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Organolanthanide and Organoactinide Oxidative Additions Exhibiting Enhanced Reactivity. 5. Stoichiometry, Kinetic, and Mechanistic Studies of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ Oxidative-Addition Reactions and of $(C_5Me_5)_2Yb^{III}R$ (R = R, X) "Yb^{III}-Grignard" Reactions with Alkyl and Aryl Halides. Evidence for the Dominance of Inner-Sphere Mechanisms

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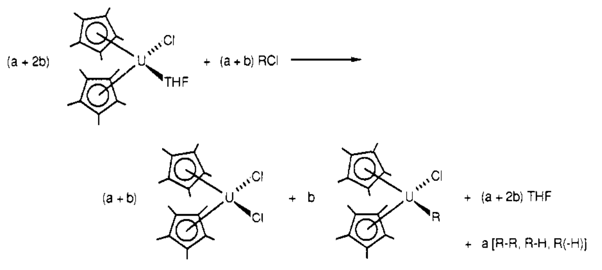
$(C_5Me_5)_2Yb^{II}\cdot OEt_2$ undergoes atom-abstraction oxidative addition with alkyl and aryl halides according to the generalized stoichiometry $1.0(C_5Me_5)_2Yb^{II}\cdot OEt_2 + (1 + a)RX \rightarrow (1 - a)(C_5Me_5)_2Yb^{III}X + (a)(C_5Me_5)_1Yb^{III}X_2 + (a)C_5Me_5R + 1.0Et_2O + 1.0$[R–R, R–H(alkanes), R(–H)(olefins)]. A reactive Yb–alkyl intermediate, $(C_5Me_5)_2Yb^{III}R$, is formed from $R^{\bullet}$ trapping by diamagnetic $(C_5Me_5)_2Yb^{II}$. This $(C_5Me_5)_2Yb^{III}R$ intermediate and the initial product $(C_5Me_5)_2Yb^{III}X$ react further with RX in subsequent "Yb^{III}-Grignard" reactions that are retarded by added Et_2O and, therefore, apparently operate via an inner-sphere pathway. The observed "Yb^{III}-Grignard" stoichiometries are $(C_5Me_5)_2Yb^{III}R + 2RX \rightarrow (C_5Me_5)_2Yb^{III}X_2 + C_5Me_5R + R–R$ and $(C_5Me_5)_2Yb^{III}X + RX \rightarrow (C_5Me_5)_1Yb^{III}X_2 + C_5Me_5R$. The absolute rates of reaction of RX with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ are found to be first-order each in $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and RX, with an added inverse dependence upon Et_2O. The Et_2O dependence is consistent with a requirement for a site of coordinative unsaturation and an inner-sphere pathway. Comparison of the rates of reactions of $(C_5Me_5)_2U^{III}(Cl)(THF)$ and $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX provides compelling evidence for participation of electron transfer in these net atom-abstraction reactions.

Introduction

Oxidative-addition reactions constitute one of the most important methods of forming transition metal to carbon bonds.[1] As a part of an effort to systematically study organoactinide and organolanthanide oxidative-addition[2,3] reactions, in 1981 we reported[4] the one-electron oxidative addition of alkyl and aryl halides to $(C_5Me_5)_2U(Cl)(THF)$ (eq 1). These reactions were shown to proceed with rates 10^4–10^7 times faster than d-block organotransition-metal atom abstractors such as Co^{II}, coenzyme B_{12r}, and $Cr(en)_2^{2+}$.[5] Subsequent mechanistic work[4b,6a] provided strong evidence for an inner-sphere pathway and for an atom-abstraction transition state similar to that proposed for group 14 radicals.[6b–e] In the case of $(C_5Me_5)_2UCl$ the rate-determining transition state was shown to contain



(1)

[†] Contribution no. 4204.

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contributions from electron transfer, carbon–halogen bond cleavage, and U–X bond formation.

The organoactinide oxidative-addition studies raised a number of questions concerning possible but little investigated $(C_5Me_5)_2Ln^{II}\cdot OEt_2$ organolanthanide oxidative additions. Specifically, the following questions are of interest: (i) How do the stoichiometries and products compare between the organoactinides and organolanthanides? (ii) What are the absolute rates, do the $(C_5Me_5)_2Ln^{II}\cdot OEt_2$ complexes show enhanced reactivity as found for U^{III}? (iii) What are the relative rates as a function of RX for Ln^{II} vs U^{III}? (iv) Which is more important, the number of unpaired electrons, the metal's redox potential, the ionic size of the central metal, or some other property in determining the similarities or the differences in reactivity and products? (v) Finally, what are the mechanistic details? Are the organolanthanide reactions inner or outer sphere, and do they proceed by an overall "atom-abstraction" mechanism as observed for U^{III}?

Table I. Stoichiometries[a] for Oxidative Additions of Alkyl and Aryl Halides to $(C_5Me_5)_2Yb^{II}\bullet OEt_2$ at 23 °C in Benzene-d_6 by ^1H NMR

substrate	stoichiometry	yield R–R (±0.05 equiv)
$PhCH_2Br$	0.56[b]	0.48
$PhCH_2Cl$	0.55[b]	0.50
$PhCH_2Cl$	0.69[c]	0.49
$PhCH_2F$	0.58[b]	0.49
t-BuCl[d]	0.50[b]	
t-BuCl[d]	0.61[b]	
n-BuCl	0.74[b]	
i-PrCl	1.0	
CH_3I	1.0	
PhI	0.71[b]	0.46

[a] Final stoichiometries (see text) defined from eq 2 as 1.0/(1.0 + *a*). [b] Single addition of ≥2.0 equiv of substrate. [c] Sequential additions of ≃0.25 equiv of substrate until 1.75 equiv were added. [d] The C_5Me_5R product for *t*-BuCl is R = H. For all other substrates, R = alkyl or aryl.

Three organolanthanide complexes were selected for comparison to $5f^3$ $(C_5Me_5)_2U^{III}Cl\cdot THF$ with its three unpaired electrons, its $E_{1/2} = -1.3$ V vs SCE reduction potential,[7] and its 1.1–1.2 Å U^{III} ionic radius.[10] The three Ln complexes and a summary of their relevant properties are shown below:

Ln complex	f^n configuration	no. of unpaired electrons	Ln^{III}/Ln^{II} $E_{1/2}$ (vs SCE)[8,9]	Ln^{II} ionic radius[10]
$(C_5Me_5)_2Yb^{II}\cdot OEt_2$	$4f^{14}$	0	≃−1.4 V	1.1–1.2
$(C_5Me_5)_2Sm^{II}\cdot OEt_2$	$4f^6$	6	≃−2.0 V	1.2–1.3
$(C_5Me_5)_2Eu^{II}\cdot OEt_2$	$4f^7$	7	≃−0.8 V	1.2–1.4

All three compounds have identical ligands and similar ionic radii,[10] but the reduction potentials vary considerably, as do the 4f electron configurations and the number of unpaired electrons. We were interested in how the above differences, between $(C_5Me_5)_2UCl\cdot THF$ and the more ionic organolanthanides (with their 4f orbitals buried in filled 5s and 5p shells[11,12]), would manifest themselves in the observed rates, products, and oxidative-addition mechanism(s).

More recently[13] we reported $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ does in

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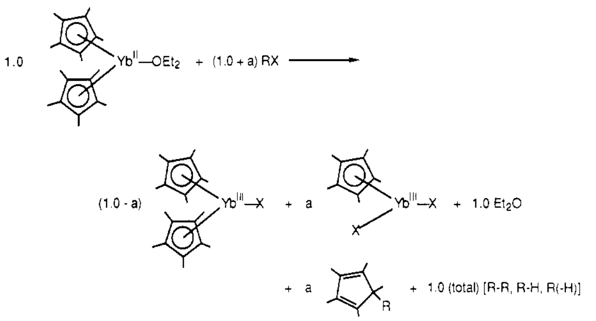
fact undergo rapid oxidative-addition reactions with alkyl and aryl halides. Among the key findings was evidence for the formation of Yb^{III} alkyls, $(C_5Me_5)_2Yb^{III}(R)$, via an unusual[14] radical trapping reaction by closed-shell, $4f^{14}$ Yb^{II}. The ability of this and the other Yb^{III} products to participate in subsequent "Yb^{III}-Grignard" reactions with additional alkyl halide was another important observation.

Herein we provide the necessary details of our investigation of the oxidative addition of alkyl and aryl halides to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, with an emphasis upon previously unreported kinetic and mechanistic studies and emphasis upon the experimental procedures and conditions which turn out to be quite important. The results for the analogous reactions of $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ and $(C_5Me_5)_2Eu^{II}\cdot OEt_2$ with alkyl and aryl halides have been described elsewhere.[6a,15]

Results

$(C_5Me_5)_2Yb^{II}\cdot OEt_2$ Oxidative Additions: Products and Stoichiometry. Following an examination of 15 alkyl and aryl halides, benzyl chloride emerged as a typical and convenient substrate for ^1H NMR product and stoichiometry studies. The oxidative-addition stoichiometry observed, once a slight excess of $PhCH_2Cl$ has been added to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, is shown in eq 2 ($a$ = 0.52); it accounts for 98 ± 5% of the reactants. This generalized stoichiometry of eq 2 is obeyed by $PhCH_2Cl$ and the other alkyl and aryl halides examined (Table I) as long as RX is added as described in the Experimental Section and until a slight excess is present.



(2)

In addition to the above general and *final* stoichiometry, evidence was obtained for the presence of a meta-stable $(C_5Me_5)_2Yb^{III}–R$[16] *intermediate* that undergoes "Yb^{III}-Grignard"[17] reactions with excess RX to give C_5Me_5R and R–R (plus Yb) products. Three lines of evidence support the presence of this intermediate. First, the difference (by ^1H NMR), when comparing the mass balance of a reaction with 1.60 equiv (excess) of $PhCH_2Cl$ to one performed by using only 0.68 equiv of $PhCH_2Cl$, requires formation of ca. 25% of an intermediate of net composition $(C_5Me_5)_{1.9\pm0.4}Yb_{1.0\pm0.2}(CH_2Ph)_{1.0\pm0.4}$. (The precision of this experiment is limited by overlapping resonances in the ^1H NMR.) Second, independent evidence for a $Yb–CH_2Ph$ intermediate was obtained by quenching the 0.68-equiv $PhCH_2Cl$ reaction with MeOH and GLC analysis for toluene (82 ± 8% of the expected 1/4 equiv of toluene is observed). Third, a reaction designed to maximize the apparent $PhCH_2\bullet$ trapping by $(C_5Me_5)_2Yb^{II}$ was performed by using a 12:1 ratio of $(C_5Me_5)_2Yb$ to $PhCH_2Cl$ ($[PhCH_2Cl] = 8.7 \times 10^{-3}$ M). Methanol quench and GLC analysis of this reaction shows the expected formation of additional toluene (62 ± 8% based on $PhCH_2Cl$), providing strong evidence for $(C_5Me_5)_2Yb^{III}–CH_2Ph$ formation, apparently by the novel[14] $PhCH_2^\bullet$ radical trapping reaction by *diamagnetic*, $4f^{14}$ Yb^{II}.

Evidence for the formation of Yb^{III}–alkyl intermediates in the reactions of other alkyl and aryl halides was also obtained. For example, in the reaction of n-BuCl with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, anomalously high amounts of butane are obtained relative to that expected from n-Bu•.[18] Moreover, GLC-determined $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ to RX $(1.0/(1.0 + a))$ values, eq 2, *greater* than 1.0 are observed for reactions of n-BuCl, phenyl halide (PhX), and neopentyl chloride under (lower concentration) conditions reproducing those of the absolute rate experiments (vide infra). Such stoichiometries occur only when the $R^\bullet$ produced by the initial atom-abstraction reaction is captured by a second equivalent of $(C_5Me_5)_2Yb^{II}$ to yield, at least initially, $(C_5Me_5)_2Yb^{III}–R$.

As noted previously[13] and as documented in the Experimental Section, intermediate and final stoichiometries are sensitive to a variety of factors, especially the method of addition and the initial concentrations of both $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and RX and the amount of added coordinating ligands such as Et_2O or THF. In each case, these results are readily explained by the apparent inner-sphere nature of most—if not all—of the key steps in the mechanism. For example, factors that favor Et_2O-free Yb^{II} increase the efficiency of $R^\bullet$ trapping by Yb^{II}.

When $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ is in excess, the *initial, limiting stoichiometry* approaches that previously observed[4] for $(C_5Me_5)_2UCl\cdot THF$ when all the $R^\bullet$ is captured by the metal, that is $2(C_5Me_5)_2Yb^{II}\cdot OEt_2 + RX \rightarrow (C_5Me_5)_2YbX + (C_5Me_5)_2Yb–R$. The $(C_5Me_5)_2Yb^{III}–R$ intermediate formed in these reactions then undergoes rapid followup Grignard reactions with additional RX, eventually resulting in the formation of blue $(C_5Me_5)YbCl_2$ and accounting, in part (vide infra), for the purple to blue color change in the reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with excess $PhCH_2Cl$. The observed stoichiometry in generalized form is shown in eq 3.

"Yb^{III}-Grignard Reactions": Product and Rate Studies of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ and $(C_5Me_5)_2Yb^{III}–R$

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[14] (a) A related reductive radical trapping by $SmI_2(THF)_n$ in Kagan's chemistry has been postulated although its probable inner-sphere mechanism[4,6a] was not previously pointed out.[31] (b) Interestingly, Ln^0 reductive capture of $CH_3^\bullet$ provided the first evidence for the formation of Ln alkyls (Ln = La). Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 474.

[15] Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1987**, *6*, 1356.

[16] (a) Due to the lack of ^1H NMR resonances assignable to $(C_5Me_5)_2Yb^{III}(CH_3)(OEt_2)$, quantification of the products by ^1H NMR was not practical. It is interesting that $(C_5Me_5)_2Yb^{III}–R$ ($R = CH_2Ph$) is not seen by ^1H NMR in contrast to some recently synthesized $(C_5H_5)_2Yb–R$ analogues.[16b,d] However, an authentic sample of the red crystalline methyl complex $(C_5Me_5)_2YbCH_3(OEt_2)$ *is* undetectable under the same conditions of concentration, solvent, and temperature: Watson, P. L.; Herskovitz, T. *ACS Symp. Ser.* **1983**, *No. 212*, 459–479. Moreover, the analogous compounds $(C_5Me_5)_2Ln(\mu\text{-}X)_2Y$ ($X = Cl, CH_3, CH_2SiMe_3$; $Y = Na, Li, Li(dme)_3$, respectively) and $[(C_5Me_5)LnR_3][Li(tmed)_2]$ ($R = CH_3$; Ln = Lu, Yb) are all ^1H NMR active *except* for the Yb compound.[16c] (b) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194. Deacon, G. B.; Fallon, G. D.; MacKinnon, P. I.; Newnham, R. H.; Pain, G. N.; Tuong, T. D.; Wilkinson, D. L. *J. Organomet. Chem.* **1984**, *277*, C21. (c) Albrecht, I.; Hahn, E.; Pickardt, J.; Schumann, H. *Inorg. Chim. Acta* **1985**, *110*, 145. (d) The synthesis of LiCl free $(C_5Me_5)_2YbCH_3(THF)$ (using a hot toluene extraction procedure) and its X-ray structure have been reported: Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263.

[17] The behavior of organolanthanide compounds as Grignard reagents is amply precedented for Yb^{II} complexes such as "RYbX"[17a,c,e] and "RYbR"[17b] and for the Ln^{III} complex $X_2Ln^{III}–R$[17d] but not specifically for $(C_5Me_5)_2Yb^{III}–R$ or $(C_5Me_5)_2Yb^{III}–X$. (a) Reference 30. (b) Evans, D. F.; Fazakerly, G. V.; Phillips, R. F. *J. Chem. Soc. A* **1971**, 1931. (c) Deacon, G. B.; Tuong, T. D. *J. Organomet. Chem.* **1981**, *205*, C4. (d) Kauffmann, T.; Pahde, C.; Tannert, A.; Wingbermuhle, D. *Tetrahedron Lett.* **1985**, *26*, 4063. (e) Hou, Z.; Mine, N.; Fujiwara, Y.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1985**, 1700.

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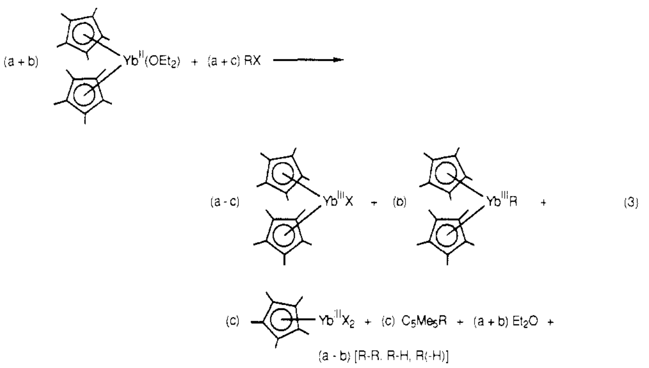
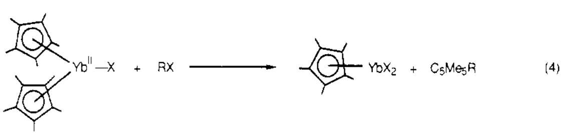


with RX. The "Yb^{III}-Grignard" reactions were probed and verified via independent studies. For example, the reaction of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with 1.0 equiv of $PhCH_2Cl$ yields 1.0 equiv each of $(C_5Me_5)YbCl_2$ and $C_5Me_5CH_2Ph$ (eq 4).



The rate constant for this reaction is at least 500 times slower than that observed for $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ plus $PhCH_2Cl$ ($k_{2obsd} \geq 40\ M^{-1}\ s^{-1}$) and ca. 11 ± 3 times slower than the analogous $(C_5Me_5)_2Yb^{III}$–R + $PhCH_2Cl$ reaction (vide infra). This means that participation of this specific $(C_5Me_5)_2Yb^{III}$–Cl "Grignard" reaction in the overall pathway (eq 3) is significant only toward the end of reaction or when excess $PhCH_2Cl$ is present, that is when the reactants for eq 4 are at relatively high concentrations.

The Yb^{III}–alkyl complexes proved to be more reactive "Grignard" reagents than $(C_5Me_5)_2Yb^{III}X(OEt_2)$. The methyl complex $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ reacts immediately with $PhCH_2Cl$ to give $C_5Me_5CH_2Ph$ and $PhCH_2CH_3$ as the only organic products[16] by ^1H NMR. This complex exhibits the following decreasing activity trend (by ^1H NMR): isopropyl chloride ($t_{1/2} \simeq 2$ h) > n-BuCl ($t_{1/2} \simeq 3$ h) > phenyl iodide ($t_{1/2} \simeq 6$ h) > neopentyl chloride ($t_{1/2} \simeq 10$ h). The reaction of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with $PhCH_2Cl$ shows that the formation of $PhCH_2CH_3$ is favored over that of $C_5Me_5CH_2Ph$ by a factor of 3.4 ± 0.3 (by GLC; since there are two C_5Me_5 ligands vs one CH_3, this number includes a statistical correction factor of 2). A reaction of a 1:1 mixture of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ in toluene competing for $PhCH_2Cl$ (monitored by GLC during the initial stages of the reaction) shows that the $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ reaction is favored over that of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ by a factor of 106 ± 27.

Unfortunately, even with considerable effort we were unable to independently prepare and isolate a pure sample of the Yb^{III}–CH_2Ph complex $(C_5Me_5)_2Yb^{III}$–CH_2Ph for studies analogous to those performed for the Yb^{III}–CH_3 complex.[19] However, competition studies[13a] performed with $(C_5Me_5)_2Yb^{III}$–CH_3 and impure[19] $(C_5Me_5)_2Yb^{III}$–CH_2Ph show their relative rates toward $PhCH_2Cl$ are quite similar, 1.0 ± 0.2. (This ratio probably also reflects the differential Et_2O affinities of the R = $PhCH_2$ vs the CH_3 complex.) These $(C_5Me_5)_2Yb^{III}R$ Grignard reactions are summarized in eq 5 and 6.

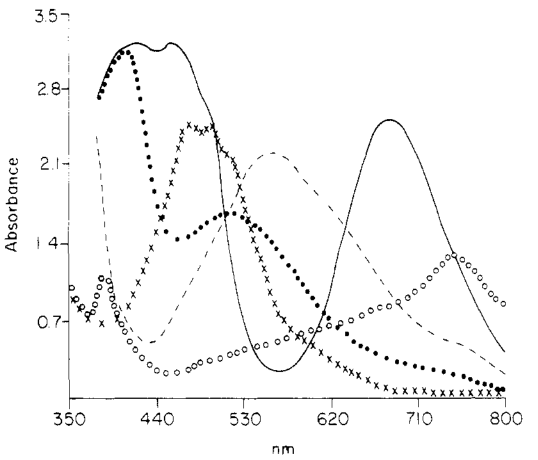
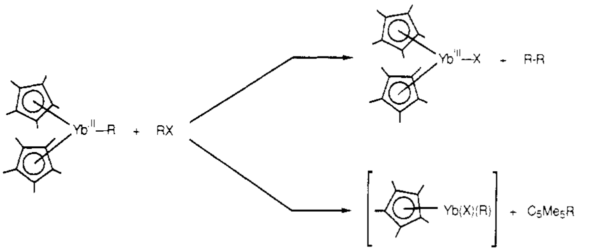


Figure 1. Overlaid visible spectra for the organoytterbium complexes at 22.0 °C in toluene: - - -, 0.0125 M $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$; —, 0.012 M $(C_5Me_5)_2Yb^{II}(OEt_2)$; ○, 0.0124 M $(C_5Me_5)Yb^{III}Cl_2$; ●, impure $(C_5Me_5)_2Yb^{III}CH_2Ph$; ×, 0.011 M $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$.



$(C_5Me_5)_2Yb^{II}\cdot OEt_2$ Reactions: Kinetic and Mechanistic Studies. The complex $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ displays the visible spectrum shown in Figure 1, $\lambda_{max} = 680$ nm. Beer's law is obeyed over the concentration range examined, $(3.42–9.77) \times 10^{-3}$ M, $\epsilon_{680(toluene)} = 214 \pm 6\ M^{-1}\ cm^{-1}$. The absolute rates of reaction of RX with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ were determined by monitoring the decrease in absorbance due to $[Yb^{II}]_T$ at 680 nm at 22.0 °C in toluene. Comparable concentrations of both $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and RX (i.e. second-order conditions) were used in all cases in order to minimize the follow-up Yb^{III} plus RX Grignard reactions. The products $(C_5Me_5)_2Yb^{III}X(OEt_2)$, $(C_5Me_5)_2Yb^{III}R(OEt_2)$, and $(C_5Me_5)_1Yb^{III}X_2$ all have substantial absorbances at the 680-nm wavelength used for the kinetic determinations (Figure 1); hence a correction compensating for the product absorbances has to be made. In addition, the rate law contains a stoichiometry factor, Q, defined as $Q = (a + b)/(a + c)$ (from eq 3), which had to be obtained independently from GLC experiments performed under conditions *identical* with those of the absolute rate experiments.

Furthermore, design and interpretation of the kinetic studies require (a) a knowledge of whether or not significant concentrations of the bis Et_2O adduct $(C_5Me_5)_2Yb^{II}(OEt_2)_2$ is present under the conditions of the kinetic experiments, and (b) a knowledge of its relative

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(19) (a) Approaches to $(C_5Me_5)_2Yb^{III}CH_2Ph$ included the ionic reactions of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with $LiCH_2Ph$ and $ClMgCH_2Ph$ and the redox driven reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with $Cu(CH_2Ph)$[38b] and $Hg(CH_2Ph)_2$ and with $Te(CH_2Ph)_2$.[19b] (The Cu–CH_2Ph compound was unstable as a solid above ca. −20 °C, and the conditions required were incompatible for in situ reaction utilizing Yb^{II}.) In all cases the reaction yields products less pure than the HgR_2 reaction or does not occur ($Te(CH_2Ph)_2$). The impurities present by ^1H NMR appear to be bibenzyl and a C_5Me_5R compound. The impure $(C_5Me_5)_2Yb^{III}CH_2Ph$ appears unstable when isolated and stored at room temperature, decolorizing when sealed in a darkened bottle in the drybox to give a hexane-insoluble orange solid and increased amounts of bibenzyl and C_5Me_5R. (b) Gysling, H. J. *Coord. Chem. Rev.* **1982**, *42*, 133. Gysling, H. J.; Luss, H. R.; Smith, D. L. *Inorg. Chem.* **1979**, *18*, 2696.

Scheme I. Proposed Mechanism (Initial Steps) for the Reactions of $(C_5Me_5)_2Yb^{II}\bullet OEt_2$ with Alkyl and Aryl Halides at 22 °C in Toluene

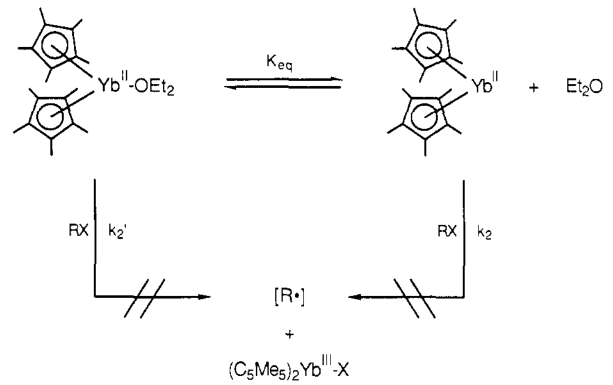

Table II. Absolute Rates (M^{-1} s^{-1}) of Alkyl and Aryl Halide Oxidative Additions to $(C_5Me_5)_2Yb^{II}\bullet OEt_2$ at 22 °C in Toluene

substrate	k_{2obsd}[c]
n-BuCl	1.9 ± 0.2
n-BuCl[a]	0.037 ± 0.004
neopentyl Cl	0.30 ± 0.04
isopropyl Cl[b]	23 ± 5
iodobenzene	2.4 ± 0.8
bromobenzene	0.039 ± 0.005

[a] Et_2O solvent; stoichiometry coefficient $Q = 1.0$. [b] Determined from the last 10% to 15% of this fast reaction. [c] k_{2obsd} is a composite; $k_{2obsd} = k_2K_{eq}/(K_{eq} + [L])$; see the mechanism given in Scheme I.

oxidative addition rate constant k_2''. Early control experiments showed that added Et_2O has no effect on the $[Yb^{II}]_T$ absorbance over the concentration range used for the absolute rate experiments (0.018–0.073 M), arguing against the presence of significant amounts of a $(C_5Me_5)_2Yb^{II}(OEt_2)_2$ complex. However, upon adding Et_2O at high (>0.2 M) concentrations, decreases in the 680-nm absorbance assigned to $[Yb^{II}]_T$ (beyond what is expected from simple dilution effects) indicate, as expected based on literature precedent, that it in fact is possible to bind two Et_2O ligands[20] to $(C_5Me_5)_2Yb^{II}$ under these conditions. Fortunately, contributions to the observed *rates* of oxidative addition from the direct reaction of $(C_5Me_5)_2Yb^{II}(OEt_2)_2$ (rate constant = k_2'', Scheme I) or $(C_5Me_5)_2Yb^{II}(OEt_2)$ (rate constant = k_2', Scheme I) with RX were found to be negligible based on three lines of evidence. First, the observation of a linear $1/k_{2obsd}$ vs $[Et_2O]$ plot requires $50(k_2'' + k_2') < k_2$ (vide infra). (Simulated $1/k_{2obsd}$ vs $[Et_2O]$ plots showed that a contribution of as little as 5% from k_2' and/or k_2'' would have been detected by curvature in the plot.) Second, the rate of reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with *n*-BuCl in neat Et_2O as solvent is $(k_{2obsd}'' + k_{2obsd}') = (3.7 \pm 0.4) \times 10^{-2}$ M^{-1} s^{-1}, providing (following comparison to k_{2obsd}) the limit $51(k_{2obsd}'' + k_{2obsd}') \leq k_{2obsd}$ and thus suggesting $(k_2'' + k_2') \ll k_2$ ($k_{2obsd} = 1.9 \pm 0.2$ M^{-1} s^{-1} for the reaction of *n*-BuCl with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (Table II); k_{2obsd}, k_{2obsd}', and k_{2obsd}'' are composites; i.e., they include the effects of Et_2O on $\rightleftarrows$ off equilibria). Third, $(C_5Me_5)_2Yb^{II}\cdot$(dimethoxyethane) reacts only slowly with *n*-BuCl, $k_{2obsd}'' = (3.0 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1},[6a] providing the limit 633 $k_{2obsd}'' \leq k_{2obsd}$ and strongly suggesting $k_2'' \ll k_2$.

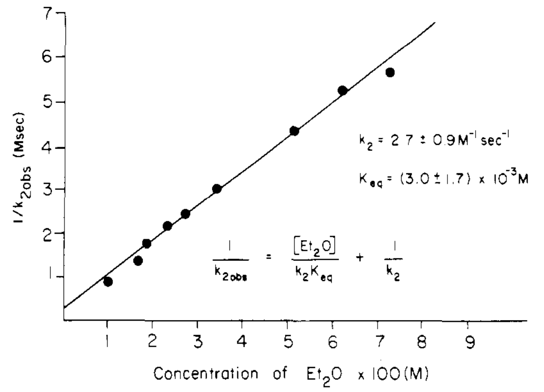

Figure 2. $1/k_{2obsd}$ vs $[Et_2O]$ plot for *n*-BuCl oxidative addition to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ at 22.0 °C in toluene (*n*-BuCl = 0.0098 M, Yb^{II} = 0.0078–0.0085 M, and stoichiometry coefficient $Q = 1.6 \pm 0.2$ as determined by GLC). Error bars for k_{2obsd} (not shown) are ±10%.

The rate laws for the reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with *n*-butyl chloride (*n*-BuCl), neopentyl chloride (NpCl), isopropyl chloride (*i*-PrCl), phenyl iodide (PhI), and phenyl bromide (PhBr) were determined in toluene at 22.0 °C (Table II); $-d[Yb^{II}]_T/dt = (Q)k_{2obsd}[Yb^{II}]_T[RX]_T$ for all concentrations of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and for each of the RX examined. Typical second-order kinetic plots are linear for at least 80% of the reaction or 2–3 half-lives (and are available as supplementary material). Trimethylsilyl chloride, PhCl, and *n*-octyl fluoride show no reaction with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, while the reactions of the other substrates listed in Table I (benzyl X, *t*-BuCl, MeI) occur too rapidly for non-stopped-flow measurements.

Added Et_2O acts to retard the rate of reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX in all cases. The full concave $[Et_2O]$ dependence was established for the reaction of *n*-BuCl with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ at 22.0 °C, consistent with a prior equilibrium where $K_{eq} \ll 1$ (Scheme I). A stoichiometry coefficient, Q, is required to interpret properly a $1/k_{2obsd}$ vs $[Et_2O]$ plot of these data, and an average of $Q = 1.6 \pm 0.2$ was determined by GLC experiments under conditions duplicating those of the absolute rate experiments. Fortunately, the *n*-BuCl oxidative-addition stoichiometry is relatively insensitive (compared to that for $PhCH_2Cl$) to added Et_2O. (Plots of the effect of added Et_2O on the product distributions for the *n*-BuCl and $PhCH_2Cl$ reactions are provided as supplementary material.) Derivation of the necessary kinetic equations[21] and the appropriate $1/k_{2obsd}$ vs $[Et_2O]$ plot (Figure 2) is linear and provides $K_{eq} = (3.0 \pm 1.7) \times 10^{-3}$ M and $k_2 = (2.7 \pm 0.9)$ M^{-1} s^{-1} and allows the limit $50k_2' \leq k_2$ to be set.

These results strongly suggest an inner-sphere mechanism. However, they are not sufficient to tell if the reaction proceeds as outlined in Scheme I or whether there is a second equilibrium present involving RX prior coordination, $(C_5Me_5)_2Yb^{II} + RX \rightleftarrows (C_5Me_5)_2Yb^{II}(RX)$, with equilibrium constant $K_{eq,RX}$. The reported $K_{eq(obsd)}$ would then actually be a composite, $K_{eq(obsd)} = (K_{eq,RX})(K_{eq,L})$ for the equilibrium $(C_5Me_5)_2Yb^{II}(OEt_2) + RX \rightleftarrows (C_5Me_5)_2Yb^{II}(RX) + Et_2O$. We mention this because we consider an initial RX binding equilibrium likely, both because complexes with alkyl and aryl halides are now well established[1] and because Yb^{III} shift reagents bind and shift alkyl fluorides.[22a,d] However, it has been omitted from

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[20] (a) Thomas, A. C.; Ellis, A. B. *J. Chem. Soc., Chem. Commun.* **1984**, 1270. (b) Schlesener, C. J.; Ellis, A. B. *Organometallics* **1983**, *2*, 529. (c) Thomas, A. C.; Ellis, A. B. *Ibid.* **1985**, *4*, 2223.

[21] (a) From Scheme I, a plot of $1/k_{2obsd}$ vs $[Et_2O]$ will be linear if $k_2' \ll k_2$ and have a slope of $1/K_{eq}k_2$ and intercept $1/k_2$. (b) At higher Et_2O concentrations the $1/k_{2obsd}$ vs $[Et_2O]$ plot begins to level off as expected.

Table III. Absolute Rates (M^{-1} s^{-1}) of Alkyl Halide Reactions with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ at 22 °C in Toluene

substrate	k_{2obsd}	solv
t-BuCl	$(3.8 \pm 0.7) \times 10^{-2}$	Et_2O
t-BuCl	$(3.2 \pm 0.6) \times 10^{-2}$	toluene
$PhCH_2Cl$	$(2.7 \pm 0.7) \times 10^{-4}$	Et_2O
$PhCH_2Cl$	$(6.5 \pm 1.5) \times 10^{-2}$	toluene

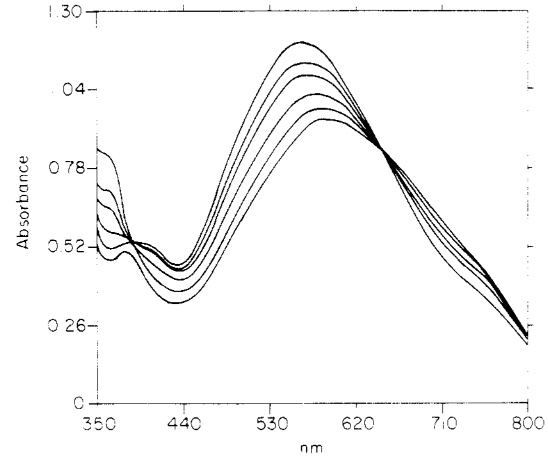

Figure 3. Visible spectra for the reaction of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with $PhCH_2Cl$ at 22.0 °C in toluene (Yb^{III}–Cl = 0.0091 M and $PhCH_2Cl$ = 0.013 M). An isosbestic point occurs at 665 nm.

Scheme I because we lack direct evidence for the participation of this equilibrium.

The k_{2obsd} for $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX decreases in the order X = I > Br > Cl ≫ F and R = benzyl ≃ tertiary > secondary > primary > neopentyl > phenyl. This trend is consistent with an atom-abstraction oxidative addition to generate an organic radical. Further evidence for the intermediacy of organic radicals is provided by the observation of dimers, olefins, and alkanes in the reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with n-BuCl, for example. The observed octane to butene, that is the $k_{combinatn}/k_{disproportionatn}$ ratio, is 0.14 ± 0.05, within experimental error of that characteristic of the n-Bu• free radical, 0.15.[18] Moreover, the reaction of RX = (chloromethyl)cyclopropane with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ shows, by ^1H NMR, the generation of significant amounts (0.21 equiv) of olefinic organic products.[23] (However, the C_5Me_5R product (0.04 equiv) is exclusively $C_5Me_5CH_2\overline{CHCH_2CH_2}$ by GLC.)

$(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ Reactions: Kinetic and Mechanistic Studies. $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ displays the visible spectrum shown in Figure 1, λ_{max} = 550 nm. It too obeys Beer's law over the concentration range examined, $(2.26–9.04) \times 10^{-3}$ M, $\epsilon_{550} = 176 \pm 2$ M^{-1} cm^{-1}. The absolute rates of reaction of selected alkyl halides with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ are summarized in Table III. The observed rate constants were obtained by monitoring the disappearance of the $[Yb^{III}–Cl]_T$ at 550 nm at 22.0 °C in toluene. Pseudo-first-order conditions (excess RX) were used for reactions of RX = t-BuCl with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$, while both pseudo-first-order and second-order conditions were used for reactions of RX = $PhCH_2Cl$.

Table IV. Relative Rates of the Reaction of $PhCH_2X$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ at 23 °C in Benzene-d_6 Determined by Pairwise ^1H NMR Competition Experiments

substrates R = CH_2Ph	k_{obsd}/k_{obsd}
RF/RCl	16 ± 3
RBr/RCl	3 ± 1
RF/RBr	3.6 ± 0.1
RF/RBr[a]	1.0 ± 0.2[a]

[a] In THF-d_8.

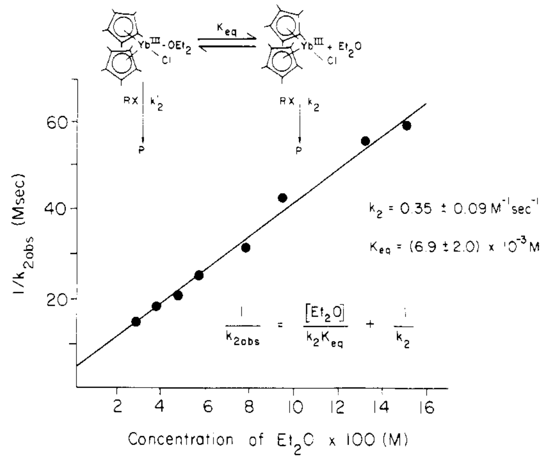

Figure 4. $1/k_{2obsd}$ vs $[Et_2O]$ plot for the reaction of $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ at 22.0 °C in toluene ($PhCH_2Cl$ = 0.013 M and Yb^{III}–Cl = 0.0079–0.010 M). Error bars for k_{2obsd} (not shown) are ±10%.

As in the $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ reactions described above, a correction had to be made to compensate for the $(C_5Me_5)_1Yb^{III}Cl_2$ product absorbance growing in at this wavelength (Figure 1). (Details are provided in the Experimental Section.) Unlike reactions of RX with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, the reactions of RX with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ show a clean isosbestic point at 665 nm for both RX = t-BuCl and $PhCH_2Cl$ (shown in Figure 3 for $PhCH_2Cl$) *as long as second-order concentration conditions in RX are used*, thereby avoiding complications due to subsequent reactions of $(C_5Me_5)_1Yb^{III}Cl$.

Only the most active substrates are found to react with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ at appreciable rates; substrates such as n-BuCl and n-BuBr react only very slowly ($k_{2obsd} \leq 10^{-4}$ M^{-1} s^{-1}), while neopentyl chloride and the phenyl halides (PhX, X = I, Br, Cl) do not react. (Chloromethyl)cyclopropane reacts rapidly to give $C_5Me_5\overline{CHCH_2CH_2}$ as the only C_5Me_5R product by ^1H NMR and GLC. This result indicates that *free* radicals, i.e. those that have escaped the solvent cage, are not involved in the Grignard reactions of $(C_5Me_5)_2Yb^{III}X(OEt_2)$.

Kinetic plots for the reaction of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with t-BuCl and $PhCH_2Cl$ are typically linear for 3–4 half lives. (Representative kinetic plots for the reaction of $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ using both pseudo-first-order and second-order concentrations of RX are available as supplementary material.) The reactions all obey the rate law $-d[Yb^{III}–Cl]/dt = k_{2obsd}[Yb^{III}–Cl][RX]$, overall second-order, first-order each in RX and $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$.

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(22) Such a trend for halide binding has been firmly established from studies utilizing organolanthanides as NMR shift reagents: (a) Kime, K. A.; Sievers, R. E. *Aldrichim. Acta* **1977**, *10*, 54. (b) Cocerkill, A. F.; Davies, G. L. O.; Harden, R. C.; Rackham, D. M. *Chem. Rev.* **1973**, *73*, 553. (c) Reuben, J. *Prog. Nucl. Magn. Reson. Spectrosc.* **1973**, *9*, 1. (d) San Filippo, J., Jr.; Nuzzo, R. G.; Romano, L. J. *J. Am. Chem. Soc.* **1975**, *97*, 2546. (e) *Nuclear Magnetic Resonance Shift Reagents*; Sievers, R. E., Ed.; Academic: New York, 1973. (f) deRenzi, A.; Morelli, G.; Panunzi, A.; Wurzburger, S. *Inorg. Chim. Acta* **1983**, *76*, L285. (g) Wenzel, T. J. *J. Org. Chem.* **1984**, *49*, 1834. (h) Abraham, R. J.; Chadwick, D. J.; Sancassan, F. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1037. (i) McGarvey, B. R. *Can. J. Chem.* **1984**, *62*, 1349. (j) Jahn, W.; Yunlu, K.; Oroschin, W.; Amberger, H.-D.; Fischer, R. D. *Inorg. Chim. Acta* **1984**, *95*, 85. (k) Wenzel, T. J.; Zaia, J. *J. Org. Chem.* **1985**, *50*, 1322.

(23) (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. (b) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (c) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395.

Interestingly, the reaction of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with $PhCH_2Cl$ is 200 times slower with Et_2O as the solvent (Table II), suggesting that these reactions also proceed via an inner-sphere mechanism analogous to that proposed for reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX (Scheme I). Suggestive evidence for prior coordination of RX to $(C_5Me_5)_2Yb^{III}X(OEt_2)$ was obtained by ^1H NMR competition experiments in benzene-d_6 and THF-d_8 utilizing $PhCH_2X$ (X = Br, Cl, F; Table IV). As can be seen, the order of reactivity $F \gg Br > Cl$ does not parallel—is in fact the opposite of—the relative leaving group abilities of the halides, $Br > Cl \gg F$. The order of reactivity resembles more closely the relative affinity of electropositive Yb^{III} for electronegative X, $F \gg Cl > Br$.[22]

The inner-sphere nature of these $(C_5Me_5)_2Yb^{III}X(OEt_2)$ Grignard reactions was verified by determining the $[Et_2O]$ dependence of the $PhCH_2Cl$ plus $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ rate in a manner analogous to that described earlier for $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ plus n-BuCl. An eight-point plot[21] of $1/k_{2obsd}$ vs $[Et_2O]$ is linear over the range examined (Figure 4). From this plot the values $k_2 = 0.35 \pm 0.09$ M^{-1} s^{-1}, $K_{eq} = 0.0069 \pm 0.0020$ M, and the limit $50k_2' \leq k_2$ are obtained.

$(C_5Me_5)_2Yb^{III}R(OEt_2)$ (R = CH_2Ph, CH_3) Reactions: Kinetic Studies for R = CH_2Ph. As stated previously, the $(C_5Me_5)_2Yb^{III}R$ complexes are more reactive than $(C_5Me_5)_2Yb^{III}X$ in "Grignard-like" reactions with RX. Numerous attempts to prepare authentic $(C_5Me_5)_2Yb^{III}CH_2Ph$ by reaction of $LiCH_2Ph$ or $Mg(Cl)(CH_2Ph)$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ or $Hg(CH_2Ph)_2$ with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ yielded samples of insufficient purity[19] for reliable absolute rate experiments. However, a rough estimate for k_{2obsd} for the reaction of $(C_5Me_5)_2Yb^{III}CH_2Ph$ with $PhCH_2Cl$ was obtained in the following GLC experiment. In this experiment, $(C_5Me_5)_2Yb^{III}CH_2Ph$ was generated in situ from (excess) $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and $PhCH_2Cl$. The $Yb^{III}-CH_3$ complex $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ was then added. (The $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ complex can also be added at the same time as $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ without complications, due to the slower reaction of the $Yb^{III}-CH_3$ complex with $PhCH_2Cl$.) $PhCH_2Cl$ was then added, and the relative amounts of the products $PhCH_2CH_2Ph$ and $PhCH_2CH_3$ were determined. The result is the estimate $k_{2obsd} \simeq 0.7 \pm 0.2$ M^{-1} s^{-1} for the reaction of $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}CH_2Ph$ (based on a k_{2obsd} value of 0.55 ± 0.10 M^{-1} s^{-1} for the reaction of the R = CH_3 complex with $PhCH_2Cl$ and assuming the R = CH_2Ph complex also exhibits second-order kinetics).

For R = CH_3. In the case of the R = CH_3 complex, it was possible to prepare authentic, crystalline material from $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ and $LiCH_3$. The visible spectrum for $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ is displayed in Figure 1, $\lambda_{max} = 475$ nm, and Beer's law is obeyed over the concentration range examined, 0.0013–0.018 M, $\epsilon_{460(toluene)} = 200 \pm 20$ M^{-1} cm^{-1}. The absolute rate for the reaction of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with $PhCH_2Cl$ was determined at 22.0 °C in toluene under second-order conditions by monitoring the $[Yb^{III}-CH_3]$ decrease at 460 nm. Individual second-order kinetic plots are typically linear for 2–3 half-lives (provided as supplementary material). The reactions obey the rate law $-d[Yb^{III}-CH_3]/dt = k_{2obsd}[Yb^{III}-CH_3][RX]$ with $k_{2obsd} = 0.55 \pm 0.10$ M^{-1} s^{-1} for $PhCH_2Cl$.

Added Et_2O acts to retard the rate of reaction of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with $PhCH_2Cl$. The preliminary $[Et_2O]$ dependence of the rate of reaction was established at 22.0 °C in toluene. Unfortunately a plot of $1/k_{2obsd}$ vs $[Et_2O]$ is not linear over the $[Et_2O]$ range examined, 0–0.12 M. We believe this is due to the higher uncertainty in the individual k_{2obsd} values and probably also due to a competitive outer-sphere reaction. Evidence for the latter is provided from the reaction of t-BuCl with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$. Here the rate is virtually unchanged on going from toluene to neat Et_2O (Table III), suggesting an outer-sphere reaction. The organic products also change to C_5Me_5H and $(CH_3)_2C{=}CH_2$, products of an apparent H^+ transfer reaction.

Discussion

The goal of these oxidative-addition studies is to determine the general reactions and mechanisms for a series of organolanthanide and organoactinide bis(pentamethylcyclopentadienyl) complexes of different f^n configuration, different number of unpaired electrons, varying ionic size,[10] and varying metal $E_{1/2}$ value,[8,9] and to determine which factors dominate their reactivity. Our survey of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, $(C_5Me_5)_2Sm^{II}\cdot OEt_2$, $(C_5Me_5)_2Eu^{II}\cdot OEt_2$, and $(C_5Me_5)_2U^{III}Cl\cdot THF$ is now complete;[4,6a,13,15] the two most thoroughly investigated systems are the $(C_5Me_5)_2U^{III}Cl\cdot THF$ organoactinide[4,6a,7] and the present $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ organolanthanide ones.

The data for $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ fully support the mechanism shown in Scheme I. In this (minimum) mechanism (for the initial steps), which is essentially the same as that found previously[4,6a] for $(C_5Me_5)_2U^{III}Cl\cdot THF$, ligand dissociation is required and is then followed by the net atom-abstraction reaction $(C_5Me_5)_2Yb^{II} + RX \rightarrow (C_5Me_5)_2Yb^{II}-X + R^\bullet$.

A second equivalent of $(C_5Me_5)_2Yb^{II}$ then must rapidly trap $R^\bullet$ competitively with diffusion-controlled self-coupling and disproportionation reactions of $R^\bullet$ (Scheme II) to give metal alkyls as additional intermediates or, in some cases, metastable products. Such a result is reasonable for U^{III} with its partially covalent U–R bonds[24] but has little precedent[14] and therefore was somewhat surprising for the largely ionic[25] organoytterbium complex—particularly in light of the closed-shell, $4f^{14}$ fully paired configuration of $(C_5Me_5)_2Yb^{II}$.[26] Given the ionic nature of the organolanthanides and their inaccessible 4f orbitals, it seems likely that such products arise from a *facile inner-sphere electron transfer* from Ln^{II} to $R^\bullet$ to give $Ln^{III}-R$ (rather than a simple recombination of unpaired electrons to give largely covalent bonds as in $R^\bullet$ trapping by Co^{II} or $R_3M^\bullet$ (M = Si, Sn)). Some precedent does exist for a single electron-transfer step of this nature. For example, electron transfer from U^{III} ions in aqueous solution to organic radicals has been found to occur, giving U^{IV} and R^-.[27]

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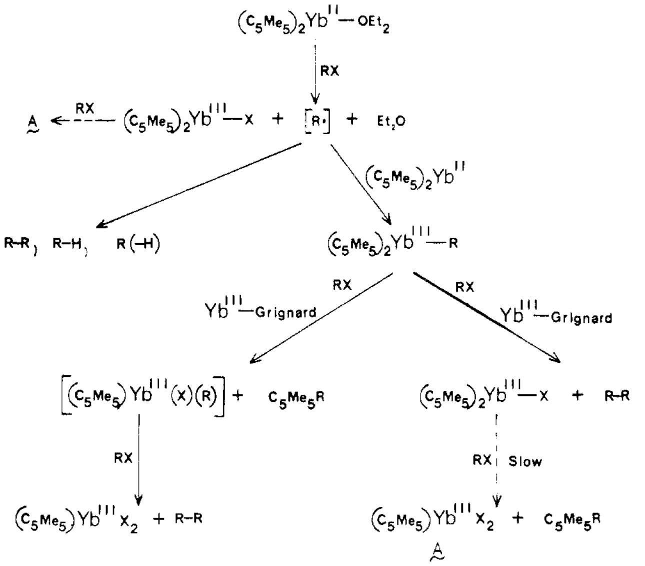
[24] (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 622. (b) See ref 11r. (c) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1984**, *23*, 1633. (d) Tatsumi, K.; Nakamura, A. *J. Organomet. Chem.* **1984**, *272*, 141.

[25] (a) Reference 11a. (b) Mauermann, H.; Swepston, P. N.; Marks, T. J. *Organometallics* **1985**, *4*, 200. (c) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 622. (d) Reference 11r. (e) Anderson, E. A.; Tilley, T. D. *J. Am. Chem. Soc.* **1982**, *104*, 1772. (f) Andersen, R. A.; Tilley, T. D.; Zalkin, A. *Ibid.* **1982**, *104*, 3725. (g) Ciliberto, E.; Condorelli, G.; Fagan, P. G.; Manriquaz, J. M.; Fragala, I.; Marks, T. J. *Ibid.* **1981**, *103*, 4755. (h) Zalkin, A.; Templeton, D. H.; Luke, W. D.; Streitwieser, A., Jr. *Organometallics* **1982**, *1*, 618. (i) Bruno, G.; Ciliberto, E.; Fischer, R. D.; Fragala, I.; Spiegl, A. W. *Ibid.* **1982**, *1*, 1060. (j) Bunzli, J.-C. G.; Klein, B.; Chapuis, G.; Schenk, K. J. *Inorg. Chem.* **1982**. *21*, 808.

[26] Interestingly, spin paired d^8 $(CH_3)_2Pt^{II}$ (1,10-phenanthroline) is found to trap bulky radicals such as isopropyl at rates of 10^7 M^{-1} s^{-1}, suggesting that trapping of less bulky radicals should approach diffusion control for this diamagnetic Pt^{II} compound. Hill, R. H.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1218. Monaghan, P. K.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 439.

[27] Golub, D.; Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1985**, 641.

Scheme II. Proposed Mechanistic Scheme for Reactions of $(C_5Me_5)_2Yb^{II}\bullet OEt_2$, $(C_5Me_5)_2Yb^{III}X(OEt_2)$, and $(C_5Me_5)_2Yb^{III}R$ with Alkyl and Aryl Halides



Moreover, such a process is consistent with the *outer-sphere* reduction potentials known from simple alkyl radicals and, then, the more favorable energetics of the inner-sphere (vs the outer-sphere) process.[28] For example, $PhCH_2^\bullet$ is reduced at ca. −1.45 V vs SCE[28] while the lanthanide II/III potential is also in this range.[8]

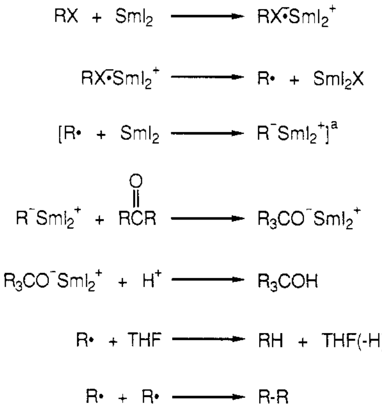
Once formed, the $(C_5Me_5)_2Yb^{III}R$ complexes undergo further, "Grignard" reactions with RX to rapidly generate R–R, C_5Me_5R, and $(C_5Me_5)Yb^{III}X_2$ (Scheme II), reactions that were independently verified (except for $[(C_5Me_5)Yb^{III}(X)R]$, hence it is shown in brackets in Scheme II). The reactions needed to account for the observed kinetic and product data are summarized in Scheme II.

It is interesting to note that the corresponding, but less ionic, U^{IV} alkyls do not show any such Grignard reaction.[4,6a] This presumably reflects the small—but significant—covalent contributions to the organoactinide bonding.[24] The U^{IV} complexes do participate in facile ionic halide exchange equilibria,[4,6a] however, of the type also known for the organolanthanides.[13b,25]

One uncertainty of the present studies is whether or not a contribution to the observed C_5Me_5R and $(C_5Me_5)Yb^{III}X_2$ products occurs by the hypothetical Yb^{II}-Grignard reaction: $(C_5Me_5)_2Yb^{II}\cdot OEt_2 + RX \rightarrow [(C_5Me_5)Yb^{II}X(OEt_2)] + C_5Me_5R$, followed by $[(C_5Me_5)Yb^{II}X(OEt_2)] + RX \rightarrow (C_5Me_5)Yb^{III}X_2 + R^\bullet$. The distribution of products from the reaction of $PhCH_2Cl$ with a 12-fold excess of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (60% $(C_5Me_5)_2Yb^{III}(CH_2Ph)$, 20% $C_5Me_5CH_2Ph$, 10% $PhCH_2CH_2Ph$) suggests that such a contribution may occur (≤20%) but is likely a minor contributor in comparison to the pathways presented in Scheme II.

The fact that the Yb^{II} and Yb^{III} reactions utilize inner-sphere mechanisms to achieve their enhanced reactivity is the single most important result from these studies. Outer-sphere electron transfer is thought to be particularly disfavored for the f elements due to the inaccessibility of the 4f valence orbitals;[29] f elements have been referred to as primary examples of non-adiabatic reactions (due to poor orbital overlap between the reactants) and are said to be prime candidates for the observation of electron tunneling (although there is some controversy regarding this subject).[29] Hence one's predictions and our findings agree in that an inner-sphere electron-transfer pathway should be,[29d] *and is*, preferred in the oxidative additions of alkyl and aryl halides to Yb^{II}. The inner-sphere mechanism is, then, intimately tied to the effects of covalency, decreasing the distance between the Yb^{II} and RX reactants provides a more favorable orbital–orbital interaction. The 5s and 5p component of this orbital interaction is thought to increase as the reaction's driving force increases.[29b,c] Detailed kinetic studies comparing $(C_5Me_5)_2Sm^{II}\cdot OEt_2$ to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ might possibly provide further evidence on this point.

Scheme III. Mechanism[31] Proposed by Kagan et al.[30,31] for the Reaction of SmI_2 with Alkyl and Aryl Halides and Ketones in THF



(a) This step was excluded for the alkyl halides presumably because the authors were unable to isolate Sm^{III}-alkyl intermediates.

It seems probable that the observed dominance of inner-sphere pathways will extend to other applications of organolanthanides (at least under certain conditions), for example, in organic synthesis.[30,31] Although a general

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[28] Wayner, D. D. M.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 7764 and references therein.

[29] (a) Taube, H. *Adv. Chem. Ser.* **1977**, *No. 162*, 127. (b) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370. (c) Furholz, U.; Haim, A. *Inorg. Chem.* **1985**, *24*, 3091. (d) Recent studies of electrochemical (outer-sphere) reductions of alkyl halides show that roughly 80% of the activation energy is C–X bond breaking. This also indicates why inner-sphere mechanisms, where metal···X bond making can occur simultaneous with C···X bond breaking (and where charge separation following electron transfer is minimized), are preferred. Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788. Andrieux, C. P.; Gallardo, I. Savéant, J.-M.; Su, K.-B. *J. Am. Chem. Soc.* **1986**, *108*, 638. Andrieux, C. P.; Merz, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 6097.

[30] The use of Ln^{II} to Ln^{III} reactions in organic synthesis has been investigated: (a) Imamoto, T.; Tawarayama, Y.; Kusumoto, T.; Yokoyama, M. *J. Synth. Org. Chem. Jpn.* **1984**, *42*, 143. (b) Yokoo, K.; Fukagawa, T.; Yamanaka, Y.; Taniguchi, H.; Fujiwara, Y. *J. Org. Chem.* **1984**, *49*, 3237. (c) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693. (d) Souppe, J.; Danon, L.; Namy, J. L.; Kagan, H. B. *J. Organomet. Chem.* **1983**, *250*, 227. (e) Yokoo, K.; Kijima, Y.; Fujwawa, Y.; Taniguchi, H. *Chem. Lett.* **1984**, 1321. (f) Souppe, J.; Namy, J. L.; Kagan, H. B. *Tetrahedron Lett.* **1984**, *25*, 2869. (g) Deacon, G. B.; Tuong, T. D. *J. Organomet. Chem.* **1981**, *205*, C4. (h) Molander, G. A.; Etter, J. B. *Tetrahedron Lett.* **1984**, *25*, 3281. (i) Molander, G. A.; LaBelle, B. E.; Hahn, G. *J. Org. Chem.* **1986**, *51*, 5259. (j) Molander, G. A.; Etter, J. B.; Zinke, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 453. (k) Imamoto, T.; Takiyama N. *Tetrahedron Lett.* **1987**, *28*, 1307. (l) Evans, W. J.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1722. (m) Namy, J. L.; Collin, J.; Zhang, J.; Kagan, H. B. *J. Organomet. Chem.* **1987**, *328*, 81. (n) *Inanaga*, J.; Ishikawa, M.; Yamaguchi, M. *Chem. Lett.* **1987**, 1485. (o) Otsubo, K.; Kawamura, K.; Inanaga, J.; Yamaguchi, M. *Chem. Lett.* **1987**, 1487.

mechanism has been proposed for the reactions of the Sm^{II} compound SmI_2 with organic halides and ketones or aldehydes[31] (Scheme III), all the steps were written as shown, apparently as outer-sphere processes. Inner-sphere processes should be preferred, although the use of THF as a solvent in these reactions may be inhibiting inner-sphere pathways just as THF and Et_2O, respectively, inhibit U^{III} and Yb^{II} atom-abstraction oxidative additions.

Comparison of the rate of organoactinide and organolanthanide reactions with alkyl and aryl halides allow some insights into the intimate mechanism of the atom-abstraction step. Comparison of $(C_5Me_5)_2U^{III}Cl\cdot THF$ to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ shows the rates of the Yb^{II} reactions with alkyl and aryl halides to be consistently slower than U^{III}, but only by ca. 1 order of magnitude—i.e., their reactivities are similar.

It is useful at this point to recall the properties given previously for Yb^{II} and U^{III}: their ionic radii and $E_{1/2}$ values are quite similar, but their f^n configurations and numbers of unpaired electrons are very different: (Yb^{II}, $4f^{14}$ closed shell; U^{III}, $5f^3$, three unpaired electrons). It follows, then, that either their similar size or their similar $E_{1/2}$ values (or some other property that is comparable) are more important in determining their similar reactivities than is their much different f^n configurations. *Indeed, if this were a simple atom-abstraction reaction as an elementary step, one would expect no relationship of a metal triradical* U^{III} *to a diamagnetic metal* (Yb^{II})! Furthermore, if one realizes that paramagnetic products (Yb^{III}) are formed from the diamagnetic Yb^{II} precursor, one is led to the seemingly inescapable conclusion that Yb^{II} unpairs an electron in the transition state of its rate-determining step. Restated, we consider this prima facie evidence for the importance of single electron transfer in these net "atom-abstraction" reactions.[6]

Further evidence for the importance of electron transfer in organolanthanide and organoactinide oxidative additions is provided by the relative oxidative-addition rates,[15] $Sm^{II} > Yb^{II} \gg Eu^{II}$ (no reaction), a trend that mirrors their decreasing reduction potentials to the limit where no oxidative-addition reaction is seen for Eu because the Eu^{II} to Eu^{III} reduction of $PhCH_2Cl$ or t-BuCl is thermochemically unfavorable.[15]

Conclusions

The major conclusions from this work can be summarized as follows:

(1) $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ undergoes atom-abstraction oxidative addition with alkyl and aryl halides 10^3–10^6 times faster than typical d-block atom-abstraction reactions, according to the initial stoichiometry: $(a + b)(C_5Me_5)_2Yb^{II}(OEt_2) + (a + c)RX \rightarrow (a - b)$"$R^\bullet$" $+ (b)(C_5Me_5)_2YbR + (a - c)(C_5Me_5)_2YbX + (c)(C_5Me_5)YbX_2 + (c)C_5Me_5R + (a + b)Et_2O$.

(2) The initial step in these oxidative-addition reactions occurs inner-sphere (Scheme I); loss of the Et_2O ligand is required for the observed enhanced reactivity. The enhanced reactivity also reflects the large $E_{1/2}$ driving force and the significant Yb···X bonding in the transition state (and strong Yb^{III}–X bonds) allowed by the inner-sphere mechanism.

(3) The intermediate $R^\bullet$ is captured by diamagnetic $4f^{14}$ Yb^{II} in competition with $R^\bullet + R^\bullet$ reactions giving reactive $(C_5Me_5)_2Yb^{III}R$ intermediates. This trapping probably occurs via an inner-sphere electron transfer from diamagnetic Yb^{II} to $R^\bullet$ to give Yb^{III}–R.

(4) The $(C_5Me_5)_2Yb^{III}R$ products undergo subsequent "Yb^{III}-Grignard" reactions with RX via an inner-sphere mechanism to give C_5Me_5R, R–R, and $(C_5Me_5)Yb^{III}X_2$ as the ultimate products.

(5) The $(C_5Me_5)_2Yb^{III}X$ products also undergo subsequent "Yb^{III}-Grignard" reactions with RX via an inner-sphere mechanism with rates approximately 10 times slower than the analogous reactions of $(C_5Me_5)_2Yb^{III}R$.

(6) Electron transfer is thought to be an important component in the overall "atom-abstraction" reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with alkyl and aryl halides.

(7) The inner-sphere mechanisms uncovered for these Yb^{II} and Yb^{III} organolanthanide reactions may extend to, and help facilitate development of, the use of organolanthanides in other areas such as in organic synthesis.[30,31]

Experimental Section

General Procedures. All reactions were carried out either in a Vacuum Atmospheres double-length drybox under purified nitrogen or in septum-capped vials, cuvettes, and NMR tubes under dry, prepurified nitrogen. Nitrogen and argon were purified by passage over a heated 20 × 1.5-in. glass column of BASF R3-11 (Chemalog Inc.) oxygen scavenger in the black (reduced) form and then dried by passage over activated Linde 4-Å molecular sieves. Oxygen levels in the drybox were always maintained at less than 5.0 ppm (generally <1.0 ppm) as monitored by a Model AO 316-C Vacuum Atmospheres O_2 analyzer.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian XL-100 NMR spectrometer operating at 23 °C or a General Electric QE-300 system operating at 23 °C. Chemical shift values were measured by using the ^1H residuals in the deuteriated solvent and reported relative to tetramethylsilane for ^1H NMR. UV/visible spectra were run on a Cary 15 spectrophotometer equipped with a Neslabs Exacal 100 and Endocal 350 temperature control unit employing 1:1 water/ethylene glycol for circulation through a jacketed cuvette holder. Later in this work a Beckman DU-7 spectrophotometer, equipped with a six-position high-temperature cell holder, was used. Unless stated otherwise, NMR and UV/visible samples were prepared by weighing solid samples (±0.5 mg) in a 2-dram vial in the drybox adding solvent(s) and transferring to an NMR tube or cuvette. The NMR tube or cuvette was then stoppered with a rubber septum and removed from the drybox for the experiment. Additions to the samples were made outside the drybox via injection through the septum cap of the sample using 50 μL to 1.0 mL gas-tight syringes. UV/visible monitored experiments were maintained at 22 °C, while ^1H NMR monitored reactions were performed at ambient temperature, ca. 23 °C.

Gas–liquid chromatography (GLC) experiments were performed on a Hewlett-Packard 5790A gas chromatograph, using a 12.5-m (0.2-mm inner diameter) Hewlett-Packard boiling point (bp) capillary column of cross-linked dimethylsilicone or a 6 ft 80/100 Porapak Q column. The gas chromatograph was equipped with flame ionization detectors and a Hewlett-Packard 3390A integrator. Unless stated otherwise, GLC monitored reactions were performed at ambient temperature, ca. 23 °C.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, 56-19 37th Ave., Woodside, NY 11377.

Solvents and Reagents. Benzene and toluene solvents were refluxed over sodium under argon for at least 2 days prior to distillation and then bubbled with purified argon for at least 30 min before being transferred to the drybox for storage. THF and Et_2O were refluxed over sodium/benzophenone under nitrogen, bubbled with argon for at least 15 minutes, and transferred into the drybox for storage. All other solvents and reagents were refluxed over CaH_2 for at least 1 h, distilled, purged with argon as above, and transferred to the drybox for storage. Substrates were purchased from Aldrich Chemical Co. Benzene-d_6 and THF-d_8 were purchased from Aldrich Chemical Co. and used without further purification.

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[31] (a) Natale, N. R. *Org. Prep. Proced. Int.* **1983**, *15*, 387. (b) Namy, J. L.; Girard, P.; Kagan, H. B. *Tetrahedron* **1981**, *37* (Supplement No. 1), 175. (c) Kagan, N. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of the Rare Earths*; Gschneider, K. A., Jr., Eyring, L. Eds.; Elsevier: 1984; Chapter 50.

Synthesis of Ytterbium Compounds. (i) $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and $(C_5Me_5)_2Yb^{III}X(OEt_2)$. The ytterbium compounds $(C_5Me_5)_2Yb^{II}\cdot L$ (L = dimethoxyethane (DME) or Et_2O).[32] were synthesized by literature methods at Du Pont by P.L.W. $(C_5Me_5)_2Yb^{III}Br(OEt_2)$ was synthesized from $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and trimethylsilyl bromide in Et_2O or toluene at Du Pont.[32] $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ was synthesized analogously from $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and $CHCl_3$ in Et_2O. All were obtained as pure compounds as judged by ^1H NMR and elemental analysis. The compounds $(C_5Me_5)_2Yb^{III}X(OEt_2)$ (X = I, F) were identified by ^1H NMR in the reactions of the appropriate RX by comparison to independently generated X = Cl and Br compounds.

Green $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ shows λ_{max} = 680 nm and obeys Beer's law over the concentration range examined, $(3.42–9.77) \times 10^{-3}$M, $\epsilon_{680} = 214 \pm 6$ M^{-1} cm^{-1}. ^1H NMR (benzene-d_6): δ 2.98 (q, 4 H, J = 6 Hz), 2.07 (s, 30 H, $lw_{1/2}$ = 14 Hz), 0.92 (t, 6 H, J = 6 Hz). Purple $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ shows λ_{max} = 550 nm and obeys Beer's law over the concentration range examined, $(2.26–9.04) \times 10^{-3}$ M, $\epsilon_{550} = 176 \pm 6$ M^{-1} cm^{-1}. Its ^1H NMR spectrum is highly variable, depending upon its concentration and the presence of coordinating solvents or ligands. $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ alone shows a broad resonance in the region δ 12.9 (bs, 30 H, $lw_{1/2}$ = 50 Hz). Similarly, $(C_5Me_5)_2Yb^{III}Br(OEt_2)$ shows a broad resonance centered at δ 9.2 (bs, 30 H, $lw_{1/2}$ = 50 Hz).

(ii) Synthesis of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$. Red, crystalline $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ was synthesized at Du Pont by established procedures from $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ and $LiCH_3$ in Et_2O. This synthesis is nontrivial; it depends critically on such factors as solvent, temperature, duration of reaction, and the amount of LiR used. (For example, the use of 1.0 equiv of $LiCH_3$ fails to yield the desired compound.) A detailed synthesis has been published.[16a] The interested reader should also consult Evan's work on $(C_5H_5)_2YbCH_3(THF)$.[16d] The complex shows an absorbance in the visible spectrum centered at λ_{max} = 475 nm and obeys Beer's law over the concentration range examined, $[Yb^{III}–CH_3]$ = 0.0013–0.018 M, $\epsilon_{460} = 200 \pm 20$ M^{-1} cm^{-1}. This complex shows no resonances in its ^1H NMR spectrum under the conditions used for the present studies and for the other complexes.

(iii) Synthesis of $(C_5Me_5)Yb^{III}X_2$. A typical preparation of blue $(C_5Me_5)Yb^{III}Cl_2$ was carried out as follows in the drybox: $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ (60 mg, 0.1 mmol), t-BuCl (10 μL, 0.1 mmol), and 1.0 mL of toluene were combined in a vial. The solution was allowed to react for 25 min at ambient temperature, during which time it turned blue. All of the solvents were then removed in vacuo; the residue was resuspended in hexane and was filtered. The light blue solid obtained was washed three times with 5-mL portions of hexane and dried in vacuo to give the product in a 70% yield. ^1H NMR (benzene-d_6): δ 19.17 (bs, 15 H, $lw_{1/2}$ = 45 Hz). In the presence of Et_2O or other Yb^{III} species, this compound becomes ^1H NMR invisible at ambient temperatures due to exchange equilibria. The visible spectrum shows λ_{max} = 740 and 380 nm, and Beer's law is obeyed over the concentration range examined, 6.0×10^{-3} to 1.6×10^{-2} M, $\epsilon_{680} = 74 \pm 6$ M^{-1} cm^{-1}. Anal. Calcd for $C_{10}H_{15}Cl_2Yb$: Yb, 45.64; C, 31.68; H, 3.99; Cl, 18.70%. Found: Yb, 45.78; C, 31.38; H, 3.83; Cl, 18.81.

$(C_5Me_5)Yb^{III}Br_2$ was synthesized in an analogous manner but on a much smaller scale. In a typical preparation $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (0.027 mmol), allyl bromide (0.035 mmol), and 0.5 mL of toluene were combined in a 2-dram vial in the drybox. After 15 min at ambient temperature the solution turned blue. The solvent was removed in vacuo, the blue solid was rinsed three times with 5-mL portions of hexane and was dried in vacuo. The yield is essentially quantitative. All of the solid product from one particular reaction was dissolved in 0.8 mL of benzene-d_6 and split evenly into two samples. The first shows the following ^1H NMR spectrum: δ 19.6 (bs, 15 H, $lw_{1/2}$ = 42 Hz). The second half was combined with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (0.031 mmol) and then placed in an NMR tube, showing the following ^1H NMR spectrum: δ 3.8 (bs, 30 H, $lw_{1/2}$ = 166 Hz), −0.64 (s, 15 H, $lw_{1/2}$ = 6 Hz).

The $(C_5Me_5)Yb^{III}X_2$ (X = I, F) compounds were not independently synthesized, their presence as products in reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX being inferred and quantified on the basis of the C_5Me_5R products observed.

(iv) Synthesis of YbX_3. Typical preparations were as follows. To each of two 2-dram vials in the drybox was added $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (50 mg, 0.097 mmol) along with 1.0 mL of toluene. To one of the vials $PhCH_2F$ (0.4 mL, 3.7 mmol) was added, while $PhCH_2Cl$ (0.4 mL, 3.5 mmol) was added to the other. Both reactions were allowed to stand at ambient temperature for 1 h. The solids which precipitated were isolated by filtration. The solid products were thoroughly washed with toluene (five 5-mL portions) and dried in vacuo. In both cases, the yields are essentially quantitative. Anal. Calcd for YbF_3: Yb, 75.22; F, 24.78. Anal. Calcd for $YbF_3(OEt_2)$: Yb, 56.89; F, 18.74. Found: Yb, 73.1; F, 24.2. Anal. Calcd for $YbCl_3$: Yb, 61.93; Cl, 38.07. Anal. Calcd for $YbCl_3(OEt_2)$: Yb, 48.85; Cl, 30.44. Found: Yb, 48.95; Cl, 30.86. The X = I or Br compounds were not independently synthesized.

A 1:1 sample of $YbCl_3$ and $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ was prepared by combining $YbCl_3$ (10 mg, 0.036 mmol), $(C_5Me_5)_2YbCl(OEt_2)$ (20 mg, 0.036 mmol), and 1.0 mL of benzene-d_6 in a 2-dram vial in the drybox. The initially purple and heterogeneous mixture quickly (<5 min) became a homogeneous, blue solution. The ^1H NMR spectrum of this blue solution shows the quantitative formation of $(C_5Me_5)YbCl_2$ (δ 19 (bs, 15 H, $lw_{1/2}$ = 50 Hz)).

Synthesis of C_5Me_2R. Pentamethylcyclopentadiene, C_5Me_5H, was synthesized by the method of Bercaw[33] in an 80% yield. The pure product was obtained as a clear colorless or slightly yellow oil by vacuum distillation (60.0 °C, 13 mmHg). ^1H NMR (benzene-d_6): δ 2.47 (q, 1 H, J = 7 Hz), 1.78 (overlapping singlets, 12 H), 1.01 (d, 3 H, J = 7 Hz).

The R = CH_2Ph analogue $C_5Me_5CH_2Ph$ was synthesized by combining $C_5Me_5MgCl\cdot THF$[33] (2.0 g, 7.5 mmol), $PhCH_2Cl$ (6 mL, 52.0 mmol), and 2 mL of toluene in a 25-mL round-bottom flask in the drybox. The reaction vessel was sealed and stirred in the drybox for 3 days at ambient temperature. All the solvents were removed in vacuo. The residue was resuspended in 6 mL of hexane and filtered. The resultant solid was washed three times with 2-mL portions of hexane. The filtrates were combined and all solvents removed in vacuo leaving a light orange oil. Careful distillation under reduced pressure (80–90 °C, 1.0 mmHg) gives approximately 0.5 mL of the pure compound as a light yellow oil, 30% yield. The reaction time is considerably reduced (to 1 day) and the yield improved (to 80%) with THF as the reaction solvent. ^1H NMR (benzene-d_6): δ 2.65 (s, 2 H), 1.77 (s, 6 H), 1.57 (s, 6 H), 0.98 (s, 3 H), 7.03 (m, 5 H). Anal. Calcd for $C_{17}H_{22}$: C, 90.18; H, 9.82. Found: C, 89.94; H, 9.76. MS calcd for $C_{17}H_{22}$: m/e 226. Found: m/e 226.

The compounds C_5Me_5R (R = n-butyl, 1-butene, and (cyclopropyl)carbinyl) were prepared in an analogous manner by using 3 mL each of n-BuBr (28.0 mmol), 4-bromo-1-butene (29.6 mmol), and (bromomethyl)cyclopropane (30.9 mmol) combined with $C_5Me_5MgCl\cdot THF$ (2 g, 7.5 mmol) in 3.0 mL of THF. The yields were 60–80%. The products were not purified beyond the removal of hexane and all volatiles in vacuo, since the products obtained proved to be >95% pure by ^1H NMR. The ^1H NMR spectrum for the R = n-butyl compound shows (benzene-d_6): δ 1.76 (overlapping singlets, 12 H), 0.94 (s, 3 H), 0.82 (t, 3 H, J = 6 Hz), 1.0–1.7 (m, 6 H).

The R = 1-butene C_5Me_5R compound shows the following ^1H NMR spectrum (benzene-d_6): δ 5.84 (m, 2 H), 5.04 (m, 1 H), 1.76 (s, 6 H), 1.54 (m, 4 H), 0.94 (s, 3 H). Anal. Calcd for $C_{14}H_{22}$: C, 88.3; H, 11.7. Found: C, 87.9; H, 11.9. MS calcd for $C_{14}H_{22}$: m/e 190. Found: m/e 190.

The R = $CH_2\overline{CHCH_2CH_2}$ compound shows the following ^1H NMR spectrum (benzene-d_6): δ 1.8 (overlapping singlets, 12 H), 1.51 (d, 2 H, J = 5 Hz), 1.36 (apparent triplet, 2 H), 0.93 (s, 3 H), 0.23 (m, 2 H), −0.06 (m, 1 H). Anal. Calcd for $C_{14}H_{22}$: C, 88.3; H, 11.7. Found: C, 88.4; H, 11.8. MS mass calcd for $C_{14}H_{22}$: m/e 190. Found: m/e 190.

Other C_5Me_5R species not made independently were identified by comparison to the above compounds. For example, the following ^1H NMR spectrum is obtained for the R = phenyl compound obtained from reaction of PhI with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ in benzene-d_6: δ 7.2 (m, 5 H), 1.78 (s, 6 H), 1.61 (s, 6 H), 1.3 (s, 3

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[32] Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652.

[33] Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.

H). Other C_5Me_5R compounds have been synthesized and reported in the literature, for example, the R = CH_2Ph[34a] and R = Et.[34b]

^1H NMR Reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with Alkyl and Aryl Halides. Only a few representative experiments are presented below. Experiments using other alkyl and aryl halides were carried out in an identical manner with completely analogous results to the examples described below. In all cases and unless noted otherwise, 100 ± 6% final mass balances are obtained. The stoichiometries observed are summarized in the Results (Table I). The substrates *n*-octyl fluoride, trimethylsilyl chloride, and PhCl show no reaction with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$.

All of the samples described below were prepared in 2-dram vials in the drybox and transferred to NMR tubes which were septum capped, and the samples were then removed from the drybox for the experiment. Experiments were performed at ca. 23 °C with ca. 15 min between successive additions of RX or ArX substrate and carefully shaking the NMR tubes (avoiding contact with the septum cap) after each addition of substrate. The reaction was then allowed to proceed for at least 5 min before the ^1H NMR spectrum was recorded. In all cases naphthalene and/or hexamethylbenzene were used as unreactive internal standards that have distinctive ^1H NMR resonances which do not interfere with the product resonances. Early control experiments showed that Yb^{II} solutions, in septa-capped NMR tubes where the septa were deliberately pierced, showed no change by NMR on the time scale of the NMR product studies described herein.

(i) Reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with $PhCH_2Cl$. (a) Determination of the Final Products and Evidence for a $(C_5Me_5)_2Yb^{III}CH_2Ph$ Intermediate. A green solution of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (20 mg, 0.039 mmol), hexamethylbenzene (2 mg, 0.012 mmol), and 0.4 mL of benzene-d_6 was prepared. Benzyl chloride (9 μL, 0.078 mmol) was added to the sample in 1-μL (0.25-equiv) increments, causing the solution first to become purple and then blue during the course of addition. The products identified were $PhCH_2CH_2Ph$, $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$, $(C_5Me_5)Yb^{III}Cl_2$, and $C_5Me_5CH_2Ph$ by comparison to authentic samples or, as often needed, mixtures of authentic materials.

In a similar experiment $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (40 mg, 0.077 mmol), naphthalene (19 mg, 0.148 mmol), hexamethylbenzene (10 mg, 0.062 mmol), and 1.2 mL of benzene-d_6 were combined in a 2-dram vial in the drybox. The resulting green solution was then split evenly into two NMR tubes. To one sample was added 0.68 equiv total $PhCH_2Cl$ (3 μL, 0.026 mmol), 1 μL (0.23 equiv) at a time. After this addition of $PhCH_2Cl$ the observed C_5Me_5 and $PhCH_2$ mass balances are ca. 75 ± 8%. The missing 25% mass is consistent with a compound of empirical formula $(C_5Me_5)_{1.9\pm0.4}Yb_{1.0\pm0.2}(CH_2Ph)_{1.0\pm0.4}$ which is not detectable by ^1H NMR under the reaction conditions. The analogous reaction of the second sample used 1.60 equiv total $PhCH_2Cl$ (7 μL, 0.061 mmol), again added 1 μL (0.23 equiv) at a time. For this second sample a 98 ± 5% final mass balance is obtained.

After the initial ^1H NMR studies, both of the above samples were taken into the drybox and washed out of the NMR tubes by using benzene-d_6 into two separate 2-dram vials. All of the volatiles were removed in vacuo. The solid residues were resuspended in 1.0 mL *ortho*-xylene. The vials were septum capped, removed from the drybox, and analyzed by GLC. The conditions used for the GLC analysis are identical with those described for other reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with $PhCH_2Cl$ in the GLC section (vide infra). The sample with 0.68 equiv total $PhCH_2Cl$ yields, after addition of 5.0 equiv of MeOH, 82% of the expected 0.25 equiv of toluene (0.2 ± 0.02 equiv based on the $PhCH_2Cl$ added). The sample with 1.60 equiv total $PhCH_2Cl$ shows no toluene (after addition of 5.0 equiv of MeOH) and a corresponding increase in the amounts of the $PhCH_2CH_2Ph$ and $C_5Me_5CH_2Ph$ products relative to those found in the 0.68-equiv $PhCH_2Cl$ sample.

(b) Dependence of the Yield of $C_5Me_5CH_2Ph$ on the Method of Addition of $PhCH_2Cl$. The effect of the method of addition of $PhCH_2Cl$ to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ on the yield of $C_5Me_5CH_2Ph$ was probed by using a series of five samples. The initial concentrations used in each sample were $[Yb^{II}]$ = 0.0995 M and $[PhCH_2Cl]$ = 0.104 M in 0.5 mL of benzene-d_6. Additions of $PhCH_2Cl$ were made to the five samples in five different ways as follows: one 6 μL addition, one 4 μL plus one 2 μL addition 2 min later, two 3 μL additions equally spaced over 2 min, three 2 μL additions equally spaced over 2 min, and six 1 μL (0.0087 mmol) additions equally spaced over 2 min. The results show that addition of less $PhCH_2Cl$ per unit time decreases the amount of $C_5Me_5CH_2Ph$ produced by ≤26% over the range of conditions described above.

(c) Effect of Added $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ on the Yield of $C_5Me_5CH_2Ph$. Since the $C_5Me_5CH_2Ph$ product is thought to arise in part from Grignard reactions of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with $PhCH_2Cl$ (operating during the later stages of the $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ reaction with RX), the effect of added $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ on the yield of $C_5Me_5CH_2Ph$ was investigated. This effect was probed by using a series of six samples. Each sample contained $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (23 mg, 0.0445 mmol), hexamethylbenzene (3 mg, 0.018 mmol), and 0.4 mL of benzene-d_6. To each of the six samples, a different amount of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ was added, ranging from 0 to 40 mg (0–0.071 mmol or 0–0.17 M). The initial ^1H NMR spectra of the resulting green to dark purple solutions were recorded. Benzyl chloride (8 μL, 0.0695 mmol) was then added to each sample as a single addition, and the reactions were allowed to proceed for 15 min before the final ^1H NMR spectra was recorded. The amount of $C_5Me_5CH_2Ph$ found in each sample was determined by integration relative to the amount of bibenzyl generated, assuming the final amount of bibenzyl was 0.5 equiv in each case. Unreacted (excess) $PhCH_2Cl$ is observed by ^1H NMR in all of the samples. The added $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ increased the yield of $C_5Me_5CH_2Ph$; e.g., 0.60 equiv is found when 0.17 M Yb^{III}–Cl has been added (compared to 0.37 equiv (±10% and based on Yb^{II}) when no Yb^{III}–Cl was added).

(ii) Reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with *n*-BuCl. A green solution containing $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (30 mg, 0.058 mmol), bibenzyl (3 mg, 0.0165 mmol, as an internal standard), and 0.4 mL of benzene-d_6 was prepared. To the sample was added 1.5 μL, 2 μL, 5 μL, and 6 μL successively. Addition of *n*-BuCl causes the solution to slowly darken to purple over the course of approximately 30 min. The major product is $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$, with a significant amount of $C_5Me_5(n\text{-Bu})$ also present (by comparison to authentic materials). The presence of an amount of $(C_5Me_5)Yb^{III}Cl_2$ equal to the amount of $C_5Me_5(n\text{-Bu})$ observed was verified by addition of more $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (15 mg, 0.029 mmol) at the end of the reaction; the characteristic resonance at δ −1.42 (bs, 15 H) due to $(C_5Me_5)Yb^{III}Cl_2$ (in the presence of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$) was observed.

Experiments performed in an identical manner, but where 2.0 equiv of 2-MeTHF or THF had been added to the samples, show no $C_5Me_5(n\text{-Bu})$ forms.

(iii) Reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with *t*-BuCl. A green solution containing $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (19 mg, 0.037 mmol) and 0.4 mL of benzene-d_6 was prepared. To this sample was added 7 μL of *t*-BuCl (0.064 mmol, 1.75 equiv total) in 1 μL (0.0092-mmol, 0.25-equiv) increments causing the solution first to turn purple and then blue. Further addition of 21 μL (0.19 mmol, 4.25 equiv) of *t*-BuCl causes the solution to turn lighter blue as a solid ($YbCl_3$) precipitates. Soluble products identified by comparison to authentic materials are $(C_5Me_5)_2YbCl(OEt_2)$, C_5Me_5H, $(CH_3)_3CH$ (δ 0.9 (d, 9 H, J = 8 Hz) (lit.[35] δ 0.89 (d, 9 H), 1.56 (m, 1 H))), and $(CH_3)_2C{=}CH_2$ (δ 1.68 (s, 6 H), 4.8 (s, 2 H) (lit.[35] δ 1.70 (s, 6 H), 4.60 (s, 2 H))).

(iv) Reaction of $(C_5Me_2)_2Yb^{II}\cdot OEt_2$ with (Chloromethyl)cyclopropane. (Chloromethyl)cyclopropane (11 μL, 0.12 mmol, Aldrich, containing <5% 4-chloro-1-butene impurity by ^1H NMR), $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (70 mg, 0.14 mmol), and 0.6 mL of benzene-d_6 were combined in a 10-mL round-bottom flask equipped with a gas adapter in the drybox. The reaction was removed from the box and stirred at room temperature for 20 min. All of the volatiles were removed in vacuo and trapped by using a simple vacuum trap (described below for GLC monitored reactions of

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(34) (a) Photolysis of $(C_5Me_5)Fe(CO)_2(CH_2Ph)$ gives $C_5Me_5CH_2Ph$ in as high as a 50% yield via the benzyl radical. Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694. (b) Dietl, H.; Reinheimer, H.; Moffat, J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2276.

(35) Bovey, F. A. *NMR Tables for Organic Compounds*; Wiley: New York, 1967; Vol. 1, pp 70–78.

$(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with *n*-BuCl). The trapped, volatile liquids were quickly and carefully transferred via pipette to an NMR tube. The total yield of volatile organic products isolated is 42% (0.42 ± 0.04 equiv) determined by ^{1}H NMR and based on the Et_2O resonances observed (taken to equal 1.0 equiv). The ^{1}H NMR of these volatile products showed both olefinic and intact cyclopropane ring resonances in approximately the same amount. A small amount (0.04 equiv) of C_5Me_5R was also present (exclusively as the ring-intact product by GLC).

^{1}H NMR Reactions of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ and $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with RX. The experiments described below were performed in the same manner and under identical conditions as those described previously for the ^{1}H NMR reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX. Samples were prepared in 2-dram vials in the drybox and then transferred to NMR tubes. The NMR tubes were septum capped and removed from the drybox; experiments were performed at ambient temperature. The reaction was allowed to proceed for at least 5 min prior to NMR analysis, 15 min typically elapsing between sequential RX additions. In the cases described below the benzene-d_6 residual resonance was used as the internal standard. Experiments with other substrates were performed in an identical manner. Trimethylsilyl chloride, neopentyl chloride, and the phenyl halides (PhX, X = Cl, Br, I) show no reaction with any $(C_5Me_5)_2Yb^{III}X(OEt_2)$ complex. In addition, reactions of *n*-BuCl are very slow ($t_{1/2} \simeq 5$ h). For all of the experiments described below, mass balances of 100 ± 5% are observed.

(i) Reaction of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with $PhCH_2Cl$. A purple solution containing $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ (18 mg, 0.032 mmol) and 0.4 mL of benzene-d_6 was prepared. Benzyl chloride (8 μL, 0.07 mmol, 2.15 equiv total) was added to the sample in the following increments: 1 μL (0.0087 mmol, 0.27 equiv), 1 μL, 1 μL, and 5 μL. The solution gradually turns blue during the course of the addition. One hour after the final addition of $PhCH_2Cl$ the solution is light blue with a suspended solid (presumably $YbCl_3$). Other products observed during the course of the reaction by comparison to authentic materials are $C_5Me_5CH_2Ph$, $(C_5Me_5)_2Yb^{III}Cl_2$, and free Et_2O.

(ii) ^{1}H NMR Competition Studies for the Reactions of $PhCH_2X$ (X = Br, Cl, F) with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$. Benzyl chloride (7.5 μL, 0.065 mmol), $PhCH_2F$ (7.0 μL, 0.065 mmol), hexamethylbenzene (3 mg, 0.018 mmol), and 0.35 mL of benzene-d_6 were each added to three NMR tubes in the drybox. The initial ^{1}H NMR spectrum was taken of each solution, 100 μL (0.018 mmol) of a solution of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ (40 mg, 0.073 mmol) in 0.4 mL of benzene-d_6 was then added to each sample, and the ^{1}H NMR spectrum of each blue product solution was recorded as soon as possible. The percent of each $PhCH_2X$ consumed was determined by integration, the ratio of the two percentages being taken as the ratio of the respective k_{obsd}. Identical experiments were performed by using $PhCH_2Cl$ (7.5 μL, 0.065 mmol) plus $PhCH_2Br$ (8.0 μL, 0.067 mmol) and $PhCH_2F$ (21 μL, 0.19 mmol), plus $PhCH_2Br$ (24 μL, 0.2 mmol). The $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ complex clearly shows the preference F ≫ Br ≥ Cl. These preferences may contain contributions from the subsequent Grignard reactions of the $(C_5Me_5)Yb^{III}X_2$ product. However, this should be a minor contribution as NMR analyses were performed rapidly on the *homogeneous blue* solutions (indicating $(C_5Me_5)Yb^{III}Cl_2$ is still the predominant Yb^{III} product). Slow precipitation of a solid (YbX_3) is observed in these experiments after ca. 20 min.

The experiment was repeated once by using 0.4 mL of THF-d_8 as the solvent and employing $PhCH_2Br$ (3 μL, 0.025 mmol) plus $PhCH_2F$ (3 μL, 0.028 mmol) in each of three NMR tubes. Similar to the above experiment, 100 μL (0.009 mmol) of a solution containing $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ (20 mg, 0.036 mmol) in 0.4 mL of THF-d_8 was added to each tube. In this case the reaction is very slow, and the samples were left at room temperature overnight before significant reaction had occurred. No strong substrate rate preference is observed, Br ≃ F, apparently indicating a change in mechanism.

(iii) Reactions of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with Alkyl and Aryl Halides. Since $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ possesses no initial ^{1}H NMR resonances under the standard conditions used, qualitative experiments were performed as follows. Samples were prepared in 2-dram vials in the dry box and were transferred to NMR tubes; the NMR tubes were septum capped and removed from the drybox for the 23 °C experiment. Reactions were allowed to proceed for at least 5 min prior to NMR analysis, ca. 15 min elapsing between successive additions of substrates.

In a typical reaction $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ (24 mg, 0.045 mmol) and hexamethylbenzene (3 mg, 0.019 mmol, as an internal standard) were combined with 0.4 mL of benzene-d_6. To this solution was added $PhCH_2Cl$ (5 μL, 0.043 mmol, 0.97 equiv total), 0.2 equiv (1 μL) at a time for the first 0.6 equiv (3 μL) and then the last 4 equiv (2 μL) was added all at once. The reaction is immediate, producing a purple solution after 0.6 equiv of $PhCH_2Cl$ had been added. The solution gradually turns blue as the final 0.4 equiv was added. Products identified by comparison to authentic materials are $(C_5Me_5)Yb^{III}Cl_2$, $C_5Me_5CH_2Ph$, and $PhCH_2CH_3$.

Reactions of other substrates were performed in the same manner. Typical samples consisted of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ (35 mg, 0.066 mmol), hexamethylbenzene (3 mg, 0.019 mmol), and 0.4 mL of benzene-d_6. The following amounts of RX were added to the samples in single, bulk additions prior to ^{1}H NMR analysis: *n*-BuCl (8 μL, 0.077 mmol), isopropyl chloride (8 μL, 0.088 mmol), neopentyl chloride (9 μL, 0.073 mmol), and PhI (8 μL, 0.072 mmol). All of these reactions are slow, the relative rates spanning $t_{1/2} \simeq 2$ h to $t_{1/2} \simeq 10$ h and following the order: isopropyl chloride > *n*-BuCl > PhI ≫ neopentyl chloride. For *n*-BuCl and PhI both the CH_3R and C_5Me_5R Grignard products are observed, while the other two substrates show only CH_3R (R = H, neopentyl).

Gas-Liquid Chromatography Experiments. All of the samples described below were prepared in 2-dram vials in the drybox. The vials were septum capped, the septa were sealed to the vials by wrapping them with black electrical tape, and the vials were then removed from the drybox for the ambient-temperature GLC experiments. The length of time between multiple additions of substrate or added ligands varied, depending on the length of time required for the GLC analyses (e.g. 15 min for reactions of *n*-BuCl). In addition, for reactions of *n*-BuCl with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, samples were allowed to react at least 15 min prior to GLC analysis. Times for other RX reactions are given below. Injections were typically 2 μL each.

Volatile products such as butane, butene, and neopentane were quantified by comparison to an octane standard. Examination of the relative FID response factors[36] shows that all such simple hydrocarbons have relative FID response factors within 10% of each other. (The relative response factor of a compound X is defined as ($\text{area}_X/\text{weight}_X$) divided by ($\text{area}_{benzene}/\text{weight}_{benzene}$).) For example (relative to benzene, 1.0): CH_4, 0.97; butane, 1.09; pentane, 1.04; octane, 0.97; $CH_2{=}CH_2$, 1.02; toluene, 1.07; *tert*-butylbenzene, 1.02; 1-hexene, 0.99.

(i) Reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with *n*-BuCl. Experiments were analyzed by GLC using a 6 ft 80/100 Porapak Q column (injector = 80.0 °C, detector = 140.0 °C, T_1 = 80.0 °C, time$_1$ = 18.0 min, T_2 = 200.0 °C, time$_2$ = 15.0 min, rate = 41.0 °C/min, flow = 40.0 mL/min, run times 40–50 min each) to determine the butene/butane ratio. Quantification of the total amount of butane and butene was accomplished via the boiling point capillary column using octane as an internal standard (injector = detector = 140.0 °C, flow = 1.5 mL/min, T_1 = 60.0 °C, time$_1$ = 2.5 min, T_2 = 110.0 °C, time$_2$ = 4.5 min, rate = 42.0 °C/min, run times 15–20 min). A standard was prepared by adding octane (8 μL, 0.49 mmol), *n*-BuCl (10 μL, 0.097 mmol), and C_5Me_5(*n*-Bu) (0.05 mmol) to 1.0 mL of toluene in a septum-capped 2-dram vial. A second standard (for retention times) was prepared by bubbling 1.0 mL of toluene simultaneously with butane and butene.

Two samples were prepared in the first experiment, each containing 0.0386 M $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and 0.0483 M *n*-BuCl in toluene. The first sample, essentially a control reaction, was carried out and left in a septum-capped 2-dram vial. The second sample was prepared in a 10-mL round-bottom flask equipped with a gas adapter. After 20 min at ambient temperature, both samples were removed from the drybox. All the volatiles were removed from the sample in the 10-mL flask by vacuum transfer to a specially constructed trap (consisting of a septum-capped

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(36) McNair, H. M.; Boncelli, E. J. *Basic Gas Chromatography*; Consolidated Printers: Berkeley, CA, 1968.

2-dram vial joined near the bottom by two $^1/_4$ in. diameter glass tubes) immersed in liquid N_2. Injections for GLC analysis were made directly from the trap which was kept at 0.0 °C to minimize losses of volatile butene and butane. The solid residue left in the 10-mL flask was returned to the drybox, dissolved in 1.0 mL of toluene, transferred to a septum-capped 2-dram vial, removed from the box, and analyzed by GLC.

The yield of butane plus butene volatiles in the 10-mL flask is 0.09 ± 0.01 equiv vs starting $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, butene/butane ratio = 0.5 ± 0.06 (using the Porapak column). This ratio remains constant over 2 h at room temperature. The solid residue from the 10-mL flask shows almost twice the amount of light organics, 0.14 ± 0.02 equiv, but it is all butane. The total *n*-Bu mass balance is 80 ± 10%. One possible, nonvolatile butane "resting state" is $(C_5Me_5)_2Yb^{III}(n\text{-Bu})$.

The first sample (the one in the 2-dram vial) shows the same *total* yield of light hydrocarbons as the sample above, 0.26 ± 0.03 equiv, plus 0.07 ± 0.01 equiv of octane and 0.43 ± 0.02 equiv of $C_5Me_5(n\text{-Bu})$ vs $(C_5Me_5)_2Yb^{II}\cdot OEt_2$). However, all the butane (e.g. from $(C_5Me_5)_2Yb\text{-}n\text{-Bu}$) is now observed; the butene to butane ratio is 0.032 ± 0.009.

By assuming that the amount of *n*-Bu• derived butane is the same as the amount of butene observed (effectively subtracting the butane derived from other sources such as a $(C_5Me_5)_2Yb(n\text{-Bu})$ complex), one obtains a value of 0.14 ± 0.05 for the (butane–butene)/octane or $k_{\text{disproportionatn}}$ to $k_{\text{recombinatn}}$ ratio for the *n*-Bu• radical.

A second experiment was performed to determine the stoichiometry of reaction of *n*-BuCl with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ *under the more dilute concentration conditions used for the kinetic experiments*, including the $[Et_2O]$ dependence experiments. One run was performed with no added Et_2O, and four separate runs were performed with $[Et_2O]$ = 0.019, 0.029, 0.058, and 0.073 M.

The dependence of the $C_5Me_5(n\text{-Bu})$ yield on the $[Et_2O]$ was probed in another set of experiments. Five runs were performed by using column conditions and standards as described above. Samples containing $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (0.078 M), *n*-BuCl (0.096 M), Et_2O (0–1.24 M), and 0.5 mL of toluene were prepared in 2-dram vials in the drybox and treated as described above. Each sample was allowed to react at least 20 min prior to beginning analyses and then left at room temperature. (Somewhat low (≃75%) organic products mass balances are obtained as before.) The amount of $C_5Me_5(n\text{-Bu})$ generated was decreased by up to a factor of 3. A plot of this effect is provided as supplementary material.

(ii) Reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with $PhCH_2Cl$ Followed by a MeOH Quench. Three different experiments were performed. The best conditions for product separation and quantification were obtained by using the bp capillary column (injector = detector = 140 °C, flow = 1.5 mL/min, T_1 = 60 °C, time$_1$ = 2.6 min, rate = 38.2 °C/min, T_2 = 140 °C, time$_2$ = 5.65 min, run times ca. 20 min). The standard consisted of toluene, $PhCH_2CH_2Ph$, Et_2O, $C_5Me_5CH_2Ph$, and C_5Me_5H (at concentrations roughly equivalent to those expected in the samples being examined), and 1.0 mL of *o*-xylene in a septum-capped 2-dram vial.

The first experiment was designed to maximize the apparent trapping of $PhCH_2\bullet$ by $(C_5Me_5)_2Yb^{II}\cdot OEt_2$. A sample containing $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (0.1 M) in 0.5 mL of *o*-xylene was prepared in a 2-dram vial in the drybox. Outside the box and at ambient temperature, $PhCH_2Cl$ (0.0087 M total) was added to the sample, the reaction was let stand 5 min, and the products were analyzed by GLC after methanolysis (5 equiv of MeOH). The product solution is found to contain 0.63 ± 0.06 equiv of toluene, 0.10 ± 0.01 equiv of bibenzyl, and 0.19 ± 0.02 equiv of $C_5Me_5CH_2Ph$ (based on the amount of $PhCH_2Cl$ added).

The effect of added Et_2O, 0–9.65 M (neat) on the yields of products from the reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with $PhCH_2Cl$, was determined in the second set of experiments. A series of samples were prepared in 0.5 mL of *o*-xylene. The initial concentrations used in each were $[Yb^{II}]$ = 0.0966 M and $[PhCH_2Cl]$ = 0.0869 M. The yields of products obtained were based on the amount of $PhCH_2Cl$ added and after methanolysis (5 equiv of MeOH). Addition of Et_2O acts to decrease the amounts of $C_5Me_5CH_2Ph$ and $(C_5Me_5)_2Yb^{III}CH_2Ph$ generated 13- and 7-fold over the range 0–9.65 M, respectively, while the amount of bibenzyl increases by a factor of 2 over the same range. A plot of this effect is included as supplementary material.

Finally, the effect of dilution on the yields of the various products was investigated. Initial concentrations of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ in 1.0 mL of *o*-xylene were from 0.0048 to 0.097 M and the corresponding initial concentrations of $PhCH_2Cl$ were from 0.0017 to 0.035 M. The yields of products were based on the amount of $PhCH_2Cl$ added. Decreasing the initial concentrations of both $PhCH_2Cl$ and $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ over the above 20-fold range shows a 0.2-equiv (±10%, based on $PhCH_2Cl$) increase in the amount of $(C_5Me_5)_2Yb^{III}CH_2Ph$ formed while the amounts of bibenzyl and $C_5Me_5CH_2Ph$ decrease by 0.03 equiv and 0.16 equiv, respectively. A plot of this effect is supplied as supplementary material.

(iii) Reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with (Bromomethyl)cyclopropane. These experiments are detailed as supplementary material for the interested reader and are also available in a thesis.[37a]

(iv) Determination of the Stoichiometry of the Reaction of Neopentyl Chloride (NpCl), Isopropyl Chloride (*i*-PrCl), Bromobenzene (PhBr), and Iodobenzene (PhI) with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ under the Conditions Used for Absolute Rate Determinations. These experiments are detailed as supplementary materials for the interested reader and are also available in a thesis.[37b]

(v) Reactions of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ and of a 1:1 Mixture of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ and $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with $PhCH_2Cl$. Both of the experiments detailed below were performed by using the boiling point capillary column described in the General Procedures (injector = detector = 140 °C, flow = 1.5 mL/min, T_1 = 60 °C, time$_1$ = 2.5 min rate = 37.5 °C/min, T_2 = 150 °C, and time$_2$ = 4.0 min, run time 15 min). Samples were prepared in the drybox in septum-capped 2-dram vials, removed from the box, let react for ≥5 min at 23 °C, and then subjected to GLC analysis.

The first experiment utilized a sample containing $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ (0.028 mmol) and 1.0 mL of toluene in a septum-capped 2-dram vial. To this sample was added $PhCH_2Cl$ (5 μL, 0.0435 mmol total), 1 μL (0.0087 mmol) at a time; ca. 15 min after each addition the products were determined by GLC. Only 67 ± 6% $PhCH_2CH_3$ (0.67 equiv vs the initial $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$) is found. The ratio $PhCH_2CH_3/C_5Me_5CH_2Ph$ = 1.72 ± 0.15 was determined during the initial part of the reaction when <0.5 equiv of $PhCH_2Cl$ had been added. A standard containing Et_2O, $C_5Me_5CH_2Ph$, $PhCH_2CH_3$, and $PhCH_2Cl$ in a 2-dram, septum-capped vial with toluene was used in the product analysis.

The second experiment utilized a standard and conditions identical with those described above. The sample consisted of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ (19 mg, 0.036 mmol), $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (20 mg, 0.039 mmol), and 1.0 mL of toluene in a 2-dram septum-capped vial. A 10% solution (by volume) of $PhCH_2Cl$ in toluene was then added 5 μL (0.0043 mmol) at a time until 40 μL (0.035 mmol total) had been added. Further additions of the 10% $PhCH_2Cl$ solution were made 10 μL (0.0086 mmol) at a time until a final total of 160 μL (0.14 mmol) had been added. The distribution of products when ≤0.013 mmol of $PhCH_2Cl$ had been added was determined by GLC 5 min after each addition of $PhCH_2Cl$. The ratio obtained for $k_{\text{obsd}}(Yb^{II})/k_{\text{obsd}}(Yb^{III}\text{–}CH_3)$ (taken as the product ratio $([PhCH_2Cl]_{\text{initial}} - [PhCH_2CH_3])/[PhCH_2CH_3]$) is 106 ± 27 (three points). (This rough estimate

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[37] (a) Reference 13b, p 199. (b) Reference 13b, p 203. (c) Reference 13b, p 219.

[38] The compounds $Ag(CH_2Ph)$[38a] and $Cu(CH_2Ph)$[38b] are unstable above −78 °C, decomposing to give bibenzyl and zerovalent metal. The corresponding $Zn(CH_2Ph)_2$[38c] and $Mg(CH_2Ph)_2$[38d] are isolable as solids but are also of limited stability. Thus the R = CH_2Ph derivatives of ionic metals appear, as one might anticipate, to be some of the least stable of the metal alkyls. (a) Hashimoto, H.; Nakano, T. *J. Org. Chem.* **1966**, *31*, 891. Glocking, F.; Kingston, D. *J. Chem. Soc.* **1959**, 3001. Beverwijk, C. D. M.; Van der Kerk, G. J. M.; Leusink, A. J.; Noltes, J. G. *Organomet. Chem. Rev. A* **1970**, *5*, 215. (b) Costa, G.; Camus, A.; Gatti, L.; Marsich, N. *J. Organomet. Chem.* **1966**, *5*, 568. Ebert, G. W.; Rieke, R. D. *J. Org. Chem.* **1984**, *49*, 5280. (c) Nutzel, K. *Methods Elem.-Org. Chem.* **1967**, *3*. Strohmeier, W. *Chem. Ber.* **1955**, *88*, 1218. (d) Kamienski, C. W.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *8*, 542; *J. Org. Chem.* **1969**, *34*, 1116. Psarras, T.; Dessy, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 5132.

assumes a bimolecular rate law for both reactions.)

Similarly, from the latter stages of the reaction (the two points, where 0.030 and 0.035 mmol total $PhCH_2Cl$ were added), a ratio approximating $k_{obsd}(Yb^{III}-CH_3)/k_{obsd}(Yb^{III}-CH_2Ph)$ of 0.97 ± 0.14 ($[PhCH_2CH_3]/[PhCH_2CH_2Ph]$) was determined (two points). (During this stage of the reaction the two $(C_5Me_5)_2Yb^{III}R$ complexes should be the major reactants; this rough estimate assumes a bimolecular rate law for both reactions.)

At the end of the reaction, when excess $PhCH_2Cl$ is observed by GLC and after 5 equiv of MeOH (vs Yb^{II} plus $Yb^{III}-CH_3$) had been added, the following final product yields are obtained: $PhCH_2CH_2Ph$ = 0.45 ± 0.05 equiv (vs initial amount of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$), $PhCH_2CH_3$ = 0.60 ± 0.05 equiv (vs initial $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$), and $C_5Me_5CH_2Ph$ = 0.8 ± 0.1 equiv (vs initial $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ plus $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$). A final $PhCH_2Cl$ mass balance of 100 ± 10% is obtained.

UV/Visible Monitored Reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$, and $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with Alkyl and Aryl Halides. (i) Determination of Isosbestic Points in Reactions of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with $PhCH_2Cl$ and *t*-BuCl. Toluene (2.0 mL) and $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ (6 mg, 0.012 mmol) were added to a cuvette in the drybox. The cuvette was septum capped and removed from the drybox and the initial visible spectrum recorded from 350 to 800 nm. A series of overlapping visible spectra were then recorded after each of seven 1-μL (0.25 equiv) additions of 33% (by volume in toluene) *t*-BuCl. Further 2-μL and 5-μL additions of 33% *t*-BuCl were made, followed finally by 1 μL of *neat* *t*-BuCl. A clean isosbestic point is observed at 665 nm.

The reaction of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ (0.0095 M) with $PhCH_2Cl$ (0.013 M) in toluene at 22.0 °C was monitored via a series of overlapping visible spectra. The reaction shows a clean isosbestic point at 665 nm. Reactions performed by using high concentrations of $PhCH_2Cl$ (pseudo-first-order condition) show no isosbestic points due to the buildup and subsequent slower reaction of $(C_5Me_5)Yb^{III}Cl_2$ with $PhCH_2Cl$.

(ii) Absolute Rates for $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ plus Alkyl and Aryl Halides. The absolute rates for the reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with *n*-BuCl, NpCl, *i*-PrCl, PhI, and PhBr were determined at 22.0 °C in toluene by monitoring the decrease in $[Yb^{II}]_T$ at 680 nm. Samples were prepared in 2-dram vials in the drybox, were then transferred to 1-cm Pyrex visible cells, septum capped, and removed from the drybox for the experiment. Considerable interference from the $(C_5Me_5)_2Yb^{III}-Cl$, $(C_5Me_5)Yb^{III}Cl_2$, and $(C_5Me_5)_2Yb^{III}R$ product complexes is present (see Figure 1, 680 nm), and, generally speaking, isosbestic points are not observed. Therefore, it was necessary to correct for the total absorbance due to these three complexes growing in under the $[Yb^{II}]_T$ absorbance. The formula shown below was used to correct the absorbances, where A_t is the absorbance due to $[Yb^{II}]_T$ at time *t* and is for the case where the bis Et_2O complex $(C_5Me_5)_2Yb^{II}(OEt_2)_2$ is not formed to any appreciable extent.

$$\frac{A_{t,680} - l\epsilon_p[Yb^{II}]_0}{l(\epsilon_s - \epsilon_p)} = [Yb^{II}]_t$$

$[Yb^{II}]_0$ is the initial concentration of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, l is the path length of the cell (1 cm), $[Yb^{II}]_t$ is the corrected concentration of ${Yb^{II}}_T$ at time t, ϵ_s is the extinction coefficient of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ at 680 nm (214 ± 6 M^{-1} cm^{-1}), and ϵ_p is an apparent extinction coefficient of the three products absorbing at 680 nm (ϵ_p is determined by using the final absorbance at the end of the kinetic runs divided by the initial concentration of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$). A full derivation of this equation is available (see pp 211–216);[13b] ϵ_p is given by

$$\epsilon_p = [(a + b)/(a - c)]\{\epsilon_1 + \epsilon_2[c/(a - c)] + \epsilon_3[b/(a - c)]\}$$

where the stoichiometry coefficients are defined in eq 3 and ϵ_1, ϵ_2, and ϵ_3 are the extinction coefficients for the three products absorbing at 680 nm. This method of correcting the absorbance effectively assumes ϵ_p is a constant, i.e., that the ratio of products is constant throughout the course of the reaction. The good linearity of the second-order plots provides excellent experimental justification for the use of the above equation for $[Yb^{II}]_t$ and confirms the constancy of the product ratios (and thus ϵ_p) obtained in GLC experiments.

The kinetics were measured (except where indicated otherwise) under second-order conditions. Integration of the rate expression $-d[Yb^{II}]_T/dt = (Q)k_{2obsd}[Yb^{II}]_T[RX]$ by the usual method of partial fractions yields[13b]

$$k_{2obsd}(t) = \frac{1}{Q(B_0 - (A_0/Q))} \ln\frac{A_0(B_0 - x)}{QB_0((A_0/Q) - x)}$$

where A_0 is the initial concentration of Yb^{II}, B_0 is the initial concentration of RX, x is the extent of reaction, and $Q = (a + b)(a + c)$ = the stoichiometry coefficient. A complete analysis and derivation of all of the equations used in the kinetics experiments is available.[13b] Data were analyzed by standard least-squares techniques;[6,13] error bars are quoted at 1 standard deviation.

The method of correcting the absorbances described above assumes that ϵ_p does not change significantly over the time that the reaction is monitored. If this assumption begins to fail; i.e., if ϵ_p changes by as little as 15–20% during the course of the reaction, simulations show that second-order kinetic plots will begin to curve. Experimentally, linear second-order kinetic plots are generally observed (examples are provided as supplementary material), although curvature after the second half-life is observed in some of the experiments described below. (In such cases data were taken from the linear portion of the reaction only.) This shows, as expected, that toward the end of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ reaction, the Grignard reactions of the Yb^{III} products do in fact occur. It is for this very reason that high (pseudo-first-order) concentrations of RX were not used.

(a) Controls for the Kinetic Studies. Since the ^1H NMR reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX suggest that the Yb complexes can at least interact in exchange equilibria and/or form stable aggregates, two control experiments were undertaken. In the first, the effect of added $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ on the rate of reaction of *n*-BuCl with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ was examined. Three runs were performed for added $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$. The $[Yb^{II}]$ was 7.35 × 10^{-3} M, the $[Yb^{III}-Cl]$ was from 4.6 × 10^{-4} to 1.82 × 10^{-3} M, and the [*n*-BuCl] used as 0.012 M. Second-order kinetic plots are linear for over 80% of the reaction and yield k_{2obsd} = 1.8 ± 0.3 M^{-1} s^{-1} (compared to a k_{2obsd} = 1.9 ± 0.2 M^{-1} s^{-1} without added $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$). Moreover, addition of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ to $(C_5Me_5)Yb^{II}\cdot OEt_2$ shows no deviations from Beer's law (increases in the absorbance at 680 nm can be fully accounted for by overlapping absorbances, $A_T = A_{Yb^{II}} + A_{Yb^{III}}$).

The second control experiment examined the effect of added $(C_5Me_5)Yb^{III}Cl_2$ on the rate of reaction of *n*-BuCl with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$. Two runs were performed, the $[Yb^{II}]$ was 5.79 × 10^{-3} M, the $[Yb^{III}Cl_2]$ was from 1.25 × 10^{-3} to 2.51 × 10^{-3} M, and the [*n*-BuCl] used was 9.6 × 10^{-3} M. Second-order kinetic plots are linear for at least 75% of the reaction and yield k_{2obsd} = 1.5 ± 0.3 M^{-1} s^{-1} (compared to a k_{2obsd} = 1.9 ± 0.2 M^{-1} s^{-1} without added $(C_5Me_5)Yb^{III}Cl_2$). Addition of $(C_5Me_5)Yb^{III}Cl_2$ to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ shows small linear increases in the absorbance at 680 nm; i.e. $A_T = A_{Yb^{II}} + A_{Yb^{III}}$ as above.

It is known that $(C_5Me_5)_2Ln^{II}\cdot OEt_2$ (Ln = Yb, Eu) can form excited-state species on irradiation with visible light.[20] Such species are capable of rapid reaction with alkyl halides such as $CHCl_3$. Therefore, the effect of variable spectrophotometer slit width was examined. Four runs were performed, the $[Yb^{II}]$ was 9.25 × 10^{-3} M and the [*n*-BuCl] used was 0.0144 M. The slit width was varied from 0.01 to 0.4 mm. Second-order kinetic plots are typically linear for at least 80% of the reaction. The result, k_{2obsd} = 2.3 ± 0.4 M^{-1} s^{-1}, is within experimental error of the k_{2obsd} = 1.9 ± 0.3 M^{-1} s^{-1} determined previously.

(b) Absolute Rates for $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ plus *n*-Butyl Chloride, Neopentyl Chloride, Isopropyl Chloride, Phenyl Iodide, and Phenyl Bromide. These experiments are detailed in the supplementary material for the interested reader and are also available in a thesis.[37c]

(c) Et_2O Dependence of the Absolute Rate of Oxidative Addition of *n*-BuCl to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$. Added Et_2O acts to retard the rate of oxidative addition of alkyl and aryl halides to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$. The $[Et_2O]$ dependence was determined under second-order concentration conditions from nine kinetic points in toluene at 22.0 °C. An average stoichiometry coefficient of $Q = 1.6 \pm 0.2$ was used as determined by the GLC experiments described earlier and performed under identical [Et_2O] conditions. The [Et_2O] used was from 0.010 to 0.0723 M, the $[Yb^{II}]_T$ ranged from 7.78×10^{-3} to 8.54×10^{-3} M, and the [*n*-BuCl] used was 9.78×10^{-3} M. A plot of $1/k_{2obsd}$ vs [Et_2O] is linear with intercept = 0.23 ± 0.11 M s and slope = 78.9 ± 3.0 s giving[21] $k_2 = 2.7 \pm 0.9$ M^{-1} s^{-1} and $K_{eq} = (3.0 \pm 1.7) \times 10^{-3}$ M and allowing the limit $50k_2' \leq k_2$ to be set. At higher (≥0.15 M) Et_2O concentrations the rate begins to level off; i.e. k_{2obsd} shows little further decrease. Each cuvette contained 4.5 mL (total volume) of toluene so as to minimize the amount of Et_2O lost to the free volume above the solution (earlier runs had shown this to be a problem). In all cases, kinetic plots are linear for at least 3 half-lives.

(iii) Absolute Rate Determinations for Reactions of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with Alkyl and Aryl Halides. (a) Absolute Rate of *t*-BuCl and $PhCH_2Cl$ plus $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$. The absolute rates for the reaction of *t*-BuCl and $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ were determined at 22.0 °C in toluene and also in neat Et_2O by monitoring the loss of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ at 550 nm. A correction for product interference ($(C_5Me_5)Yb^{III}Cl_2$) was made exactly as described above for reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX. Unlike the kinetic reactions of RX with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, high concentrations of RX (pseudo-first-order conditions) could be used in the reactions of RX with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$. This was possible as the interference from the product ($(C_5Me_5)Yb^{III}Cl_2$) at the wavelength monitored is small and the subsequent Grignard reactions of this product are slow (i.e., ϵ_p remains essentially constant). All of the reactions of *t*-BuCl and $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ examined below are found to obey the rate law $-d[Yb^{III}-Cl]/dt = k_{2obsd}[Yb^{III}-Cl][RX]$. Kinetic plots are typically linear for 2–3 half-lives.

Three runs were performed for the reaction of *t*-BuCl with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ by using high concentrations of *t*-BuCl (pseudo-first-order condition). The [Yb^{III}–Cl] used ranged from 7.26×10^{-3} to 7.73×10^{-3} M and the [*t*-BuCl] ranged from 0.092 to 0.28 M (12–36-fold excess RX). Three runs were performed for this reaction in neat Et_2O. The [Yb^{III}–Cl] used ranged from 8.86×10^{-3} to 1.12×10^{-2} M, and the [*t*-BuCl] was 0.115 M (10–13-fold excess RX).

Four runs were performed for the reaction of $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ in toluene by using high concentrations of $PhCH_2Cl$ (pseudo-first-order conditions). The [Yb^{III}–Cl] used ranged from 8.5×10^{-3} to 9.8×10^{-3} M, and the [$PhCH_2Cl$] was from 0.107 to 0.21 M (11–21-fold excess RX). One run was performed by using second-order concentration conditions (the [Yb^{III}–Cl] was 0.012 M, and the [$PhCH_2Cl$] was 0.017 M); the same rate constant was obtained as with pseudo-first-order conditions. Three runs were performed for $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ in neat Et_2O. The [Yb^{III}–Cl] used ranged from 5.9×10^{-3} to 6.7×10^{-3} M, and the [$PhCH_2Cl$] was 0.117 M (18–20-fold excess RX).

(b) Dependence of the Absolute Rate of $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ on the Concentration of Et_2O. Added Et_2O acts to retard the rate of reaction of $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$. Although the possible coordination of a second Et_2O ligand to $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ is unlikely since it has one less coordination site compared to $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ (and the latter forms $(C_5Me_5)_2Yb^{II}(OEt_2)_2$ but not $(C_5Me_5)_2Yb^{II}(OEt_2)_3$), this was checked experimentally. No change is observed in the $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ visible spectrum over the [Et_2O] range used.

The [Et_2O] dependence of the reaction of $PhCH_2Cl$ with $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ was determined as above in toluene at 22.0 °C from eight kinetic points by following the decrease of $[Yb^{III}Cl]_T$ at 550 nm. A plot of $1/k_{2obsd}$ vs [Et_2O] is linear with intercept = 2.8 ± 0.9 M s and slope 404 ± 9 s giving[21] $k_2 = 0.35 \pm 0.09$ M^{-1} s^{-1} and $K_{eq} = 0.007 \pm 0.002$ M, and allowing the limit $50k_2' \leq k_2$ to be set. The concentration of Et_2O used ranged from 0.028 to 0.23 M, the [$Yb^{III}Cl$] ranged from 0.010 to 0.0079 M, and the [$PhCH_2Cl$] was 0.013 M.

(iv) Absolute Rate of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with $PhCH_2Cl$. The absolute rate for the reaction of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with $PhCH_2Cl$ in toluene at 22.0 °C was determined by monitoring the decrease in $[Yb^{III}-CH_3]_T$ at 460 nm under second-order concentration conditions. It was not possible to use high concentrations of $PhCH_2Cl$ (pseudo-first-order conditions) because of subsequent $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ and $(C_5Me_5)(CH_3)Yb^{III}Cl(OEt_2)$ reactions with the excess $PhCH_2Cl$. A correction was made to the absorbances in a manner identical with that used for the reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX. Second-order kinetic plots are linear for up to 2 half-lives, at which point they begin to show curvature. Isosbestic points are not observed for this reaction. The absolute rate was determined from five runs. The [Yb^{III}–CH_3] used ranged from 0.0064 to 0.01 M, and the [$PhCH_2Cl$] was 1.2 times the $[Yb^{III}-CH_3]_T$. The partial rate law $-d[Yb^{III}-CH_3]/dt = k_{2obsd}[Yb^{III}-CH_3][PhCH_2Cl]$ is obeyed, with $k_{2obsd} = 0.55 \pm 0.10$ M^{-1} s^{-1}.

Added Et_2O retards the $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ plus $PhCH_2Cl$ reaction. The [Yb^{III}–CH_3] ranged from 0.005 to 0.008 M, the [$PhCH_2Cl$] was 1.2 times the $[Yb^{III}-CH_3]_T$, and the [Et_2O] ranged from 0 to 0.12 M. Unfortunately, a plot of $1/k_{2obsd}$ vs [Et_2O] is not linear, and the [Et_2O] effect on this reaction was not investigated further.

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Registry No. $(C_5Me_5)_2Yb\cdot OEt_2$, 74282-47-6; $(C_5Me_5)_2YbBr(OEt_2)$, 117470-39-0; $(C_5Me_5)_2YbCl(OEt_2)$, 99642-76-9; $(C_5Me_5)_2YbI(OEt_2)$, 117470-40-3; $(C_5Me_5)_2YbF(OEt_2)$, 117470-41-4; $(C_5Me_5)_2YbCH_3(OEt_2)$, 80145-93-3; $(C_5Me_5)YbCl_2$, 99642-75-8; $(C_5Me_5)YbBr_2$, 117470-42-5; $PhCH_2F$, 350-50-5; $PhCH_2Cl$, 100-44-7; YbF_3, 13760-80-0; $YbF_3(OEt_2)$, 117470-43-6; $YbCl_3$, 10361-91-8; $YbCl_3(OEt_2)$, 61731-06-4; $C_5Me_5CH_2Ph$, 100692-30-6; $C_5Me_5MgCl\cdot THF$, 107495-40-9; C_5Me_5(*n*-Bu), 117439-46-0; $C_5Me_5(CH_2CH_2CH{=}CH_2)$, 117439-47-1; C_5Me_5[(cyclopropyl)carbinyl], 117439-48-2; *n*-BuBr, 109-65-9; PhI, 591-50-4; $PhCH_2CH_2Ph$, 103-29-7; *n*-BuCl, 109-69-3; $PhCH_2Br$, 100-39-0; *i*-PrCl, 75-29-6; 4-bromo-1-butene, 5162-44-7; (bromomethyl)cyclopropane, 7051-34-5; (chloromethyl)cyclopropane, 5911-08-0; neopentyl chloride, 753-89-9.

Supplementary Material Available: Plots of the effect of added Et_2O on the yields of products from reactions of $PhCH_2Cl$ and *n*-BuCl with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$, plot of the effect of dilution on the yields of products obtained in reactions of $(C_5Me_5)_2Yb^{II}OEt_2$ with $PhCH_2Cl$, typical second-order kinetic plots for reactions of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ with RX = *n*-BuCl, isopropyl chloride, neopentyl chloride, PhI, and PhBr, typical kinetic plots for reactions of $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with $PhCH_2Cl$ and *t*-BuCl, a typical second-order kinetic plot for the reaction of $(C_5Me_5)_2Yb^{III}CH_3(OEt_2)$ with $PhCH_2Cl$, experimental details for the reaction of $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ and $(C_5Me_5)_2Yb^{III}Cl(OEt_2)$ with (bromomethyl)cyclopropane, experimental details for the determination of the stoichiometry of the reaction of neopentyl chloride, isopropyl chloride, bromobenzene, and iodobenzene with $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ under the conditions used for the absolute rate determinations, and the experimental details for the absolute rates for $(C_5Me_5)_2Yb^{II}\cdot OEt_2$ plus *n*-butyl chloride, neopentyl chloride, isopropyl chloride, phenyl iodide, and phenyl bromide (13 pages). Ordering information is given on any current masthead page.