process the formal oxidation state of rhodium changes from +1 to +3, which will be accompanied by a significant decrease in volume. This could also partly contribute toward the value of −16 cm$^3$ mol$^{-1}$ found in this study, which would then favor a linear transition state of the type L$_4$Rh- - -CH$_3$- - -I as suggested before.[18] We are confident that a combined solvent/pressure dependence study, presently under way in our laboratories, will enable us to differentiate between these two possible transition states.

The pressure enhancement observed for the oxidative-addition reaction is quite significant, corresponding to a doubling of the rate constant for an increase in pressure of 100 MPa. The significantly higher pressure sensitivity of the oxidative-addition reactions as compared to the substitution reactions of Rh(I) complexes is partly due to the formation of more than one bond and partly due to the polar nature of the transition state.

**Acknowledgment.** We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the SA Council for Scientific and Industrial Research, and the Research Fund for the University of the Orange Free State.

**Registry No.** Rh(acac)(cod), 12245-39-5; Rh(tfac)(cod), 32610-46-1; Rh(acac)(P(OPh)$_3$)$_2$, 25966-19-2; Rh(tfac)(P(OPh)$_3$)$_2$, 95041-07-9; Rh(cup)(CO)(PPh$_3$), 105833-24-7; 1,10-phenanthroline, 66-71-7; methyl iodide, 74-88-4.

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# Olefin Coordination with Rhodium(II) Perfluoroalkanoates in Solution

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*Received February 17, 1987*

The coordination of olefins to rhodium(II) carboxylates is not generally observed in solution, and its absence has been interpreted to indicate that these transition-metal compounds are incapable of such association.[1,2] We recently reported olefin coordination with dirhodium(II) tetrakis(trifluoroacetate) in dichloromethane solution.[3] The complexes were characterized by a slight, but significant, decrease in $\lambda_{max}$ for the $\pi^*_{RhRh} \rightarrow \sigma^*_{RhRh}$ absorption band[4] and a substantial increase in molar absorptivity, as well as by increases in the NMR chemical shifts of olefinic protons resulting from the combination of the dirhodium tetracarboxylate with alkenes. Only 1:1 adducts were formed (eq 1, L = carboxylate), and their apparent equilibrium constants for association,

$$\mathrm{RhL_4Rh} + \text{olefin} \rightleftharpoons \mathrm{RhL_4Rh(olefin)} \qquad (1)$$

which ranged over 2 orders of magnitude, increased with increasing electron-donating ability of olefin substituents. Dirhodium(II) tetraacetate gave no evidence for adduct formation under these conditions.

Recently Schurig has reminded us[5] of evidence that he obtained which established olefin coordination with a variety of dirhodium(II) tetracarboxylates that included the acetate and benzoate derivatives.[6,7] Relative stability constants were determined from retention data by complexation gas chromatography[8] rather than from spectroscopic measurement. Although the two methods operate on different phases, the lack of spectroscopic evidence for complexation of alkanes by dirhodium(II) tetraacetate in solution is disconcerting and requires explanation.

Drago and co-workers have reported that dirhodium(II) tetrakis(heptafluorobutyrate) has significantly greater covalent and electrostatic $\sigma$-acceptor properties than the corresponding butyrate.[9] This report prompted our prior use of Rh$_2$(OOCCF$_3$)$_4$ to examine olefin coordination.[3] In the present study we describe the enhanced capability of Rh$_2$(pfb)$_4$ (pfb = perfluorobutyrate) for coordination with alkenes and the linear correspondence between solution association constants and relative stability constants determined by complexation gas chromatography.

## Experimental Section

**Rhodium(II) Carboxylates.** Rh$_2$(OOCCH$_3$)$_4$ was prepared from RhCl$_3$·3H$_2$O,[10] and Rh$_2$(pfb)$_4$ was obtained from rhodium(II) acetate in refluxing perfluorobutyric acid containing perfluorobutyric anhydride.[9] The isolated product was purified by continuous extraction in anhydrous dichloromethane and, following concentration of the blue solution, Rh$_2$(pfb)$_4$ was obtained as finely divided blue crystals. Green crystals were obtained upon drying in a vacuum oven. Proton NMR spectral analyses demonstrated the absence of acetate, and spectrophotometric determinations in dichloromethane provided a $\lambda_{max}$ value of 626 nm ($a$ = 248 M$^{-1}$ cm$^{-1}$). Rhodium(II) tetrafluoroacetate was prepared according to the methods described by Telser and Drago.[11]

**Association Constants.** Rhodium(II) perfluorobutyrate is very hygroscopic, and extreme care was taken to exclude traces of water, which cause a spectral shift to $\lambda_{max}$ 615–618 nm. Dichloromethane was distilled from calcium hydride and stored over molecular sieves. Solutions of Rh$_2$(pfb)$_4$ in CH$_2$Cl$_2$ were prepared in an inert-atmosphere glovebox under nitrogen, and they were transferred to quartz cells sealed by double septa. A similar procedure was employed with the less hygroscopic Rh$_2$(OOCCF$_3$)$_4$. Olefins were distilled under reduced pressure before use and stored under nitrogen.

Spectrophotometric determinations were performed following sequential injections of 2.5–5.0 $\mu$L of a concentrated solution of the olefin in dichloromethane (0.500–1.00 M) into the rhodium(II) carboxylate solution (3.00 mL). Spectral scans were obtained from a HP 8451A diode array spectrophotometer, and olefin additions were continued through at least eight sequential injections until the limiting $\lambda_{max}$ of the rhodium(II) carboxylate–olefin complex could be determined, which in all cases was 585 ± 5 nm with no evident dependence on the structure of the olefin. The initial addition of olefin to Rh$_2$(pfb)$_4$ generally produced a shift in $\lambda_{max}$ from 626 nm to 605–610 nm, and much smaller changes in $\lambda_{max}$ occurred with subsequent olefin additions. A similar effect was not evident in olefin additions to Rh$_2$(OOCCF$_3$)$_4$, whose initial $\lambda_{max}$ was 610 nm.

Equilibrium constants were calculated from the measured absorbances at several wavelengths in the range of 550–590 nm for Rh$_2$(pfb)$_4$ complexes and in the range of 570–600 nm for Rh$_2$(OOCCF$_3$)$_4$ complexes. A plot of $1/\Delta A$ vs. $1/[\text{olefin}]$ provided a linear relationship (correlation coefficient >0.99) that described a 1:1 complex between the rhodium(II) carboxylate and olefin from which the apparent equilibrium constant was calculated. The first one or two absorbance measurements for experiments performed with Rh$_2$(pfb)$_4$ were not included in these determinations because of their apparent deviation from this relationship. At least two independent measurements were made for each determination. Reproducible values for equilibrium constants were obtained from measurements at two or more wavelengths.

**Spectral Analyses of Olefin Complexes.** In addition to spectrophotometric methods, proton NMR analyses were performed on a Varian FT-80A spectrometer to evaluate the influence of the rhodium(II) carboxylate on proton chemical shifts. The rhodium(II) carboxylate was dissolved in CDCl$_3$, and fixed amounts of the alkene were injected through a septum into the NMR tube. Spectra were taken immediately after addition and also at 30–60 min following addition of the olefin.

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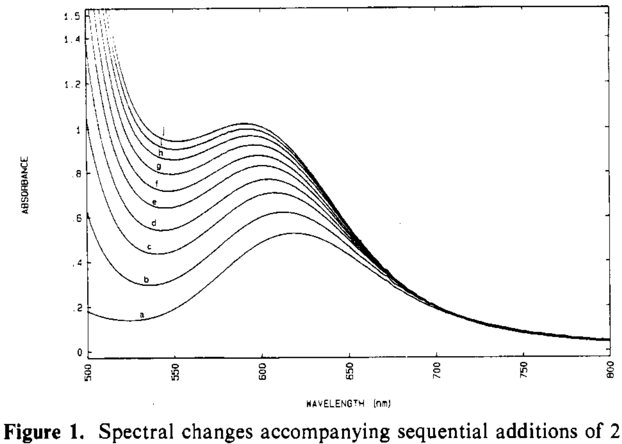

**Figure 1.** Spectral changes accompanying sequential additions of 2,5-dimethyl-2,4-hexadiene to $Rh_2(pfb)_4$ ($2.00 \times 10^{-3}$ M) in anhydrous dichloromethane at 25 °C. [$Me_2C{=}CHCH{=}CMe_2$] ($10^3$ M): (a) 0; (b)–(j) sequential increments of 0.90 up to a total of 9.00.

Spectral shifts remained constant with time except in several experiments with vinyl ethers, where trace amounts of water resulted in their conversion to equivalent amounts of ketal and ketone.

**Competitive Cyclopropanation Reactions Catalyzed by $Rh_2(pfb)_4$.** Ethyl diazoacetate (1.00 mmol) was added at a controlled rate over a 4–8-h period to a stirred solution of cyclohexene and styrene (minimum amount of each olefin 10.0 mmol) and $Rh_2(pfb)_4$ (0.010 mmol) under nitrogen at 25 °C. After addition was complete, dibenzyl ether was added to the reaction solution as the internal standard followed by 50 mL of ethyl ether. The resulting ether solution was washed twice with 50-mL portions of aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. The ether and excess olefin were distilled under reduced pressure. The product mixture was then subjected to GC analysis with an SP-2330 capillary column. Product isomer ratios were identical with those obtained from reactions with the single olefin.[12] Cyclopropane product yields were obtained with the use of experimentally measured relative response ratios for each cyclopropane pair and generally accounted for greater than 95% of the ethyl diazoacetate initially employed.

## Results

Sequential addition of aliquots of 2,5-dimethyl-2,4-hexadiene to $Rh_2(pfb)_4$ in anhydrous dichloromethane produces the spectral changes described in Figure 1. Like those with $Rh_2(OOCCF_3)_4$,[3] there is no isosbestic point to suggest a uniformity in the transition from uncoordinated rhodium(II) carboxylate to the olefin complex. However, unlike the spectral changes observed with the use of $Rh_2(OOCCF_3)_4$, where small uniform changes in $\lambda_{max}$ accompany each addition of the alkene, the first olefin addition to $Rh_2(pfb)_4$ causes a substantial change in $\lambda_{max}$ ($\Delta\lambda = 11$ nm), and subsequent aliquots produce much smaller shifts ($\Delta\lambda < 5$ nm). The same pattern is evident in spectral displays obtained with styrene and vinyl ethers. In contrast, with cyclohexene, 1-hexene, or 2-methyl-2-butene additions to $Rh_2(pfb)_4$ a different pattern of spectral changes emerges (Figure 2). Isosbestic points are observed (at 613 nm with cyclohexene, 605 nm with 1-hexene, and 612 nm with 2-methyl-2-butene), but they do not include the spectrum of $Rh_2(pfb)_4$ prior to addition of the olefin. Also, like the spectral changes observed for 2,5-dimethyl-2,4-hexadiene, the first olefin addition causes a substantial change in $\lambda_{max}$ that is uncharacteristic of those observed with further olefin additions.

Because of uncertainties associated with the spectral display above 600 nm for olefin association with $Rh_2(pfb)_4$, $\Delta A$ values were chosen from the spectral region between 550 and 590 nm. Here, uniform values for equilibrium constants could be obtained but with variation from calculations at three different wavelengths (±15%) significantly greater than those determined for $Rh_2(OOCCF_3)_4$.[1] Table I reports the apparent equilibrium constants for complex formation between $Rh_2(pfb)_4$ and a representative series of olefins together with those for association with $Rh_2(OOCCF_3)_4$. Equilibrium constants for styrene association with these rhodium(II) perfluoroalkanoates are the lowest, and those with vinyl ethers are the highest. $\alpha,\beta$-Unsaturated esters do not form complexes with these rhodium compounds. 2,5-Dimethyl-2,4-hexadiene has a higher association constant than does 2-methyl-2-butene, but this is probably due to the two double bonds of 2,5-dimethyl-2,4-hexadiene acting independently of each other.

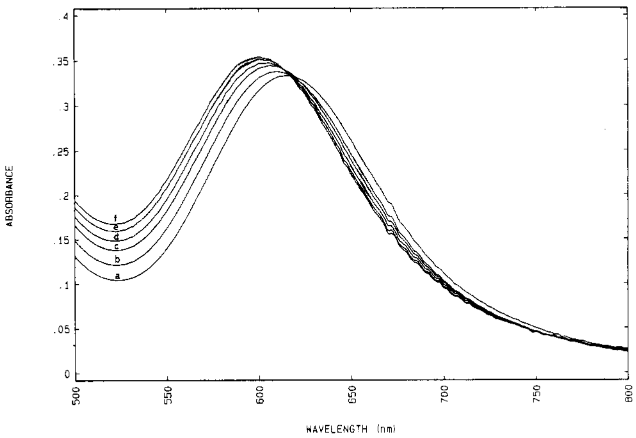

**Figure 2.** Spectral changes accompanying sequential additions of cyclohexene to $Rh_2(pfb)_4$ ($1.32 \times 10^{-3}$ M) in anhydrous dichloromethane at 25 °C. [$C_6H_{10}$] ($10^3$ M): (a) 0; (b) 0.95; (c) 1.90; (d) 2.85; (e) 3.80; (f) 4.76.

**Table I.** Equilibrium Constants for Olefin Coordination with Rhodium(II) Trifluoroacetate and Rhodium(II) Perfluorobutyrate in Dichloromethane at 25 °C

| | $10^{-2}K_{eq}$, $M^{-1}$ | |
|---|---|---|
| olefin | $Rh_2(OOCCF_3)_4$[a] | $Rh_2(OOCC_3F_7)_4$[b] |
| styrene | 0.11 | 0.70 |
| *trans*-3-hexene | 0.46 | |
| *trans*-4-octene | 0.48 | 1.11 |
| 1-hexene | 0.42 | 1.50 |
| cyclohexene | 0.62 | 2.00 |
| 2,5-dimethyl-2,4-hexadiene | 1.50 | 4.51 |
| 2-methyl-2-butene | 1.33 | 2.94 |
| *n*-butyl vinyl ether | 2.10 | 6.50 |
| ethyl vinyl ether | 2.24 | 8.60 |
| 2-methoxypropene | 5.78 | 9.32 |

[a] [$Rh_2(OOCCF_3)_4$] = $4.00 \times 10^{-4}$ M. [b] [$Rh_2(OOCC_3F_7)_4$] = $(1.00–4.00) \times 10^{-3}$ M; individual values ±15%.

When 2,5-dimethyl-2,4-hexadiene is maintained under nitrogen in the presence of $Rh_2(pfb)_4$ for extended periods of time, the solution turns bright yellow and the $\pi^*_{RhRh} \rightarrow \sigma^*_{RhRh}$ absorption band is no longer visible. The same change occurs with norbornadiene, but here the transformation is very rapid. Other olefins employed in this study did not cause this modification of the rhodium(II) perfluorobutyrate. These transformations have been previously reported for reactions between $Rh_2(OOCCF_3)_4$ and norbornadiene, but on a time scale that is much slower than the one we observe with $Rh_2(pfb)_4$, and they were attributed to a reduction of rhodium(II) to rhodium(I).[13]

Substantial NMR spectral changes for the vinyl proton of 2-methyl-2-butene result from the addition of this olefin to $Rh_2(OOCCF_3)_4$: $\Delta\delta = 1.1$ for the vinyl proton and $\Delta\delta = 0.15–0.20$ for methyl protons at 1:3 [$Rh_2(OOCCF_3)$]:[2-methyl-2-butene]. Similar effects were observed with the use of $Rh_2(pfb)_4$: $\Delta\delta = 1.3$ for the vinyl proton of 2-methyl-2-butene at 1:3 [$Rh_2(pfb)_4$]:[2-methyl-2-butene]. In addition, downfield shifts of olefinic and methyl protons were observed with 2-methoxypropene ($\Delta\delta = 1.62$ for each of the two vinyl protons, $\Delta\delta = 0.20$ for the methyl protons, and $\Delta\delta = 0.30$ for the methoxy protons at 1:5 [$Rh_2(OOCCF_3)_4$]:[2-methoxypropene]) and $\alpha$-methoxystyrene ($\Delta\delta = 0.62$ and 0.60 for the two vinyl protons and $\Delta\delta = 0.10$ for the methoxy protons at 1:8 [$Rh_2(OOCCF_3)_4$]:[$\alpha$-methoxy-

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styrene]). Downfield shifts of 0.1–0.3 ppm were observed even when the concentration of alkene was 20 times that of the rhodium(II) carboxylate.

Competitive cyclopropanation reactions of ethyl diazoacetate with two alkenes, cyclohexane and styrene, were performed to evaluate the influence of olefin association on the catalytic function of $Rh_2(pfb)_4$. We have previously shown that relative reactivities in these transformations were dependent on the molar ratio of reactant olefins in reactions catalyzed by copper(I) triflate,[2] which is known to form olefin complexes,[14] but not with rhodium(II) acetate. Schurig has suggested that metal–olefin interactions in rhodium(II) carboxylate catalyzed cyclopropanation reactions should be further scrutinized in view of the propensity of the rhodium(II) compounds to coordinate with olefins.[5] Results similar to those obtained with $Rh_2(OAc)_4$ are observed with $Rh_2(pfb)_4$. There is a linear dependence of the product ratio on the molar ratio of reactants (relative reactivity 0.70), suggesting that olefin coordination is not involved in this transformation, but olefin coordination with $Rh_2(pfb)_4$ does inhibit catalyst turnover as demonstrated by the rate for nitrogen evolution as a function of olefin concentration or olefin coordinating ability. Apparently the coordinated olefin is replaced by the diazo compound and has no directive role in these reactions.

## Discussion

Dirhodium(II) tetrakis(trifluoroacetate) and the corresponding perfluorobutyrate form $\pi$ complexes with alkenes in a 1:1 stoichiometry. Equilibrium constants for olefin coordination in dichloromethane show that the $Rh_2(pfb)_4$–olefin complexes are approximately 3 times more stable than those derived from $Rh_2(OOCCF_3)_4$. The olefin proton NMR spectral shifts resulting from the combination of alkenes with rhodium(II) carboxylates provide further evidence for these olefin complexes. Bonding occurs at the carbon–carbon double bond rather than at oxygen in vinyl ethers, and as suggested by the identical downfield chemical shifts for the two olefinic protons of 2-methoxypropene and $\alpha$-methoxystyrene, association of these alkenes with $Rh_2(OOCCF_3)_4$ places the two olefinic protons in identical environments. The vinyl ethers examined were more responsive than 2-methyl-2-butene to rhodium(II)-induced vinyl proton chemical shifts, and this could be due to electronic or steric effects on the closeness of axial approach of the carbon–carbon double bond to rhodium or to a combination of these effects.

Rhodium(II) carboxylates are uniquely designed for axial coordination with electron-donor ligands.[15] Adduct formation with n-donor molecules is a two-step process involving initial formation of a 1:1 complex.[16] Once the 1:1 adduct has formed, the second axial ligand is less strongly bound to rhodium at the second coordination site.[17] The formation of only 1:1 adducts between $Rh_2(OOCCF_3)_4$ or $Rh_2(pfb)_4$ and olefins is consistent with these observations.

The spectral changes observed upon successive addition of aliquots of an alkene to $Rh_2(pfb)_4$, particularly those evident in Figure 2, suggest that the initial association of an olefin with the rhodium(II) carboxylate is more complex than simply the combination of the two species (eq 1). If $Rh_2(pfb)_4$ is unassociated in solution, we should have observed a spectral display that exhibited an isosbestic point that included the initial uncomplexed rhodium carboxylate. That we do not observe this condition suggests that the rhodium compound which forms $\pi$ complexes with alkenes is coordinated either to a weaker electron-donor molecule, such as the solvent dichloromethane, or to itself. Drago and co-workers have established that electron withdrawal from perfluorocarboxylate complexes of rhodium(II) enhances the Lewis acidity of the axial coordination sites.[9,18] However, water is not the "weaker" electron-donor molecule since even traces of water cause a substantial spectral shift to lower wavelengths, and water as a ligand of $Rh_2(pfb)_4$ is not displaced by alkene. In addition, if dichloromethane is the responsible ligand, we would have expected a uniform spectral transition (eq 2) upon addition of the

$$Rh_2(pfb)_4(CH_2Cl_2) + \text{olefin} \rightleftharpoons Rh_2(pfb)_4(\text{olefin}) + CH_2Cl_2 \tag{2}$$

alkene. We are left to suggest that $Rh_2(pfb)_4$ is coordinated to itself and exists as an oligomer in solution (eq 3). Such association

$$[Rh_2(pfb)_4]_n + \text{olefin} \rightleftharpoons (n-1)Rh_2(pfb)_4 + Rh_2(pfb)_4(\text{olefin}) \tag{3}$$

has been reported to occur in the solid state for $Rh_2(OOCH)_4$,[19] where the oxygen atom of one rhodium(II) carboxylate unit is an axial ligand for another rhodium(II) carboxylate, but a detailed structure has not appeared. This explanation, coupled with the relative ability of rhodium(II) carboxylates to form complexes with n-donor molecules as opposed to $\pi$-electron donors,[6] might account for the absence of observable olefin $\pi$ complexes with rhodium(II) alkanoates in solution but not on stationary supports in the gas phase.[5]

The association constants for several of the alkenes reported in Table I have also been determined by complexation gas chromatography.[5] A plot of these values shows remarkable linearity and signifies that the same associative processes are being measured by the two methods. The slope of the line is 3.0, which is consistent with the temperature difference between these two measurements and corresponds to $\Delta H_{assoc} = 3$ kcal/mol.

**Acknowledgment.** The support of the National Science Foundation for this research is gratefully acknowledged. We thank the Johnson Matthey Co. for their loan of rhodium(III) chloride.

**Supplementary Material Available:** Proton NMR chemical shift data for $Rh_2(OOCCF_3)_4(CH_3C(CH_3)CHCH_3)$ (Figure 3), a plot of relative reactivity data for $Rh_2(pfb)_4$-catalyzed cycloprotonation of cyclohexene/styrene (Figure 4), and a plot of association constants for $Rh_2(pfb)_4$ and selected olefins obtained in dichloromethane and by complexation gas chromatography (Figure 5) (3 pages). Ordering information is given on any current masthead page.

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# A Ruthenium Tris(diimine) Complex with Three Different Ligands

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*Received March 2, 1987*

There has been a great deal of recent interest in the chemistry of ruthenium polypyridine complexes.[1] Much of this interest has centered around the utility of such complexes as photocatalysts for the decomposition of water into its elements.[2] The absorption of sunlight by a ruthenium polypyridine catalyst results in the

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