and in contrast to the geometry displayed in solution, which has trans triphenylphosphines, has a cis arrangement of triphenylphosphine ligands. The $Ir\text{-}CF_2CF_2H$ bond distance is 2.145 (8) Å.

Introduction

The tetrafluoroethylene ligand has proved to be an excellent precursor for σ-bonded transition-metal fluorocarbon complexes.[1] One possibility is the insertion of tetrafluoroethylene into a metal–ligand bond. This reaction has been demonstrated for several different types of ligands but is observed most frequently for the hydride ligand.[2] Metal hydrides react with a large number of olefins and acetylenes, giving products that are a result of formal insertion of the olefin or acetylene into the metal–hydride bond.[3]

The reaction of hydride–carbonyl complexes with alkenes has relevance to the intermediate species in transition-metal-catalyzed hydroformylation,[2c,d] and the insertion of olefins into transition-metal–hydrogen bonds is an important step in a number of other catalytic processes, such as hydrogenation, oligomerization, and polymerization. The reaction of tetrafluoroethylene with rhodium hydrides has been shown to give σ-bonded fluorocarbon complexes in a number of cases (eq 1).[2c,d] Rh-



(1)

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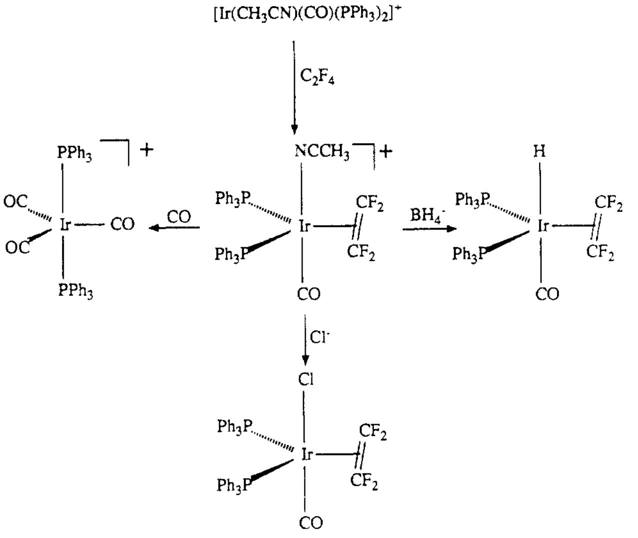
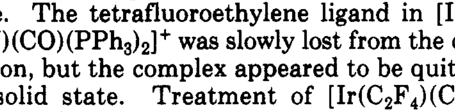
Scheme I



$(CF_2CF_2H)(CO)(PPh_3)_2$ undergoes several reactions characteristic of rhodium(I) complexes, including reactions with SO_2 and HCl.[2d] As part of our studies of the conversion of fluorinated alkyl ligands to halocarbene complexes through α-fluoride abstraction[4] we have examined $Rh(CF_2CF_2H)(CO)(PPh_3)_2$. Unfortunately, $Rh(CF_2CF_2H)(CO)(PPh_3)_2$ did not show the same reactivity of the α-fluorines as was found for $Rh(CF_3)(CO)(PPh_3)_2$.[5] The reaction of $Rh(CF_2CF_2H)(CO)(PPh_3)_2$ with HCl gave $RhHCl(CF_2CF_2H)(CO)(PPh_3)_2$. This complex was not stable and decomposed to $RhCl(CO)(PPh_3)_2$ and CF_2HCF_2H. In the hope of finding more stable tetrafluoroethyl complexes the insertion reaction of tetrafluoroethylene has been carried out with the analogous iridium complex and the results are described in this paper.

Results and Discussion

The reaction of $RhH(CO)(PPh_3)_3$ with tetrafluoroethylene was carried out at room temperature and was complete within 1 h. Under the same conditions there was no reaction with $IrH(CO)(PPh_3)_3$. Increasing the reaction temperature to 80 °C and the reaction time to 8 h did, however, result in the conversion of $IrH(CO)(PPh_3)_3$ to $IrH(C_2F_4)(CO)(PPh_3)_2$ (eq 2). $IrH(C_2F_4)(CO)(PPh_3)_2$ is

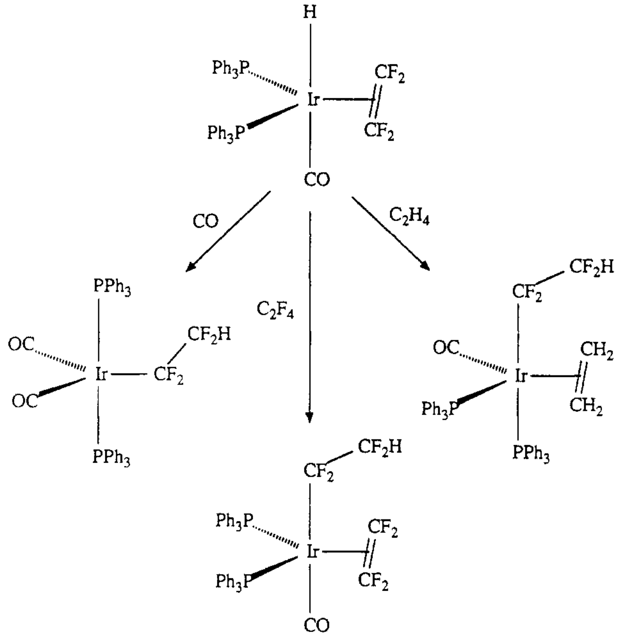


(2)

a white crystalline solid, which could also be produced in good yield from the reaction of $NaBH_4$ with $[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]^+$ (see Scheme I).

$[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]^+$ was formed when $[Ir(CH_3CN)(CO)(PPh_3)_2]^{+}$[6] was treated with tetrafluoroethylene. The tetrafluoroethylene ligand in $[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]^+$ was slowly lost from the complex in solution, but the complex appeared to be quite stable in the solid state. Treatment of $[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]^+$ with CO resulted in rapid displacement of the tetrafluoroethylene ligand and formation of $[Ir(CO)_3(PPh_3)_2]^+$ (Scheme I). The geometry of $[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]^+$ was confirmed by NMR spectroscopy, with the ^{13}C NMR spectrum providing unequivocal proof of the geometry. The ipso carbons of the triphenylphosphine ligands appeared as a doublet ($^1J_{PC}$ = 46.2 Hz) at 128.9 ppm. If the complex had contained trans equivalent triphenylphosphine ligands, the ipso carbon would be expected to appear as a triplet due to virtual coupling between the phosphorus atoms. The tetrafluoroethylene ligand was also evident as a ddd pattern, characteristic of the geometry depicted above.

Scheme II



The addition of X^- to $[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]^+$ gave the neutral complexes $IrX(C_2F_4)(CO)(PPh_3)_2$ (X = Cl, H). $IrCl(C_2F_4)(CO)(PPh_3)_2$ is a known compound, having been prepared by direct addition of tetrafluoroethylene to $IrCl(CO)(PPh_3)_2$.[7] The reaction of chloride with $[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]^+$ was slow, and the product was always contaminated with $IrCl(CO)(PPh_3)_2$ resulting from loss of C_2F_4 during the reaction. In contrast, the addition of a hydride (through reaction with $NaBH_4$) to $[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]^+$ occurred rapidly in good yield. The IR spectrum of $IrH(C_2F_4)(CO)(PPh_3)_2$ showed ν(IrH) at 2142 cm^{-1} along with ν(CO) at 2007 cm^{-1}. The hydride ligand appeared in the ^1H NMR spectrum as a multiplet at -9.92 ppm. Again, the geometry of $IrH(C_2F_4)(CO)(PPh_3)_2$ was determined from the ^{13}C NMR spectrum, with the ipso carbon of the triphenylphosphine occurring as a doublet ($^1J_{CP}$ = 48.9 Hz) at 134.8 ppm. It is worth noting that the rhodium complex analogous to $IrH(C_2F_4)(CO)(PPh_3)_2$ has not been described, although it is assumed to be the intermediate in the formation of $Rh(CF_2CF_2H)(CO)(PPh_3)_2$.[2c,d]

When $IrH(C_2F_4)(CO)(PPh_3)_2$ was treated with more tetrafluoroethylene under much more vigorous conditions (90 °C for 3 days), the tetrafluoroethylene ligand inserted into the iridium–hydrogen bond to give the tetrafluoroethyl complex $Ir(C_2F_4)(CF_2CF_2H)(CO)(PPh_3)_2$ (Scheme II). In the ^1H NMR spectrum the tetrafluoroethyl proton signal is seen at 5.37 ppm. The geometry of the complex was assigned as depicted in Scheme II on the basis of the ^{13}C and ^{19}F NMR spectra, that is, the same relative geometry as for the structurally characterized $Ir(C_2F_4)(CF_3)(CO)$-

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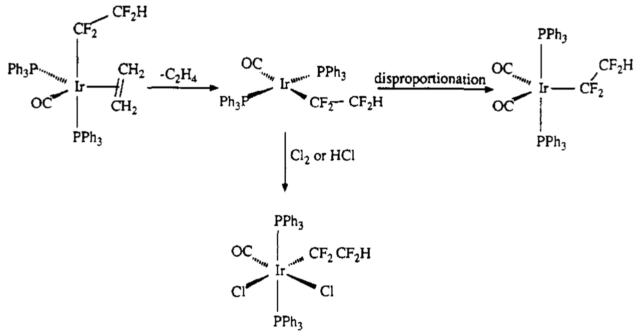
Scheme III

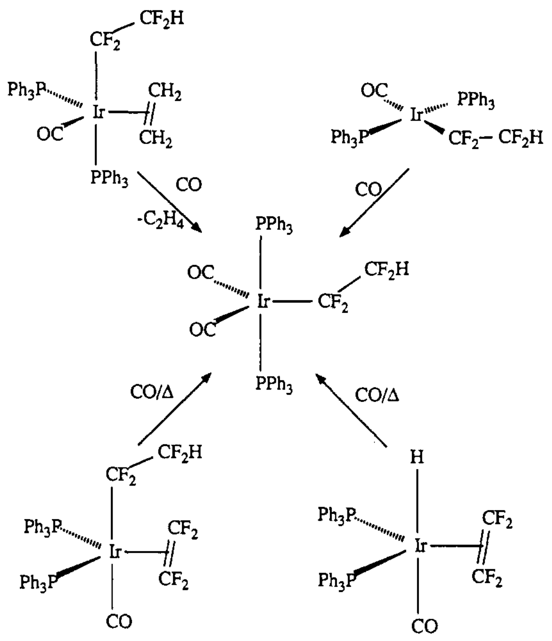


$(PPh_3)_2$.[8] $Ir(C_2F_4)(CF_2CF_2H)(CO)(PPh_3)_2$ appeared to be indefinitely stable in solution, with the tetrafluoroethylene ligand being displaced only under vigorous conditions. Although other olefins containing electron-withdrawing substituents have been reacted with $IrH(CO)(PPh_3)_3$ before, and the intermediate hydride–olefin complexes have been isolated, their further reactions via hydride migration to olefin had not been demonstrated.[3b]

The insertion of olefins into the iridium–hydrogen bond is apparently dependent upon the electron-withdrawing ability of the substituents on the olefin. The more electron deficient the olefin, the less likely the insertion is to proceed spontaneously. The reaction of $IrH(CO)(PPh_3)_3$ with ethylene has not been reported. However, a similar reaction, where $IrH(CO)(PPh_3)_3$ was treated with ethylene and carbon monoxide, has been shown to give $Ir(C(O)CH_2CH_3)(CO)_2(PPh_3)_2$[2d] with no detectable intermediates.

The reaction of $IrH(C_2F_4)(CO)(PPh_3)_2$ with ethylene, under the conditions that caused tetrafluoroethylene to be inserted, resulted in the formation of $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ (Scheme II). $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ was a moderately stable solid and had an unusual geometry in solution, as determined by multinuclear NMR spectroscopy. $Ir(CF_3)(C_2H_4)(CO)(PPh_3)_2$ has a geometry featuring trans triphenylphosphine ligands with the ethylene ligand undergoing rapid free rotation on the NMR time scale.[8] The hindered rotation of the ethylene ligand in $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ was therefore unexpected. Hindered rotation of coordinated olefins is usually associated with increased metal–ligand interactions. The relative stability of the ethylene adduct increased from $R_f = CF_3$ to $R_f = CF_2CF_2H$. This increase in stability was accompanied by a change in metal geometry and an increase in the barrier to rotation of the ethylene adduct. The trifluoromethyl complex has the geometry in solution where the triphenylphosphine groups are trans and are in the axial sites. This leaves the ethylene, the trifluoromethyl group, and the carbonyl ligand to share the electron density in the equatorial plane. The presence of the electron-withdrawing CF_3 and CO ligands does not leave sufficient electron density available on the iridium for strong back-bonding to the ethylene. The different geometry in the tetrafluoroethyl complex results in the electron-withdrawing tetrafluoroethyl ligand being replaced by a σ-donating triphenylphosphine. This provides more electron density for the metal to back-donate to the ethylene. The result is a more tightly held ethylene in $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$, which was revealed in the greater stability and the hindered rotation of the ethylene ligand.

Scheme IV



$Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ was only moderately stable in solution, with the ethylene ligand being lost over several days. The product resulting from the removal of the ethylene in the solid state was $Ir(CF_2CF_2H)(CO)(PPh_3)_2$. Unfortunately the sensitivity of $Ir(CF_2CF_2H)(CO)(PPh_3)_2$ prevented accurate analytical figures being obtained, so the complex was characterized only by spectroscopy and by its chemical reactivity (Scheme III). This instability was unexpected, considering that $Ir(CF_3)(CO)(PPh_3)_2$ is quite stable in solution.[8] $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ could also be formed in low yield from $IrH(C_2F_4)(CO)(PPh_3)_2$ by heating at high temperatures. $Ir(CF_2CF_2H)(CO)(PPh_3)_2$ behaves like other 16-electron d^8 complexes, in that it reacts with neutral coordinating ligands such as carbon monoxide to give $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ (Scheme IV). Also, it was oxidized by reagents such as HCl and Cl_2. The reaction of $Ir(CF_2CF_2H)(CO)(PPh_3)_2$ with chlorine yielded *cis*-$IrCl_2(CF_2CF_2H)(CO)(PPh_3)_2$ (where cis refers to the chloride ligands) (Scheme III). This complex is an isomer of the one formed by addition of CO to $IrCl_2(CF_2CF_2H)(PPh_3)_2$.[9] Reaction of $Ir(CF_2CF_2H)(CO)(PPh_3)_2$ with HCl gave $IrHCl(CF_2CF_2H)(CO)(PPh_3)_2$ as the initial product. This complex could be detected only by NMR spectroscopy, as it reacted with any excess HCl present to form *cis*-$IrCl_2(CF_2CF_2H)(CO)(PPh_3)_2$ (Scheme III). *cis*-$IrCl_2(CF_2CF_2H)(CO)(PPh_3)_2$ was apparent in the ^1H NMR spectrum with a hydride signal at −9.14 ppm as a triplet of multiplets ($^2J_{PH}$ = 11 Hz), with the coupling to the fluorocarbon ligand not resolved. The tetrafluoroethyl ligand could also be observed as a triplet of triplets ($^2J_{FH}$ = 53.8 Hz, $^3J_{FF}$ = 7.4 Hz). The ^{31}P signal occurred at −21.48 ppm as triplet of multiplets ($^3J_{PF}$ = 20.5 Hz).

The change in stability of $Ir(R_f)(CO)_2(PPh_3)_2$ ($R_f = CF_3$, CF_2CF_2H) must be associated with the possibility of β-elimination in changing from a trifluoromethyl to a tetrafluoroethyl ligand. $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ was also produced from the addition of carbon monoxide to $Ir(CF_2CF_2H)(CO)(PPh_3)_2$, $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$, $IrH(C_2F_4)(CO)(PPh_3)_2$, and $Ir(CF_2CF_2H)(C_2F_4)(CO)(PPh_3)_2$ (Scheme IV).

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[8] Brothers, P. J.; Burrell, A. K.; Rickard, C. E. F.; Roper, W. R. Submitted for publication in *J. Organomet. Chem.*

[9] Burrell, A. K.; Roper, W. R. Unpublished results.

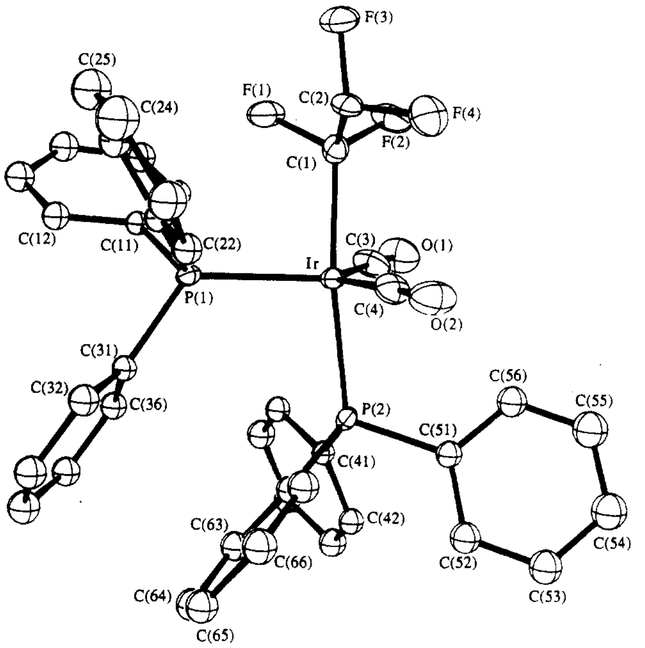

Figure 1. ORTEP drawing of the molecular geometry of $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$.

Table I. Selected Geometrical Parameters for $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$

(a) Bond Lengths (Å)

Ir-P1	2.414 (2)	Ir-C4	1.902 (8)
Ir-P2	2.363 (2)	C1-C2	1.54 (1)
Ir-C1	2.145 (8)	C1-F(1,2)	1.387 (9)
Ir-C3	1.904 (8)	C2-F(3,4)	1.365 (9)

(b) Bond Angles (deg)

P1-Ir-P2	97.7 (1)	Ir-C1-C2	118.6 (3)
P1-Ir-C1	89.4 (2)	C1-Ir-C3	86.3 (3)
P1-Ir-C3	118.2 (3)	C1-Ir-C4	90.1 (3)
P1-Ir-C4	113.1 (3)	Ir-C1-F(1,2)	112.7 (5)
P2-Ir-C1	172.9 (2)	C1-C2-F(3,4)	108.7 (6)
P2-Ir-C3	89.7 (3)	C3-Ir-C4	128.5 (4)

Crystals suitable for a single-crystal X-ray examination of $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ were obtained, and the structure was determined.

Description of the X-ray Structure of $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$. $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ crystallized as colorless cubes in the triclinic space group $P\bar{1}$. The data were collected at −100 °C, and the refinement, with all except the phenyl ring atoms anisotropic, had $R = 0.0400$ and $R_w = 0.0407$. The structure (Figure 1) is that of a distorted trigonal bipyramid, with the axial positions occupied by a triphenylphosphine and the tetrafluoroethyl ligand. The equatorial plane contains the remaining triphenylphosphine and the two carbonyl groups. The bond lengths for this complex are all within the expected values (Table I). The metal–phosphorus bond trans to the tetrafluoroethyl ligand is slightly longer than the cis metal–phosphorus bond. This is presumably an indication of the trans influence of the tetrafluoroethyl ligand, along with the differing electronic requirements of the axial and equatorial ligands. The α-carbon– and β-carbon–fluorine bond lengths, while well defined, do not show any significant differences.

The geometry of $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ in the solid state is not the geometry of the complex in solution. The solid-state isomer and the isomer identified in solution could be interconverted in solution by a simple Berry rotation. However, the isomer of $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ that exists in the solid state could not be detected in solution. The only complex that could be seen in solution was the isomer with trans triphenylphosphine ligands. All of the other isomers possible by Berry rotation may have existed in solution, but in such small concentrations that they remained undetected. The isomer that crystallized from such an equilibrium mixture would be the one that is least soluble.

Conclusions

The insertion of tetrafluoroethylene into metal–hydrogen bonds provides an effective method of introducing a σ-bonded fluorocarbon ligand into a transition-metal complex. While reactions of tetrafluoroethylene with rhodium–hydrogen bonds were extremely facile, similar reactions with iridium complexes required forcing conditions. However, extending this reactivity to iridium enabled the isolation of the complex $IrH(C_2F_4)(CO)(PPh_3)_2$, which is a model complex for the intermediates in the insertion of olefins into metal–hydrogen bonds. The reaction of $IrH(C_2F_4)(CO)(PPh_3)_2$ with ethylene to form $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ rather than $Ir(CH_2CH_3)(C_2F_4)(CO)(PPh_3)_2$ is compatible with the idea that an olefin must coordinate prior to insertion into the iridium–hydrogen bond of $IrH(CO)(PPh_3)_3$.

Experimental Section

General Data. Standard Schlenk techniques were used for all manipulations involving oxygen-sensitive compounds. Solvents used were purified as follows: benzene and *n*-hexane were distilled from sodium/benzophenone; dichloromethane was distilled from calcium hydride.

When procedures involved materials that were not air-sensitive, solvents were purified by chromatography on alumina (Spence type H, 100–200 mesh) or filtered prior to use. In these cases, solvent removal under reduced pressure was achieved with use of a rotary evaporator. Routine recrystallizations were achieved by the following method: The sample was dissolved in a low-boiling-point solvent, and a higher boiling point solvent, in which the compound was insoluble, was added. Evaporation at reduced pressure effected gradual crystallization.

^1H NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400 MHz and are quoted in ppm downfield from TMS. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer at 100 MHz and are quoted relative to TMS. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer at 162 MHz and are quoted relative to 85% phosphoric acid solution (external). ^{19}F NMR spectra were recorded on a JEOL FX-90 spectrometer at 84.6 MHz and are reported referenced to $CFCl_3$. Melting points were determined on a Reichert microscope hot stage and are uncorrected. Elemental analyses for carbon and hydrogen were made by the microanalytical laboratory of the University of Otago. $IrH(CO)_2(PPh_3)_3$[10] and $[Ir(CH_3CN)(CO)(PPh_3)_2]ClO_4$[6] were prepared with use of literature procedures. Small amounts of tetrafluoroethylene were obtained from the vacuum pyrolysis of poly(tetrafluoroethylene)[12] (approximately 1 g at any one time). *Caution!* Tetrafluoroethylene can polymerize explosively.

Reactions. $IrH(C_2F_4)(CO)(PPh_3)_2$. (a) $IrH(CO)(PPh_3)_3$ (500 mg, 0.5 mmol) was dissolved in benzene (30 mL) and heated, at 80 °C, under tetrafluoroethylene pressure (approximately 500 kPa) in a Fischer–Porter bottle (volume 300 mL) for 8 h. The solution was then cooled, and the tetrafluoroethylene was vented. The benzene was removed in vacuo, and the residue was recrystallized from dichloromethane and ethanol to give the product as white crystals (390 mg, 93%), mp 164–166 °C. Anal. Calcd for $C_{39}H_{31}F_4IrOP_2$: C, 55.38; H, 3.69; F, 8.99. Found: C, 55.34; H, 3.79; F, 8.75. IR (Nujol, cm^{-1}): ν(CO) 2007; ν(IrH) 2147; ν(CF), 1412, 1094, 1041, 808. ^1H NMR ($CDCl_3$, ppm): −9.92 (m, 1 H, IrH). ^{31}P NMR ($CDCl_3$, ppm): 0.97 (m). ^{19}F ($CDCl_3$, ppm): −108.2–114.3 (m). ^{13}C NMR ($CDCl_3$, ppm): 175.7 (m, CO), 92.4 (td, $^1J_{FC}$ = 322.6 Hz, $^1J_{FC}$ = 322.6 Hz, $^2J_{CP}$ = 90.6 Hz, C_2F_4), 134.7 (d, $^1J_{CP}$ = 48.9 Hz, ipso PPh_3), 133.4 (d, $^2J_{CP}$ = 12.1 Hz, ortho

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(10) Wilkinson, G. *Inorg. Synth.* **1973**, *13*, 126.

Table II. Crystal Data and Details of the Structure Determination of $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$

Crystal Data			
formula	$C_{40}H_{31}F_4IrP_2O_2$	α	103.9 (4)°
mol wt	873.83	β	94.14 (4)°
space group	$P\bar{1}$	γ	113.09 (3)°
cryst syst	triclinic	V	1704 Å^3
a	9.868 (5) Å	Z	2
b	11.527 (5) Å	d(calcd)	1.699 g cm^{-3}
c	17.083 (9) Å	F(000)	860
		μ	43.1 cm^{-1}

Data Collection and Reduction	
diffractometer	Nicolet
radiation	Mo Kα (λ = 0.71069 Å)
temperature	194–196 K
scan technique	$2\theta/\omega$
2θ (min–max)	2–42°
scan speed	4.88° min^{-1}
no. of unique reflns	5992
no. of unique obsd rflns	4876
σ criterion	$I > 3\sigma(I)$
R(merg)	0.0161

Structure Determination and Refinement	
R and R_w[a]	0.0400, 0.0407
weight	$1.3273/(\sigma^2(F) + 0.000940F^2)$

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

PPh_3), 138.1 (d, $^3J_{CP}$ = 10.1 Hz, meta PPh_3), 130.1 (s, para PPh_3).

(b) $[Ir(C_2F_4)(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (100 mg, 0.1 mmol) was suspended in ethanol (15 mL), and a filtered solution of sodium borohydride (50 mg) in ethanol was added. The suspension was stirred for 5 min, and then the product was collected by filtration (84 mg, 98%).

$Ir(CF_2CF_2H)(C_2F_4)(CO)(PPh_3)_2$. (a) $IrH(C_2F_4)(CO)(PPh_3)_2$ (500 mg, 0.59 mmol) was dissolved in benzene (10 mL) and heated, at 90 °C, under tetrafluoroethylene pressure (approximately 500 kPa) in a Carius tube (volume 25 mL) for 3 days. The solution was then cooled, and the tetrafluoroethylene was vented. The benzene was removed in vacuo and the residue recrystallized from dichloromethane and ethanol to give the product as white crystals (498 mg, 89%), mp 171–173 °C. Anal. Calcd for $C_{41}H_{31}F_8IrOP_2$: C, 52.06; H, 3.30; F, 16.07. Found: C, 51.81; H, 3.58; F, 14.54. IR (Nujol, cm^{-1}): ν(CO) 2060; ν(CF), 1435, 1104, 1087, 1044, 983, 951, 814. ^1H NMR ($CDCl_3$, ppm): 5.37 (tt, 1 H, $^2J_{FH}$ = 53.9 Hz, $^3J_{FH}$ = 7.1 Hz, CF_2CF_2H). ^{31}P NMR ($CDCl_3$, ppm): −10.59 (m). ^{19}F ($CDCl_3$, ppm): −130.2 (dt, $^2J_{HF}$ = 54 Hz, $^3J_{FF}$ = 7.3 Hz, CF_2CF_2H), −73.5 (dtt, $^2J_{PF}$ = 31.5 Hz, $^3J_{HF}$ = 7.7 Hz, $^3J_{FF}$ = 7.3 Hz, $C\mathit{F}_2CF_2H$), −102.2 (ddd, $^2J_{FF}$ = 167 Hz, $^3J_{FF}$ = 43 Hz, $^3J_{PF}$ = 33 Hz, $C_2\mathit{F}_4$ (F trans to CO)), −119.4 (ddd, $^2J_{FF}$ = 167 Hz, $^3J_{FF}$ = 43 Hz, $^3J_{PF}$ = 38 Hz, $C_2\mathit{F}_4$ (F trans to CF_2CF_2H)). ^{13}C NMR ($CDCl_3$, ppm): 170.4 (m, CO), 89.5 (td, $^1J_{FC}$ = 321.3 Hz, $^1J_{F'C}$ = 335.1 Hz, $^2J_{CP}$ = 95.0 Hz, C_2F_4), 133.5 (d, $^1J_{CP}$ = 43.1 Hz, ipso PPh_3), 134.1 (d, $^2J_{CP}$ = 10.9 Hz, ortho PPh_3), 128.1 (d, $^3J_{CP}$ = 9.9 Hz, meta PPh_3), 130.3 (d, $^4J_{CP}$ = 1.6 Hz, para PPh_3), 113.0 (tt, $^1J_{FC}$ = 251.0 Hz, $^2J_{FC}$ = 23.1 Hz, CF_2CF_2H), 116.2 (t, $^1J_{FC}$ = 280.0 Hz, $CF_2\mathit{C}F_2H$).

(b) $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$ (100 mg, 0.11 mmol) was treated as in part a to give the product as white crystals (41 mg, 84%).

$Ir(C_2H_4)(CF_2CF_2H)(CO)(PPh_3)_2$. $IrH(C_2H_4)(CO)(PPh_3)_2$ (500 mg, 0.59 mmol) was dissolved in benzene (30 mL) and heated, at 90 °C, under ethylene pressure (approximately 500 kPa) in a Carius tube (volume 25 mL) for 2 days. The solution was then cooled, and the ethylene was vented. The benzene was removed in vacuo, and the residue was recrystallized from dichloromethane and ethanol to give the product as white crystals (480 mg, 93%), mp 148–154 °C. Anal. Calcd for $C_{41}H_{35}F_4IrOP_2$: C, 56.35; H, 4.04; F, 8.70. Found: C, 55.34; H, 4.32; F, 7.77. IR (Nujol, cm^{-1}): ν(CO) 1964; ν(CF) 1166, 1150, 1087, 1019, 976, 968, 935; ν(C=C) 1364. ^1H NMR ($CDCl_3$, ppm): 5.27 (tdd, 1 H, $^2J_{FH}$ = 49.4 Hz, $^3J_{FH}$ = 5.75 Hz, $^3J_{F'H}$ = 8.14 Hz, CF_2CF_2H), 2.49 (m, 1 H, C_2H_4), 1.99 (m, 1 H, C_2H_4), 1.53 (m, 1 H, C_2H_4), 0.22 (m, 1 H, C_2H_4). ^{31}P NMR ($CDCl_3$, ppm): −2.78 (m, $^2J_{PP}$ = 20 Hz), −6.90 (m, $^2J_{PP}$ = 20 Hz). ^{13}C NMR ($CDCl_3$, ppm): 182.7 (m, CO), 27.4 (m, C_2H_4), 26.4 (m, C_2H_4), 115.5 (tt, $^1J_{FC}$ = 246.0 Hz, $^2J_{CP}$ = 47.1 Hz, CF_2CF_2H).

Table III. Atom Positions for $Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$

atom	x/a	y/b	z/c	B_{eqv}, Å^2
Ir	0.22072 (3)	0.35966 (3)	0.25984 (2)	1.30
P1	0.4209 (2)	0.3375 (2)	0.1936 (1)	1.27
P2	0.2946 (2)	0.5870 (2)	0.2770 (1)	1.30
O1	−0.0782 (7)	0.2997 (7)	0.1575 (4)	3.50
O2	0.2930 (8)	0.4304 (6)	0.4468 (4)	3.48
F1	0.1595 (6)	0.0785 (5)	0.1821 (3)	2.84
F2	−0.0252 (5)	0.0969 (5)	0.2364 (3)	2.97
F3	0.1205 (6)	−0.0253 (5)	0.2991 (3)	2.97
F4	0.1186 (7)	0.1453 (6)	0.3854 (3)	3.54
C1	0.1294 (8)	0.1536 (8)	0.2501 (5)	1.80
C2	0.182 (1)	0.1114 (8)	0.3207 (5)	2.22
C3	0.037 (1)	0.3212 (9)	0.1925 (6)	2.63
C4	0.266 (1)	0.4014 (8)	0.3761 (5)	2.31
C11	0.3667 (8)	0.2279 (7)	0.0874 (4)	1.32
C12	0.4780 (9)	0.2061 (8)	0.0471 (5)	1.84
C13	0.439 (1)	0.1190 (8)	−0.0324 (5)	2.25
C14	0.288 (1)	0.0547 (8)	−0.0723 (5)	2.28
C15	0.177 (1)	0.0819 (8)	−0.0342 (5)	2.22
C16	0.2182 (9)	0.1679 (8)	0.0454 (5)	1.94
C21	0.5113 (8)	0.2630 (8)	0.2509 (4)	1.70
C22	0.5765 (8)	0.3306 (8)	0.3355 (4)	1.79
C23	0.641 (1)	0.275 (1)	0.3820 (5)	2.73
C24	0.642 (1)	0.152 (1)	0.3461 (6)	3.47
C25	0.576 (1)	0.083 (1)	0.2631 (6)	3.04
C26	0.509 (1)	0.1389 (8)	0.2168 (5)	2.28
C31	0.5827 (8)	0.4778 (7)	0.1800 (4)	1.40
C32	0.7252 (9)	0.5302 (8)	0.2275 (5)	2.05
C33	0.844 (1)	0.6341 (8)	0.2100 (5)	2.21
C34	0.817 (1)	0.6848 (9)	0.1476 (5)	2.36
C35	0.6722 (9)	0.6307 (8)	0.1000 (5)	1.95
C36	0.5570 (8)	0.5293 (8)	0.1161 (4)	1.69
C41	0.2464 (8)	0.6345 (7)	0.1872 (4)	1.36
C42	0.2403 (8)	0.7564 (8)	0.1963 (4)	1.66
C43	0.2060 (9)	0.7924 (8)	0.1268 (5)	2.13
C44	0.1801 (9)	0.7069 (8)	0.0488 (5)	2.08
C45	0.184 (1)	0.5857 (8)	0.0389 (5)	2.23
C46	0.2164 (8)	0.5491 (7)	0.1078 (4)	1.62
C51	0.2109 (8)	0.6601 (8)	0.3556 (4)	1.61
C52	0.2841 (9)	0.7967 (8)	0.3989 (5)	2.15
C53	0.217 (1)	0.8539 (9)	0.4562 (5)	2.54
C54	0.078 (1)	0.775 (1)	0.4734 (5)	2.90
C55	0.010 (1)	0.640 (1)	0.4317 (5)	2.92
C56	0.074 (1)	0.5833 (8)	0.3731 (5)	2.15
C61	0.4956 (8)	0.6950 (7)	0.3153 (4)	1.53
C62	0.5824 (8)	0.7771 (8)	0.2725 (4)	1.82
C63	0.733 (1)	0.8605 (8)	0.3062 (5)	2.11
C64	0.7973 (9)	0.8587 (8)	0.3812 (5)	2.11
C65	0.711 (1)	0.7768 (8)	0.4231 (5)	2.36
C66	0.5612 (9)	0.6938 (8)	0.3903 (5)	2.03

$Ir(CF_2CF_2H)(CO)_2(PPh_3)_2$. (a) $IrH(C_2F_4)(CO)(PPh_3)_2$ (500 mg, 0.59 mmol) was dissolved in benzene (30 mL) and heated, at 90 °C, with triphenylphosphine (465 mg, 1.7 mmol) for 2 days in a Carius tube (volume 25 mL). The solution was then cooled. The benzene was removed in vacuo, and the residue was recrystallized from dichloromethane and ethanol to give the product as white crystals (222 mg, 43%), mp 152–154 °C. Anal. Calcd for $C_{40}H_{31}F_4IrO_2P_2\cdot{}^1/_2CH_2Cl_2$: C, 53.08; H, 3.52; F, 8.30. Found: C, 53.12; H, 3.81; F, 9.55. IR (Nujol, cm^{-1}): ν(CO) 1987, 1935; ν(CF) 1156, 1090, 1080, 986, 939, 789. ^1H NMR ($CDCl_3$, ppm): 5.23 (tt, 1 H, $^2J_{FH}$ = 57.0 Hz, $^3J_{FH}$ = 5.51 Hz, CF_2CF_2H). ^{31}P NMR ($CDCl_3$, ppm): 2.33 (tt, $^3J_{PF}$ = 30.5 Hz, $^4J_{PF}$ = 5 Hz).

(b) $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ (50 mg, 0.05 mmol) was dissolved in dichloromethane (10 mL), and carbon monoxide was bubbled through the solution for 5 min. Ethanol (20 mL) was then added, and the dichloromethane was removed at reduced pressure to give the product as white crystals (41 mg, 82%).

(c) $Ir(CF_2CF_2H)(C_2F_4)(CO)(PPh_3)_2$ (500 mg, 0.53 mmol) was dissolved in benzene (30 mL) and heated, at 90 °C, under carbon monoxide (500 kPa) in a Fischer–Porter (volume 300 mL) bottle for 3 h. The solution was then cooled and the pressure vented. The benzene was removed in vacuo and the residue recrystallized from dichloromethane and ethanol to give the product as white crystals (199 mg, 43%).

(d) $Ir(CF_2CF_2H)(CO)(PPh_3)_2$ (50 mg, 0.05 mmol) was dissolved in dichloromethane (10 mL), and carbon monoxide was bubbled through the solution for 5 s. Ethanol (20 mL) was then added, and the dichloromethane was removed at reduced pressure to give the product as white crystals (45 mg, 98%).

$[Ir(CH_3CN)(C_2F_4)(CO)(PPh_3)_2]ClO_4$. $[Ir(CH_3CN)(CO)(PPh_3)_2]ClO_4$ (500 mg, 0.57 mmol) was dissolved in benzene (30 mL) and stirred under tetrafluoroethylene pressure (500 kPa) in a Fischer–Porter bottle (volume 300 mL) for 3 h. The tetrafluoroethylene was then vented, and the benzene was removed in vacuo. The residue was recrystallized from dichloromethane and ethanol to give the product as white crystals (544 mg, 97%), mp 185–187 °C. Anal. Calcd for $C_{41}H_{33}ClF_4IrO_5NP_2$: C, 49.98; H, 3.38; N, 1.42; F, 7.71. Found: C, 50.31; H, 3.60; F, 6.97. IR (Nujol, cm^{-1}): ν(CO) 2068; ν(CF) 1139, 1072, 801; ν(CN) 2335. ^1H NMR ($CDCl_3$, ppm): 2.06 (s, 3 H, CH_3CN). ^{31}P NMR ($CDCl_3$, ppm): −7.04 (m). ^{19}F ($CDCl_3$, ppm): −113.3 (ddm, $^2J_{FF} = 165$ Hz, $^3J_{FF} = 39$ Hz, $C_2\mathit{F}_4$ (F trans to CO)), −119.4 (dm, $^2J_{FF} = 165$ Hz, $C_2\mathit{F}_4$ (F trans to CH_3CN)). ^{13}C NMR ($CDCl_3$, ppm): 161.5 (m, CO), 174 (m, $CH_3\mathit{C}N$), 2.8 (s, $\mathit{C}H_3CN$), 93.1 (ddd, $^1J_{FC} = 328.0$ Hz, $^1J_{F'C} = 339.1$ Hz, $^2J_{CP} = 87.6$ Hz, C_2F_4), 128.9 (d, $^1J_{CP} = 46.2$ Hz, ipso PPh_3), 133.0 (d, $^2J_{CP} = 11.2$ Hz, ortho PPh_3), 129.4 (d, $^3J_{CP} = 10.6$ Hz, meta PPh_3), 132.0 (d, $^4J_{CP} = 1.9$ Hz, para PPh_3).

$Ir(CF_2CF_2H)(CO)(PPh_3)_2$. $Ir(CF_2CF_2H)(C_2H_4)(CO)(PPh_3)_2$ (200 mg, 0.2 mmol) was heated, at 90 °C, under dynamic vacuum for 2 h. During this time the color changed from white to yellow. The complex was characterized spectroscopically. IR (Nujol, cm^{-1}): ν(CO) 1964; ν(CF) 1166, 1150, 1087, 1019, 976, 968, 935, 776. ^1H NMR ($CDCl_3$, ppm): 4.88 (tt, 1 H, $^2J_{FH} = 54.8$ Hz, $^3J_{FH} = 6.7$ Hz, CF_2CF_2H). ^{31}P NMR ($CDCl_3$, ppm): 4.04 (t, $^3J_{PF} = 15.3$ Hz).

***cis*-$IrCl_2(CF_2CF_2H)(CO)(PPh_3)_2$.** $Ir(CF_2CF_2H)(CO)(PPh_3)_2$ (100 mg, 0.1 mmol) was dissolved in dichloromethane (10 mL). Iododichlorobenzene (0.1 mmol) was added and the solution stirred for 5 min, during which time the yellow color faded. Ethanol (20 mL) was added, and the dichloromethane was removed at reduced pressure. The product was isolated as colorless crystals (62 mg, 77%), mp 195–198 °C. Anal. Calcd for $C_{39}H_{31}Cl_2F_4IrOP_2$: C, 51.10; H, 3.40; F, 8.29. Found: C, 51.33; H, 3.59; F, 8.08. IR (Nujol, cm^{-1}): ν(CO) 2073; ν(CF) 1162, 1094, 999, 907, 846. ^1H NMR ($CDCl_3$, ppm): 4.92 (tt, 1 H, $^2J_{FH} = 53.7$ Hz, $^3J_{FH} = 7.21$ Hz, CF_2CF_2H). ^{31}P NMR ($CDCl_3$, ppm): −21.48 (t, $^3J_{PF} = 20.5$ Hz).

X-ray Collection and Refinement. Crystals suitable for data collection were grown from a dichloromethane/ethanol solution. The cell parameters were determined by a least-squares refinement of 25 accurately centered reflections. Crystal stability was monitored by recording three check reflections every 100 reflections, and no significant variations were observed. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied, on the basis of the ψ-scan data and the crystal dimensions. A Patterson synthesis revealed the position of the heavy atom, and the remaining non-hydrogen atoms were located with use of Fourier maps. Atomic scattering factors were for neutral atoms. Anisotropic thermal parameters were assigned to all but the atoms of the phenyl rings. The structure solution and refinement utilized SHELX-76.[11] Details of the crystal data and intensity data collection parameters are summarized along with atom positions in Tables II and III.

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Supplementary Material Available: Thermal factors (Tables IV and V), bond lengths (Table VI), and bond angles (Table VII) (5 pages); a listing of the structure factors (11 pages). Ordering information is given on any current masthead page.

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Cooperative Activation of CO by Early/Late Heterobimetallics: Reactions of $[Cp_2M(\mu\text{-}PR_2)]_2$ (M = Ti, Zr) with $[CpMo(CO)_3]_2$

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The reactions of the Ti(III) and Zr(III) species $[Cp_2M(\mu\text{-}PEt_2)]_2$ with $[CpMo(CO)_3]_2$ have been studied. In the Zr case, the reaction proceeds with reduction of the Mo–Mo bond and concurrent oxidation of the Zr(III) center to Zr(IV). The product is formulated as $Cp_2Zr(\mu\text{-}PEt_2)(\mu\text{-}\eta^1,\eta^2\text{-}OC)Mo(CO)Cp$ (**1**). Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.644$ (2) Å, $b = 9.795$ (2) Å, $c = 14.667$ (3) Å, $\beta = 104.27$ (1)°, $Z = 4$, and $V = 2039$ (1) Å^3. The reaction of the Ti(III) phosphide species with $[CpMo(CO)_3]_2$ proceeds via an alternate pathway. Reduction of the Mo–Mo bond occurs with oxidation of the phosphide ligand on Ti, affording the complex $Cp_2Ti(THF)(\mu\text{-}\eta^1,\eta^1\text{-}OC)Mo(CO)_2Cp$ (**2**) and P_2Et_4. The Ti(III)/Mo(0) complex **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 16.320$ (4) Å, $b = 7.907$ (2) Å, $c = 10.882$ (3) Å, $\alpha = 115.39$ (1)°, $\beta = 82.99$ (2)°, $\gamma = 124.66$ (2)°, $Z = 2$, and $V = 1029$ (1) Å^3. The spectral and structural characterizations of complexes **1** and **2** are presented. The differing modes of CO activation in species **1** and **2** are described, and the implications regarding heterobimetallic activation of CO are discussed.

Introduction

Recently, numerous studies have described complexes containing both early, oxophilic and late, electron-rich metals.[1] Interest in such heterobimetallic complexes has arisen, as such metal pairings combine the Lewis acidity of the early metals and the known ability of late-metal centers to activate hydrogen, thus offering the potential of carbon oxide activation and reduction. A number of synthetic routes to homogeneous early/late heterobimetallic complexes have been reported.[1] Although a number of complexes have been described where the constituent metals are linked by metal–metal bonds,

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(1) The subject of early/late heterobimetallics has been recently reviewed: Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.