Comparison of the Thermal and Reductive Decarbonylation of a Rhodium Trifluoroacetyl Diphosphine Complex

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Acyl complexes of rhodium(III) with chelating diphosphine ligands are well known for their stability toward decarbonylation. However, we have found that the corresponding perfluoro complexes do decarbonylate under mild conditions. In this report we address specifically Rh(dppp)-(COCF₃)I₂ (dppp = 1,3-bis(diphenylphosphino)propane). Another difference between this compound and rhodium acyl complexes containing monodentate phosphines is that it does not undergo reductive elimination of alkyl halide after decarbonylation. Instead, slow CO dissociation from Rh(dppp)(CO)(CF₃)I₂ occurs to yield Rh(dppp)(CF₃)I₂ as the final product. Reduction of the trifluoroacetyl complex is a net two-electron process that also involves decarbonylation, but through a quite different mechanism. The products consist of Rh(dppp)(CO)I, CF₃⁻ anion, and iodide. X-ray crystal structures of both Rh(dppp)(COCF₃)I₂ and Rh(dppp)(CF₃)I₂ have been obtained and show the expected square-pyramidal geometry with the acyl/alkyl group in the apical position.

Introduction

Rhodium acyl complexes function as homogeneous catalysts or intermediates in many important organic transformations on both the laboratory and industrial scales.¹ These reactions typically involve migratory insertion and/or decarbonylation steps. It has been known for quite some time that five-coordinate rhodium(III) acyl dihalide complexes containing chelating diphosphine ligands, particularly 1,3-bis(diphenylphosphino)propane (dppp), are unusually stable with respect to decarbonylation.^{2–4} The reason for this stability has been proposed to be the unlikely occurrence of a complex containing an alkyl group trans to a phosphorus, which would necessarily result from decarbonylation of the dppp complex.⁴ However, while one may infer that this claim is based in some way upon the strong trans effect of both phosphine and alkyl ligands,⁵ it was presented without any supporting evidence and we consider this explanation to be far from an established fact.

We have a longstanding interest in organometallic reactions initiated or catalyzed by electron transfer, and it occurred to us that the decarbonylation of rhodium acyl complexes containing dppp might be amenable to study. In particular, we were curious to see whether these complexes could undergo electron transfer chain catalyzed (ETC^{6-9}) decarbonylation. The reaction might be expected to proceed as

$$Rh(dppp)(COR)X_2 + e^- \rightarrow [Rh(dppp)(COR)X_2]^-$$
 (1)

$$[Rh(dppp)(COR)X_2]^- \rightarrow [Rh(dppp)(CO)(R)X_2]^- (2)$$

$$[Rh(dppp)(CO)(R)X_2]^- + Rh(dppp)(COR)X_2$$

$$\rightarrow Rh(dppp)(CO)(R)X_2 + [Rh(dppp)(COR)X_2]^- (3)$$

The Rh(III) acyl complexes can be expected to be reducible,¹⁰ and once they are reduced to odd-electron species their reactivity would likely be enhanced. Such rate enhancements have been observed for migratory insertion reactions,^{11–15} but not so far as we are aware for decarbonylation, other than a reductively initiated radical chain decarbonylation of a rhenium formyl complex.¹⁶ Initiation by reduction in eq 1 was expected to be followed by a catalytic cycle consisting of eqs 2 and 3. It is generally held that such a process can be catalytic only if the reduction potential of the product is more negative than that of the



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reactant, making reaction 3 thermodynamically favorable.¹⁷ However, we have shown that this is not strictly true if there are other factors favoring the forward reaction.¹⁸ In any event, it is not obvious which species, the five-coordinate acyl complex or the six-coordinate alkyl carbonyl complex, would have the more negative reduction potential. We therefore decided to investigate this reaction using both electrochemical and chemical reduction.

Unfortunately, preliminary studies of the reduction of the well-known acetyl complex Rh(dppp)(COCH₃)I₂ failed to show any evidence for the proposed ETC decarbonylation reaction and also proved difficult to follow by NMR. We therefore used our experience with perfluoroalkyl complexes to prepare the previously unreported $Rh(dppp)(COCF_3)I_2(1)$, which would allow both ³¹P and ¹⁹F NMR to be conveniently used to follow the course of the reaction and the fate of the acyl group. Such an approach proved quite successful in our studies of the similar Co(CO)₃(PPh₃)(COCF₃) system.¹⁹ Much to our surprise, while studying its electrochemistry we discovered that complex 1 underwent thermal decarbonylation in solution under ambient conditions, though at a rate slow enough that it did not interfere with the reductive studies. Therefore, we have also studied this unexpected thermal decarbonylation and found that it proceeds via a path quite different from that of the reduction reaction. The results of both studies are presented below.

Results and Discussion

Thermal Decarbonylation of 1. Complex **1** was synthesized using a variation of the procedure reported by Miller and Nelson²⁰ to initially produce the trifluoroacetate complex Rh- $(dppp)(COCF_3)(CO_2CF_3)I$, followed by in situ replacement of the trifluoroacetate ligand with iodide. This complex was characterized by IR, NMR, elemental analysis, and X-ray crystallography (Figure 1, Table 1). As with previously reported rhodium acyl complexes of this type,^{3,21-24} complex **1** adopts an essentially square-pyramidal geometry with the trifluoroacetyl group in the apical position. Other than the somewhat enlarged C–Rh–I bond angles, the structure is an essentially ideal square pyramid (vide infra).

The thermal reactivity of **1** was followed by NMR, with the starting complex showing a doublet at 16.8 ppm in its ³¹P NMR and a singlet at -69.6 ppm in its ¹⁹F NMR spectrum in CD₂Cl₂. Over the course of 3 days in CD₂Cl₂ solution at room temperature these peaks decreased in intensity and major new ones appeared at -21.7 (pd) and 0.5 (ddq) ppm in the ³¹P NMR and 1.7 (dt) ppm in ¹⁹F NMR. Coupling constants of these peaks are presented in Table 2. During this time IR showed that the carbonyl stretching band of **1** at 1679 cm⁻¹ decreased in intensity and was replaced by a new band at 2079 cm⁻¹. These NMR and IR results are consistent with decarbonylation of **1** to give Rh(dppp)(CO)(CF₃)I₂ (**2**). While this type of reaction has been



Figure 1. ORTEP diagram of Rh(dppp)(COCF₃)I₂ (1). Phenyl groups and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected distances (Å) and angles (deg): Rh1–I1 = 2.6926(6), Rh1–I2 = 2.6798(7), Rh1–C6 = 1.946(3), Rh1–P2 = 2.3102(9), Rh1–P1 = 2.3140(9), O1–C6 = 1.207(3), C6–C2 = 1.579(4), P1–C11 = 1.820(3), P1–C21 = 1.825(3), P1–C3 = 1.832(3), P2–C41 = 1.823(3), P2–C31 = 1.824(3), P2–C5 = 1.831(3), C3–C4 = 1.528(4), C4–C5 = 1.538(4), F1–C2 = 1.319(4), F2–C2 = 1.333(3), F3–C2 = 1.331(4), O1–C6–C2 = 112.2(3); O1–C6–Rh1 = 127.8(2), C6–Rh1–P2 = 92.08(9), C6–Rh1–P1 = 91.31(9), P2–Rh1–P1 = 89.86(3), C6–Rh1–I2 = 104.06(8), P2–Rh1–I2 = 163.75(2), P1–Rh1–I2 = 87.90(3), C6–Rh1–I1 = 100.17(9), P2–Rh1–I1 = 89.65(2), P1–Rh1–I1 = 168.52(2), I2–Rh1–I1 = 89.370(18), C11–P1–C21 = 105.20(13), C41–P2–C31 = 107.06(13).

used to prepare trifluoromethyl complexes of a number of other metals,²⁵ so far as we know it is the first time it has been used for rhodium. Other Rh(III) trifluoromethyl complexes have been prepared via oxidative addition of CF_3I ,²⁶ Me₃SiCF₃,²⁷ or an aryl-CF₃ diphosphine to Rh(I).²⁸

Presumably at least initially the CF₃ of **1** migrates to a position trans to one of the phosphorus atoms, displacing one of the iodides. It has been reported that trans phosphorus–fluorine three-bond coupling constants are larger than those of cis isomers.²⁷ We observed both large (${}^{3}J_{P-F} = 60$ Hz) and small (${}^{3}J_{P-F} = 12$ Hz) phosphorus–fluorine three-bond coupling in the NMR spectra of complex **2**, indicating that the CF₃ must be trans to one of the phosphorus atoms and cis to the other. This arrangement would require the terminal CO to be trans to the displaced iodide. We were able to grow single crystals of **2**, but X-ray crystallography failed to distinguish between the CF₃ and iodide ligands trans to the two phosphorus atoms, and thus a suitable solution could not be obtained.²⁷ Nevertheless, the partial solution confirmed our proposed decarbonylation step. The CO stretching frequency

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characteristic of a terminal carbonyl, the inequivalence of the phosphine NMR resonances, and the appearance of Rh–F coupling in the ¹⁹F NMR spectrum are all consistent with the proposed structure. Nevertheless, it should be noted that the ¹⁹F NMR spectrum, for which the signal-to-noise ratio was quite good, displayed additional minor resonances very similar to the major resonances but at different chemical shifts, perhaps representing different isomers of the trifluoromethyl complex produced as minor products.

Despite the fact that we were able to grow single crystals of complex **2**, it was not stable in solution at room temperature. Over long periods of time (ca. 20 days or more) the carbonyl stretching band of **2** disappeared from the IR spectrum and NMR spectra showed the formation of a new compound. The ³¹P NMR spectrum showed a single resonance at 14.8 (dq) ppm indicative of equivalent phosphorus atoms, and ¹⁹F NMR showed a new resonance at 14.5 (q) ppm with identical Rh–F and P–F coupling constants. The logical conclusion is that over time the carbonyl ligand dissociates, leaving Rh(dppp)(CF₃)I₂ (**3**). In fact, we were able to grow single crystals of **3**, and the structure is shown in Figure 2. As with compound **1**, compound **3** displays an almost ideal square-pyramidal geometry (vide infra). Compound **3** was not produced in sufficient quantities to allow its characterization by

Table 1. Summary of Crystallographic Data for Rh(dpp)-(COCF₃)I₂ (1) and Rh(dpp)(CF₃)I₂ (3)

	$1 \cdot CH_2Cl_2$	$3 \cdot 3 CH_2 Cl_2$
empirical formula	C ₃₀ H ₂₈ Cl ₂ F ₃ I ₂ OP ₂ Rh	$C_{31}H_{32}Cl_6F_3I_2P_2Rh$
formula wt	951.07	1092.92
cryst size (mm)	$0.21 \times 0.19 \times 0.13$	$0.13\times0.09\times0.07$
cryst syst	triclinic	monoclinic
space group	$P\overline{1}$	$P2_1/m$
a (Å)	9.500(2)	8.7676(5)
$b(\mathbf{A})$	13.385(4)	22.1871(13)
c(Å)	14.187(4)	10.3947(6)
α (deg)	74.522(14)	90.0
β (deg)	79.145(12)	110.587(2)
γ (deg)	70.165(12)	90.0
$V(Å^3)$	1625.8(7)	1892.93(19)
Z	2	2
temp (K)	110(2)	110(2)
$d_{\rm calcd}$ (Mg m ⁻³)	1.943	1.917
$\mu (\text{mm}^{-1})$	2.728	2.628
θ range for data collecn (deg)	1.66-25.34	1.84-25.35
no of data measd	26253	24 4 56
no. of unique data	5890	3561
no. of data/restraints/ params	5890/0/370	3561/0/211
max/min transmissn	0.7113/0.5942	0.8354/0.7230
R _{int}	0.0440	0.0335
wR2, R1 (all data)	0.0505, 0.0266	0.0478, 0.0239
wR2, R1 $(I > 2\sigma(I))$	0.0480, 0.0223	0.0451, 0.0194
GOF on F^2	1.040	1.051
max/min $\Delta \rho$ (e Å ⁻³)	0.806/-0.691	0.779/-0.362

elemental analysis, but a high-resolution mass spectrum was obtained using ESI on a solution of **3** in methanol. While the compound is not capable of forming a molecular ion due to the lack of an appropriate protonation/deprotonation site, the spectrum exhibited peaks for $[3 - CF_3]^+$ and $[3 - I]^+$, confirming the compound's identity.

The thermal reactivity of compound **1** can thus be summarized by Scheme 1. Decarbonylation of the square-pyramidal trifluoroacetyl complex yields the octahedral trifluoromethyl carbonyl complex **2**, most likely with the trifluoromethyl group trans to one of the phosphines. Given time, this complex dissociates CO to yield the square-pyramidal complex **3**. It is interesting to note that when nonfluorinated rhodium acyl complexes containing monodentate phosphine ligands decarbonylate to alkyl complexes, the alkyl group subsequently reductively eliminates with one of the halides to leave *trans*-RhP₂(CO)X type complexes.²⁹ It is unclear whether the different reactivity of **2** stems from the enforced cis geometry of the phosphines or the much stronger metal–carbon bond of the CF₃ group.³⁰ Note also that while the geometry of the complexes alternates between square pyramidal and octahedral, the oxidation state of rhodium remains constant at +3.

Electrochemistry of 1. Cyclic voltammetry of complex 1 was performed in dichloromethane and tetrahydrofuran.



Figure 2. ORTEP diagram of Rh(dppp)(CF₃)I₂(**3**). Phenyl groups and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected distances (Å) and angles (deg): Rh1–I1 = 2.6884(3), Rh1–P1 = 2.3012(6), Rh1–C1 = 2.014(4), P1–C11 = 1.825(2), P1–C21 = 1.825(2), P1–C2 = 1.827(2), F1–C1 = 1.327(3), F2–C1 = 1.341(4), C2–C3 = 1.526(3); C1–Rh1–P1=93.36(7), P1–Rh1–P1A = 91.84(3), P1– Rh1–I1A = 166.619(19), C1–Rh1–I1 = 99.98(7), P1–Rh1– I1 = 88.391(17), P1A–Rh1–I1 = 166.619(19), I1A–Rh1–I1 = 88.319(11), C11–P1–C21 = 105.32(11).

Table 2. Summary of ³¹ P and ¹⁹ F NMR E)ata
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complex	³¹ P (ppm); <i>J</i> (Hz)	¹⁹ F (ppm); <i>J</i> (Hz)
$Rh(dppp)(COCF_3)I_2(1)^a$	16.8 (d); 117 (Rh–P)	-69.6 (s)
$Rh(dppp)(CO)(CF_3)I_2(2)^a$	-21.7 (pd, P _A), 0.5 (ddq, P _B); 60 (Rh-P _A , F-P _A), 102 (Rh-P _B), 11 (F-P _B), 29 (P _A -P _B)	1.7 (dt); 56 (P _A -F), 12 (Rh-F, P _B -F)
$Rh(dppp)(CF_3)I_2(3)^a$	14.8 (dq); 114 (Rh–P), 13 (F–P)	14.5 (q); 12 (Rh-F, P-F)
$[Rh(dppp)(CO)(CF_3)I]^- (E)^b$	9.2 (ddq, P _A), 13.8 (ddq, P _B); 141 (Rh–P _A), 19 (F–P _A), 95 (Rh–P _B), 48 (F–P _B), 53 (P _A –P _B)	-10.2 (dt); 19 (Rh-F, P _A -F), 45 (P _B -F)
$Rh(dppp)(CO)I^b$	$3.5 (dd, P_A), 22.0 (dd, P_B); 115 (Rh-P_A),$	
	$156 (Rh-P_B), 56 (P_A-P_B)$	

^a Solvent CD₂Cl₂. ^b Solvent THF-d₈.





The peak potential for the chemically irreversible reduction observed in both solvents was -1.36 V vs Fc⁺/Fc. When cyclic voltammograms were recorded at a slow scan rate (200 mV/s), only one oxidation peak at ca. -0.1 V was observed on the return scan, and it was confirmed to originate from iodide by adding tetrabutylammonium iodide as an additional source of iodide.³¹ At faster scan rates (e.g., 2 V/s) an additional oxidation peak for a short-lived intermediate could be observed at -0.75 V on the return scan. When the forward scan toward negative potentials was reversed at a potential just before the reduction of **1**, no oxidation peaks were observed during the return scan. These results demonstrate that a short-lived oxidizable intermediate and iodide are produced by the reduction of compound **1**.

The number of electrons transferred during the reduction of complex 1 was investigated electrochemically by linear scan voltammetry (LSV) in dichloromethane and acetonitrile and controlled-potential electrolysis in THF and acetonitrile. The LSV limiting current of 1 was compared with those of cyclopentadienyliron dicarbonyl dimer (2e) and tris(dibenzoylmethanato)iron (1e) using 0.1 and 0.01 mm microelectrodes. While not an exact match, the LSV limiting current of compound 1 corresponded most closely with that of the two-electron reduction. Likewise, controlled-potential electrolyses consumed approximately 2 mol of electrons/mol of 1 reduced. We thus conclude from its electrochemistry that the reduction of compound 1 is a two-electron process with iodide as one of the major products.

Chemical Reduction of 1. Complex 1 was reduced in THF*d*₈ with THF solutions of the mono- and dipotassium salts of benzophenone (KBP and K₂BP), and the progress of the reaction was monitored by IR, ³¹P NMR, and ¹⁹F NMR. IR spectra showed that during the reduction of 1 its carbonyl stretching band at 1680 cm⁻¹ (cf. 1679 cm⁻¹ in CH₂Cl₂) disappeared and was replaced by a peak at 2009 cm⁻¹. This new IR band is in the region expected for a terminal metal–carbonyl stretching frequency and in fact matches that of Rh(dppp)(CO)I.² No intermediate species were detected by IR, perhaps because IR lacked either the sensitivity or the selectivity to do so.

NMR spectroscopy proved to be a much more sensitive way to follow the progress of the reduction reaction. After partial reduction of **1** with K₂BP, the ³¹P NMR spectrum displayed resonances at 3.5 (dd), 9.2 (ddq), 13.8 (ddq), and 22.0 (dd) ppm, in addition to that of compound **1** at 16.8 (d) ppm (Figure 3). Coupling constants of these peaks are presented in Table 2. As more reductant was added, the starting material disappeared, followed by loss of the peaks at 9.2 and 13.8 ppm, leaving those at 3.5 and 22.0 ppm from the primary product after complete reduction. A singlet at 32.3 ppm corresponding to 1,3bis(diphenylphosphino)propane dioxide was the sole remaining ³¹P NMR resonance after exposing the product mixture to air. The ¹⁹F NMR spectrum after partial reduction with K₂BP



Figure 3. ³¹P NMR spectrum after partial reduction of Rh-(dppp)(COCF₃)I₂ (1) with K₂BP in THF- d_8 .



Figure 4. ¹⁹F NMR spectrum after partial reduction of Rh-(dppp)(COCF₃)I₂ (1) with K₂BP in THF- d_8 .

(Figure 4) displayed peaks at -10.2 (dt), -74.9 (s), -78.1 (d), and -78.8 (1:1:1 t) ppm, in addition to that of compound 1 at -68.7 (s) ppm (cf. -69.6 ppm in CD₂Cl₂). As more reductant was added, the starting material disappeared, followed by loss of the peak at -10.2 ppm, leaving those at -74.9, -78.1, and -78.8 ppm from the primary fluorine-containing products after complete reduction. These ¹⁹F NMR peaks correspond to Ph₂C(OH)CF₃, CF₃H, and CF₃D, respectively.¹⁹

When compound 1 was reduced with K₂BP in the presence of ethyl acetate, the ¹⁹F NMR peak for CF₃H was much larger than that in its absence while those for Ph₂C(OH)CF₃ and the intermediate at -10.2 ppm were much smaller. This result suggests a rapid reaction between the intermediate and ethyl acetate, most likely consisting of proton transfer from the ethyl acetate to CF₃⁻. A similar result was obtained when compound 1 was reduced in acetone-*d*₆, though in this case the yield of CF₃D was enhanced. Both esters with α -hydrogens and acetone have been reported to react with CF₃⁻ to produce CF₃H and deprotonated solvent as major products.³²

In order to quantify the number of electrons transferred during the chemical reduction of 1, it was titrated with a standardized solution of KBP. Experiments were performed in which the consumption of 1 was followed by either NMR or CV, and in each case titrations consumed 2 equiv of KBP/mol of compound 1. These results are in agreement with the electrochemical studies, which indicated that the reduction of 1 is a net two-electron process.

Proposed Mechanism for the Reduction of 1. Scheme 2 shows the proposed mechanism for the reduction of compound

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1. The initial electron transfer produces an unstable 17e anion (A). It is clear from both IR and NMR that decarbonylation occurs eventually, but it is unlikely to do so at this point, since the resulting anionic trifluoromethyl complex would be a 19e species. The anion A thus almost certainly undergoes loss of iodide next to yield a neutral 15e intermediate (B). This complex may then decarbonylate to yield a 17e trifluoromethyl complex (C). However, there is no evidence to support the intermediacy of C. In fact, it is also possible that complex B instead undergoes a second electron transfer. This second reduction would produce the intermediate labeled D, a 16e anion, through a typical ECE mechanism.³³ This complex should be observable by NMR, but no appropriate resonances, inequivalent ³¹P signals lacking P-F coupling, were observed. Cyclic voltammetry does give evidence for a short-lived oxidizeable intermediate. Such an intermediate would more likely be D than C, given its ease of oxidation and observable lifetime. However, we cannot conclusively state whether the reduction of 1 passes through either intermediate C or D.

Either decarbonylation of **D** or a second electron transfer to **C** would yield an 18e anionic trifluoromethyl complex (**E**). Good NMR evidence does exist to support the intermediacy of complex **E** (see Table 2). The ³¹P resonances observed at 9.2 and 13.8 ppm after partial reduction of **1** as well as the ¹⁹F resonance at -10.2 ppm are consistent with the proposed structure in terms of both chemical shifts and coupling constants. The ³*J*_{P-F} values of 45 and 19 Hz are consistent with one phosphorus atom being trans to the CF₃ and one being cis. A terminal CO stretch which could be associated with complex **E** was not observed, but this may be due to its low intensity and/or overlap with the stretching frequency of the final product, Rh(dppp)(CO)I.

While NMR spectra consistent with complex E were observed, this compound was not stable. Over time its ³¹P NMR resonances gave way to those of Rh(dppp)(CO)I, while ¹⁹F NMR indicated the formation of compounds derived from the CF₃ group, including CF₃H, CF₃D, and the anion of trifluoromethyl benzhydrol. We have reported these same products from the one-electron reduction of Co(CO)₃(PPh₃)COCF₃, which

produces CF₃ radicals.¹⁹ However, in this case both chemical and electrochemical evidence confirm the two-electron nature of the reduction, requiring CF₃⁻ anion as the product. The increased yield of CF₃H in the presence of ethyl acetate and CF₃D in the presence of acetone- d_6 also support the production of CF₃⁻. Thus, we feel confident in assigning the final step in the mechanism of the reduction of **1** to CF₃⁻ dissociation from complex **E**. The fact that this step involves loss of CF₃⁻ rather than iodide may be the result of a trans effect of phosphine weakening the Rh–CF₃ bond.

It should be noted that Rh(dppp)(CO)I could also be produced by loss of CF_3^- directly from intermediate **D**. This pathway would produce the correct products, derived from CF_3^- , with the correct electron stoichiometry and is analogous to the loss of CF_3^- from the trifluoroacetyl ligand of $Cp*Ir(PMe_3)(H)(COCF_3)$.³⁴ However, the observation of an intermediate with NMR spectroscopy consistent with the structure shown for **E**, but not **D**, makes this pathway an unlikely alternative.

X-ray Crystal Structures of Complexes 1 and 3. Crystals of 1 and 3 suitable for X-ray crystallography were grown by slow diffusion of hexanes into dichloromethane solutions at low temperature. Compound 1 crystallized in the triclinic space group $P\overline{1}$ with two formula units per unit cell, while compound 3 crystallized in the monoclinic space group $P2_1/$ *m* with two formula units per unit cell. The crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are presented in the captions of Figures 1 and 2, which show perspective views of $Rh(dppp)(COCF_3)I_2$ (1) and $Rh(dppp)(CF_3)I_2$ (3), respectively. As can be seen in Figures 1 and 2, both compounds have a square-pyramidal geometry with the phosphorus and iodine atoms occupying the basal sites and either a trifluoroacetyl or a trifluoromethyl group occupying the apical position. This has been reported to be the preferred orientation, over trigonal bipyramidal, for fivecoordinate d⁶ complexes.³⁵

When the bond angles in complexes 1 and 3 are compared with those of an ideal square-pyramidal structure, the major deviation from ideality is in the larger than expected apical carbon-rhodium-iodine angles. This distortion most likely results from contact between the iodine atoms and C2 and F1 in 1 and F1 and F1A in 3. Contact between the acyl oxygen and the phosphorus atoms in 1 and the single F2 atom and the phosphorus atoms in 3 is less significant, and so those angles are closer to the ideal 90° value. These slight distortions are quite typical of this class of rhodium complexes and agree with several related structures that we have solved,³⁶ as well as literature reports for similar dichloro complexes.^{3,22} Interestingly, Moloy and Petersen's reported structure for Rh(dppp)(COCH₃)I₂ shows significant distortion toward a trigonal bipyramid,²¹ but Søtofte and Hjortkjær have reported the structure as having only minor deviations from square-pyramidal geometry.²⁴ We have independently solved the structure of this compound and found it in agreement with that of $1.^{36}$

The bond lengths in complexes 1 and 3 are quite typical. When the two complexes are compared, the average Rh-I bond length of complex 3 is very slightly longer than that of 1, while the average Rh-P bond length of 3 is slightly shorter

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than that of **1**. The major difference, as expected, is in the Rh–C bond length, with the acyl complex having the shorter bond (1.946 vs 2.014 Å). This trend is in agreement with two previously reported pairs of perfluoroacyl and perfluoroalkyl complexes of rhodium and platinum^{37–39} but is in contrast to our results with cobalt, where the Co–C bond length of the trifluoroacetyl complex.⁴⁰ On the other hand, the Rh–C bond length for the acetyl complex reported by Moloy and Petersen (1.981 Å)²¹ is, as expected, significantly longer than the trifluoroacetyl bond length of **1**. However, the carbon–oxygen (1.182 Å) and carbon–carbon (1.513 Å) bond lengths of the acyl ligand are shorter in the acetyl complex than in the trifluoroacetyl complex (1.207 and 1.579 Å, respectively).

Conclusions

Unlike previously reported acyl complexes of rhodium with diphosphine ligands,²⁻⁴ the trifluoroacetyl complex **1** undergoes spontaneous thermal decarbonylation at room temperature. And unlike acyl complexes with monodentate phosphine ligands which do decarbonylate, the resulting alkyl carbonyl complex loses CO instead of undergoing reductive elimination of alkyl halide.²⁹ Thus, the reactivity of this perfluoro complex is quite different from that of nonfluorinated analogues, in line with results from a number of other organometallic systems.³⁰ The reduction of **1** also results in decarbonylation, though we cannot say whether this step occurs from a 15e Rh(II) or a 16e Rh(I) intermediate. In either case, a net two-electron reduction yields a Rh(I) carbonyl complex, iodide, and trifluoromethyl anion. Good evidence exists for the intermediacy of an unstable 18e Rh(I) trifluoromethyl complex in this reaction.

Experimental Section

General Procedures. Chlorodicarbonylrhodium(I) dimer and 1,3-bis(diphenylphosphino)propane were obtained from Strem Chemicals. Trifluoroacetic anhydride was obtained from Acros Organics. Solutions of K_2BP (potassium salt of benzophenone dianion)⁴¹ were prepared by reaction of benzophenone in THF with an excess of potassium metal and were standardized by reaction with aqueous ethanol followed by titration with standardized HCl. Solutions of KBP (potassium salt of benzophenone monoanion) were prepared by 1:1 dilution of K₂BP with a THF solution of excess benzophenone and were also standardized with HCl. The THF was first dried with CaH2 and then distilled under nitrogen from sodium benzophenone anion before use. Dichloromethane and acetonitrile were distilled from CaH2 under nitrogen. The supporting electrolyte for electrochemical experiments, [Bu₄N]PF₆, was obtained from Alfa Aesar and was dried at 100 °C under vacuum before use. All other reagents were obtained commercially and were used as received. All chemical reactions were carried out in a nitrogen atmosphere glovebox.

Instrumentation. NMR spectra were acquired on a Varian VNMRS 500 instrument. Proton chemical shifts were referenced to residual protons in the solvent, ¹⁹F chemical shifts to external CFCl₃, and ³¹P chemical shifts to external 85% H₃PO₄. IR spectra were obtained using a Mattson Instruments Genesis II FTIR or Thermo Nicolet Avatar 370 FTIR instrument and a cell having CaF₂ windows separated by a 0.1 mm spacer. Electrochemical measurements were performed with a CH Instruments Model 1140 electrochemical analyzer using a Ptdisk working electrode, a Pt-wire auxiliary electrode, and a silver-wire quasi-reference electrode. Solutions contained approximately 0.1 M [Bu₄N]PF₆ supporting electrolyte. All potentials are expressed relative to the formal potential of the ferrocenium-ferrocene couple (Fc⁺/Fc). Controlled-potential electrolyses were conducted in a standard H cell with compartments separated by a medium-porosity glass frit using 25 \times 25 mm platinum-foil working and auxiliary electrodes and a silver-wire reference electrode. The working electrode potential was set at a value ca. 0.2 V more negative than the CV peak potential, and electrolysis was continued until CV indicated that the starting material had been consumed. The total charge consumed was corrected for a background current taken as equal to the final current. High-resolution mass spectra were obtained in the Baylor University Mass Spectrometry Core Facility on a Thermo Scientific LTQ Orbitrap Discovery using an ESI source in positive ion mode.

X-ray Crystallography. Diffraction data were acquired at 110(2) K using a Bruker-Nonius X8 Apex CCD area-detector diffractometer (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å). Several sets of data frames were collected at different θ values for various initial values of ϕ and ω , each frame covering a 0.5° increment in ϕ or ω . The data frames were integrated using SAINT;⁴² the substantial redundancy in data allowed empirical absorption corrections (SADABS⁴²) to be applied on the basis of multiple measurements of equivalent reflections.

The structures were solved (SHELXS-97) via conventional direct methods and were refined (SHELXL-97) by full-matrix least squares on all F^2 data using SHELXTL.⁴³ All non-hydrogen atoms were assigned anisotropic displacement parameters. All of the hydrogen atoms were set riding on their parent atoms in calculated positions and were assigned fixed isotropic thermal parameters calculated as $U_{iso}(H) = 1.2[U_{iso}(parent)]$.

Rh(dppp)(COCF₃)I₂ (1). First, Rh(dppp)(CO)I was synthesized from $[Rh(CO)_2Cl]_2$ and dppp by the published procedure.² $Rh(dppp)(COCF_3)(CO_2CF_3)I$ was then synthesized by a procedure adapted from Miller and Nelson.²⁰ Rh(dppp)(CO)I (0.452 g, 0.21 mmol), trifluoroacetic anhydride (0.5 mL, 3.6 mmol), and 10 mL of toluene were added to a 100 mL roundbottom flask, and the mixture was stirred for about 3 h inside the glovebox. The trifluoroacetate complex was converted to 1 in situ by adding an excess of solid NaI (0.2 g, 1.3 mmol). After the mixture was stirred for about 4 h, 15 mL of hexanes was added and the solution was taken out of the glovebox and cooled in a freezer for about 1/2 h. The resulting precipitate was then filtered and washed with hexanes. The collected precipitate was dissolved in a small amount of methylene chloride and the solution filtered. The filtrate was concentrated under reduced pressure, and an orange precipitate of Rh(dppp)(COCF₃)I₂ was obtained by the addition of hexanes. This precipitate was filtered, washed with hexanes, and dried overnight under vacuum at room temperature. The yield was 0.455 g (0.52 mmol, 78% based on Rh(dppp)(CO)I). Single crystals suitable for X-ray structural determination were grown by the slow diffusion of hexanes into a solution of 1 in CH₂Cl₂ at low temperature. Anal. Calcd for C₂₉H₂₆F₃I₂OP₂Rh (866.12): C, 40.21; H, 3.03; F, 6.58. Found: C, 39.78; H, 3.01; F, 6.86. IR (CH₂Cl₂): 1679 cm⁻¹. ¹H NMR

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(CD₂Cl₂): 1.8 (m), 2.5 (m), 3.3 (m), 7.2–8.0 (m) ppm. ¹⁹F NMR (CD₂Cl₂): -69.6 (s) ppm. ³¹P NMR (CD₂Cl₂): 16.8 (d) ppm ($J_{Rh-P} = 117$ Hz).

Rh(dppp)(CF₃)I₂ (3). Single crystals of Rh(dppp)(CF₃)I₂ were grown in an NMR tube by layering hexanes over a CH₂Cl₂ solution of the solid residue remaining after evaporation of CD₂Cl₂ from a solution of **1** used for NMR studies of the thermal decarbonylation reaction. The mass spectrum of this residue was also collected in methanol solution. The compound was not otherwise isolated but was studied by NMR during the approximately 20 days it took for decarbonylation to go to completion. ¹H NMR (CD₂Cl₂): 1.9 (m), 2.7 (m), 3.0 (m), 7.2–7.7 (m) ppm. ¹⁹F NMR (CD₂Cl₂): 14.5 (q) ppm (J_{Rh-F} , J_{P-F} = 12 Hz). ³¹P NMR (CD₂-Cl₂): 14.8 (dq) ppm (J_{Rh-P} = 114 Hz, J_{F-P} = 13 Hz). High-resolution ESI/MS (MeOH): [M – CF₃]⁺ found 768.8643 (calcd

768.8649, dev 0.75 ppm), $[M - I]^+$ found 710.9547 (calcd 710.9556, dev 1.2 ppm).

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Supporting Information Available: A CIF file giving all crystal data and refinement parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for complexes **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.