acyl function back to titanium as in the cyclic transition state C′. Figure 2 gives a picture of the X-ray structure of **3**, with some relevant structural parameters.[13] The cyclization of **2** to **3** requires mainly a rotation of ~111° around the C17–C19 bond, as indicated by the values for the C16–C17–C19–O3 torsion angle: 168.1 (7) and 56.9 (7)° for **2** and **3**, respectively. The structural parameters of **3** do not reveal any significant deviation from those of some known derivatives of iron[6] and titanium[11] in the same coordination environment. The metallacycle adopts a half-chair conformation, being folded by 45.3 (4)° along the C17···O3 line (the folding is defined by the dihedral angle between the C17–C19–O3 and C17, C16, O1, Ti, O3 planes). The conformation of the metallacycle is expected to be very close to that of the cyclic transition state, the bond sequence being the same and the cyclization changing nothing in the stereochemistry of the two chiral centers. A geometrical difference between C′ and **3** may exist only because of the different coordination numbers of titanium, which is pentacoordinate in C′ and tetracoordinate in **3**.

Complexes **2** and **3** confirm general assumptions, which have never been structurally proved before, on the role of the countercation in metal enolates. They exclude metal–enolate aggregations or equilibria as playing any role and show how a transition-metal moiety such as $[(cp)_2Ti(Cl)]$ orients the substrate toward the enolate and determines the geometry of the transition state. The design of transition-metal moieties to be used as countercations, keeping in mind geometry requirements at the metal and metal–oxygen bond strength, might be important in enolate chemistry.

Attempts to understand the steric control exerted by the second metal site by using the structural information from complexes **1**–**3**, the introduction of a second chiral metal, and the parallel use of the bimetallic keto form of the iron anion are in progress.

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (SNF Grant No. 2000-005536) for financial support.

Supplementary Material Available: Tables of X-ray data, fractional atomic coordinates, anisotropic thermal parameters, and bond distances and angles for complexes **2** and **3**, a table of bond distances for **1**, and a figure showing the structure of complex **1** (18 pages); listings of observed and calculated structure factor amplitudes for complexes **2** and **3** (19 pages). Ordering information is given on any current masthead page.

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(12) Procedure for **3**: to a THF suspension (100 mL) of **2** (1.47 g, 1.90 mmol) was added $NaBPh_4$ (0.68 g, 2.0 mmol). A red solution suddenly formed, and a white solid precipitated. The suspension was stirred for 4 h at room temperature, and the white solid was removed by filtration. The IR spectrum of the solution showed the shift of the acylic function from 1621 cm^{-1} down to 1581 cm^{-1} and of the carbonylic one from 1903 cm^{-1} in **2** up to 1945 cm^{-1}. The solution after partial evaporation gave, by addition of Et_2O (30 mL), a red crystalline solid (yield 1.36 g, 68%). The solid recrystallized from CH_2Cl_2/hexane contains CH_2Cl_2 of crystallization. ^1H NMR (ABX-type spectrum) for the $[FeCOCH_2CH(Ph)OTi]$ fragment (200 MHz, CD_2Cl_2): δ 2.58 (q,* 1 H, J_{XA} = 10.51 Hz, J_{XB} = 17.81 Hz, J_{H-P} = 0.80 Hz), 4.09 (q,* 1 H, J_{BX} = 17.30 Hz, J_{BA} = 2.20 Hz, J_{H-P} = 0.60 Hz), 4.67 (d, 5 H, cp–Fe, J_{cp-P} = 1.20 Hz), 5.16 (d,* 1 H, J_{AB} = 2.00 Hz, J_{AX} = 10.41 Hz), 6.29 (s, 5 H), 6.24 (s, 5 H), 6.44–7.55 (m, 40 H). An asterisk indicates that each peak is split into a doublet derived from coupling with phosphorus. Anal. Calcd for $C_{68}H_{60}BCl_2FeO_3PTi$: C, 71.53; H, 5.30; Cl, 6.21; P, 2.71. Found: C, 71.29; H, 5.30; Cl, 6.10; P, 2.67.

(13) Structure of **3**: $C_{68}H_{60}BCl_2FeO_3PTi$, monoclinic, space group $P2_1/n$, $a = 15.300$ (1) Å, $b = 14.196$ (2) Å, $c = 27.105$ (2) Å, $\beta = 100.77$ (12)°, $V = 5783.5$ (7) Å^3, $Z = 4$, $\rho_{calcd} = 1.311$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 5.52 cm^{-1}, crystal dimensions $0.37 \times 0.48 \times 0.61$ mm^3. The structure was solved by the heavy-atom method and refined anisotropically for all non-hydrogen atoms. All the hydrogen atoms were directly located from a difference Fourier map and introduced into the final refinement as fixed contributors ($U_{iso} = 0.08$ Å^2); 4187 unique observed reflections ($I > 2\sigma(I)$) collected at room temperature ($6 < 2\theta < 46°$) were used ($R = 0.049$). All calculations were carried out with use of SHELX 76.

Catalytic Hydration of Alkynes with Zeise's Dimer

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Summary: **Pt(II) in the form of Zeise's dimer has been shown to be an efficient and facile hydration catalyst or catalyst precursor for the hydration of alkyl-substituted alkynes.**

Unactivated alkynes are an abundant hydrocarbon resource, and hydration represents an excellent means of functionalization. Classically, they are hydrated to ketones or aldehydes by use of Hg(II) complexes with added catalytic amounts of H_2SO_4 or pTsOH.[1,2] Further, Regen,[3] in 1982, reported that phenylmercuric hydroxide was a highly selective reagent for the hydration of nonconjugated terminal alkynes. In this latter methodology, it was not necessary to employ acid but the reaction required stoichiometric amounts of mercury. Other metals have also been employed to hydrate acetylenes and alkynes, including copper(I),[4] silver(I),[4] palladium(II),[4] ruthenium(III),[4] rhodium(III),[4] and osmium(II).[5] These hydrolyses are accelerated by protonic acids and give a variety of products from acetylene such as crotonaldehyde and polymers thereof, in addition to the simple hydration products.

In regard to platinum-facilitated addition reactions with alkynes, Clark and Chisholm concentrated on the addition of methanol to cationic complexes.[6,7] Trogler[8] has reported the analogous hydration of nitriles with a hydridoplatinum(II) hydroxide complex. Finally, in a paper by Chatt[9] in 1961, dealing with the preparation of alkyne

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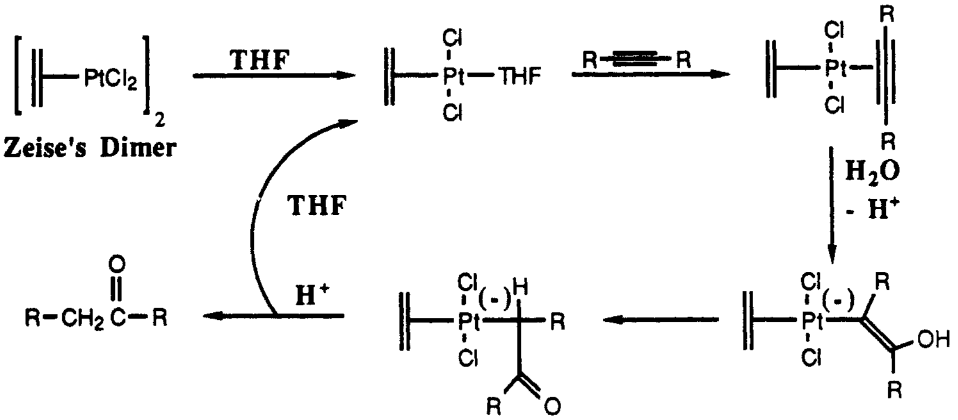
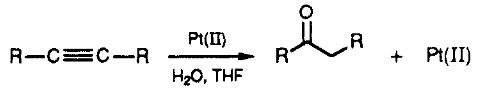
Scheme I



derivatives of Pt(II) complexes, he briefly reported that ethanolic $Na_2PtCl_4 \cdot 4H_2O$ reacted with several alkynes to form ketones. They speculated that hydration was catalyzed by colloidal platinum generated by reduction of the above-mentioned salt.

In this communication, we wish to demonstrate that Pt(II), in the form of Zeise's dimer, is an active and selective catalyst or catalyst precursor in the hydration of several unactivated alkynes (eq 1).



(1)

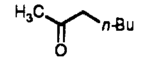
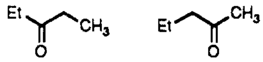
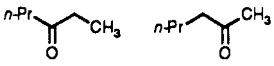
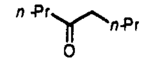
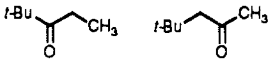
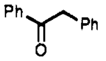
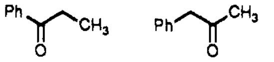
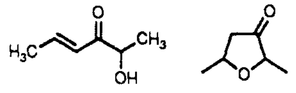
R = alkyl; Pt(II) = Zeise's dimer

Optimum conditions for the reaction involve addition of 0.7 mol % of Zeise's dimer to 3 g (27 mmol) of 4-octyne in 20 mL of THF containing 1.6 equiv of H_2O/mol of alkyne. After 24 h of reflux, there was quantitative reaction as determined by ^1H NMR spectroscopy. Subsequent isolation by distillation gave a 93% yield of pure 4-octanone as compared to an authentic sample (^1H and ^{13}C NMR spectroscopy). Data for the other alkyne substrates investigated are shown in Table I.

It is clear that electron-donating substituents are more effective in the reaction than are electron-withdrawing substituents. Unsymmetrically substituted alkynes hydrate to yield both ketones, with a bias favoring the more hindered (internal) side, and a *tert*-butyl moiety slows the reaction considerably. Hept-1-yne has a feature that is noteworthy. If the Pt(II) catalyst is added to a solution of the alkyne and THF with minimal water present, polymeric product (uncharacterized) is obtained. However, is *excess* water is present in the THF solution prior to the addition of Pt(II), an excellent yield of the methyl ketone is obtained with only a trace of heptanal.

While the mechanistic details of this reaction are not complete, there are a few significant and unique features that have been elaborated. (1) It is not accelerated by acid (5% H_2SO_4 or 2.6% pTsOH). (2) It is specific for water, even in the presence of alcohol. For example, in an attempt to add methanol to the alkyne, the only product observed was a trace of ketone from adventitious water. (3) There is no isotope effect on reaction progress (H_2O vs D_2O) with use of 4,4-dimethyl-2-pentyne. Kinetic experiments show the reaction to be first order overall (independent of $[H_2O]$ and first order in [alkyne]). The selectivity of H_2O vs MeOH is a dominant feature. There are two explanations. First, MeOH is poorer than H_2O at coordinating to Pt(II). However, Pt(II) does not strongly coordinate oxygen moieties of any type. Second, if external attack on the alkyne occurs, these data would suggest that ketalization of the enol intermediate is a critical product-forming step as shown in the proposed Scheme I.[10]

Table I. Alkyne Substrates, Products, and Yields

alkyne	product (ratio)	extent of reacn,[a] % (isolated yield, %)
1-heptyne		93 (78)
2-pentyne	 (1.8:1)	100 (76)
2-hexyne	 (2:1)	100 (84)
4-octyne		100 (93)
4,4-dimethyl-2-pentyne	 (2.7:1)	95 (86)
diphenylacetylene		30 (25)
1-phenylpropyne	 (2:1)	50 (35)
2,5-hexynediol	 (4:1)	60 (45)
dimethyl acetylenedicarboxylate	a myriad of products in extremely low yield	<10

[a] From ^1H NMR spectroscopy.

In summary, Pt(II) in the form of Zeise's dimer is an excellent catalyst or catalyst precursor for the hydration of unactivated alkynes. Modest regioselectivity has been observed to date on unsymmetrically substituted substrates, and electron-withdrawing groups severely retard the reaction. Addition of acid, which is common with other hydration catalysts, is neither necessary nor advantageous in this case.

Registry No. $H_3CC{\equiv}CCH_2CH_3$, 627-21-4; $H_3CC{\equiv}C(CH_2)_2CH_3$, 764-35-2; $H_3C(CH_2)_2C{\equiv}C(CH_2)_2CH_3$, 1942-45-6; $H_3CC{\equiv}C$-

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[10] In this scheme, we favor external attack of H_2O on the coordinated alkyne leading to the trans vinyl alcohol. Since there is no strong evidence for this mode of addition, we recognize the option of internal attack from a platinum-coordinated water molecule.

$C(CH_3)_3$, 999-78-0; $PhC{\equiv}CPh$, 501-65-5; $PhC{\equiv}CCH_3$, 673-32-5; $H_3CCH(OH)C{\equiv}CCH(OH)CH_3$, 3031-66-1; $H_3CO_2CC{\equiv}CCO_2CH_3$, 762-42-5; $H_3CCO(CH_2)_4CH_3$, 110-43-0; $EtCOCH_2CH_3$, 96-22-0; $EtCH_2COCH_3$, 107-87-9; *n*-$PrCOCH_2CH_3$, 589-38-8; *n*-$PrCH_2COCH_3$, 591-78-6; *n*-$PrCOCH_2Pr$, 589-63-9; *t*-$BuCOCH_2CH_3$, 564-04-5; *t*-$BuCH_2COCH_3$, 590-50-1; $PhCOCH_2Ph$, 451-40-1; $PhCOCH_2CH_3$, 93-55-0; $PhCH_2COCH_3$, 103-79-7; $H_3C\text{-}CH{=}CHCOCH(OH)CH_3$, 127229-40-7; $HC{\equiv}C(CH_2)_4CH_3$, 628-71-7; 2,5-dimethyldihydro-3(2*H*)-furanone, 64026-45-5; Zeise's dimer, 12073-36-8.

Articles

Defluorination of Perfluoroolefins by Divalent Lanthanoid Reagents: Activating C–F Bonds

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Divalent lanthanoid complexes $MCp^*_2{\cdot}L$ (M = Yb, Eu, Sm; L = diethyl ether or THF; Cp* = η^5-pentamethylcyclopentadienyl) and $YbCp'_2{\cdot}L$ (Cp′ = η^5-methylcyclopentadienyl; L = tetrahydrofuran) rapidly abstract fluorine atoms from a variety of perfluoroolefins including perfluoro-2,4-dimethyl-3-ethylpent-2-ene, perfluoro-2,3-dimethylpent-2-ene, and perfluorocyclohexene. A similar abstraction of fluorine atoms from perfluorobenzene is much slower. However, visible light enhances the rate of fluorine abstraction from perfluorobenzene by $MCp^*_2{\cdot}OEt_2$ (M = Yb, Eu, Sm). Qualitative observation shows that the relative fluorine abstraction reactivity of the four lanthanoid complexes increases with increasingly negative reduction potential for reasonably unhindered fluoroolefin substrates. The Yb(III)/Yb(II) reduction potential of $YbCp'_2$ solvated in acetonitrile is determined here to be −1.65 V (relative to ferrocene) by cyclic voltammetry. The fully characterized organometallic products from the fluorine atom abstraction reactions are solvated trivalent lanthanoid fluorides $MCp^*_2F{\cdot}L$ (M = Yb, Eu, Sm; L = diethyl ether or THF) and $YbCp'_2F{\cdot}THF$. The molecular structures of $YbCp^*_2F{\cdot}OEt_2$ and $YbCp^*_2F{\cdot}THF$ determined by X-ray crystallography reveal the first terminal lanthanoid–fluoride bonds. However, three different environments for bridging lanthanoid–fluoride bonds are seen in the X-ray determined structure of the trivalent pentaytterbium cluster $[Yb_5Cp^*_6(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu\text{-}F)_6]$, which is a secondary product from the further reaction of $YbCp^*_2F$ with perfluoroolefins. From the X-ray data of these three trivalent ytterbium compounds the *averaged* Yb–F distances are 2.02 Å for the terminal Yb–F bonding mode, 2.20 Å for an F atom bridging between two Yb atoms, and 2.37 Å for an F atom bridging between three of four Yb atoms.

Introduction

Homolytic bond energies of carbon–fluorine bonds are substantially higher than for analogous hydrocarbons. For example, the homolytic bond dissociation energy for $CF_4 \rightarrow CF_3 + F$ is 130.5 ± 3 kcal/mol,[1,2] whereas for $CH_4 \rightarrow CH_3 + H$ the energy is substantially less, 105 ± 1 kcal/mol.[2,3] The bond dissociation energy for $C_6F_6 \rightarrow C_6F_5 + F$ is even higher, 154.6 kcal/mol,[1] and the allylic bond dissociation energy for $CF_2CFCF_3 \rightarrow CF_2CFCF_2 + F$ is estimated to be around 120–126 kcal/mol.[4] However, since lanthanoid–fluorine bonds are also very strong (124–135 kcal/mol for trivalent Eu, Yb, and Sm[5]), the possibility of productive defluorination of fluorocarbons under mild conditions seems feasible. Indeed, in lanthanoid chemistry, Deacon[6] demonstrated selective intramolecular removal of fluorine from the ortho position of pentafluorobenzoic acid coordinated to ytterbium(II) during a complex protonolysis reaction. On the other hand, simple alkyl fluorides were shown by Finke et al. to be unreactive with divalent lanthanoid complexes[7] under mild conditions. Andersen[8] recently published a report of the fluorine atom abstraction reactions of the unsolvated divalent lanthanoid $YbCp^*_2$ with perfluorobenzene. Our

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[†] Contribution No. 4690.

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(4) (a) The allylic $CF_2CFCF_2{-}F$ bond dissociation energy (BDE) was roughly estimated (by B. E. Smart, Du Pont Central Research and Development Department) as $BDE(CF_2CFCF_2{-}F) \sim BDE(CF_3CF_2{-}F)$, 126.8 kcal/mol[4c] − ΔG_{rot} (CF_2CFCF_2), 6.1 kcal/mol,[4d] = 120.7 kcal/mol. The corresponding hydrocarbon equation requires a correction factor of 2.4 kcal/mol, i.e. $BDE(CH_2CHCH_2{-}H)$, 86.8 kcal/mol,[4e] = $BDE(CH_3CH_2{-}H)$,[4e] 100.1 kcal/mol − $\Delta G_{rot}(CH_2CHCH_2)$, 15.7 kcal/mol,[4f] + 2.4 kcal/mol; the fluorocarbon reaction if corrected by the same amount gives $BDE(CF_2CFCF_2{-}F)$ = 123.1 kcal/mol. (b) An alternative method gives a similar result. With an estimate in the JANAF tables[4g] for the heat of formation of CF_2CFCF_2, −159 kcal/mol, and the heats of formation of CF_2CFCF_3, −266.4 kcal/mol,[4h,i] and F, 18.9 kcal/mol, $BDE(CF_2CFCF_2{-}F)$ = 125.9 kcal/mol. (c) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532. (d) Smart, B. E.; Krusic, P. J.; Meakin, P.; Bingham, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 7382–7383. (e) Griller, D.; Kanabus-Kaminska, J. M.; Maccoll, A. *J. Mol. Struct.* **1988**, *163*, 125–131. (f) Forth, H. G.; Trill, H.; Sustmann, H. *J. Am. Chem. Soc.* **1981**, *103*, 4483–4489. (g) *JANAF Thermochemical Tables*; Stull, D. R., Ed.; Dow Chemical: Midland, MI, 1965. (h) Duus, H. C. *Ind. Eng. Chem.* **1955**, *47*, 1445. (i) Dixon, D. A.; Fukunaga, T.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 4027–4031.

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