Bond activation and catalysis with organolanthanides

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5 Exploration of the Reactivity of $(Cp^*_2LaH)_2$ toward Pyridine; Catalytic Alkylation of Pyridine with Ethene to 2,6-Diethylpyridine

5-1. Introduction

In the previous chapter, the reactivity of the Cp^*_2Y-system was compared with the analogous system where the two cyclopentadienyl rings are linked through a Me_2Si-bridge, the $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Y$-system. The linking of the Cp-ligands opens up the coordination sphere of the metal by reducing the Ct-Y-Ct (Ct = centroid) angle. It was found that the yttrium hydride $\{[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Y(\mu\text{-}H)\}_2$[1] reacts with pyridine by 1,2-insertion,[2] while $(Cp^*_2YH)_2$ gives the *ortho*-metallated product.[3] The C-C coupling of pyridyl and pyridine by the 1,2-insertion product $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Y(NC_5H_6)(NC_5H_5)$ (**4.2a**) results in formation of the 2-hydro-2,2'-bipyridyl complex $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Y(\eta^2\text{-}1\text{-}N_2C_{10}H_9)$ (**4.2d**).

Reaction of Me_2Si-bridged 1,2-insertion product $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Y(NC_5H_6)(NC_5H_5)$ (**4.2a**) with ethene in the presence of excess pyridine leads to bis-alkylation of pyridine. $Cp^*_2Y(\eta^1\text{-}2\text{-}NC_5H_4)$ reacts with ethene in the presence of pyridine into the mono insertion product $Cp^*_2Y(\eta^2\text{-}CH_2CH_2\text{-}2\text{-}NC_5H_4)$,[3] but cleavage of the Y-C bond by C-H bond activation of pyridine is very slow. This is due to the strong intramolecular coordination of nitrogen in $Cp^*_2Y(\eta^2\text{-}CH_2CH_2\text{-}2\text{-}NC_5H_4)$. In the Me_2Si-bridged yttrocene system the cleavage of the Y-C bond probably takes place though hydrogenolysis since dihydrogen is formed in a stoichiometric amount upon reaction of the 1,2-insertion product $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Y(NC_5H_6)(NC_5H_5)$ (**4.2a**) with ethene to give complex $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Y(\eta^2\text{-}CH_2CH_2\text{-}2\text{-}NC_5H_3\text{-}6\text{-}Et)$ (**4.7**) and 2,6-diethylpyridine (§ 4-7, Fig 4.2). Only when the single ethene insertion product $Cp^*_2Y(\eta^2\text{-}CH_2CH_2\text{-}2\text{-}C_5H_4N)$ reacts with ethene and excess pyridine in the presence of H_2 (to promote M-C cleavage[4]) good conversions to 2-ethyl and 2,6-diethylpyridine were observed (§ 4-7).

Another way of increasing the available space around the reactive centre is to replace yttrium by the larger metal lanthanum (ionic radius: Y^{3+} (1.019 Å), La^{3+} (1.16 Å)).[5] In the catalytic alkylation of pyridine by the permethyl lanthanocene system, a higher activity toward C-H bond activation of pyridine and multiple insertions of ethene into the La-C(pyridyl) bond are expected due to the larger ionic radius of lanthanum compared to yttrium. It is also possible that H_2 is not needed to cleave the M-C bond in the Cp^*_2La-system. In this chapter, the reactivity of $(Cp^*_2LaH)_2$[6] with pyridine and pyridine/ethene is explored, and compared to the corresponding reactions of the Cp^*_2Y- and $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Y$-hydrides.

5-2-1. Reactivity toward Pyridine. Reaction of $(Cp^*_2LaH)_2$ (**5.1**) with pyridine (1 equiv per La) leads to formation of the *ortho*-metallated pyridyl $Cp^*_2La(\eta^2\text{-}2\text{-}C_5H_4N)$ (**5.2**) and the 1-(2,3,4-tetrahydropyridyl) $Cp^*_2La(NC_5H_8)$ (**5.3**) in a 1:1 ratio (NMR spectroscopy, benzene-d_6, Fig 5.1).

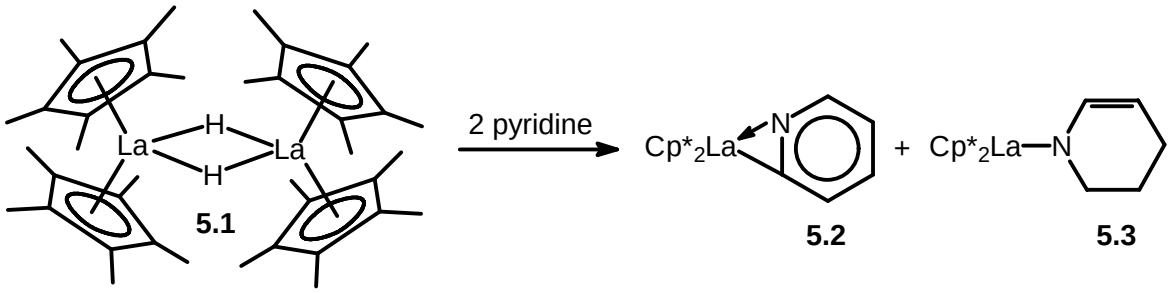


Figure 5.1. Reaction of $(Cp^*_2LaH)_2$ (**5.1**) with 2 equivalents of pyridine.

The ^{1}H NMR data of the *ortho*-metallated pyridyl compound indicate an η^2-coordination, since the resonances for the pyridyl ring are very similar to $Cp^*_2Ln(\eta^2\text{-}2\text{-}C_5H_4N)$ (Ln = Y[3], Lu[7]) and to those of the crystallographically characterised $Cp^*_2Sc(\eta^2\text{-}2\text{-}C_5H_4N)$.[8] Addition of a second equivalent of pyridine to the reaction mixture gives the Lewis base adducts $Cp^*_2La(\eta^1\text{-}2\text{-}C_5H_4N)(C_5H_5N)$ (**5.2· C_5H_5N**) and $Cp^*_2La(NC_5H_8)(NC_5H_5)$ (**5.3· C_5H_5N**). In the Cp^*_2La-system, the H_2 that is eliminated upon *ortho*-metallation of pyridine, is quantitatively captured by a lanthanum mediated reduction of pyridine (0.5 mol/La) to give a 1:1 mixture of **5.2** and **5.3** (Fig 5.1). Another example of efficient hydrogen trapping by pyridine, mediated by an early transition metal complex, was observed in the titanocene catalysed hydrosilylation of pyridines, described by Harrod and Samuel *et al*.[9] In the catalytic cycle, the proposed 1,2-inserted pyridine species was further reduced with dihydrogen that was generated during the silane dehydrocoupling reaction before Si-N/Ti-H transdisposition occurred.

$(Cp^*_2LaH)_2$ reacts with an excess of pyridine (4-9 equiv) in benzene-d_6 to a mixture of 1,2-inserted product $Cp^*_2La(NC_5H_6)(C_5H_5N)$ (**5.4· C_5H_5N**), *ortho*-metallated pyridyl (**5.2· C_5H_5N**), and 1-(2,3,4-tetrahydropyridyl) (**5.3· C_5H_5N**) complexes in ratios depending on the amount of pyridine used (see Fig 5.2). Use of 9 equivalents of pyridine leads initially to an increase of the 1,2-insertion product **5.4· C_5H_5N** in the reaction mixture compared to the reaction with 4 equivalents. Further hydrogenation of the 1,2-insertion product **5.4· C_5H_5N** is apparently retarded by excess pyridine. Heating the reaction mixtures at 50°C for 7h resulted in a mixture of 3 complexes: $Cp^*_2La(NC_5H_8)(NC_5H_5)$ (**5.3· C_5H_5N**), $Cp^*_2La(\eta^1\text{-}2\text{-}NC_5H_4)(NC_5H_5)$ (**5.2· C_5H_5N**) and 2-hydro-2,2'-bipyridyl complex $Cp^*_2La((\eta^2\text{-}1\text{-}N_2C_{10}H_9)$[10] (**5.5**) in a 0.5:0.1:0.4

ratio. This implies that after a period of time the equilibrium 1:1 ratio of complexes **5.2· C_5H_5N** and **5.3· C_5H_5N** is achieved (see Fig 5.2), but that the *ortho*-metallated pyridyl **5.2· C_5H_5N** is not stable under the conditions applied and undergoes 1,2-insertion of pyridine to give the C-C coupled complex **5.5** (Fig 5.3, see for comparison Scheme 4.1 in § 4-3-2). Further heating at 50°C shows that $Cp^*_2La(NC_5H_8)(C_5H_5N)$ (**5.3· C_5H_5N**) is inert to further reaction while compound **5.5** yields a complicated reaction mixture with a broad resonance at δ 3.40, which is attributed to $Cp^*_2La(\eta^2$-2,2'-bipyridyl) (purple) (**5.6**, Fig. 5.3).[11]

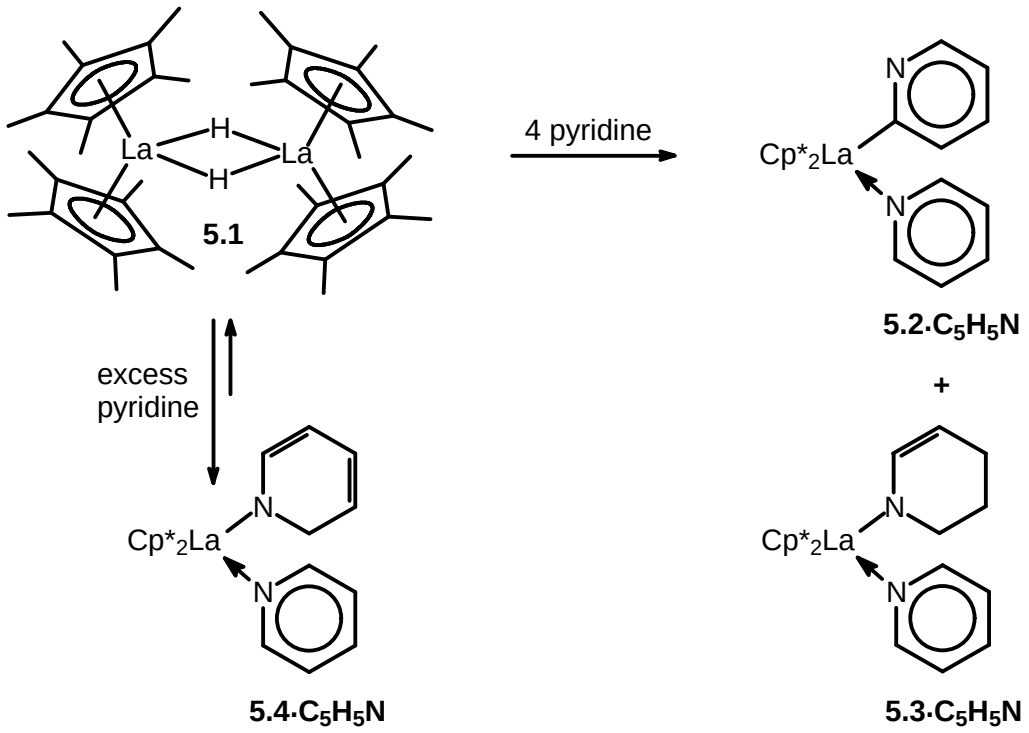


Figure 5.2. Reaction of $(Cp^*_2LaH)_2$ with 4-9 equivalents of pyridine.

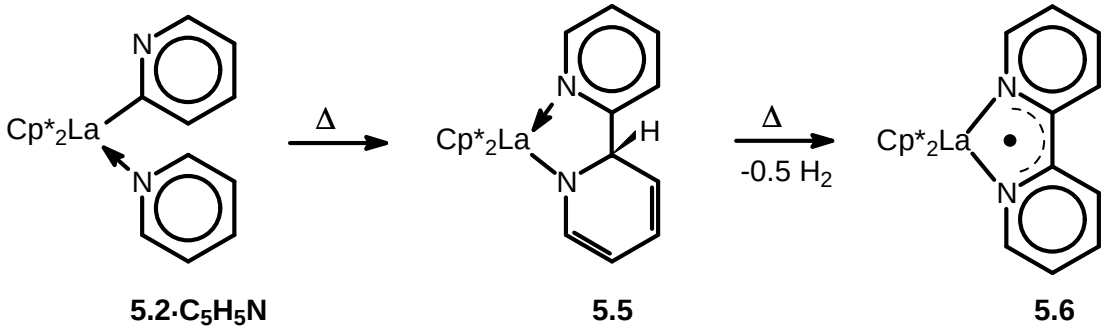
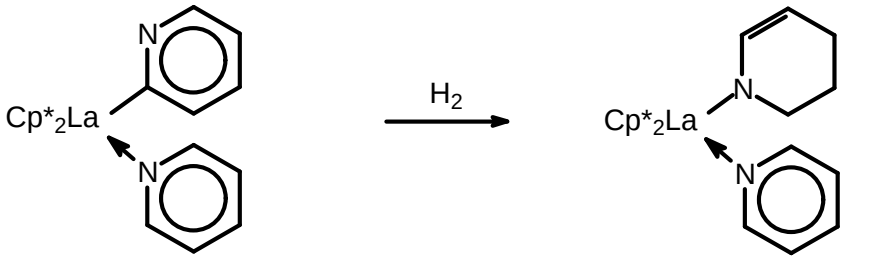


Figure 5.3. Thermolysis of $Cp^*_2La(\eta^1$-2-$NC_5H_4)(NC_5H_5)$ (**5.2· C_5H_5N**).

Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**), which is stable at room temperature for at least 1 day in benzene-d_6, can be quantitatively reduced to Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**) by exposing the solution to H_2 (4 atm, 1d, 20°C) (Fig 5.4).



5.2·C_5H_5N **5.3·C_5H_5N**

Figure 5.4. Hydrogenation of Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**).

5-2-2. Reactivity with Ethene and Pyridine. The reactions were carried out on NMR scale in benzene-d_6 and monitored by ^{1}H NMR spectroscopy at regular time intervals at 50°C. The 1:1 mixtures of Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**) and Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**) were generated *in situ* from (Cp*$_2$LaH)$_2$ (**5.1**) and pyridine as described above. In general, an excess of pyridine (4 mol) relative to the metal and ethene was added. When the ethene reacted completely the mixture was quenched with MeOH and analysed by GC/GC-MS. Product yields and ratios were determined by NMR spectroscopy and GC-MS analysis of hydrolysis products.

Addition of 10 equiv ethene to a 1:1 mixture of Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**) and Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**) in benzene-d_6 (1d, 50°C) without additional pyridine resulted after quenching in 2,6-diethylpyridine (66%), 2-ethyl-6-butyl-pyridine (28%) and 2-ethyl-6-hexyl-pyridine (6%). In addition, a small amount of polyethene was formed. Before quenching, the ^{1}H NMR spectrum showed a mixture of Cp*$_2$La(h^2-$CH(CH_3)$-2-NC_5H_3-6-Et) (**5.7**), C-C coupling products due to reaction of Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**) with pyridine and formation of *N*-ethyl-2,3,4-tetrahydropyridine (0.5 mol/La). Complex **5.7** showed for the La-$CH(CH_3)$-pyridyl moiety in the ^{1}H NMR spectrum a doublet (δ 1.60, J = 5.5 Hz, 3H) and a quartet (δ 2.94, J = 5.5 Hz, 1H), which compare well with the ^{1}H NMR resonances for the M-$CH(CH_3)$-Ar moiety in [$Me_2Si(NCMe_3)(OCMe_3)$]$_2$Y(h^2-$CH(CH_3)$-2-NC_5H_4)[12], Cp*$_2$Y(h^2-$CH(CH_3)$-2-NC_5H_4),[3] and {(MBP)Ti[h^2-$CH(CH_3)$-C_6H_4(*o*-CH_2NMe_2)]}$^+$ (MBP = 2,2'-methylenebis(4-methyl-6-*tert*-butylphenolate).[13] The formation of *N*-ethyl-2,3,4-tetrahydropyridine was deduced from its ^{1}H,^{1}H-COSY spectrum and GC-MS analysis.

The lanthanocene amide Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**) alone reacts with 10 equiv of ethene in benzene-d_6 (1d, 50°C) to give, after quenching, a similar product distribution

(2,6-diethylpyridine (79%), 2-ethyl-6-butyl-pyridine (16%) and 2-ethyl-6-hexyl-pyridine (5%)) as observed for reaction of the 1:1 mixture of **5.2· C_5H_5N** and **5.3· C_5H_5N** with ethene. In contrast, neither polyethene formation nor C-C coupling of pyridyl with pyridine were found.

Catalytic alkylation of pyridine with ethene by the Cp^*_2La-system was investigated using 1:1 mixtures of the h^1-pyridyl complex **5.2· C_5H_5N** and 1-(2,3,4-tetrahydropyridyl) complex **5.3· C_5H_5N** with an excess of pyridine (4 mol per La) and excess ethene. After 3d at 50°C all pyridine had been converted into 2,6-diethylpyridine (99%) and 2-ethyl-6-butyl-pyridine (1%).

Catalytic alkylation of pyridine with ethene to 2,6-diethylpyridine can take place via olefin insertion into an *ortho*-metallated pyridyl lanthanum complex followed by C-H bond activation of pyridine (or a pyridine derivative). Formation of $Cp^*_2La(h^2\text{-}2\text{-}C_5H_4N)$ in the 1:1 mixture of $Cp^*_2La(h^1\text{-}2\text{-}C_5H_4N)(C_5H_5N)$ (**5.2· C_5H_5N**) and $Cp^*_2La(NC_5H_8)(C_5H_5N)$ (**5.3· C_5H_5N**) can take place either by pyridine dissociation from $Cp^*_2La(h^1\text{-}2\text{-}C_5H_4N)(C_5H_5N)$ (**5.2· C_5H_5N**) or by insertion of ethene into the La-amide bond of $Cp^*_2La(NC_5H_8)(C_5H_5N)$ (**5.3· C_5H_5N**) upon which *N*-ethyl-2,3,4-tetrahydropyridine is eliminated. Marks *et al* showed that in lanthanocene mediated amino-olefin hydroamination/cyclization, the rate-determining step is the intramolecular insertion of the alkene function into the Ln-amide bond, which is followed by a rapid Ln-alkyl protonolysis.[14] It is not possible to exclude hydrogenolysis as a chain transfer mechanism in the catalytic alkylation of pyridine in the Cp^*_2La-system since C-C coupling products such as **5.5** (Fig 5.3) were observed and this implies that H_2 could be formed as well. However, when the 1-(2,3,4-tetrahydropyridyl) (**5.3· C_5H_5N**) alone was tested with excess ethene under the same conditions as the 1:1 mixture of (**5.2· C_5H_5N**) and (**5.3· C_5H_5N**), no products due to C-C coupling of pyridyl and pyridine were observed. It is also not very likely that the 1-(2,3,4-tetrahydropyridyl) complex **5.3· C_5H_5N** eliminates H_2. This suggests that bis-alkylation of pyridine to 2,6-diethylpyridine, 2-ethyl-6-butyl-pyridine and 2-ethyl-6-hexyl-pyridine can proceed without the presence of H_2 and confirms C-H bond activation of pyridine as an operative chain transfer mechanism.

5-3. Concluding Remarks

The bis(pentamethylcyclopentadienyl) lanthanum hydride, $(Cp^*_2LaH)_2$, readily metallates pyridine at the *ortho*-position with concomitant formation of H_2. In contrast to the yttrium analogue, the H_2 formed upon *ortho*-metallation of pyridine was effectively captured by the larger La to quantitatively form a 1:1 mixture of $Cp^*_2La(h^2\text{-}2\text{-}C_5H_4N)$ (**5.2**) and $Cp^*_2La(NC_5H_8)$ (**5.3**). $(Cp^*_2LaH)_2$ is more tending to give metallation of pyridine than the yttrium hydride $\{[Me_2Si(h^5\text{-}C_5Me_4)_2]Y(m\text{-}H)\}_2$, which quantitatively forms the 1,2-insertion product $[Me_2Si(h^5\text{-}C_5Me_4)_2]Y(NC_5H_6)(NC_5H_5)$ (**4.2a**).

The lanthanocene *ortho*-metallated pyridyl **5.2· C_5H_5N** is much more reactive than the yttrium analogue. Complex **5.2· C_5H_5N** was reduced in the presence of H_2 (4 atm, 1d, 20°C) to give the 1-(2,3,4-tetrahydropyridyl) Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**), while in the Cp*$_2$Y-system the same reaction only resulted in the formation of the 1,4-addition product.[3] In the catalytic alkylation of pyridine with ethene, lanthanum can in contrast to the yttrium congener easily coordinate and activate 2-ethylpyridine to give 2,6-diethylpyridine.

Since for the La analogue, compared to Y in Cp*$_2$Ln/pyridine/ethene system, a much higher reactivity is found toward C-H activation of pyridine and insertion of ethene resulting in the formation of higher alkylated pyridines such as 2-ethyl-6-butyl-pyridine and 2-ethyl-6-hexyl-pyridine, it would be interesting to extend the reactivity of Cp*$_2$La-system to other heterocycles. In chapter 3, in the Cp*$_2$Y/thiophene/ethene system, [Cp*$_2$Y(*m*-2-C_4H_3S)]$_2$ (**2.14**) slowly catalytically converts ethene into a mixture of thiophene-capped, saturated and olefinic ethene oligomers H(CH_2CH_2)$_n$(2-C_4H_3S) (n = 1-12), and saturated regular ethene oligomers H(CH_2CH_2)$_n$H and polymers. The effect on the reactivity of the Cp*$_2$Ln/thiophene/ethene system when yttrium is substituted for the larger lanthanum on the polymerisation of ethene and C-H bond activation of thiophene is described in the next chapter.

5-4. Experimental Section

***General Considerations*.** All compounds are extremely oxygen and moisture sensitive. Manipulations were therefore carried out under nitrogen using glove-box (Braun MB-200) and standard Schlenk techniques. Solvents were predried over Na wire and distilled from Na (toluene), K (THF) or Na/K alloy (ether, pentane, hexane, benzene) and stored under nitrogen. Benzene-d_6 and THF-d_8 were distilled from Na/K alloy and degassed prior to use. Pyridine was distilled from KOH under nitrogen before use. (Cp*$_2$LaH)$_2$[6] was prepared according to a published procedure. NMR spectra were recorded on a Gemini-200 (^{1}H: 200 MHz, ^{13}C: 50.3 MHz) or a Varian VXR-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances. GC analyses were performed on a HP 6890 instrument equipped with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC-MS spectra were recorded at 70 eV using a HP 5973 mass-selective detector attached to a HP 6890 GC as described above.

Reaction of (Cp*$_2$LaH)$_2$ with 2 equiv of pyridine. In an NMR tube pyridine (18 *m*mol, 1.5 *m*L) was added to (Cp*$_2$LaH)$_2$ (7.5 mg, 9.1 *m*mol) in benzene-d_6 (0.5 mL). A mixture of two complexes instantaneously formed in a 1:1 ratio: Cp*$_2$La(η^2-2-C_5H_4N) (**5.2**) and the partly hydrogenated complex Cp*$_2$La(NC_5H_8) (**5.3**). ^{1}H NMR (300 MHz, benzene-d_6) of **5.2**: δ 8.15 (d, 1H, $^3J_{HH}$ = 5.1 Hz, pyridyl H6); 7.85 (d, 1H, $^3J_{HH}$ = 7.3 Hz, pyridyl H); 7.13 (m, 1H, pyridyl H); 6.70 (m, 1H, pyridyl H); 1.84 (s, 30H, Cp*). ^{1}H NMR (300 MHz, benzene-d_6) of **5.3**: δ 6.56 (d, 1H, $^3J_{HH}$ = 5.1 Hz, pyridyl H); 3.49-3.09 (4s, 5H, pyridyl H); 2.06 (s, 30H, Cp*); 1.64 (s, 2H, pyridyl H). Addition of a second equivalent of pyridine (per La) instantly gave a 1:1 mixture of Cp*$_2$La(η^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**) and Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**). ^{1}H NMR (300 MHz, benzene-d_6) of **5.2· C_5H_5N**: δ 8.54 (s, 2H, pyridine *ortho* H); 8.48 (d, 1H, $^3J_{HH}$ = 4.8 Hz, pyridyl H); 8.03 (d, 1H, $^3J_{HH}$ = 6.6 Hz, pyridyl H); 7.25 (m, 1H, pyridyl H); 6.89

(m, 1H, pyridine *para* H); 6.81 (m, 1H, pyridyl H); 6.63 (m, 2H, pyridine *meta* H); 1.87 (s, 30H, Cp*). ^{1}H NMR of **5.3· C_5H_5N** (300 MHz, benzene-d_6, assignment of the resonances was aided by a ^{1}H-^{1}H COSY spectrum): δ 8.38 (s, 2H, pyridine *ortho* H); 6.84 (m, 1H, pyridine *para* H); 6.58 (m, 2H, *meta* H); 6.45 (d, 1H, $^3J_{HH}$ = 7.0 Hz, pyridyl H6); 4.51 (m, 1H, pyridyl H5); 3.69 (m, 2H, pyridyl H2); 2.55 (m, 2H, pyridyl H4); 2.04 (overlap with Cp*, pyridyl H3); 1.97 (s, 30H, Cp*).

Reaction of (Cp*$_2$LaH)$_2$ with 4 equiv of pyridine. In an NMR tube pyridine (36 ㎛mol, 3.0 ㎛L) was added to (Cp*$_2$LaH)$_2$ (7.5 mg, 9.1 ㎛mol) in benzene-d_6 (0.5 mL). After 1d at room temperature and 7h at 50ºC a mixture was obtained containing Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**), 2-hydro-2,2'-bipyridyl complex Cp*$_2$La(h^2-1-$N_2C_{10}H_9$) (**5.5**) and Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**) in a 0.5: 0.4: 0.1 ratio. After 2d at 50ºC a complicated reaction mixture resulted with several resonances in the vinylic (4-6 ppm) and aromatic (7-9 ppm) region and a broad resonance at 3.40 ppm. ^{1}H NMR (300 MHz, benzene-d_6) of **5.5**: δ 7.65 (d, 1H, $^3J_{HH}$ = 5.5 Hz, 2,2'-bipyridyl H); 7.02 (d, 1H, $^3J_{HH}$ = 8.1 Hz, 2,2'-bipyridyl H); 6.86 (m, 1H, overlap with pyridine, 2,2'-bipyridyl H); 6.53-6.44 (m, 3H, 2,2'-bipyridyl H); 5.60 (t, 1H, $^3J_{HH}$ = 5.7 Hz, 2,2'-bipyridyl H); 5.26 (s, 1H, 2,2'-bipyridyl H); 4.46 (d, 1H, overlap with H5 of **5.3· C_5H_5N**, 2,2'-bipyridyl H); 1.88 and 1.84 (2s, 30H, Cp*).

***Hydrogenation of* Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (5.2· C_5H_5N).** Addition of H_2 (ca. 4 atm) to a 1:1 benzene-d_6 (0.5 mL) solution of Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**) and Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**), prepared via the procedure described above using (Cp*$_2$LaH)$_2$ (7.5 mg, 9.1 ㎛mol) and pyridine (36 ㎛mol, 3.0 ㎛L), resulted after 1d at room temperature in the quantitative formation of **5.3· C_5H_5N**. The 1,2-insertion product Cp*$_2$La(NC_5H_6)(C_5H_5N) (**5.4· C_5H_5N**) was observed as an intermediate after 15 min. ^{1}H NMR (300MHz, benzene-d_6) of **5.4· C_5H_5N**: δ 8.44 (s, 2H, pyridine *ortho* H); 6.86 (m, 1H, pyridine *para* H); 6.76 (d, 1H, $^3J_{HH}$ = 6.2 Hz, pyridyl H); 6.60 (m, 2H, pyridine *meta* H); 6.49 (m, 1H, pyridyl H); 5.38 (t, 1H, $^3J_{HH}$ = 5.7 Hz, pyridyl H); 4.97 (m, 1H, pyridyl H); 4.16 (d, 1H, $^3J_{HH}$ = 4.4 Hz, pyridyl H); 1.93 (s, 30H, Cp*).

Reaction of 1:1 mixture of* Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (5.2· C_5H_5N) and Cp*$_2$La(NC_5H_8)(C_5H_5N) (5.3· C_5H_5N) *with excess ethene. Addition of ethene (10 equiv/La) to a 1:1 mixture of Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N) (**5.2· C_5H_5N**) and Cp*$_2$La(NC_5H_8)(C_5H_5N) (**5.3· C_5H_5N**) in benzene-d_6 (0.5 mL) (prepared via the procedure described above using (Cp*$_2$LaH)$_2$ (15 mg, 18 ㎛mol) and pyridine (5.9 ㎛L, 72 ㎛mol)) gave after 0.5h at 50°C formation of a white fluffy precipitate (polyethene), ethene was not fully consumed. After 1d at 50°C the ^{1}H NMR spectrum showed Cp*$_2$La(h^2-$CH(CH_3)$-2-NC_5H_3-6-Et) (**5.7**), a mixture of C-C coupling products due to reaction of pyridine with Cp*$_2$La(h^1-2-C_5H_4N)(C_5H_5N), 2,6-diethylpyridine and CH_3CH_2(1-NC_5H_8), no free pyridine was left. GC/GC-MS after quenching with MeOH showed the bis-alkylated pyridines: 2,6-diethylpyridine (66% (GC); m/z = 134), 2-ethyl-6-butyl-pyridine (28% (GC); m/z = 162) and 2-ethyl-6-hexyl-pyridine (6% (GC); m/z = 190) and 1-ethyl-2,3,4-tetrahydropyridine (m/z = 111). ^{1}H NMR of **5.7** (300 MHz, benzene-d_6): δ 6.89 (t, 1H, $^3J_{HH}$ = 7.9 Hz, pyridyl H4); 6.46 (d, 1H, $^3J_{HH}$ = 8.8 Hz, pyridyl H3 or H5); 5.80 (d, 1H, $^3J_{HH}$ = 6.6 Hz, pyridyl H5 or H3); 2.94 (q, 1H, $^3J_{HH}$ = 5.5 Hz, La*CH*(CH_3)); 1.96 (s, 30H, Cp*); 1.60 (d, 3H, $^3J_{HH}$ = 5.5 Hz, LaCH(*CH*$_3$)); 0.89 (t, 3H, $^3J_{HH}$ = 7.0 Hz, CH_2*CH*$_3$). *CH*$_2$$CH_3$ resonance not observed due to overlap with Cp* resononances. ^{1}H NMR of *N*-ethyl-2,3,4-tetrahydropyridine (300 MHz, benzene-d_6, assignment of the resonances was aided by a ^{1}H-^{1}H COSY spectrum): δ 6.95 (d, 1H, $^3J_{HH}$ = 5.9 Hz, pyridine H6); 6.45 (m, 2H, pyridine H4); 5.24 (t, 1H, pyridine H5); 4.76 (dd, 2H, $^3J_{HH}$ = 8.4 Hz and 8.4 Hz, pyridine H3); 3.76 (m, 2H, pyridine H2); 2.37 (overlap, CH_3*CH*$_2$N); 1.25 (overlap with 2,6-diethylpyridine, *CH*$_3$$CH_2$N).

Reaction of Cp*$_2$La(NC$_5$H$_8$)(C$_5$H$_5$N) (5.3· C$_5$H$_5$N***) with excess ethene.*** To an NMR tube with a benzene-d_6 (0.5 mL) solution of complex **5.3· C$_5$H$_5$N** (18 ㎛mol) was added ethene (180 ㎛mol) at -196°C. The reaction was monitored by NMR spectroscopy at 50°C for 1d. The reaction mixture was subsequently quenched with MeOH and analysed by GC. The product distribution is similar to that found for addition of ethene (10 equiv/La) to a 1:1 mixture of Cp*$_2$La(h^1-2-C$_5$H$_4$N)(C$_5$H$_5$N) (**5.2· C$_5$H$_5$N**) and Cp*$_2$La(NC$_5$H$_8$)(C$_5$H$_5$N) (**5.3· C$_5$H$_5$N**): 2,6-diethylpyridine (79%), 2-ethyl-6-butyl-pyridine (16%) and 2-ethyl-6-hexyl-pyridine (5%). No formation of polyethene and C-C coupling products due to reaction of pyridine with Cp*$_2$La(h^1-2-C$_5$H$_4$N)(C$_5$H$_5$N) (**5.2· C$_5$H$_5$N**) were observed.

Reaction of 1:1 mixture of* Cp*$_2$La(h^1-2-C$_5$H$_4$N)(C$_5$H$_5$N) (5.2· C$_5$H$_5$N) and Cp*$_2$La(NC$_5$H$_8$)(C$_5$H$_5$N) (5.3· C$_5$H$_5$N) *with 4 equiv of pyridine and excess ethene at 50ºC. In an NMR tube ethene (440 ㎛mol) was condensed onto a 1:1 mixture of Cp*$_2$La(h^1-2-C$_5$H$_4$N)(C$_5$H$_5$N) (**5.2· C$_5$H$_5$N**) and Cp*$_2$La(NC$_5$H$_8$)(C$_5$H$_5$N) (**5.3· C$_5$H$_5$N**) (prepared via the procedure described above using (Cp*$_2$LaH)$_2$ (15 mg, 18 ㎛mol) and pyridine (17.7 ㎕L, 216 ㎛mol)) in benzene-d_6 (0.5 mL) at -196°C. The progress of the reaction was followed by ^{1}H NMR spectroscopy. After 3d at 50°C the ^{1}H NMR spectrum showed that ethene had been fully converted with pyridine into 2,6-diethylpyridine. The volatiles were vacuum transferred and GC/GC-MS showed 2,6-diethylpyridine (99%) and 2-ethyl-6-butyl-pyridine (1%).

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(11) The broad resonance at δ 3.40 is assigned to Cp*$_2$La(h^2-2,2'-bipyridyl) in analogy to the crystallographically characterised Cp*$_2$Y(h^2-2,2'-bipyridyl) (**4.1h**, δ 4.15).

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