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Insertion Chemistry of Cp*$_2$Y(2-pyridyl) and Molecular Structure of the Unexpected CO Insertion Product (Cp*$_2$Y)$_2$(μ-η^2:η^2-OC(NC$_5$H$_4$)$_2$)

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Pyridine is metalated selectively at the 2-position by (Cp*$_2$YH)$_2$ to yield Cp*$_2$Y(2-pyridyl)
(**1**). Compound **1** reacts with H$_2$ to give the hydride addition product Cp*$_2$Y(NC$_5$H$_6$) (**2**).
With THF and pyridine the adducts Cp*$_2$Y(η^2-2-pyridyl)(THF) (**3**) and Cp*$_2$Y(η^1-2-pyridyl)-
(py) (**4**) are formed. The pyridine complex **4** is not stable at higher temperatures, and after
organic work up a stoichiometric amount of the C−C coupling product 2,2′-bipyridine is
obtained. Ethylene and propylene react with **1** to give the monoinsertion products Cp*$_2$-
YCH$_2$CH$_2$(2-NC$_5$H$_4$) (**5**) and Cp*$_2$YCH$_2$CHMe(2-NC$_5$H$_4$) (**6**). With alkynes HCCR, C−H
activation to form the acetylides Cp*$_2$Y(CCR)(py) (**7**, R = H; **8**, R = Me) is the dominant
reaction. Also with 2-butyne C−H activation is observed yielding the propargylic metalation
product Cp*$_2$YCH$_2$CCMe (**9**). 2-Pentyne gives a mixture of insertion products Cp*$_2$Y-
(CEtCMe(2-NC$_5$H$_4$)) (**10**) and Cp*$_2$Y(CMeCEt(2-NC$_5$H$_4$)) (**11**). A surprising reaction with
CO to form (Cp*$_2$Y)$_2$(μ-η^2:η^2-OC(2-NC$_5$H$_4$)$_2$) (**12**) was observed. The molecular structure of
12 was determined by X-ray diffraction: Space group $P2_1/c$ with unit cell parameters $a =$
14.194(4) Å, $b =$ 17.559(4) Å, $c =$ 18.717(5) Å, $\beta =$ 109.61(2)°, and $Z =$ 4. Least-squares
refinement based on 6867 reflections converged to $R_1 =$ 0.09. Compound **5** gives σ-bond
metathesis with pyridine to form **1** and 2-ethylpyridine. By using **1** as a catalyst, alkylation
of pyridine to 2-ethylpyridine is possible. Also minor amounts of 2-*n*-butylpyridine, 2-*n*-
hexylpyridine, and polyethylene were formed in this catalytic process. Compound **5** is not
thermally stable and decomposes to the isomers Cp*$_2$Y(2-NC$_5$H$_3$(6-Et)) (**13**) and Cp*$_2$YCHMe-
(2-NC$_5$H$_4$) (**14**) at 80 °C (60:40). Attempts to convert **5** to **1** and 2-ethylpyridine by
hydrogenolysis of the Y−C bond also resulted in the formation of a mixture of **13** and **14**
(55:45). In this reaction the formation of an intermediate hydride complex seems likely
because (Cp*$_2$YH)$_2$ and 2-ethylpyridine also give products **13** and **14**.

Introduction

The activation of C−H bonds and the subsequent
functionalization of hydrocarbons is a field of consider-
able current interest in organometallic chemistry. Oxi-
dative addition of C−H bonds with late transition
metals is well-known,[1] and more recently, the hetero-
lytic activation of these bonds by electrophilic high-
valent early transition metal complexes has been de-
veloped.[2] Especially interesting in this area are the very
electrophilic group 3 compounds (including the lan-
thanides).

Recently we have shown that group 3 and lanthanide
alkyl and hydride complexes very easily activate aro-

matic C−H bonds in a wide variety of substrates leading
to metallacycles containing new M−C bonds.[3] Insertion
of unsaturated substrates in metallacyclic M−C bonds
is very interesting since it might lead to C−C coupling
at the aromatic ring. Especially when the metalation
step can be performed in a regioselective fashion, such
a process could be of interest for organic synthesis and
provide an alternative for the well-known Pd-mediated
functionalization of C−H bonds like the Heck type
reaction.[4]

Jordan *et al.* nicely demonstrated a zirconium-medi-
ated functionalization of pyridines based on cationic Cp$_2$-
Zr(2-pyridyl)(L)$^+$ systems.[5] Recently we found that the
hydride (Cp*$_2$YH)$_2$ gives facile cyclometalation with a
variety of arenes including pyridine,[6] which offers
opportunities for the functionalization of arenes and
heterocycles. This led us to study the reactivity of the
cyclometalated products toward a variety of (unsatur-

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‡ University of Utrecht.
⊗ Abstract published in *Advance ACS Abstracts*, August 15, 1994.
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Principles and Applications of Organotransition Metal Chemistry;
University Science Books: Mill Valley, CA, 1987; p 295.
(2) For a general introduction in the field see: (a) Crabtree, R. H.
Chem. Rev. **1985**, *85*, 245. (b) Tanaka, M.; Sakakura, T. In *Homoge-
neous Transition Metal Catalyzed Reactions*; Moser, W. R., Slocum,
D. W., Eds.; American Chemical Society: Washington, DC, 1992; p
181. (c) Jones, W. D. In *Selective Hydrocarbon Activation*; Davies, J.
A., Watson, P. L., Liebman, J. F., Greenberg, A., Eds.; VCH Publish-
ers: New York, 1990; p 113.

(3) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meets-
ma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531.
(4) Reference 1, p 720.
(5) (a) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics*
1990, *9*, 1546. (b) Guram, A. S.; Jordan, R. F. *Organometallics* **1991**,
*10*, 3470.
(6) Den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics*
1987, *6*, 2053.

ated) substrates. In this contribution we focus on the insertion chemistry of the pyridyl complex $Cp*_2Y(2$-pyridyl) (**1**) and compare it with the isoelectronic Cp_2-$Zr(2$-pyridyl)(L)$^+$.[5]

Results and Discussion

Synthesis and Properties of $Cp*_2Y(2$-pyridyl) (**1**).

When $(Cp*_2YH)_2$ was allowed to react with pyridine, compound **1** could be isolated in 55% yield (eq 1).[7] The

$$(Cp*_2YH)_2 + 2\ pyridine \longrightarrow 2\ Cp*_2Y\overset{N}{\underset{}{\bigcirc}} \quad (1)$$

1
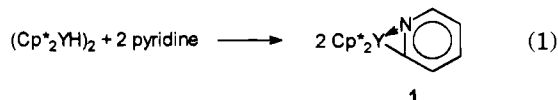
^1H- and ^{13}C-NMR spectra of **1** show resonances for the *ortho* C—H fragment (8.02 and 145.27 ppm, respectively) upfield from those of free pyridine (8.53 and 150.0 ppm, respectively). Since the NMR spectra of **1** are in close analogy with those of the corresponding Sc and Lu complexes,[8] in which the pyridyl ligand was found to be η^2-bonded to the metal center by X-ray diffraction, we assume an analogous bonding for the pyridyl ligand in our yttrium compound.

Compound **1** dissolves well in organic solvents like pentane, cyclohexane, benzene, and toluene, and **1** is thermally very robust. No thermal decomposition was observed after 24 h at 120 °C in benzene-d_6. However, extensive H/D scrambling between the pyridyl ligand and solvent had taken place and no resonances of the pyridyl ligand were observed in the ^1H-NMR spectrum. The Cp* ligands were unaffected. This H/D scrambling is only operative at relatively high temperatures; at 75 °C (24 h) no H/D scrambling was detected.

H/D scrambling most likely involves metalation of solvent producing $Cp*_2YPh$ and free pyridine in an equilibrium reaction (eq 2). Such an equilibrium should

$$Cp*_2Y\overset{N}{\underset{}{\bigcirc}} \underset{pyridine}{\overset{benzene}{\rightleftharpoons}} Cp*_2YPh \quad (2)$$

1
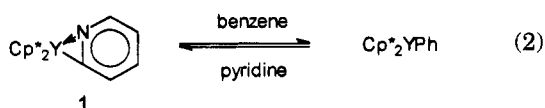
strongly favor the starting compound since in the ^1H-NMR spectrum no indication for the presence of $Cp*_2$-YPh was observed. The observation that H/D scrambling is not restricted to the *ortho* positions but that other positions are affected as well suggests that also *meta*- and *para*-metalated yttrium pyridyl species are involved and are kinetically within reach.

Reaction with Hydrogen. With H_2 (1 bar), **1** reacts in about 3 d at room temperature to form in 50% yield the 1,4-hydride addition product $Cp*_2Y(NC_5H_6)$ (**2**) and some unidentified material (eq 3). A comparable observation has been made in the reaction of $[Cp_2YH(THF)]_2$ with pyridine in THF.[9] Here the first step is the formation of the 1,2-addition product which is slowly

$$Cp*_2Y\overset{N}{\underset{}{\bigcirc}} \xrightarrow{H_2} Cp*_2Y\overset{H}{\underset{N}{\bigcirc}} \longrightarrow Cp*_2Y-N\langle\rangle \quad (3)$$

1   **2**
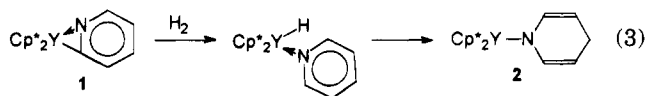
converted into the 1,4-isomer. Therefore we propose that the first step in eq 3 is hydrogenolysis of the Y—C bond of **1** to form an intermediate hydride pyridine adduct, which then reacts further to the 1,4-addition product **2**. In the Ziegler alkylation of pyridines by alkyllithium,[10] intermediate 1,2-addition products have been observed. In our case, however, no indication for a 1,2-addition product was found, suggesting that the reaction involves direct 1,4-addition. Nucleophilic attack on both the 2- and the 4-positions is well-known for pyridine rings.[10b] The unidentified material in the reaction mixture was due to reaction of **1** with pyridine. The ^1H-NMR signals of this unidentified compound were identical to those observed in the reaction of **1** with pyridine in the absence of H_2 (*vide infra*).

Reaction with Lewis Bases. The Lewis acidity of **1** was tested by studying the complexation behavior toward Et_2O, THF, and pyridine. No complexation of Et_2O was observed, but with the stronger bases, THF and pyridine, the 1:1 adducts $Cp*_2Y(\eta^2$-2-pyridyl)(THF) (**3**) and $Cp*_2Y(\eta^1$-2-pyridyl)(NC_5H_5) (**4**) were formed (eq 4 and Scheme 1). The strong downfield shift of the H6

$$Cp*_2Y\overset{N}{\underset{}{\bigcirc}} + \text{THF} \longrightarrow Cp*_2Y(\eta^2\text{-2-pyridyl})(\text{THF}) \quad (4)$$

1   **3**

resonance of **4** relative to the corresponding resonance of **1** (8.50 ppm for **4** vs 8.02 ppm for **1**) is close to that of the *ortho* protons of free pyridine (8.53 ppm) and suggests that the pyridyl ligand is η^1-bonded to Y. With Et_2O and THF no further reaction was observed, even when heated at 80 °C for several days.

The pyridine adduct, on the other hand, is not very stable and converts in the course of 3 d at 50 °C into a mixture of products. In the ^1H-NMR spectrum of this mixture several olefinic signals were present in the region between 6 and 3 ppm indicating that the reaction involves partial reduction of a pyridine ring. Isolation and purification of these products on a preparative scale was severely hampered by the high solubility in hydrocarbon solvents, however. When performed with an excess of pyridine (10 equiv), analysis of the reaction mixture by GC/MS and ^1H-NMR after quenching with water revealed the formation of a stoichiometric amount of 2,2′-bipyridine (1 equiv per Y), indicating that C—C coupling between the pyridyl ligand and pyridine had taken place. The amount of 2,2′-bipyridine did not increase after prolonged heating, which means that the reaction is not catalytic under these conditions.

This formation of 2,2′-bipyridine is remarkable since to our knowledge no examples of dehydrogenative C—C coupling reactions with arenes are known for group 3 and 4 organometallic compounds. There is a precedent in organolithium chemistry, where attempted lithiation of pyridine with lithium diisopropylamide also led to the

(7) Better yields of **1** are possible (73%) when the hydride complex is generated *in situ* from $Cp*_2YCH(SiMe_3)_2$ and hydrogen in the presence of pyridine. See Experimental Section for details. The *ortho* metalation of pyridine starting from $Cp*_2YCH(SiMe_3)_2$ has been mentioned before by our group,[6] but **1** could not be isolated analytically pure.

(8) (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276.

(9) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.

(10) (a) March, J. *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 3rd ed.; John Wiley and Sons: New York, 1985; p 598. (b) Joule, J. A.; Smith, G. F. *Heterocyclic Chemistry*; Van Nostrand Reinhold Co.: London, 1972; Chapter 4 and references cited there.

Scheme 1
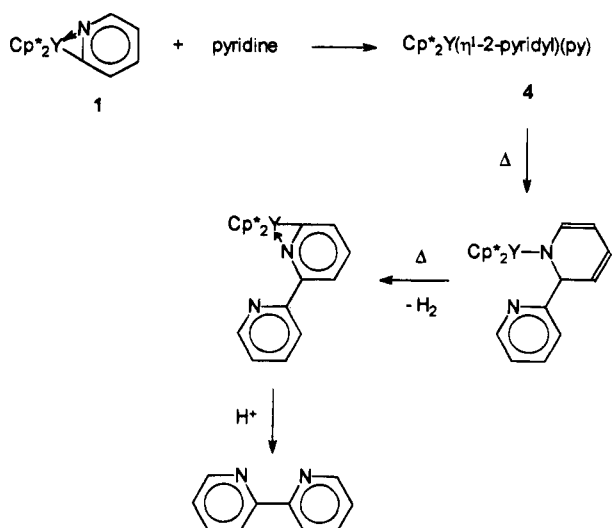
formation of 2,2'-bipyridine.[11] Another example is the alkylation or arylation of pyridine mentioned above, which involves the 1,2-addition of RLi and subsequent elimination of LiH. Therefore Scheme 1 gives a plausible reaction sequence which also explains the reduction of pyridine. The close analogy with eq 3 also supports the proposed addition step.

Reaction with Alkenes. With excess ethylene, **1** reacts to form the monoinsertion product $Cp*_2YCH_2CH_2$-(2-NC_5H_4) (**5**) (eq 5). The conversion is complete within

$$(5)$$
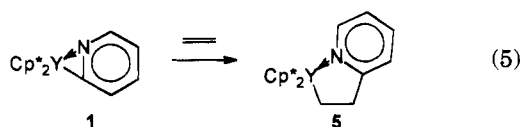
1 h at room temperature, and no further insertion of ethylene is observed (*vide infra*). Reaction with propylene is slower (4 d at 60 °C) and leads selectively to the 1,2-insertion product $Cp*_2YCH_2CHMe$(2-NC_5H_4) (**6**) (eq 6). For both **5** and **6** the nitrogen lone pair of the pyridyl

$$(6)$$
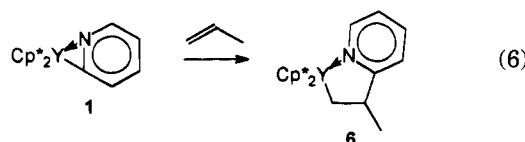
group is expected to coordinate to the metal since the chemical shifts of the hydrogen atoms in the *ortho* position to N are different from that of free pyridine and 2-ethylpyridine (δ = 7.45 ppm for **5** and **6** vs 8.53 ppm for free pyridine). The close spectroscopic analogy with $Cp_2ZrCH_2CH_2$(2-NC_5H_3(6-Me))$^+$, where intramolecular coordination of the pyridine function has been found,[5a] supports this.

The stability of the five-membered ring toward consecutive insertion of olefin is remarkable bearing in mind the high activity of M—H and M—C (M = group 3 element) bonds toward the polymerization of olefins.[12] The higher stability of five-membered rings compared

to compounds with larger or smaller ring size is very well-known in cyclometalation reactions.[13] Apparently the metallacycles **5** and **6** are stabilized toward further reaction with olefin.[14]

No reaction of **1** with butadiene (1 bar) was observed (3 d at 75 °C).

Reaction with Alkynes. Acetylene reacts with **1** by C—H activation and formation of pyridine (eq 7). The

$$(7)$$
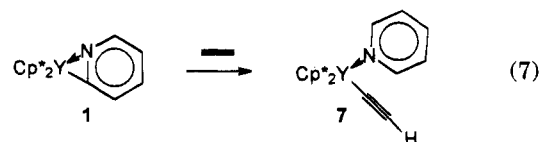
organoyttrium species was identified as the monomeric pyridine acetylide complex $Cp*_2Y(CCH)$(py) (**7**) and was obtained in 29% yield. The formation of monomeric **7** is unique since the only yttrium ethynyl complex known so far, $\{[C_6H_5C(NSiMe_3)_2]_2Y(\mu$-CCH)$\}_2$,[15] is a dimer whereas the scandium analogue, $Cp*_2ScCCH$,[16] has only been observed by NMR. Clearly the coordinated pyridine stabilizes **7** as a monomer. It also inhibits catalytic activity since, in contrast to $Cp*_2ScCCH$, polymerization of the excess of acetylene to polyacetylene has not been observed.

Also with excess of propyne (1 bar), C—H activation took place to form acetylide $Cp*_2Y(CCMe)$(py) (**8**) (68% yield) which is again monomeric due to coordination of pyridine (eq 8). In contrast to what was observed for

$$(8)$$
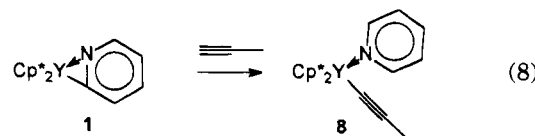
$Cp*_2YCH(SiMe_3)_2$,[6] no dimerization of propyne is found here, again indicating that the coordinated pyridine effectively blocks catalytic activity.

To investigate the reactivity of **1** toward internal C—C triple bonds, **1** was allowed to react with 2-butyne and 2-pentyne. With 2-butyne the major reaction was propargylic metalation to form $Cp*_2YCH_2CCMe$ (**9**)[17] and pyridine (eq 9). The pyridine formed is coordinated

$$1 : 1$$

$$(9)$$

to **1** which results in only 50% conversion of the starting material. As stated before, the pyridine adduct **4** is not very stable and starts to decompose under the reaction
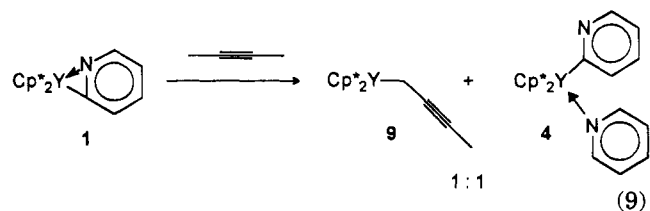
(11) Clarke, A. J.; McNamara, S.; Meth-Cohn, O. *Tetrahedron Lett.* **1974**, 2373.

(12) (a) Den Haan, K. H.; Wielstra, Y.; Eshuis, J. J. W.; Teuben, J. H. *J. Organomet. Chem.* **1987**, *323*, 181. (b) Eshuis, J. J. W. Ph.D. Thesis, University of Groningen, 1991.

(13) (a) Constable, E. C. *Polyhedron* **1984**, *3*, 1037. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.

(14) To test this stability toward further insertions of olefin, solutions of **5** and **6** were reacted with excess ethylene (1 bar). Only when heated to 130 °C was reaction and formation of a white solid, polyethylene (IR), observed.

(15) Duchateau, R.; Van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931.

(16) St. Clair, M.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1991**, *10*, 525.

(17) Heeres, H. J.; Heeres, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 1508.

conditions applied. Adduct **4** is apparently resistant toward decomplexation of pyridine because with an excess of 2-butyne (20 equiv) still only 50% conversion was reached. Another remarkable observation is that the pyridine gets coordinated to **1** and not to the metalation product as in eq 8.

When the reaction of **1** with 2-pentyne was monitored by ^{1}H-NMR spectroscopy, it was found that within 2 d at 75 °C **1** had been converted completely into a mixture of products.[18] The identity of this mixture could not be determined, but the appearance of a quartet at $\delta = 2.42$ ($^3J_{HH} = 7.3$ Hz) and two triplets at $\delta = 1.13$ and $\delta = 1.09$ ($^3J_{HH} = 7.3$ Hz for both signals) indicates the presence of a $CH_3CH_2C\equiv C$ moiety and suggests that 2,3- and 3,2-insertion of 2-pentyne has taken place (70%). Attempts to purify the insertion products by crystallization were unsuccessful. Therefore the product mixture was quenched with water and the pyridyl-containing organics were purified by acid/base extraction. Analysis of the resulting oil by GC, GC-MS, and ^{1}H-NMR showed it to consist of 2,2′-bipyridine, 2-(1-methyl-1-butenyl)pyridine, and 2-(1-ethyl-1-propenyl)-pyridine (molar ratio 1.0:1.5:1.9).

From the presence of 2-(1-methyl-1-butenyl)pyridine and 2-(1-ethyl-1-propenyl)pyridine in the reaction mixture after quenching we conclude that the major reaction is insertion of 2-pentyne to form the regioisomers Cp*$_2$YCEtCMe(2-NC$_5$H$_4$) (**10**) and Cp*$_2$YCMeCEt(2-NC$_5$H$_4$) (**11**) in a 1.0:1.3 ratio (63%, eq 10). The fact that
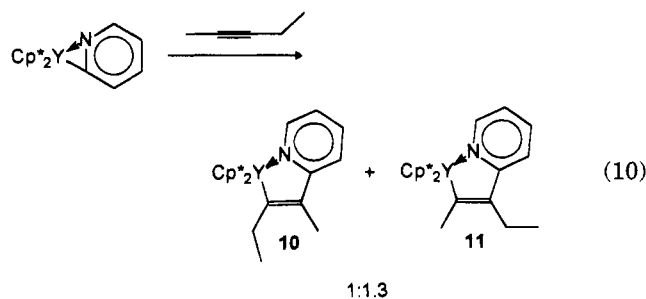
11 is the major isomer can be understood on the basis of steric factors favoring the isomer with the larger alkyl substituent on the β-carbon.[6] The formation of 2,2′-bipyridine is most likely the result of propargylic C—H activation of 2-pentyne analogous to eq 9. The pyridine liberated during this process could then enter the C—C coupling reaction with **1** (Scheme 1). On the basis of the amount of 2,2′-bipyridine formed, propargylic C—H activation accounts for 37% of the reaction of **1** with 2-pentyne and is far less important than in the case of 2-butyne.

Electronically, the triple bonds in 2-butyne and 2-pentyne are not very different and therefore this is not expected to cause a drastic change in selectivity. It seems that steric hindrance in the transition state for C—H activation of 2-pentyne is more severe. For C—H activation of 2-pentyne in the 1-position, the ethyl group has to be situated between the wedge of the Cp* ligands, which will be sterically unfavorable. For 3,2-insertion the 2-pentyne molecule can be situated more out of the wedge of the Cp* ligands leading to less steric hin-

drance, and in the case of 2,3-insertion no interaction of the ethyl group with the Cp* ligands is expected. These effects could lead to a reversal of the selectivity going from 2-butyne to 2-pentyne. Another explanation could be the unique allene structure of **9**,[17] which apparently also inhibits coordination of pyridine. When this structure is less preferred for metalated 2-pentyne as a result of the larger alkyl substituent, insertion of alkyne might be able to compete.

From these results it can be concluded that the intramolecular coordination of the pyridyl group of **1** has little effect on the reactivity of the Y—C bond toward alkynes because similar C—H activations were observed for Cp*$_2$YCH(SiMe$_3$)$_2$ and (Cp*$_2$YH)$_2$.[6,17,19] Compared to Cp*$_2$YCH(SiMe$_3$)$_2$, which shows no reaction with 2-butyne and other disubstituted alkynes, **1** is more reactive however. In addition, the stabilization of the monomeric metalation products by the pyridine formed is quite different from the reactions with Cp*$_2$YR and (Cp*$_2$YH)$_2$, which led to dimeric acetylides.

Reaction with Carbon Monoxide. Group 3 alkyl complexes normally react with CO to form unstable η^2-acyl compounds which, in the presence of excess CO, enter a consecutive reaction with a second equivalent of CO to form dinuclear ene dione diolate complexes.[20] Ketene intermediates are believed to be involved in this second step, but conclusive evidence has not yet been obtained. In view of the ability of the pyridyl ligand in **1** to stabilize insertion products we reasoned that it might be possible to capture an intermediate in the reaction of **1** with CO. We were able to isolate a product formed by consecutive reaction of the η^2-acyl, but this was not the expected ketene or acyl intermediate.

Both with excess (1 bar) and 1 equiv of CO **1** reacts in 24 h to form an intensely purple compound (Cp*$_2$Y)$_2$-(μ-η^2:η^2-OC(2-NC$_5$H$_4$)$_2$) (**12**). The ^{1}H- and ^{13}C-NMR spectra of this compound show a 2-substituted pyridine ligand and two inequivalent Cp* rings. A strong IR absorption at 1406 cm^{-1} indicates a severely reduced bond order of the carbonyl functionality.[21] The UV–vis spectrum shows a strong absorption at 576 nm (ϵ_{max} = 2400 cm^2/mol). Since these data were not sufficient to identify the structure of **12**, a crystal structure determination was undertaken.

The molecular structure consists of two normal bent Cp*$_2$Y units that are bridged by a μ-η^2:η^2-dipyridyl ketone fragment (Figures 1 and 2) and is close to C_2 symmetry, which explains the two Cp* resonances in the NMR spectra. The Y1—O8 and Y2—O8 distances (Table 1) are in the range for bridging alkoxide ligands, while the C7—O8 distance is close to that of a C—O single bond (1.43 Å). The C6—C7 and C7—C9 distances clearly possess some double bond character,[22] while the Y1—N1 and Y2—N10 bond lengths are close to that of a Y—N σ bond. The Y—N distances compare well with those in [(C$_5$H$_4$R)$_2$Y(HCNCCMe$_3$)]$_2$ (2.325(4) Å), in

(18) Three Cp* resonances were present in the ^{1}H-NMR (300 MHz, cyclohexane-d_{12}) at $\delta = 1.91$, 1.75, and 1.74 with relative intensities 1.0:1.2:1.5.

(19) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980.
(20) (a) Evans, W. J.; Wayda, A. D.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. *J. Am. Chem. Soc.* **1985**, *107*, 8091.
(21) For comparison, the vibrations of the reduced carbonyl groups in the η^2-acyls Cp$_2$Lu(COCMe$_3$) and Cp$_2$Zr(COMe)Me are found at 1490 and 1545 cm^{-1}, respectively. See ref 20a and the following: Fachinetti, G.; Floriani, C.; Marchetti, F.; Merlino, S. *J. Chem. Soc., Chem. Commun.* **1976**, 522.
(22) C—C = 1.54 Å and C=C = 1.34 Å: Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper and Row: New York, 1978; p 847.

Figure 1. ORTEP view drawn at the 50% probability level and atom-labeling scheme for $(Cp*_2Y)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ **(12)**.
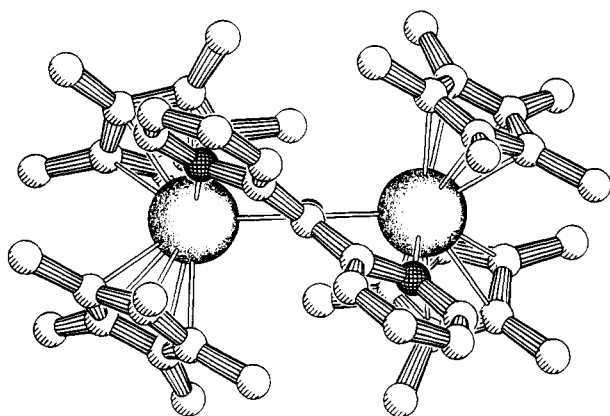

Figure 2. PLUTON view of **12** showing the twist angle between the pyridyl rings.

which Y—N single bond character has been established,[23] and with the Y—N bond distances in $[(C_5H_4R)_2Y\text{-}(N\text{=}CHR)]_2$ (2.314(9) and 2.386(1) Å).[9] However, the Y—N single bond distances in $Cp*_2YN(SiMe_3)_2$ (2.274-(5) and 2.253(5) Å)[24] are significantly shorter.

In addition, both the geometries around O8 and C7 are sp^2, although there is a torsion angle of 39(1)° along C6—C7—O8—Y1 (Figure 2). Also the planes of the two pyridyl rings are twisted by 36(6)° relative to each other, which is most likely the result of minimizing the strain energy in the two five-membered metallacycles. As a result these metallacyclic rings are slightly puckered. On the basis of these data, we would describe the structure as intermediate between the two resonance forms depicted in Figure 3. This description explains the short Y—N interactions, the partial double bond character of C6—C7 and C7—C9, and the absorption in

the visible spectrum of **12** which is caused by the delocalized π system. Also the low ν_{CO} is in agreement with this structure in which the dipyridyl ketone fragment has formally undergone two electron reduction relative to the free ketone.

Several dpk (dpk = di-2-pyridyl ketone) complexes have been reported in the literature and include complexes of the rear earths, Co, Zn, Cd, Hg, and Au.[25a-e] However, in these complexes the dpk ligand serves as

Table 1. Selected Bond Distances (Å) and Angles (°) for $(Cp*_2Y)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ (12)[a]

Y1—O8	2.356(8)	C5—C6	1.437(16)
Y1—N1	2.348(9)	C6—C7	1.422(18)
Y2—O8	2.353(8)	C7—C9	1.410(18)
Y2—N10	2.344(9)	C9—C14	1.427(16)
O8—C7	1.424(13)	C11—C12	1.373(17)
N1—C2	1.372(17)	C12—C13	1.41(2)
N1—C6	1.381(16)	C13—C14	1.33(2)
N10—C9	1.386(17)	Y1—Ct1	2.428(5)
N10—C11	1.344(18)	Y1—Ct2	2.416(6)
C2—C3	1.333(17)	Y2—Ct3	2.414(5)
C3—C4	1.39(2)	Y2—Ct4	2.409(5)
C4—C5	1.341(18)		
O8—Y1—N1	72.0(3)	C2—N1—C6	118(1)
O8—Y2—N10	71.7(3)	Y2—N10—C9	111.4(8)
Y1—O8—Y2	149.4(3)	Y2—N10—C11	127.3(9)
Y1—O8—C7	105.4(7)	C9—N10—C11	119(1)
Y2—O8—C7	105.1(7)	Ct1—Y1—Ct2	131.5
Y1—N1—C2	128.7(8)	Ct3—Y2—Ct4	135.4
Y1—N1—C6	111.2(7)		
C6—C7—O8—Y1	−39(1)	C9—C7—O8—Y1	140.1(9)
C6—C7—O8—Y2	139.3(9)	C9—C7—O8—Y2	−42(1)

[a] Ct1 = C101—C105 centroid, Ct2 = C111—C115 centroid, Ct3 = C201—C205 centroid, and Ct4 = C211—C215 centroid.

(23) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 1252.

(24) Den Haan, K. H.; De Boer, J. L.; Teuben, J. H. *Organometallics* **1986**, *5*, 1726.

(25) (a) Jagannathan, R.; Soundararajan, S. *J. Inorg. Nucl. Chem.* **1980**, *42*, 145. (b) Ortego, J. D.; Waters, D. D.; Steele, C. S. *J. Inorg. Nucl. Chem.* **1974**, *36*, 751. (c) Ortego, J. D.; Seymour, M. *Polyhedron* **1982**, *1*, 21. (d) Ortego, J. D.; Upalawanna, S.; Amanollahi, S. *J. Inorg. Nucl. Chem.* **1979**, *41*, 593. (e) Byers, P. K.; Canty, A. J. *J. Chem. Soc., Dalton Trans.* **1985**, 981.
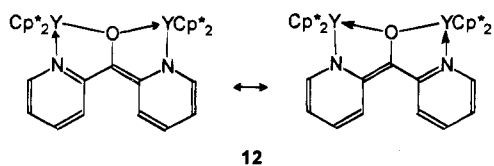
Figure 3. Two resonance forms of $(Cp*_2Y)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ (**12**).

a simple N,N-coordinated Lewis base with an intact carbonyl functionality (IR). None of these complexes shows the very unique bonding mode of the dpk ligand with the reduced carbonyl functionality as in **12**. Complex **12** shows some similarity with the formyl complex $Ta_2Cp'_2Cl_4(H)(CHO)^{26}$ in which the C—O bond order (C—O = 1.496(16) Å) of the $\mu\text{-}\eta^2\text{:}\eta^2$-bonded formyl ligand is also significantly reduced.

Molecular orbital calculations on dpk and $[dpk]^{2-}$ were carried out to find out whether the dpk ligand in **12** could be approximated by a $[dpk]^{2-}$ dianion description. The geometry of $[dpk]^{2-}$ was optimized using the MOPAC program starting from the geometry of the dpk ligand in the crystal structure of **12**. The calculated geometry of the $[dpk]^{2-}$ dianion closely resembles that of the dpk ligand in **12**. The C—O bond order (C—O = 1.281 Å) is significantly reduced compared to the free ketone (C—O = 1.23 Å^{27}) although the C—O bond order in **12** (C—O = 1.424(13) Å) is decreased even further.

Using the optimized geometry the IR and UV—vis spectra of $[dpk]^{2-}$ were calculated using the appropriate options in the MOPAC and ZINDO programs. The position of the C—O stretching mode of dpk was calculated at 2078 cm^{-1} whereas for $[dpk]^{2-}$ a value of 1806 cm^{-1} was calculated. This is in agreement with a decrease in C—O bond order upon two electron reduction of dpk to $[dpk]^{2-}$. Although absolute wave numbers cannot be compared directly with experimental values because of the approximate nature of the Hartree—Fock method, the calculated 272 cm^{-1} difference in wave number of the C—O stretching vibrations of dpk and $[dpk]^{2-}$ compares well with the 269 cm^{-1} difference observed experimentally for the C—O stretching frequencies of dpk (1675 cm^{-1}) and **12** (1406 cm^{-1}). Therefore the description of the dpk ligand in **12** as a dpk molecule which has undergone two electron reduction and the assignment of the band at 1406 cm^{-1} in the IR spectrum of **12** seems to be justified. Also the UV—vis spectrum of **12** could successfully be approximated using $[dpk]^{2-}$ as a model. The calculated spectrum of $[dpk]^{2-}$ shows an absorption at 636 nm due to a $\pi \rightarrow \pi^*$ transition. This agrees well with the observed absorption of **12** at 576 nm. Therefore the absorption of **12** in the visible region of the electronic spectrum can be assigned to a $\pi \rightarrow \pi^*$ transition in the dpk ligand excluding the possibility of a ligand-to-metal charge-transfer band.

The formation of compound **12** is remarkable because the common reaction path seen for group 3 alkyl complexes is insertion of a second equivalent of CO to form ene dione diolate complexes. However for **1**, even

Scheme 2
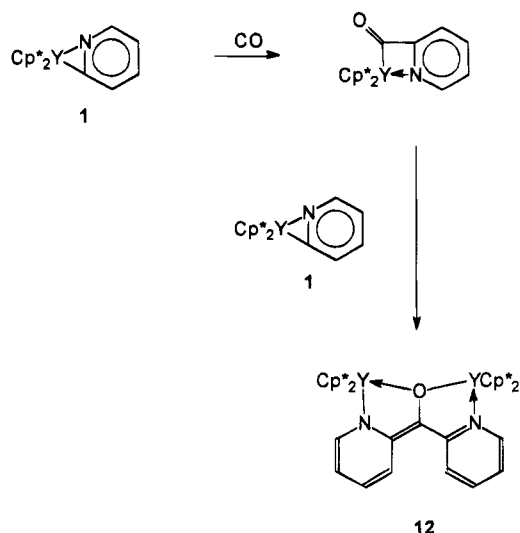
with excess of CO, only product **12** is observed (¹H-NMR). The product formation can be explained by a scheme in which nucleophilic attack of the starting compound on the acyl species takes place (Scheme 2). Such a nucleophilic attack on M(η^2-acyl) and formation of ketone complexes has some precedent in a heterobimetallic Zr—Mo acyl complex in which a Zr—Me bond has added across the CO bond of the acyl functionality^{28} (eq 11). The nucleophilic attack on the acyl has been associated with the presence of a good σ-donating ligand in this system.
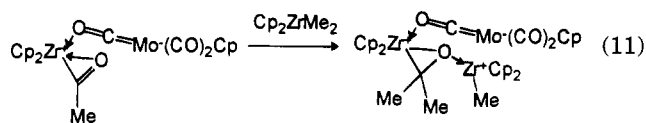
Also the formation of aldehyde complexes from nucleophilic attack on the acyl carbon has been observed (eq 12).^{29} In all cases one of the metal centers forms a
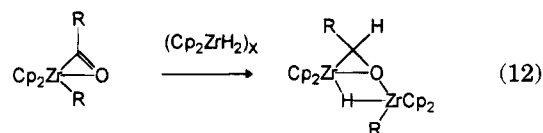
σ bond with the former acyl carbon atom. For **12** there is no interaction of C7 with either of the yttrium centers. This can be explained by the delocalized π-system of the pyridyl rings and C7 which leads to increased σ bond character in the Y—N bonds.

Nucleophilic attack on acyl carbon atoms has been explained in molecular orbital terms by Hoffmann *et al.*^{30} These authors showed that acyl carbon atoms of early transition metal η^2-acyls are electrophilic rather than carbenic in character due to a low-lying π^*_{CO} orbital and therefore might show carbenium-type reactivity. The fact that **12** shows no tendency to react with another equivalent of CO is evidently again caused by

(26) (a) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 226. (b) Belmonte, P. A.; Cloke, F. G. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 2643.

(27) This corresponds well with C—O distances of 1.23 Å reported for free ketones: Weast, R. C., Astle, M. J., Eds. *CRC Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1980; p F 219.

(28) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952.

(29) (a) Erker, G.; Kropp, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447. (b) Wolczanksi, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121.

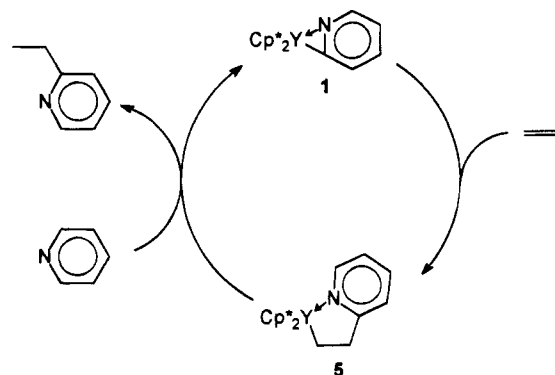(30) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440.

Figure 4. Catalytic cycle for formation of 2-ethylpyridine from pyridine and ethylene.

the donor properties of the pyridyl ring which results in the formation of (two) stable five-membered metallacycles similar to the insertion reactions with ethylene and propylene. The interaction of 1 with CO is another example in which the Y—pyridyl bond reacts in a totally different manner compared to unfunctionalized Ln—C bonds.

Reactivity of Cp*₂YCH₂CH₂(2-NC₅H₄) (5) and Catalytic Conversion of Pyridine to 2-Ethylpyridine. When the starting compound 1 can be regenerated from 5 by hydrogenolysis of the Y—C bond and subsequent metalation of pyridine, catalytic formation of 2-ethylpyridine from pyridine might become feasible. This strategy has been successfully exploited by Jordan *et al.* for Cp₂Zr(2-pyridyl)(L)⁺ systems.[31] An even simpler method for the regeneration of 1 from 5 would be direct σ-bond metathesis of 5 with pyridine (eq 13).

$$(13)$$
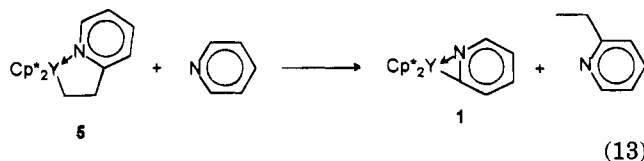
As anticipated, this regeneration of 1 with pyridine (3 equiv) was possible (50 °C, 2 d). However, the slower consecutive reaction of 1 with excess pyridine took place as well (*vide supra*).

With the necessary steps available, catalytic conversion of pyridine to 2-ethylpyridine was attempted. In an experiment under catalytic conditions (40 bar ethylene, [1]:[pyridine] = 1:33, 110 °C) it was found that the pyridine was converted into 2-ethylpyridine (44%) and small amounts of 2-*n*-butylpyridine (4%) and 2-*n*-hexylpyridine (traces) were present (GC/MS, ¹H-NMR). Also a small amount of polyethylene (IR) was formed indicating that multiple insertions are possible. The remainder of the pyridine was left unreacted.

A probable catalytic cycle is depicted in Figure 4, which consists of the two reaction steps observed under noncatalytic conditions. The formation of small amounts of 2-*n*-butylpyridine, 2-*n*-hexylpyridine, and polyethylene can be explained by multiple insertions of ethylene into the Y—C bond of 5. Since 5 was found to be very stable toward insertion of ethylene, polymerization with a very low rate of initiation is expected to be operative.[32]

When one ethylene molecule has been inserted, polymerization is triggered because now the stabilizing coordination of the pyridyl ring is lifted. After initiation, chain termination by σ-bond metathesis with pyridine is apparently insignificant since, except for 2-*n*-butylpyridine and 2-*n*-hexylpyridine, no other low molecular weight oligomers were found. In the products from the initiation and the first propagation step there is apparently still some stabilization through coordination of the pyridyl ligand present, which allows chain termination by σ-bond metathesis with pyridine to compete, resulting in the formation of 2-*n*-butylpyridine and 2-*n*-hexylpyridine.

Finding the optimal reaction conditions for this catalytic alkylation of pyridine is the subject of our current research along with the functionalization of other arenes and heterocycles. It is clear that, in contrast to Cp₂Zr(2-pyridyl)(L)⁺ systems,[5] in our yttrium system hydrogen is not necessary for regeneration of the catalyst.

To investigate which organoyttrium species are present under the catalytic reaction conditions, the thermal stability of 5 was examined. It was found that 5 reacts in 4 d at 80 °C to form a mixture of the two isomers Cp*₂Y(2-NC₅H₃(6-Et)) (13) and Cp*₂YCHMe(2-NC₅H₄) (14) (ratio 60:40; eq 14). No attempts were made to

$$(14)$$

60 : 40
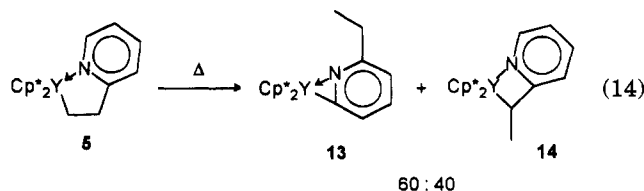
isolate these compounds because they could be completely identified on the basis of NMR data. The rate of thermolysis was enhanced when Lewis bases THF or Et₂O were added in stoichiometric amounts (see Experimental Section). During the reaction, no Lewis base adducts of 5 were observed in the ¹H-NMR spectrum, however.

The formation of 13 and 14 may involve the generation of an incipient fulvene species Cp*(η⁶-CH₂C₅Me₄)Y which metalates 2-ethylpyridine in both the benzylic and the *ortho* positions. Evidence of intermediate Cp*-(η⁶-CH₂C₅Me₄)Y has been obtained in the thermolysis of Cp*₂YCH(SiMe₃)₂[6,33] and in benzene and methane metalation reactions of (Cp*₂YMe)₂[34] under similar reaction conditions. The rate enhancement with added Lewis base suggests that decomplexation of the pyridyl group might be necessary for Cp* activation to take place. The Lewis base might stabilize an intermediate Cp*₂YCH₂CH₂(2-NC₅H₄) species in which the intramolecular coordination of the pyridyl group has been lifted. This would allow the Y—CH₂ fragment to reach the favored orientation for Cp* ligand metalation. Isomerization of 5 to 13 and 14 is also expected to take place in the catalytic formation of 2-ethylpyridine, which might lead to deactivation of the catalyst.

Regeneration of 1 from 5 with H₂ was also tried, but this again resulted in the formation of a mixture of 13 and 14 with a slightly different product ratio however
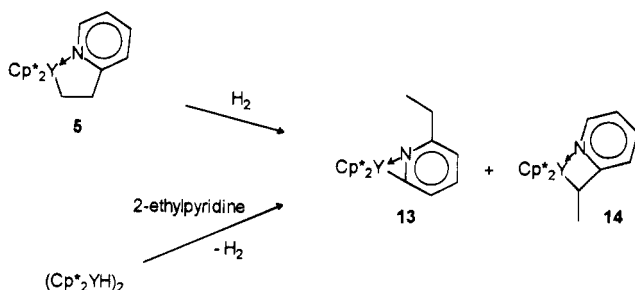
(31) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778.
(32) See for instance: Szwarc, M. *Carbanions, Living Polymers and Electron Transfer Processes*; Interscience Publishers: New York, 1986; p 50.

(33) Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3246.
(34) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491.

Scheme 3

(45:55; Scheme 3). Since this reaction is expected to involve the formation of a Y—H bond by hydrogenolysis, we also reacted the hydride (Cp*$_2$YH)$_2$ with 2-ethylpyridine and a similar product distribution was found (Scheme 3). This confirms the formation of a common hydride intermediate for both reactions. From this it is clear that hydrogenolysis of the Y—C bond in **5** is not a good route for the regeneration of **1** since it leads to the formation of other metalation products.

Concluding Remarks

The Y—pyridyl bond in **1** is in principle very reactive, but this reactivity seems to be limited to small molecules because of steric saturation at the yttrium center. Insertions of olefins and alkynes are especially sensitive to this steric inaccessibility of the yttrium center, which prevents approach of the π-system of these substrates; a prerequisite for insertion. However, when using small molecules like CO, ethylene, and propene, interesting reactivity of the insertion products is observed leading to unexpected compounds. The use of a sterically less demanding ligand system or a larger metal center (a lanthanide for instance) might result in a wider scope for this chemistry by allowing the insertion of alkynes in the Y—pyridyl bond.

Experimental Section

General Considerations. All experiments were performed under nitrogen using standard Schlenk, glovebox (Braun MB200), and vacuum line techniques. Pentane, THF, cyclohexane, benzene, benzene-d_6, and toluene-d_8 were distilled from Na/K alloy and degassed prior to use. Cp*$_2$YCH(SiMe$_3$)$_2$ and (Cp*$_2$YH)$_2$ were prepared according to published procedures.[6] H$_2$ (99.9995%, Hoek-Loos), ethylene, propylene, acetylene, CO (UCAR), butadiene, and propyne (Matheson) were used without further purification. Pyridine and 2-ethylpyridine were distilled from KOH. Other reagents and cyclohexane-d_{12} were stored over molecular sieves (4 Å) and degassed prior to use. Chloroform-d_1 was used as purchased.

NMR spectra were recorded on Gemini 200 (^{1}H, 200 MHz) and Varian VXR-300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz) spectrometers at ambient temperatures. 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 Mattson FT-IR spectrophotometer. Elemental analyses were carried out at the Micro-Analytical Department of the University of Groningen. The determinations are the average of two independent determinations.

Synthesis of Cp*$_2$Y(2-pyridyl) (1). A 5.20 g amount (10.0 mmol) of Cp*$_2$YCH(SiMe$_3$)$_2$ was dissolved in 100 mL of pentane, and the solution was stirred for 4 h under H$_2$ (1 bar) at 0 °C. The pentane layer was decanted, and the white residue was dried in vacuum. This material was suspended in 30 mL of fresh pentane, and 0.80 mL (9.9 mmol) of pyridine was added with stirring. The color of the reaction mixture

changed to yellow, and gas evolution was observed. After 18 h, volatiles were removed in vacuum, the yellow solid was washed with 2.5 mL of pentane and dissolved in 25 mL of pentane, and the mixture was filtered. Crystallization at −80 °C yielded 1.86 g (4.25 mmol) of yellow crystals. Concentration of the mother liquor yielded a second crop of 0.54 g (1.2 mmol). The total yield was 55%. ^{1}H-NMR (200 MHz, benzene-d_6): 8.02 (d, $^3J_{HH}$ = 5.2 Hz, 1H, pyridyl H), 7.82 (d, $^3J_{HH}$ = 7.2 Hz, 1H, pyridyl H), 7.08 (t, $^3J_{HH}$ = 7.2 Hz, 1H, pyridyl H), 6.64 (m, 1H, pyridyl H), 1.83 (s, 30H, C$_5$Me$_5$). ^{1}H-NMR (200 MHz, cyclohexane-d_{12}): δ 8.20 (d, $^3J_{HH}$ = 5.1 Hz, 1H, pyridyl H), 7.70 (d, $^3J_{HH}$ = 7.3 Hz, 1H, pyridyl-H), 7.21 (t, $^3J_{HH}$ = 6.0 Hz, 1H, pyridyl H), 6.86 (t, $^3J_{HH}$ = 6.5 Hz, 1H, pyridyl H), 1.71 (s, 30H, C$_5$Me$_5$). ^{13}C-NMR (75.4 MHz, cyclohexane-d_{12}): δ 225.53 (d, $^1J_{CY}$ = 33.2 Hz, Y—C), 145.27 (d, $^1J_{CH}$ = 173.9 Hz, pyridyl C), 133.55 (d, $^1J_{CH}$ = 162.0 Hz, pyridyl CH), 133.24 (d, $^1J_{CH}$ = 158.3 Hz, pyridyl CH), 121.14 (d, $^1J_{CH}$ = 161.1 Hz, pyridyl CH), 116.66 (s, C$_5$Me$_5$), 10.63 (q, $^1J_{CH}$ = 125.5 Hz, C$_5$Me$_5$). Anal. Calcd for C$_{25}$H$_{34}$NY: C, 68.64; H, 7.83; Y, 20.32. Found: C, 68.76; H, 7.90; Y, 20.43.

1 could also be prepared directly from Cp*$_2$YCH(SiMe$_3$)$_2$: 1.5 mL (19 mmol) of pyridine was added to a solution of 9.5 g (18 mmol) of Cp*$_2$YCH(SiMe$_3$)$_2$ in 100 mL of pentane. This mixture was stirred for 6 h under H$_2$ (1 bar), and the light-brown solid which formed was isolated and identified by ^{1}H-NMR. Yield: 5.83 g (13.3 mmol, 73%).

Reaction of 1 with H$_2$. A solution of 15 mg (0.034 mmol) of **1** in 0.5 mL of benzene-d_6 was exposed to 1 bar of H$_2$. The progress of the reaction was followed with ^{1}H-NMR spectroscopy. After 3 d at room temperature **1** had been completely converted into **2** (50%) and some unidentified material due to reaction of **1** with pyridine (remaining 50%). ^{1}H-NMR of **2** (300 MHz, benzene-d_6): δ 5.70 (d, $^3J_{HH}$ = 7.7 Hz, 2H, NCH=), 4.01 (m, 2H, =CHCH$_2$), 3.10 (t, $^3J_{HH}$ = 2.9 Hz, 2H, CH$_2$), 1.80 (s, 30H, C$_5$Me$_5$).

Cp*$_2$Y(η²-2-pyridyl)(THF) (3). To a solution of 44 mg (0.10 mmol) of **1** in 0.5 mL of benzene-d_6 was added 8.1 μL (0.10 mmol) of THF which resulted in the instantaneous formation of **3**. No decomposition was observed during several days at 80 °C. ^{1}H-NMR (200 MHz, benzene-d_6): δ 8.15 (d, $^3J_{HH}$ = 5.2 Hz, 1H, H6), 7.79 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H3), 7.14 (m, 1H, H4), 6.69 (m, 1H, H5), 3.67 (m, 4H, α-THF), 1.84 (s, 30H, C$_5$Me$_5$), 1.43 (m, 4H, β-THF).

Reaction of 1 with Pyridine. To a solution of 25 mg (0.057 mmol) of **1** in 0.5 mL of benzene-d_6 was added 4.6 μL (0.057 mmol) of pyridine which resulted in the instantaneous formation of **4**. ^{1}H-NMR (300 MHz, benzene-d_6): δ 8.74 (m, 2H, pyridine ortho H), 8.50 (d, $^3J_{HH}$ = 7.1 Hz, 1H, H6), 7.98 (d, $^3J_{HH}$ = 5.1 Hz, 1H, H3), 7.23 (t, $^3J_{HH}$ = 7.1 Hz, 1H, H4), 6.95 (m, 1H, pyridine para H), 6.79 (m, 1H, H5), 6.69 (m, 2H, pyridine meta H), 1.77 (s, 30H, C$_5$Me$_5$). The thermolysis of **4** was monitored by ^{1}H-NMR for several days at 50 °C. After 2 d, **4** had been converted completely into a mixture of unidentified compounds (see text).

Reaction of 1 with Excess Pyridine. To a solution of 50 mg (0.11 mmol) of **1** in 10 mL of cyclohexane was added 180 μL (2.22 mmol) of pyridine. The reaction mixture was stirred for 1 day under reflux, and a sample of the mixture was analyzed by GC and GC/MS after quenching with water and drying over MgSO$_4$. This showed the presence of 2,2′-bipyridine (1 equiv per Y), pyridine, and Cp*H. GC/MS of 2,2′-bipyridine (EI, 70 eV): m/e 157 (15), 156 (100) (molecular ion), 155 (46), 130 (10), 129 (20), 128 (27), 104 (7), 103 (8), 102 (9), 101 (7), 79 (22), 78 (70), 77 (13), 76 (15), 75 (12), 74 (7), 64 (6), 63 (7), 52 (17), 51 (40), 50 (15), 28 (6). Further heating of the reaction mixture for 3 d did not show any increase in the amount of 2,2′-bipyridine. The remaining reaction mixture was quenched with water and extracted with ether. The ether layer was dried over MgSO$_4$, and volatiles were removed in vacuum. The remaining yellow oil was unequivocally identified by ^{1}H-NMR as a mixture of 2,2′-bipyridine and Cp*H. ^{1}H-NMR of 2,2′-bipyridine (300 MHz, chloroform-d_1): δ 8.83

(broad d, $^3J_{HH}$ = 4.0 Hz, 2H), 8.55 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.97 (td, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz, 2H), 7.46 (ddd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.1 Hz, 2H).

Synthesis of Cp*₂YCH₂CH₂(2-NC₅H₄) (5). A solution of 0.91 g (2.1 mmol) of **1** in 15 mL of pentane was stirred for 1 h under ethylene (1 bar). A yellow precipitate formed, and the liquid was filtered off. Yield: 0.54 g (1.2 mmol, 55%) of a yellow powder. IR (cm⁻¹): 2955 (vs), 2924 (vs), 2857 (vs), 2723 (w), 1599 (s), 1562 (w), 1527 (w), 1462 (s), 1377 (s), 1321 (w), 1282 (m), 1153 (w), 1017 (w), 995 (w), 754 (m), 741 (w), 721 (m), 659 (m), 638 (m), 532 (m). ¹H-NMR (300 MHz, toluene-d_8): δ 7.45 (d, 1H, $^3J_{HH}$ = 5.4 Hz, pyridyl H), 6.95 (m, 1H, pyridyl H), 6.67 (d, 1H, $^3J_{HH}$ = 7.8 Hz, pyridyl H), 6.44 (m, 1H, pyridyl H), 3.36 (t, 2H, $^3J_{HH}$ = 7.4 Hz, YCH₂C*H₂*), 1.97 (s, 30H, C₅Me₅), 0.36 (td, 2H, $^3J_{HH}$ = 7.6 Hz, $^2J_{HY}$ = 3.1 Hz, YCH₂). ¹³C-NMR (75.4 MHz, toluene-d_8): δ 172.7 (s, pyridyl C), 146.2 (d, $^1J_{CH}$ = 176 Hz, pyridyl CH), 137.7 (d, $^1J_{CH}$ = 157 Hz, pyridyl CH), 124.4 (overlaps with solvent signal, pyridyl CH), 119.7 (d, $^1J_{CH}$ = 165 Hz, pyridyl CH), 115.7 (s, C₅Me₅), 38.1 (t, $^1J_{CH}$ = 123 Hz, YCH₂C*H₂*), 27.0 (dt, $^1J_{CH}$ = 113 Hz, $^1J_{CY}$ = 49 Hz, YCH₂), 11.3 (q, $^1J_{CH}$ = 125 Hz, C₅*Me₅*). Anal. Calcd for C₂₇H₃₈NY: C, 69.66; H, 8.32; Y, 19.10. Found: C, 69.81; H, 8.28; Y, 19.19.

Synthesis of Cp*₂YCH₂CHMe(2-NC₅H₄) (6). A 0.959 g amount (2.19 mmol) of **1** was dissolved in 5 mL of cyclohexane, and the solution was stirred under propylene (1 bar) at 60 °C for 4 d during which the color of the reaction mixture became brown and crystals of the same color formed. Volatiles were removed in vacuum, and the remaining solid was extracted once with pentane. The extract was concentrated, and crystallization at −80 °C yielded 0.485 g (1.01 mmol, 46%) of brown crystals. IR (cm⁻¹): 3050 (w), 2924 (vs), 2955 (vs), 2855 (vs), 2722 (w), 1599 (s), 1567 (w), 1462 (s), 1377 (s), 1294 (w), 1161 (w), 1143 (w), 1051 (w), 1013 (m), 976 (w), 962 (w), 779 (m), 752 (m), 737 (m), 723 (m), 642 (w), 602 (w), 521 (w), 500 (w). ¹H-NMR (200 MHz, benzene-d_6): δ 7.32 (m, 1H, pyridyl H), 6.93 m, 2H, pyridyl H), 6.44 (m, 1H, pyridyl H), 3.23 (m, 1H, CH₂C*H*Me), 1.91 (s, 30H, C₅Me₅), 1.55 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH₂CHM*e*), 0.60 (m, 1H, YCH), 0.05 (m, 1H, YCH). ¹³C-NMR (75.4 MHz, benzene-d_6): δ 175.06 (pyridyl C), 145.38 (pyridyl CH), 137.93 (pyridyl CH), 123.03 (pyridyl CH), 119.56 (pyridyl CH), 115.69 (C₅Me₅), 115.61 (C₅Me₅), 41.53 (CH₂CHMe), 40.69 (d, $^1J_{CY}$ = 49.0 Hz, YCH₂), 27.51 (CHM*e*), 11.50 (C₅*Me₅*), 11.16 (C₅*Me₅*). Anal. Calcd for C₂₈H₄₀NY: C, 70.13; H, 8.41; Y, 18.54. Found: C, 69.69; H, 8.38; Y, 18.58.

Synthesis of Cp*₂Y(CCH)(py) (7). A stirred solution of 0.54 g (1.2 mmol) of **1** in 20 mL of pentane was cooled to −80 °C and exposed to an atmosphere of acetylene (0.5 bar, 10 equiv). Then the reaction mixture was allowed to warm to room temperature, which resulted in the formation of a red solution. The mixture was stirred at room temperature for 3 d upon which a yellow solid formed. The reaction mixture was cooled to −30 °C, and the pentane layer was decanted. The residue was washed with 5 mL of pentane and recrystallized from 30 mL of pentane at −80 °C. Yield: 0.16 g (0.35 mmol, 29%) of a yellow material. IR (cm⁻¹): 3264 (m), 3059 (m), 2955 (s), 2924 (s), 2854 (s), 2723 (m), 1601 (s), 1489 (sh), 1460 (s), 1446 (s), 1377 (s), 1217 (m), 1066 (m), 1039 (m), 1020 (m), 1008 (m), 756 (s), 721 (m), 705 (s), 659 (s), 626 (m). ¹H-NMR (benzene-d_6, 200 MHz): δ 8.59 (broad s, lw₁/₂ = 193 Hz, 2H, *ortho* H's of pyridine), 6.75 (tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, *para* H of pyridine), 6.49 (t, $^3J_{HH}$ = 6.8 Hz, 2H, *meta* H's of pyridine), 2.55 (d, $^2J_{HY}$ = 2.1 Hz, 1H, YCCH), 2.02 (s, 30 H, C₅Me₅). ¹³C-NMR (benzene-d_6, 75.4 MHz): δ 149.37 (d br, *ortho* C's of pyridine), 138.11 (d, $^1J_{CH}$ = 168 Hz, *para* C of pyridine), 124.02 (d, $^1J_{CH}$ = 168 Hz, *meta* C's of pyridine), 117.07 (s, C₅Me₅), 95.34 (dd, $^1J_{CH}$ = 212 Hz, $^2J_{CY}$ = 13 Hz, YCCH), 11.75 (q, $^1J_{CH}$ = 126 Hz, C₅*Me₅*), α-C resonance not found. Anal. Calcd for C₂₇H₃₆NY: C, 69.97; H, 7.83; Y, 19.18. Found: C, 69.43; H, 7.77; Y, 19.10.

Synthesis of Cp*₂Y(CCMe)(py) (8). A solution of 0.686 g (1.57 mmol) of **1** in 25 mL of pentane was stirred under

propyne (1 bar) for 2.5 h. The propyne was replaced by nitrogen, and crystallization at −80 °C afforded 0.510 g (1.07 mmol, 68%) of **7** as brown-yellow crystals. IR (cm⁻¹): 2957 (vs), 2924 (vs), 2903 (vs), 2723 (w), 2069 (w), 1601 (m), 1462 (vs), 1377 (s), 1305 (w), 1217 (m), 1155 (w), 1069 (w), 1038 (w), 1020 (w), 1006 (m), 949 (m), 754 (s), 723 (m), 706 (s), 626 (m), 588 (w). ¹H-NMR (300 MHz, benzene-d_6): δ 8.5 (broad singlet, 2H, pyridyl H), 6.77 (m, 1H, pyridyl H), 6.52 (m, 2H, pyridyl H), 2.07 (s, 3H, C≡CMe), 2.03 (s, 30H, C₅Me₅). ¹³C-NMR (75.4 MHz, benzene-d_6): δ 149.56 (d, $^1J_{CH}$ = 168.1 Hz, 2 pyridyl CH), 138.10 (d, $^1J_{CH}$ = 168.2 Hz, pyridyl CH), 133.68 (d, $^1J_{CY}$ = 70.3 Hz, YC≡CMe), 124.01 (d, $^1J_{CH}$ = 167.0 Hz, 2 pyridyl CH), 116.82 (s, C₅Me₅), 103.30 (dq, $^2J_{CY}$ = 12.7 Hz, $^2J_{CH}$ = 9.2 Hz, YC≡CMe), 11.77 (q, $^1J_{CH}$ = 124.4 Hz, C₅*Me₅*), 6.17 (q, $^1J_{CH}$ = 129.0 Hz, C≡C*Me*). Anal. Calcd for C₂₈H₃₈NY: C, 70.43; H, 8.02; Y, 18.62. Found: C, 70.27; H, 8.05; Y, 18.65.

Reaction of 1 with 2-Butyne. 2-Butyne (5.0 μL, 0.064 mmol) was added to a solution of 25 mg (0.056 mmol) of **1** in 0.5 mL of benzene-d_6. After 5 min at room temperature, characteristic resonances of **9** (29%) were observed in the ¹H-NMR spectrum which were identical to those reported earlier.[17] The ¹H-NMR spectrum, after 2 h at room temperature, showed no changes. However, after 15 h at 75 °C, 50% of **9** and 50% of the unidentified Cp*₂Y product resulting from reaction of **1** with pyridine were present. Of the 2-butyne 0.64 equiv remained. Addition of a 20-fold excess of 2-butyne did not lead to an increase of the amount of **9**.

Reaction of 1 with 2-Pentyne. 2-Pentyne (9.0 μL, 0.094 mmol) was added to a solution of 40.3 mg (0.092 mmol) of **1** in 0.6 mL of cyclohexane-d_{12}. The resulting solution was transferred to an NMR tube which was kept at 75 °C. The progress of the reaction was monitored by ¹H-NMR, and after 2 d the reaction was complete. The NMR tube was opened, and the reaction mixture was quenched with 2 mL of water. The mixture was extracted three times with 1 mL of Et₂O. The ether extracts were washed with water and back-extracted three times with 0.5 mL of 5% HCl(aq). The combined extracts were washed with Et₂O and neutralized with 5 N KOH(aq) upon which a yellow oil formed. This mixture was extracted three times with 0.5 mL of Et₂O, the extract was dried over MgSO₄, and volatiles were removed in vacuum affording a yellow oil. ¹H-NMR, GC, and GC/MS analysis showed this oil to consist of 2,2′-bipyridine, 2-(1-methyl-1-butenyl)pyridine, and 2-(1-ethyl-1-propenyl)pyridine (molar ratio 1.0:1.5:1.9). ¹H-NMR for 2-(1-methyl-1-butenyl)pyridine and 2-(1-ethyl-1-propenyl)pyridine (200 MHz, chloroform-d_1): δ 8.41 (dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, H6), 7.62 (tt, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.7 Hz, H4), 7.32 (m, H3), 7.12 (m, H5), 6.39 (q, $^3J_{HH}$ = 7.9 Hz, C=C*H*CH₂), 6.32 (q, $^3J_{HH}$ = 7.3 Hz, C=C*H*Me), 2.65 (q, $^3J_{HH}$ = 7.7 Hz, CH₃C*H₂*(C₅H₄N)C=C), 2.29 (quint, $^3J_{HH}$ = 7.3 Hz, CH₃C*H₂*(H)C=C), 2.11 (d, $^4J_{HH}$ = 1.3 Hz, *Me*(C₅H₄N)C=C), 1.87 (d, $^3J_{HH}$ = 6.8 Hz, *Me*(H)C=C). For NMR data of 2,2′-bipyridine, see reaction of **1** with pyridine. GC/MS for 2-(1-ethyl-1-propenyl)pyridine (EI, 70 eV): *m/e* 148 (7), 147 (27) (molecular ion), 146 (17), 133 (25), 132 (59), 131 (5), 130 (8), 118 (30), 117 (52), 105 (9), 104 (29), 78 (17), 53 (23), 52 (27), 51 (40), 41 (11), 40 (16), 39 (47), 32 (22), 29 (23), 28 (100), 27 (23). GC/MS for 2-(1-methyl-1-butenyl)pyridine (EI, 70 eV): *m/e* 148 (8), 147 (31) (molecular ion), 146 (21), 133 (15), 132 (37), 131 (13), 130 (10), 118 (16), 117 (36), 104 (7), 79 (7), 78 (9), 53 (15), 52 (29), 51 (32), 50 (12), 41 (14), 40 (9), 39 (29), 38 (6), 32 (22), 29 (26), 28 (100), 27 (17). For GC/MS data of 2,2′-bipyridine, see reaction of **1** with pyridine.

Synthesis of (Cp*₂Y)₂(μ-η²:η²-OC(2-NC₅H₄)₂) (12). A solution of 0.269 g (0.615 mmol) of **1** in 24 mL of pentane was exposed to 0.65 mmol of CO. After 24 h at room temperature the purple crystals which had formed were filtered off, washed with pentane, and dried in vacuum. Yield: 0.125 g (0.269 mmol, 44%). IR (cm⁻¹): 2955 (vs), 2924 (vs), 2855 (vs), 1602 (vw), 1588 (m), 1458 (s), 1406 (s), 1375 (s), 1283 (w), 1260 (w), 1240 (w), 1150 (s), 1055 (w), 991 (m), 918 (s), 750 (m), 723

Table 2. Details of the X-ray Structure Determination of $(Cp^*_2Y)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ (12)

formula	$C_{51}H_{68}N_2OY_2$
M_n	902.92
cryst system	monoclinic
space group	$P2_1/c$
a, Å	14.194(4)
b, Å	17.559(4)
c, Å	18.717(5)
β, deg	109.61(2)
V, Å^3	4394(2)
D_{calc}, g cm^{-3}	1.365
Z	4
$F(000)$	1896
μ, cm^{-1}	26.8
cryst size, mm	$0.40 \times 0.40 \times 0.50$
T, K	150
θ range, deg	1.15–24.20
scan type	$\omega/2\theta$
scan, deg	$1.04 + 0.35 \tan\theta$
hor, ver aperture, mm	4.06, 4.00
X-ray exposure time, h	40
linear decay, %	1
ref reflcns	$\bar{2}26, \bar{2}2\bar{4}, \bar{1}52$
data set	$-16{:}0, -20{:}20, -20{:}20$
no. of reflcns collcd	14 323
no. of unique reflcns	6867
DIFABS corr range	0.80–1.12
no. of refined params	517
final $R_1{}^a$	0.094 [for 2831, $F_o > 4\sigma(F_o)$]
final $wR_2{}^b$	0.168
goodness of fit	0.97
weighting scheme	$w^{-1} = \sigma(F^2) + (0.0388P)^2$ ^{c}
$(\Delta/\sigma)_{mean}$, $(\Delta/\sigma)_{max}$	0.003, 0.077
min residual density, e Å^{-3}	-0.65
max residual density, e Å^{-3}	0.68

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = [\sum[w(F^2{}_o - F^2{}_c)^2]/\sum[w(F^2{}_o)^2]]^{1/2}$. ^{c} $P = ((\max(F^2{}_o),0) + 2F^2{}_c)/3$.

(m), 561 (w). ^{1}H-NMR (benzene-d_6, 300 MHz): δ 7.47 (d, $^3J_{HH}$ = 9.0 Hz, 1H, pyridyl H), 7.39 (d, $^3J_{HH}$ = 5.6 Hz, 1H, pyridyl H), 6.58 (m, 1H, pyridyl H), 5.90 (t, $^3J_{HH}$ = 6.0 Hz, 1H, pyridyl H), 2.05 (s, 15H, C_5Me_5), 1.91 (s, 15H, C_5Me_5). ^{13}C-NMR (benzene-d_6, 75.4 MHz): δ 153.94 (pyridyl C), 145.79 (pyridyl C), 133.18 (pyridyl C), 118.43 (pyridyl C), 118.0 (C_5Me_5), 117.94 (C_5Me_5), 13.08 (C_5Me_5), 12.07 (C_5Me_5). One pyridyl C signal and the C–O carbon signal were not found. Anal. Calcd for $C_{51}H_{68}N_2OY_2$: C, 67.84; H, 7.59; Y, 19.69. Found: C, 68.10; H, 7.76; Y, 19.79.

X-ray Structure Determination of 12. Crystal data and summarized experimental procedures are collected in Table 2. Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 3. A crystal suitable for X-ray structure determination was covered by an inert oil, glued to the tip of a glass fiber and immediately placed in the cold dinitrogen stream (150 K). Data were collected in $\omega-2\theta$ mode using an Enraf-Nonius CAD4-Turbo diffractometer with rotating anode. The crystals were found to diffract poorly. Unit cell dimensions and standard deviations were obtained by least-squares fit (SET4) to 25 reflections (8.61 < θ < 15.43°). Reduced-cell calculations did not indicate higher lattice symmetry.[35] Three standard reflections were monitored periodically and showed minor variations in intensity during data collection. The 14 323 reflections collected were processed to give 6867 unique reflections (R_{int} = 0.184). These were corrected for Lorentz, polarization, and absorption effects. An empirical absorption/extinction correction was applied (DIFABS[36]). The systematic reflection conditions ($h0l$, l = 2n; $0k0$, k = 2n) indicated space group $P2_1/c$. The structure was solved by automated Patterson methods and subsequent

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Table 3. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms for $(Cp^*_2Y)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}OC(2\text{-}NC_5H_4)_2)$ (12)

atom	x	y	z	U_{eq},^{a} Å^2
Y1	0.11237(9)	0.40641(7)	0.28730(7)	0.0184(4)
Y2	0.42644(9)	0.33896(7)	0.29957(7)	0.0212(4)
O8	0.2563(5)	0.3732(4)	0.2583(4)	0.020(3)
N1	0.0616(7)	0.3331(6)	0.1759(5)	0.024(4)
N10	0.3900(8)	0.4048(6)	0.1845(5)	0.031(4)
C2	−0.0308(9)	0.3026(7)	0.1383(7)	0.032(5)
C3	−0.0598(10)	0.2772(7)	0.0671(7)	0.030(5)
C4	0.0086(9)	0.2801(7)	0.0290(7)	0.033(5)
C5	0.1005(9)	0.3091(6)	0.0617(7)	0.027(5)
C6	0.1292(9)	0.3387(7)	0.1376(6)	0.023(4)
C7	0.2248(9)	0.3699(6)	0.1777(6)	0.020(4)
C9	0.2896(9)	0.3990(7)	0.1414(7)	0.025(5)
C11	0.4549(10)	0.4271(7)	0.1503(7)	0.036(6)
C12	0.4284(11)	0.4510(7)	0.0763(7)	0.037(6)
C13	0.3258(11)	0.4479(7)	0.0341(7)	0.033(5)
C14	0.2583(10)	0.4237(7)	0.0643(6)	0.036(5)
C101	0.0856(8)	0.2717(6)	0.3457(6)	0.018(4)
C102	0.1682(9)	0.3070(6)	0.3993(6)	0.018(4)
C103	0.1288(8)	0.3703(6)	0.4293(6)	0.015(3)
C104	0.0244(8)	0.3718(6)	0.3950(6)	0.020(4)
C105	−0.0029(8)	0.3091(7)	0.3424(6)	0.021(4)
C106	0.0900(8)	0.1941(6)	0.3095(7)	0.031(5)
C107	0.2744(8)	0.2793(7)	0.4238(7)	0.035(5)
C108	0.1848(8)	0.4182(7)	0.4973(6)	0.028(5)
C109	−0.0504(8)	0.4096(7)	0.4232(6)	0.026(5)
C110	−0.1062(8)	0.2818(7)	0.3051(6)	0.025(4)
C111	0.1106(9)	0.5407(7)	0.2139(7)	0.025(5)
C112	0.1167(8)	0.5603(6)	0.2890(6)	0.015(4)
C113	0.0275(9)	0.5404(7)	0.2973(7)	0.024(5)
C114	−0.0343(9)	0.5054(7)	0.2292(7)	0.027(5)
C115	0.0188(9)	0.5085(7)	0.1780(6)	0.019(4)
C116	0.1847(9)	0.5628(7)	0.1774(7)	0.040(6)
C117	0.1946(8)	0.6096(6)	0.3443(5)	0.026(4)
C118	−0.0057(9)	0.5702(6)	0.3617(6)	0.030(5)
C119	−0.1434(8)	0.4836(6)	0.2105(7)	0.026(5)
C120	−0.0252(9)	0.4898(7)	0.0951(6)	0.033(5)
C201	0.4622(9)	0.4411(7)	0.4057(6)	0.020(4)
C202	0.4927(9)	0.4779(7)	0.3498(6)	0.022(4)
C203	0.5814(9)	0.4430(7)	0.3499(6)	0.021(4)
C204	0.6065(9)	0.3853(7)	0.4055(6)	0.025(4)
C205	0.5295(9)	0.3837(7)	0.4400(6)	0.027(5)
C206	0.3744(9)	0.4665(7)	0.4286(6)	0.031(5)
C207	0.4478(9)	0.5489(6)	0.3064(7)	0.036(5)
C208	0.6530(8)	0.4728(7)	0.3137(6)	0.027(4)
C209	0.7073(7)	0.3496(7)	0.4334(6)	0.026(4)
C210	0.5338(9)	0.3361(7)	0.5070(6)	0.034(5)
C211	0.3681(9)	0.1999(6)	0.2417(7)	0.021(4)
C212	0.4264(8)	0.2296(6)	0.2039(6)	0.014(3)
C213	0.5251(9)	0.2333(7)	0.2519(7)	0.026(5)
C214	0.5274(9)	0.2038(7)	0.3232(7)	0.024(4)
C215	0.4299(10)	0.1840(6)	0.3182(6)	0.023(5)
C216	0.2600(8)	0.1775(6)	0.2123(6)	0.027(4)
C217	0.3895(9)	0.2424(7)	0.1164(6)	0.036(5)
C218	0.6157(8)	0.2546(7)	0.2299(7)	0.036(5)
C219	0.6173(9)	0.1774(8)	0.3876(7)	0.046(6)
C220	0.4039(9)	0.1381(7)	0.3756(6)	0.036(5)

^{a} $U_{eq} = {}^1/_3$ of the trace of the orthogonalized U.

difference Fourier synthesis (DIRDIF[37]). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93[38]). All reflections were considered observed. Anisotropic thermal parameters were used for all non-hydrogen atoms except two cyclopentadienyl carbon atoms. The anisotropic displacement parameters for some of the remaining carbon atoms were found to be somewhat compressed. This is ascribed to the weak data set. Hydrogen

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atoms were included in the refinement cycle at calculated positions, riding on their carrier atoms. A fixed isotropic displacement parameter of 1.5 or 1.2 times the equivalent isotropic displacement parameter of the carrier atom was used for the methyl hydrogen atoms and other hydrogen atoms, respectively. The final model includes four symmetry-related voids, each of 54(1) Å³. The nearest non-hydrogen atom was found at 3.44 Å from the center of each void. The BYPASS[39] procedure, as implemented in PLATON,[40] found no electron density within these regions. Geometrical calculations and the ORTEP illustration were performed with PLATON.[40] Computing was conducted on a DECstation 500 cluster.

Calculations on dpk and [dpk]²⁻. Geometries of dpk and [dpk]²⁻ were optimized using the MOPAC 94 program[41] as implemented in the CAChe[42] Worksystem with the AM1[43] set of parameters. The geometry of the dpk ligand in **12** was used as the starting geometry in both cases. Vibrational spectra were also calculated with MOPAC. Electronic spectra were calculated with the standard INDO/1[44] set of parameters using the configurational interaction calculation of the ZINDO program as implemented in the CAChe Worksystem. Calculations were run on a Macintosh System II computer.

Reaction of 5 with Pyridine. A 12 μL volume (0.15 mmol) of pyridine was added to a solution of 0.021 g (0.045 mmol) of **5** in 0.5 mL of benzene-d_6. ¹H-NMR after 3 d at 50 °C showed that a mixture of pyridine, **5** (37%), **4** (28%), 2-ethylpyridine (63%), and thermolysis products of **4** (35%) had been formed. Further heating resulted in complete conversion to 2-ethylpyridine and thermolysis products of **4**.

Catalytic Conversion of Pyridine to 2-Ethylpyridine. A solution of 0.33 g (0.76 mmol) of **1** and 2.0 mL (25 mmol) of pyridine in 85 mL of benzene was placed into an autoclave (with glass insert) and pressurized with ethylene (40 bar). After the mixture was stirred for 18 h at 110 °C, during which the pressure remained essentially constant, the pressure was released and the reaction mixture was quenched with 2 mL of methanol. A sample of the resulting mixture was filtrated and analyzed by GC and GC/MS. The small amount of white material (30 mg) which had been formed was washed with methanol, dried at 100 °C, and identified by IR (KBr pellet) to be polyethylene.[45] End group determination by IR was not possible due to occlusion of water in the polymer.

Thermolysis of Cp*₂YCH₂CH₂(2-NC₅H₄) (5). A solution of **5** (25 mg, 0.054 mmol) in 0.5 mL of cyclohexane-d_{12} was

kept at 80 °C. The progress of the thermolysis was monitored by ¹H-NMR. After 4 d, **5** had been converted completely into a mixture of **13** (60%) and **14** (40%). ¹H-NMR for **13** (300 MHz): δ 7.50 (pd, $^3J_{HH}$ = 5.6 Hz, 1H, H5), 7.20 (t, 1H, H4), 6.77 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H3), 2.69 (q, 2H, CH_2CH₃), 1.72 (s, 30H, C₅Me₅), 1.29 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH₂CH_3). ¹³C-NMR for **13** (75.4 MHz): δ 224.71 (d, $^1J_{CY}$ = 33 Hz, C2), 159.48 (s, C6), 135.71 (d, $^1J_{CH}$ = 158 Hz, pyridyl CH), 134.05 (d, $^1J_{CH}$ = 157 Hz, pyridyl CH), 119.00 (d, $^1J_{CH}$ = 162 Hz, pyridyl CH), 116.69 (s, C_5Me₅), 31.61 (t, $^1J_{CH}$ = 125 Hz, CH₂CH₃), 13.30 (q, $^1J_{CH}$ = 127 Hz, CH₂CH₃), 10.85 (q, $^1J_{CH}$ = 125 Hz, C₅Me₅). ¹H-NMR for **14** (300 MHz): δ 7.28 (pd, $^3J_{HH}$ = 4.9 Hz, 1H, H6), 7.04 (m, 1H, H5), 6.60 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H3), 6.12 (m, 1H, H4), 2.46 (pseudo q, J = 5.6 Hz, 1H, YCHCH₃), 1.80 (s, C₅Me₅), 1.44 (d, $^3J_{HH}$ = 5.6 Hz, 3H, YCHCH_3). ¹³C-NMR of **14** (75.4 MHz): δ 167.31 (s, C2), 146.06 (d, $^1J_{CH}$ = 171 Hz, C6), 130.95 (d, $^1J_{CH}$ = 162 Hz, C4), 117.33 (s, C_5Me₅), 115.50 (d, $^1J_{CH}$ = 158 Hz, C3 or C5), 109.83 (d, $^1J_{CH}$ = 167 Hz, C3 or C5), 47.54 (dd, $^1J_{CH}$ = 130 Hz, $^2J_{CY}$ = 11 Hz, YCHCH₃), 11.71 (YCHCH_3, overlaps with C₅Me₅ signal), 10.80 (q, $^1J_{CH}$ = 125 Hz, C₅Me₅).

The influence of equimolar amounts of Lewis base on thermolysis was studied at 50 °C in benzene-d_6. The times necessary for complete thermolysis were as follows: THF, 5 d; Et₂O, 10 d; PMe₃, 1 month. In all cases the 60:40 ratio of **13**:**14** was observed.

Treatment of 5 with H₂. An NMR tube containing a solution of **5** (25 mg, 0.054 mmol) in 0.5 mL of benzene-d_6 was exposed to 1 equiv of H₂ using a vacuum line. After 10 min at room temperature, ¹H-NMR (200 MHz) of the yellow solution showed that **5** had been completely converted into a mixture of **13** (45%) and **14** (55%).

Reaction of (Cp*₂YH)₂ with 2-Ethylpyridine. To a suspension of 25 mg (0.035 mmol) of (Cp*₂YH)₂ in 0.5 mL of benzene-d_6 was added 7.9 μL (0.070 mmol) of 2-ethylpyridine. Immediately gas evolution was observed and a yellow solution formed. ¹H-NMR (200 MHz) showed the quantitative formation of a mixture of **13** (40%) and **14** (60%).

Supplementary Material Available: Lists of hydrogen coordinates and U values, all bond lengths and angles, torsion angles, and anisotropic thermal parameters of **12** (25 pages). Ordering information is given on any current masthead page.

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