Heterocyclic Carbenes

A Stable P-Heterocyclic Carbene**

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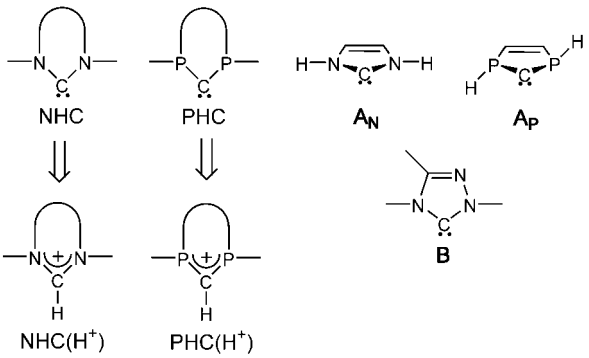
The availability of catalysts that can perform specific transformations is critical for both industry and academia. Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of a variety of systems. Recently, spectacular achievements have been made using cyclic diaminocarbenes, usually called N-heterocyclic carbenes (NHCs; Scheme 1), as ligands for transition-metal-based catalysts,[1–3] and even as catalysts in their own right.[4,5] Compared to most classical ligands, such as phosphanes, NHCs bind more strongly to metal centers (thus avoiding the necessity for the use of excess ligand), and the resulting NHC-based catalysts are less sensitive to air and moisture, and have proven remarkably resistant to oxidation.[6]



Scheme 1. N- and P-Heterocyclic carbenes and their classical precursors.

It is noteworthy that although NHC–transition-metal complexes have been known since the Sixties,[7–9] the recent developments in their application as scaffolds in catalysis have only been made possible because of the availability of isolable NHCs.[10,11] The unusual stability of NHCs (for a long time carbenes were considered as prototypical reactive intermediates, their instability being due to their six-valence-electron shell that defies the octet rule)[12] results from the ability of nitrogen to act as a π-donor, which decreases the electron deficiency at the adjacent carbene center. This electronic stabilization produces the strong σ-donor and weak π-acceptor properties of NHCs that explain their efficiency as ligands for transition-metal-based catalysts.

In a seminal paper, Schleyer et al.[13] concluded that the inherent π-donor capabilities of the heavier elements (such as phosphorus) are as large as, or larger than, those of their second-row counterparts (such as nitrogen), and that their apparently inferior donor ability is due to the difficulty in achieving the optimum planar configuration. Therefore, one of the obvious interesting candidates to compete with and/or complement NHCs as ligands for transition-metal-based catalysts are P-heterocyclic carbenes (PHCs),[14–18] providing that there is a driving force for the planarization of the phosphorus centers. Previous calculations have shown that the nitrogen centers of the parent NHC $\mathbf{A_N}$ (Scheme 1) are in a perfectly planar environment,[19,20] whereas the phosphorus centers of the corresponding PHC $\mathbf{A_P}$ are strongly pyramidalized, as expected.[21,22] Consequently, the singlet–triplet gap drops from 79 kcal mol^{-1} for $\mathbf{A_N}$[19] to 21 kcal mol^{-1} for $\mathbf{A_P}$[22] although the latter is predicted to be highly unstable with respect to dimerization.[21] However, there are several ways to decrease the inversion barrier at phosphorus, as discussed recently in a comprehensive review,[23] the simplest being to use bulky substituents. Here, we report the synthesis and ligand properties of a stable diphosphorus analogue of Enders' NHC **B**.[24]

The classical precursors for NHCs are the well-known corresponding protonated species NHC(H$^+$) (Scheme 1). In contrast, the phosphorus analogues of such species, PHC(H$^+$), are unknown.[25–28] Moreover, the synthetic methods used in the nitrogen series cannot be extended to compounds of its heavier congener. We therefore designed an original synthetic approach: a formal [3+2] cycloaddition of the transient diphosphaallylic cation **2** with a dipolarophile (Scheme 2). Addition of silver trifluoromethanesulfonate or gallium trichloride to a dichloromethane solution of the readily available phosphaalkene **1**,[29,30] at −78 °C, in the presence of a large excess of acetonitrile (30–45 equiv) afforded the desired salts **3a** and **3b**, respectively. They were isolated after recrystallization as white crystals (see Experimental Section). Deprotonation of derivative **3a** was then carried out in THF at −78 °C with lithium bis(trimethylsilyl)amide. The resulting carbene **4** was isolated after recrystallization from a concentrated THF/toluene solution at −30 °C as light-yellow crystals.

The X-ray diffraction analyses of compounds **3b** and **4** (Figure 1 and 2) revealed the almost planar environment of the phosphorus centers in both molecules (sum of the angles, **3b**: 354° and 348°; **4**: 353° and 348°).[31] However, the slight deviation from planarity (*trans* arrangement of the 2,4,6-tri-*tert*-butylphenyl substituents) makes **3b** and **4** chiral in the solid state. In solution both ^{1}H and ^{13}C NMR spectroscopy showed the equivalency of the diastereotopic *tert*-butyl

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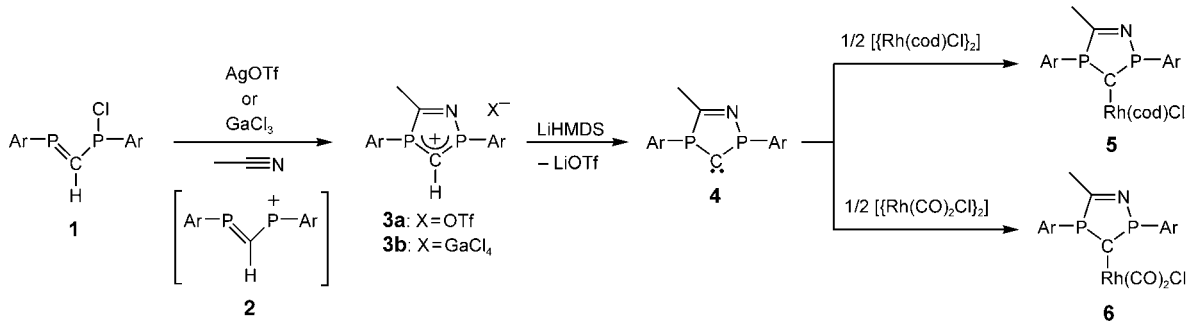


Scheme 2. Synthesis and complexation of P-heterocyclic carbene **4**. Ar = 2,4,6-tri-*tert*-butylphenyl, cod = cycloocta-1,5-diene, HMDS = hexamethyldisilazide, Tf = trifluoromethanesulfonyl.

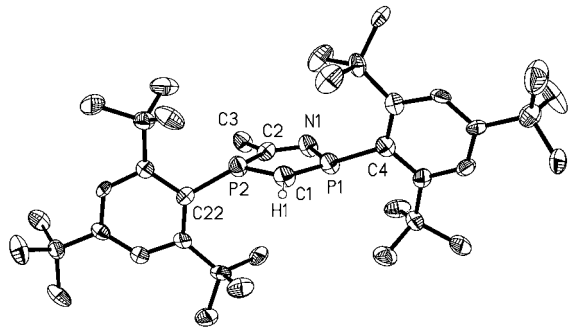


Figure 1. Molecular view of **3b** in the solid state. Selected bond lengths [Å] and angles [°]: P1–C1 1.693(11), P2–C1 1.720(11), P1–N1 1.662(8), P2–C2 1.799(10), C2–N1 1.318(12); P1-C1-P2 106.2(5), C1-P1-N1 106.2(5), C1-P1-C4 126.2(5), C4–P1–N1 121.7(4), C1-P2-C2 99.2(5), C1-P2-C22 129.6(5), C22-P2-C2 119.5(5), P1-N1-C2 112.6(7), P2-C2-N1 114.7(8).

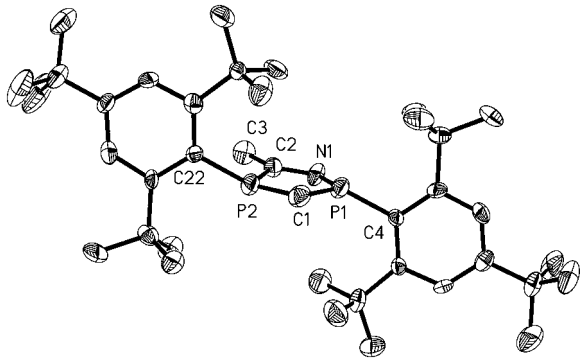


Figure 2. Molecular view of **4** in the solid state. Selected bond lengths [Å] and angles [°]: P1–C1 1.673(6), P2–C1 1.710(6), P1–N1 1.708(5), P2–C2 1.796(6), C2–N1 1.306(6); P1-C1-P2 98.2(3), C1-P1-N1 113.9(3), C1-P1-C4 124.9(3), C4-P1-N1 114.1(3), C1-P2-C2 105.7(3), C1-P2-C22 128.7(3), C22-P2-C2 113.4(3), P1-N1-C2 107.3(4), P2-C2-N1 113.7(4).

groups, even at −100 °C, thereby suggesting that the two enantiomers are in rapid equilibrium, in agreement with the expected low inversion barriers at the phosphorus centers. The strong donation of the phosphorus lone-pairs to the electron-deficient carbene center is clearly apparent from the P–C1 bond lengths (1.693(11) and 1.720(11) Å (**3b**); 1.673(6) and 1.710(6) Å (**4**)), which are significantly shorter than normal P–C single bonds (> 1.80 Å). Since the N1–C2 and the P1–N1 and P2–C2 bonds are only marginally longer and shorter than typical double and single bonds, respectively, the interaction between the N1–C2 unit and the P1–C1–P2 fragment is weak for both **3b** and **4**. The same conclusions have been drawn for the Enders-type carbene **B**.[24] Interestingly, the same differences that are observed between NHCs and their NHC(H^+) precursors can be found between **3b** and **4**. The P1–C1–P2 bond angle for **4** (98.2°) is more acute than in its cationic precursor (106.2°), and is in fact very similar to the carbene bond angle recently reported for a four-membered NHC (96.7°).[32] The ^{13}C NMR signal for the carbene carbon ($\delta = 184$ ppm) of **4** is strongly deshielded compared to that of **3** ($\delta = 119$ ppm), and is observed at a slightly higher field than those of NHCs ($\delta = 205$–244 ppm).

Ab initio calculations[33] were performed on carbene **4** and on its derivatives **4a** and **4b**, which feature hydrogen and phenyl substituents, respectively, instead of 2,4,6-tri-*tert*-butylphenyl substituents. As expected, the sum of the angles around P increases significantly as the steric demand of the substituent increases (**4a**: 328° and 342°; **4b**: 341° and 341°; **4**: 351° and 352°). As a consequence of the enforced planarization of the phosphorus centers, the singlet–triplet energy gap increases strongly (**4a**: 22.6; **4b**: 26.7; **4**: 41.4 kcal mol^{-1}) as does the energy of the HOMOs (Kohn–Sham (KS) orbital energies) (**4a**: −5.9; **4b**: −5.3; **4** −5.0 eV). Interestingly, the HOMO of the experimentally observed carbene **4** is even higher in energy than that calculated at the same level of theory for Enders' NHC **B** (−5.1 eV); this can be regarded as a first indication of the strongly basic character of **4**.

In initial attempts to evaluate the ligand properties of **4**, we prepared the [RhCl(cod)(**4**)] complex **5** and compared its geometric parameters with those of corresponding NHC complexes.[34–38] Complex **5** was isolated as highly thermally stable single crystals (78% yield; m.p.: 187–189 °C). Notably, no significant decomposition was observed when a dichloromethane solution of **5** was stirred for several hours in air. As observed for NHCs, the complexation induces a very small lengthening of the P–C bonds, which, however, stay shorter than those in the corresponding cation **3b** (Figure 3).[31] Importantly, the phosphorus centers are not pyramidalized, the sum of the angles around phosphorus (350° and 351°) being essentially identical to those observed for the free PHC

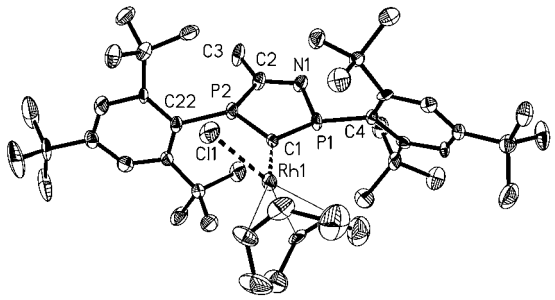


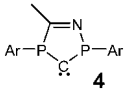
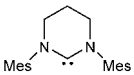
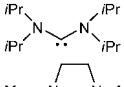
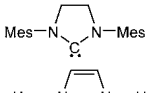
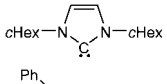
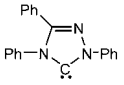
Figure 3. Molecular view of **5** in the solid state. Selected bond lengths [Å] and angles [°]: C1–Rh 2.064(8), P1–C1 1.730(7), P2–C1 1.701(8), P1–N1 1.657(6), P2–C2 1.782(8), C2–N1 1.325(10); P1-C1-P2 100.7(4), C1-P1-N1 109.2(4), C1-P1-C4 124.5(4), C4-P1-N1 116.2(3), C1-P2-C2 104.6(4), C1-P2-C22 131.7(4), C22-P2-C2 114.4(4), P1-N1-C2 111.5(5), P2-C2-N1 112.6(6).

4. These data suggest a very weak π-donation from the metal to the carbene ligand. This is confirmed by the $C_{carbene}$–Rh bond length (2.064(8) Å), which is at the upper limit of those observed for [RhCl(cod)(NHC)] complexes (2.00–2.06 Å), and distinctly longer than that found for the analogous complex with Enders' NHC **B** as ligand (2.004 Å).[36]

The carbonyl stretching frequencies of *cis*-[$RhCl(CO)_2(L)$] complexes are recognized as an excellent measure of the σ-donor and π-acceptor properties of the carbene ligand L.[38,39] Complex **6** was easily prepared by addition of half an equivalent of [{$RhCl(CO)_2$}$_2$] to the free PHC **4**. The values of the carbonyl stretching frequencies for complex **6** are lower than those observed for the analogous complex with Enders' NHC **B** as ligand (Table 1). In fact, the observed values for **6** are as low as those reported for complexes featuring the most basic NHC and even acyclic diaminocarbene ligands.[40,41]

PHC **4** is an analogue of one of the less-basic NHCs, although its basicity already appears to be comparable to those of saturated five- and six-membered NHCs. Therefore, it is quite likely[42] that saturated PHCs will push upward the electronic parameter scale characterizing NHC-type ligands. Any catalytic application requiring electron-rich ligands might benefit from the use of PHC ligands.

Table 1: IR carbonyl stretching frequencies $\tilde{\nu}$ [cm^{-1}] for *cis*-[$RhCl(CO)_2L$] complexes.

L	ν(CO) I	ν(CO) II	Ref.
 **4**	2059	1985	this work
	2062	1976	[39]
	2057	1984	[40]
	2081	1996	[42]
	2076	2006	[42]
	2089	2009	this work

Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC80, AC200, Avance 300, or AMX400 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm relative to $SiMe_4$ as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4.

3a: A solid mixture of 3-chloro-1,3-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphaprop-1-ene (**1**; 1.06 g, 1.7 mmol) and silver triflate (0.453 g, 1.7 mmol) was cooled to −78 °C. Acetonitrile (4 mL, 76 mmol) and dichloromethane (10 mL) were then added with vigorous stirring and the reaction mixture was warmed to room temperature. After 30 min the mixture was filtered and the solvent removed under vacuum. The crude product was crystallized from a CH_2Cl_2/Et_2O mixture at −30 °C to give the title compound as white needles (yield: 80%); m.p.: 157–159 °C; ^1H NMR (300 MHz, $CDCl_3$, 298 K): $\delta = 1.39$ (s, 18H; CCH_3), 1.45 (s, 36H; CCH_3), 2.63 (dd, $J_{P,H} = 20$ and 2 Hz, 3H; $NCCH_3$), 7.73 (d, $^4J_{P,H} = 4$ Hz, 2H; CH_{arom}), 7.75 (d, $^4J_{P,H} = 3$ Hz, 2H; CH_{arom}), 8.60 ppm (dd, $^2J_{P,H} = 16$ and 7 Hz, 1H; PCHP); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K): $\delta = 22.2$ (dd, $J_{P,C} = 25$ and 30 Hz, $NCCH_3$), 30.8 (s, CH_{3para}), 30.9 (s, CH_{3para}), 33.0 (s, CH_{3ortho}), 33.4 (s, CH_{3ortho}), 38.5 (d, $J_{P,C} = 3$ Hz, C_qCH_3), 38.6 (d, $J_{P,C} = 8$ Hz, C_qCH_3), 119.3 (dd, $J_{P,C} = 51$ and 44 Hz, PCHP), 124.4 (d, $J_{P,C} = 16$ Hz, $C_{arom}H$), 124.8 (d, $J_{P,C} = 14$ Hz, $C_{arom}H$), 159.8 (d, $J_{P,C} = 3$ Hz, C_{arom}), 160.3 (d, $J_{P,C} = 4$ Hz, C_{arom}), 160.6 (dd, $J_{P,C} = 3$ and 13 Hz, C_{arom}), 160.6 (d, $J_{P,C} = 10$ Hz, C_{arom}), 172.2 ppm (dd, $J_{P,C} = 7$ and 29 Hz, $NCCH_3$); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, 298 K): $\delta = 104$ and 85 ppm ($^2J_{P,P} = 266$ Hz).

3b: Compound **1** (0.8 g; 1.3 mmol) was dissolved in a mixture of dichloromethane (10 mL) and acetonitrile (2 mL, 38 mmol). One equivalent of $GaCl_3$ (0.235 g) in 2 mL of dichloromethane was added, with vigorous stirring, at −78 °C. The reaction mixture was then warmed up to room temperature. The solvents were removed under vacuum and the crude product was crystallized from a CH_2Cl_2/Et_2O mixture at −30 °C. White needles (yield: 67%); m.p.: 173–175 °C.

4: A solution of **3a** (1 g, 1.4 mmol) in THF (5 mL) was cooled to −78 °C. A solution of lithium hexamethyldisilazide (0.335 g, 1.4 mmol) in THF (3 mL) was added dropwise. After warming up to room temperature, the reaction was complete. The solvent was removed under vacuum, and the solid was extracted with pentane. The resultant solution was concentrated and cooled to −30 °C to afford a yellow powder, which was dried under vacuum. Single crystals suitable for X-ray analysis were obtained from a concentrated solution in THF/toluene cooled to −30 °C. Yellow crystals (yield: 72%); m.p.: 123–127 °C; ^1H NMR (400 MHz, [D_8]THF; 263 K): $\delta = 1.35$ (s, 18H; CCH_3), 1.40 (s, 18H; CCH_3), 1.41 (s, 18H; CCH_3), 2.26 (dd, $J_{P,H} = 13$ and 3 Hz, 3H; $NCCH_3$), 7.61 (d, $^4J_{P,H} = 4$ Hz, 2H; CH_{arom}), 7.63 ppm (d, $^4J_{P,H} = 4$ Hz, 2H; CH_{arom}); $^{13}C\{^1H\}$ NMR (100 MHz, [D_8]THF, 263 K): $\delta = 19.8$ (dd, $J_{P,C} = 30$ and 34 Hz, N=CCH_3), 30.6 (s, CH_3), 32.0(s, CH_3), 32.5(s, CH_3), 35.3 (s, CCH_3), 38.3 (s, CCH_3), 121.1 (d, $J_{P,C} = 34$ Hz, C_{arom}), 121.3 (d, $J_{P,C} = 34$ Hz, C_{arom}), 122.3 (d, $J_{P,C} = 12$ Hz, HC_{arom}), 122.5 (d, $J_{P,C} = 11$ Hz, HC_{arom}), 153.8 (d, $J_{P,C} = 4$ Hz, C_{arom}), 153.9 (d, $J_{P,C} = 3$ Hz, C_{arom}), 157.8 (m, C_{arom}), 179.1 (dd, $J_{P,C} = 16$ and 31 Hz, C=N), 184.4 ppm (pseudo t, $J_{P,C} = 147$ Hz, PCP); $^{31}P\{^1H\}$ NMR (162 MHz, [D_8]THF, 263 K): $\delta = 85$ and 73 ppm ($^2J_{P,P} = 135$ Hz).

5 and **6**: A solution of **4** in THF was added to a solution of 0.5 equivalents of the corresponding chlororhodium(I) dimer ([{Rh(cod)Cl}$_2$] for **5**, [{$Rh(CO)_2Cl$}$_2$] for **6**) in THF at −78 °C. After the mixture had been warmed up to room temperature, the solvent was removed under vacuum and the product extracted with pentane.

Single crystals suitable for X-ray analysis were obtained from a pentane/toluene solution cooled to −30 °C.

5: Deep red crystals (yield: 78 %); m.p.: 187–189 °C; ^{1}H NMR (300 MHz, C_6D_6, 298 K): $\delta = 1.21$ (s, 18 H; CH_3), 1.31 (s, 18 H; CH_3), 1.66 (s, 18 H; CH_3), 1.74 (s, 18 H; CH_3), 1.0–2.0 (m, 6 H; H_2C_{allyl}), 2.31 (dd, $J_{P,H} = 13$ and 8 Hz, 3 H; N=CCH_3), 3.17 (br, 2 H; H_2C_{allyl}), 4.29 (br, 2 H; HC_{vinyl}), 5.14 (br, 2 H; HC_{vinyl}), 7.74 ppm (m, 4 H; HC_{arom}); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): $\delta = 21.4$ (dd, $J_{P,C} = 25$ and 27 Hz, N=CCH_3), 29.1 (s, H_2C_{allyl}), 30.7(s, H_2C_{allyl}), 30.8 (s, CH_3), 31.0 (s, CH_3), 33.2 (s, H_2C_{allyl}), 33.9 (s, CH_3), 34.4 (s, CH_3), 35.0 (s, CCH_3), 35.3 (s, CCH_3), 39.3 (d, $J_{P,C} = 4$ Hz, CCH_3), 40.2 (d, $J_{P,C} = 2$ Hz, CCH_3), 69.3 (d, $J_{C,Rh} = 14$ Hz, CH_{vinyl}), 78.2 (d, $J_{C,Rh} = 14$ Hz, CH_{vinyl}), 93.8 (d, $J_{C,Rh} = 8$ Hz, CH_{vinyl}), 117.0 (dd, $J_{P,C} = 16$ and 28 Hz, C_{arom}), 119.0 (dd, $J_{P,C} = 14$ and 33 Hz, C_{arom}), 123.5 (dd, $J_{P,C} = 3$ and 9 Hz, HC_{arom}), 125.2 (dd, $J_{P,C} = 6$ and 9 Hz, HC_{arom}), 153.9 (d, $J_{P,C} = 3$ Hz, C_{arom}), 155.1 (d, $J_{P,C} = 3$ Hz, C_{arom}), 157.7 (dd, $J_{P,C} = 5$ and 8 Hz, C_{arom}), 159.2 (dd, $J_{P,C} = 5$ and 8 Hz, C_{arom}), 170.9 (ddd, $J_{P,C} = 61$ and 72 Hz, $J_{C,Rh} = 41$ Hz, CRh), 176.8 ppm (pseudo t, $J_{P,C} = 14$ Hz, N=C) ^{31}P{^{1}H} NMR (81 MHz, C_6D_6, 298 K): $\delta = 89$ and 88 ppm (AB system, $^2J_{P,P} = 173$ Hz).

6: Yellow crystals (yield: 69 %); m.p.: 175–178 °C; IR (KBr): $\tilde{\nu} = 1985$ and 2059 cm^{-1} (CO); ^{1}H NMR (300 MHz, C_6D_6, 298 K): $\delta = 1.23$ (s, 9 H; CCH_3), 1.26 (s, 9 H; CCH_3), 1.60 (s, 18 H; CCH_3), 1.62 (s, 18 H; CCH_3), 2.33 (dd, $J_{P,H} = 17$ and 4 Hz, 3 H; $NCCH_3$), 7.71 (d, $^4J_{P,H} = 5$ Hz, 2 H; CH_{arom}), 7.74 ppm (d, $^4J_{P,H} = 6$ Hz, 2 H; CH_{arom}); ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): $\delta = 22.2$ (dd, $J_{P,C} = 25$ and 330 Hz, N=CCH_3), 31.5 (s, CH_3), 31.8 (s, CH_3), 34.6(s, CH_3), 34.8 (s, CH_3), 36.2 (s, CCH_3), 36.0 (s, CCH_3), 40.0 (d, $J_{P,C} = 4$ Hz, CCH_3), 40.6 (d, $J_{P,C} = 4$ Hz, CCH_3), 116.3 (dd, $J_{P,C} = 11$ and 39 Hz, C_{arom}), 118.6 (dd, $J_{P,C} = 4$ and 58 Hz, C_{arom}), 124.6 (d, $J_{P,C} = 14$ Hz, HC_{arom}), 125.7 (dd, $J_{P,C} = 1$ and 14 Hz, HC_{arom}), 156.2 (d, $J_{P,C} = 4$ Hz, C_{arom}), 157.1 (d, $J_{P,C} = 3$ Hz, C_{arom}), 159.0 (dd, $J_{P,C} = 5$ and 9 Hz, C_{arom}), 159.9 (dd, $J_{P,C} = 3$ and 9 Hz, C_{arom}), 175.9 (ddd, $J_{P,C} = 2$ and 8 Hz, $J_{C,Rh} = 24$ Hz, CRh), 183.9 (ddd, $J_{C,Rh} = 75$ Hz, $J_{P,C} = 3$ and 6 Hz, RhCO), 185.9 ppm (dt, $J_{C,Rh} = 86$ Hz, $J_{P,C} = 3$ Hz, RhCO); ^{31}P{^{1}H} NMR (81 MHz, C_6D_6, 298 K): $\delta = 101$ and 93 ppm ($^2J_{P,P} = 187$ Hz).

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