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Dehydrogenation of a Cyclohexyl Group in Tricyclohexylphosphine Complexes of Ruthenium. X-ray Crystal Structure of $[Ru(C_6H_9PCy_2)(CF_3COO)]_2(\mu\text{-}CF_3COO)_2(\mu\text{-}OH_2)$

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Summary: $RuH(H_2)(OCOCF_3)(PCy_3)_2$ (**1**) is unreactive toward D_2 and ${}^tBuCH{=}CH_2$, whereas $RuH_2(OCOCF_3)_2(PCy_3)_2$ (**2**) reacts instantly with D_2 to exchange H_2 for D_2 and with cyclooctene to yield cyclooctane and $[Ru(C_6H_9PCy_2)(OCOCF_3)]_2(\mu\text{-}OCOCF_3)_2(\mu\text{-}OH_2)$ (**5**). The crystal structure of $\mathbf{5}\cdot(C_8H_{14})_2$ demonstrates the dehydrogenation of a cyclohexyl group of PCy_3 and the presence in **3** of a rare example of a bridging water molecule strongly hydrogen-bonded to the terminal trifluoroacetato groups. In solution, **5** is shown to adopt three isomeric forms. $P2/c$, $Z = 2$, $a = 13.034$ Å, $b = 14.751$ Å, $c = 18.261$ Å, $\beta = 105.49°$, $V = 3383$ Å^3, $R = 0.025$, $R_w = 0.030$ for 3357 reflections with $F_o^2 > 3\sigma(F_o^2)$.

Hydrogen transfer is a classical process in organometallic chemistry. It is usual in catalytic reactions such as hydrogenation, isomerization, oligomerization of olefins, etc.[1] The recent development of the chemistry of dihydrogen compounds[2] has stressed the question of a possible novel reactivity of such species. The greater reactivity of dihydrogen complexes when compared to their polyhydride counterparts is well-established and results from the ready dissociation of a dihydrogen molecule.[3] Equally well-established is the acidity of coordinated dihydrogen in cationic complexes.[3a,4]

A novel cis stabilizing interaction between a hydride and coordinated dihydrogen has been discovered by Caulton and Eisenstein,[5] which may be related to the recent demonstration by Crabtree of an associating fluxional process for the interconversion of hydride and dihydrogen.[6]

We have been studying for a few years the synthesis and reactivity of ruthenium dihydrogen derivatives,[7] and in related studies, we have observed hydrogen-elimination reactions that could occur through unstable dihydrogen derivatives.[8] We describe in this note the reactivity of two complexes, $RuH(H_2)(OCOCF_3)(PCy_3)_2$ (**1**) and $RuH_2(OCOCF_3)_2(PCy_3)_2$ (**2**), for which we have proposed a dihydride/dihydrogen equilibrium[7b] in hydrogen-transfer and hydrogen-elimination reactions. The crystal structure of a new μ-aquo derivative resulting from these reactions is also reported. These reactions have been briefly mentioned in a preliminary communication.[7b]

Results and Discussion

Compound **1** has been shown recently to contain coordinated dihydrogen.[7b,d] One of the arguments for the presence of undissociated dihydrogen is the observation of roughly the same T_1 minimum as for $RuH(H_2)I(PCy_3)_2$ (**3**) recently characterized by an X-ray crystal structure.[7c]

However, we have found that **1** is very stable. It does not eliminate H_2 upon heating in vacuo up to 100 °C nor does it react with D_2 to exchange H_2 for D_2. Similarly, **1** does not react at 100 °C with *tert*-butylethylene. In contrast, **2** and **3** react instantly with D_2 at room temperature. Thus, bubbling D_2 in a solution of **2** or **3** in C_6D_6 at room temperature for 2 min results in the complete disappearance of the hydride signals. In the case of **2**, attempts to prepare partially deuteriated derivatives were unsuccessful.

Furthermore, **2** slowly loses H_2 in solution as monitored by ^{31}P NMR, and in vacuo, the complex $Ru(OCOCF_3)_2(PCy_3)_2$ (**4**) could be obtained according to eq 1. This compound shows as expected two bidentate trifluoroacetato groups by infrared spectroscopy and two trans equivalent phosphorus by ^{31}P NMR.

$$RuH_2(OCOCF_3)_2(PCy_3)_2 \rightarrow Ru(OCOCF_3)_2(PCy_3)_2 + H_2 \qquad (1)$$

This hydrogen-elimination reaction is slow and stops with the formation of **4**. However, in the presence of an olefin, a hydrogen-transfer reaction takes place. This reaction was performed with cyclooctene since hydrogen transfer from PCy_3 to cyclooctene has been demonstrated on an iridium complex.[9] Thus, the reaction of **2** in neat cyclooctene for 3 h leads to the formation of 2 mol of cyclooctane/mole of complex (GLC analysis) and a new complex (**5**) as yellow crystals. The X-ray crystal structure (see Figure 2 and Table I) shows compound **5** to be dimeric, with two Ru^{II} units bridged by two trifluoroacetato groups and one water molecule. The octahedral geometry around each ruthenium is achieved by a monodentate trifluoroacetato group and a phosphine acting as a bidentate ligand through phosphorus and the double bond of a cyclohexenyl group. The latter results from the dehydrogenation of a cyclohexyl ring. Thus, C(3)–C(4) is short (1.376 (7) Å) as expected for a coordinated olefinic group. The intermetallic Ru···Ru distance is very long (3.851 (6) Å) and rules out any direct metal–metal interaction. The most unexpected aspect of this structure is the presence of a bridging water molecule hydrogen-bonded to the terminal trifluoroacetato groups (Ru–O(1),

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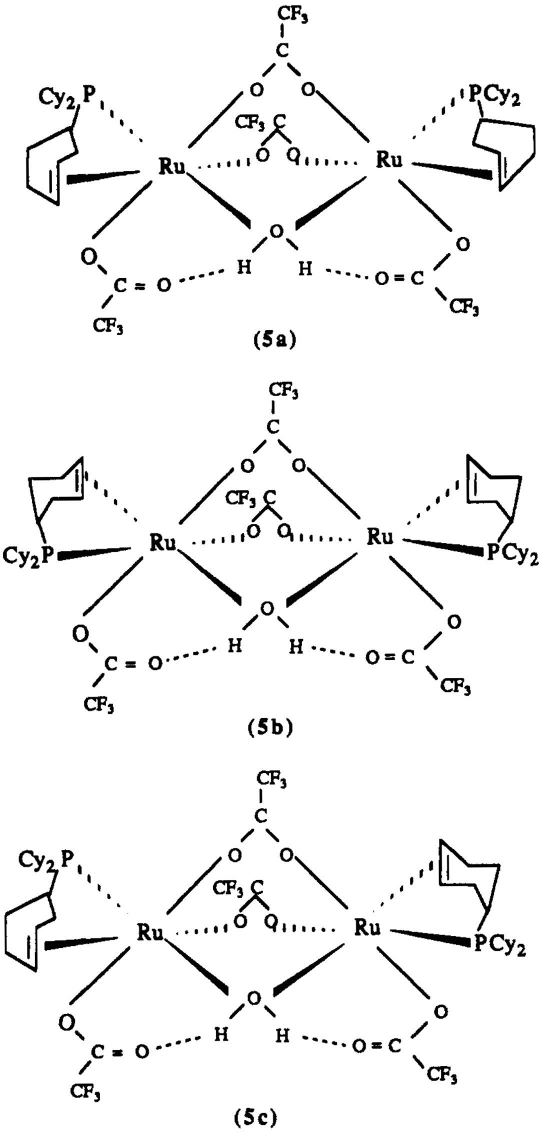

Figure 1. Three possible isomers for the structure of 5 in solution.

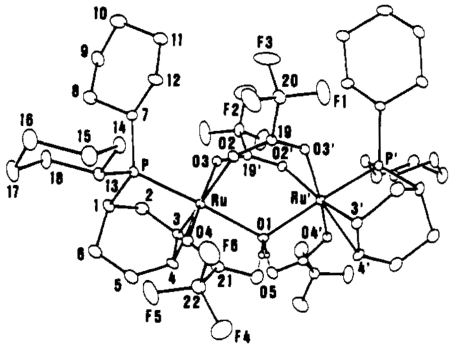

Figure 2. ORTEP view of $[Ru_2(C_6H_9PCy_2)(OCOCF_3)]_2(\mu\text{-}H_2O)$ (5). All hydrogen atoms except those of the water molecule have been omitted for clarity.

2.216 (1) Å; O(1)-H(O(1)), 0.95 Å; O(1)···O(5), 2.526(4) Å).

It is interesting to note that this molecule adopts a "hemerythrin-like" core structure. Thus, a lot of interest has recently been devoted to the understanding and synthesis of model compounds of hemerythrin.[10-14] Numerous

Table I. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for 11[a]

Ru-P	2.2601 (8)	Ru-O(4)	2.091 (2)
Ru-O(1)	2.216 (1)	Ru-C(3)	2.188 (4)
Ru-O(2)	2.147 (2)	Ru-C(4)	2.186 (4)
Ru-O(3)	2.096 (2)	Ru-M(C(34))	2.075 (4)
P-Ru-O(1)	176.84 (6)	O(2)-Ru-O(3)	85.39 (9)
P-Ru-O(2)	96.26 (6)	O(2)-Ru-O(4)	81.93 (9)
P-Ru-O(3)	90.71 (6)	O(2)-Ru-C(3)	163.1 (1)
P-Ru-O(4)	89.42 (6)	O(2)-Ru-C(4)	159.4 (1)
P-Ru-C(3)	85.28 (9)	O(2)-Ru-M(C(34))	176.1 (1)
P-Ru-C(4)	89.68 (9)	O(3)-Ru-O(4)	167.26 (9)
P-Ru-M(C(34))	87.34 (9)	O(3)-Ru-C(3)	77.7 (1)
O(1)-Ru-O(2)	86.74 (7)	O(3)-Ru-C(4)	114.3 (1)
O(1)-Ru-O(3)	90.51 (7)	O(3)-Ru-M(C(34))	96.0 (1)
O(1)-Ru-O(4)	90.03 (7)	O(4)-Ru-C(3)	115.0 (1)
O(1)-Ru-C(3)	92.13 (9)	O(4)-Ru-C(4)	78.4 (1)
O(1)-Ru-C(4)	87.2 (1)	O(4)-Ru-M(C(34))	96.7 (1)
O(1)-Ru-M(C(34))	89.6 (1)	C(3)-Ru-C(4)	36.9 (1)
P-C(1)	1.860 (4)		
P-C(7)	1.859 (4)	P-C(13)	1.851 (4)
Ru-P-C(1)	100.6 (1)	C(1)-P-C(7)	103.1 (2)
Ru-P-C(7)	114.0 (1)	C(1)-P-C(13)	109.0 (2)
Ru-P-C(13)	116.8 (1)	C(7)-P-C(13)	111.6 (2)
C(1)-C(2)	1.528 (6)	C(10)-C(11)	1.518 (7)
C(2)-C(3)	1.541 (5)	C(11)-C(12)	1.504 (6)
C(3)-C(4)	1.384 (6)	C(12)-C(7)	1.502 (6)
C(4)-C(5)	1.464 (5)	C(13)-C(14)	1.532 (6)
C(5)-C(6)	1.500 (6)	C(14)-C(15)	1.519 (6)
C(6)-C(1)	1.520 (6)	C(15)-C(16)	1.533 (6)
C(7)-C(8)	1.503 (5)	C(16)-C(17)	1.526 (7)
C(8)-C(9)	1.529 (7)	C(17)-C(18)	1.515 (6)
C(9)-C(10)	1.518 (7)	C(18)-C(13)	1.532 (5)
P-C(1)-C(2)	103.0 (2)	P-C(13)-C(18)	115.6 (3)
P-C(1)-C(6)	116.1 (3)	Ru-C(3)-C(2)	107.4 (3)
P-C(7)-C(8)	118.6 (3)	Ru-C(3)-C(4)	71.5 (2)
P-C(7)-C(12)	112.4 (3)	Ru-C(4)-C(3)	71.7 (2)
P-C(13)-C(14)	113.4 (2)	Ru-C(4)-C(5)	115.6 (3)
C(6)-C(1)-C(2)	109.1 (3)	C(9)-C(10)-C(11)	110.5 (4)
C(1)-C(2)-C(3)	108.0 (4)	C(10)-C(11)-C(12)	112.2 (4)
C(2)-C(3)-C(4)	119.3 (3)	C(11)-C(12)-C(7)	111.7 (4)
C(3)-C(4)-C(5)	124.4 (3)	C(18)-C(13)-C(14)	109.1 (3)
C(4)-C(5)-C(6)	114.4 (4)	C(13)-C(14)-C(15)	109.2 (3)
C(5)-C(6)-C(1)	110.6 (3)	C(14)-C(15)-C(16)	110.4 (4)
C(12)-C(7)-C(8)	111.3 (3)	C(15)-C(16)-C(17)	108.9 (4)
C(7)-C(8)-C(9)	110.2 (3)	C(16)-C(17)-C(18)	109.9 (4)
C(8)-C(9)-C(10)	109.9 (4)	C(17)-C(18)-C(13)	109.7 (4)
C(19)-O(2)	1.226 (4)	O(2)-C(19)-O(3)′	133.5 (3)
C(19)-O(3)′	1.223 (4)	O(2)-C(19)-C(20)	113.1 (3)
C(19)-C(20)	1.526 (6)	O(3)′-C(19)-C(20)	113.4 (3)
Ru-O(1)-Ru′	120.9 (1)	Ru-O(3)-C(19)′	135.0 (2)
Ru-O(2)-C(19)	134.5 (2)	Ru-O(4)-C(21)	125.5 (2)
O(1)-H(O(1))	0.95 (3)	H(O(1))-O(O(1))-H(O(1))′	113 (2)
Ru-O(1)-H(O(1))	93 (2)	Ru-O(1)-H(O(1))′	119 (2)
O(1)...O(5)	2.533 (3)		
H(O(1))...O(5)	1.59 (3)	O(1)-H(O1)...O(5)	169 (2)
O(4)-C(21)	1.262 (4)	C(21)-O(5)	1.216 (4)
C(21)-C(22)	1.536 (6)		
C(20)-F(1)	1.279 (5)	C(22)-F(4)	1.276 (5)
C(20)-F(2)	1.284 (5)	C(22)-F(5)	1.274 (4)
C(20)-F(3)	1.289 (6)	C(22)-F(6)	1.288 (6)
C(19)-C(20)-F(1)	112.9 (4)	C(21)-C(22)-F(4)	112.1 (3)
C(19)-C(20)-F(2)	110.1 (4)	C(21)-C(22)-F(5)	114.7 (4)
C(19)-C(20)-F(3)	106.6 (4)	C(21)-C(22)-F(6)	109.3 (3)
F(1)-C(20)-F(2)	109.8 (4)	F(4)-C(22)-F(5)	109.8 (3)
F(1)-C(20)-F(3)	109.2 (4)	F(4)-C(22)-F(6)	104.7 (4)
F(2)-C(20)-F(3)	108.1 (4)	F(5)-C(22)-F(6)	105.6 (3)

[a] M(C(34)) is the midpoint of C(3)-C(4) bond. ′ denotes the symmetry operation 1 − x, y, 1/2 − z.

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Table II. NMR Data for the Three Isomers of Compound 5

isomers[a]	NMR, ppm				
	^1H		$^{31}P\{^1H\}$	$^{13}C\{^1H\}$	
5a	11.5 (s)[b]	5.0 (d t; H_4)[c] 4.8 (d t; H_3)[c]	70.6 (s)	85.6 (C_4);[c] 77.5 (C_3)[d]	18–35 (m)[e]
5b	10.9 (s)[b]	5.2 (d t; H_4)[c] 4.7 (d t; H_3)[c]	69.8 (s)	not seen	18–35 (m)[e]
5c	11.1 (s)[b]	5.0 (d t; H_4)[c] 4.8 (d t; H_3)[c]	69.4 (s)	85.3 (C_4);[c] 78.9 (C_3)[d]	18–35 (m)[e]
	11.2 (s)[b]	5.3 (d t; H_4)[c] 4.6 (d t; H_3)[c]	70.8 (s)	85.5 (C_4);[c] 76.8 (C_3)[d]	

[a] NMR in C_6D_6. [b] Protons of water. [c] Olefinic protons. [d] Olefinic carbons. [e] Carbons not olefinic.

diiron(III,III) derivatives[11] and a few diruthenium(III,III)[12] analogues have been reported. Mixed-valence species have also been reported and even a diiron(II,III) complex containing a bridging hydroxo ligand.[13]

Only a few structurally characterized complexes have been shown to contain coordinated water.[15] Very recently, the presence of a bridging water molecule has been demonstrated in a mixed valence Ru^{II}–Ru^{III} derivative.[16]

Singleton and co-workers have reported a few years ago a preliminary account of the crystal structure of a complex very close to ours, namely, $Ru_2(C_8H_{12})_2(O_2CCF_3)_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}H_2O)$.[17] Like 5, this complex shows a long intermetallic distance (3.733 (1) Å) and hydrogen bonding between the bridging water molecule and the terminal trifluoroacetato groups.

The reason for the stability of coordinated water probably lies in the two strong hydrogen bonds formed with the terminal trifluoroacetato ligands. Similar hydrogen bonding between water and carboxylate groups can also be present in biological systems.

Although it cannot be considered as an enzyme model, the successful isolation of complex 5 demonstrates the possible existence of such aquo-bridged reduced species. As expected for a diruthenium(II,II) complex, 5 is diamagnetic and we have studied its NMR spectroscopic properties.

The ^{31}P NMR spectrum shows four peaks in an approximate 1:2:2:4 ratio (see Table II). Surprising at first, this behavior was also observed for the olefinic carbons in the ^{13}C spectrum and for the H_2O and olefinic protons in the ^1H NMR spectrum. We propose the existence of three isomers (see Figure 1). Since in the three cases we can observe the aquo protons near δ 11 ppm, we think that strong hydrogen bonding is present in the three isomers between the terminal trifluoroacetato groups and these protons of water (as suggested here above, the stability of the coordination of water is probably related to this hydrogen bonding).

Therefore, only three possibilities remain for the structure of the complex: the two phosphorus trans to water as on the X-ray structure (**5a**), the two double bonds trans to water (**5b**) or an asymmetric structure with the water molecule trans to phosphorus on one side and trans to a C═C double bond on the other (**5c**) (see Figure 1).

Considering the presence of these three isomers, it is easy to attribute the NMR spectra. Thus, the ^{31}P NMR spectrum shows the three isomers as a singlet (or two singlets in the case of **5c** near δ 70 ppm), while the ^{13}C NMR spectrum shows a singlet (or two singlets) for the olefinic carbons respectively near δ 77 (C_3) and δ 85 ppm (C_4), the water molecule near δ 11 ppm, and the olefinic protons near δ 5 ppm (Table II).

The mechanism of the formation of 5 involves a transfer of hydrogen from a cyclohexyl ring of PCy_3 to cyclooctene. Evidence for this mechanism comes from the right amount of cyclooctane found by GLC. In cyclooctene solution, there is probably an equilibrium of dissociation of PCy_3; the presence of two phosphines would prevent any organic molecules from approaching the metal center. Dimerization is a common feature of carboxylate chemistry. Finally a water molecule, which most probably arises from the trifluoroacetic acid, completes the coordination sphere of both ruthenium atoms (eq 2).

$$2RuH_2(OCOCF_3)_2(PCy_3)_2 + 4C_8H_{14} + H_2O \rightarrow [Ru(OCOCF_3)(C_6H_9PCy_2)]_2(\mu\text{-}OCOCF_3)_2(\mu\text{-}H_2O) + 4C_8H_{16} + 2PCy_3 \quad (2)$$

Conclusion

In conclusion, this note demonstrates the low reactivity of $RuH(H_2)(OCOCF_3)(PCy_3)_2$ toward both olefins and exchange with deuterium. This observation is surprising for a dihydrogen complex but can be related to the electronic saturation of the complex and steric protection by the bulky tricyclohexylphosphine ligands. The reaction with $RuH_2(OCOCF_3)_2(PCy_3)_2$ is a classical transfer of hydrogen. Dissociation of PCy_3 from the crowded heptacoordinate species or from the dihydrogen tautomer as initial step could explain the much higher reactivity of the dihydride complex and the formation of the unexpected dinuclear species. Finally, the isolation of this species demonstrates the possibility for water to occupy a bridging site in related reduced biological systems containing dinuclear active sites bridged by carboxylate ligands.

Experimental Section

General Considerations. Microanalyses were performed in the lab. All manipulations were carried out under dry argon by using standard Schlenk tube techniques. The solvents were degassed and distilled before used. Infrared spectra were recorded in the solid state as Nujol mulls or KBr disks on a Perkin-Elmer 983 spectrometer. NMR spectra were recorded on Bruker WH90, WM250, or AC 200 spectrometers operating in the Fourier transform mode.

$RuH(H_2)(OCOCF_3)(PCy_3)_2$ (1) and $RuH_2(OCOCF_3)_2(PCy_3)_2$ (2) were prepared following published methods.[7b,d]

$[Ru(OCOCF_3)_2(PCy_3)_2]$ (4). $RuH_2(OCOCF_3)_2(PCy_3)_2$ (0.15 g, 0.168 mmol) was dissolved in 10 mL of hexane. The resulting solution was heated at 60 °C under reduced pressure for 1 h. It was then cooled at −18 °C, depositing yellow microcrystals of the complex. Isolated yield: 40%. The reaction was also followed by ^{31}P NMR (spectroscopic yield. 90%). IR: 1620, 1404 cm^{-1} (chelating $OCOCF_3$ group). ^{31}P NMR: δ 44.20 ppm (s). ^1H NMR: δ 0.8–2.2 ppm (br). Microanalytical data calcd for $4\cdot{}^1/_2C_6H_{14}$: C, 55.42; H, 8.92. Found: C, 55.55; H, 8.54.

$[Ru(OCOCF_3)(C_6H_9PCy_2)]_2(\mu\text{-}OCOCF_3)_2(\mu\text{-}H_2O)$ (5). $RuH_2(OCOCF_3)_2(PCy_3)_2$ (0.18 g, 0.202 mmol) was added to 5 mL (excess) of cyclooctene freshly passed over an alumina column. The yellow solution was heated for 3 h at 60 °C during which it

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Table III. Summary of Crystal and Intensity Collection Data for 11

compd	$[Ru(C_6H_9PC_6H_9Cy_2)(OCOCF_3)]_2(\mu\text{-}OCOCF_3)_2(\mu\text{-}OH_2)(C_8H_{14})_2$
formula	$C_{60}H_{92}F_{12}O_9P_2Ru_2$
fw	1449.45
a, Å	13.034 (2)
b, Å	14.751 (2)
c, Å	18.261 (3)
β, deg	105.49 (1)
V, Å^3	3383 (1)
Z	2
F(000)	1500
d_{calcd}, g·cm^{-3}	1.423
space group	C_{2h}^4–$P2/c$ (No. 13)
radiation	Mo Kα from graphite monochromator (λ = 0.71073 Å)
linear abs coeff, cm^{-1}	μ = 5.6
temp, °C	20
receiving aperture, mm	4.0 × 4.0
takeoff angle, deg	3.85
scan mode	θ–2θ
scan range, deg	1.00 + 0.35 tan θ
scan speed, deg·min^{-1}	1.1–10.1
2θ limits, deg	50

Table IV. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å^2 × 100) with Esd's in Parentheses for 11[a,b]

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
Ru	0.38599 (2)	0.12975 (2)	0.15761 (1)	3.03 (4)
P	0.26979 (7)	0.19872 (6)	0.05913 (5)	3.5 (1)
C(1)	0.2997 (3)	0.1388 (3)	−0.0224 (2)	5.4 (7)
C(2)	0.4212 (4)	0.1346 (3)	0.0003 (2)	6.8 (8)
C(3)	0.4568 (3)	0.0740 (2)	0.0713 (2)	4.5 (6)
C(4)	0.3865 (3)	0.0109 (2)	0.0862 (2)	4.6 (6)
C(5)	0.2838 (4)	−0.0123 (3)	0.0335 (3)	6.7 (8)
C(6)	0.2555 (4)	0.0432 (3)	−0.0379 (2)	6.5 (8)
C(7)	0.3039 (3)	0.3185 (2)	0.0445 (2)	4.4 (6)
C(8)	0.2546 (5)	0.3620 (3)	−0.0312 (2)	7.4 (9)
C(9)	0.3082 (5)	0.4530 (3)	−0.0367 (2)	7.5 (9)
C(10)	0.2965 (5)	0.5152 (3)	0.0268 (3)	9 (1)
C(11)	0.3429 (5)	0.4709 (3)	0.1036 (3)	8 (1)
C(12)	0.2956 (4)	0.3789 (3)	0.1088 (2)	6.5 (8)
C(13)	0.1266 (3)	0.1856 (3)	0.0531 (2)	4.1 (6)
C(14)	0.0942 (3)	0.2286 (3)	0.1200 (2)	5.0 (7)
C(15)	−0.0187 (3)	0.2000 (4)	0.1173 (3)	6.8 (8)
C(16)	−0.0961 (3)	0.2308 (4)	0.0426 (3)	7.2 (9)
C(17)	−0.0628 (3)	0.1883 (4)	−0.0237 (3)	7.4 (9)
C(18)	0.0496 (3)	0.2173 (4)	−0.0214 (2)	6.1 (8)
O(1)	$^1/_2$	0.0557 (2)	$^1/_4$	3.4 (5)
H(O(1))	0.446 (2)	0.0202 (4)	0.262 (2)	7.9 (3)
O(2)	0.3532 (2)	0.2132 (2)	0.2450 (1)	3.7 (4)
O(3)	0.5030 (2)	0.2262 (1)	0.1548 (1)	3.5 (4)
C(19)	0.4063 (3)	0.2413 (2)	0.3067 (2)	3.5 (6)
C(20)	0.3465 (3)	0.3092 (3)	0.3430 (3)	6.1 (8)
F(1)	0.3779 (3)	0.3091 (3)	0.4156 (2)	13.7 (9)
F(2)	0.2461 (2)	0.2934 (3)	0.3212 (2)	11.8 (8)
F(3)	0.3633 (4)	0.3881 (2)	0.3181 (3)	16 (1)
O(4)	0.2606 (2)	0.0537 (2)	1.773 (1)	3.8 (4)
C(21)	0.2665 (3)	0.0027 (2)	0.2337 (2)	4.2 (6)
O(5)	0.3444 (2)	−0.0209 (2)	0.2832 (2)	5.3 (5)
C(22)	0.1562 (3)	−0.0297 (3)	0.2381 (2)	5.3 (7)
F(4)	0.1612 (2)	−0.1041 (2)	0.2745 (2)	10.1 (7)
F(5)	0.0871 (2)	−0.0361 (2)	0.1741 (2)	9.1 (6)
F(6)	0.1178 (2)	0.0278 (2)	0.2768 (2)	9.9 (6)
*C(23)	0.5091 (10)	0.3065 (8)	0.6634 (7)	9.5 (3)
*C(24)	0.4067 (9)	0.2878 (8)	0.6665 (6)	8.4 (3)
*C(25)	0.3804 (20)	0.1970 (17)	0.6820 (16)	17.7 (9)
*C(26)	0.3714 (21)	0.1928 (18)	0.7651 (16)	20 (1)
*C(27)	0.4572 (22)	0.1398 (16)	0.8107 (14)	19.5 (9)
*C(28)	0.5544 (22)	0.2078 (17)	0.8379 (13)	18.9 (9)
*C(29)	0.6074 (11)	0.2146 (10)	0.7719 (10)	9.7 (4)
*C(30)	0.5972 (13)	0.3033 (11)	0.7256 (9)	13.5 (5)
*C(31)	0.0643 (13)	0.4068 (12)	0.6837 (10)	10.6 (5)
*C(32)	0.0062 (15)	0.4874 (12)	0.6725 (9)	10.7 (5)
*C(33)	0.0656 (12)	0.5723 (10)	0.7069 (8)	11.5 (4)
*C(34)	0.0495 (12)	0.5835 (11)	0.7859 (8)	12.8 (5)
*C(35)	0.0569 (17)	0.4948 (13)	0.8266 (11)	14.5 (7)
*C(36)	−0.0527 (14)	0.4446 (13)	0.8135 (9)	9.9 (5)
*C(37)	−0.0650 (12)	0.3693 (11)	0.7553 (9)	10.0 (5)
*C(38)	0.0400 (13)	0.3396 (11)	0.7387 (10)	10.8 (6)

[a] The * denotes atoms with an occupancy factor of 0.5. [b] U_{eq} – (1/3) Trace $\tilde{U}$.

turned reddish. It was then concentrated to 2 mL and left for 15 h at room temperature, during which time yellow crystals were obtained. Yield 75%. Anal. Calcd for $Ru_2C_{44}H_{64}F_{12}O_9\cdot(C_8H_{14})_2$: C, 51.95; H, 6.64. Anal. Calcd for $Ru_2C_{44}H_{64}F_{12}O_9\cdot(C_8H_{14})_3$: C, 54.54; H, 7.08. Found: C, 52.91; H, 7.42. The crystal structure shows the presence of two molecules of cyclooctene per molecule of complex. However, the microcrystalline samples used for microanalysis may contain more residual cyclooctene, and we did not succeed in obtaining a better result.

X-ray Crystal Structure of 5·$(C_8H_{14})_2$. (a) Collection and Reduction of X-ray Data. The crystals belong to the monoclinic system, space group *P*2/*c*. The selected crystal of 0.60 × 0.20 × 0.20 mm dimensions was sealed in a Lindemann glass capillary under argon atmosphere and mounted on an Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data is given in Table III. A total of 6228 reflections were recorded to a 2θ (Mo) maximum of 50° by procedures described elsewhere.[18] Intensity standards, recorded periodically, showed only random, statistical fluctuations. Intensity data were corrected for Lorentz polarization[19] and for empirical absorption[20] ($T_{min-max}$ = 0.97–1.00). Equivalent reflections 0*kl* and 0*k*$\bar{l}$ were merged (R_{av} = 0.016), and 5948 independent reflections, 3337 for which $F_o^2 > 3\sigma(F_o^2)$, were used in subsequent calculations.

(b) Structure Solution and Refinement. The structure was solved[21] by the heavy-atom method. Successive Fourier maps and least-squares refinement cycles revealed the positions of all non-hydrogen atoms and the presence of crystallization solvent, i.e., cyclooctene. The presence of cyclooctane rather than cyclooctene in the lattice, although unlikely, cannot entirely be ruled out. The geometry and the height of the 16 formed peaks led to the introduction of two disordered molecules of cyclooctene with an occupancy factor of 0.5. Cyclooctene hydrogen atoms were not found and not calculated theoretically. All other hydrogen atoms were located on a difference Fourier map. They were introduced in calculations in idealized positions (C–H = 0.97 Å) except those bonded to C(3), C(4), and O(1), which were nevertheless constrained to remain at "distances" of 0.97 Å for H(C(3)) and H(C(4)) and 0.95 Å for H(O(1)). A general isotropic temperature factor was refined to 0.079 (3) Å^2 for all H atoms. Other atoms were refined anisotropically, except solvent atoms refined isotropically.

The atomic scattering factors used were those proposed by Cromer and Waber[22] with anomalous dispersion effects.[23] Scattering factors for the hydrogen atoms were taken from Stewart et al.[24]

The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$ converged to $R = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.025 and $R_w = [\sum(|F_o| - |F_c|)^2|/\sum|F_o|^2]^{1/2}$ = 0.030 with the weighting scheme $w = [\sigma^2(F_o) + 0.0004F_o^2]^{-1}$. The error in an observation of unit weight was $S = [\sum(|F_o| - |F_c|)^2|/(n - m)]^{1/2}$ = 0.98 with *n* = 3337 observation and *m* = 386 variables. An

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analysis of variance showed no unusual trends. In the last cycle of refinement, the shifts for all parameters were less than 0.007σ, except for H and cyclooctene parameters. A final difference Fourier map showed a residual electron density of 0.7 e/Å^3 near disordered cyclooctenes. All calculations were performed on a VAX-11/730 DEC computer.

The final fractional atomic coordinates are listed in Table IV.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes for $5\cdot(C_8H_{14})_2$ (16 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Rhenocene Derivatives

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Summary: An improved preparation of Cp_2ReH (**1**) is reported, which employs the reaction of $ReCl_5$ with $Na(C_5H_5)$ and a borohydride reducing agent in dimethoxyethane, affording **1** in 40% yield. Lithiation of **1** with BuLi in THF gives Cp_2ReLi. Alkylation of Cp_2ReLi with primary alkyl halides affords the alkyl derivatives $Cp_2Re–R$ in excellent yields and high purity. The alkyl derivatives react with protic acids to afford thermally labile Re(V) alkyl hydrides, which readily eliminate the corresponding alkane.

The attempt to synthesize the rhenium analogue of manganocene by Wilkinson and Birmingham in 1955[1] led to the isolation of Cp_2ReH (1) (Cp = η^5-C_5H_5). The isolation of 1 was of some importance in the early development of transition-metal organometallic chemistry, since it was the first hydride complex not containing carbonyl coligands and was the first such complex to be characterized by ^1H NMR spectroscopy. Perhaps as a consequence of the difficult synthesis[2] of 1, relatively few studies of 1 and its derivatives have been reported.[3] In this paper, we report an improved preparation of 1, which allows for a convenient entry into the chemistry of rhenocene derivatives.

The rhenocene alkyls $Cp_2Re–R$ are found to be thermally stable (with the exception of R = benzyl) but reactive species. We have found that the alkyls react with protic acids to afford thermally labile cationic Re(V) alkyl hydride complexes, which can in some cases be isolated as microcrystalline solids at low temperature. The alkyl hydride complexes are found to readily undergo reductive elimination in the solid state or in solution to give the corresponding alkane. With chloride as the counterion, the final product is Cp_2ReCl.

Experimental Section

General Considerations. All reactions were carried out by standard Schlenk, drybox, or vacuum line techniques. An inert atmosphere was provided by purified argon. All solvents were dried and distilled from Na/K benzophenone or activated 4-Å molecular sieves. Rhenium metal (powder, 30–200 mesh) was purchased from Rhenium Alloys Inc., Elyria, OH. Chlorine gas (UHP) was purchased from Matheson. Alkyl halides were freshly distilled from 4-Å molecular sieves. Elemental analyses were performed by Galbraith Analytical Laboratory and by Mikroanalytisches Labor Pascher.

Synthesis of Cp_2ReH from $ReCl_5$. Rhenium pentachloride was prepared by the method of Lincoln and Wilkinson.[11] The product of chlorination of 18.6 g (0.1 mol) of Re metal was collected in a 2-L flask fitted with a 24/40 taper joint and a sidearm with a vacuum valve. The collection flask was flame-sealed under reduced pressure. The flask was cooled to −78 °C and 100 mL of 1,2-dimethoxyethane (DME) was added. The mixture was stirred while being warmed to 0 °C. A suspension of 0.6 mol of $Na(C_5H_5)$ in DME (1 L) at 0 °C was added. The dark purple mixture was stirred for 1 h at room temperature. The flask was fitted with a reflux condenser and heated to reflux for 12 h. At this point 100 mL of $KBH(i\text{-}OPr)_3$ solution (1 M in THF) was added and heating continued for 12 h. The mixture was transferred while hot through a wide-bore cannula to a 2-L flask equipped with a vacuum valve and a large O-ring flange. Volatiles were removed by pumping, resulting in a dark purple residue. The flask was fitted with a heating mantle and gently heated with continuous pumping until yellow crystals were observed on the upper surfaces of the flask. A large cold finger was fitted to the O-ring joint. Sublimation at 100–120 °C (10^{-4} mmHg) gave 12.1 g of 1 (40% based on Re metal). The material can be recrystallized from Et_2O/heptane (1:5) to remove traces of triisopropoxyborane and resublimed at 60 °C. Anal. Calc for $C_{10}H_{11}Re$: C, 37.84; H, 3.49. Found: C, 38.05; H, 3.50. ^1H NMR, δ: (CD_2Cl_2) 4.38 (d, J = 1 Hz, Cp, 10 H), −13.41 (br s, Re–H, 1 H); (C_6D_6) 4.20 (d, J = 1 Hz, Cp, 10 H), −12.92 (br m, Re–H, 1 H).

Synthesis of 1 from $ReCl_4(THF)_2$. To a solution of $K(C_5H_5)$ (20 mmol) in 100 mL of DME at 0 °C was added 3.2 g (6.7 mmol) of $ReCl_4(THF)_2$.[6] After stirring at 0 °C for 1 h, $LiBH_4$ (0.147 g, 6.7 mmol) was added and the mixture was warmed to room temperature for 3 h. Volatiles were removed by pumping and 1 was isolated by sublimation (80 °C, 10^{-4} mmHg). Yield: 0.86 g (40%).

Synthesis of 1 from Cp_2ReCl. To a solution of 0.100 g of Cp_2ReCl in 20 mL of DME at 0 °C was added 3 mL of a 1 M solution of tris(isopropoxy)borohydride. The solution was stirred at room temperature for 3 h. The volatiles were removed, and compound 1 was recovered by vacuum sublimation. Yield: 0.51 g (57% based on Cp_2ReCl).

Synthesis of Rhenocene Alkyls. The procedures are exemplified by that adopted for the methyl complex. A solution of

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