From *P*-Metalated *trans*-Iminodiphosphanes to *N*-Metalated *cis*-Iminodiphosphanes: An Unprecedented Rearrangement

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The reaction of chlorophosphanes with azazirconacyclopentenes provides an unique way to cyclic *P*-metalated *trans*-iminodiphosphanes, which rearrange to give unprecedented *N*-metalated *cis*-iminodiphosphanes.

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Introduction

The search for new derivatives incorporating phosphorus and nitrogen continues to receive considerable attention due to the versatility of these ligands (combination of hard and soft donor atoms) towards complexation. Classical nitrogen ligands (amine, pyridine, oxazoline, quinoline, pyrazole etc.) and classical phosphanes constitute the coordinating skeleton of the majority of these P,N species.[1] Similarly, β- or γ-iminophosphanes in which the imine acts as a weak π-acceptor and the phosphane as a good σ-donor are also being used more and more frequently. Palladium(II) complexes of these phosphorus-nitrogen mixed donors ligands have been found, for example, to be efficient catalysts for the Heck reaction,[2] for the carbostannylation of alkynes,[3] for the copolymerisation of CO/ethylene and CO/norbornylene[4] or for allylic alkylation.[5]

In contrast, very few iminodiphosphanes, namely the linear *trans*-*C*-phosphanyl, *N*-phosphanyl imines **I**, are known[6] and no complexes of this potential ligand or free or complexed *trans* or *cis* cyclic analogs of these derivatives have been described.

We report herein a powerful and versatile one-pot synthesis of cyclic *P*-metalated *trans*-iminodiphosphanes from azazirconacyclopentenes and chlorophosphanes and the quite unusual rearrangement of the former derivatives to cyclic *N*-metalated *cis*-iminodiphosphanes.

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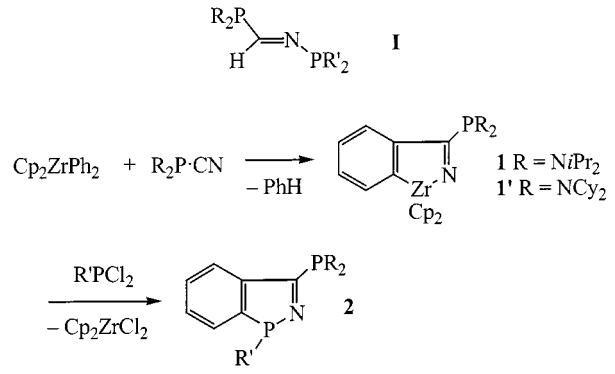
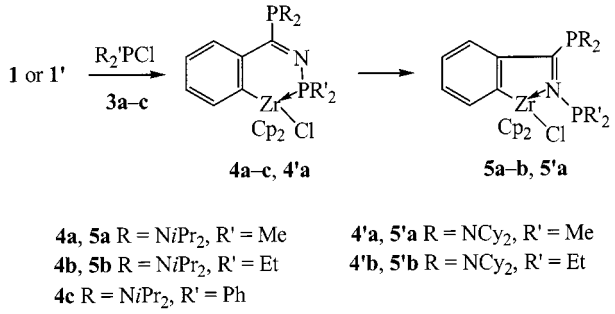
Results and Discussion

We have already reported that the thermolysis of diphenylzirconocene in the presence of bis(amino)cyanophosphane leads to the formation of the azazirconacyclopentenes **1** and **1′**. These complexes can then be reacted with various dichlorophosphanes to give the 1,2-azaphosphindoles **2** and Cp_2ZrCl_2 (Scheme 1).[7] The same reaction performed with chlorophosphanes R'_2PCl (**3a−c: a** R′ = Me, **b** R′ = Et, **c** R′ = Ph) instead of dichlorophosphanes proceeds differently. In this case no exchange reaction takes place. Indeed, the addition of chlorophosphanes **3a−c** to **1** (R = N*i*Pr$_2$) in toluene at −20 °C affords the unexpected cyclic *P*-metalated *trans* (the two phosphanyl groups) iminodiphosphanes **4a−c** (Scheme 2). The reaction can be monitored by ^{31}P NMR spectroscopy which shows the disappearance of the signal due to **1** (δ = 45) and the appearance of two doublets at δ = 74.0 [P(NiPr$_2$)$_2$] and 67.5 (PMe$_2$) ($J_{P,P}$ = 6.9 Hz) for **4a**, δ = 78.4 (PEt$_2$) and 74.1 [P(NiPr$_2$)$_2$] ($J_{P,P}$ = 8 Hz) for **4b** and δ = 78.8 [P(NiPr$_2$)$_2$] and 63.3 (PPh$_2$) ($J_{P,P}$ = 8.6 Hz) for **4c**. The direct complexation of the R$_2$P phosphanyl group to the 16e$^-$ zirconium moiety is shown in the ^{1}H NMR spectrum by the presence of two doublets for the Cp groups due to the coupling between phosphorus and the Cp protons ($1.9 < J_{H,P} < 2.2$ Hz). Such $J_{H,P}$ values are characteristic of compounds with a P→ZrCp$_2$ dative bond.[8] The formation of **4a−c** can be viewed as the 1,2-addition of the chlorophosphane to the zirconium-nitrogen covalent bond of **1** initiated by the halophilicity of the zirconium moiety and the nucleophilicity of the cyclic imino-nitrogen bond, followed by direct complexation of the phosphanyl group at zirconium. However, the resulting *P*-metalated *trans*-iminodiphosphanes appear to be the kinetic products of the reaction. In solution at room temperature, **4a−b** afford the thermodynamically favored complexes **5a−b** (Scheme 2). Such an evolution de-

pends strongly on the nature of the phosphanyl group linked to zirconium: it takes 24 h for the transformation **4a** → **5a** and 24 days for **4b** → **5b**. The evolution of **4c** gave numerous unidentified products.



Scheme 1



Scheme 2

These transformations can be monitored by ^{31}P NMR spectroscopy. As an example, the two doublets for **4a** disappeared and two new doublets appeared at δ = 74.0 (PMe_2) and 41.7 [$P(NiPr_2)_2$] ($J_{P,P}$ = 6.2 Hz) for **5a**. As expected, only a singlet is detected for the Cp groups in the ^1H NMR spectrum, strongly indicating that the phosphanyl group is not linked to the Cp_2Zr unit. A similar observation can be made for the evolution of **4b** into **5b**, with an analogous characteristic shielding effect in the ^{31}P NMR spectrum for the $P(NiPr_2)_2$ group (Δδ = 30.1 ppm).

The stability of *P*-metalated *trans*-iminodiphosphanes and their transformation to the corresponding *N*-metalated *cis*-iminodiphosphanes depends also on the nature of the substituents directly linked to the exocyclic phosphorus atom. Thus, treatment of the azazirconacyclopentene **1′** with chlorodimethylphosphane **3a** at −20 °C leads to the unstable *P*-metalated *trans*-iminodiphosphane **4′a** which was only characterized by ^{31}P NMR spectroscopy {doublets at δ = 81.3 [$P(N(Cy)_2$] and 64.9 (PMe_2) with $J_{P,P}$ = 7.0 Hz}. The evolution of **4′a** is fast (a few hours at room temperature) and leads to the thermodynamically stable complex **5′a** which was fully characterized by NMR spectroscopy, mass spectrometry and elemental analysis. In marked contrast the same reaction performed with **1′** and **3b** allowed us to isolate the *P*-metalated iminodiphosphane **4′b** {$\delta^{31}P$ = 80.7 [$P(N(Cy)_2]_2$ and 77.1 (PEt_2) ($J_{P,P}$ = 8.5 Hz)}. The formation of a dative bond between the Et_2P group and Zr is again confirmed by the presence in the ^1H NMR spectrum of the characteristic two doublets for the Cp groups at δ = 5.87 and 6.25 with $J_{H,P}$ = 2.0 and 1.9 Hz. The full transformation of **4′b** to **5′b** occurs at room temperature after 6 h (Scheme 2). Here again a typical shielding effect is observed for the $P[N(Cy)_2]_2$ group when moving from the six- to the five-membered ring (Δδ = 34.6 ppm).

Attempts to grow suitable crystals for an X-ray diffraction study have so far been unsuccessful.

Conclusion

The treatment of cyanophosphanes successively with diphenylzirconocene and then a chlorophosphane allows the clean reduction of the cyano group to an imino group, the formation of cyclic *P*-metalated *trans*-iminodiphosphanes and their unprecedented rearrangement to cyclic *N*-metalated *cis*-iminodiphosphanes. Such a sequence of reactions can be performed as a one-pot process.

Investigations concerning the generality of this unique synthetic methodology, studies concerning the complexation of the *N*-metalated *cis*-iminodisphosphanes and the use of the resulting complexes in catalytic processes are currently underway.

Experimental Section

General: All reactions were carried out under argon using standard Schlenk techniques and vacuum-line manipulations. All solvents were dried degassed and distilled before use. A Perkin−Elmer 1725X spectrometer was used to record the FT-IR spectra. NMR spectra were recorded on Bruker AC80, AC200, or AM250 spectrometers for ^1H, ^{13}C and ^{31}P NMR, with $SiMe_4$ and H_3PO_4, as references. The assignment of the signals in the ^{13}C NMR spectrum was done using Jmod, two dimensional HMBC and HMQC, broad band or CW ^{31}P decoupling experiments when necessary.

Compound 4a: Chlorodimethylphosphane (0.079 g, 64.8 μL, 0.82 mmol) was added to a solution of azazirconacyclopentene **1** (0.455 g, 0.82 mmol) in toluene at −20 °C. The mixture was stirred at room temperature for 30 min, and then evaporated to dryness. The resulting solid residue was extracted with pentane (2 × 20 mL) and filtered. The volatiles were removed from the solution to give **4a** as a yellow solid in 92% yield (0.491 g). ^1H NMR (C_6D_6): δ = 0.62 (d, $J_{H,P}$ = 5.7 Hz, 3 H, CH_3), 1.01 (d, $J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 1.14 (d, $J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 1.31 (d, $J_{H,P}$ = 4.2 Hz, 3 H, CH_3), 3.4 (sept, $J_{H,H}$ = 6.7 Hz, 4 H, CH), 5.74 (d, $J_{H,P}$ = 2.0 Hz, 5 H, CH_{Cp}), 6.09 (d, $J_{H,P}$ = 1.9 Hz, 5 H, CH_{Cp}), 7.14 (m, 1 H, CH_{arom}), 7.53 (m, 1 H, CH_{arom}), 7.89 (d, $J_{H,P}$ = 1.1 Hz, $J_{H,H}$ = 7.7 Hz, CH_{arom}), 8.5 (d, $J_{H,H}$ = 7.7 Hz, CH_{arom}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 15.4 (d, $J_{C,P}$ = 16.7 Hz, CH_3P), 17.7 (d, $J_{C,P}$ = 16.6 Hz, CH_3P), 25.4 (d, $J_{C,P}$ = 11.1 Hz, CH_3), 26.6 (d, $J_{C,P}$ = 8.5 Hz, CH_3), 26.8 (d, $J_{C,P}$ = 10.6 Hz, CH_3), 51.4 (d, $J_{C,P}$ = 8 Hz, CH), 58.4 (d, $J_{C,P}$ = 11.9 Hz, CH), 109.8 (s, CH_{Cp}), 109.9 (s, CH_{Cp}), 124.1, 125.2, 137.6 (s, CH_{arom}), 156.1 (dd, $J_{C,P}$ = 7.5 Hz, $J_{C,P}$ = 20.9 Hz, C_{arom}), 172.9 (dd, $J_{C,P}$ = 26.9 Hz, C_{arom}), 204.3 (dd, $J_{C,P}$ = 12.2 Hz, $J_{C,P}$ = 8.9 Hz, C=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 74.0 [d, $J_{P,P}$ = 6.9 Hz, $P(NiPr_2)_2$], 67.5 (d, $J_{P,P}$ = 6.9 Hz,

PMe_2). $C_{31}H_{48}ClN_3P_2Zr$ (651.36): calcd. C 57.16, H 7.42, N 6.45; found C 57.01, H 7.38, N 6.39.

Compound 4b: Same experimental procedure as for **4a** starting from **1** (0.416 g, 0.75 mmol) and chlorodiethylphosphane (0.094 g. 91 μL, 0.75 mmol); **4b** was obtained in 88% yield (0.484 mg). ^1H NMR (C_6D_6): δ = 0.65 (dt, $J_{H,H}$ = 7.5 Hz, $J_{H,P}$ = 18.8 Hz, 3 H, CH_3, Et), 0.68 (dt, $J_{H,H}$ = 7.7 Hz, $J_{H,P}$ = 13.3 Hz, 3 H, CH_3, Et), 1.10 (d, $J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 1.20 (d, $J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 2.20 (m, 4 H, CH_2), 3.50 (sept, $J_{H,H}$ = 6.7 Hz, 4 H, CH), 5.94 (d, $J_{H,P}$ = 2.0 Hz, 5 H, $CH_{C,P}$), 6.17 (d, $J_{C,P}$ = 2.2 Hz, 5 H, CH_{Cp}), 7.30 (m, 1 H, CH_{arom}), 8.00 (dd, $J_{H,P}$ = 1.2 Hz, $J_{H,H}$ = 7.7 Hz, 1 H, CH_{arom}), 8.21 (d, $J_{H,H}$ = 7.9 Hz, 1 H, CH_{arom}), 8.64 (d, $J_{H,H}$ = 7.6 Hz, 1 H, CH_{arom}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 8.2 (d, $J_{C,P}$ = 8.1 Hz, CH_2CH_3), 18.5 (d, $J_{C,P}$ = 8.8 Hz, CH_2CH_3), 25.5 (d, $J_{C,P}$ = 12.1 Hz, CH_3), 27.6 (d, $J_{C,P}$ = 12.1 Hz, CH_3), 51.5 (d, $J_{C,P}$ = 8.9 Hz, CH), 58.7 (d, $J_{C,P}$ = 12.6 Hz, CH), 110.5 (s, CH_{Cp}), 109.8 (s, CH_{Cp}), 124.2, 126.6, 128, 146.5 (s, CH_{arom}), 146.2 (d, $J_{C,P}$ = 3.5 Hz, CH), 173.7 (d, $J_{C,P}$ = 27.1 Hz, C_{arom}), 205.1 (dd, $J_{C,P}$ = 10.0 Hz, $J_{C,P}$ = 9.8 Hz, C=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 78.4 (d, $J_{P,P}$ = 8.0 Hz, PEt_2), 74.1 [d, $J_{P,P}$ = 8.0 Hz, $P(NiPr_2)_2$]. $C_{33}H_{52}ClN_3P_2Zr$ (679.4): calcd. C 58.34, H 7.71, N 6.18; found C 58.16, H 7.60, N 6.04.

4c: ^1H NMR (C_6D_6): δ = 1.09 (d, $J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 1.20 (d, $J_{H,H}$ = 6.7 Hz, 12 H, CH_3), 3.40 (sept $J_{H,H}$ = 6.7 Hz, 4 H, CH), 6.12 (d, $J_{H,P}$ = 1.9 Hz, 5 H, Cp), 6.17 (d, $J_{H,P}$ = 2.1 Hz, 5 H, Cp), 7.1−7.6 (m, 12 H, CH_{arom}), 8.22 (m, 1 H, CH_{arom}), 8.83 (d, $J_{H,H}$ = 6.9 Hz, 1 H, CH_{arom}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.4 (d, $J_{C,P}$ = 5.7 Hz, CH_3), 24.2 (d, $J_{C,P}$ = 5.8 Hz, CH_3), 49.5 (d, $J_{C,P}$ = 12.0 Hz, CH), 111.6 (s, CH, Cp), 124.4 (d, $J_{C,P}$ = 24.3 Hz, C_{ipso}), 124.9 (d, $J_{C,P}$ = 23.8 Hz, C_{ipso}), 127.6, 127.8, 128.0, 128.4 (s, CH_{arom}, PPh), 124.1, 126.7, 138.6 (s, CH_{arom}), 178.9 (s, *C*−C=N), 199.9 (dd, $J_{C,P}$ = 12 Hz, $J_{C,P}$ = 9 Hz, C=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 78.8 [d, $J_{P,P}$ = 8.6 Hz, $P(NiPr_2)_2$], 63.3 (d, $J_{P,P}$ = 8.6 Hz, PPh_2). $C_{41}H_{52}ClN_3P_2Zr$ (775.50): calcd. C 63.50, H 6.76, N 5.42; found C 63.31, H 6.51, N 5.34.

Compound 5a: Evolution of **4a** at room temperature in toluene for 24 h gave rise quantitatively to **5a**. ^1H NMR (C_6D_6): δ = 1.20 (d, $J_{H,H}$ = 6.6 Hz, 12 H, CH_3), 1.24 (d, $J_{H,H}$ = 6.6 Hz, 12 H, CH_3), 1.27 (d, $J_{H,P}$ = 3.0 Hz, 6 H, CH_3P), 3.30 (m, 4 H, CH), 5.80 (s, 10 H, CH_{Cp}), 7.0−7.2 (m, 2 H, CH_{arom}), 7.52 (m, 1 H, CH_{arom}), 8.41 (dd, $J_{H,H}$ = 7.8 Hz, $J_{H,P}$ = 0.9 Hz, 1 H, CH_{arom}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 14.0 (dd, $J_{C,P}$ = 5 Hz, $J_{C,P}$ = 23.0 Hz, CH_3), 24.3 (d, $J_{C,P}$ = 5.4 Hz, CH_3), 24.5 (d, $J_{C,P}$ = 5.8 Hz, CH_3), 48.1 (d, $J_{C,P}$ = 10.4 Hz, CH), 112.2 (s, CH_{Cp}), 112.6 (s, CH_{Cp}), 124.9, 125.7, 126.8, 139.0 (s, CH_{arom}), 145.1 (dd, $J_{C,P}$ = 41.9 Hz, $J_{C,P}$ = 17.8 Hz, *C*−C=N), 156.1 (dd, $J_{C,P}$ = 4.6 Hz, $J_{C,P}$ = 17.8 Hz, C-Zr), 185.8 (dd, $J_{C,P}$ = 15.7 Hz, $J_{C,P}$ = 15.7 Hz, C=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 74.0 (d, $J_{P,P}$ = 6.2 Hz, PMe_2), 41.7 [d, $J_{P,P}$ = 6.2 Hz $P(NiPr_2)_2$]. $C_{31}H_{48}ClN_3P_2Zr$ (651.4): calcd. C 57.16, H 7.42, N 6.45; found C 56.97, H 7.35, N 6.31.

Compound 5b: The evolution of **4b** to **5b** was very slow (24 days) and the formation of **5b** (NMR yield: 60%) was accompanied by that of numerous unidentified by-products. **5b** was only characterized by ^{31}P NMR [δ = 86.9 (d, $J_{P,P}$ = 6.5 Hz), 43.9 (d, $J_{P,P}$ = 6.5 Hz)].

Compounds 4′a and 5′a: Chlorodimethylphosphane (0.068 g, 56 μL, 0.7 mmol) was added to a solution of azazirconacyclopentene **1′** (0.364 g, 0.7 mmol) in toluene at −20 °C. The mixture was stirred at room temperature for 15 min and then evaporated to dryness. The resulting solid residue was extracted with pentane (20 mL) and filtered. The volatiles were removed from the solution to give a mixture of **4′a** and **5′a** in a 4:1 ratio. Compound **4′a** was only characterized by ^{31}P NMR: δ = 81.3 (d, $J_{P,P}$ = 7.0 Hz, $P(NCy_2)_2$, 64.9 (d, $J_{P,P}$ = 7.0 Hz, PMe_2). Evolution of **4′a** to **5′a** is fast and complete within 24 h at room temperature.

5′a: ^1H NMR (C_6D_6): δ = 1.06 (d, $J_{H,P}$ = 3.2 Hz, 3 H, CH_3), 1.29 (d, $J_{H,P}$ = 3.2 Hz, 3 H, CH_3), 1.39−2.11 (m, 40 H, CH_2), 3.21−3.30 (m, 4 H, CHN), 6.00 (s, 10 H, CH_{Cp}), 6.45−7.20 (m, 2 H, CH_{arom}), 7.51 (d, $J_{H,H}$ = 6.5 Hz, 1 H, CH_{arom}), 8.51 (d, $J_{H,H}$ = 5.5 Hz, 1 H, CH_{arom}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.6 (d, $J_{C,P}$ = 23.6 Hz, CH_3), 13.7 (d, $J_{C,P}$ = 23.6 Hz, CH_3), 26.0, 26.8, 27.0 (s, CH_2), 35.0 (br. s, CH_2), 57.6 (d, $J_{C,P}$ = 9.4 Hz, CH), 57.9 (d, $J_{C,P}$ = 8.5 Hz, CH), 113.8 (s, CH, C_{Cp}), 125.6, 125.8, 126.7, 138.6 (s, CH_{arom}), 145.3 (dd, $J_{C,P}$ = 43.4 Hz, $J_{C,P}$ = 21.8 Hz, CCN), 155.5 (dd, $J_{C,P}$ = 3.7 Hz, $J_{C,P}$ = 17.7 Hz, C-Zr), 185.6 (dd, $J_{C,P}$ = 17.4 Hz, $J_{C,P}$ = 17.4 Hz, C=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 70.2 (d, $J_{P,P}$ = 8.4 Hz, PMe_2), 40.3 [d, $J_{P,P}$ = 8.4 Hz, $P(NCy_2)_2$]. $C_{43}H_{64}ClN_3P_2Zr$ (811.6): calcd. C 63.63, H 7.95, N 5.18; found C 63.41, H 7.89, N 5.09.

Compound 4′b: Chlorodiethylphosphane (0.077 g, 76 μL, 0.62 mmol) was added to a solution of azazirconacyclopentene **1′** (0.323 g, 0.62 mmol) in toluene at −20 °C. The mixture was stirred at room temperature for 20 min and then the solvents evaporated to dryness. The resulting solid residue was extracted with pentane (2 × 20 mL) and filtered. The volatiles were removed from the solution to give **4′b** as an orange-yellow solid in 68% yield (0.272 mg). ^1H NMR (C_6D_6): δ = 1.57 (t, $J_{H,H}$ = 3.1 Hz, 3 H, CH_3), 1.64 (t, $J_{H,H}$ = 3.1 Hz, 3 H, CH_3), 2.15 (dq, $J_{H,P}$ = $J_{H,H}$ = 3.1 Hz, 4 H, CH_2), 1.20−2.10 (m, 40 H, CH_2), 2.95 (br. s, 4 H, CHN)5.87 (d, $J_{H,P}$ = 2.0 Hz, 5 H, CH_{Cp}), 6.25 (d, $J_{H,P}$ = 1.9 Hz, 5 H, CH_{Cp}), 7.02−7.40 (m, 2 H, CH_{arom}), 7.70 (m, 1 H, CH_{arom}), 8.50 (d, $J_{H,H}$ = 9.2 Hz, 1 H, CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 10.3 (s, CH_3), 10.6 (s, CH_3), 20.9 (d, $J_{C,P}$ = 11.7 Hz, CH_2), 26.4, 27.5, 27.7 (s, CH_2), 35.7 (br. s, CH_2), 56.6 (d, $J_{C,P}$ = 9.2 Hz, CHN), 58.5 (d, $J_{C,P}$ = 8.2 Hz, CHN), 59.6 (d, $J_{C,P}$ = 8.3 Hz, CHN), 62.0 (d, $J_{C,P}$ = 8.4 Hz, CHN), 110.2 (s, CH_{Cp}), 110.4 (s, CH_{Cp}), 124.7, 125.6, 126.0, 137.4 (s, CH_{arom}), 147.1 (s, C_{arom}), 172.8 (d, $J_{C,P}$ = 25.7 Hz, C_{arom}), 205.0 (dd, $J_{C,P}$ = 12.73 Hz, $J_{C,P}$ = 9 Hz, C=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 80.7 (d, $J_{P,P}$ = 8.5 Hz, PEt_2), 77.1 [d, $J_{P,P}$ = 8.5 Hz, $P(NCy_2)_2$]. $C_{45}H_{68}ClN_3P_2Zr$ (839.67): calcd. C 64.37, H 8.16, N 5.00; found C 64.21, H 7.98, N 4.92.

Compound 5′b: Compound **4′b** evolves quickly (6 h, room temperature) to give **5′b**. ^1H NMR (C_6D_6): δ = 0.92 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 0.99 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.31−1.95 (m, 40 H, CH_2), 3.25 (q, $J_{H,H}$ = 7.0 Hz, 4 H, CH_2), 3.15−3.35 (m, 4 H, CH), 5.81 (s, 10 H, CH_{Cp}), 7.02−7.20 (m, 2 H, CH_{arom}), 7.60 (d, $J_{H,H}$ = 6.8 Hz, 1 H, CH_{arom}), 8.55 (d, $J_{H,H}$ = 8.7 Hz, 1 H, CH_{arom}). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 10.1 (d, $J_{C,P}$ = 14.0 Hz, CH_3), 21.0 (d, $J_{C,P}$ = 12.7, CH_2), 26.7, 27.5, 27.7, 35.7 (s, CH_2), 58.5 (br. s, CH), 114.6 (s, CH_{Cp}), 125.4, 125.6, 126.4, 138.2, (s, CH_{arom}), 146.0 (dd, $J_{C,PN}$ = 41.6 Hz, $J_{C,PEt}$ = 21.4 Hz, C_{arom}), 154.1 (dd, $J_{C,P}$ = 5.3 Hz, $J_{C,P}$ = 19.2 Hz, C_{arom}), 186.8 (dd, $J_{C,P}$ = 17.4 Hz, C=N). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 83.2 (d, $J_{P,P}$ = 6.9 Hz, PEt_2), 42.5 (d, $J_{P,P}$ = 6.9 Hz, $P(NCy_2)_2$. $C_{45}H_{68}ClN_3P_2Zr$ (839.67): calcd. C 64.37, H 8.16, N 5.00; found C 64.17, H 7.82, N 4.86.

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