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# Transition Metal Complexes of Bulky, Electron-Rich *N*-Phosphanyl-Substituted N-Heterocyclic Carbenes (NHCP Ligands). Small Bite Angle Four-Membered (*κ-C,κ-P*) Chelate Structures

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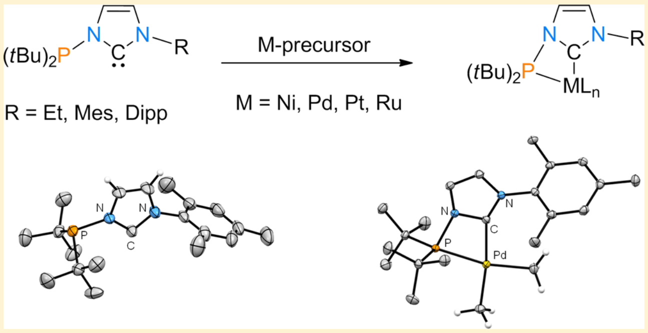
*Supporting Information*

**ABSTRACT:** Bulky, electron-rich *N*-phosphanyl-substituted N-heterocyclic carbenes (NHCP ligands: $^{Et}$CNP **3**, $^{Mes}$CNP **5a**, $^{Dipp}$CNP **5b**) are potential ligands for strained, very small bite angle four-membered transition metal chelate complexes with (*κ*-C,*κ*-*P*) metal coordination. Various compounds of this type have been synthesized and were fully characterized *inter alia* by X-ray crystallography. Reactions of isolated NHCP species **3**, **5a**, and **5b** with appropriate metal precursors furnished a series of (*κ*-C,*κ*-*P*)-coordinated four-membered NHCP chelate complexes for the metals of the nickel triad and for ruthenium. The *cis*-dimethyl Pd(II) complex ($^{Mes}$CNP-*κ*C,*κ*-*P*)PdMe$_2$ (**8**) reacted at room temperature with acceptor-substituted alkenes such as fumaronitrile and maleic anhydride to yield the corresponding $\eta^2$-olefin complexes **9** and **10** with reductive elimination of ethane. Palladacyclopentadiene complex **11** was formed by addition of two equivalents of dimethyl acetylene dicarboxylate to complex **8** via alkyne−alkyne coupling.



## INTRODUCTION

Since the first applications of NHC ligands in coordination chemistry by Wanzlick and Öfele[1] and the first isolation of a free crystalline N-heterocyclic carbene (NHC) by Arduengo,[2] N-heterocyclic carbenes have gained increasing importance in transition metal catalysis.[3] Regarding their ligand properties, NHC ligands show a remarkable resemblance to electron-rich alkylphosphines.[4] Both are considered to be strong $\sigma$-donors and weak $\pi$-acceptors, however with different steric characteristics and with NHC ligands forming stronger metal−ligand bonds. Using bulky, alkyl-substituted, electron-rich diphosphinomethanes as chelating, small bite angle ligands, such as bis(di-*tert*-butylphosphino)methane (dtbpm),[5] we have shown that their complexes with metals of the nickel triad or with Ru feature unusually high reactivity in bond activation chemistry[6] and catalysis, e.g., for olefin metathesis (ROMP),[7] for olefin polymerization, or CO/ethylene copolymerization.[8,9] Adopting the structural motif of four-membered bisphosphine chelate transition metal complexation and trying to combine the electronic characteristics of NHC ligands with those of electron-rich phosphine moieties should lead to *N*-phosphanyl-substituted NHC hybrid ligand systems capable of forming (*κ*-C,*κ*-*P*)-bound, four-membered chelate structures with appropriate transition metal fragments. We use the general acronym NHCP for all NHC ligands with a second, P-based coordination site such as *N*-phosphanyl-substituted (or *N*-phosphinomethyl-substituted[10]) NHCs. To the best of our knowledge, so far only complexes with five-membered,[10,11] six-membered,[12] or even larger[13] NHCP-type chelate ligands have been published.

Of course chelate complexation at metals forming four-membered chelate substructures is well known for many types of $\kappa^2$-coordinating three-atom ligand units, but there is only one structural motif of four-membered chelate systems disclosed in the literature, by Grotjahn et al.,[14] which is closely related to the systems we report in this paper. In the context of their studies of bulky imidazolyl phosphane ligands for Pd chemistry, these authors have prepared a C2-phosphanyl-substituted *N*-methylimidazole (phosphanyl = P(*t*-Bu)$_2$), which in a couple of cases was found to bind to palladium through the P- and N-donor atom of the imidazolyl phosphine, generating (*κ*-*N*,*κ*-*P*) four-membered chelate structures with small N−Pd−P bite angles between 69° and 70°.

Here we report our successful first attempts to employ a specific group of NHCP ligands, those with a direct *N*-phosphanyl link, for transition metal coordination to the metals of the Ni triad and to Ru. We disclose the synthesis and structural characterization of the first four-membered chelate ring NHCP complexes with (*κ*-C,*κ*-*P*) metal coordination and with extraordinarily small bite angles between 65° and 70°. Compared to the systems of Grotjahn et al.[14] the replacement

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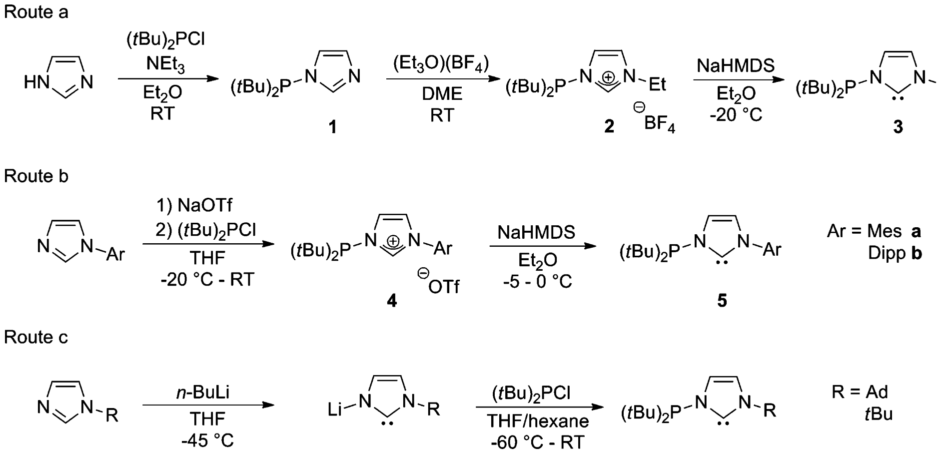
**Scheme 1. Synthetic Pathways for NHCP Ligands with a N−P Linkage**



of the imidazole N-donor center by a NHC carbene (imidazolylidene) carbon is expected to significantly change the electronic structure and thus presumably reactivity patterns of transition metal complexes.

## ■ RESULTS AND DISCUSSION

**Ligand Synthesis.** The first synthesis of an NHCP ligand with a direct N−P linkage was achieved in our group some time ago.[15] The simple three-step synthetic strategy is shown in Scheme 1 (route a).

After a modified procedure of Fischer et al.,[16] imidazole was first P-functionalized at one nitrogen with di-*tert*-butylchlorophosphine in the presence of triethylamine, yielding **1**. The reaction could be easily followed through the high-field shift of the phosphorus singlet signal from 148 ppm to 89 ppm in $^{31}P$ NMR. Subsequent alkylation with Meerwein's salt $(Et_3O)^+(BF_4)^-$ in DME at the other nitrogen gave the *N*-ethyl, *N*′-P(*t*-Bu)$_2$-substituted imidazolium salt **2**. The completion of the alkylation reaction was determined by the downfield shift of the phosphorus nucleus from 89 ppm to 121 ppm in the $^{31}P$ NMR spectrum and of proton H2 (NC*H*N) from 7.7 ppm to 8.8 ppm in the proton NMR. In the last step the imidazolium salt was deprotonated with NaHMDS in $Et_2O$ at low temperature, giving the desired NHCP system $^{Et}$CNP (**3**). We use the general acronym NHCP for various NHC chelate ligands[10] with a second, P-based coordination site, and we specify the NHCP systems with an N−R unit and with direct N−P(*t*-Bu)$_2$ substitution used in the present paper as $^{R}$CNP to indicate their three-atom, four-membered (*κ*-*C*,*κ*-*P*) chelate metal coordination. Compound **3** is characterized by a singlet in its $^{31}P$ NMR at 97 ppm and by the absence of the H2 signal in the $^{1}H$ NMR. The molecular structure of compound **3** could be characterized by X-ray diffraction (*vide infra*). Our route a is a modular approach toward $^{R}$CNP systems, allowing a broad variation of N-bound phosphanyl units other than P(*t*-Bu)$_2$, but is somewhat limited by the availability of appropriate carbon electrophiles such as $(Et_3O)^+(BF_4)^-$, $(Me_3O)^+(BF_4)^-$, $CH_3SO_2CF_3$, or the like for the second N-substitution (step 2) leading to imidazolium salts.

Recently, the group of Kostyuk et al.[17a,b] has disclosed two further elegant pathways leading to bulky *N*-phosphanyl-substituted N-heterocyclic NHCPs (routes b, c). In contrast to our route a, where the carbon substituent on the N atom was introduced in the second step by N-alkylation, we used *N*-aryl-substituted imidazoles (aryl = Mes, Dipp) as starting materials on route b.[17a] Treatment of these imidazoles with sodium triflate and di-*tert*-butylchlorophosphine led to the imidazolium salts **4a**/**b**. The precipitation of NaCl drives the reaction to the desired product. Full conversion is indicated by a broad signal in the $^{31}P$ NMR at 123 (**4a**) and 124 ppm (**4b**). In order to access the free NHCP ligands $^{Mes}$CNP (**5a**) and $^{Dipp}$CNP (**5b**), the salts were treated with NaHMDS in diethyl ether. The deprotonation process can again conveniently be followed by $^{1}H$ and $^{31}P$ NMR. There is also a large downfield shift of the carbene carbon in $^{13}C$ NMR from around 142 ppm to ca. 226 ppm. The NHCP derivatives **3**, **5a**, and **5b** are colorless crystalline solids with rather high melting points (without decomposition), in the case of the latter two at 106 °C (**5a**) and 156 °C (**5b**). All imidazolium salts and the free NHCPs are air and moisture sensitive; therefore they were handled in dry solvents and under dry argon.

As displayed in Scheme 1 (route c), the third approach to make NHCP ligands for (*κ*-*C*,*κ*-*P*) four-membered chelate metal coordination available, also published by Kostyuk et al.,[17b] involves deprotonation of N-substituted imidazoles (or benzimidazoles) carrying bulky N-substituents (adamantyl, *t*-Bu) with *n*-BuLi and reaction of the resulting Li-imidazolides with di-*tert*-butylchlorophosphine. Unfortunately a severe limitation of route c lies in the observation that for imidazoles with less bulky N-substitution (e.g., aryl) a rearrangement with phosphanyl group migration from N to C2 is facile, while for $^{R}$CNP systems isolated in routes a and b this isomerization requires rather high temperatures. Also in our hands attempts to synthesize analogues of **5a** and **5b** in route c, for instance by deprotonation of N-*t*-Bu imidazole with *n*-BuLi and by reaction of the imidazolide with (*t*-Bu)(Me)PCl even at −40 °C, led directly and exclusively to the rearranged product with the phosphanyl group at C2 instead of yielding the expected NHCP system. This clearly reveals that not only is a bulky N-substituent of the N-substituted imidazole, which is deprotonated, required, as found by Kostyuk et al., but that the substitution pattern and presumably the steric demand of the phosphorus halide also plays an important role for route c and the yield of the desired NHCP ligands.

As clearly indicated by Scheme 1, NHCP ligand structures of the $^{R}$CNP type, required for our intended studies of their small bite angle (*κ*-*C*,*κ*-*P*) metal coordination behavior, are conveniently accessible in a reasonably broad variability. Here we focus on $^{Et}$CNP (**3**), $^{Mes}$CNP (**5a**), and $^{Dipp}$CNP (**5b**).

The solid-state X-ray structures of **3**, **5a**, and **5b** could be determined and are shown in Figure 1, and selected bond lengths and angles are listed in Table 1.

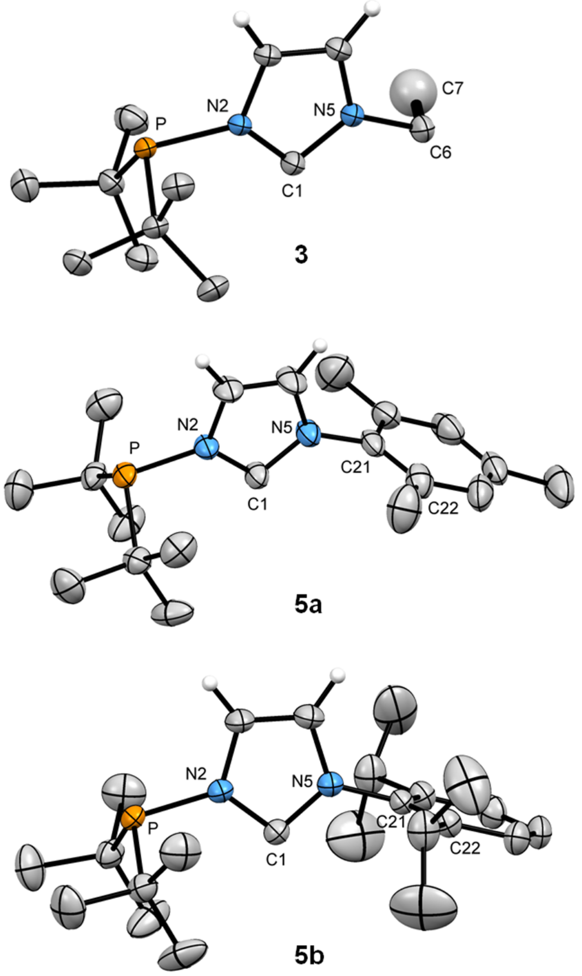


**Figure 1.** ORTEP diagrams of the solid-state structures of **3**, **5a**, and **5b** with 50% ellipsoids. Hydrogen atoms (except imidazolylidene H atoms) are omitted for clarity.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Ligands 3, 5a, and 5b**

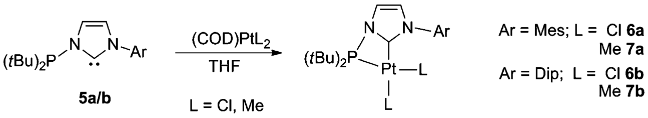
| | $^{Et}$CNP (**3**) | $^{Mes}$CNP (**5a**) | $^{Dipp}$CNP (**5b**) |
|---|---|---|---|
| P−N2 | 1.753(2) | 1.749(2) | 1.7485(16) |
| N2−C1 | 1.386(3) | 1.383(3) | 1.378(2) |
| C1−N5 | 1.360(3) | 1.359(3) | 1.361(2) |
| N5−C6/C21 | 1.451(3) | 1.445(3) | 1.437(2) |
| P−N2−C1 | 128.89(17) | 127.72(17) | 127.57(13) |
| N2−C1−N5 | 102.1(2) | 102.0(2) | 101.88(15) |
| C1−N5−C6/C21 | 123.1(2) | 121.9(2) | 123.47(15) |
| C1−N5−C6/C21−C7/C22 | 95.3 | 89.65 | 90.34 |

The *N*-ethyl-substituted carbene **3** displays an abnormally large displacement parameter for the ethyl group's methyl unit. (See comments in the CIF file in the Supporting Information.)

The solid-state X-ray structures of the aryl-substituted carbenes **5a** and **5b** show symmetric molecules with the imidazole rings in mirror planes. Comparing the bond lengths and angles of the three carbenes, only very small, nonsignificant structural differences are apparent. The lone pairs of the phosphine and of the carbene unit are oriented in an *anti* fashion. This geometry is similar to the one in bulky diphosphinomethanes[5d] and is as expected since the electronic repulsion between the lone pairs is minimized in this conformation.

**Synthesis of Neutral ($^{R}$CNP *κ-C,κ-P*) Platinum Complexes.** Metal complexes of Pt were obtained by adding the isolated pure carbenes **5a/b** to a suspension or solution of a suitable metal precursor such as (COD)PtCl$_2$ or (COD)PtMe$_2$ in THF (Scheme 2).

**Scheme 2. Synthesis of Neutral ($^{R}$CNP *κ-C,κ-P*) Platinum Complexes**



Platinum dichloro complexes **6a** and **6b** showed a singlet resonance in the $^{31}$P NMR with characteristic Pt-satellites ($^{1}J_{P,Pt}$ = 3439.9 Hz for **6a**, $^{1}J_{P,Pt}$ = 3440.5 Hz for **6b**). Both complexes were poorly soluble and could only be dissolved in polar aprotic solvents such as acetonitrile or DMSO. Complex **6a** was crystallized by slow evaporation of acetonitrile and DCM out of a saturated solution in this solvent mixture. It was not yet possible to obtain crystals suitable for X-ray diffraction for complex **6b**.

$^{R}$CNP platinum dimethyl complexes **7a** and **7b** also are characterized by singlet resonances in their $^{31}$P NMR spectra at 104 and 100 ppm, respectively, with Pt-satellites. Expectedly, the $^{1}J_{P,Pt}$ coupling constants of the dimethyl complexes ($^{1}J_{P,Pt}$ = 1279.4 Hz for **7a**, $^{1}J_{P,Pt}$ = 1288.4 Hz for **7b**) were much smaller compared to those of the dichloro complexes. The different resonances for the methyl groups *cis* and *trans* to P were assigned by the different coupling constants from $^{1}$H, $^{13}$C NMR and NOESY experiments. The coupling constants $^{3}J_{H,P}$ of the methyl protons of **7a** and **7b** are approximately 7 Hz, whereas the coupling constants $^{2}J_{C,P}$ of the methyl carbons differ a lot and are 107 Hz for the *trans*-P- and 4 Hz for the *cis*-P-bonded methyl group.

The most remarkable feature of all structures is the small chelate bite angle, which for all three compounds is the same within experimental error. Due to the fact that four-membered-ring chelate ligands generally lead to small bite angles, in this case smaller than 70°, the molecular structures of the complexes put the platinum center in a rather distorted square-planar geometry. This also distinctly affects the P−N2−C1 bond angle, which decreases by metal coordination from around 128° in the free carbenes (Table 1) to approximately 100° in the complexes (Table 2). Interestingly, no remarkable difference between the *trans* influence of the NHC unit and the P-moiety, respectively, is observed since bond lengths from platinum to both chloro or methyl ligands are nearly identical.

**Synthesis of Neutral ($^{R}$CNP *κ-C,κ-P*) Palladium Complexes.** ($^{Mes}$CNP *κ-C,κ-P*)PdMe$_2$ **8** was obtained via a ligand exchange reaction by adding the free carbene **5a** to a solution of (tmeda)PdMe$_2$ in THF at room temperature (Scheme 3). Due to $^{3}J$-coupling of the methyl group protons with the phosphorus atom, the methyl ligands exhibit two doublets in the $^{1}$H NMR. The methyl group *cis* to P has a larger coupling constant (8.0 Hz at −0.28 ppm) than the methyl group *trans* to P (6.9 Hz at −0.25 ppm). In the $^{13}$C NMR the coupling constants are

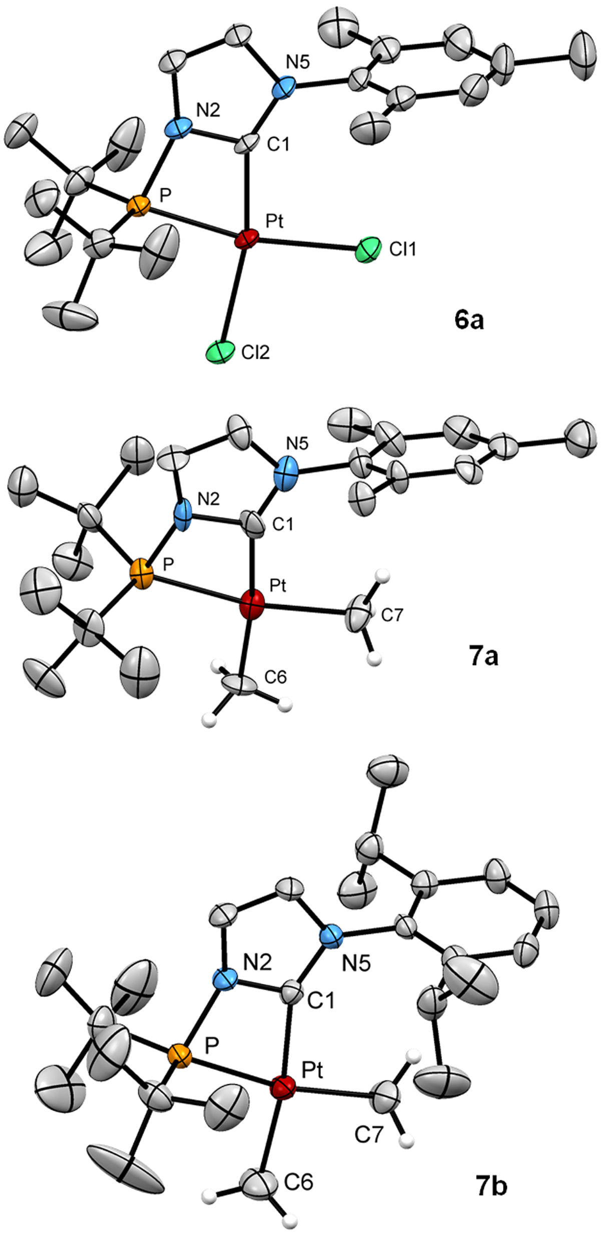


**Figure 2.** ORTEP diagrams of the solid-state structures of **6a**, **7a**, and **7b** with 50% ellipsoids. Hydrogen atoms (except H atoms of the Pt-bound methyl groups) are omitted for clarity.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for Platinum Complexes 6a, 7a, and 7b**

| | $(^{Mes}CNP)PtCl_2$ (**6a**) | $(^{Mes}CNP)PtMe_2$ (**7a**) | $(^{Dipp}CNP)PtMe_2$ (**7b**) |
|---|---|---|---|
| Pt−C1 | 1.974(8) | 2.042(17) | 2.048(3) |
| Pt−P | 2.216(2) | 2.287(4) | 2.2767(8) |
| Pt−Cl1/C7 (*trans*-P) | 2.349(2) | 2.067(15) | 2.081(3) |
| Pt−Cl2/C6 (*trans*-C) | 2.357(2) | 2.059(16) | 2.092(3) |
| P−N2 | 1.747(8) | 1.745(14) | 1.742(3) |
| N2−C1 | 1.366(11) | 1.388(19) | 1.370(4) |
| P−Pt−C1 | 69.2(3) | 68.0(4) | 67.90(8) |
| C1−Pt−Cl1/C7 | 98.2(3) | 99.4(6) | 100.58(13) |
| Cl1/C7−Pt−Cl2/C6 | 94.09(8) | 87.4(7) | 87.68(15) |
| P−Pt−Cl2/C6 | 98.48(8) | 105.2(5) | 103.84(11) |
| Pt−C1−N2 | 106.3(6) | 105.5(10) | 105.2(2) |
| Pt−P−N2 | 84.9(3) | 85.2(4) | 85.16(10) |
| P−N2−C1 | 99.5(6) | 101.1(10) | 101.6(2) |

**Table 3. Selected Bond Length (Å) and Angles (deg) for Palladium Complexes 9 and 10 (for both independent molecules)**

| | $(^{Mes}CNP)Pd(0)FN$ (**9**) | $(^{Mes}CNP)Pd(0)MA$ (**10**) |
|---|---|---|
| Pd−C1 | 2.112(2)/2.114(2) | 2.099(3)/2.073(3) |
| Pd−P | 2.3261(2)/2.3205(6) | 2.3209(7)/2.3409(7) |
| Pd−C7 (*trans*-P) | 2.081(2)/2.099(2) | 2.116(3)/2.101(3) |
| Pd−C6 (*trans*-C) | 2.069(2)/2.057(2) | 2.079(3)/2.096(3) |
| C6−C7 | 1.443(3)/1.452(3) | 1.4274(4)/1.422(5) |
| P−N2 | 1.750(2)/1.742(2) | 1.744(2)/1.755(2) |
| N2−C1 | 1.371(3)/1.374(3) | 1.373(3)/1.365(3) |
| P−Pd−C1 | 68.13(7)/68.01(6) | 67.93(7)/67.85(8) |
| C6−Pd−C7 | 40.67(9)/40.87(9) | 39.79(11)/39.60(13) |
| P−N2−C1 | 105.37(15)/105.20(15) | 104.57(14)/104.23(18) |

smaller for the *cis*-P methyl group (4.8 Hz at −10.3 ppm) and larger for the *trans*-P one (105.2 Hz at −3.8 ppm), as anticipated.

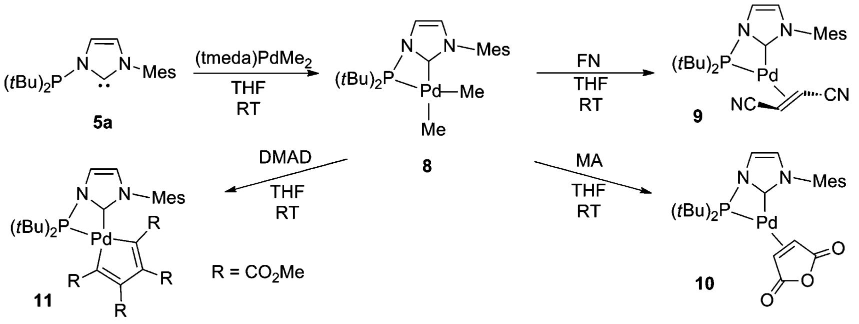
Single crystals of **8** were obtained by slow evaporation of diethyl ether from a saturated solution. The molecular structure in the crystal is shown in Figure 3. The geometry around the metal center is again distorted square planar, the bite angle is 67.59(7)°, and again no *trans* influence difference can be detected; the two $Pd-CH_3$ bond lengths, 2.066(3) (*trans*-P) and 2.056(3) Å (*trans*-C), are practically identical (Table 4).

The dimethyl complex **8** can serve as a convenient precursor for further transformations. Electron-poor olefins, e.g., fumaronitrile (FN) and maleic anhydride (MA), induce reductive elimination of exclusively ethane (NMR) at room temperature and lead to the palladium(0) olefin complexes **9** and **10**. The reaction of **8** with two equivalents of an electron-poor alkyne, such as dimethyl acetylene dicarboxylate (DMAD), affords the palladacyclopentadiene complex **11** (Scheme 3). The product formation is indicated by a color change from colorless to yellowish.

The olefin complexes **9** and **10** are characterized by a singlet in their $^{31}P$ NMR at 127 and 130 ppm, respectively. The olefin protons of complex **9** show two doublets at around 2.5 ppm in their $^1H$ NMR, and complex **10** displays two singlets at around 3.6 ppm for the MA protons. Since the NHCP ligand of **9** and **10** with its two very strong $\sigma$-donor coordination sites is tailor-made for efficient back-bonding to the low-lying olefin $\pi^*$-orbitals; the olefin hydrogens are shifted to distinctly higher field compared to the uncoordinated olefins FN and MA and thus indicate the expected relevant contribution of a metallacyclopropane resonance structure in these systems. The palladacyclopentadiene **11** shows a signal close to the free carbene at 99 ppm in its $^{31}P$ NMR spectrum. The $^1H$ resonances of three methyl ester methyl groups are observed between 3.4 and 3.5 ppm, whereas one ester signal is shifted to higher field (2.8 ppm) as a consequence of its location over the face of the aromatic system of the *N*-mesityl substituent, which is oriented perpendicular to the NHC ring.

Crystals of **9** and **10** could be obtained by slow evaporation of THF and diethyl ether from a solution of the palladium complexes and were suitable for X-ray diffraction analysis. Their molecular structures are shown in Figure 4. In both cases two independent molecules crystallized in the unit cell, and their

**Scheme 3. Synthesis of ($^{R}$CNP κ-C,κ-P) Palladium Complexes**



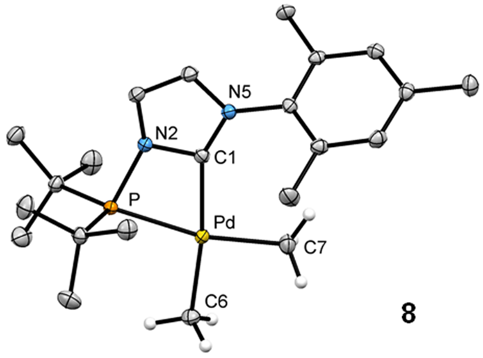


**Figure 3.** ORTEP diagram of the solid-state structures of **8** with 50% ellipsoids. Hydrogen atoms (except H atoms of the Pd-bound methyl groups) are omitted for clarity.

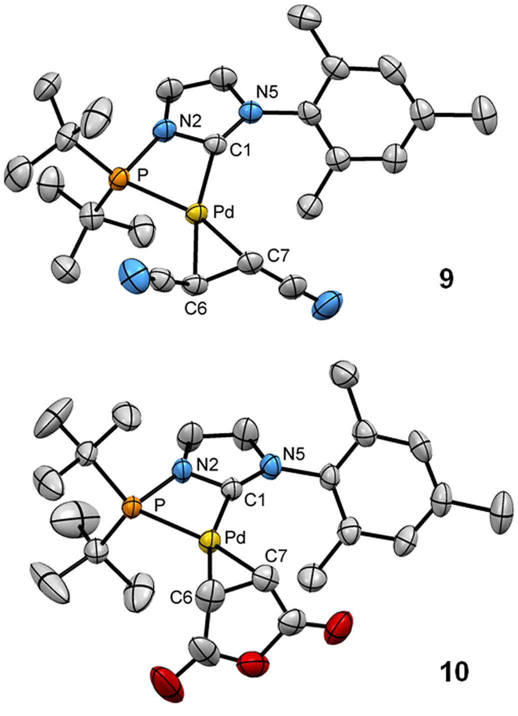


**Figure 4.** ORTEP diagrams of the solid-state structures of **9** and **10** with 50% ellipsoids. Hydrogens are omitted for clarity.

bond lengths and angles partially differ somewhat (Table 3). The C═C double bond (1.443(3)/1.452(3) Å) in the fumaronitrile complex **9** is elongated compared to the free olefin (1.249 Å).[18] This is also observed in the maleic anhydride complex **10**, where the C═C double bond (1.427(4)/1.422(5) Å) is also longer than in the uncoordinated olefin (1.3322(9) Å).[19] This feature is clear evidence for the above-mentioned resonance contribution of metallacyclopropane character. Compound **11** was also crystallized, but the data obtained were of moderate quality and only useful as a proof of the overall constitution.

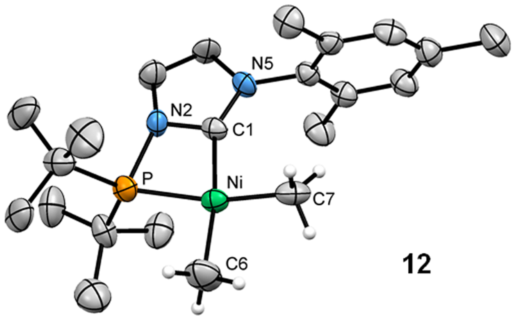
**Synthesis of a Neutral NHCP Nickel Complex.** The *cis*-dimethyl compound ($^{Mes}$CNP κ-C,κ-P)$NiMe_2$ **12** was obtained similarly to the palladium complex **8**. The free carbene **5a** was reacted with (tmeda)$NiMe_2$ in pentane at low temperature in a heterogeneous reaction. The methyl ligands show two doublets at −0.83 and −0.64 ppm in the $^1H$ NMR with coupling constants of 12.2 and 4.6 Hz. The phosphorus resonance is at

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for Methyl Complexes of the Nickel Triad 7a, 8, and 12**

| | ($^{Mes}$CNP)$PtMe_2$ (**7a**) | ($^{Mes}$CNP)$PdMe_2$ (**8**) | ($^{Mes}$CNP)$NiMe_2$ (**12**) |
|---|---|---|---|
| M−C1 | 2.042(17) | 2.097(2) | 1.920(6)/1.946(6) |
| M−P | 2.287(4) | 2.3310(6) | 2.2508(17)/2.2363(17) |
| M−C7 (*trans*-P) | 2.067(15) | 2.066(3) | 1.915(6)/1.927(6) |
| M−C6 (*trans*-C) | 2.059(16) | 2.056(3) | 1.926(6)/1.952(7) |
| P−N2 | 1.745(14) | 1.746(2) | 1.743(5)/1.749(5) |
| N2−C1 | 1.388(19) | 1.372(3) | 1.354(7)/1.370(7) |
| P−M−C1 | 68.0(4) | 67.59(7) | 69.91(19)/70.15(19) |
| C1−M−C7 | 99.4(6) | 100.50(10) | 98.8(3)/99.2(3) |
| C7−M−C6 | 87.4(7) | 87.15(11) | 89.4(3)/89.4(3) |
| P−M−C6 | 105.2(5) | 104.81(8) | 102.0(2)/101.3(2) |
| M−C1−N2 | 105.5(10) | 103.71(16) | 106.8(5)/105.7(4) |
| M−P−N2 | 85.2(4) | 84.08(7) | 82.05(18)/83.02(17) |
| P−N2−C1 | 101.1(10) | 104.18(16) | 101.1(4)/100.8(4) |

112 ppm. The complex decomposes partially in solution and does so even as a solid at temperatures higher than −20 °C.

X-ray quality crystals of **12** could be grown out of the reaction mixture. Again, two independent molecules are found in the unit cell, and the structure of the complex is shown in Figure 5. As all dimethyl complexes of the nickel triad (**7a**, **8**, **12**) were crystalline and could be successfully subjected to X-ray analysis, their relevant structural data are listed in Table 4. Compared with the corresponding platinum (**7a**, 68.0(4)°) and palladium (**8**, 67.59(7)°) complexes, the nickel complex **12** features the largest bite angle, with 69.91(19)° and 70.15(19)°. We interpret this as due to the fact that the bond lengths of the ligating NHCP atoms to the Ni center are shorter, just like the methyl to Ni distances. The geometries of the platinum (**7a**) and the palladium complex (**8**) are quite similar and different from the Ni compound (**12**).



**12**

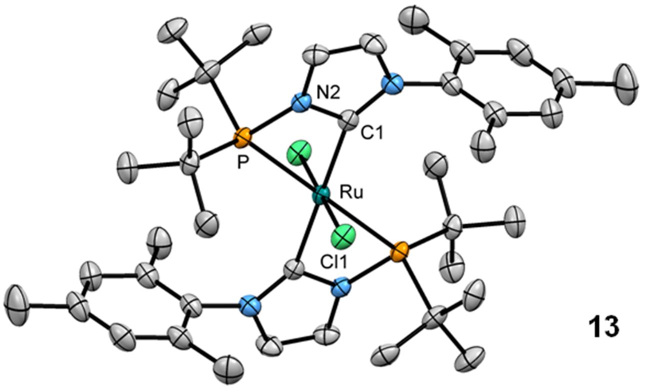
**Figure 5.** ORTEP diagram of the solid-state structures of **12** with 50% ellipsoids. Hydrogen atoms (except H atoms of the Ni-bound methyl groups) are omitted for clarity.

**Synthesis of a Neutral NHCP Ruthenium Complex.** The octahedral bis-chelate complex ($^{\text{Mes}}$CNP *κ-C*,*κ-P*)$_2$RuCl$_2$ **13** was synthesized by the reaction of two equivalents of $^{\text{Mes}}$CNP **5a** with (PPh$_3$)$_3$RuCl$_2$ in THF. The reaction with only one equivalent of the free NHCP also led to the precipitation of complex **13** and a nonseparable mixture of unidentifiable compounds in solution.

Crystals of **13** suitable for X-ray analysis were obtained directly from a preliminary NMR test reaction in $d_8$-THF and had grown in the NMR tube. The molecular structure of **13** is shown in Figure 6. The complex has an octahedral geometry with the two chloro ligands *trans* and an inversion center; hence the two chelate ligands are arranged in *trans* P−P position. The bond lengths within the coordination sphere are longer compared to the square-planar platinum complex **6a**. Especially the Ru−P bond is around 0.2 Å longer (Ru 2.4096(5), Pt 2.216(2) Å), and therefore this complex exhibits the smallest bite angle (65.25(6)°) of all four-membered chelate NHCP complexes presented here.

## CONCLUSIONS

Bulky, electron-rich *N*-phosphanyl-functionalized NHCP ligands ($^{\text{R}}$CNP systems) are accessible in a few steps and in good yields. Their transition metal complexes (Ni, Pd, Pt, Ru) feature four-membered chelate (*κ-C*,*κ-P*) metal coordination with extraordinarily small P−M−C bite angles, around 65−69°, but these compounds are quite stable despite their apparent ring strain. They were synthesized by the replacement of other ligands such as COD, tmeda, or PPh$_3$ of appropriate precursor complexes, employing the isolated NHCP ligands. The Pd(II) dimethyl complex (**8**) reacted readily with electron-poor olefins at room temperature under ethane elimination, leading to novel Pd(0) olefin complexes. With an electron-deficient alkyne a Pd(II) metallacyclopentadiene complex was formed. The chemistry and in particular the potential for metal-catalyzed reactions of this class of NHCP complexes are currently being investigated in our lab.



**13**

**Figure 6.** ORTEP diagram of the solid-state structure of **13** with 50% ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard derivations: Ru−C1 = 2.073(2), Ru−P = 2.4096(5), Ru−Cl1 = 2.4466(5), P−N2 = 1.7412(18), N2−C1 = 1.370(3), P−Ru−C1 = 65.25(6), C1−Ru−Cl1 = 79.12(6), P−Ru−Cl1 = 90.181(19), Ru−C1−N2 = 106.37(13), Ru−P−N2 = 82.75(6), P−N2−C1 = 102.24(13).

## EXPERIMENTAL SECTION

**General Comments.** All manipulations were carried out under an atmosphere of dry argon using standard Schlenk- and syringe-cannula techniques or in a glovebox containing dry argon and less than 1 ppm oxygen and water. Solvents were dried over an appropriate drying agent, distilled under an atmosphere of argon, and stored over molecular sieves (3 Å). Di-*tert*-butylchlorophosphine,[5d] 1-mesitylimidazole,[20] 1-(2,6-diisopropylphenyl)imidazole,[20] (COD)PtCl$_2$,[21] (COD)PtMe$_2$, (tmeda)PdMe$_2$,[22] and (tmeda)NiMe$_2$[23] were prepared according to the literature. NMR spectra were recorded using a Bruker DRX 300 or DRX 500 or a Bruker AVANCE III 600 spectrometer with both the $^{31}$P and $^{13}$C spectra being measured in the $^1$H decoupled mode. Chemical shifts are given in ppm referenced to solvent ($^1$H, $^{13}$C). Abbreviations used are s = singlet, d = doublet, t = triplet, pt = pseudotriplet, q = quartet, dd = doublet of doublets, sept = septet, s + sat = singlet + satellites, d + sat = doublet + satellites. Infrared spectra were measured on a Nicolet Magna IR 550 (ATR) or on a Bruker FT-IR Equinox 55 spectrometer in KBr pellets. Mass spectra were recorded on a JEOL JMS-700 or Bruker ApexQe hybrid 9.4 T FT-ICR instrument. Elemental analyses were performed in the "Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg".

*1-(Di-tert-butylphosphino)imidazole (**1**).* To a solution of imidazole (0.68 g, 10.0 mmol) and triethylamine (1.06 g, 10.5 mmol) in Et$_2$O (7 mL) was added a solution of di-*tert*-butylchlorophosphine (1.81 g, 10.0 mmol) in Et$_2$O (7 mL). The reaction mixture was stirred for 24 h at room temperature. Precipitated triethylamine hydrochloride was filtered off and extracted three times with Et$_2$O. The filtrate was concentrated *in vacuo* until dryness and was subjected twice to a Kugelrohr distillation to give **1** as a colorless solid (2.04 g, 96%). $^1$H NMR (300.1 MHz, CDCl$_3$): $\delta$ 1.20 (d, 18H, $^3J_{\text{H,P}}$ = 12.8 Hz, CH$_3$-*t*Bu), 7.14 (s, 1H, CH4/5-Im), 7.18 (s, 1H, CH4/5-Im), 7.71 (s, 1H, CH2-Im). $^{13}$C{$^1$H} NMR (75.5 MHz, CDCl$_3$): $\delta$ 28.8 (d, $^2J_{\text{C,P}}$ = 16.0 Hz, CH$_3$-*t*Bu), 34.5 (d, $^1J_{\text{C,P}}$ = 34.5 Hz, C$_{\text{quart}}$-*t*Bu), 123.1 (CH4/5-Im), 130.1 (CH4/5-Im), 144.1 (CH2-Im). $^{31}$P{$^1$H} NMR (101.3 MHz, CDCl$_3$): $\delta$ 88.6 (s). MS (CI): *m*/*z* 213.2 (M$^+$ + H), 229.3 (M$^+$ + O + H). IR (KBr): $\nu$ (cm$^{-1}$) 3120 m, 3105 m, 2960 s, 2864 s, 1702 w, 1633 w, 1457 s, 1371 s, 1361 s, 1230 s, 1152 s, 1066 s, 671 s, 517 s . Anal. Calcd for $C_{11}H_{21}N_2P$: C, 62.24; H, 9.97; N, 13.20; P, 14.59. Found: C, 61.97; H, 10.12; N, 13.07; P, 14.48.

*3-(Di-tert-butylphosphino)-1-ethylimidazolium Tetrafluoroborate (**2**).* **1** (465 mg, 2.19 mmol) and ethyl Meerwein's salt (415 mg, 2.19 mmol) were placed in a Schlenk tube and cooled to 0 °C in an ice bath. Then 8 mL of equally cooled DME was added, and the reaction mixture was allowed to warm to room temperature and stirred for 8 d. The solution was concentrated *in vacuo* until dryness, and the resulting solid was washed with pentane and recrystallized from DME at low temperatures. The product was washed twice with pentane and dried *in vacuo*, to give **2** as a colorless powder (647 mg, 90%), which was stored at −20 °C. $^{1}$H NMR (300.1 MHz, $CD_2Cl_2$): $\delta$ 1.26 (d, 18H, $^{3}J_{H,P}$ = 13.5 Hz, $CH_3$-*t*Bu), 1.57 (t, 3H, $^{3}J_{H,H}$ = 7.4 Hz, $CH_3$-Et), 4.43 (q, 2H, $^{3}J_{H,H}$ = 7.4 Hz, $CH_2$-Et), 7.52 (d, 1H, $J$ = 1.6 Hz, CH4/5-Im), 7.60 (s, 1H, CH4/5-Im), 9.02 (s, 1H, CH2-Im). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CD_2Cl_2$): $\delta$ 15.7 ($CH_3$-Et), 28.7 (d, $^{2}J_{C,P}$ = 16.0 Hz, $CH_3$-*t*Bu), 35.6 (d, $^{1}J_{C,P}$ = 30.0 Hz, $C_{quart}$-*t*Bu), 46.1 ($CH_2$-Et), 123.7 (CH4/5-Im), 127.3 (CH4/5-Im), 141.3 (CH2-Im). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CD_2Cl_2$): $\delta$ 120.6 (s). MS (ESI MS/MS): $m/z$ 241.2 ($M^+$), 184.4 ($M^+$ − *t*Bu), 97.2 ($M^+$ − P(*t*Bu)$_2$). IR (KBr): $\nu$ (cm$^{-1}$) 3133 s, 2997 s, 2962 s, 1571 m, 1527 m, 1475 s, 1371 m, 1174 m, 1125 vs, 1098 vs, 1014 vs, 807 m, 770 m, 650 m, 502 m. Anal. Calcd for $C_{13}H_{26}BF_4N_2P$: C, 47.58; H, 7.99; N, 8.54; P, 9.44. Found: C, 47.08; H, 7.90; N, 8.70; P, 9.41.

*3-(Di-tert-butylphosphino)-1-ethylimidazol-2-ylidene (**3**).* To a suspension of the salt **2** (164 mg, 0.5 mmol) in $Et_2O$ (3 mL) was added dropwise at −20 °C over 30 min a solution of sodium bis(trimethylsilyl)amide (92 mg, 0.5 mmol) in $Et_2O$ (2 mL). The reaction mixture was stirred at this temperature for 30 min. The solvent was removed *in vacuo*, and the product was extracted with pentane (3 × 3 mL) and filtered off. The filtrate was concentrated *in vacuo* until the product started to precipitate. The solution was put into a freezer (−40 °C) for full crystallization. The solvent was filtered off at −40 °C, and the product was dried *in vacuo* to give **3** as a colorless crystalline solid (75 mg, 63%), which was stored at −20 °C. $^{1}$H NMR (500.1 MHz, *d*-THF): $\delta$ 1.21 (d, 18H, $^{3}J_{H,P}$ = 12.4 Hz, $CH_3$-*t*Bu), 1.36 (t, 3H, $^{3}J_{H,H}$ = 7.3 Hz, $CH_3$-Et), 4.08 (q, 2H, $^{3}J_{H,H}$ = 7.3 Hz, $CH_2$-Et), 6.93 (s, 1H, CH5-Im), 6.98 (d, 1H, $^{3}J_{H,P}$ = 3.9 Hz, CH4-Im). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, *d*-THF): $\delta$ 17.7 ($CH_3$-Et), 29.6 (d, $^{2}J_{C,P}$ = 16.2 Hz, $CH_3$-*t*Bu), 35.4 (d, $^{1}J_{C,P}$ = 35.4 Hz, $C_{quart}$-*t*Bu), 46.5 ($CH_2$-Et), 117.4 (d, $^{3}J_{C,P}$ = 8.1 Hz, CH5-Im), 128.6 (d, $^{2}J_{C,P}$ = 35.7 Hz, CH4-Im), 223.5 ($C_{carbene}$). $^{31}P\{^{1}H\}$ NMR (202.5 MHz, *d*-THF): $\delta$ 97.2 (s). MS (HR-EI): $m/z$ 240.1773 ($M^+$). Due to the sensitivity of **3**, a correct elemental analysis was not obtained.

*3-(Di-tert-butylphosphino)-1-mesitylimidazolium Triflate (**4a**).* To a solution of 1-mesitylimidazole (4.66 g, 25.0 mmol) and sodium triflate (4.73 g, 27.5 mmol, 1.1 equiv) in THF (40 mL) was added dropwise at −20 °C di-*tert*-butylchlorophosphine (5.21 g, 27.5 mmol, 1.1 equiv). The reaction mixture was allowed to warm slowly to room temperature and stirred for 24 h. After evaporation of the solvent the product was extracted with $CH_2Cl_2$ (3 × 30 mL) and filtered off. The filtrate was concentrated *in vacuo* until dryness and washed with pentane (2 × 40 mL) to give **4a** as colorless powder (10.10 g, 84%). Mp: 171 °C. $^{1}$H NMR (300.1 MHz, $CD_2Cl_2$): $\delta$ 1.32 (d, 18H, $^{3}J_{H,P}$ = 13.7 Hz, $CH_3$-*t*Bu), 2.04 (s, 6H, *o*-$CH_3$-Mes), 2.37 (s, *p*-$CH_3$-Mes), 7.02 (s, 2H, CH-Mes), 7.61 (s, 1H, CH5-Im), 7.95 (s, 1H, CH4-Im), 8.79 (s, 1H, CH2-Im). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CD_2Cl_2$): $\delta$ 17.6 (*o*-$CH_3$-Mes), 21.4 (*p*-$CH_3$-Mes), 28.7 (d, $^{2}J_{C,P}$ = 16.1 Hz, $CH_3$-*t*Bu), 35.7 (d, $^{1}J_{C,P}$ = 30.3 Hz, $C_{quart}$-*t*Bu), 126.4 (CH5-Im), 128.1 (CH4-Im), 130.3 (CH-Mes), 130.7 ($C_{quart}$-Mes), 134.5 ($C_{quart}$-Mes), 142.1 ($C_{quart}$-Mes), 142.3 (CH2-Im). $^{31}P\{^{1}H\}$ NMR (121.6 MHz, $CD_2Cl_2$): $\delta$ 122.7 (s). MS (ESI$^+$): $m/z$ 331.22987 ($M^+$). IR (ATR): $\nu$ (cm$^{-1}$) 3085 w, 2958 w, 2872 w, 2361 w, 1540 w, 1515 m, 1471 w, 1368 w, 1264 vs, 1224 m, 1152 s, 1111 s, 1065 m, 1030 vs, 864 w, 774 w, 675 m. Anal. Calcd for $C_{21}H_{32}F_3N_2O_3PS$: C, 52.49; H, 6.71; N, 5.83; P, 6.45. Found: C, 52.65; H, 6.75; N, 5.93; P, 6.16.

*3-(Di-tert-butylphosphino)-1-mesitylimidazol-2-ylidene (**5a**).* To a suspension of the salt **4a** (6.84 g, 14.2 mmol) in $Et_2O$ (20 mL) was added dropwise at −5 °C over 1 h a solution of sodium bis(trimethylsilyl)amide (2.61 g, 14.2 mmol) in THF (20 mL). The reaction mixture was stirred at this temperature for 30 min. The solvent was removed *in vacuo*, and the product was extracted with pentane (3 × 20 mL) and filtered off. The filtrate was concentrated *in vacuo* until the product started to precipitate. The solution was put into a freezer (−40 °C) for full crystallization. The solvent was filtered off at −40 °C, and the product was dried *in vacuo* to give **5a** as a colorless crystalline solid (4.04 g, 86%), which was stored at −20 °C. Mp: 106 °C. $^{1}$H NMR (300.1 MHz, $C_6D_6$): $\delta$ 1.37 (d, 18H, $^{3}J_{H,P}$ = 12.4 Hz, $CH_3$-*t*Bu), 2.02 (s, 6H, *o*-$CH_3$-Mes), 2.14 (s, *p*-$CH_3$-Mes), 6.35 (pt, 1H, $^{4}J_{H,P}$ = 1.5 Hz, $^{3}J_{H,H}$ = 1.5 Hz, CH5-Im), 6.76 (s, 2H, CH-Mes), 7.08 (dd, 1H, $^{3}J_{H,P}$ = 4.8 Hz, $^{3}J_{H,H}$ = 1.5 Hz, CH4-Im). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $C_6D_6$): $\delta$ 16.5 (*o*-$CH_3$-Mes), 21.4 (*p*-$CH_3$-Mes), 29.4 (d, $^{2}J_{C,P}$ = 16.1 Hz, $CH_3$-*t*Bu), 35.3 (d, $^{1}J_{C,P}$ = 24.1 Hz, $C_{quart}$-*t*Bu), 119.3 (d, $^{3}J_{C,P}$ = 8.0 Hz, CH5-Im), 128.4 (d, $^{2}J_{C,P}$ = 35.1 Hz, CH4-Im), 129.4 (CH-Mes), 135.6 ($C_{quart}$-Mes), 137.5 ($C_{quart}$-Mes), 139.5 ($C_{quart}$-Mes), 225.8 ($C_{carbene}$). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, $C_6D_6$): $\delta$ 99.9 (s). MS (HR-FAB$^+$): $m/z$ 331.2290 ($M^+$ + 1). IR (ATR): $\nu$ (cm$^{-1}$) 3138 w, 2946 m, 2855 m, 1585 w, 1493 m, 1460 m, 1361 m, 1238 w, 1170 s, 1124 s, 1077 s, 1032 w, 1009 m, 922 m, 850 s, 808 s, 740 vs. Anal. Calcd for $C_{20}H_{31}N_2P$: C, 72.69; H, 9.46; N, 8.48; P, 9.37. Found: C, 72.49; H, 9.55; N, 8.55; P, 9.33.

*3-(Di-tert-butylphosphino)-1-(2,6-di-isopropylphenyl)-imidazolium Triflate (**4b**).* To a solution of 1-(2,6-diisopropylphenyl)-imidazole (5.71 g, 25.0 mmol) and sodium triflate (4.73 g, 27.5 mmol, 1.1 equiv) in THF (40 mL) was added dropwise at −20 °C di-*tert*-butylchlorophosphine (5.21 g, 27.5 mmol, 1.1 equiv). The reaction mixture was allowed to warm slowly to room temperature and stirred for 48 h. After evaporation of the solvent the product was extracted with $CH_2Cl_2$ (3 × 30 mL) and filtered off. The filtrate was concentrated *in vacuo* until dryness and washed with pentane (2 × 40 mL) to give **4b** as colorless powder (8.34 g, 64%). Mp: 186 °C. $^{1}$H NMR (300.1 MHz, $CD_2Cl_2$): $\delta$ 1.17 (d, 6H, $^{3}J_{H,H}$ = 7.0 Hz, $CH_3$-*i*Pr), 1.20 (d, 6H, $^{3}J_{H,H}$ = 6.9 Hz, $CH_3$-*i*Pr), 1.33 (d, 18H, $^{3}J_{H,P}$ = 13.4 Hz, $CH_3$-*t*Bu), 2.22 (sept, 2H, $^{3}J_{H,H}$ = 6.9 Hz, CH-*i*Pr), 7.37 (d, 2H, $^{3}J_{H,H}$ = 7.7 Hz, CH-Ar), 7.60 (t, 1H, $^{3}J_{H,H}$ = 7.8 Hz, CH-Ar), 7.69 (s, 1H, CH5-Im), 8.05 (s, 1H, CH4-Im), 8.73 (s, 1H, CH2-Im). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CD_2Cl_2$): $\delta$ 24.0 ($CH_3$-*i*Pr), 24.5 ($CH_3$-*i*Pr), 28.7 (d, $^{2}J_{C,P}$ = 16.1 Hz, $CH_3$-*t*Bu), 29.5 (CH-*i*Pr), 35.8 (d, $^{1}J_{C,P}$ = 30.1 Hz, $C_{quart}$-*t*Bu), 125.3 (2C, CH-Ar), 127.6 (CH5-Im), 128.3 (CH4-Im), 130.2 ($C_{quart}$-Ar), 132.7 (1C, CH-Ar), 142.3 (CH2-Im), 145.5 ($C_{quart}$-Ar). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CD_2Cl_2$): $\delta$ 123.8 (s). MS (ESI$^+$): $m/z$ 373.27644 ($M^+$). IR (ATR): $\nu$ (cm$^{-1}$) 3081 w, 2963 w, 2868 w, 1508 w, 1471 w, 1369 w, 1263 vs, 1225 m, 1150 m, 1094 m, 1066 m, 1032 s, 907 w, 806 m, 783 w, 760 m, 682 w. Anal. Calcd for $C_{24}H_{38}F_3N_2O_3PS$: C, 55.16; H, 7.33; N, 5.36; S, 6.14; P, 5.93. Found: C, 55.08; H, 7.21; N, 5.37; S, 5.86; P, 5.78.

*3-(Di-tert-butylphosphino)-1-(2,6-di-isopropylphenyl)imidazol-2-ylidene (**5b**).* To a suspension of the salt **4b** (1.57 g, 3.0 mmol) in $Et_2O$ (15 mL) was added dropwise at −5 °C over 30 min a solution of sodium bis(trimethylsilyl)amide (0.58 g, 3.15 mmol) in THF (7 mL). The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The solvent was removed *in vacuo*, and the product was extracted with pentane (3 × 10 mL) and filtered off. The filtrate was concentrated *in vacuo* until the product started to precipitate, and the solution was put in a freezer (−40 °C) for full crystallization. The solvent was filtered off at −40 °C, and the product was dried *in vacuo* to give **5b** as colorless crystalline solid (0.68 g, 61%), which was stored at −20 °C. Mp: 156 °C. $^{1}$H NMR (500.1 MHz, *d*-THF): $\delta$ 1.12 (d, 6H, $^{3}J_{H,H}$ = 6.9 Hz, $CH_3$-*i*Pr), 1.13 (d, 6H, $^{3}J_{H,H}$ = 6.9 Hz, $CH_3$-*i*Pr), 1.28 (d, 18H, $^{3}J_{H,P}$ = 12.2 Hz, $CH_3$-*t*Bu), 2.57 (sept, 2H, $^{3}J_{H,H}$ = 6.9 Hz, CH-*i*Pr), 6.99 (dd, 1H, $^{4}J_{H,P}$ = 1.2 Hz, $^{3}J_{H,H}$ = 1.5 Hz, CH5-Im), 7.22 (dd, 1H, $^{3}J_{H,P}$ = 5.0 Hz, $^{3}J_{H,H}$ = 1.5 Hz, CH4-Im), 7.23 (d, 2H, $^{3}J_{H,H}$ = 7.7 Hz, CH-Ar), 7.34 (t, 1H, $^{3}J_{H,H}$ = 7.7 Hz, CH-Ar). $^{13}C\{^{1}H\}$ NMR (125.8 MHz, *d*-THF): $\delta$ 23.9 ($CH_3$-*i*Pr), 25.0 ($CH_3$-*i*Pr), 29.2 (CH-*i*Pr), 29.6 (d, $^{2}J_{C,P}$ = 16.1 Hz, $CH_3$-$^{t}$Bu), 35.6 (d, $^{1}J_{C,P}$ = 24.7 Hz, $C_{quart}$-*t*Bu), 121.2 (d, $^{3}J_{C,P}$ = 8.0 Hz, CH5-Im), 124.1 (2C, CH-Ar), 128.6 (d, $^{2}J_{C,P}$ = 35.6 Hz, CH4-Im), 129.3 (1C, CH-Ar), 139.7 ($C_{quart}$-Ar), 146.8 ($C_{quart}$-Ar), 226.4 ($C_{carbene}$). $^{31}P\{^{1}H\}$ NMR (121.7 MHz, *d*-THF): $\delta$ 98.7 (s). MS (ESI$^+$): $m/z$ 373.2805 ($M^+$ + 1). IR (ATR): $\nu$

(cm$^{-1}$) 3134 w, 3089 w, 3052 w, 2963 s, 2865 w, 1593 w, 1495 w, 1471 s, 1382 s, 1359 m, 1254 w, 1171 s, 1107 m, 1084 vs, 1060 m, 1011 m, 956 m, 806 vs, 761 vs, 748 vs, 731 m. Anal. Calcd for $C_{23}H_{37}N_2P$: C, 74.15; H, 10.01; N, 7.52; P, 8.31. Found: C, 74.30; H, 10.06; N, 7.59; P, 8.21.

***(${}^{Mes}$CNP κ-C,κ-P)PtCl$_2$ (6a).*** ${}^{Mes}$CNP **5a** (79 mg, 240 μmol) was added in portions to a suspension of (COD)PtCl$_2$ (75 mg, 200 μmol) in THF (3 mL) and stirred for 24 h. The solvent was filtered off, and the solid was washed with THF (5 mL) and pentane (5 mL) and dried *in vacuo* to give **6a** as a colorless powder (123 mg, 88%). Mp: 305 °C (dec). $^1$H NMR (300.1 MHz, *d*-DMSO): δ 1.49 (d, 18H, $^3J_{H,P}$ = 17.0 Hz, CH$_3$-*t*Bu), 1.98 (s, 6H, *o*-CH$_3$-Mes), 2.29 (s, *p*-CH$_3$-Mes), 6.98 (s, 2H, CH-Mes), 7.30 (s, 1H, CH5-Im), 8.17 (s, CH4-Im). $^{13}$C{$^1$H} NMR (75.5 MHz, *d*-DMSO): δ 17.2 (*o*-CH$_3$-Mes), 20.7 (*p*-CH$_3$-Mes), 27.1 (d, $^2J_{C,P}$ = 4.6 Hz, CH$_3$-*t*Bu), 37.4 (d, $^1J_{C,P}$ = 13.8 Hz, C$_{quart}$-*t*Bu), 124.2 (CH5-Im), 124.9 (CH4-Im), 128.5 (CH-Mes), 132.8 (C$_{quart}$-Mes), 134.1 (C$_{quart}$-Mes), 138.5 (C$_{quart}$-Mes), (C$_{carbene}$) could not be detected due to low solubility. $^{31}$P{$^1$H} NMR (101.3 MHz, *d*-DMSO): δ 85.5 (s + sat, $^1J_{P,Pt}$ = 3439.9 Hz). MS (HR-FAB$^+$): *m*/*z* 596.1270 (M$^+$), 560.1555 (M$^+$ − Cl). IR (ATR): ν (cm$^{-1}$) 3150 w, 3091 s, 2966 s, 2921 m, 2223 w, 1610 w, 1536 m, 1470 s, 1417 m, 1395 w, 1373 m, 1316 m, 1300 m, 1172 m, 1156 s, 1098 w, 1025 w, 978 w, 914 w, 849 m, 808 w, 758 w, 729 s, 700 m, 640 m. Anal. Calcd for $C_{20}H_{31}Cl_2N_2PPt_2$: C, 40.27; H, 5.24; N, 4.70; P, 5.19. Found: C, 40.15; H, 5.26; N, 4.56; P, 5.34.

***(${}^{Mes}$CNP κ-C,κ-P)PtMe$_2$ (7a).*** ${}^{Mes}$CNP **5a** (73 mg, 220 μmol) was added in portions to a solution of (COD)PtMe$_2$ (67 mg, 200 μmol) in THF (5 mL) and stirred for 2 h. After evaporation of the solvent, the solid was washed with pentane (5 mL) and dried *in vacuo* to give **7a** as colorless powder (98 mg, 88%). Mp: 170 °C (dec). $^1$H NMR (500.1 MHz, *d*-THF): δ 0.01 (d + sat, 3H, $^2J_{H,Pt}$ = 83.0 Hz, $^3J_{H,P}$ = 7.3 Hz, CH$_{3(trans-P)}$-Pt), 0.30 (d + sat, 3H, $^2J_{H,Pt}$ = 71.9 Hz, $^3J_{H,P}$ = 7.0 Hz, CH$_{3(cis-P)}$-Pt), 1.42 (d, 18H, $^3J_{H,P}$ = 13.7 Hz, CH$_3$-*t*Bu), 2.06 (s, 6H, *o*-CH$_3$-Mes), 2.30 (s, *p*-CH$_3$-Mes), 6.74 (s, 1H, CH5-Im), 6.94 (s, 2H, CH-Mes), 7.32 (s, 1H, CH4-Im). $^{13}$C{$^1$H} NMR (125.8 MHz, *d*-THF): δ −13.7 (d, $^2J_{C,P}$ = 4.0 Hz, CH$_{3(cis-P)}$-Pt), −6.2 (d, $^2J_{C,P}$ = 106.7 Hz, CH$_{3(trans-P)}$-Pt), 18.0 (*o*-CH$_3$-Mes), 21.3 (*p*-CH$_3$-Mes), 28.9 (d, $^2J_{C,P}$ = 8.0 Hz, CH$_3$-*t*Bu), 36.2 (d, $^1J_{C,P}$ = 3.4 Hz, C$_{quart}$-*t*Bu), 122.8 (CH5-Im), 124.1 (d, $^2J_{C,P}$ = 7.5 Hz, CH4-Im), 129.6 (CH-Mes), 135.9 (C$_{quart}$-Mes), 136.2 (C$_{quart}$-Mes), 139.4 (C$_{quart}$-Mes), 175.9 (d, $^2J_{C,P}$ = 4.6 Hz, C$_{carbene}$). $^{31}$P{$^1$H} NMR (101.3 MHz, *d*-THF): δ 104.0 (s + sat, $^1J_{P,Pt}$ = 1279.4 Hz). MS (HR-FAB$^+$): *m*/*z* 555.2300 (M$^+$), 540.2095 (M$^+$ − Me), 524.1799 (M$^+$ − 2Me). IR (ATR): ν (cm$^{-1}$) 3072 w, 3027 w, 2860 m, 2353 w, 1610 w, 1528 w, 1469 m, 1390 m, 1367 m, 1307 m, 1291 m, 1262 w, 1155 s, 1094 w, 1022 m, 972 w, 933 m, 853 s, 808 s, 734 s, 675 m. Anal. Calcd for $C_{22}H_{37}N_2PPt_2$: C, 47.56; H, 6.71; N, 5.04; P, 5.57. Found: C, 47.43; H, 6.69; N, 5.00; P, 5.49.

***(${}^{Dipp}$CNP κ-C,κ-P)PtCl$_2$ (6b).*** ${}^{Dipp}$CNP **5b** (75 mg, 200 μmol) was added in portions to a suspension of (COD)PtCl$_2$ (75 mg, 200 μmol) in THF (5 mL) and stirred for 24 h. The solvent was filtered off, and the solid was washed with THF (5 mL) and pentane (5 mL) and dried *in vacuo* to give **6b** as a colorless powder (98 mg, 77%). Mp: 307 °C (dec). $^1$H NMR (600.1 MHz, CD$_3$CN): δ 1.12 (d, 6H, $^3J_{H,H}$ = 6.9 Hz, CH$_3$-*i*Pr), 1.29 (d, 6H, $^3J_{H,H}$ = 6.9 Hz, CH$_3$-*i*Pr), 1.54 (d, 18H, $^3J_{H,P}$ = 17.2 Hz, CH$_3$-*t*Bu), 2.45 (sept, 2H, $^3J_{H,H}$ = 6.9 Hz, CH-*i*Pr), 6.94 (dd, 1H, $^3J_{H,H}$ = 2.0 Hz, $^3J_{H,P}$ = 1.0 Hz CH5-Im), 7.28 (d, 2H, $^3J_{H,H}$ = 7.7 Hz, CH-Ar), 7.47 (t, 1H $^3J_{H,H}$ = 7.7 Hz, CH-Ar), 7.53 (pt, 1H $^3J_{H,H}$ = 2.0 Hz, $^3J_{H,P}$ = 2.0 Hz, CH4-Im). $^{13}$C{$^1$H} NMR (150.9 MHz, *d*-CD$_3$CN): δ 23.9 (CH$_3$-*i*Pr), 24.0 (CH$_3$-*i*Pr), 28.1 (d, $^2J_{C,P}$ = 4.9 Hz, CH$_3$-*t*Bu), 29.6 (CH-*i*Pr), 38.8 (d, $^1J_{C,P}$ = 13.2 Hz, C$_{quart}$-*t*Bu), 124.4 (d, $^2J_{C,P}$ = 6.2 Hz, CH4-Im), 124.6 (2C, CH-Ar), 126.6 (d, $^3J_{C,P}$ = 2.8 Hz, CH5-Im), 131.3 (1C, CH-Ar), 133.7 (C$_{quart}$-Ar), 146.3 (C$_{quart}$-Ar), (C$_{carbene}$) could not be detected due to low solubility. $^{31}$P{$^1$H} NMR (101.3 MHz, CD$_3$CN): δ 84.7 (s + sat, $^1J_{P,Pt}$ = 3440.5 Hz). MS (HR-FAB$^+$): *m*/*z* 602.2080 (M$^+$ − Cl). IR (ATR): ν (cm$^{-1}$) 3142 w, 3091 w, 2960 w, 2361 m, 2341 m, 1739 w, 1536 w, 1460 m, 1446 w, 1417 w, 1373 w, 1364 w, 1321 w, 1301 w, 1184 w, 1159 m, 1095 w, 974 w, 938 w, 802 m, 761 s, 700 m, 668 w. Despite several attempts, the microanalysis values are outside the range associated with analytical purity, probably due to some unidentified impurities, not visible in the spectra.

***(${}^{Dipp}$CNP κ-C,κ-P)PtMe$_2$ (7b).*** ${}^{Dipp}$CNP **5b** (62 mg, 165 μmol) was added in portions to a solution of (COD)PtMe$_2$ (50 mg, 150 μmol) in THF (3 mL) and stirred for 5 h. After evaporation of the solvent, the solid was washed with pentane (5 mL) and dried *in vacuo* to give **7b** as colorless powder (72 mg, 80%). Mp: 197 °C (dec). $^1$H NMR (300.1 MHz, *d*-THF): δ −0.06 (d + sat, 3H, $^2J_{H,Pt}$ = 82.4 Hz, $^3J_{H,P}$ = 7.6 Hz, CH$_{3(trans-P)}$-Pt), 0.28 (d + sat, 3H, $^2J_{H,Pt}$ = 72.2 Hz, $^3J_{H,P}$ = 6.8 Hz, CH$_{3(cis-P)}$-Pt), 1.12 (d, 6H, $^3J_{H,H}$ = 6.9 Hz, CH$_3$-*i*Pr), 1.26 (d, 6H, $^3J_{H,H}$ = 6.9 Hz, CH$_3$-*i*Pr), 1.43 (d, 18H, $^3J_{H,P}$ = 13.7 Hz, CH$_3$-*t*Bu), 2.65 (sept, 2H, $^3J_{H,H}$ = 6.9 Hz, CH-*i*Pr), 6.87 (pt, 1H, $^3J_{H,H}$ = 1.9 Hz, $^4J_{H,P}$ = 1.9 Hz, CH5-Im), 7.22 (d, 2H, $^3J_{H,H}$ = 7.7 Hz, CH-Ar), 7.33 (dd, 1H $^3J_{H,H}$ = 1.9 Hz, $^3J_{H,P}$ = 0.9 Hz, CH4-Im), 7.38 (t, 1H $^3J_{H,H}$ = 7.7 Hz, CH-Ar). $^{13}$C{$^1$H} NMR (75.5 MHz, *d*-THF): δ −13.7 (d, $^2J_{C,P}$ = 4.3 Hz, CH$_{3(cis-P)}$-Pt), −5.0 (d, $^2J_{C,P}$ = 106.9 Hz, CH$_{3(trans-P)}$-Pt), 24.0 (CH$_3$-*i*Pr), 24.3 (CH$_3$-*i*Pr), 28.8 (d, $^2J_{C,P}$ = 8.1 Hz, CH$_3$-*t*Bu), 29.5 (CH-*i*Pr), 36.3 (d, $^1J_{C,P}$ = 3.7 Hz, C$_{quart}$-*t*Bu), 123.8 (d, $^2J_{C,P}$ = 7.5 Hz, CH4-Im), 124.2 (CH5-Im), 124.3 (2C, CH-Ar), 130.5 (1C, CH-Ar), 136.2 (C$_{quart}$-Ar), 146.6 (C$_{quart}$-Ar), 176.9 (d, $^2J_{C,P}$ = 4.3 Hz, C$_{carbene}$). $^{31}$P{$^1$H} NMR (121.6 MHz, *d*-THF): δ 100.4 (s + sat, $^1J_{P,Pt}$ = 1288.4 Hz). MS (HR-FAB$^+$): *m*/*z* 597.2631, (M$^+$), 582.2443 (M$^+$ − Me), 567.2316 (M$^+$ − 2Me). IR (ATR): ν (cm$^{-1}$) 3117 w, 2962 w, 2864 w, 2782 w, 2361 w, 1464 m, 1397 m, 1368 w, 1295 w, 1259 w, 1180 w, 1152 m, 1115 w, 1023 m, 966 w, 807 s, 765 m, 723 m, 675 w. Despite several attempts, the microanalysis values for this compound, which has been characterized by X-ray, are outside the range associated with analytical purity, probably due to some unidentified impurities, not visible in the spectra.

***(${}^{Mes}$CNP κ-C,κ-P)PdMe$_2$ (8).*** ${}^{Mes}$CNP **5a** (1.43 g, 1.43 mmol) was added in portions to a solution of (tmeda)PdMe$_2$ (0.95 g, 3.76 mmol) in THF (20 mL) and stirred for 4 h. After evaporating the solvent, the solid was washed with pentane (2 × 10 mL) at 0 °C and Et$_2$O (2 × 10 mL) at −20 °C and dried *in vacuo* to give **8** as a colorless powder (1.39 g, 80%), which was stored at −20 °C. Mp: 152 °C (dec). $^1$H NMR (300.5 MHz, *d*-THF): δ −0.28 (d, 3H, $^3J_{H,P}$ = 8.0 Hz, CH$_{3(cis-P)}$-Pd), −0.25 (d, 3H, $^3J_{H,P}$ = 6.9 Hz, CH$_{3(trans-P)}$-Pd), 1.41 (d, 18H, $^3J_{H,P}$ = 13.2 Hz, CH$_3$-*t*Bu), 2.03 (s, 6H, *o*-CH$_3$-Mes), 2.30 (s, *p*-CH$_3$-Mes), 6.94 (s, 2H, CH-Mes), 6.94 (pt, 1H, $^3J_{H,H}$ = 1.8 Hz, $^4J_{H,P}$ = 1.8 Hz, CH5-Im), 7.43 (pt, 1H, $^3J_{H,H}$ = 1.8 Hz, $^3J_{H,P}$ = 1.8 Hz, CH4-Im). $^{13}$C{$^1$H} NMR (75.5 MHz, *d*-THF): δ −10.3 (d, $^2J_{C,P}$ = 4.8 Hz, CH$_{3(cis-P)}$-Pd), −3.8 (d, $^2J_{C,P}$ = 105.2 Hz, CH$_{3(trans-P)}$-Pd), 18.0 (*o*-CH$_3$-Mes), 21.2 (*p*-CH$_3$-Mes), 29.0 (d, $^2J_{C,P}$ = 10.4 Hz, CH$_3$-*t*Bu), 36.5 (d, $^1J_{C,P}$ = 12.5 Hz, C$_{quart}$-*t*Bu), 122.7 (d, $^2J_{C,P}$ = 6.9 Hz, CH4-Im), 123.3 (CH5-Im), 129.5 (CH-Mes), 135.6 (C$_{quart}$-Mes), 136.3 (C$_{quart}$-Mes), 139.1 (C$_{quart}$-Mes), 189.7 (C$_{carbene}$). $^{31}$P{$^1$H} NMR (121.5 MHz, *d*-THF): δ 101.5 (s). MS (HR-FAB$^+$): *m*/*z* 466.1461 (M$^+$), 451.1474 (M$^+$ − Me), 436.1200 (M$^+$ − 2Me). IR (ATR): ν (cm$^{-1}$) 3126 w, 2945 w, 2901 w, 2858 w, 1572 w, 1471 m, 1386 m, 1366 m, 1273 w, 1174 m, 1150 s, 1111 m, 1090 w, 1022 w, 931 w, 860 m, 807 m, 745 s, 732 s, 658 w. Anal. Calcd for $C_{22}H_{37}N_2PPd_2$: C, 56.59; H, 7.99; N, 6.00; P, 6.63. Found: C, 56.64; H, 8.11; N, 6.05; P, 6.37.

***(${}^{Mes}$CNP κ-C,κ-P)Pd(η$^2$-FN) (9).*** ${}^{Mes}$CNP **5a** (69 mg, 210 μmol) was added in portions to a solution of (tmeda)PdMe$_2$ (51 mg, 200 μmol) in THF (3 mL) and stirred for 4 h. Then fumaronitrile (16 mg, 200 μmol) was added in small portions, and the reaction mixture was stirred for 24 h. After evaporation of the solvent, the solid was washed with pentane (3 × 5 mL) and dried *in vacuo* to give **9** as a pale yellow powder (96 mg, 93%). Mp: 176 °C (dec). $^1$H NMR (300.1 MHz, *d*-THF): δ 1.41 (d, 9H, $^3J_{H,P}$ = 8.0 Hz, CH$_3$-*t*Bu), 1.46 (d, 9H, $^3J_{H,P}$ = 8.0 Hz, CH$_3$-*t*Bu), 2.03 (s, 3H, *o*-CH$_3$-Mes), 2.08 (s, 3H, *o*-CH$_3$-Mes), 2.32 (s, 3H, *p*-CH$_3$-Mes), 2.46 (d, 1H, $^3J_{H,H}$ = 9.3 Hz, CH-FN), 2.55 (d, 1H, $^3J_{H,H}$ = 9.3 Hz, CH-FN), 6.99 (s, 1H, CH-Mes), 7.02 (s, 1H, CH-Mes), 7.32 (pt, 1H, $^3J_{H,H}$ = 1.9 Hz, $^4J_{H,P}$ = 1.9 Hz, CH5-Im), 7.65 (dd, 1H, $^3J_{H,H}$ = 1.9 Hz, $^3J_{H,P}$ = 1.1 Hz, CH4-Im). $^{13}$C{$^1$H} NMR (75.5 MHz, *d*-THF): δ 18.1 (*o*-CH$_3$-Mes), 18.3 (CH-FN), 21.3 (*p*-CH$_3$-Mes), 21.7 (CH-FN), 28.8 (d, $^2J_{C,P}$ = 9.7 Hz, CH$_3$-*t*Bu), 30.0 (d, $^2J_{C,P}$ = 10.4 Hz, CH$_3$-*t*Bu), 36.6 (d, $^1J_{C,P}$ = 9.7 Hz, C$_{quart}$-*t*Bu), 37.5 (d, $^1J_{C,P}$ = 10.4 Hz, C$_{quart}$-*t*Bu), 123.4 (d, $^2J_{C,P}$ = 5.5 Hz, CH4-Im), 125.3 (d, $^3J_{C,P}$ = 2.8 Hz, CH5-Im), 129.6 (CH-Mes), 130.4 (CH-Mes), 134.9

(C$_{quart}$-Mes), 136.0 (C$_{quart}$-Mes), 136.1 (C$_{quart}$-Mes), 139.5 (C$_{quart}$-Mes), 191.2 (C$_{carbene}$). $^{31}$P{$^{1}$H} NMR (121.5 MHz, *d*-THF): δ 126.7 (s). MS (HR-FAB$^+$): *m*/*z* 514.1553 (M$^+$), 436.1269 (M$^+$ − FN). IR (ATR): ν (cm$^{-1}$) 2958, 2905, 2860, 2360 w, 2329 w, 2194 m, 1605 w, 1472 m, 1390 m, 1368 w, 1274 w, 1246 w, 1152 s, 1090 w, 1022 w, 933 w, 854 w, 807 m, 739 m, 723 m, 682 m. Anal. Calcd for $C_{24}H_{33}N_4PPd$: C, 55.98; H, 6.46; N, 10.88; P, 6.02. Found: C, 56.13; H, 6.52; N, 10.87; P, 5.74.

*($^{Mes}$CNP κ-C,κ-P)Pd($\eta^2$-MA) (**10**).* $^{Mes}$CNP **5a** (69 mg, 210 μmol) was added in portions to a solution of (tmeda)PdMe$_2$ (51 mg, 200 μmol) in THF (3 mL) and stirred for 4 h. Then maleic anhydride (20 mg, 200 μmol) was added in small portions, and the reaction mixture was stirred for 24 h. After evaporation of the solvent, the solid was washed with pentane (3 × 5 mL) and dried *in vacuo* to give **10** as a pale orange powder (96 mg, 91%). Mp: 183 °C (dec). $^{1}$H NMR (300.5 MHz, *d*-THF): δ 1.39 (d, 18H, $^{3}J_{H,P}$ = 14.3 Hz, CH$_3$-*t*Bu), 1.98 (s, 6H, *o*-CH$_3$-Mes), 2.33 (s, 3H, *p*-CH$_3$-Mes), 3.59 (s, 1H, CH-MA), 3.67 (s, 1H, CH-MA), 6.96 (s, 1H, CH-Mes), 7.03 (s, 1H, CH-Mes), 7.27 (dd, 1H, $^{3}J_{H,H}$ = 1.9 Hz, $^{4}J_{H,P}$ = 2.7 Hz, CH5-Im), 7.63 (dd, 1H, $^{3}J_{H,H}$ = 1.9 Hz, $^{3}J_{H,P}$ = 1.1 Hz, CH4-Im). $^{13}$C{$^{1}$H} NMR (75.5 MHz, *d*-THF): δ 17.7 (*o*-CH$_3$-Mes), 17.9 (*o*-CH$_3$-Mes), 21.2 (*p*-CH$_3$-Mes), 28.7 (d, $^{2}J_{C,P}$ = 7.6 Hz, CH$_3$-*t*Bu), 28.8 (d, $^{2}J_{C,P}$ = 9.0 Hz, CH$_3$-*t*Bu), 36.5 (d, $^{1}J_{C,P}$ = 11.1 Hz, C$_{quart}$-*t*Bu), 37.5 (d, $^{1}J_{C,P}$ = 10.4 Hz, C$_{quart}$-*t*Bu), 42.9 (CH-MA), 46.3 (CH-MA), 123.3 (d, $^{2}J_{C,P}$ = 6.2 Hz, CH4-Im), 125.3 (d, $^{3}J_{C,P}$ = 2.8 Hz, CH5-Im), 129.3 (CH-Mes), 130.3 (CH-Mes), 135.8 (C$_{quart}$-Mes), 136.4 (C$_{quart}$-Mes), 139.3 (C$_{quart}$-Mes), 173.3 (CO-MA), 190.4 (C$_{carbene}$). $^{31}$P{$^{1}$H} NMR (121.5 MHz, *d*-THF): δ 130.0 (s). MS (HR-FAB$^+$): *m*/*z* 534.1291 (M$^+$), 506.1357 (M$^+$ − CO), 436.1233 (M$^+$ − MA). IR (ATR): ν (cm$^{-1}$) 3138 w, 2946 w, 2893 w, 2864 w, 2357 w, 2329 w, 1789 vs, 1723 vs, 1601 w, 1471 w, 1392 m, 1334 m, 1219 s, 1174 m, 1149 s, 1060 m, 999 m, 931 w, 868 m, 803 s, 747 m, 702 s, 732 m, 683 m. Anal. Calcd for $C_{24}H_{33}N_2O_3PPd$: C, 53.89; H, 6.22; N, 5.24; P, 5.79. Found: C, 53.70; H, 6.38; N, 5.20; P, 5.57.

*($^{Mes}$CNP κ-C,κ-P)Pd($C_4(CO_2Me)_4$) (**11**).* DMAD (57 mg, 50 μL, 400 μmol) was added in portions to a solution of $^{Mes}$CNP-PdMe$_2$ **8** (70 mg, 150 μmol) in THF (3 mL) and stirred for 2 d. After evaporating the solvent and the excess DMAD at 70 °C, the solid was washed with Et$_2$O (3 × 5 mL) and pentane (3 × 5 mL) and dried *in vacuo* to give **11** as a yellow powder (100 mg, 92%). Mp: 223 °C (dec). $^{1}$H NMR (500.1 MHz, *d*-THF): δ 1.46 (d, 18H, $^{3}J_{H,P}$ = 14.9 Hz, CH$_3$-$^{t}$Bu), 2.02 (s, 6H, *o*-CH$_3$-Mes), 2.31 (s, 3H, *p*-CH$_3$-Mes), 2.81 (s, 3H, CH$_3$-O), 3.39 (s, 3H, CH$_3$-O), 3.45 (s, 3H, CH$_3$-O), 3.50 (s, 3H, CH$_3$-O), 6.94 (s, 1H, CH-Mes), 7.04 (dd, 1H, $^{3}J_{H,H}$ = 1.9 Hz, $^{4}J_{H,P}$ = 1.1 Hz, CH5-Im), 7.63 (pt, 1H, $^{3}J_{H,H}$ = 1.9 Hz, $^{3}J_{H,P}$ = 1.9 Hz, CH4-Im). $^{13}$C{$^{1}$H} NMR (125.8 MHz, *d*-THF): δ 18.2 (*o*-CH$_3$-Mes), 21.1 (*p*-CH$_3$-Mes), 28.9 (d, $^{2}J_{C,P}$ = 7.9 Hz, CH$_3$-*t*Bu), 38.0 (d, $^{1}J_{C,P}$ = 2.8 Hz, C$_{quart}$-*t*Bu), 50.5 (CH$_3$-O), 50.5 (CH$_3$-O), 50.6 (CH$_3$-O), 50.6 (CH$_3$-O), 124.6 (d, $^{2}J_{C,P}$ = 5.1 Hz, CH4-Im), 126.7 (CH5-Im), 130.0 (CH-Mes), 135.9 (C$_{quart}$-Mes), 136.0 (C$_{quart}$-Mes), 139.1 (C$_{quart}$-Mes), 147.3 (d, $J_{C,P}$ = 6.5 Hz, C═C), 147.5 (d, $J_{C,P}$ = 6.7 Hz, C═C), 164.3 (d, $J_{C,P}$ = 117.0 Hz, C═C$_{trans-P}$), 164.9 (d, $J_{C,P}$ = 1.4 Hz, C═O), 165.4 (d, $J_{C,P}$ = 8.6 Hz, C═O), 167.3 (d, $J_{C,P}$ = 6.5 Hz, C═C), 174.4 (d, $J_{C,P}$ = 8.3 Hz, C═O), 176.5 (d, $^{2}J_{C,P}$ = 9.5 Hz, C$_{carbene}$), 177.6 (d, $J_{C,P}$ = 6.0 Hz, C═O). $^{31}$P{$^{1}$H} NMR (205.5 MHz, *d*-THF): δ 98.7 (s). MS (HR-FAB$^+$): *m*/*z* 720.1850 (M$^+$), 693.1628 (M$^+$ − OCH$_3$). IR (ATR): ν (cm$^{-1}$) 3142 w, 2946 w, 1716 s, 1693 s, 1532 w, 1428 m, 1393 w, 1307 w, 1192 vs, 1157 vs, 1062 m, 1008 m, 934 w, 850 w, 808 w, 757 w, 690 w. Anal. Calcd for $C_{32}H_{43}N_2O_8PPd$: C, 53.30; H, 6.01; N, 3.88; P, 4.30. Found: C, 53.19; H, 5.97; N, 3.87; P, 4.48.

*($^{Mes}$CNP κ-C,κ-P)NiMe$_2$ (**12**).* A solution of $^{Mes}$CNP **5a** (182 mg, 550 μmol) in pentane (3 mL) was added slowly to a suspension of (tmeda)NiMe$_2$ (102 mg, 500 μmol) in pentane (3 mL) at −20 °C and was put in a freezer (−20 °C) for 2 d. The solvent was filtered off, and the solid was washed with pentane (3 × 5 mL) at 0 °C and dried *in vacuo* to give **12** as yellow solid (135 mg, 65%), which was stored at −20 °C. Mp: 90 °C (dec). $^{1}$H NMR (300.1 MHz, *d*-THF): δ −0.83 (d, 3H, $^{3}J_{H,P}$ = 12.2 Hz, CH$_3$-Ni), −0.64 (d, 3H, $^{3}J_{H,P}$ = 4.6 Hz, CH$_3$-Ni), 1.47 (d, 18H, $^{3}J_{H,P}$ = 12.9 Hz, CH$_3$-*t*Bu), 2.06 (s, 6H, *o*-CH$_3$-Mes), 2.29 (s, *p*-CH$_3$-Mes), 6.83 (s, 1H, CH5-Im), 6.92 (s, 2H, CH-Mes), 7.26 (s, 1H, CH4-Im). $^{13}$C{$^{1}$H} NMR (75.5 MHz, *d*-THF): δ −10.4 (CH$_{3(cis-P)}$-Ni), −3.8 (d, $^{2}J_{C,P}$ = 74.0 Hz, CH$_{3(trans-P)}$-Ni), 18.0 (*o*-CH$_3$-Mes), 21.2 (*p*-CH$_3$-Mes), 30.0 (d, $^{2}J_{C,P}$ = 9.0 Hz, CH$_3$-*t*Bu), 36.8 (d, $^{1}J_{C,P}$ = 10.1 Hz, C$_{quart}$-*t*Bu), 121.5 (d, $^{2}J_{C,P}$ = 8.3 Hz, CH4-Im), 123.7 (CH5-Im), 129.4 (CH-Mes), 135.7 (C$_{quart}$-Mes), 136.4 (C$_{quart}$-Mes), 138.9 (C$_{quart}$-Mes), 187.9 (d, $^{2}J_{C,P}$ = 2.8 Hz, C$_{carbene}$). $^{31}$P{$^{1}$H} NMR (121.5 MHz, *d*-THF): δ 112.5 (s). MS (HR-FAB$^+$): *m*/*z* 403.1496 (M$^+$ − Me). IR (KBr): ν [cm$^{-1}$] 2960 m, 2917 m, 2865 m, 1699 m, 1576 m, 1478 s, 1397 m, 1285 w, 1135 s, 1024 s, 935 w, 851 w, 821 m, 669 m. Due to the pronounced thermal instability of the compound, a correct elemental analysis could not be obtained. The values always were outside the range associated with analytical purity, although **12** could be characterized by X-ray.

*($^{Mes}$CNP κ-C,κ-P)$_2$RuCl$_2$ (**13**).* $^{Mes}$CNP **5a** (139 mg, 420 μmol) was added in portions to a solution of (PPh$_3$)$_3$RuCl$_2$ (192 mg, 200 μmol) in THF (5 mL) and stirred for 3 d. After evaporation of the solvent, the solid was washed with pentane (3 × 5 mL) and Et$_2$O (3 × 5 mL) and dried *in vacuo* to give **13** as a pale brown powder (100 mg, 60%). Mp: 236 °C (dec). $^{1}$H NMR (300.1 MHz, CD$_3$CN): δ 1.31 (d, 9H, $^{3}J_{H,P}$ = 7.4 Hz, CH$_3$-*t*Bu), 1.17 (d, 9H, $^{3}J_{H,P}$ = 7.2 Hz, CH$_3$-*t*Bu), 2.02 (s, 6H, *o*-CH$_3$-Mes), 2.33 (s, *p*-CH$_3$-Mes), 7.09 (s, 2H, CH-Mes), 7.26 (d, 1H, $^{3}J_{H,H}$ = 1.9 Hz, CH5-Im), 7.84 (d, 1H, $^{3}J_{H,H}$ = 1.9 Hz, CH4-Im). $^{13}$C{$^{1}$H} NMR (75.5 MHz, CD$_3$CN): δ 18.6 (*o*-CH$_3$-Mes), 21.1 (*p*-CH$_3$-Mes), 29.3 (d, $^{2}J_{C,P}$ = 3.3 Hz, CH$_3$-*t*Bu), 29.4 (d, $^{2}J_{C,P}$ = 3.0 Hz, CH$_3$-*t*Bu), 40.9 (d, $^{1}J_{C,P}$ = 2.3 Hz, C$_{quart}$-*t*Bu), 41.0 (d, $^{1}J_{C,P}$ = 2.3 Hz, C$_{quart}$-*t*Bu), 127.2 (pt, $^{2}J_{C,P}$ = 2.9 Hz, CH4-Im), 127.5 (CH5-Im), 130.7 (CH-Mes), 136.0 (C$_{quart}$-Mes), 136.4 (C$_{quart}$-Mes), 141.5 (C$_{quart}$-Mes), 180.4 (C$_{carbene}$). $^{31}$P{$^{1}$H} NMR (121.5 MHz, CD$_3$CN): δ 102.8 (s). MS (HR-FAB$^+$): *m*/*z* 831.2872 (M$^+$), 797.3201 (M$^+$ − Cl). IR (ATR): ν (cm$^{-1}$) 3113 w, 2950 w, 2901 w, 2860 w, 2365 w, 1601 w, 1482 w, 1383 m, 1273 s, 1145 s, 1070 w, 1025 w, 931 m, 852 m, 806 w, 703 vs. Anal. Calcd for $C_{40}H_{62}Cl_2N_4P_2Ru$: C, 57.68; H, 7.50; N, 6.73; P, 7.44. Found: C, 57.98; H, 7.48; N, 6.56; P, 7.32.

**X-ray Structure Determinations.** For the X-ray diffraction studies data sets were collected at 200 K (100 K for **3**). A complete sphere in reciprocal space was covered by narrow ω-scans in all cases. For all data sets the intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on the Laue symmetry of the reciprocal space, was applied using SADABS (2009/1).[24] All structures were solved by direct methods and refined against $F^2$ with a full-matrix least-squares algorithm using the SHELXTL (version 2008/4) software package.[25] If not noted differently below, hydrogen atoms were treated using appropriate riding models. All structures have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**1:** colorless crystal (polyhedron), dimensions 0.40 × 0.26 × 0.08 mm$^3$, crystal system orthorhombic, space group $P2_12_12$, $Z$ = 4, $a$ = 14.5402(2) Å, $b$ = 14.8124(1) Å, $c$ = 5.9994(1) Å, $V$ = 1292.12(3) Å$^3$, $\rho$ = 1.091 g/cm$^3$, theta$_{max}$ = 27.50°, 13 446 reflections measured, 2962 unique ($R$(int) = 0.0340), 2684 observed ($I > 2\sigma(I)$), $\mu$ = 0.18 mm$^{-1}$, $T_{min}$ = 0.93, $T_{max}$ = 0.99, 145 parameters refined, imidazole-hydrogen atoms were refined isotropically, Flack absolute structure parameter −0.14(11), goodness of fit 1.05 for observed reflections, final residual values R1($F$) = 0.036, $wR(F^2)$ = 0.092 for observed reflections, residual electron density −0.19 to 0.23 e Å$^{-3}$. CCDC 905608.

**2:** colorless crystal (polyhedron), dimensions 0.26 × 0.24 × 0.12 mm$^3$, crystal system monoclinic, space group $C2/c$, $Z$ = 8, $a$ = 16.2513(4) Å, $b$ = 13.7380(2) Å, $c$ = 15.5104(3) Å, $\beta$ = 93.814(1)°, $V$ = 3455.19(12) Å$^3$, $\rho$ = 1.262 g/cm$^3$, theta$_{max}$ = 25.37°, 15 061 reflections measured, 3161 unique ($R$(int) = 0.0401), 2412 observed ($I > 2\sigma(I)$), $\mu$ = 0.19 mm$^{-1}$, $T_{min}$ = 0.95, $T_{max}$ = 0.98, 200 parameters refined, hydrogen atom H1 at C1 refined isotropically, goodness of fit 1.03 for observed reflections, final residual values R1($F$) = 0.043, $wR(F^2)$ = 0.106 for observed reflections, residual electron density −0.28 to 0.38 e Å$^{-3}$. CCDC 905609.

**3:** colorless crystal (polyhedron), dimensions 0.30 × 0.23 × 0.22 mm$^3$, crystal system monoclinic, space group $P2_1/c$, $Z$ = 4, $a$ = 12.3300(15) Å, $b$ = 10.2347(12) Å, $c$ = 10.9981(13) Å, $\beta$ =

98.157(2)°, $V$ = 1373.9(3) Å$^3$, $\rho$ = 1.162 g/cm$^3$, $T$ = 100(2) K, theta$_{max}$ = 27.87°, 13 551 reflections measured, 3282 unique ($R$(int) = 0.0282), 2694 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.18 mm$^{-1}$, $T_{min}$ = 0.95, $T_{max}$ = 0.96, 150 parameters refined, goodness of fit 1.15 for observed reflections, final residual values R1($F$) = 0.062, $wR(F^2)$ = 0.178 for observed reflections, residual electron density −0.48 to 0.91 e Å$^{-3}$. CCDC 905610.

**4a:** colorless crystal (polyhedron), dimensions 0.31 × 0.14 × 0.08 mm$^3$, crystal system monoclinic, space group $P2_1/c$, $Z$ = 4, $a$ = 9.7535(15) Å, $b$ = 25.436(4) Å, $c$ = 10.2815(15) Å, $\beta$ = 105.874(3)°, $V$ = 2453.5(6) Å$^3$, $\rho$ = 1.301 g/cm$^3$, theta$_{max}$ = 28.36°, 25 766 reflections measured, 6109 unique ($R$(int) = 0.0441), 4753 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.24 mm$^{-1}$, $T_{min}$ = 0.93, $T_{max}$ = 0.98, 289 parameters refined, goodness of fit 1.10 for observed reflections, final residual values R1($F$) = 0.066, $wR(F^2)$ = 0.148 for observed reflections, residual electron density −0.32 to 0.50 e Å$^{-3}$. CCDC 905611.

**4b:** colorless crystal (needle), dimensions 0.30 × 0.03 × 0.02 mm$^3$, crystal system orthorhombic, space group $P2_12_12_1$, $Z$ = 4, $a$ = 10.139(3) Å, $b$ = 16.338(4) Å, $c$ = 17.216(5) Å, $V$ = 2852.0(13) Å$^3$, $\rho$ = 1.217 g/cm$^3$, theta$_{max}$ = 25.42°, 24 175 reflections measured, 5242 unique ($R$(int) = 0.0876), 4011 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.22 mm$^{-1}$, $T_{min}$ = 0.94, $T_{max}$ = 1.00, 317 parameters refined, Flack absolute structure parameter 0.34(12), goodness of fit 1.06 for observed reflections, final residual values R1($F$) = 0.064, $wR(F^2)$ = 0.133 for observed reflections, residual electron density −0.30 to 0.36 e Å$^{-3}$. CCDC 905612.

**5a:** colorless crystal (polyhedron), dimensions 0.38 × 0.14 × 0.07 mm$^3$, crystal system monoclinic, space group $P2_1/m$, $Z$ = 2, $a$ = 6.0223(2) Å, $b$ = 13.6935(3) Å, $c$ = 12.2697(4) Å, $\beta$ = 94.944(1)°, $V$ = 1008.07(5) Å$^3$, $\rho$ = 1.089 g/cm$^3$, theta$_{max}$ = 25.03°, 8642 reflections measured, 1862 unique ($R$(int) = 0.0521), 1384 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.14 mm$^{-1}$, $T_{min}$ = 0.95, $T_{max}$ = 0.99, 122 parameters refined, goodness of fit 1.04 for observed reflections, final residual values R1($F$) = 0.042, $wR(F^2)$ = 0.092 for observed reflections, residual electron density −0.22 to 0.19 e Å$^{-3}$. CCDC 905613.

**5b:** colorless crystal (polyhedron), dimensions 0.28 × 0.23 × 0.13 mm$^3$, crystal system monoclinic, space group $P2_1/m$, $Z$ = 2, $a$ = 5.9579(11) Å, $b$ = 17.518(3) Å, $c$ = 11.241(2) Å, $\beta$ = 90.984(4)°, $V$ = 1173.1(4) Å$^3$, $\rho$ = 1.055 g/cm$^3$, theta$_{max}$ = 28.32°, 12 456 reflections measured, 2984 unique ($R$(int) = 0.0333), 2566 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.13 mm$^{-1}$, $T_{min}$ = 0.97, $T_{max}$ = 0.98, 135 parameters refined, goodness of fit 1.06 for observed reflections, final residual values R1($F$) = 0.047, $wR(F^2)$ = 0.121 for observed reflections, residual electron density −0.17 to 0.40 e Å$^{-3}$. CCDC 905614.

**6a:** colorless crystal (polyhedron), dimensions 0.46 × 0.07 × 0.02 mm$^3$, crystal system orthorhombic, space group $Pnma$, $Z$ = 4, $a$ = 27.553(4) Å, $b$ = 11.6443(16) Å, $c$ = 8.6785(12) Å, $V$ = 2784.3(7) Å$^3$, $\rho$ = 1.657 g/cm$^3$, theta$_{max}$ = 28.33°, 27 994 reflections measured, 3637 unique ($R$(int) = 0.0633), 3253 observed ($I$ >2$\sigma$($I$)), $\mu$ = 5.53 mm$^{-1}$, $T_{min}$ = 0.19, $T_{max}$ = 0.90, 187 parameters refined, goodness of fit 1.25 for observed reflections, final residual values R1($F$) = 0.052, $wR(F^2)$ = 0.109 for observed reflections, residual electron density −5.07 to 2.38 e Å$^{-3}$. CCDC 905615.

**7a:** colorless crystal (platte), dimensions 0.28 × 0.06 × 0.02 mm$^3$, crystal system monoclinic, space group $P2_1/c$, $Z$ = 4, $a$ = 19.916(11) Å, $b$ = 8.120(4) Å, $c$ = 15.056(8) Å, $\beta$ = 108.867(10)°, $V$ = 2304(2) Å$^3$, $\rho$ = 1.602 g/cm$^3$, theta$_{max}$ = 25.79°, 18 474 reflections measured, 4354 unique ($R$(int) = 0.1310), 3183 observed ($I$ >2$\sigma$($I$)), $\mu$ = 6.17 mm$^{-1}$, $T_{min}$ = 0.28, $T_{max}$ = 0.89, 240 parameters refined, goodness of fit 1.05 for observed reflections, final residual values R1($F$) = 0.084, $wR(F^2)$ = 0.162 for observed reflections, residual electron density −4.53 to 2.65 e Å$^{-3}$. CCDC 905616.

**7b:** colorless crystal (polyhedron), dimensions 0.26 × 0.24 × 0.14 mm$^3$, crystal system monoclinic, space group $P2_1/n$, $Z$ = 4, $a$ = 13.1842(2) Å, $b$ = 9.1134(2) Å, $c$ = 23.1448(4) Å, $\beta$ = 105.3170(10)°, $V$ = 2682.13(9) Å$^3$, $\rho$ = 1.480 g/cm$^3$, theta$_{max}$ = 27.48°, 26 845 reflections measured, 6145 unique ($R$(int) = 0.0477), 4951 observed ($I$ >2$\sigma$($I$)), $\mu$ = 5.30 mm$^{-1}$, $T_{min}$ = 0.34, $T_{max}$ = 0.52, 279 parameters refined, goodness of fit 1.05 for observed reflections, final residual values R1($F$) = 0.027, $wR(F^2)$ = 0.049 for observed reflections, residual electron density −0.73 to 0.54 e Å$^{-3}$. CCDC 905617.

**8:** colorless crystal (polyhedron), dimensions 0.28 × 0.16 × 0.09 mm$^3$, crystal system monoclinic, space group $P2_1/n$, $Z$ = 4, $a$ = 7.7405(9) Å, $b$ = 37.916(4) Å, $c$ = 8.0646(9) Å, $\beta$ = 109.008(2)°, $V$ = 2237.8(4) Å$^3$, $\rho$ = 1.386 g/cm$^3$, theta$_{max}$ = 28.34°, 23 473 reflections measured, 5565 unique ($R$(int) = 0.0250), 5359 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.91 mm$^{-1}$, $T_{min}$ = 0.78, $T_{max}$ = 0.92, 246 parameters refined, goodness of fit 1.40 for observed reflections, final residual values R1($F$) = 0.037, $wR(F^2)$ = 0.077 for observed reflections, residual electron density −0.74 to 0.84 e Å$^{-3}$. CCDC 905618.

**9:** colorless crystal (plate), dimensions 0.41 × 0.28 × 0.07 mm$^3$, crystal system triclinic, space group $P\bar{1}$, $Z$ = 4, $a$ = 9.6292(12) Å, $b$ = 14.9191(18) Å, $c$ = 18.310(2) Å, $\alpha$ = 99.270(2)°, $\beta$ = 97.460(2)°, $\gamma$ = 94.770(2)°, $V$ = 2559.5(5) Å$^3$, $\rho$ = 1.336 g/cm$^3$, theta$_{max}$ = 28.31°, 27 166 reflections measured, 12 589 unique ($R$(int) = 0.0250), 9751 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.80 mm$^{-1}$, $T_{min}$ = 0.73, $T_{max}$ = 0.95, 562 parameters refined, hydrogen atoms H6 and H7 of the olefin were refined isotropically, goodness of fit 1.02 for observed reflections, final residual values R1($F$) = 0.032, $wR(F^2)$ = 0.075 for observed reflections, residual electron density −0.29 to 0.99 e Å$^{-3}$. CCDC 905619.

**10:** colorless crystal (plate), dimensions 0.11 × 0.08 × 0.02 mm$^3$, crystal system monoclinic, space group $P2_1/c$, $Z$ = 8, $a$ = 37.238(2) Å, $b$ = 8.0707(5) Å, $c$ = 16.9874(10) Å, $\beta$ = 101.3760(10)°, $V$ = 5005.0(5) Å$^3$, $\rho$ = 1.420 g/cm$^3$, theta$_{max}$ = 28.79°, data collected with a mean redundancy of 4.38 and a completeness of 99.7% to a resolution of 0.74 Å, 58 837 reflections measured, 12 991 unique ($R$(int) = 0.0395), 10 331 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.83 mm$^{-1}$, $T_{min}$ = 0.91, $T_{max}$ = 0.98, 581 parameters refined, hydrogen atoms of the coordinated olefins were refined isotropically, goodness of fit 1.03 for observed reflections, final residual values R1($F$) = 0.037, $wR(F^2)$ = 0.078 for observed reflections, residual electron density −0.58 to 0.79 e Å$^{-3}$. CCDC 905620.

**12:** yellow crystal (polyhedron), dimensions 0.14 × 0.09 × 0.06 mm$^3$, crystal system monoclinic, space group $Cc$, $Z$ = 8, $a$ = 17.0836(12) Å, $b$ = 17.1274(12) Å, $c$ = 18.0587(13) Å, $\beta$ = 97.331(2)°, $V$ = 5240.7(6) Å$^3$, $\rho$ = 1.154 g/cm$^3$, theta$_{max}$ = 20.84°, data collected with a mean redundancy of 9.07 and a completeness of 98.3% to a resolution of 1.00 Å, 25 367 reflections measured, 5259 unique ($R$(int) = 0.0528), 4608 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.81 mm$^{-1}$, $T_{min}$ = 0.89, $T_{max}$ = 0.95, 524 parameters refined, Flack absolute structure parameter 0.008(15), goodness of fit 1.04 for observed reflections, final residual values R1($F$) = 0.039, $wR(F^2)$ = 0.079 for observed reflections, residual electron density −0.21 to 0.41 e Å$^{-3}$. CCDC 905621.

**13:** red-brown crystal (polyhedron), dimensions 0.25 × 0.11 × 0.09 mm$^3$, crystal system monoclinic, space group $P2_1/n$, $Z$ = 2, $a$ = 12.0530(13) Å, $b$ = 13.9007(15) Å, $c$ = 12.3697(13) Å, $\beta$ = 104.854(2)°, $\gamma$ = 90°, $V$ = 2003.2(4) Å$^3$, $\rho$ = 1.381 g/cm$^3$, theta$_{max}$ = 28.44°, 21 064 reflections measured, 5020 unique ($R$(int) = 0.0465), 4356 observed ($I$ >2$\sigma$($I$)), $\mu$ = 0.64 mm$^{-1}$, $T_{min}$ = 0.86, $T_{max}$ = 0.94, 226 parameters refined, goodness of fit 1.08 for observed reflections, final residual values R1($F$) = 0.036, $wR(F^2)$ = 0.078 for observed reflections, residual electron density −0.29 to 0.58 e Å$^{-3}$. CCDC 905700.

## ■ ASSOCIATED CONTENT

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### Notes

The authors declare no competing financial interest.

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