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C–H Activation of Arenes and Substituted Arenes by the Yttrium Hydride $(Cp^*_2YH)_2$: Competition between Cp* Ligand Metalation, Arene Metalation, and H/D Exchange. Molecular Structures of $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ and $Cp^*_2Y(o\text{-}C_6H_4PPh_2CH_2)$

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Summary. Several C—H activation reactions with $(Cp^*_2YH)_2$ (1) are reported. Thermolysis of 1 in *n*-octane, cyclohexane, or benzene leads to formation of the thermodynamically favored product $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (2). The molecular structure of 2 was determined by X-ray diffraction. The compound crystallizes in space group $P\bar{1}$ with unit cell parameters $a = 10.433(3)$ Å, $b = 13.661(3)$ Å, $c = 15.076(5)$ Å, $\alpha = 113.76(3)°$, $\beta = 90.62(3)°$, $\gamma = 100.45(2)°$. The unit cell contains two molecules of 2 ($Z = 2$) and one benzene molecule. Least-squares refinement based on 4240 reflections converged to $R_F = 0.065$. With deuterated aromatic solvents fast H/D exchange takes place between the solvent and hydride ligands of 1, without intermediate metalation of solvent molecules. For toluene, a preference for H/D exchange on the para and meta positions was found. Metalation of benzene and toluene is possible when the hydrogen gas generated is removed quickly, leading to compounds Cp^*_2YPh (3) and $Cp^*_2YCH_2Ph$ (4), respectively. This process is much slower than the H/D scrambling reaction, and formation of 2 competes. It is proposed that the H/D exchange with benzene and toluene and the formation of 3 and 4 proceed through different σ-bond metathesis pathways. With aromatic molecules PhX (X = OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, $-PPh_2{=}CH_2$, F, Cl, Br), ortho-metalation of the phenyl group is the dominant reaction, although formation of 2 is also observed (X = NMe_2, CH_2NMe_2). For halobenzenes (X = F, Cl, Br) instantaneous reaction was observed but the products appeared to be complicated mixtures which could not be identified. Organic workup and analysis of the organic products showed that C—C coupling leading to biphenyl derivatives is taking place. The product resulting from ortho-metalation of $Ph_3P{=}CH_2$, $Cp^*_2Y(o\text{-}C_6H_4\text{-}PPh_2CH_2)$ (10), crystallizes in space group $P2_1/n$ with unit cell parameters $a = 13.449(2)$ Å, $b = 16.522(2)$ Å, c 15.410(2) Å, $\beta = 108.73(1)°$. The unit cell contains four molecules of 10 ($Z = 4$). Least-squares refinement based on 5198 reflections converged to $R_F = 0.043$.

Introduction

The 14 electron group 3 and lanthanide compounds Cp^*_2LnR ($Cp^* = \eta^5\text{-}C_5Me_5$, R = H, alkyl) are strong Lewis acids[2] which, in the absence of Lewis bases, even may attack the electron density of C–H bonds, thus forming agostic interactions[3] and activating these bonds.[2b,4] Activation of C–H bonds is limited to predominantly hydrocarbyl substrates without heteroatom functionalities however. Activation of C–X bonds (X = heteroatom) is also well-known for these complexes. For X = halogen it has frequently been observed[5] and activation of C–O[6] and C–P[7] bonds has been reported. Activation of C–C bonds has been observed by several groups as a termination process for propene polymerization by lanthanide and group 4 complexes.[8] This β-alkyl elimination has been applied successfully for the isomerization of *n*-diolefins to branched and cyclic olefins by Bercaw and co-workers.[9] C–X agostic interactions have been found for X = Si[10] and N,[11] but activation of these bonds has only been reported for β-Si–C bonds in sila–alkyl complexes of which the

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reversible activation in a cationic zirconium complex [*rac*-$C_2H_4(indenyl)_2ZrCH(SiMe_3)_2]^+$ is the most relevant for our work.[12]

Thermodynamically, C–X activation is strongly favored because of the formation of strong Ln–X bonds.[5a] Should C–H activation be preferred over C–X activation, then this is expected to be kinetic in origin. Indeed, there are indications that functionalized substrates do not always undergo C–X activation. The catalytic hydroamination/cyclization of aminoolefins with organosamarium compounds,[13] cyclization of functionalized dienes[14] and hydrogenation[15] of functionalized olefins by an organoyttrium system, and the living polymerization of methyl methacrylate by group 3 and lanthanide organometallics[16] are examples in which C–X bonds are tolerated despite the highly favorable Ln–X bond formation.

During our work on hydrocarbyl and hydride compounds Cp^*_2LnR and $(Cp^*_2LnH)_2$ with Ln = Y, La, Ce, we studied the activation of C–H bonds and observed that the crowded metal alkyls $Cp^*_2LnCH(SiMe_3)_2$, though much less reactive, show a reactivity very related to that of the hydrides $(Cp^*_2LnH)_2$. The yttrium compound $(Cp^*_2YH)_2$ (1) appeared to be the most reactive of the series and therefore we focused on this compound. Its reactivity in solvents like alkanes, benzene, and toluene and its reactions with aromatic molecules having heteroelement containing substituents attached to them was studied to determine the selectivity of C–H activation and possible competition between C–H and C–X activation with this type of compounds. The results are described in this publication.

Results and Discussion

Competition between C–H Activation of a Cp* Ligand and C–H Activation in Benzene and Toluene. Thermolysis of 1 in *n*-octane, cyclohexane, or benzene leads to the internally metalated complex $Cp^*_2Y(\mu\text{-H})(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (2)[17] (eq 1). This reaction occurs

$$\underset{1}{(Cp^*_2YH)_2} \rightleftharpoons \underset{2}{Cp^*_2Y(\mu\text{-H})(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*} + H_2 \quad (1)$$

in closed vessels but also when the hydrogen evolved is removed slowly. Binuclear complex 2 contains bridging hydride and tetramethylfulvene (Fv = η^1,η^5-$C_5Me_4CH_2$) ligands, the latter formed via hydrogen abstraction from a Cp* ligand. A similar observation has been made for the analogous samarium hydride $(Cp^*_2SmH)_2$[6b] which emphasizes the strong resemblance of 1 and lanthanide hydrides.[2b] The formation of 2 is reversible, and in closed systems a solution of 1, although it contains in part 2, reacts as if it were the intact dimeric hydride.

In aromatic solvents a second C–H activation process is observed. When 1 is dissolved in deuterated benzene or toluene at room temperature, instantaneous H/D scrambling between hydride ligands and solvent takes place, leading to formation of the deuteride $(Cp^*_2YD)_2$, and it is impossible to observe hydride resonances in the ^{1}H-NMR spectrum.[18,19]

The H/D exchange with benzene and toluene was monitored with ^{1}H-NMR spectroscopy by adding stoichiometric quantities of benzene-d_6 or toluene-d_8 to cyclohexane-d_{12} solutions of 1. The loss of hydride intensity was attended with a matching increase in intensity of the benzene and toluene resonances, respectively. Superimposed on this scrambling reaction is the thermolysis to 2. With toluene-d_8, after 26 h at room temperature, 20% of the hydride ligands of 1 were still present while 30% had been exchanged for deuteride ligands. The remaining 50% of 1 had been converted to 2. The intensity ratio H(para):H(meta):H(ortho):H(methyl) = 1.1:2.3:1.1:1.0 was observed, indicating a clear preference for H/D scrambling on the para and meta positions. These observations are in close agreement with the corresponding scandium system.[5b]

These results indicate that 1 is an efficient catalyst for the activation of C–D/C–H bonds in aromatic hydrocarbons. For nondeuterated aromatic hydrocarbons it is not a productive process however. In contrast to deuterated benzene and toluene, the sp^3 C–H bonds of cyclohexane-d_{12} are more inert towards H/D exchange since no significant H/D exchange was observed during the thermolysis of 1 in this solvent (several days at room temperature).

In addition to fast H/D exchange and the slow intramolecular C–H activation which gives 2, a third reaction was observed which, at an intermediate rate, leads to metalation of solvent molecules under formation of hydrogen (eq 2). This C–H activation competes with Cp* metalation

$$(Cp^*_2YH)_2 + 2RH \rightleftharpoons \underset{\substack{3,\ R\,=\,Ph\\ 4,\ R\,=\,CH_2Ph}}{2Cp^*_2YR} + 2H_2 \quad (2)$$

and compounds Cp_2^*YR (R = Ph (3), $PhCH_2$ (4)) can be trapped as the kinetic products when the hydrogen is removed sufficiently rapidly. The method is not clean, as small amounts of the bridged hydride fulvene 2 are obtained as well. For benzene this leads to a 6:1 mixture of 3 and 2. Toluene is metalated faster, resulting in an 11:1 ratio of 4 and 2. It is clear from competition experiments that 2 is the thermodynamic product, obtained when thermolysis of 1 is carried out slowly, *i.e.* when hydrogen is removed gradually during a couple of days at room temperature. Equation 2 is positioned strongly at the side of the starting material 1, and in closed NMR tubes less than 1% of 1 is converted to metalation products.

In principle, H/D scrambling could take place via metalation (Scheme I). After dissociation of 1,[10c] an arene molecule is metalated under formation of HD. The new Y–C bond can be hydrogenolyzed in the second step by

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(18) In contrast to what was published earlier by our group,[19] the ^{1}H-NMR data (300 MHz, methylcyclohexane-d_{14}, 300 K) for 1 are as follows: δ 5.45 (broad s, 2 H, Y–H–Y), 2.06 (s, 60 H, $C_5(CH_3)5$). Heating the solution to 355 K did lead to a slightly sharpened resonance, the high temperature limit could however not been reached due to severe thermal decomposition of the compound. On cooling, the broad singlet hydride resonance splits into a triplet ($^1J_{HY}$ = 37.5 Hz) already at 288 K. Subsequent cooling to 195 K does not lead to further substantial changes of the NMR spectrum. This implicates that below room temperature 1 exists as a dimer with symmetrically bridging hydride ligands.

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Scheme I

$$Cp^*_2YH + RD \rightleftharpoons Cp^*_2YR + HD$$

$$Cp^*_2YR + HD \rightleftharpoons Cp^*_2YD + RH$$

HD to give Cp^*_2YD and protonated solvent. Another possibility is that after dissociation of 1, H/D scrambling involves the direct exchange of a proton for a deuteron between monomeric hydride and solvent. The fact that H/D scrambling between 1 and toluene-d_8 takes place dominantly at the aryl C–H positions while only the benzyl product can be obtained under dynamic vacuum suggests that the pathway for H/D (H/H) exchange is different from that of the metalation, because otherwise a mixture of yttrium tolyls $Cp^*_2YC_6H_4Me$ and the benzyl 4 is expected. The observation that H/D scrambling between H_2 (4 atm) and toluene-d_8 in the presence of 1 is slow, while in the same experiment scrambling between 1 and toluene-d_8 is fast, indicates that H_2, D_2, and HD are not intermediates in the latter process. Ring metalation of toluene is therefore probably not on the reaction coordinate for H/D scrambling between 1 and solvent.

One way to account for the different observations within the framework of the well-known σ-bond metathesis mechanism[4] is that there are two possibilities for the incoming molecule RH to form a transition state. The most easily achieved, considering steric interactions upon approaching molecule RH, is situation A (Figure 1), with R symmetrically positioned between two hydrogen atoms, leading to nonproductive metathesis when hydrogen atoms are involved and to catalytic H/D scrambling when deuterated substrates R–D are introduced. Situation B is the transition state normally anticipated and leads to a metalated species and H_2 (or HD). So far, transition state A has hardly been mentioned as a possibility in early transition metal chemistry and theoretical analyses,[20] but it has been proposed to explain H/D exchange between CpCp*M(H)Cl (M = Zr, Hf) and $PhSiD_3$.[21]

The reactions with benzene and toluene show that 1 behaves very much like the Sc, Lu, and other lanthanide analogues. Both $(Cp^*_2ScH)_2$[5b] and $(Cp^*_2LuH)_2$[6a] give facile H/D scrambling between the hydride ligands and deuterated benzene or toluene. They also form phenyl complexes when H_2 is purged from the reaction mixture. Metalation of toluene to form the benzyl $Cp^*_2MCH_2Ph$ has also been observed for the cerium alkyl $Cp^*_2CeCH(SiMe_3)_2$[22] and for the dimeric samarium hydride $(Cp^*_2SmH)_2$.[6b]

The formation of hydride fulvene complexes $Cp^*_2M(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)MCp^*$ has not been reported for M = Sc and Lu, although these systems have been studied under conditions comparable to those under which we studied the thermolysis of 1. Bercaw et al.[5b] observed that, in aliphatic hydrocarbon solvents and under reduced hydrogen pressures, $(Cp^*_2ScH)_n$ decomposes but the nature of the product(s) was not established. Formation of a scandium fulvene complex $(Cp^*(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)Sc)_2$ was observed however in the thermolysis of Cp^*_2ScR species.[23] In light of our results it seems likely that also for scandium the formation of a fulvene hydride $Cp^*_2Sc(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)ScCp^*$ can take place when other possibilities are blocked.

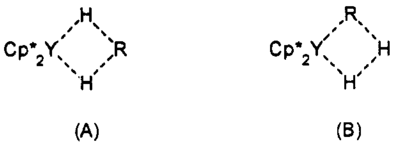

Figure 1. Transition states in nonproductive (A) and productive (B) σ-bond metathesis.

Evans et al.[6b] observed the formation of an analogous hydride fulvene complex from $(Cp^*_2SmH)_2$ in alkanes and benzene, *i.e.* under conditions close to those described by us for yttrium. These authors do not mention a transient side product Cp^*_2SmPh, but in toluene they observe formation of a mixture of $Cp^*_2Sm(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)SmCp^*$ and the benzyl $Cp^*_2SmCH_2Ph$, which strongly suggests that the various C–H activation processes take place at samarium and therefore at other analogous lanthanide centers as well. The main difference will be the relative rates, which will determine the kinetic products, but also the thermodynamics may vary from metal to metal, leading to variations in final product composition, although the differences probably will be marginal.

A requisite for high H/D scrambling and metalation activity seems to be the presence of a terminal hydride ligand.[6b,8b,10c] For $(Cp^*_2MH)_2$ complexes with small metal centers (M = Sc, Lu) this is realized by dissociation of the dimeric hydride in solution. The similarities in the behavior of 1 and the scandium and lutetium analogues suggest that dissociation is at least kinetically within range. These considerations can also explain why the bridging hydride ligand in 2 does not suffer H/D exchange with benzene-d_6 (18 h, room temperature), since breaking up of the hydride bridge is expected to be more difficult here.

The observations discussed above illustrate how subtle differences in experimental conditions can drastically influence the ultimate products from C–H activation reactions of 1. This is caused by the small differences in kinetics of the various C–H activation routes available. It is evident that 1 and the species derived from it through thermolysis and solvent metalation are very reactive. Their role should be taken into account when reactions of 1 with other substrates are studied.

Metalation of Substituted Arenes PhX. We were interested to see whether the presence of a heteroatom containing substituent X in the substrate molecule would influence the selectivity of the C—H activation and especially whether activation of group X would compete. Therefore we studied the reaction of 1 with substituted aromatic compounds PhX (X = OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, $PPh_2{=}CH_2$, F, Cl, Br). From organolithium chemistry it is known that several substituents on the aryl ring can function as an ortho-directing group, *e.g.* –OMe, $-NMe_2$, and $-CH_2NMe_2$.[24]

The dominant reaction observed appeared to be orthometalation (eq 3 and 4), demonstrating the strong preference for attack on sp^2 C–H bonds. No activation of sp^3 C–H bonds or of substituent X was observed. For anisole

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$$\underset{\mathbf{1}}{(\mathrm{Cp^*}_2\mathrm{YH})_2} + 2\mathrm{PhX} \rightarrow 2\mathrm{Cp^*}_2\mathrm{Y}(o\text{-}\mathrm{C_6H_4X}) + 2\mathrm{H_2} \qquad (3)$$

$$\begin{array}{l} \mathbf{5}, \mathrm{X} = \mathrm{OMe} \\ \mathbf{6}, \mathrm{X} = \mathrm{SMe} \\ \mathbf{7}, \mathrm{X} = \mathrm{NMe_2} \\ \mathbf{8}, \mathrm{X} = \mathrm{CH_2NMe_2} \\ \mathbf{9}, \mathrm{X} = \mathrm{PMe_2} \end{array}$$

$$\underset{\mathbf{1}}{(\mathrm{Cp^*}_2\mathrm{YH})_2} + 2\mathrm{PPh_3{=}CH_2} \rightarrow \underset{\mathbf{10}}{2\mathrm{Cp^*}_2\mathrm{Y}(o\text{-}\mathrm{C_6H_4PPh_2CH_2})} + 2\mathrm{H_2} \qquad (4)$$

the reaction is instantaneous at room temperature and strictly analogous to the reaction with organolithium reagents.[24] The ortho-metalation of methyl phenyl sulfide is also fast and quite interesting, because with other metalating reagents preferential metalation at the methyl group is found.[25] This α-metalation of methyl phenyl sulfide is probably thermodynamically favored, because the negative charge on the α-carbon is stabilized by empty d-acceptor orbitals on sulfur.[26] During reaction of *n*-BuLi with methyl phenyl sulfide, the ortho-metalated product has been observed as an intermediate, but isomerization to the more stable α-metalated product takes place. This sequence is not observed for the yttrium system studied here. With *N,N*-dimethylaniline only minor amounts of ortho-metalation product **7** were formed along with the fulvene hydride **2**. When the reaction was monitored by ^{1}H-NMR spectroscopy, also extensive H/D exchange between solvent and the aryl positions of *N,N*-dimethylaniline but not with the methyl groups was observed. On a preparative scale, **7** was obtained in low yield from **1** in pure *N,N*-dimethylaniline. This is in remarkable contrast with the quantitative ortho-metalation of *N,N*-dimethylaniline with *n*-BuLi.[24]

The reason that formation of **2** is favored over metalation of *N,N*-dimethylaniline is most probably thermodynamic in origin and might be caused by steric hindrance between the methyl substituents on the amine function and the pentamethylcyclopentadienyl ligands. This prevents internal stabilization by coordination of the nitrogen lone pair. A similar effect might explain the reaction of **1** with benzyldimethylamine. Some ortho-metalation and formation of **8** was found, but again the major reaction product was **2**.[27]

On the other hand, the reaction with dimethylphenylphosphine produced cleanly the ortho-metalated product **9**. ^{1}H-NMR spectroscopy indicated coordination of the phosphorus atom to yttrium. A small yttrium coupling on the P–CH_3 resonance ($^3J_{\mathrm{HY}}$ = 0.4 Hz) was observed and provides the second example of a phosphine adduct of yttrium.[28] The observation that for phosphorus the formation of a four-membered chelate ring is very well possible whereas for nitrogen it is not, cannot be explained on the basis of the relative Lewis base strength of phosphorus and nitrogen ligating atoms. If that would be the determining effect, ortho-metalated products would have been expected both for *N,N*-dimethylaniline and benzyldimethylamine, rather than for dimethylphenylphosphine. The results obtained are more in line with steric effects, since the longer Y–P distance will place the methyl groups on phosphorus sufficiently far from the cyclopentadienyl ligands to diminish the steric interaction so that the interaction between yttrium and phosphorus can become strong enough to stabilize the ortho-metalated product with respect to the fulvene hydride **2**.

The strong preference of the Y–H bond to attack aryl C–H bonds is also demonstrated by its reaction with methylenetriphenylphosphorane, where ortho-metalation of a phenyl group and formation of a five-membered metallacycle **10** was observed, despite the crowded transition state necessary for direct attack on the aryl C–H bond. Ortho-metalation of methylenetriphenylphosphorane has also been reported for hydride and alkyl complexes of lutetium,[6a,29] but in contrast to lanthanide compounds, d^0-complexes of group 4 elements give metalation on the methylene carbon.[30]

The reaction of **1** with PhX (X = F, Cl, Br) in cyclohexane-d_{12} was instantaneous but a complicated mixture of yet unidentified compounds was formed. Formation of benzyne was indicated from GC/MS analysis after quenching the fluorobenzene reaction with water. In addition to a significant amount of 2-fluorobiphenyl, three other major components were observed which, according to the molecular mass, were provisionally identified as resulting from attack of benzyne on the Cp* ligands. Due to the complexity of the reaction and the resulting hydrolysis mixture, a detailed investigation of these systems was not pursued. However, in a preparative reaction of **1** with fluorobenzene, a biphenyl derivative $\mathrm{Cp^*_2Y(–C_6H_4–C_6H_4F)}$ (^{1}H-NMR) was isolated in low yield (6%). This indicates that C–X bonds are activated, possibly after initial ortho-metalation of fluorobenzene. C–C coupling can then take place either by attack of benzyne on a Cp* ligand or by insertion into the Y–C bond of the initial metalation product $\mathrm{Cp^*_2Y}(o\text{-}\mathrm{C_6H_4F})$. Since the ^{1}H-NMR spectra of the chloro- and bromobenzene reactions with **1** are very similar to that with fluorobenzene, an analogous reactivity of these benzenes is assumed.

Molecular Structure of $\mathrm{Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*}$ (2). The red compound **2** crystallizes from benzene in the triclinic space group $P\bar{1}$, with $Z = 2$, and the unit cell contains one additional benzene molecule. The molecular structure is shown in Figure 2, and relevant bond distances and angles are given in Table I. The structure is as suggested on the basis of the NMR data[17] and almost identical with that of the samarium analogue $\mathrm{Cp^*_2Sm(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)SmCp^*}$.[6b]

One yttrium atom (Y2) is surrounded by two intact Cp* ligands, forming a normal $\mathrm{Cp^*_2Y}$ moiety. The other yttrium atom (Y1) is η^5-bonded to both a normal Cp* and a tetramethylfulvene ligand, giving also a $\mathrm{Cp^*_2Y}$-like structure. The methylene carbon of the fulvene ligand is bonded to Y1 and coplanar with the five ring carbon atoms of the fulvene ligand. The hydride ligand, although

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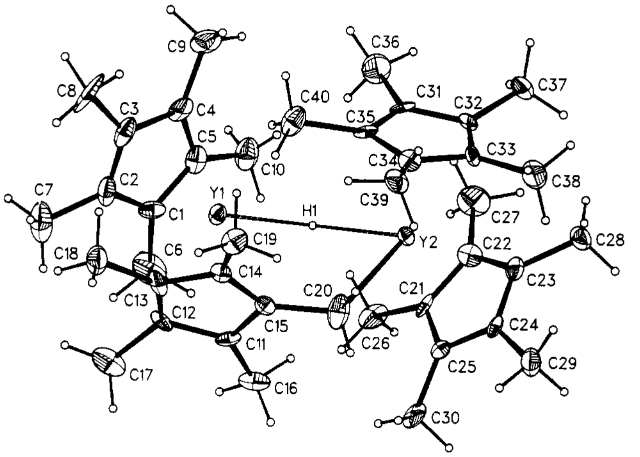

Figure 2. ORTEP diagram of $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (2) with the probability ellipsoids drawn at the 50% level.

Table I. Selected Distances and Angles for $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (2)[a]

	Distances (Å)		
Y1–Ct1	2.37(2)	Y2–Ct2	2.39(2)
Y1–Ct(Fv)	2.33(1)	Y2–Ct3	2.37(2)
Y1–C(ring 1)$_{av}$	2.66(2)	Y2–C(ring 2)$_{av}$	2.67(4)
Y1–C(Fv)$_{av}$	2.62(3)	Y1–C(ring 3)$_{av}$	2.66(4)
Cp*1(C–C)$_{int,av}$	1.41(2)	Cp*2(C–C)$_{int,av}$	1.41(1)
Fv(C–C)$_{int,av}$	1.42(3)	Cp*3(C–C)$_{int,av}$	1.42(1)
Cp*1(C–C)$_{ext,av}$	1.50(2)	Cp*2(C–C)$_{ext,av}$	1.51(2)
Fv(C–C)$_{ext,av}$	1.51(3)	Cp*3(C–C)$_{ext,av}$	1.49(1)
Y1–H1	2.14(7)	Y2–H1	2.10(7)
C15–C20	1.52(1)	Y2–C20	2.631(9)
	Angles (deg)		
Y1–H1–Y2	135(3)	H1–Y2–C20	79.8(16)
Y1–C15–C20	117.7(5)	Y2–C20–C15	116.4(5)

[a] Cp*1 = C1–C10, Cp*2 = C21–C30, Cp*3 = C31–C40, Fv = C11–C20.

bridging, appears to form a regular Cp^*_2YH fragment around Y1. The Y–Ct1 distances (Table I) for the Cp* rings are comparable to those found in the similar complexes Cp^*_2YR (R = $N(SiMe_3)_2$, $CH(SiMe_3)_2$, Me·THF, Cl·THF).[31] The Y–Ct(Fv) distance (2.33(1) Å) is slightly shorter than the other Y–Ct(Cp*) distances. The methylene-carbon–ring-carbon distance, C15–C20 (1.52(1) Å), is typical for a regular C–C single bond.[32] Therefore the fulvene ligand in 2 is essentially a metalated Cp* ligand. The Y2–C20 distance (2.631(9) Å) is quite long for an Y–C σ-bond (a value of 2.45 Å would be normal[31a,c]). The longest yttrium–carbon σ-bond reported so far is in $(Cp_2YMe)_2$ (2.553(10) Å)[33] where the methyl ligands are bridging. Nevertheless, ^1H- and ^{13}C-NMR data (*vide infra*) indicate a cyclopentadienyl–alkyl type of bonding for the fulvene. The long Y2–C20 σ-bond most likely originates from the high steric congestion. The bulky Cp* and Fv ligands are forced to come closely together by the combined action of the Fv and hydride bridges.

Very interesting is the location of the hydride ligand. The Y1–H1 and Y2–H1 distances are 2.14(7) and 2.10(7) Å, respectively, comparable to values found in $[(C_5H_4Me)_2Y(THF)(\mu\text{-}H)]_2$ and $[(1,3\text{-}Me_2C_5H_3)Y(\mu\text{-}H)(THF)]_2$,[34] indicating that the hydride ligand is bridging symmetrically. The Y1–H–Y2 angle of 135(3)° however is much larger than the corresponding angles (114(3) and 118(3)°, respectively) in these complexes. This large angle was also found in the samarium analogue (135(4)°).[6b] Finally, two agostic interactions[3] are present (Y1···H402 (2.62(6) Å) and Y1···H403 (2.69(6) Å)).

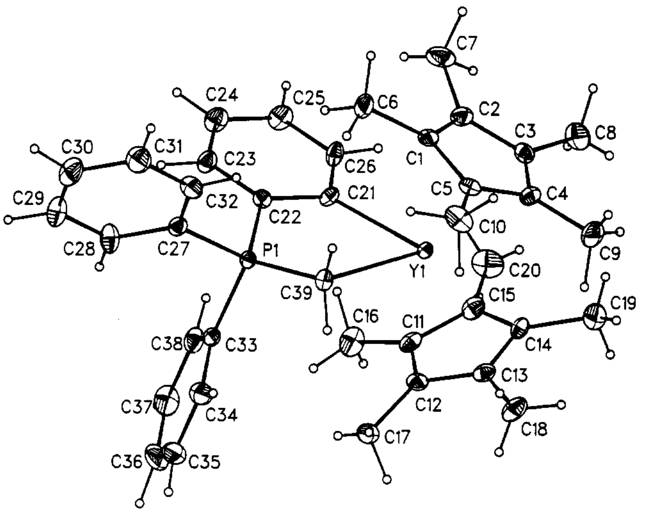

Figure 3. ORTEP diagram of $Cp^*_2Y(o\text{-}C_6H_4PPh_2CH_2)$ (10) with the probability ellipsoids drawn at the 50% level.

In the ^{13}C-NMR spectrum of 2, chemical shift and coupling constants of the $Y\text{–}CH_2$ resonance indicate that this methylene group forms a nonbridging σ-bond[35] since the signal appears as a triplet of doublets with $^1J_{CH}$ = 116.3 Hz and $^1J_{CY}$ = 35.3 Hz at 36.33 ppm. In accordance with this, the ^1H NMR spectrum displays a doublet ($^2J_{HY}$ = 3.7 Hz) for the methylene group at 0.81 ppm and a double doublet for the hydride ($^1J_{HY}$ = 48.0 and 29.0 Hz). This, together with the structural data, indicates that the fulvene ligand is bonded as a bridging $\eta^1,\eta^5\text{-}C_5Me_4CH_2$ cyclopentadienyl–alkyl ligand.

Molecular Structure of $Cp^*_2Y(o\text{-}C_6H_4PPh_2CH_2)$ (10). The structure of this compound is very interesting with respect to the bonding of the $C_6H_4PPh_2CH_2$ ligand to yttrium. Several ways of bonding are possible for the hydrogen abstracted Wittig's reagent, and since no structural data on this ligand were available, an X-ray structure determination was carried out.

The compound crystallizes from toluene in the monoclinic space group $P2_1/n$ with Z = 4. The molecular structure is given in Figure 3; relevant bond lengths and angles are presented in Table II. The molecule is a regular, bent metallocene compound with the characteristics of a normal Cp^*_2YR derivative.[31] The most interesting part is a chelating five-membered ring Y–C21–C22–P–C39 which is located in the plane bisecting the angle between the two pentamethylcyclopentadienyl ligands. Four of the chelate ring atoms (Y, C21, C22 and C39) are coplanar within 0.02(1) Å, and the phosphorus atom is 0.34(1) Å out of this plane.

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Table II. Selected Distances and Angles for $Cp^*{}_2Y(o\text{-}C_6H_4PPh_2CH_2)$ (10)[a]

	Distances (Å)		
Y–Ct1	2.42(1)	Y–Ct2	2.38(2)
Y–C(ring 1)$_{av}$	2.70(3)	Y–C(ring 2)$_{av}$	2.67(1)
Cp*1(C–C)$_{int,av}$	1.41(1)	Cp*2(C–C)$_{int,av}$	1.42(1)
Cp*1(C–C)$_{ext,av}$	1.50(1)	Cp*2(C–C)$_{ext,av}$	1.50(1)
Y–C21	2.452(3)	Y–C39	2.563(3)
P–C22	1.806(3)	P–C27	1.828(3)
P–C33	1.806(3)	P–C39	1.737(3)
	Angles (deg)		
C21–Y–C39	77.1(2)	C22–P–C27	107.4(1)
Y–C21–C22	121.5(2)	C22–P–C33	108.1(1)
C21–C22–P	116.2(2)	C22–P–C39	110.9(1)
C22–P–C39	110.9(1)	C27–P–C33	102.8(1)
P–C39–Y	109.9(1)	C27–P–C39	117.3(1)
		C33–P–C39	109.7(1)

[a] Cp*1 = C1–C10, Cp*2 = C11–C20.

The extreme situations for the bonding of the ortho-metalated phosphorus ylide ligand to the $Cp^*{}_2Y$ unit are the Zwitterionic dialkyl structure with a positive charge on phosphorus and the alkyl heteroolefin adduct with the P=C double bond coordinated to yttrium. The distances Y—C21 (2.452(3) Å) and Y—C39 (2.563(3) Å) indicate a normal and a long yttrium carbon σ-bond. The P—C39 distance of 1.737(3) Å is elongated with respect to that in methylenetriphenylphosphorane itself (1.661(8) Å)[36] but still indicates that there is a significant contribution of π-bonding, as is evident when it is compared to the P—C single bonds (1.806(3), 1.828(3), 1.806(3) Å).[37] However the bonding geometry of C39 comes close to an sp^3 hybridization of this carbon atom as follows from the bonding angles Y—C39—H391 (101(2)°), Y—C39—H392 (122(2)°), P—C39—H391 (108(1)°), P—C39—H392 (108(2)°), and H391—C39—H392 (108(3)°). Despite the fact that **10** is formally a 16 electron compound and close to coordinative saturation, a short intramolecular Y···H distance between yttrium and H391 (2.90(2) Å) indicates an agostic interaction,[3] quite normal in organometallic lanthanide compounds.

^{13}C-NMR spectroscopy also indicates significant sp^3 hybridization of C39. The Y–CH_2–P resonance appears as a triplet of pseudotriplets ($^1J_{CH}$ = 124.3 Hz, $^1J_{CY}$ = $^1J_{CP}$ = 28.7 Hz) with the $^1J_{CH}$ coupling in the range for an sp^3 hybridized carbon atom. This suggests significant σ-character of the Y–C39 bond. The yttrium coupling on the Y–*C*(aryl) carbon ($^1J_{CY}$ = 48.8 Hz) is as expected for an Y–C σ-bond.[35] ^1H-NMR spectroscopy shows the expected splitting of the Y–C*H*$_2$–P resonance (dd, $^2J_{HP}$ = 13.8 Hz, $^2J_{HY}$ = 2.4 Hz) with an yttrium–hydrogen coupling in the range observed for α-hydrogens of yttrium-bonded alkyl groups.[35]

Concluding Remarks. The yttrium hydride $(Cp^*{}_2YH)_2$ (**1**) very easily enters various C–H activation processes and, in addition to nonproductive H/H (H/D) exchange, competition between intramolecular activation of a pentamethylcyclopentadienyl ligand and intermolecular attack of aromatic solvents is observed. For most possibilities the activation barriers are comparable, thus leading to mixtures of kinetic products. Also the differences in free energies between the various products appear not to be very pronounced, so that frequently complicated equilibria result and separation of the various components is virtually impossible. In relatively inert solvents (alkanes) the dominant product is the fulvene hydride $Cp^*{}_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (**2**), formed by extrusion of H_2 through activation of a methyl group on one of the pentamethylcyclopentadienyl ligands of the dimeric hydride.

In deuterated aromatic solvents fast H/D exchange between the hydride ligand and all solvent positions takes place, indicating a low activation energy pathway for this, in general terms, nonproductive σ-bond metathesis. This high H/D scrambling activity seems to be related to the facile dissociation of **1** into reactive monomers. The metalation of benzene, toluene, and heteroatom containing aromatic substrates PhX as well as the intramolecular sp^3 C—H activation of the methyl group of a Cp* ligand to give the fulvene hydride **2** follow another pathway. With benzene and toluene the kinetic products are the phenyl complex $Cp^*{}_2YPh$ (**3**) and the benzyl $Cp^*{}_2YCH_2Ph$ (**4**), respectively. With benzene derivatives PhX containing Lewis base substituents (X = OMe, SMe, NMe_2, CH_2NMe_2, PMe_2, $PPh_2{=}CH_2$) ortho-metalation is the thermodynamically favored process, except when steric congestion (X = NMe_2, CH_2NMe_2) decreases the stability of the compound. In that case the thermodynamic product is **2**. The ortho-metalation product of $Ph_3P{=}CH_2$, $Cp^*{}_2Y(o\text{-}C_6H_4PPh_2CH_2)$ (**10**), appears to be stabilized by interaction of yttrium with the P=C double bond. Only with PhX substrates with X = F, Cl, Br were there indications for activation of C—X bonds, indicating that in general sp^2 C—H and in some cases even sp^3 C—H activation of the pentamethylcyclopentadienyl ligand is preferred over activation of the heteroatom substituents.

Experimental Section

General Considerations. All experiments were performed under nitrogen using standard Schlenk, glovebox (Braun MB200), and vacuum line techniques. Benzene, toluene, pentane, cyclohexane, benzene-d_6, toluene-d_8, and THF-d_8 were distilled from Na/K alloy and degassed prior to use. $Cp^*{}_2YCH(SiMe_3)_2$,[31a] **1**,[19] and methylenetriphenylphosphorane[38] were prepared according to published procedures. Hydrogen (Hoek-Loos, 99.9995%) was used without further purification. Other reagents, cyclohexane-d_{12} and methylcyclohexane-d_{14}, were stored over molecular sieves (4 Å) and degassed prior to use.

NMR spectra were recorded on Bruker WH-90 (^1H, 90 MHz), Nicolet NT-200 (^1H, 200 MHz; ^{13}C, 50.3 MHz), Gemini 200 (^1H, 200 MHz; ^{31}P, 80.9 MHz), and Varian VXR-300 (^1H, 300 MHz; ^{13}C, 75.4 MHz) spectrometers at ambient temperatures unless stated otherwise. GC/MS analyses (EI) were carried out on a Ribermag R 10-10 C instrument using a CP Sil 5 CB column. IR spectra were recorded as Nujol mulls between KBr disks on a Pye-Unicam SP3-300 spectrophotometer. Elemental analyses were carried out at the Micro-Analytical Department of the University of Groningen. The determinations are the average of at least two independent determinations.

$Cp^*{}_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (2). A solution of 3.19 g (6.1 mmol) of $Cp^*{}_2YCH(SiMe_3)_2$ in 50 mL of pentane was stirred under H_2 (1 atm) for 3 h at room temperature, during which time a white precipitate of **1** formed. The pentane was filtered off, and the residue was washed with 50 mL of pentane and subsequently dried in vacuum. The remaining pink powder was dissolved in 30 mL of benzene, and the solution was stirred at room temperature for 4 days. The evolving hydrogen was removed by a daily freeze–pump–thaw cycle. The resulting deep-red, clear solution was slowly cooled to 7 °C and 0.77 g (1.0 mmol, 33%) of **2** was isolated as red, block-shaped crystals. Concen-

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tration of the mother liquor afforded a second crop of 1.24 g (1.6 mmol, 53%). IR (cm^{-1}): 2910 (s), 2725 (w), 1450 (s), 1375 (s), 1260 (m, br), 1165 (m), 1060 (w), 1020 (m), 950 (w), 920 (s), 815 (s), 800 (s), 725 (m), 675 (s), 645 (w), 590 (s), 560 (w). ^{1}H-NMR (cyclohexane-d_{12}): δ 7.19 (s, 3 H, C_6H_6), 3.66 (dd, $^1J_{HY}$ = 48.0 respectively 29.0 Hz, 1 H, Y–$H \rightarrow$ Y), 2.02 and 1.91 (both s, each 6 H, $CH_2C_5(CH_3)_4$), 1.99 (s, 45 H, $C_5(CH_3)_5$), 0.81 (d, $^1J_{HY}$ = 3.7 Hz, 2 H, Y–CH_2). ^{13}C-NMR (cyclohexane-d_{12}): δ 149.33 (s, YCH_2C), 128.80 (d, $^1J_{CH}$ = 157.9 Hz, C_6H_6), 120.21 (s, C_5Me_5), 118.44 and 114.62 (both s, $CH_2C_5Me_4$), 116.64 (s, $(C_5Me_5)_2$), 36.33 (td, $^1J_{CH}$ = 116.3 Hz, $^1J_{CY}$ = 35.3 Hz, YCH_2), 14.44 and 11.87 (both q, $^1J_{CH}$ = 125.1 Hz respectively 123.6 Hz, $CH_2C_5(CH_3)_4$), 12.07 (q, $^1J_{CH}$ = 124.3 Hz, $(C_5(CH_3)_5)_2$), 11.84 (q, $^1J_{CH}$ = 125.1 Hz, $C_5(CH_3)_5$). Anal. Calcd for $C_{40}H_{60}Y_2 \cdot {}^1/_2(C_6H_6)$: C, 68.16; H, 8.38; Y, 23.46. Found: C, 67.97; H, 8.29; Y, 23.66.

H/D Scrambling Reactions of $(Cp^*_2YH)_2$ (1) with Benzene and Toluene. A 12-mg (0.017-mmol) sample of 1 was dissolved in 0.5 mL of benzene-d_6. Within 5 min volatiles were removed in vacuum and the residue was dissolved in 0.5 mL of cyclohexane-d_{12}. When the ^{1}H-NMR spectrum of this solution was compared to that of 1 in cyclohexane-d_{12} the hydride resonances turned out to be absent. The $C_5(CH_3)_5$ resonance however was observed at the same chemical shift.

H/D scrambling reactions were followed by monitoring solutions of 0.037 mmol of benzene-d_6 or toluene-d_8 and 13.2 mg (0.018 mmol) of 1 in 0.6 mL of cyclohexane-d_{12} with ^{1}H-NMR spectroscopy at room temperature. For toluene the volatiles were pumped off after 26 h, and from the ^{1}H-NMR spectrum the ratio of proton incorporation into the different positions of toluene was established.

To investigate the H/D scrambling between H_2 and toluene-d_8 by 1, an NMR tube containing 17 mg (0.024 mmol) of 1 in 0.61 mL (5.6 mmol) of toluene-d_8 was sealed under 4 atm (0.3 mmol) of H_2. The increase in the integration of the aryl resonances of the solvent was monitored by ^{1}H-NMR spectroscopy at regular intervals during 5 days at room temperature. The methyl resonance of toluene was not observed due to overlap with the $C_5(CH_3)_5$ resonance of 1. Immediately after preparation of the NMR tube the intensity of the aryl–hydrogen signals of toluene corresponded to 0.05 mmol of hydrogen atoms and the hydride signal was absent. After 30 min the intensity of the aryl–hydrogen signals of toluene corresponded to 0.088 mmol of hydrogen atoms. After 68 h at room temperature this value had increased to 0.17 mmol.

Metalation of Benzene by $(Cp^*_2YH)_2$ (1). A 15-mg (0.021-mmol) sample of 1 was dissolved in 20 mL of benzene and stirred for 4 h under dynamic vacuum at room temperature. Volatiles were removed under vacuum and the ^{1}H-NMR spectrum of the remaining oil in cyclohexane-d_{12} indicated that a mixture of 68% of 3, 11% of 2, and some unidentified material had been formed. ^{1}H-NMR of 3 (cyclohexane-d_{12}, 300 MHz): δ 7.08 (t, $^3J_{HH}$ = 7 Hz, 2 H, meta H's), 6.98 (t, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 1 H, para H), 6.72 (dd, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 2 H, ortho H's), 1.78 (s, 30 H, $C_5(CH_3)_5$).

Metalation of Toluene by $(Cp^*_2YH)_2$ (1). A stirred solution of 50 mg (0.069 mmol) of 1 in 2.5 mL of toluene was evaporated to dryness in $^1/_2$ h at room temperature. The yellow oil which remained was dissolved in cyclohexane-d_{12}, and the ^{1}H-NMR spectrum indicated that a mixture of 80% of 4, 13% of unreacted 1, and 7% of 2 had been formed. ^{1}H-NMR of 4 (cyclohexane-d_{12}, 200 MHz): δ 6.92 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, meta H's), 6.63 ($^3J_{HH}$ = 6.8 Hz, 1 H, para H), 6.53 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, ortho H's), 1.91 (d, $^2J_{YH}$ = 6.0 Hz, 2 H, YCH_2), 1.83 (s, 30 H, $C_5(CH_3)_5$).

$Cp^*_2Y(o\text{-}C_6H_4OMe)$ (5). A solution of 2.03 g (3.9 mmol) of $Cp^*_2YCH(SiMe_3)_2$ in 50 mL of pentane was stirred under H_2 (1 atm) for 3 h at room temperature, during which time a white precipitate was formed. The hydrogen atmosphere was replaced by nitrogen, and 0.40 mL (0.40 g, 3.7 mmol) of anisole was added. The reaction mixture was stirred at room temperature for 16 h, during which time a gas evolved and an orange solution was formed. Filtration and cooling to −30 °C yielded 0.88 g (1.9 mmol, 49%) of 5 as pale orange crystals. Concentration of the mother liquor afforded a second fraction of 0.12 g (0.3 mmol, 7%). IR (cm^{-1}): 3070 (w), 3060 (w), 3040 (w), 2960 (sh), 2920 (s), 2850 (s), 2720 (w), 1600 (w), 1565 (m), 1545 (m), 1490 (sh), 1480 (sh), 1460 (sh), 1435 (s), 1410 (s), 1380 (s), 1265 (m), 1250 (m), 1190 (m), 1155 (w), 1140 (w), 1120 (s), 1100 (s), 1040 (m), 1015 (s), 755 (s), 705 (m), 630 (w), 565 (w), 470 (sh), 425 (sh), 340 (sh). ^{1}H-NMR (benzene-d_6/TMS): δ 7.72 (m, 1 H, aryl CH), 7.18 (m, 2 H, aryl CH), 6.41 (m, 1 H, aryl CH), 3.16 (s, OCH_3), 1.84 (s, $C_5(CH_3)_5$). ^{13}C-NMR (benzene-d_6): δ 173.59 (d, $^1J_{CY}$ = 51.6 Hz, Y–C), 161.39 (s, C–OMe), 139.13 (d, $^1J_{CH}$ = 152.8 Hz, aryl CH), 125.79 (d, $^1J_{CH}$ = 158.4 Hz, aryl CH), 123.44 (d, $^1J_{CH}$ = 154.7 Hz, aryl CH), 116.95 (s, C_5Me_5), 104.12 (d, $^1J_{CH}$ = 152.8 Hz, aryl CH), 53.49 (q, $^1J_{CH}$ = 144.9 Hz, OCH_3), 11.01 (q, $^1J_{CH}$ = 125.2 Hz, $C_5(CH_3)_5$). Anal. Calcd for $C_{27}H_{37}OY$: C, 69.52; H, 7.99; Y, 19.06. Found: C, 69.44; H, 8.02; Y, 19.14.

$Cp^*_2Y(o\text{-}C_6H_4SMe)$ (6). A solution of 1.32 g (2.5 mmol) of $Cp^*_2YCH(SiMe_3)_2$ in 40 mL of pentane was stirred under H_2 (1 atm) for 3 h at room temperature, during which time a white precipitate was formed. The hydrogen atmosphere was replaced by nitrogen by two freeze–pump–thaw cycles, and 0.30 mL (0.32 g, 2.6 mmol) of methyl phenyl sulfide was added. The reaction mixture was stirred at room temperature for 48 h, during which time a gas evolved and a clear orange solution was formed. The solution was concentrated to ca. 20 mL, filtered, and cooled to −30 °C. Yield: 0.22 g (0.5 mmol, 19%) of 6 as white crystals. Concentration of the mother liquor afforded a second fraction of 0.23 g (0.5 mmol, 19%). IR (cm^{-1}): 3040 (m), 2960 (s), 2930 (s), 2860 (s), 2720 (w), 1455 (s), 1410 (m), 1380 (s), 1315 (w), 1255 (w), 1230 (m), 1050 (w), 1020 (m), 1010 (w), 960 (w), 805 (w), 750 (w), 705 (m), 680 (w), 435 (m), 340 (sh). ^{1}H-NMR (cyclohexane-d_{12}): δ 7.32 (m, 1 H, aryl CH), 7.01 (m, 3 H, aryl CH), 6.94 (m, 1 H, aryl CH), 2.47 (s, SCH_3), 1.78 (s, C_5Me_5). ^{13}C-NMR (cyclohexane-d_{12}): δ 192.93 (d, $^1J_{CY}$ = 52.1 Hz, Y–C), 138.42 (d, $^1J_{CH}$ = 160.0 Hz, aryl CH), 137.29 (s, C–SMe), 127.18 (d, $^1J_{CH}$ = 160.0 Hz, aryl CH), 127.01 (d, $^1J_{CH}$ = 160.0 Hz, aryl CH), 126.78 (d, $^1J_{CH}$ = 160.0 Hz, aryl CH), 117.79 (s, C_5Me_5), 20.07 (q, $^1J_{CH}$ = 140.0 Hz, SCH_3), 11.54 (q, $^1J_{CH}$ = 125.0 Hz, $C_5(CH_3)_5$). Anal. Calcd for $C_{27}H_{37}SY$: C, 67.20; H, 7.73; Y, 18.42. Found: C, 66.93; H, 7.75; Y, 18.68.

$Cp^*_2Y(o\text{-}C_6H_4NMe_2)$ (7). A solution of 0.72 g (1.4 mmol) of $Cp^*_2YCH(SiMe_3)_2$ in 20 mL of pentane was stirred under H_2 (1 atm) for 3 h at room temperature, while a white precipitate of 1 formed. The precipitate was filtered and dried in vacuum and then 5 mL of *N,N*-dimethylaniline was added. The mixture was stirred for 16 h at room temperature. The resulting red solution was evaporated under vacuum to leave a red oil. Addition of 15 mL of pentane gave a yellow precipitate which was filtered off, washed with 5 mL of cold pentane, and dried in vacuum to yield 0.13 g (0.3 mmol, 21%) of 7. IR (cm^{-1}): 3030 (m), 2710 (w), 1595 (w), 1545 (w), 1240 (m), 1230 (m), 1170 (w), 1150 (m), 1120 (w), 1090 (m), 1030 (m), 1015 (s), 925 (s), 800 (w), 770 (s), 740 (m), 715 (s), 660 (m), 595 (w), 560 (w), 430 (m). ^{1}H-NMR (benzene-d_6/TMS, 300 MHz): δ 7.72 (m, 1 H, C_6H_4), 7.23–7.08 (m, 2 H, C_6H_4), 6.94 (m, 1 H, C_6H_4), 2.35 (s, 6 H, N–CH_3), 1.82 (s, 30 H, $C_5(CH_3)_5$). ^{13}C-NMR (benzene-d_6, 75.4 MHz): δ 184.47 (d, $1J_{YC}$ = 49.5 Hz, Y–C(aryl)), 155.70 (s, C(aryl)–NMe_2), 138.56 (dd, $^1J_{CH}$ = 155.4 Hz, $^2J_{CH}$ = 6.9 Hz, aryl CH), 126.22 (dd, $^1J_{CH}$ = 157.7 Hz, $^2J_{CH}$ = 8.1 Hz, aryl CH), 125.65 (dd, $^1J_{CH}$ = 154.2 Hz, $^2J_{CH}$ = 3.5 Hz, aryl CH), 117.44 (s, C_5Me_5), 114.73 (dd, $^1J_{CH}$ = 151.9 Hz, $^2J_{CH}$ = 5.8 Hz, aryl CH), 50.84 (q, $^1J_{CH}$ = 135.8 Hz, NCH_3), 12.03 (q, $^1J_{CH}$ = 125.1 Hz, $C_5(CH_3)_5$). Anal. Calcd for $C_{28}H_{40}NY$: C, 70.13; H, 8.41; Y, 18.54. Found: C, 69.20; H, 8.39; Y, 19.18.

$Cp^*_2Y(o\text{-}C_6H_4CH_2NMe_2)$ (8). A solution of 3.05 g (5.9 mmol) of $Cp^*_2YCH(SiMe_3)_2$ in 40 mL of pentane was stirred under H_2 (1 atm) for 3 h at room temperature, while a precipitate of 1 formed. The hydrogen atmosphere was replaced by nitrogen and then 0.5 mL of *N,N*-dimethylbenzylamine was added. The mixture was stirred for 4 days at room temperature. The red solution was filtered, concentrated, and cooled to −30 °C to give 0.49 g (1.0 mmol, 17%) of white crystalline 8 slightly contaminated with 2 (^{13}C NMR spectroscopy). IR (cm^{-1}): 3100 (w), 3040 (m), 2960 (s), 2920 (s), 2850 (s), 2720 (w), 1455 (s), 1435 (sh), 1420 (m),

Table III. Details of the Structure Determinations of $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (2) and $Cp^*_2Y(o\text{-}C_6H_4PPh_2CH_2)$ (10)

	a. Crystal Data	
chem formula	$C_{40}H_{60}Y_2\cdot{}^1/_2(C_6H_6)$	$C_{39}H_{46}PY$
mol wt	757.79	634.67
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a, Å	10.433(3)	13.449(2)
b, Å	13.661(3)	16.522(2)
c, Å	15.076(5)	15.410(2)
α, deg	113.76(3)	
β, deg	90.62(3)	108.73(1)
γ, deg	100.45(2)	
V, Å^3	1926(1)	3242.8(8)
Z	2	4
D_{calc}, g·cm^{-3}	1.307	1.300
$F(000)$, electrons	798	1366
μ(Mo K$\bar{\alpha}$), cm^{-1}	30.4	18.8
approx cryst dimens, mm	0.10 × 0.13 × 0.18	0.17 × 0.18 × 0.50
	b. Data Collection	
diffractometer	Enraf-Nonius CAD-4F	Enraf-Nonius CAD-4F
radiation (λ, Å)	Mo K$\bar{\alpha}$ (0.710 73)	Mo K$\bar{\alpha}$ (0.710 73)
monochromator	graphite	graphite
temp, K	130	130
θ range: min max, deg	1.48, 26.0	1.23, 28.0
$\omega/2\theta$ scan, deg	$\Delta\omega = 0.75 + 0.35 \tan\theta$	$\Delta\omega = 0.75 + 0.35 \tan\theta$
data set	$h, -12 \rightarrow 12$; $k, -1 \rightarrow 16$; $l, -18 \rightarrow 17$	$h, -1 \rightarrow 17$, $k, -1 \rightarrow 21$; $l, -20 \rightarrow 19$
crystal to receiving aperture dist, mm	173	173
horizontal, vertical aperture, mm	$3.2 + \tan\theta$, 4.0	$3.2 + \tan\theta$, 4.0
ref reflctns, rms dev. in %	$\bar{3}12$, 1.3 $\bar{3}0\bar{2}$, 1.4	561, 1.74 $7\bar{4}\bar{4}$, 1.76
instability constant P	0.018	0.024
drift correction	1.00–1.10	0.99–1.00
$R1$ $(=\sum(I - \bar{I})/\sum I)$	0.126	0.033
$R2$ $(=\sum\sigma/\sum I)$	0.118	0.060
no. of equivalent reflns	1926	3084
X-ray exposure time, h	134.9	210.6
total no. of data	8501	9680
no. of unique data	7538	7804
no. of obsd data $(I > 2.5\sigma(I))$	4240	5198
	c. Refinement	
no. of reflctns	4240	5198
no. of refined params	584	556
isotropic sec ext coeff, g		$0.91(4) \times 10^{-4}$
final R_F $(=\sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|)$	0.065	0.043
final R_w $(=[\sum(w(\|F_o\| - \|F_c\|)^2)/\sum\|wF_o^2\|]^{1/2})$	0.050	0.035
weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
S $(=[\sum w(\|F_o\| - \|F_c\|)^2/(m-n)]^{1/2})$[a]	1.918	1.584
residual electron density in final diff Fourier map, e/Å^3	−1.27, 0.98	−0.59, 0.91
max shift/σ, final cycle	0.673	0.006
av shift/σ, final cycle	0.069	0.0006

[a] m = no. of observations; n = no. of variables.

1380 (s), 1350 (w), 1235 (w), 1090 (w), 1065 (w), 1020 (m), 985 (w), 735 (s), 710 (m), 595 (w). ^{1}H-NMR (benzene-d_6, 300 MHz): δ 7.70 (m, 1 H, C_6H_4), 7.21 (m, 2 H, C_6H_4), 6.91 (m, 1 H, C_6H_4), 3.30 (s, 2 H, N–CH_2), 1.88 (s, 36 H, $C_5(CH_3)_5$ overlapping with $N(CH_3)_2$). ^{13}C-NMR (benzene-d_6, 75.4 MHz): δ 189.91 (d, $^1J_{CY}$ = 56.3 Hz, Y–C(aryl)), 144.64 (s, N–CH_2–C(aryl)), 138.09 (dd, $^1J_{CH}$ = 152.4 Hz, $^2J_{CH}$ = 6.2 Hz, aryl CH), 126.38 (dd, $^1J_{CH}$ = 152.4 Hz, $^2J_{CH}$ = 3.0 Hz, aryl CH), 124.94 (d, $^1J_{CH}$ = 154.3 Hz, aryl CH), 124.59 (dd, $^1J_{CH}$ = 157.6 Hz, $^2J_{CH}$ = 8.1 Hz, aryl CH), 117.66 (s, C_5Me_5), 67.85 (t, $^1J_{CH}$ = 129.6 Hz, N–CH_2), 46.93 (q, $^1J_{CH}$ = 139.5 Hz, N–CH_3), 12.12 (q, $^1J_{CH}$ = 125.1 Hz, $C_5(CH_3)_5$). Anal. Calcd for $C_{29}H_{42}NY$: C, 70.57; H, 8.58. Found: C, 70.61; H, 8.66.

$Cp^*_2Y(o\text{-}C_6H_4PMe_2)$ (9). A 0.56-mL (4.0-mmol) aliquot of dimethylphenylphosphine was added at room temperature to a stirred suspension of 1.00 g (1.4 mmol) of 1 in 25 mL of pentane. After stirring for 24 h the orange solution was filtered, concentrated, and slowly cooled to −30 °C. The white needle-shaped crystals were washed with cold pentane to yield 0.40 g (0.8 mmol, 30%) of **9**. Concentration of the mother liquor and cooling gave a second crop (0.44 g, 33%). IR (cm^{-1}): 2980 (s), 2720 (w), 1460 (s), 1380 (s), 1295 (w), 1240 (w), 1225 (w), 1070 (w), 1025 (w), 1010 (w), 950 (m), 900 (m), 720 (m), 600 (w), 425 (w). ^{1}H-NMR (90 MHz, benzene-d_6): δ 7.59–7.14 (m, 4 H, C_6H_4), 1.88 (s, 30 H, $C_5(CH_3)_5$), 1.16 (dd, $^2J_{HP}$ = 4.4 Hz, $^3J_{HY}$ = 0.7 Hz, 6 H, P–CH_3). ^{13}C-NMR (75.4 MHz, benzene-d_6): δ 202.87 (dd, $^1J_{CY}$ = 50.6 Hz, $^2J_{CP}$ = 66.8 Hz, Y–C(aryl)), 138.89 (d, $^1J_{CP}$ = 27.6 Hz, aryl CH), 137.80 (ddd, $^1J_{CH}$ = 145.8 Hz, $^2J_{PC}$ = 28.8 Hz, $^2J_{CH}$ = 6.9 Hz, aryl CH), 127.88 (d, $^1J_{CH}$ = 154.2 Hz, aryl CH), 125.80 (d, $^1J_{CH}$ = 158.8 Hz, aryl CH), 125.33 (ddd, $^1J_{CH}$ = 157.7 Hz, $^2J_{CH}$ = 6.9 Hz, $^3J_{PC}$ = 4.6 Hz, aryl CH), 117.14 (s, C_5Me_5), 15.23 (qd, $^1J_{CH}$ = 130.8 Hz, $^1J_{CP}$ = 4.6 Hz, P–CH_3), 11.73 (q, $^1J_{CH}$ = 125.5 Hz, $C_5(CH_3)_5$). Anal. Calcd for $C_{28}H_{40}PY$: C, 67.73; H, 8.12; Y, 17.91. Found: C, 68.51; H, 8.30; Y, 18.25.

$Cp^*_2Y(o\text{-}C_6H_4PPh_2CH_2)$ (10). A solution of 1.83 g (3.5 mmol) of $Cp^*_2YCH(SiMe_3)_2$ in 40 mL of pentane was stirred under H_2 (1 atm) for 3 h at room temperature, and a white precipitate of 1 formed. The hydrogen atmosphere was replaced by nitrogen, and 1.09 g (3.9 mmol) of $CH_2{=}PPh_3$ was added. Gas was evolved immediately. The mixture was stirred overnight, dried in vacuum, and then extracted with hot toluene. On standing at room temperature, large, colorless crystals formed and 0.79 g of product was isolated after washing with pentane. Further workup of the mother liquor gave additional product. Total yield: 1.12 g (1.8 mmol, 51%). IR (cm^{-1}): 3960 (m), 2950 (s), 2910 (s), 2850 (s), 2720 (w), 1595 (w), 1570 (w), 1485 (m), 1460 (s), 1440 (vs), 1420 (sh), 1380 (s), 1345 (w), 1220 (m), 1180 (w), 1165 (w), 1115 (m), 1105 (m), 1080 (m), 1035 (w), 1005 (m), 960 (w), 845 (m), 835 (m), 770 (vs), 745 (vs), 720 (m), 710 (s), 695 (s), 635 (w), 600 (w), 535 (s), 520 (s), 495 (m), 460 (sh), 450 (s). ^{1}H-NMR (benzene-d_6, 90 MHz): δ 7.75–6.95 (several m, 14 H, C_6H_4 and C_6H_5), 1.94 (s, 30 H, $C_5(CH_3)_5$), 0.48 (dd, 2 H, $^2J_{HP}$ = 13.8 Hz, $^2J_{HY}$ = 2.4 Hz, Y—CH_2—P). ^{13}C-NMR (THF-d_8, 75.4 MHz): δ 208.00 (pseudo t, $^2J_{CP}$ = 49.8 Hz, Y—C(aryl)), 142–124 (aryl C, not assigned due to overlap of resonances), 115.86 (s, C_5Me_5), 11.91 (q, $^1J_{CH}$ = 124.5 Hz, $C_5(CH_3)_5$), 4.12 (t pseudo t, $^1J_{CH}$ = 124.3 Hz, $^1J_{CY} = {}^1J_{CP}$ = 28.6 Hz, Y—CH_2—P). ^{31}P-NMR (THF-d_8, 80.9 MHz) δ 29.81 (d, $^2J_{PY}$ = 14 Hz). Anal. Calcd for $C_{39}H_{46}PY$: C, 73.81; H, 7.31; Y, 14.01. Found: C, 74.35; H, 7.45; Y, 13.86.

NMR and GC/MS Analysis of the Reaction of $(Cp^*_2YH)_2$ (1) with Fluorobenzene. An 8.8-μL (0.093-mmol) aliquot of fluorobenzene was added to a suspension of 34 mg (0.047 mmol) of 1 in 0.5 mL of cyclohexane-d_{12}. Immediately, gas evolution was observed and 1 dissolved completely. ^{1}H-NMR spectroscopy indicated that 1 had been converted to a complicated mixture of unidentified products. The NMR tube was opened, and 1.5 mL of cyclohexane and 6 μL of water were added. After filtration over a column of $MgSO_4$ the mixture was analyzed by GC/MS. In addition to 2-fluorobiphenyl, three compounds with M^+ peaks at m/z = 212 were present.

Preparative Scale Reaction of $(Cp^*_2YH)_2$ (1) with Fluorobenzene. A suspension of 1.09 g (1.51 mmol) of 1 in 40 mL of pentane was cooled to −70 °C, and 284 μL (3.03 mmol) of fluorobenzene was added. The reaction mixture was allowed to warm to room temperature in ca. 30 min during which gas evolution was observed and 1 dissolved completely. Volatiles were removed in vacuum and the remaining oil gave a cream-colored precipitate after washing with 2.5 mL of pentane. Crystallization from 25 mL of pentane at −80 °C gave 0.100 g of cream-colored crystals (0.19 mmol, 6%). ^{1}H-NMR (200 MHz, benzene-d_6): δ 7.77–7.66 (m, 2 H, aryl H), 7.33–7.24 (m, 2 H, aryl

Table IV. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for Non-H Atoms (with Esd's in Parentheses) for $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (2) and $Cp^*_2Y(o\text{-}C_6H_4PPh_2CH_2)$ (10)

	x	y	z	U_{eq} (Å^2)^a		x	y	z	U_{eq} (Å^2)^a
				Data for **2**					
Y1	0.20817(8)	0.19742(7)	0.31548(6)	0.0171(2)	C22	0.3744(7)	–0.2118(7)	0.1737(5)	0.019(3)
Y2	0.17008(8)	–0.11993(7)	0.21215(6)	0.0136(2)	C23	0.2656(7)	–0.2987(6)	0.1310(5)	0.021(3)
C1	0.4408(7)	0.3288(7)	0.3613(5)	0.021(3)	C24	0.2085(7)	–0.2873(6)	0.0513(5)	0.016(3)
C2	0.3510(7)	0.3988(6)	0.3991(6)	0.028(3)	C25	0.2849(7)	–0.1966(6)	0.0425(5)	0.018(3)
C3	0.2927(7)	0.3787(7)	0.4741(6)	0.027(3)	C26	0.5020(8)	–0.0565(7)	0.1300(6)	0.031(3)
C4	0.3493(7)	0.2993(7)	0.4899(5)	0.024(3)	C27	0.4698(8)	–0.1946(8)	0.2572(6)	0.041(4)
C5	0.4416(7)	0.2694(6)	0.4178(6)	0.022(3)	C28	0.2302(8)	–0.4009(7)	0.1485(6)	0.028(3)
C6	0.5298(8)	0.3256(8)	0.2825(7)	0.044(4)	C29	0.0938(8)	–0.3656(6)	–0.0199(6)	0.027(3)
C7	0.3442(9)	0.4965(7)	0.3778(7)	0.049(4)	C30	0.2733(8)	–0.1722(7)	–0.0434(6)	0.029(3)
C8	0.1993(9)	0.4395(8)	0.5367(7)	0.052(4)	C31	0.1549(7)	–0.0812(6)	0.3980(5)	0.018(3)
C9	0.3368(8)	0.2745(7)	0.5761(6)	0.035(3)	C32	0.1174(7)	–0.1963(6)	0.3512(5)	0.017(3)
C10	0.5362(8)	0.1966(7)	0.4141(6)	0.033(3)	C33	–0.0012(7)	–0.2237(6)	0.2926(5)	0.017(3)
C11	0.1592(7)	0.1427(6)	0.1298(5)	0.019(3)	C34	–0.0409(7)	–0.1250(6)	0.3068(5)	0.018(3)
C12	0.1504(7)	0.2555(6)	0.1788(5)	0.018(3)	C35	0.0555(7)	–0.0367(6)	0.3706(5)	0.015(3)
C13	0.0391(7)	0.2604(6)	0.2275(6)	0.021(3)	C36	0.2701(8)	–0.0176(7)	0.4702(6)	0.036(3)
C14	–0.0211(7)	0.1546(6)	0.2154(5)	0.020(3)	C37	0.1775(8)	–0.2705(7)	0.3811(6)	0.038(4)
C15	0.0509(7)	0.0804(6)	0.1569(5)	0.016(3)	C38	–0.0823(8)	–0.3359(7)	0.2384(6)	0.034(3)
C16	0.2563(8)	0.0973(7)	0.0647(6)	0.030(3)	C39	–0.1733(7)	–0.1209(7)	0.2729(6)	0.026(3)
C17	0.2259(8)	0.3385(8)	0.1439(6)	0.037(3)	C40	0.0537(7)	0.0832(7)	0.4117(6)	0.028(3)
C18	–0.0166(8)	0.3610(7)	0.2794(6)	0.029(3)			benzene positions		
C19	–0.1546(7)	0.1282(7)	0.2468(6)	0.026(3)	C41	0.498(1)	0.597(1)	–0.009(1)	0.063(5)
C20	0.0283(7)	–0.0430(7)	0.1199(6)	0.032(3)	C42	0.5818(8)	0.5947(7)	0.0611(5)	0.065(4)
C21	0.3876(7)	–0.1492(6)	0.1192(5)	0.017(3)	C43	0.419(2)	0.502(1)	–0.070(1)	0.067(5)
				Data for **10**					
Y1	0.19795(2)	0.16594(2)	0.41237(2)	0.0107(1)	C20	–0.0462(3)	0.0648(2)	0.2848(2)	0.0293(11)
P1	0.19783(6)	0.35270(5)	0.52659(5)	0.0119(2)	C21	0.0890(2)	0.28656(17)	0.36015(9)	0.0133(9)
C1	0.3349(2)	0.23469(18)	0.34053(19)	0.0147(9)	C22	0.1096(2)	0.35961(18)	0.41044(18)	0.0125(9)
C2	0.2577(2)	0.20164(19)	0.26412(19)	0.0169(9)	C23	0.0605(3)	0.43321(18)	0.3783(2)	0.0186(10)
C3	0.2635(2)	0.11664(19)	0.27043(19)	0.0156(9)	C24	–0.0163(3)	0.43672(19)	0.2930(2)	0.0225(11)
C4	0.3457(2)	0.09664(18)	0.35262(19)	0.0143(9)	C25	–0.0421(2)	0.3665(2)	0.24166(19)	0.0199(10)
C5	0.3894(2)	0.1702(2)	0.39568(18)	0.0148(9)	C26	0.0094(2)	0.29507(18)	0.2739(2)	0.0178(9)
C6	0.3616(3)	0.3231(2)	0.3541(2)	0.0251(11)	C27	0.2610(2)	0.45141(18)	0.55673(19)	0.0142(9)
C7	0.1933(3)	0.2486(2)	0.1812(2)	0.0297(11)	C28	0.2131(2)	0.51370(19)	0.5891(2)	0.0202(10)
C8	0.2052(3)	0.0605(2)	0.1944(2)	0.0287(11)	C29	0.2598(3)	0.58865(19)	0.6095(2)	0.0273(11)
C9	0.3931(3)	0.0144(2)	0.3811(2)	0.0258(11)	C30	0.3558(3)	0.60318(19)	0.5972(2)	0.0269(11)
C10	0.4845(2)	0.1747(2)	0.4800(2)	0.0251(10)	C31	0.4048(3)	0.5419(2)	0.5656(2)	0.0262(12)
C11	0.0272(2)	0.11759(18)	0.4524(2)	0.016(1)	C32	0.3578(3)	0.46653(19)	0.5461(2)	0.0211(11)
C12	0.1133(2)	0.09867(18)	0.5305(2)	0.0162(10)	C33	0.1198(2)	0.34459(17)	0.60218(19)	0.0143(9)
C13	0.1729(2)	0.03732(18)	0.5068(2)	0.0155(10)	C34	0.1715(2)	0.3320(2)	0.69608(19)	0.0207(9)
C14	0.1229(2)	0.01649(18)	0.4140(2)	0.0169(10)	C35	0.1139(3)	0.3258(2)	0.7557(2)	0.0298(11)
C15	0.0337(3)	0.06779(18)	0.3795(2)	0.0184(10)	C36	0.0052(3)	0.3316(2)	0.7235(2)	0.0329(11)
C16	–0.0649(3)	0.1709(2)	0.4465(2)	0.0274(11)	C37	–0.0454(3)	0.3446(2)	0.6314(2)	0.0279(11)
C17	0.1303(3)	0.1287(2)	0.6264(2)	0.0242(11)	C38	0.0110(3)	0.35114(18)	0.5712(2)	0.0203(10)
C18	0.2663(3)	–0.0047(2)	0.5715(2)	0.0263(11)	C39	0.2791(2)	0.26874(18)	0.54015(18)	0.0137(9)
C19	0.1445(3)	–0.0566(2)	0.3648(2)	0.0281(11)					

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i a_j \mathbf{a}_i\cdot\mathbf{a}_j$.

H), 6.94–6.57 (m, 3 H, aryl H), 1.83 (s, 30 H, $C_5(CH_3)_5$), an additional aryl signal overlapped with the solvent signal.

Structure Determination of $Cp^*_2Y(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}CH_2C_5Me_4)YCp^*$ (2). Suitable crystals were obtained from benzene. A red, block-shaped crystal was glued on the top of a glass fiber in a drybox and transferred directly into the cold nitrogen stream of the low temperature unit mounted on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23 computer. Unit cell dimensions and their standard deviations were determined from the setting angles of 22 reflections in the range 6.63° < θ < 17.17°. Reduced cell calculations did not indicate any higher lattice symmetry.[39] The unit cell was identified as triclinic, space group $P\bar{1}$. This choice was confirmed by the solution and the successful refinement in this space group of the structure. Two reference reflections measured every 3 h of X-ray exposure indicated a linear decay of 10% over 134.9 h of X-ray exposure time. The net intensities of the data were corrected for the decay, Lorentz, and polarization effects, but not for absorption. The correction for absorption was judged to be not necessary in view of the observed small intensity variation up to 6% for a 360° ψ-scan of the close to axial reflection ($\bar{1}2\bar{1}$). Variance $\sigma^2(I)$ was calculated on the basis of counting statistics and the term (P^2I^2), where P (=0.018) is the instability constant[40] as derived from the excess variance in the reference reflections. Pertinent numerical data on the structure determination are summarized in Table III. The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86[41]) and completed by Fourier techniques. Refinement using anisotropic thermal parameters followed by difference Fourier synthesis resulted in the location of the hydride atom and most of the 59 methyl hydrogen atoms. The remaining hydrogen atoms were calculated at idealized geometric positions where the found hydrogen atoms served to determine the conformation of all methyl groups. The benzene molecule showed some disorder and was included in the final refinement as an idealized rigid group (C41–H43). The hydrogen atoms were included in the refinement with one isotropic thermal parameter and subsequently refined satisfactorily. Weights were introduced in the final refinement cycles. Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and one overall temperature factor for the hydrogen atoms converged at R_F = 0.065 (R_w = 0.050). A

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final difference Fourier synthesis revealed residual densities between −1.27 and 0.98 e/Å^3. The details of the final refinements are included in Table III. Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table IV. Scattering factors[42] and anomalous dispersion factors[43] were obtained from the literature. All calculations were carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages XTAL,[44] EUCLID[45] (calculation of geometric data), ORTEP,[46] and a locally modified version of the program PLUTO[47] (preparation of illustrations).

Structure Determination of $Cp^*_2Y(o\text{-}C_6H_4PPh_2CH_2)$ (10). The general procedure for solving the structure was as outlined above. Precise lattice parameters and their standard deviation were derived from the angular settings of 25 reflections in the range 8.48° < θ < 17.47°. The monoclinic unit cell was checked for the presence of higher lattice symmetry.[39] A correction for absorption was judged not to be necessary in view of the observed small intensity variation (5%) for a 360° ψ-scan of the close to axial reflection (3$\bar{2}$1). Crystal data and experimental information of the structure determination are given in Table III. Refinement using anisotropic thermal parameters, followed by difference Fourier synthesis, resulted in the location of all the hydrogen atoms. Refinement on F by block-diagonal least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms converged at $R_F = 0.043$ ($R_w = 0.035$). The crystal exhibited some secondary extinction for which the F values were corrected by refinement of an empirical isotropic extinction parameter.[48] A final difference Fourier map did not show any significant residual features. Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table IV.

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Supplementary Material Available: Tables of all atomic coordinates, thermal parameters, bond distances, bond angles, and torsion angles and molecular packing diagrams for **2** and **10** (37 pages). Ordering information is given on any current masthead page.

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