Organo f-Element Thermochemistry. Thorium–Ligand Bond Disruption Enthalpies in Tris(cyclopentadienyl)thorium Hydrocarbyls

David C. Sonnenberger,[1a,b] Lester R. Morss,[1b] and Tobin J. Marks[1a]*

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, and the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Received June 12, 1984

Thorium–ligand bond disruption enthalpies (D(Th–R)) have been determined in the series of complexes Cp_3ThR, where Cp = η^5-C_5H_5 and R = an alkyl group. Thermochemical data were obtained by anaerobic batch–titration solution calorimetry from enthalpies of solution of the Cp_3ThR complexes in toluene followed by enthalpies of alcoholysis with CF_3CH_2OH. $D(\text{Th–R})_{\text{gas}}$ values obtained (2σ) were as follows: $CH_2Si(CH_3)_3$, 86.1 (3.6) kcal/mol; CH_3, 82.7 (1.1) kcal/mol; $CH_2C(CH_3)_3$, 77.9 (3.0) kcal/mol; $CH_2C_6H_5$, 77.9 (2.2) kcal/mol; $CH(CH_3)_2$, 77.3 (2.7) kcal/mol. These disruption enthalpies parallel but are significantly larger than those for the identical R functionalities in the Cp'_2ThR_2 series, Cp′ = η^5-$(CH_3)_5C_5$.

An accurate delineation of the thermodynamic aspects of a chemical transformation (ΔH, ΔS, energies of bonds being formed and ruptured) is essential for a complete understanding of the transformation. For a homologous and/or chemically connected series of organometallic molecules, metal–ligand bond disruption enthalpies (D) can be especially important for understanding the course of known chemical transformations as well as for predicting new ones.[2-5] We recently reported thorium–ligand bond disruption enthalpies in the series Cp'_2ThR_2,[5] where R = alkyl, aryl, metallacycle, hydride, and dialkylamide. These data provide an informative perspective[5,6] on organo-actinide-centered reactions that involve C–H activation,[6,7] β-hydride elimination,[5,8] olefin polymerization,[9] and CO insertion,[10] and why these reaction patterns sometimes differ from those of middle and late first-row transition elements. The first step toward assessing how general some of these observations are as well as gauging the sensitivity which the D(Th–R) values may have to other supporting ligands in the metal coordination sphere is provided in the present contribution. Herein we report thermochemically derived bond disruption enthalpy data for a different, more sterically congested, and less reactive series of thorium hydrocarbyls, Cp_3ThR, where R = CH_3, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, $CH_2C_6H_5$, and $CH(CH_3)_2$. Data for the latter complex represent the first for a secondary alkyl-to-actinide bond.

Experimental Section

Synthetic Methodology. All organoactinides were prepared and handled in Schlenk glassware on a dual manifold Schlenk line or interfaced to a high vacuum (10^{-5} torr) system. Solid transfers were accomplished under nitrogen in a Vacuum Atmospheres Corp. inert-atmosphere box equipped with a recirculating atmosphere purification system. Argon (Matheson, prepurified) and nitrogen (Matheson, prepurified) were purified by passage through sequential columns of MnO on vermiculite and Davison 4A molecular sieves. The complexes Cp_3ThCH_3,[11] $Cp_3ThCH(CH_3)_2$,[11] $Cp_3ThCH_2C(CH_3)_3$,[10b] $Cp_3ThCH_2Si(CH_3)_3$,[10b] and $Cp_3ThCH_2C_6H_5$[10b] were prepared and purified by the literature procedures.

Toluene, heptane, pentane, benzene (Aldrich Gold Label), and diethyl ether (Mallinckrodt) were dried over sodium and molecular sieves, distilled from Na/K/benzophenone under a nitrogen atmosphere, and condensed into evacuated storage bulbs on the vacuum line. For calorimetric studies, toluene was further purified by an additional distillation on the vacuum line from Na/K alloy. 2,2,2-Trifluoroethanol was dried and deoxygenated by vacuum transferring three times onto freshly activated Davison 3A molecular sieves, followed by additional freeze–thaw degassing.

Analytical Methods. Proton and carbon NMR spectra were obtained on a JEOL FX 270 (FT, 270 MHz, ^{13}C 69.80 MHz), JEOL FX 90 (FT, 90 MHz), Perkin-Elmer R20-B (CW, 60 MHz), or Varian EM-360 (CW, 60 MHz) instrument. Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls sandwiched between KBr plates in an O-ring sealed airtight holder. Spectra were calibrated with polystyrene film.

Elemental analyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany.

Synthesis of $Th(C_5H_5)_3OCH_2CF_3$. To 0.21 g (0.43 mmol) of $Cp_3ThCH_2CH_2CH_2CH_3$[10b] dissolved in 30 mL of toluene at room temperature was added 0.040 mL (0.50 mmol) of dry F_3CCH_2OH. After being stirred for 1 h, the solution was filtered and the volume of the filtrate reduced, yielding a white, microcrystalline solid. The solid was washed with pentane and dried in vacuo to give $Cp_3ThOCH_2CF_3$ in 65% yield: ^1H NMR (C_6D_6) δ 6.06 (15 H, s), 3.80 (2 H, q, J_{H-F} = 9.3 Hz); IR (Nujol mull, cm^{-1}) 1360 (m), 1165

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Table I. Experimental Enthalpies of Solution[a]

compound	ΔH_{soln}, kcal/mol	compound	ΔH_{soln}, kcal/mol
Cp_3ThCH_3	2.3 (7)	$Cp_3ThCH_2C_6H_5$	3.9 (4)
$Cp_3ThC(CH_3)_2H$	2.1 (4)	$Cp_3ThOCH_2CF_3$	2.8 (2)
$Cp_3ThCH_2C(CH_3)_3$	3.1 (2)	F_3CCH_2OH	2.9 (3)
$Cp_3ThCH_2Si(CH_3)_3$	2.8 (3)		

[a] Quantities in parentheses refer to the number of determinations.

(s), 1135 (sh), 1010 (m), 950 (m), 795 (sh), 770 (s), 670 (m), 580 (w), 450 (s). Anal. Calcd for $C_{17}H_{17}OF_3Th$: C, 38.78; H, 3.23. Found: C, 38.43; H, 3.83.

Titration Calorimetry. The specially designed anaerobic isoperibol solution titration calorimeter has been described elsewhere.[5] Procedures were similar to those for the Cp'_2ThR_2 series except that CF_3CH_2OH was used as the titrant. The accuracy of the calorimeter was checked by measuring (i) the enthalpy of solution of potassium chloride (NBS Standard, Reference Material 999) in water and (ii) the enthalpy of reaction of tris(hydroxymethyl)aminomethane (NBS Standard, Reference Material 724), THAM, with 2.015 M hydrochloric acid. In the former, our value, based upon four measurements, for $\Delta H°$ (∞, 298.15 K) is 4.13 ± 0.02 kcal/mol, which compares well with the accepted value of 4.118 ± 0.004 kcal/mol.[12a] In the latter case, our value for ΔH_i of $THAM^+$ is 11.33 ± 0.03 kcal/mol, which agrees excellently with the value reported by Öjelund and Wadsö of 11.34 ± 0.01 kcal/mol.[12b]

Results and Discussion

The details of the experimental design and procedure for anaerobic isoperibol solution batch-titration calorimetry were discussed in our Cp'_2ThR_2 study.[5] A key chemical requirement for this approach is that the alcoholysis of the Th–R bond (eq 1) be rapid, quantitative,

$$L_nTh\text{-}R + R'OH \rightarrow L_nTh\text{-}OR' + RH \qquad (1)$$

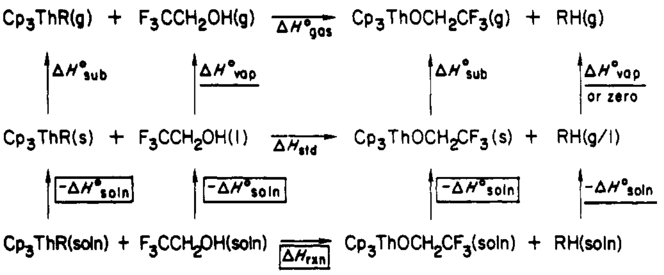
selective for the Th–R linkage, and exothermic. Although *tert*-butyl alcohol proved to be an excellent titrant for the Cp'_2ThR_2 series, no reaction occurred with Cp_3ThR compounds. However, it was found from NMR studies that under the calorimetry conditions, alcoholysis with 2,2,2-trifluoroethanol is quantitative, selective, and exothermic (eq 2). The complex tris(cyclopentadienyl)thorium trifluoroethoxide (1) can be isolated and characterized by standard techniques (see Experimental Section for details). It is also shown that *tert*-butyl alcohol and 2,2,2-trifluoroethanol derived calorimetry data can be intercompared with confidence (vide infra).

$$Cp_3ThR + CF_3CH_2OH \rightarrow \underset{1}{Cp_3ThOCH_2CF_3} + RH \qquad (2)$$

Enthalpies of solution (ΔH_{soln}) of the Cp_3ThR complexes in toluene and enthalpies of alcoholysis with CF_3CH_2OH (ΔH_{rxn}) are compiled in Tables I and II, respectively. The relationships of these measured quantities to other pertinent thermodynamic parameters are illustrated in Scheme I. With use of Scheme I, the gas-phase reaction enthalpy ($\Delta H°_{gas}$) can be equated to the measured ΔH_{rxn} by eq 3. We did not require $\Delta H°_{soln}$ or $\Delta H°_{rxn}$ (i.e., at infinite dilution) since dilution corrections are expected to be negligible, and, in any case, the dilution corrections tend to cancel on opposite sides of Scheme I. In addition, we make a reasonable, well-supported assumption[5,13] that all of the $\Delta H°_{sub}(Cp_3ThR)$ values are approximately the same and equal to $\Delta H°_{sub}(Cp_3ThOCH_2CF_3)$. On the basis of this assumption, the $\Delta H°_{sub}$ terms cancel in eq 3. Alternatively, the gas-phase component of the scheme can be neglected, and $D(Th\text{-}R)_{soln}$ values[5] can be calculated from the solution data. Within both the present (vide infra) and the Cp'_2ThR_2 series, $D(Th\text{-}R)_{soln}$ and $D(Th\text{-}R)_{gas}$ values are in close agreement.[5]

$$\begin{aligned}\Delta H°_{gas} = \Delta H_{rxn} + \Delta H°_{sub}(Cp_3ThOCH_2CF_3) + \\ \Delta H°_{vap}(RH) - \Delta H°_{sub}(Cp_3ThR) - \\ \Delta H°_{vap}(F_3CCH_2OH) - \Delta H°_{soln}(Cp_3ThOCH_2CF_3) - \\ \Delta H°_{soln}(RH) + \Delta H°_{soln}(Cp_3ThR) + \\ \Delta H°_{soln}(F_3CCH_2OH) \quad (3)\end{aligned}$$

Scheme I. Cycle for Determination of $D(Th\text{-}R)$[a]



[a] Entries in boxes: data measured in this research. Underlined entries: experimental data from the literature.

Information about F_3CCH_2OH and the RH components of the reaction system is also needed. For toluene, tetramethylsilane, and 2,2,2-trifluoroethanol, the enthalpies of vaporization are 9.07, 5.85, and 10.5 kcal/mol, respectively.[14] In the other cases, where the RH species are gaseous at 25 °C, the quantity $\Delta H°_{vap}$ (RH) is zero. The enthalpies of solution for all of the RH species are not known, but sufficient data exist to approximate the values and all are relatively small.[15] The values of $\Delta H°_{gas}$, from eq 3 and the assumptions described above, are compiled in Table II.

The bond disruption enthalpies $D(Th\text{-}R)_{gas}$ and $D(Th\text{-}R)_{soln}$[5] are related to $\Delta H°_{gas}$ and ΔH_{rxn} via eq 4 and 5,[5] respectively. Since the reactant alcohol and the product organoactinide, $Cp_3ThOCH_2CF_3$, are constant throughout the series and the value of $D(R\text{-}H)$ is known for all the RH species,[16] a relative value of $D(Th\text{-}R)$ in the various Cp_3ThR complexes can be immediately obtained by using the appropriate $\Delta H°_{gas}$ or ΔH_{rxn}. To determine absolute $D(Th\text{-}R)$ values requires both the $D(Th\text{-}O)$ in

$$-\Delta H°_{gas} = D(Th\text{-}O) + D(R\text{-}H) - D(Th\text{-}R) - D(O\text{-}H) \qquad (4)$$

$$-\Delta H_{rxn} = D(Th\text{-}O)_{soln} + D(R\text{-}H)_{soln} - D(Th\text{-}R)_{soln} - D(O\text{-}H)_{soln} \qquad (5)$$

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Table II. Experimental Alcoholysis Thermochemical Data and Derived Bond Disruption Enthalpies (kcal/mol)[a]

compound	ΔH_{rxn}	$\Delta H^\circ_{\mathrm{gas}}$[b]	$D(\mathrm{Th{-}R})_{\mathrm{soln}}$[b]	$D(\mathrm{Th{-}R})_{\mathrm{gas}}$[b]
Cp_3ThCH_3	−35.3 (1.1)	−42.2 (1.1)	89.6 (1.1)	82.7 (1.1)
$Cp_3ThCH(CH_3)_2$	−33.1 (2.4)	−37.6 (2.5)	81.8 (2.6)	77.3 (2.7)
$Cp_3ThCH_2C(CH_3)_3$	−40.2 (1.9)	−41.9 (2.1)	79.6 (2.8)	77.9 (3.0)
$Cp_3ThCH_2Si(CH_3)_3$	−30.9 (1.9)	−32.7 (1.9)	87.9 (3.6)	86.1 (3.6)
$Cp_3ThCH_2C_6H_5$	−32.5 (1.9)	−29.9 (1.8)	75.3 (2.2)	77.9 (2.2)

[a] Quantities in parentheses refer to 2σ for 6–10 determinations. [b] Error limits do not include uncertainties that are constant throughout the series.

$Cp_3ThOCH_2CF_3$ and the $D(\mathrm{O{-}H})$ in F_3CCH_2OH. As in our study on the $Cp_2'ThR_2$ systems, we estimate the value of $D(\mathrm{Th{-}O})$ to be 124 kcal/mol.[5] Next, although $D(\mathrm{O{-}H})$ in 2,2,2-trifluoroethanol is not known, a value of 104.2 kcal/mol, that for ethanol,[16a] is estimated for it. We believe this to be a reasonable approximation because, in all R_3COH species studied to date, it has been observed that $D(\mathrm{O{-}H})$ falls in the range of 104 ± 2 kcal/mol.[16a] These two approximations as well as the intercomparability of CF_3CH_2OH and *tert*-butyl alcohol calorimetry data were further substantiated by a control experiment consisting of a redetermination of the value of $D(\mathrm{Th{-}R})_{\mathrm{gas}}$ in $Cp'_2Th(C_2H_5)Cl$. With F_3CCH_2OH as the titrant, a value for $D(\mathrm{Th{-}R})_{\mathrm{gas}}$ of 65.9 ± 2.5 kcal/mol was obtained,[17] which is in excellent agreement with the previously reported value of 68.3 ± 2.0 kcal/mol,[5] where *tert*-butyl alcohol was the titrant. Again, although these values are mutually consistent, we estimate that the absolute $D(\mathrm{Th{-}O})$ is probably not accurate to better than 10 kcal/mol.

The experimentally determined $D(\mathrm{Th{-}R})_{\mathrm{soln}}$ and $D(\mathrm{Th{-}R})_{\mathrm{gas}}$ values for the present series of Cp_3ThR complexes are compiled in Table II, recalling that $D(\mathrm{Cp_3Th{-}R})$ is formally defined as in eq 6 for the gas-phase reaction portrayed in eq 7. It can be seen that the measured

$$D(\mathrm{Cp_3Th{-}R}) = \Delta H_f^\circ(\mathrm{Cp_3Th})(g) + \Delta H_f^\circ(\mathrm{R\cdot})(g) - \Delta H_f^\circ(\mathrm{Cp_3Th{-}R})(g) \tag{6}$$

$$\mathrm{Cp_3ThR}(g) \rightarrow \mathrm{Cp_3Th}(g) + \mathrm{R\cdot}(g) \tag{7}$$

$D(\mathrm{Th{-}R})$ values are rather large—on the order of 80 kcal/mol. These values parallel but are slightly, yet significantly, larger (by ca. 5 kcal/mol) than for the analogous first Th–R bonds in the Cp'_2ThR_2 series.[5] These relationships are portrayed graphically in Figure 1. For the present Cp_3ThR series, the relative ordering of $D(\mathrm{Th{-}R})$ values is $CH_2Si(CH_3)_3 \geq CH_3 > CH_2C(CH_3)_3 \approx CH_2C_6H_5 \approx CH(CH_3)_2$, which parallels that found for the Cp'_2ThR_2 series (where corresponding data are available). This trend seems somewhat surprising, since spectroscopic (e.g., hindered rotation about M–C bonds) and structural information suggests far greater steric crowding in the tris(cyclopentadienyl) hydrocarbyls.[7,18] Hence, deviations from the parallel trends might be expected, especially for sterically demanding groups. In regard to the exothermicity of eq 3, existing structural data[10d,18] argue that steric effects should be less important in the corresponding Cp_3ThOR' and $Cp'_2Th(OR')_2$ alcoholysis products; i.e., the actinide–O–R′ bond angles frequently approach 180°.[18,19]

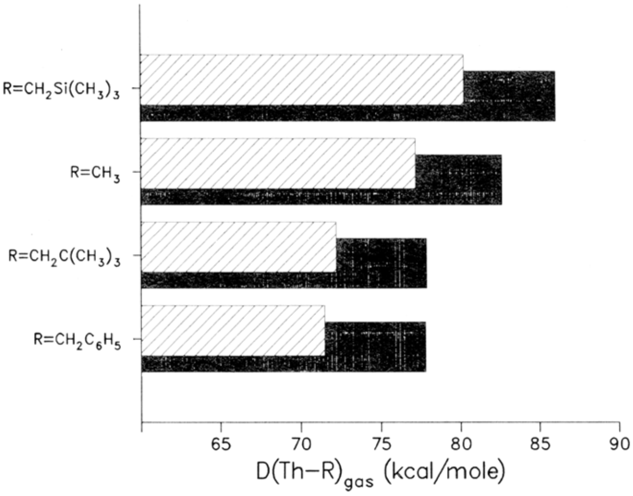
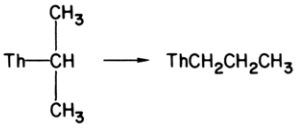


Figure 1. Histogram comparing gas-phase thorium–alkyl bond disruption enthalpies in $Cp_3Th{-}R$ compounds (dark bars) and in Cp'_2ThR_2 compounds (light bars).

The present results reveal rather similar Cp_3ThR bond disruption enthalpies for R = isopropyl, neopentyl, and benzyl. Interestingly, $D(\mathrm{Co{-}R})$ values in the L(Saloph)CoR series[2a,20] follow the same trend, although the magnitudes are considerably less: 20 kcal/mol (R = isopropyl), 18 kcal/mol (R = neopentyl), and 22 kcal/mol (R = benzyl). Extrapolating $D(\mathrm{Th}{-}n\text{-propyl})$ from the Cp'_2ThR_2 series,[5,21] the present results indicate that, within experimental error, $D(\mathrm{Th}{-}n\text{-propyl})$ and $D(\mathrm{Th{-}isopropyl})$ are comparable: 75.5 (2.0) and 77.1 (2.7) kcal/mol, respectively. Thus, the enthalpic driving force for reactions such as in eq 8[5] appears to be rather small. For the Cp′Ir[P(CH$_3$)$_3$](H)R series,[22] $D(\mathrm{Ir}{-}n\text{-}C_5H_{11}) - D(\mathrm{Ir{-}cyclohexyl}) \approx$ 5.5 kcal/mol. For the $Ir[P(CH_3)_3]_2(CO)(Cl)(I)R$ series,[23] $D(\mathrm{Ir}{-}n\text{-propyl}) - D(\mathrm{Ir{-}isopropyl}) \approx 4.0\ (3.7)$ kcal/mol. $D(\mathrm{Co}{-}n\text{-propyl}) - D(\mathrm{Co{-}isopropyl})$ is reported to be 5 kcal/mol in the L(Saloph)CoR series.[2a,20]



$$\mathrm{Th{-}CH(CH_3)_2} \longrightarrow \mathrm{ThCH_2CH_2CH_3} \tag{8}$$

The reason why $D(\mathrm{Th{-}R})$values are consistently higher for the Cp_3ThR series than for the Cp'_2ThR_2 series is presently open to speculation. Certainly, any destabilizing steric congestion in the former series is overridden by other factors. For example, the three cyclopentadienyl rings in Cp_3ThR may additionally stabilize the tetravalent or de-

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[17] $\Delta H_{\mathrm{rxn}} = -46.6$ (2.0) kcal/mol; $\Delta H^\circ_{\mathrm{gas}} = -51.9$ (2.2) kcal/mol.

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[21] The average of $D(\mathrm{Th{-}C_2H_5}) = 70.4$ (2.0) kcal/mol and $D(\mathrm{Th}{-}n\text{-}C_4H_9) = 71.6$ (1.7) kcal/mol was taken.

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stabilize the trivalent thorium oxidation state, rendering eq 7 more endothermic. Equally important may be differences in metal–hydrocarbyl ligand orbital overlap (bonding), although these are not immediately obvious in observables such as He I, II photoelectron spectra.[24] Likewise, differential π-accepting tendencies of the Cp_3Th[25] and Cp'_2Th[10e] centers may significantly affect the bonding of alkoxide ligands,[26] hence the measured exothermicity of eq 3. In any case, it is clear that the nature of the ancillary hydrocarbon ligands does affect $D(M–R)$ values for organoactinides.

Acknowledgment. This research was supported by the National Science Foundation under Grant CHE8306255 to T.J.M. and by the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under Contract No. W-31-109-ENG-38 at Argonne National Laboratory.

Registry No. $CP_3ThOCH_2CF_3$, 92473-15-9; CP_3ThCH_3, 92473-15-9; $CP_3ThC(CH_3)_2H$, 58920-14-2; $CP_3ThCH_2Si(CH_3)_3$, 89746-39-4; $CP_3ThCH_2C_6H_5$, 89746-40-7; $CP_3ThCH_2CH_2CH_2CH_3$, 54067-92-4; F_3CCH_2OH, 75-89-8.

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[26] Both d and f orbitals of appropriate symmetry are available for π bonding in Cp_3ThOR and $Cp'_2Th(OR)_2$ compounds.

Addition of Small Molecules to $(\eta\text{-}C_5H_5)_2Rh_2(CO)(CF_3C_2CF_3)$. 2.[1] Intramolecular Reactions between μ-Alkylidene Groups and the μ-Alkyne in Some Complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$. Crystal and Molecular Structure of $(\eta\text{-}C_5H_5)_2Rh_2[\mu\text{-}C(CF_3){=}C(CF_3)OC(OEt){=}C(CO_2Et)]$

Ron S. Dickson,* Gary D. Fallon, Rhonda J. Nesbit, and Geoff N. Pain

Department of Chemistry, Monash University, Clayton, Victoria, 3168 Australia

Received June 5, 1984

Treatment of $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (1) with diazoalkanes $N_2CR^1R^2$ in diethyl ether at 0 °C gives the μ-alkylidene complexes $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$ ($R^1 = R^2 = H$, **2a**; $R^1 = R^2 = CO_2Et$, **2b**). Migration of the alkylidene group to the coordinated alkyne occurs when each of the complexes is kept in solution at room temperature. With **2a**, there is formation of a new C–C bond to give a σ,π-allyl complex, $(\eta\text{-}C_5H_5)_2Rh_2(CO)[\mu\text{-}C(CF_3)C(CF_3)CH_2]$ (**3**). In contrast, **2b** gives $(\eta\text{-}C_5H_5)_2Rh_2[\mu\text{-}C(CF_3){=}C(CF_3)OC(OEt){=}C(CO_2Et)]$ (**4**) in which a new C—O bond has been formed. Determination of the crystal and molecular structure of **4** establishes that the bridging group is a divinyl ether which spans the Rh–Rh bond in "flyover" fashion. Crystal data: $C_{21}H_{20}F_6O_4Rh_2$, $M_r = 656.2$, monclinic, $P2_1/n$, $a = 17.666\ (8)$ Å, $b = 13.679\ (6)$ Å, $c = 9.526\ (4)$ Å, $\beta = 103.62\ (8)°$, $U = 2237.3$ Å^3, $D_{calcd} = 1.95$ ($Z = 4$), $D_{measd} = 1.90\ (3)$ g cm^{-3}, λ(Mo Kα) = 0.7107 Å, μ(Mo Kα) = 14.0 cm^{-1}, final $R = 0.052$, $R_w = 0.051$, from 2945 observed reflections (6518 measured).

Introduction

The first (μ-methylene)dimetal complex was reported[2] as recently as 1975, but already there is a substantial review[3] on the topic. This high level of interest and activity has been stimulated by the possible involvement of these and related compounds in important catalytic reactions such as alkene metathesis, Fischer–Tropsch chemistry, and alkyne polymerization.[3,4]

Recently, we described[1] the synthesis of a coordinatively unsaturated dirhodium complex $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CF_3C_2CF_3)$ (1) and the coordinative addition of some π-acid ligands to yield the complexes $(\eta\text{-}C_5H_5)_2Rh_2(CO)L(\mu\text{-}CF_3C_2CF_3)$. These reactions include the additions of CO and CNR, and it therefore seemed likely that related complexes should be formed with $=CR_2$. In fact, the reactions of 1 with various diazoalkanes, $N_2CR^1R^2$, lead to elimination of N_2 and formation of μ-alkylidene complexes of formula $(\eta\text{-}C_5H_5)_2Rh_2(\mu\text{-}CO)(\mu\text{-}CR^1R^2)(\mu\text{-}CF_3C_2CF_3)$. Some of these complexes undergo interesting intramolecular reactions in which the alkylidene migrates to the coordinated alkyne. In this paper, we describe two such reactions; these results have been briefly communicated.[5]

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer 521 spectrometer. ^1H and ^{19}F NMR spectra were recorded at 90 and 84.66 MHz, respectively, on a Brüker WH-90 spectrometer; the ^1H spectra are reported as δ values, and the ^{19}F chemical shifts are upfield from CCl_3F internal reference. A V.G. Micromass 7070-F spectrometer was used to measure the mass

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