Diaminocarbene- and Fischer-Carbene Complexes of Palladium and Nickel by Oxidative Insertion: Preparation, Structure, and Catalytic Activity

Doris Kremzow, Günter Seidel, Christian W. Lehmann, and Alois Fürstner*[a]

Abstract: Oxidative insertion of $[Pd(PPh_3)_4]$ or $[Ni(cod)_2]/PPh_3$ into the C–Cl bond of various 2-chloroimidazolinium- and other -amidinium salts affords metal–diaminocarbene complexes in good to excellent yields. This procedure is complementary to existing methodology in which the central metal does not change its oxidation state, and therefore allows to incorporate carbene fragments that are difficult to access otherwise. The preparation of a variety of achiral as well as enantiomerically pure, chiral metal–NHC complexes (NHC = N-heterocyclic carbene) and metal complexes with acyclic diaminocarbene ligands illustrates this aspect. Furthermore it is shown that oxidative insertion also paves a way to prototype Fischer carbenes of Pd^{II}. Since the required starting materials are readily available from urea- or thiourea derivatives, this novel approach allows for substantial structural variations of the ligand backbone. The catalytic performance of the resulting library of nickel- and palladium–carbene complexes has been evaluated by applications to prototype Suzuki-, Heck-, and Kumada–Corriu cross-coupling reactions as well as Buchwald–Hartwig aminations. It was found that even Fischer carbenes show appreciable catalytic activity. Moreover, representative examples of all types of neutral and cationic metal–carbene complexes formed in this study have been characterized by X-ray crystallography.

Keywords: carbenes · cross-coupling · homogeneous catalysis · nickel · palladium

Introduction

Metal complexes of *N*-heterocyclic carbenes (NHCs) were pioneered in the 1960 s by Wanzlick[1] and Öfele.[2] Although their organometallic chemistry has been intensively studied early on,[3] it was not until the last decade that the favorable properties of such complexes were fully appreciated by the scientific community. This development was triggered by Arduengo's seminal discovery that various NHCs can be isolated in pure form,[4,5] and by the recognition of their potential as ancillary ligands for many metal catalyzed transformations.[6,7] Not only represent NHCs mere substitutes for phosphine ligands, but it became increasingly evident that they impart superior properties to various metal templates in terms of stability and activity. Moreover, the ease of synthesis allows for structural variations which may be used to adjust the electronic as well as steric properties of the complex to the specific requirements of a given metal-catalyzed transformation. Although many recent reports bear witness for the favorable profile of metal–NHC complexes in synthesis,[6] applications to olefin metathesis,[8] palladium- and nickel-catalyzed cross-coupling reactions,[9] and hydrosilylation[10] deserve particular mentioning.

The most general procedure for the preparation of metal–NHC complexes known to date relies on simple ligand exchange and therefore hinges upon the ability to form the corresponding carbenes as a discrete or a transient species by the methods depicted in Scheme 1.[11–14] This is one of the reasons why the highly stabilized five-membered NHCs **A**–**C** are most commonly used because they are particularly well amenable to this synthesis route. They constitute, however, only one particular class of "stable" (or metastable) carbene species;[15–17] other types are depicted in Scheme 2. Despite some highly promising chemical and physical properties,[18] such species have only rarely been used as ancillary ligands in catalysis, not least because they are somewhat more delicate to handle and therefore less suited for processing via ligand exchange.[19,20] To explore the full potential of (acyclic) diaminocarbene–metal catalysts with ligands such as **D**–**H**, it seems necessary to develop practical alternative methods for their preparation.

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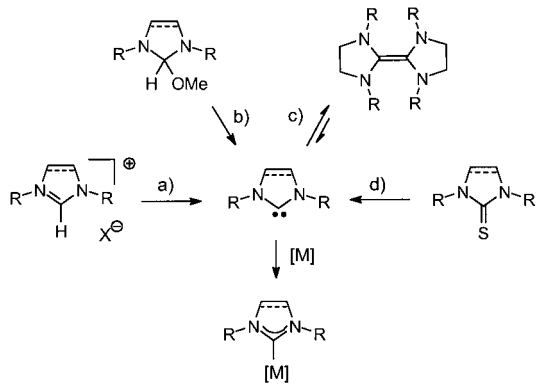
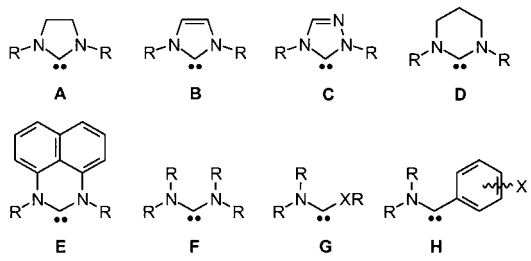


Scheme 1. Common routes to metal–imidazol(idin)-2-ylidene complexes: a) base (e. g. KO*t*Bu, KH, BuLi) in THF or liquid NH_3; b) thermolysis (α-elimination); c) cf. ref. [3]; [d] K in THF.



Scheme 2. Prototype diaminocarbene and related carbene fragments.

As part of our ongoing studies in this field,[21–23] we considered that oxidative insertion of a low-valent metal into an appropriate 2-halo-amidinium salt may open an as yet largely unexplored but potentially very useful entry. Outlined below is the reduction of this concept to practice which provides access to a wide variety of metal-diaminocarbene- and even prototype Fischer-carbene complexes of palladium and nickel that are difficult to make otherwise.[24] Their structural properties and potential as catalysts for cross-coupling reactions are also outlined.

Results and Discussion

Palladium–NHC complexes: As shown in Scheme 1, the most common synthesis route for metal–diaminocarbene complexes in general and metal–NHC complexes in particular involves a ligand exchange or salt metathesis in which the metal template does not change its oxidation state. Therefore it seemed likely at the outset of this project that any route based on oxidative insertion might potentially be complementary in scope.[25]

The formation of Fischer-carbene complexes by oxidative addition has precedence in early investigations by Lappert,[26] Stone[27] and others[28] who showed that certain metal templates are able to react with for example iminium-, 2-chlorothiazolium- or 2-chloro-1-methylpyridinum salts to afford the corresponding carbene complexes. Surprisingly though, it seems that this potentially general method has not been applied to the synthesis of metal–imidazol(idin)-2-ylidene complexes except for one special case.[29] This approach, however, promises a broad substrate scope and might allow for substantial structural variations since the required precursor salts are easily obtained from cyclic ureas or thioureas on treatment with for example oxalyl chloride.[30] Moreover, the *N,N′*-dimethyl imidazolinium derivatives **1a–c** (X = PF_6, BF_4, Cl) are even commercially available and have been widely used as excellent dehydrating agents for a host of esterification-, chlorination-, oxidation-, and rearrangement reactions as well as for heterocycle synthesis.[31,32]

Treatment of the imidazolinium salt **1a** (X = PF_6) with an equimolar amount of [$Pd(PPh_3)_4$] in refluxing CH_2Cl_2 leads to a clean reaction which can be nicely monitored by ^{31}P NMR spectroscopy. Initially, two sets of signals at δ_P = 31.8 (d, J = 24 Hz) and δ_P = 21.2 (d, J = 24 Hz) are detected which converge over a period of about 6 h to a singlet at δ_P = 22.5 ppm; two equivalents or PPh_3 are released concomitantly. This course reflects the formation of *cis*-**2a** as the primary product which isomerizes with time to the more stable *trans*-**2a**. After extraction of the free PPh_3, *trans*-**2a** was isolated as a white solid in analytically pure form (72%) by recrystallization from $CHCl_3$. The structure of this *ionic* palladium–NHC complex in the solid state is depicted in Figure 1. The imidazolinium salt **1b** (X = BF_4) reacts analogously affording compound *trans*-**2b** (δ_P = 22.8 ppm) in similar yield (Scheme 3).[33]

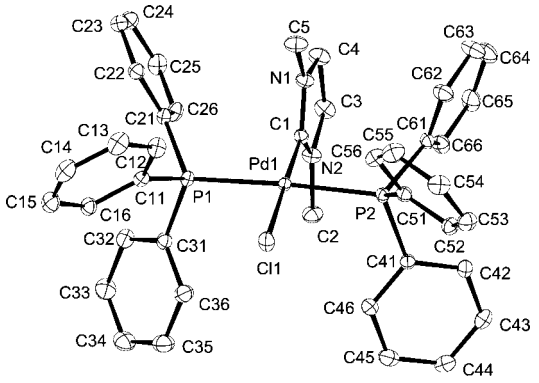
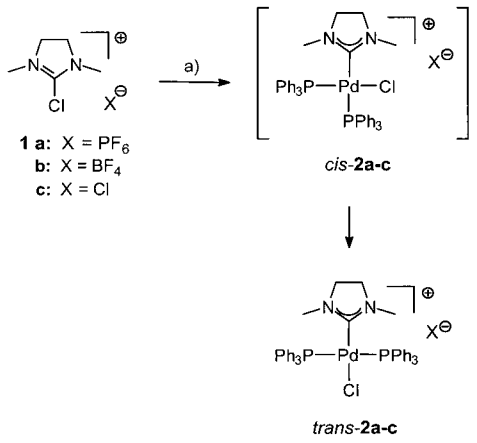


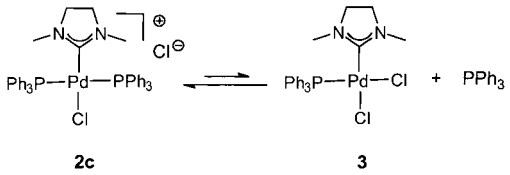
Figure 1. Molecular structure of complex **2a**. The PF_6^- counterion is omitted for clarity.

The reactivity of chloride **1c** (X = Cl) follows the same trend giving rise to the expected cationic complex *trans*-**2c** (δ_P = 22.8 ppm) which was again fully characterized by X-ray crystallography.[24] The solution structure must be similar because the carbene center in *trans*-**2c** resonates as a triplet at δ_C = 194.9 ppm (J = 6.9 Hz), thus indicating the presence of two phosphorous atoms at degenerate positions. However, the crude mixture formed from **1c** and [$Pd(PPh_3)_4$] invariably contains small amounts of other complexes in addition



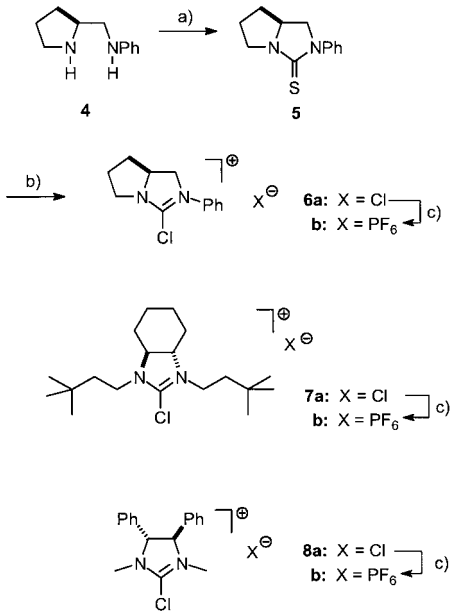
Scheme 3. a) $[Pd(PPh_3)_4]$, CH_2Cl_2, reflux, 72% (*trans*-**2a**), 74% (*trans*-**2b**), 87% (*trans*-**2c**).

to **2c**; one of them ($\delta_P = 27.7$ ppm) cleanly regenerates when recrystallized **2c** is dissolved in CD_2Cl_2 or THF. Although we were unable so far to isolate this new compound on a preparative scale, crystals were picked out from a co-precipitate and were analyzed by X-ray crystallography,[34] which showed that this product is the *neutral*, *cis*-configured palladium *di*chloride complex **3** (Scheme 4).[35,36] Therefore the particular behavior of **2c** in solution is deemed to reflect the higher affinity of the chloride ion to Pd^{II} compared with the only weakly coordinating anions PF_6^- or BF_4^- escorting compounds **2a**,**b**, respectively.

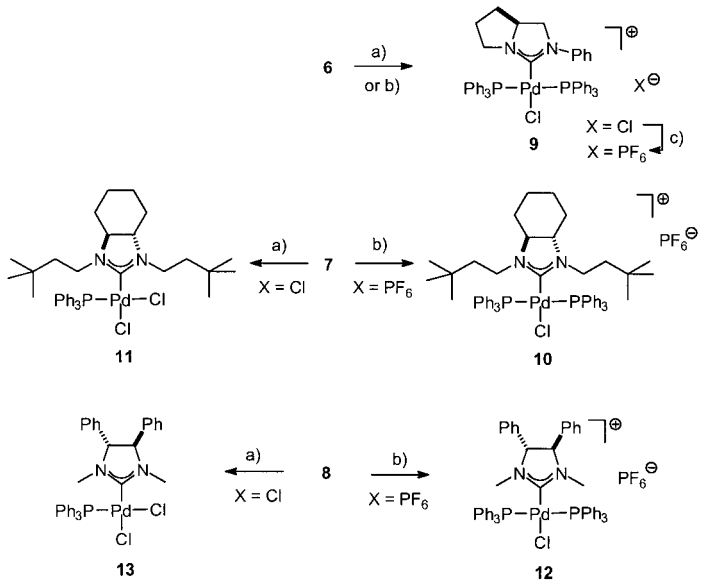


Scheme 4. Equilibrium between the cationic and the neutral form of the palladium–NHC complex.

Next, we probed the applicability of this novel method to the formation of chiral Pd^{II}–NHC complexes.[37] To this end, the enantiomerically pure 1,2-diamine **4** was converted into the corresponding thiourea derivative **5** (Figure 2). Exposure of **5** to oxalyl chloride in toluene at 60°C cleanly afforded the desired imidazolinium chloride **6a** (X = Cl) (Scheme 5). Compounds **7** and **8** were prepared analogously. All of them reacted smoothly with $[Pd(PPh_3)_4]$ in CH_2Cl_2 at ambient temperature to afford the corresponding enantiopure palladium–NHC complexes. Interestingly though, substrates **7** and **8** (Scheme 6) favor the *neutral*, *cis*-configured palladium dichloride complexes **11** (Figure 5) and **13** (Figure 7), respectively,[35] whereas the closely related proline derived salt **6a** (X = Cl) furnished the *cationic trans*-configured complex **9** (X = Cl) as the major product. Its structure was also unambiguously confirmed by X-ray analysis (Figure 3). In analogy to the results described above for the achiral complex **2c**,



Scheme 5. a) Thiophosgene, Et_3N, CH_2Cl_2, 82%; b) oxalyl chloride, toluene, 60°C; c) $AgPF_6$, CH_2Cl_2, 71% (**6b**), 79% (**7b**), 70% (**8b**).



Scheme 6. a) $[Pd(PPh_3)_4]$, CH_2Cl_2, RT, 67% (**9a**, X = Cl), 85% (**11**), 70% (**13**); b) $[Pd(PPh_3)_4]$, toluene, 100°C, 71% (**9b**), 63% (**10**), 43% (**12**).

dissolution of **9** in CH_2Cl_2 re-establishes an equilibrium between the cationic form and the corresponding neutral version as judged by ^{31}P NMR spectroscopy. The subtle preferences of the different precursors to form either neutral or cationic complexes are not yet clear.

Exchange of the chloride counter-ion in **6**–**8a** for PF_6^- was easily achieved on treatment with $AgPF_6$ in CH_2Cl_2. The resulting chiral imidazolinium hexafluorophosphates **6b**, **7b** and **8b** are equally amenable to oxidative insertion of Pd^0, although more forcing conditions had to be used.

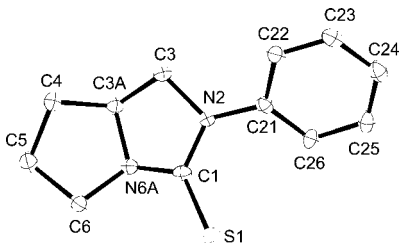


Figure 2. Molecular structure of thiourea **5**.

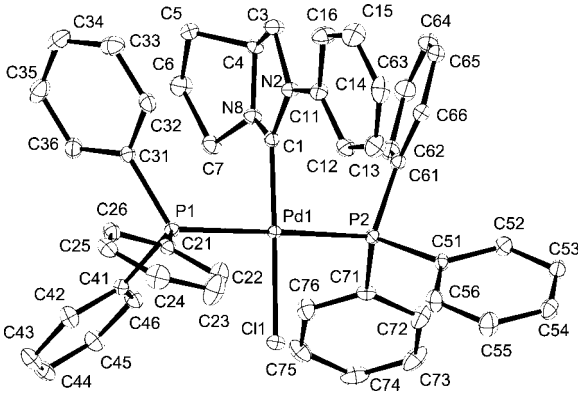


Figure 3. Molecular structure of complex **9a**. The chloride counterion is omitted for clarity.

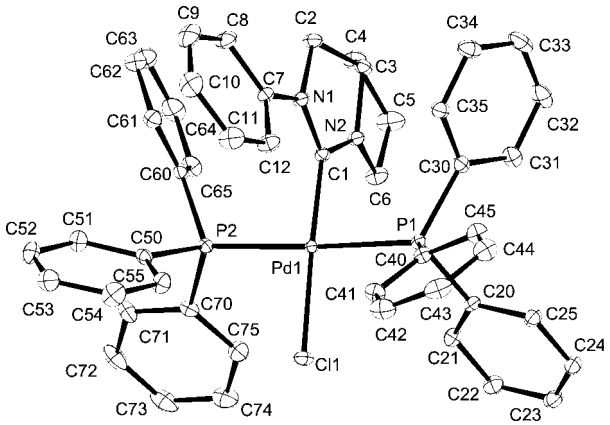


Figure 4. Molecular structure of complex **9b**. The PF_6^- counterion is omitted for clarity.

Best results were obtained in toluene at 100 °C. In two cases were the resulting cationic NHC-complexes characterized by X-ray crystallography. In line with their achiral counterparts **2a**,**b**, both of them are *trans*-configured, likely due to the strong *trans*-influence exerted by the carbene fragment (Figures 4 and 6).

Other palladium–diaminocarbene complexes: Since many amidinium salts other than the imidazolinium compounds mentioned above are readily accessible on large scale, a generalization of this concept seemed possible. Therefore we explored if oxidative addition can provide palladium complexes bearing less common diaminocarbene ligands.

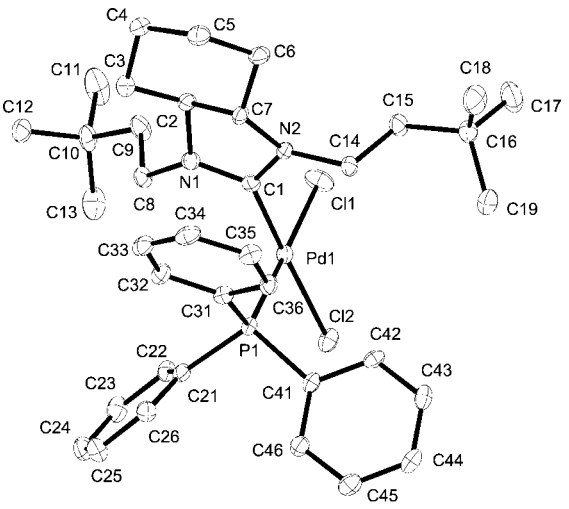


Figure 5. Molecular structure of complex **11**.

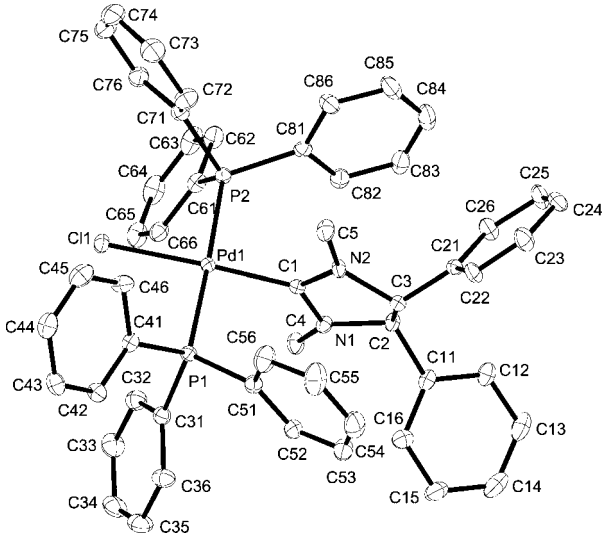


Figure 6. Molecular structure of complex **12**. The escorting PF_6^- counterion is omitted for clarity.

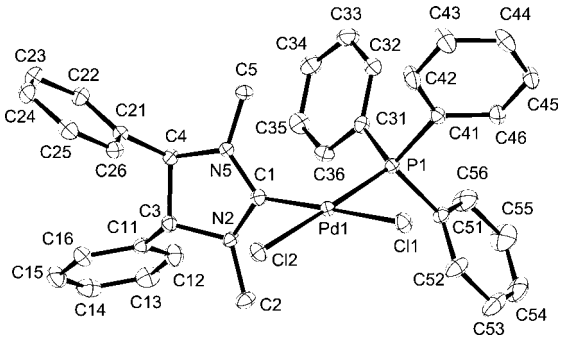
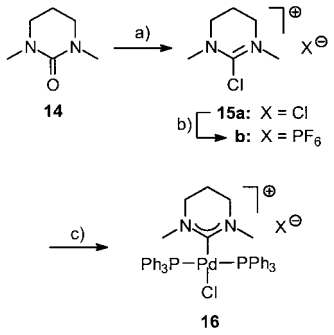


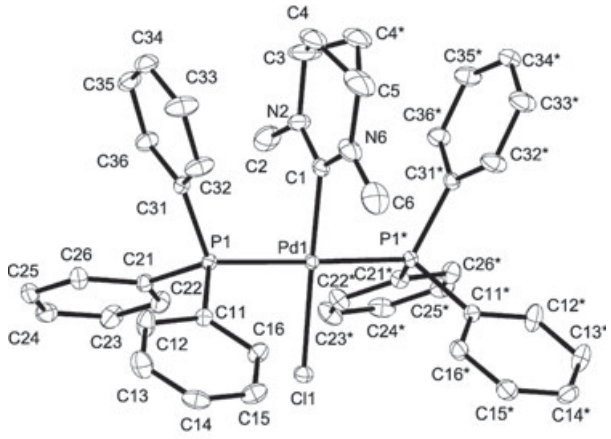
Figure 7. Molecular structure of complex **13**.

The first aspect to be investigated was the effect of the ring size. For this purpose, commercial DMPU **14** was converted into **15a** (X = Cl) on treatment with oxalyl chloride;

subsequent reaction with $[Pd(PPh_3)_4]$ under standard conditions gave the desired Pd^{II}–1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2-ylidene complex **16a** (X = Cl) in good yield (Scheme 7). The corresponding PF_6^- salt **15b** behaved similarly well, thus lending credence to the notion that the ring size of the backbone has no significant effect on the outcome of the reaction.[38] The structure of these complexes in the solid state is depicted in Figures 8 and 9.



Scheme 7. a) Oxalyl chloride, CCl_4, 60 °C, 59 %; b) $AgPF_4$, CH_2Cl_2, 90 %; c) $[Pd(PPh_3)_4]$, 62 % (**16a**), 61 % (**16b**).



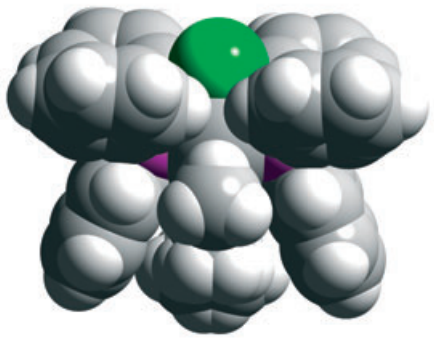


Figure 8. Top: Molecular structure of complex **16a**. The chloride counterion is omitted for clarity. Carbon atom C4 is disordered due to the crystallographic mirror symmetry. Bottom: Space filling representation of **16a**. The 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2-ylidene ligand is sandwiched between two phenyl rings. The chlorine (green) in *trans* position to the carbene is readily accessible.

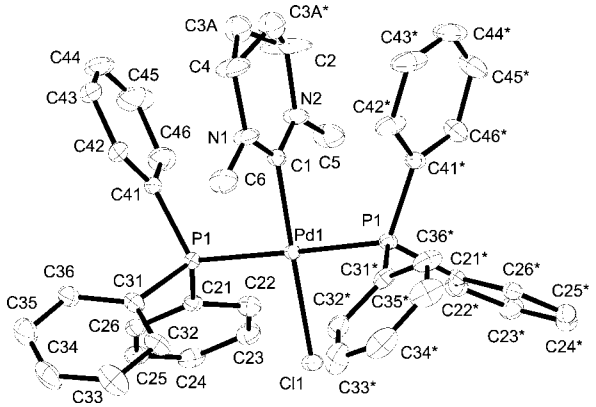
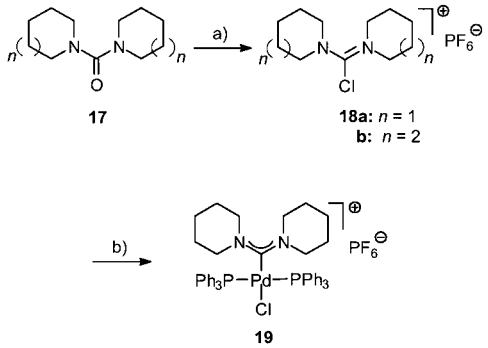


Figure 9. Molecular structure of complex **16b**. The PF_6^- counterion is omitted for clarity.

Even more gratifyingly, the commercial amidinium salt **18** derived from *N,N′*-carbonyldipiperidine **17** was exposed to $[Pd(PPh_3)_4]$ in toluene at 100 °C, thus furnishing the diaminocarbene complex **19** in 50 % yield after recrystallization of the crude product (Scheme 8 and Figure 10). This result must be seen in the light of previous experiences with the corresponding free carbene **F-1** (Scheme 9); although this



Scheme 8. a) Oxalyl chloride, toluene, 60 °C; b) $[Pd(PPh_3)_4]$, toluene, 100 °C, 50 %.

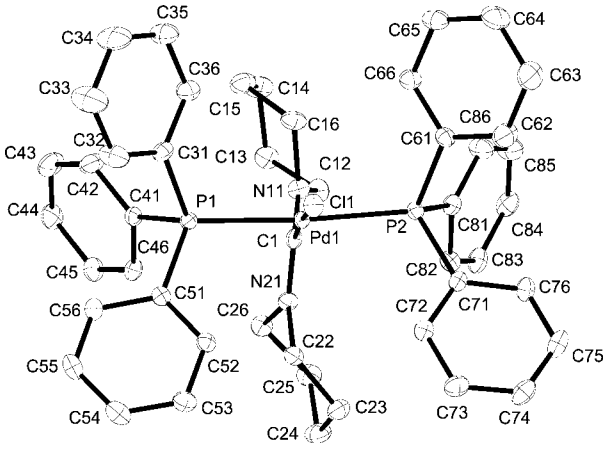
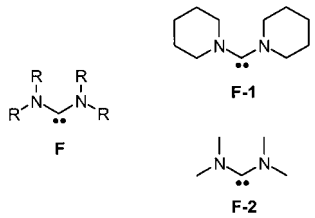
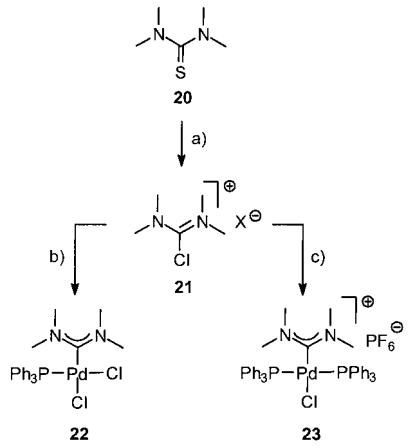


Figure 10. Molecular structure of complex **19**. The PF_6^- counterion is omitted for clarity.



Scheme 9. Diaminocarbenes with acyclic backbone.

species was previously described by Alder et al.,[39] it is known to be rather unstable and has not yet found any application as ancillary ligand for catalytically relevant metal complexes. The same pertains to bis(dimethylamino)carbene **F-2**. Although accessible in situ, this particular carbene could not be isolated in pure form[40] and was incorporated into a metal complex only once.[28a] Scheme 10 shows that



Scheme 10. a) Oxalyl chloride, toluene, 60 °C, 90 %; b) $[Pd(PPh_3)_4]$, CH_2Cl_2, RT, 40 %; c) $[Pd(PPh_3)_4]$, toluene, 100 °C, 48 %.

oxidative insertion makes it easy to generate the corresponding neutral or cationic Pd^{II}-complexes **22** and **23** of this interesting ligand from the readily available amidinium salts **21**. The proposed structures were again confirmed by X-ray crystallography (Figures 11 and 12).

Fischer-carbene complexes of palladium: Encouraged by the results summarized above, a further extension of the scope of this novel method was envisaged. Specifically, formal replacement of one of the *N*-atoms in a diaminocarbene by heteroatoms X other than nitrogen or by an aromatic ring renders the resulting carbenes of types **G** or **H** semistable at best (Scheme 2); the corresponding metal complexes are prototype Fischer carbenes.

Access to this series was gained on treatment of suitable precursor salts with $[Pd(PPh_3)_4]$ in CH_2Cl_2 at ambient temperature (for the chloride salts) or in toluene at 100 °C (for the hexafluorophosphates) as shown in Schemes 11–13. Although the yields were somewhat lower than before—in particular for the cationic species **28**, **33** and **35**—this method is

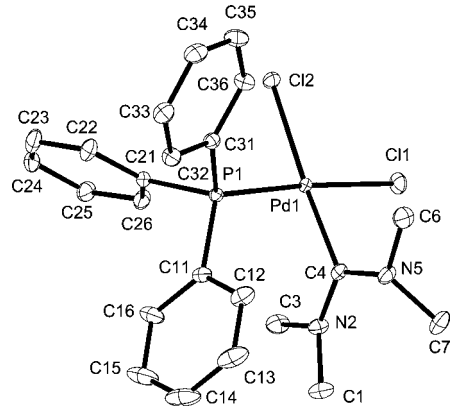


Figure 11. Molecular structure of complex **22**.

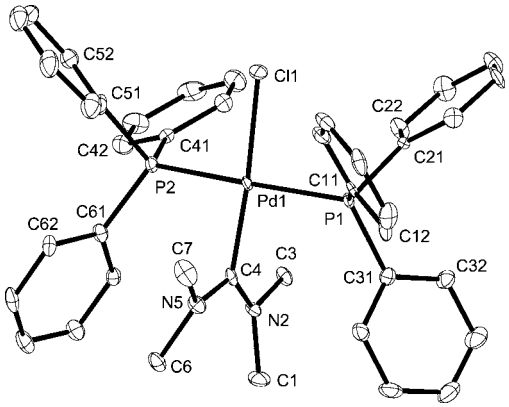
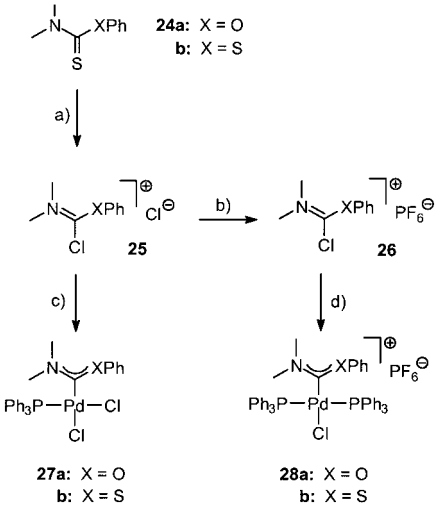
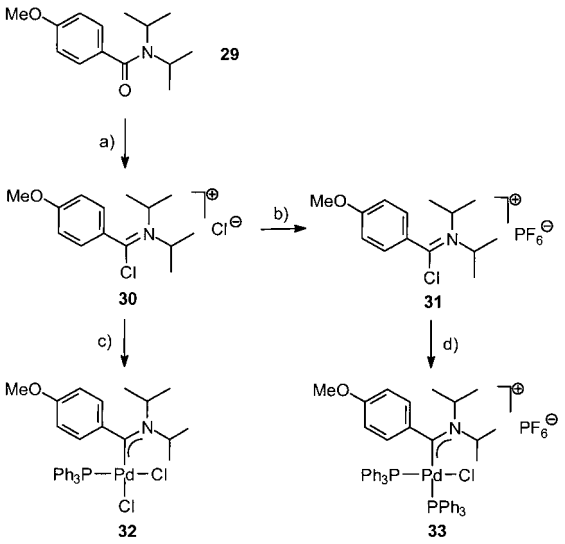


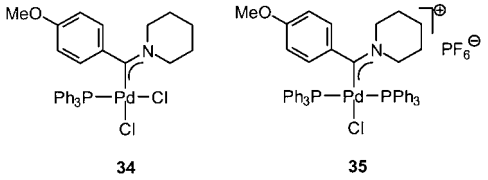
Figure 12. Molecular structure of complex **23**. The PF_6^- counterion is omitted for clarity.



Scheme 11. a) Oxalyl chloride, toluene, 60 °C, 91 % (**25a**), 85 % (**25b**); b) $AgPF_4$, CH_2Cl_2, 76 % (**26a**), 86 % (**26b**); c) $[Pd(PPh_3)_4]$, CH_2Cl_2, RT, 35 % (**27a**), 64 % (**27b**); d) $[Pd(PPh_3)_4]$, toluene, 100 °C, 30 % (**28a**), 24 % (**28b**).



Scheme 12. a) Oxalyl chloride, toluene, 60 °C, 69 %; b) $AgPF_4$, CH_2Cl_2, 65 %; c) $[Pd(PPh_3)_4]$, CH_2Cl_2, RT, 56 %; d) $[Pd(PPh_3)_4]$, toluene, 100 °C, 43 %.



Scheme 13. Further Fischer-carbene complexes of Pd^{II} formed by oxidative insertion.

highly flexible in structural terms due to the ready accessibility of the required precursor salts from simple benzoic acid amides, thiocarbamates or dithiocarbamates, respectively. Figures 13–18 show the structure of representative mem-

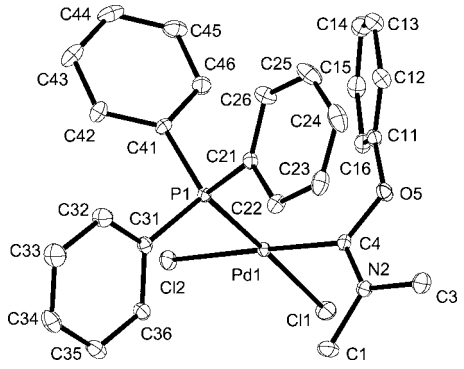


Figure 13. Molecular structure of complex **27a**.

bers of such Fischer carbenes of Pd^{II} in the solid state. It is interesting to note that compound **33** is the only cationic complex prepared during this study which is *cis*- rather than *trans*-configured.

Nickel–carbene complexes: The proven flexibility of the new approach to palladium carbene complexes of different

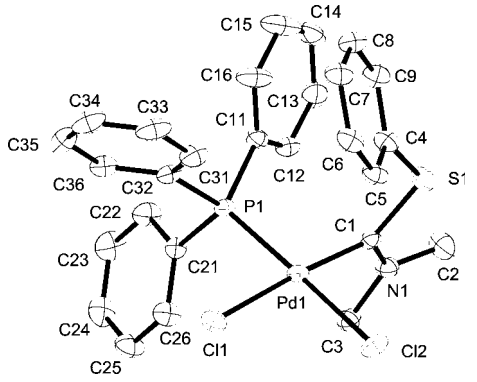


Figure 14. Molecular structure of complex **27b**.

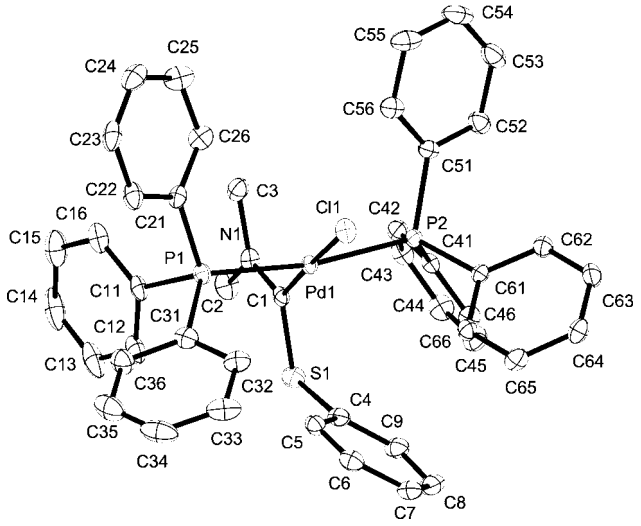


Figure 15. Molecular structure of complex **28b**. The PF_6^- counterion is omitted for clarity.

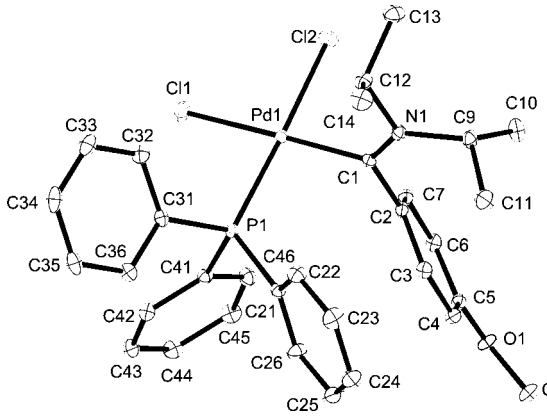


Figure 16. Molecular structure of complex **32**.

types by oxidative addition suggested that the concept should be applicable to other transition metals as well. In contrast to our expectations, however, preliminary attempts to replace $[Pd(PPh_3)_4]$ by $[Rh(Ph_3P)_3Cl]$, $[RhCl(cod)]_2$, $[RhCp(C_2H_4)_2]$, $[CoCp(C_2H_4)_2]$, or $[FeCp(CO)_2]_2$ essentially

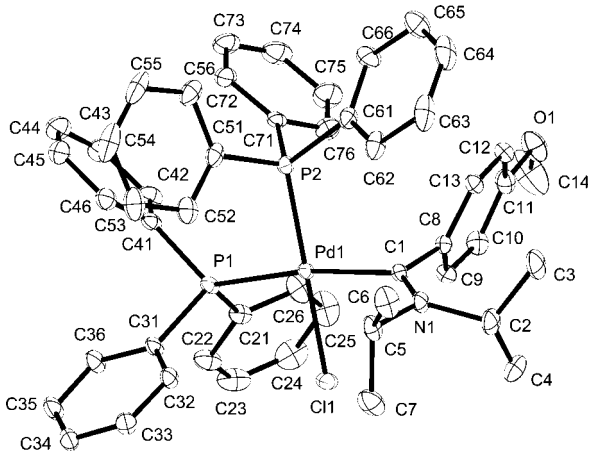


Figure 17. Molecular structure of the *cis*-configured complex **33**. The PF_6^- counterion is omitted for clarity.

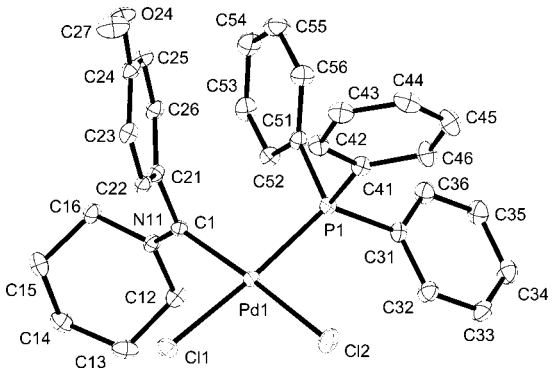
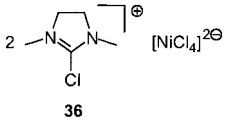


Figure 18. Molecular structure of complex **34**.

met with failure. Particularly surprising was the fact that the reaction of $[Ni(PPh_3)_4]$ or $[Ni(cod)_2]$ with **1** as a prototype carbene source led to rather complex mixtures under various experimental conditions. The only product that could be isolated in analytically pure form was the imidazolinium tetrachloronickelate salt **36**, the structure of which is shown in Figure 19.



36

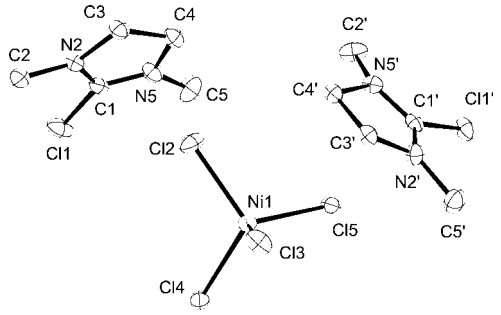
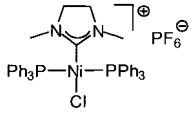
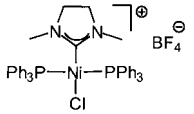
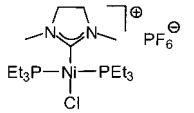
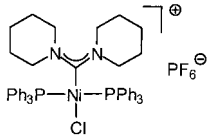
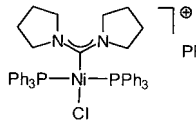
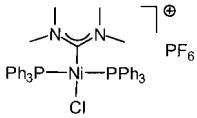


Figure 19. Molecular structure of the nickelate complex **36**.

Despite these setbacks, the importance of nickel catalysts for various types of bond forming reactions spurred further efforts to prepare carbene complexes of this metal via oxidative addition.[41] After some experimentation it was found that the use of $[Ni(cod)_2]$ in combination with PPh_3 (2 equiv) in THF at ambient temperature led to clean conversions and allowed for the formation of a variety of cationic nickel–diaminocarbene complexes in good to excellent yields. The use of PEt_3 instead of PPh_3 works equally well, suggesting that further variations of the accompanying phosphine ligands might be possible (Table 1, entry 3). Products

Table 1. Preparation of nickel-diaminocarbene complexes by oxidative insertion into various amidinium salts. All reactions were performed in THF at ambient temperature using $[Ni(cod)_2]$ and PPh_3 as the reagents unless stated otherwise.

Entry	Substrate	Product		Yield [%]
1	**1a**		**37**	86
2	**1b**		**38**	62
3	**1a**		**39**	78[a]
4	**18a**		**40**	41
5	**18b**		**41**	50
6	**21**		**42**	64

[a] Using $PEt_3/[Ni(cod)_2]$ as the reagent combination.

37–**42** formed by this protocol are summarized in Table 1. In several cases was it possible to grow crystals suitable for X-ray analysis. The structures of representative complexes are depicted in Figures 20–22.

Structural aspects: Several carbene complexes yielded crystals suitable for single crystal structure determination. All of them are distorted square-planar with root mean square deviations from planarity ranging from 0.005 to 0.068 Å. Although the square planar geometry allows for *cis–trans* isomerism, the neutral dichloro complexes invariably show *cis* geometry placing one chlorine *trans* to the PPh_3 ligand and the other one *trans* to the carbene. In the series of charged

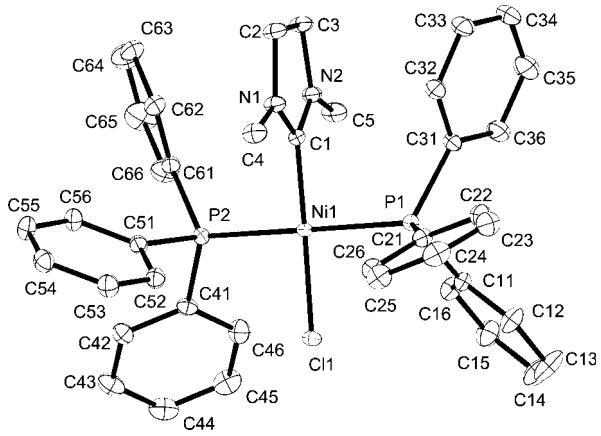


Figure 20. Molecular structure of the nickel complex **37**. The PF_6^- counterion is omitted for clarity.

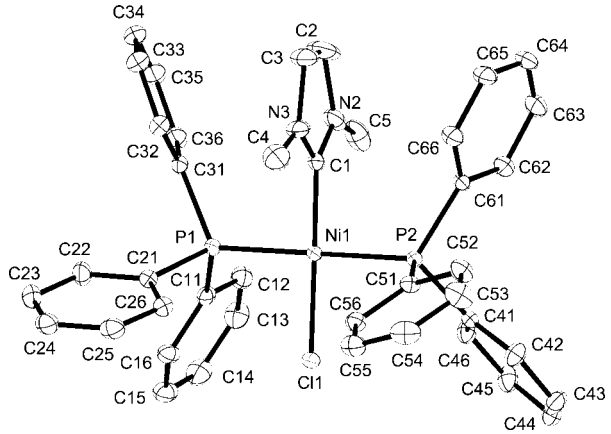


Figure 21. Molecular structure of the nickel complex **38**. The BF_4^- counterion is omitted for clarity.

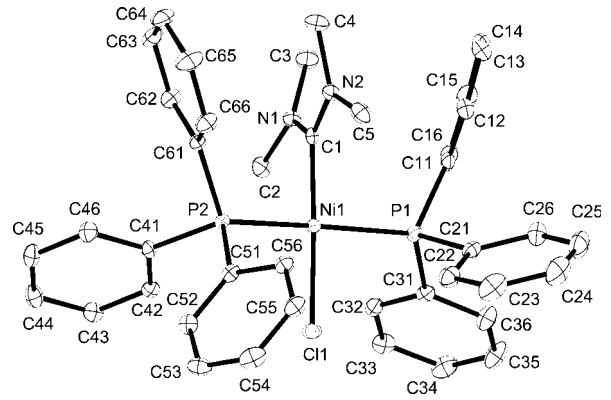


Figure 22. Molecular structure of the nickel complex **42**. The PF_6^- counterion omitted for clarity.

complexes, the two PPh_3 ligands are mutually *trans* to each other except for **33** in which the two phosphines have a *cis* arrangement (Figure 17).

For the palladium complexes a strong *trans*-effect is noted which shortens the metal–phosphorous bond by almost 0.1 Å from an average of 2.344(16) Å for those complexes with two phosphine ligands *trans* to each other, to 2.259(8) when a chlorine is *trans* to the phosphine. The metal–chlorine distances are not affected significantly, the average is 2.358(12) ranging from 2.341 to 2.378 Å. A much smaller and statistically less significant influence on bond length is observed for the palladium–carbene distance. This distance is on average 1.990(15) Å ranging from 1.969 to 2.023 Å for the 15 complexes where a chlorine is *trans* to the carbene, and the one example **33** which has a phosphine *trans* to the carbene where the Pd–C distance is 2.047(3) Å. From the nickel complexes, all of which have two PPh_3 ligands in *trans* orientation, no trends can be deduced. In line with the results of previous crystallographic investigations of diaminocarbenes and metal complexes thereof, the bond angle *N*-$C_{carbene}$-X (X = N, O, S, C) is significantly widened in all structures in which this element is not part of a cyclic motif; likewise, complexes **16a**,**b** bearing the heterocyclic carbene with a six-membered backbone also feature such a rather large bond angle. Selected data together with the characteristic shifts of the carbene atoms in the ^{13}C NMR spectra are compiled in Table 2.

Table 2. Selected structural data and compilation of the ^{13}C NMR shifts of the carbene centers of all metal carbene complexes characterized by X-ray crystallography.

Complex	M–$C_{carbene}$ [Å]	N-$C_{carbene}$-X [°]	Tilt angle [°][a]	δ_C [$C_{carbene}$, ppm]
2a	1.9805(18)	109.70(16)	87.87	194.9
9a	1.975(2)	108.65(18)	84.79	193.2
9b	1.9687(17)	108.95(15)	78.94	190.0
11	1.971(3)	109.0(3)	86.39	194.5
12	1.986(4)	109.6(3)	87.86	195.4
13	1.981(2)	109.1(2)	78.77	195.0
16a	2.005(2)	120.1(2)	90.00	187.4
16b	2.005(4)	119.6(4)	90.00	187.7
19	2.023(3)	122.3(3)	81.06	193.8
22	1.9825(13)	119.20(12)	80.85	201.3
23	2.003(5)	121.6(5)	84.87	198.8
27a	1.9791(11)	111.63(9)	82.45	204.8
27b	1.985(5)	113.8(3)	89.31	228.7
28b	1.998(3)	113.5(2)	82.84	230.3
32	1.9937(12)	122.44(11)	74.93	232.4
33	2.047(3)	124.0(2)	80.24	235.1
34	1.975(2)	121.8(2)	81.29	226.4
37	1.8650(17)	109.0(16)	87.93	197.1
38	1.8626(14)	109.85(13)	85.91	197.0
42	1.894(5)	121.3(3)	81.81	199.9

[a] Refers to the dihedral angle between the square plane defined by the ligands around the metal and the plane of the carbene ligand formed by N-$C_{carbene}$-X.

The crystal structures encompass both charged and neutral complexes, but no significant differences in metal carbene distance are found. The average palladium–carbene distance for the charged complexes is 1.998(21) Å and for neutral complexes 1.979(8) Å, respectively. For individual pairs of neutral/charged complexes it is observed that the charged complex always has a slightly longer metal–carbene distance (e.g. **3**/*trans*-**2a**; **22**/**23**; **33**/**32**; **13**/**12**).

Although the carbene ligands encompass a wide variety of different functional groups and steric demand, there is a general tendency for the plane formed by N-C-(N,C,O,S) to be rotated away from the square-planar arrangement of the metal ligands. The dihedral angle between these two planes ranges from 74.93 to 90° for the palladium complexes and is between 81.81 and 89.93° for the nickel complexes.

This perpendicular arrangement would certainly be expected for the more bulky carbene ligands like the one in complexes **10** and **11**. However, it is interesting to speculate whether there would be sufficient space for the bis(dimethylamino)methylene ligand in **22** and **23** or the similar sized carbene ligand in complex **16** to adopt a conformation placing the N-C-N plane more or less parallel to the metal coordination plane. This orientation permits the overlap of the empty p_π orbital of the carbene with the $4d_{z^2}$-orbital of palladium. To achieve this conformation it would be necessary for the triphenylphosphines to rotate around the Pd–P bond and to re-orient the phenyl rings. An analysis of the arrangement of triphenylphosphines binding to tetra-coordinated palladium in *cis* geometry to chlorine based on 170 crystal structures reveals, however, that there is a clear preference for a staggered orientation of the PPh_3 group with respect to the Pd–Cl bond. This becomes even more pronounced if only those 40 structures are considered where the remaining two palladium ligands are carbon and either another phosphorous or another chlorine atom (Figure 23). Based on this preferred dihedral angle distribution it is reasonable to assume that the phosphine's phenyl rings exert a significant directing influence on the orientation of the carbene.

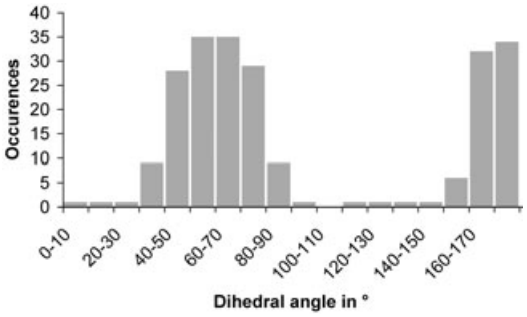
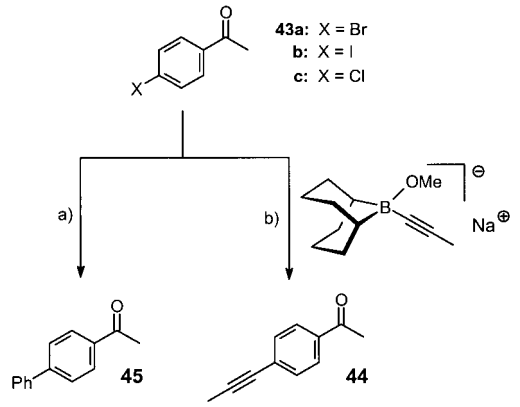


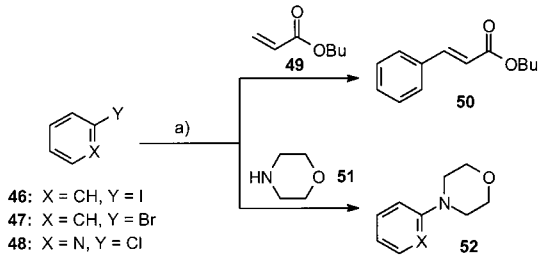
Figure 23. Distribution of the C-P-Pd-Cl dihedral angles in complexes with the extended substructure Ph_3P-Pd-$(X,C,Cl)_3$, where X is either phosphorous or chlorine and the carbon atom may be any type of carbon. The P-Pd-Cl as well as the P-Pd-C angles are restricted to values between 75 and 105°.

Catalytic performance in cross-coupling reactions: Although the main purpose of this study was the development of a novel synthesis route for metal–carbene complexes rather than the optimization of their catalytic properties, the small library of compounds formed during this investigation was screened in prototype cross-coupling reactions.

Preliminary experiments showed that the cationic Pd–NHC complex **2a** serves as active catalyst for Suzuki reactions (Scheme 14).[42,43] Specifically, cross-coupling of 4-bromoacetophenone **43a** with $PhB(OH)_2$ in the presence of 1 mol% of **2a** afforded the expected product **45** in 79% yield. Likewise, the borate formed in situ from 9-MeO-9-BBN and NaC≡CMe[44] transferred its alkynyl unit with similar ease to give product **44**. Furthermore, this catalyst effected the Heck coupling[43,45,46] of bromo- or iodobenzene with butyl acrylate as well as the Buchwald-Hartwig amination[47,48] of either bromobenzene or 2-chloropyridine with morpholine in satisfactory yields (Scheme 15). Therefore these prototype reactions were used to evaluate and compare the performance of the different catalysts.



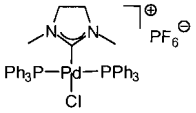
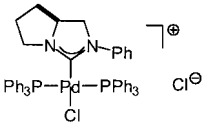
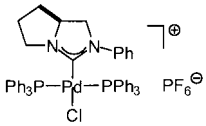
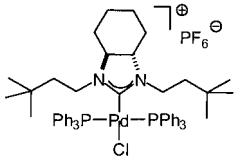
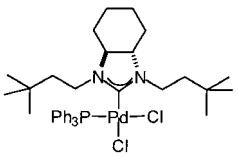
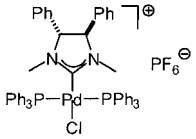
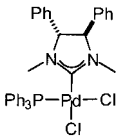
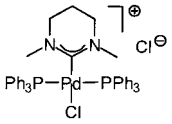
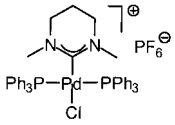
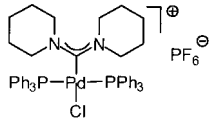
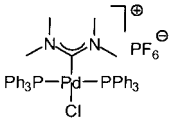
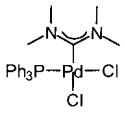
Scheme 14. a) *trans*-**2a** (1 mol%), $PhB(OH)_2$, K_2CO_3, THF, reflux, 79%; b) *trans*-**2a** (1 mol%), [(9-BBN)(OMe)(C≡CMe)], THF, reflux, 82% (GC).



Scheme 15. Model reactions to evaluate the catalytic performance of different metal carbene complexes; for the reaction conditions see Table 3.

As can be seen from the results compiled in Table 3, all complexes investigated showed good to excellent activity in the chosen test reactions. While this may not be surprising for the palladium complexes bearing NHC- and related diaminocarbene ligands in view of the proven efficiency of such species in various kinds of metal-catalyzed cross-couplings, it is interesting to note that even prototype Fischer carbenes such as **32** and **34** showed appreciable reactivity, although they are likely less electron rich at the metal center than their NHC counterparts (entries 41–46). Likewise, carbenes with heteroelements other than nitrogen gave promising results (entries 30–40). This is particularly true for complex **22b** incorporating a phenylthioether motif (entries 36–40). In evaluating these data, it must be kept in mind that the steric properties of all catalysts tested herein are almost cer-

Table 3. Evaluation of the catalytic performance of various palladium–carbene complexes in prototype cross-coupling reactions. All transformations were carried out by using 1 mol% of the metal complex. The yields refer to GC data unless stated otherwise.

Entry	Catalyst	Substrate	Suzuki [%][a]	Heck [%][b]	Amination[c]
1		**43a**	79[d]	86	
2		**47**			84
3		**48**			100
4		**43a**	89		
5		**43c**	88		
6		**46**		100	
7		**47**		90	
8		**46**		100	
9		**47**		81	
10		**46**		97	
11		**47**		59	
12		**43a**	93		
13		**46**		100	
14		**47**		51	
15		**46**		96	
16		**47**		79	
17		**46**		98	
18		**47**		98	
19		**46**		87	
20		**47**		72	
21		**46**		91	
22		**47**		88	
23		**46**		92	
24		**47**		77	
25		**46**		80	
26		**47**		75	89
27		**48**			100
28		**46**		82	
29		**47**		56	

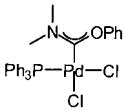
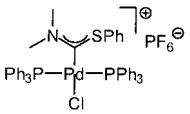
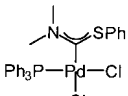
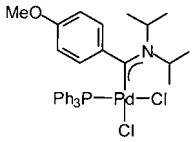
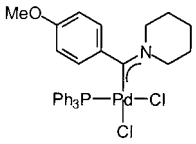
tainly not ideal, thus leaving room for further optimization.[49]

The same holds true for the novel nickel carbene complexes which were found to effect the Kumada–Corriu cross-coupling[43,50,51] of *p*-methoxyphenylmagnesium bromide with chloro- or bromobenzene as well as 2-chloropyridine (Table 4). Although small amounts of 4,4′-dimethoxybiphenyl formed by homocoupling of the Grignard reagent were invariably detected in the crude mixtures (15–25%), the desired products were obtained in good yields in all cases investigated.

Conclusion

Oxidative insertion of $[Pd(PPh_3)_4]$ or $[Ni(cod)_2]/PPh_3$ into the C–Cl bond of 2-chloroamidinium and related salts constitutes a fairly general and highly flexible entry into neutral as well as cationic diaminocarbene complexes of Pd^{II} and Ni^{II}, respectively. This approach is complementary to existing methodology which relies on metathetic ligand exchange reactions without altering the oxidation state of the central metal, and therefore provides access to ligand sets that are difficult to prepare otherwise. Moreover, it can also be applied to the formation of Fischer-carbene complexes of nickel and palladium. A representative subset of the products formed by this novel route was characterized by X-ray crystallography and was found to exhibit appreciable catalytic activity in Suzuki-, Heck-, Kumada- and Buchwald–Hartwig reactions. In view of the ready availability of the required amidinium salts (even in enantiopure form) from simple urea or thiourea

Table 3. (Continued)

Entry	Catalyst	Substrate	Suzuki [%][a]	Heck [%][b]	Amination[c]
30		**43b**	83		
31		**43a**	81		
32		**47**			82
33		**48**			100
34		**43b**	72		
35		**43a**	69		
36		**43b**	82		
37		**43a**	78		
38		**43c**	81[e]		
39		**47**			92
40		**48**			47
41		**43b**	68		
42		**43a**	55		
43		**47**			73
44		**48**			100
45		**43b**	80		
46		**43a**	78		

[a] Unless stated otherwise, the Suzuki reactions were performed in refluxing THF using K_2CO_3 as the base. [b] Heck reactions were performed in NMP at 120 °C for 16 h using Cs_2CO_3 as the base. [c] The amination reactions were performed in DME with NaO(*t*Bu) as the base at ambient temperature with substrate **48** and at 70 °C with substrate **47**. [d] Isolated yield. [e] In toluene at 120 °C.

precursors, it is reasonable to expect that this method might find broader applications in the future.

Experimental Section

General: All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF, DMA (Desmodur, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.24 ppm; CD_2Cl_2: δ_C = 53.8 ppm; residual CH_2Cl_2 in CD_2Cl_2: δ_H = 5.32 ppm). IR: Nicolet FT-7199 spectrometer, wave numbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

Starting materials

Compound 5: Thiophosgene (0.48 mL, 6.24 mmol) was slowly added to a solution of diamine **4** (1.0 g, 5.67 mmol) in CH_2Cl_2 (25 mL) and Et_3N (1.6 mL, 11.34 mmol) and the resulting mixture was stirred for 3 h at ambient temperature. For work-up, the mixture was diluted with CH_2Cl_2 and the reaction was quenched with water. The aqueous phase was repeatedly extracted with CH_2Cl_2, the combined organic layers were dried (Na_2SO_4), the solvent was evaporated and the residue was purified by flash chromatography (hexane/ethyl acetate 6:1) to give thiourea **5** as a white solid (1.02 g, 4.67 mmol, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.53 (m, 2H), 7.41–7.36 (m, 2H), 7.24–7.20 (m, 1H), 4.18–4.06 (m, 3H), 3.99–3.96 (m, 1H), 3.48–3.42 (m, 1H), 2.21–2.12 (m, 2H), 2.06–1.94 (m, 1H), 1.63–1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.2 (C), 141.1 (C), 129.1 (CH), 126.4 (CH), 124.7 (CH), 59.8 (CH), 55.6 (CH_2), 48.2 (CH_2), 31.6 (CH_2), 25.6 (CH_2); IR (KAP): $\tilde{\nu}$ = 3102, 3064, 3037, 2965, 2945, 2913, 2877, 1594, 1581, 1498, 1475, 1436, 1396, 1362, 1332, 1314, 1295, 1259, 1183, 1165, 1081, 1047, 945, 900, 878, 830, 764, 693, 644, 631, 567, 545, 492 cm^{-1}; MS (EI): m/z (%): 218 (100) [M^+], 217 (90), 189 (5), 185 (3), 177 (4), 175 (3), 151 (2), 145 (3), 136 (7), 135 (16), 132 (6), 130 (3), 117 (5), 109 (5), 104 (11), 77 (29), 55 (10), 41 (10); HRMS: calcd for $C_{12}H_{14}N_2S$: 218.0878, found: 218.0877; elemental analysis calcd (%) for: C 66.02, H 6.46, N 12.83; found: C 66.21, H 6.40, N 12.69.

General procedure for the conversion of thioureas into amidinium chlorides:[31c] Oxalyl chloride (1.2 equiv) was added to a solution of the thiourea in anhydrous toluene (5 mL per mmol of thiourea). The resulting bright yellow solution was stirred for 16 h at 60 °C, causing the precipitation of a pale brown solid. This precipitate was allowed to settle, the solution was siphoned off, and the solid was repeatedly washed with Et_2O. The following compounds were prepared according to this general procedure.

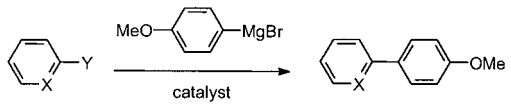
Compound 6a (X = Cl): colorless solid (96 mg, 80 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.77–7.72 (m, 2H), 7.51–7.43 (m, 3H), 4.82–4.61 (m, 3H), 4.20–4.13 (m, 1H), 3.67–3.61 (m, 1H), 2.76–2.66 (m, 1H), 2.51–2.43 (m, 1H), 2.31–2.15 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 156.6 (C), 135.5 (C), 130.2 (CH), 130.0 (CH), 126.4 (CH), 63.9 (CH), 59.5 (CH_2), 47.9 (CH_2), 30.1 (CH_2), 26.4 (CH_2); IR (KBr): $\tilde{\nu}$ = 3057, 2963, 2947, 2873, 1599, 1581, 1503, 1482, 1448, 1412, 1365, 1328, 1318, 1282, 1218, 1137, 1120, 1075, 1043, 1024, 995, 912, 898, 877, 816, 770, 752, 693, 628, 606, 562, 535, 511 cm^{-1}; MS (ESI-pos., CH_2Cl_2): m/z: 221.2 [M^+ −Cl]; elemental analysis calcd (%) for: C 56.00, H 5.35, N 10.96; found: C 56.05, H 5.49, N 10.89.

Compound 7a (X = Cl): colorless solid (529 mg, 82 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.94–3.91 (m, 2H), 3.68–3.54 (m, 4H), 2.26–2.23 (m, 2H), 1.97–1.92 (m, 2H), 1.75–1.66 (m, 2H), 1.56 (ddd, J = 13.0, 11.4, 6.3 Hz, 2H), 1.50–1.38 (m, 4H), 0.96 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 158.1, 67.9, 43.7, 41.2, 29.9, 28.9, 27.5, 23.7; IR (KBr): $\tilde{\nu}$ = 3000, 2868, 1578, 1466, 1419, 1383, 1366, 1328, 1309, 1269, 1250, 1176, 1112, 1065, 1022, 966, 912, 834, 757, 645, 518; MS (ESI-pos., CH_2Cl_2): m/z: 327.3 [M^+−Cl]; elemental analysis calcd (%) for: C 62.80, H 9.98, N 7.71; found: C 62.63, H 9.98, N 7.74.

Compound 21a:[52] colorless solid (1.16 g, 90 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.47 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 159.0 (C), 44.8 (CH_3); IR (KBr): $\tilde{\nu}$ = 3442, 3023, 2945, 2434, 2171, 1653, 1544, 1506, 1467, 1404, 1301, 1260, 1170, 1118, 1064, 1038, 939, 898, 872, 719, 638, 562 cm^{-1}; MS (ESI-pos.): m/z: 135.1 [M^+−Cl]; elemental analysis calcd (%) for: C 35.11, H 7.07, N 16.38; found: C 35.25, H 7.15, N 16.29.

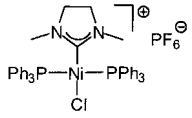
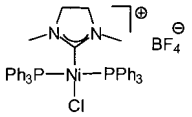
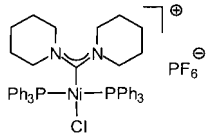
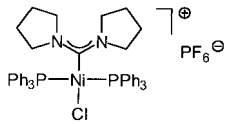
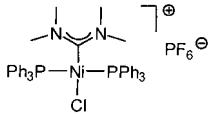
General procedure for the conversion of ureas into amidinium chlorides:[31c] Oxalyl chloride (1.2 equiv) was added to a solution of the urea in anhydrous CCl_4 (2 mL per mmol). The resulting bright yellow solution

Table 4. Kumada cross-coupling reactions catalyzed by different nickel–carbene complexes. All reactions were performed in THF at ambient temperature for 18 h, by using 3 mol% of the catalyst; the yields refer to GC data.



47: X = CH, Y = Br
48: X = N, Y = Cl
53: X = CH, Y = Cl

54

Entry	Catalyst	Substrate	Yield [%]
1		**47**	70
2		**53**	69
3		**48**	78
4		**47**	61
5		**53**	69
6		**48**	71
7		**47**	81
8		**53**	77
9		**48**	76
10		**47**	80
11		**53**	77
12		**48**	78
13		**47**	67
14		**53**	61
15		**48**	74

was stirred for 16 h at 60 °C under argon, causing the precipitation of a white solid. This precipitate was allowed to settle, the solution was siphoned off, and the solid was repeatedly washed with Et_2O. The following compounds were prepared according to this procedure:

Compound 8a (X = Cl):[53] colorless solid (356 mg, 60%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.58–7.55 (m, 2H), 7.45–7.43 (m, 3H), 7.34–7.31 (m, 3H), 7.15–7.12 (m, 2H), 5.29 (s, 1H), 4.05 (s, 1H), 3.16 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 158.1 (C), 138.3 (C), 133.1 (C), 130.4 (CH), 129.7 (CH), 128.9 (CH), 128.9 (CH), 128.4 (CH), 127.5 (CH), 75.2 (CH), 70.4 (CH), 34.0 (CH_3), 29.9 (CH_3); IR (KBr): $\tilde{\nu}$ = 3389, 3061, 3026, 3004, 2945, 2865, 1615, 1586, 1482, 1455, 1434, 1409, 1389, 1359, 1307, 1284, 1251, 1195, 1149, 1078, 1029, 1018, 835, 777, 762, 711, 634, 615, 583, 554, 505, 473 cm^{-1}; MS (ESI-pos.): m/z: 285.1 [M^+−Cl].

Compound 15a (X = Cl): colorless solid (423 mg, 59%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.86 (dt, J = 5.9, 1.2 Hz, 4H), 3.40 (d, J = 1.2 Hz, 6H), 2.2 (dquint., J = 5.9, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 153.0 (C), 51.0 (CH_2), 43.2 (CH_3), 19.4 (CH_2); IR (KAP): $\tilde{\nu}$ = 2944, 2874, 2363, 2059, 1648, 1508, 1445, 1411, 1364, 1324, 1235, 1123, 1033, 863, 844, 756, 624, 565 cm^{-1}; MS (ESI-pos.): m/z: 147.2 [M^+−Cl]; elemental analysis calcd (%) for: C 39.36, H 6.61, N 15.30; found: C 39.37, H 6.68, N 15.24.

Compound 25a (X = O):[54] Prepared in toluene as the solvent; colorless solid (249 mg, 91%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.74–7.70 (m, 2H), 7.49–7.39 (m, 3H), 3.75 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 161.7 (C), 153.0 (C), 130.4 (CH), 128.9 (CH), 121.7 (CH), 44.0 (CH_3); IR (KBr): $\tilde{\nu}$ = 3054, 3019, 2943, 1723, 1664, 1586, 1533, 1488, 1457, 1389, 1326, 1247, 1208, 1170, 1070, 1026, 939, 915, 845, 827, 814, 770, 752, 691, 663, 637, 615, 603, 502 cm^{-1}; MS (ESI-pos.): m/z: 184.2 [M^+−Cl]; elemental analysis calcd (%) for: C 49.11, H 5.04, N 6.36; found C 48.98, H 5.11, N 6.43.

Compound 25b (X = S):[55] Prepared in toluene as the solvent; colorless solid (202 mg, 85%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.80–7.77 (m, 2H), 7.66–7.62 (m, 1H), 7.57–7.52 (m, 2H), 4.02 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 177.8 (C), 136.5 (CH), 133.1 (CH), 130.7 (CH), 124.8 (C), 49.1 (CH_3); IR (KBr): $\tilde{\nu}$ = 3050, 2995, 2930, 1667, 1596, 1476, 1441, 1405, 1365, 1311, 1257, 1246, 1178, 1102, 1087, 1070, 1023, 990, 909, 872, 750, 708, 687, 653, 548, 525, 504 cm^{-1}; MS (ESI-pos.): m/z: 200.2 [M^+−Cl]; elemental analysis calcd (%) for: C 45.77, H 4.69, N 5.93; found: C 45.70, H 4.63, N 6.04.

Compound 30: Prepared in toluene as the solvent; colorless solid (573 mg, 69%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.86–7.82 (m, 2H), 7.14–7.10 (m, 2H), 4.87–4.79 (m, 2H), 3.91 (s, 3H), 1.83 (d, J = 7.0 Hz, 6H), 1.61 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 173.4 (C), 164.7 (C), 131.3 (CH), 124.5 (C), 115.0 (CH), 65.4 (CH_3), 58.8 (CH), 56.1 (CH), 20.3 (CH_3), 20.2 (CH_3); IR (KBr): $\tilde{\nu}$ = 3085, 3014, 2972, 2938, 2877, 2841, 1593, 1571, 1510, 1460, 1438, 1379, 1369, 1339, 1308, 1268, 1244, 1182, 1126, 1016, 894, 852, 843, 805, 773, 724, 689, 627, 605, 555, 535, 507 cm^{-1}; MS (ESI-pos.): m/z: 254.2 [M^+−Cl]; elemental analysis calcd (%) for: C 57.94, H 7.29, N 4.83; found: C 57.76, H 7.39, N 4.81.

Representative procedure for the formation of hexafluorophosphate salts—Compound 7b (X = PF_6): $AgPF_6$ (147 mg, 0.58 mmol) was added to a solution of chloride salt **7a** (X = Cl, 210 mg, 0.58 mmol) in CH_2Cl_2 (4 mL) and the resulting suspension was stirred for 1 h at ambient temperature under argon. The mixture was filtered and the solvent was evaporated to give the corresponding hexafluorophosphate salt **7b** in analytically pure form (219 mg, 79%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.63–3.60 (m, 2H), 3.58–3.52 (m, 4H), 2.26–2.23 (m, 2H), 2.03–1.98 (m, 2H), 1.63–1.60 (m, 2H), 1.59–1.51 (m, 2H), 1.47–1.36 (m, 4H), 0.96 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 157.8 (C), 67.7 (CH), 43.3 (CH_2), 40.9 (CH_2), 29.9 (C), 28.8 (CH_3), 27.4 (CH_2), 23.7 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 2950, 2873, 1571, 1494, 1474, 1458, 1444, 1366, 1328, 1313, 1271, 1253, 1178, 1165, 1110, 1054, 999, 969, 912, 877, 839, 778, 652, 557, 485 cm^{-1}; MS (ESI-pos.): m/z: 327.3 [M^+−PF_6]; elemental analysis calcd (%) for: C 48.25, H 7.67, N 5.92; found: C 48.31, H 7.74, N 5.96.

The following compounds were prepared analogously:

Compound 6b (X = PF_6): pale brown solid (203 mg, 71%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.57–7.49 (m, 3H), 7.44–7.41 (m, 2H), 4.78–4.69 (m, 1H), 4.54 (t, J = 11.0 Hz, 1H), 4.39 (dd, J = 11.1, 8.9 Hz, 1H), 3.93–3.86 (m, 1H), 3.72 (dt, J = 9.6, 2.9 Hz, 1H), 2.48–2.37 (m, 2H), 2.32–2.19 (m, 1H), 2.17–2.06 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 156.0 (C), 134.8 (C), 130.6 (CH), 130.4 (CH), 125.5 (CH), 68.7 (CH), 58.3 (CH_2), 47.4 (CH_2), 30.5 (CH_2), 25.7 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = −143.8 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3071, 2964, 2883, 1604, 1590, 1507, 1490, 1471, 1451, 1367, 1333, 1298, 1285, 1223, 1140, 1047, 1027, 833, 772, 696, 639, 608, 558, 536 cm^{-1}; MS (ESI-pos.): m/z: 221.0

[M^+-PF_6]; elemental analysis calcd (%) for: C 39.31, H 3.85, N 7.64; found: C 39.46, H 3.81, N 7.60.

Compound 8b (X = PF_6): colorless solid (121 mg, 70%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.50–7.46 (m, 3H), 7.40–7.36 (m, 3H), 7.34–7.32 (m, 2H), 7.20–7.17 (m, 2H), 5.08 (s, 1H), 4.30 (s, 1H), 3.11 (s, 3H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 157.0 (C), 137.6 (C), 132.8 (C), 130.7 (CH), 130.0 (CH), 129.1 (CH), 128.8 (CH), 128.2 (CH), 127.4 (CH), 74.8 (CH), 70.6 (CH), 33.6 (CH_3), 29.9 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = −143.7 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3066, 3035, 2950, 2881, 2813, 1697, 1655, 1619, 1587, 1519, 1498, 1457, 1413, 1358, 1308, 1279, 1235, 1214, 1144, 1081, 1030, 1004, 971, 839, 759, 703, 656, 635, 588, 557 cm^{-1}; MS (ESI-pos.): m/z: 285.2 [M^+-PF_6]; elemental analysis calcd (%) for: C 47.40, H 4.21, N 6.50; found: C 47.56, H 4.34, N 6.63.

Compound 15b (X = PF_6):[56] colorless solid (157 mg, 90%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.67 (t, J = 6.0 Hz, 4H), 3.37 (s, 6H), 2.21 (quint., J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 153.0 (C), 53.0 (CH_2), 43.0 (CH_3), 19.1 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 2956, 2892, 2263, 1651, 1511, 1452, 1416, 1368, 1326, 1306, 1239, 1129, 1057, 1037, 833, 742, 635, 610, 558, 494, 481 cm^{-1}; MS (ESI-pos.): m/z: 147.1 [M^+-PF_6]; elemental analysis calcd (%) for: C 24.63, H 4.13, N 9.57; found: C 24.57, H 4.18, N 9.48.

Compound 21b (X = PF_6):[57] colorless solid (224 mg, 91%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.33 (s, 12H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 159.9 (C), 44.3 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = −144.0 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 2960, 2928, 1655, 1508, 1473, 1408, 1395, 1263, 1179, 1122, 1064, 1005, 836, 645, 617, 557 cm^{-1}; MS (ESI-pos.): m/z: 135.0 [M^+-PF_6]; elemental analysis calcd (%) for: C 21.40, H 4.31, N 9.98; found: C 21.36, H 4.27, N 10.06.

Compound 26a (X = O): colorless oil (111 mg, 75%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.57–7.48 (m, 3H), 7.21–7.16 (m, 2H), 3.71 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 161.7 (C), 152.6 (C), 129.6 (CH), 125.3 (CH), 121.0 (CH), 44.7 (CH_3), 42.9 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3063, 2955, 2917, 2849, 2645, 1668, 1602, 1585, 1490, 1462, 1418, 1392, 1332, 1248, 1210, 1172, 1144, 1070, 1030, 1005, 939, 838, 815, 766, 688, 664, 630, 608, 558, 499, 467 cm^{-1}; MS (ESI-pos.): m/z: 184.1 [M^+-PF_6]; elemental analysis calcd (%) for: C 32.80, H 3.36, N 4.25; found: C 32.74, H 3.43, N 4.16.

Compound 26b (X = S): pale yellow solid (191 mg, 86%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.69–7.65 (m, 3H), 7.61–7.57 (m, 2H), 3.81 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 176.7 (C), 136.5 (CH), 133.6 (CH), 130.3 (CH), 124.2 (C), 49.0 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3060, 2919, 2849, 1666, 1605, 1477, 1446, 1411, 1366, 1335, 1261, 1236, 1137, 1104, 1089, 1059, 1026, 990, 879, 838, 758, 707, 688, 657, 558, 525, 505, 494 cm^{-1}; MS (ESI-pos.): m/z: 200.2 [M^+-PF_6]; elemental analysis calcd (%) for: C 31.27, H 3.21, N 4.05; found: C 31.21, H 3.16, N 3.88.

Compound 31: colorless solid (176 mg, 65%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.63–7.59 (m, 2H), 7.16–7.12 (m, 2H), 4.87 (hept., J = 6.6 Hz, 1H), 4.61 (hept., J = 7.1 Hz, 1H), 3.93 (s, 3H), 1.79 (d, J = 7.0 Hz, 6H), 1.54 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 165.6 (C), 161.9 (C), 131.1 (CH), 128.2 (C), 114.5 (CH), 65.7 (CH_3), 56.3 (CH), 55.7 (CH), 20.2 (CH_3), 20.1 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = −143.8 (hept., J(P,F) = 710.6 Hz); IR (KBr): ν = 2975, 2939, 2848, 1625, 1610, 1576, 1546, 1511, 1470, 1443, 1371, 1339, 1302, 1256, 1213, 1180, 1161, 1107, 1027, 925, 887, 842, 819, 801, 767, 733, 596, 558, 491 cm^{-1}; MS (ESI-pos): m/z: 254.2 [M^+-PF_6], 212.2 [M^+-PF_6-iPr]; elemental analysis calcd (%) for: C 42.06, H 5.30, N 3.50; found: C 42.16, H 5.26, N 3.41.

Representative procedure for the preparation of palladium complexes by oxidative insertion into amidinium hexafluorophosphate salts—Compound 10: A suspension of the hexafluorophosphate salt **7b** (X = PF_6, 129 mg, 0.27 mmol) and [$Pd(PPh_3)_4$] (312 mg, 0.27 mmol) in toluene (20 mL) was stirred under argon for 2 h at 100 °C. After cooling, the solvent was removed in vacuo, the waxy residue was suspended in pentane and stirred for 1 h at ambient temperature to form a fine powder. The pentane was discarded and the residue was extracted with pentane to remove the remaining PPh_3. The crude product was then recrystallized from CH_2Cl_2 to precipitate impurities. After filtration, crystallization of the product was induced by slowly diffusing pentane into the CH_2Cl_2 solution to afford complex **10** as a yellow solid (183 mg, 63%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.65–7.58 (m, 18H), 7.54–7.50 (m, 12H), 3.67–3.59 (m, 2H), 2.88–2.80 (m, 2H), 2.00 (br, 2H), 1.70 (d, J = 6.1 Hz, 4H), 0.97–0.86 (m, 8H), 0.74 (s, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 195.0 (C), 134.7 (CH), 132.2 (CH), 130.6 (C), 129.2 (t, J(C,P) = 5.2 Hz, CH), 68.6 (CH), 47.2 (CH_2), 41.5 (CH_2), 29.6 (CH_2), 28.7 (CH_3), 28.6 (C), 23.7 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 23.1, −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3056, 2954, 2866, 1585, 1573, 1482, 1436, 1396, 1367, 1324, 1310, 1260, 1187, 1162, 1093, 1027, 1000, 873, 839, 748, 695, 637, 617, 557, 520, 495 cm^{-1}; MS (ESI-pos.): m/z: 957.5 [M^+-PF_6]; elemental analysis calcd (%) for: C 59.84, H 6.03, N 2.54; found: C 59.73, H 5.95, N 2.48.

Complex *trans*-**2a**[24] and the following were prepared analogously.

Compound 12: pale yellow solid (151 mg, 43%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.73–7.63 (m, 18H), 7.59–7.55 (m, 12H), 7.32–7.28 (m, 2H), 7.22–7.18 (m, 4H), 6.24–6.22 (m, 4H), 3.82 (s, 2H), 3.01 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 195.4 (C), 134.6 (t, J(C,P) = 6.1 Hz, CH), 132.1 (CH), 131.9 (CH), 129.8 (C), 129.7 (d, J(C,P) = 22.2 Hz, C), 129.4 (t, J(C,P) = 5.2 Hz, CH), 129.2 (CH), 127.8 (CH), 76.6 (CH), 36.3 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 24.4, −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3056, 2914, 1586, 1573, 1523, 1496, 1483, 1455, 1436, 1395, 1352, 1310, 1273, 1230, 1189, 1162, 1095, 1029, 1000, 960, 911, 875, 838, 750, 695, 642, 616, 594, 558, 521, 494 cm^{-1}; MS (ESI-pos.): m/z: 915.25 [M^+-PF_6]; elemental analysis calcd (%) for: C 59.95, H 4.56, N 2.64; found: C 59.90, H 4.48, N 2.56.

Compound 16b (X = PF_6): pale yellow solid (301 mg, 61%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.74–7.69 (m, 12H), 7.60–7.50 (m, 18H), 3.31 (s, 6H), 2.25 (t, J = 6.1 Hz, 4H), 0.91 (quint., J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 187.7 (C), 134.4 (t, J(C,P) = 6.2 Hz, CH), 131.9 (CH), 129.5 (d, J(C,P) = 25.0 Hz, C_q), 129.1 (t, J(C,P) = 5.1 Hz, CH), 46.1 (CH_2), 45.9 (CH_3), 18.0 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 21.9, −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3047, 2952, 2915, 2875, 1579, 1494, 1482, 1435, 1406, 1361, 1321, 1265, 1240, 1220, 1188, 1159, 1095, 1027, 999, 925, 837, 764, 748, 708, 695, 619, 599, 558, 520, 494 cm^{-1}; MS (ESI-pos.): m/z: 779.2 [M^+-PF_6]; elemental analysis calcd (%) for: C 54.62, H 4.58, N 12.34; found: C 54.58, H 4.63, N 12.36.

Compound 19: pale yellow solid (139 mg, 50%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.60–7.49 (m, 30H), 4.03 (t, J = 5.4 Hz, 4H), 2.21 (t, J = 4.8 Hz, 4H), 1.39 (quint., J = 5.4 Hz, 4H), 1.20 (quint., J = 5.5 Hz, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 193.8 (C), 134.5 (CH), 131.9 (CH), 129.4 (C), 129.2 (t, J(C,P) = 5.4 Hz, CH), 57.0 (CH_2), 24.4 (CH_2), 23.3 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 24.2, −143.9 (hept., J(P,F) = 710.6 Hz); IR (KBr): $\tilde{\nu}$ = 3057, 2947, 2853, 1587, 1573, 1538, 1481, 1436, 1409, 1346, 1321, 1281, 1259, 1244, 1188, 1161, 1130, 1095, 999, 838, 790, 746, 705, 693, 602, 557, 520, 498 cm^{-1}; MS (ESI-pos.): m/z: 847.3 [M^+-PF_6]; elemental analysis calcd (%) for: C 56.92, H 5.08, N 2.82; found: C 57.08, H 5.03, N 2.75.

Compound 23: pale yellow solid (255 mg, 48%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.70–7.66 (m, 12H), 7.60–7.50 (m, 18H), 3.43 (s, 6H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 198.8 (C), 134.4 (t, J(C,P) = 6.2 Hz, CH), 132.0 (CH), 129.6 (d, J(C,P) = 25.0 Hz, C), 129.3 (t, J(C,P) = 5.2 Hz, CH), 47.1 (CH_3), 42.9 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 22.4, −143.9 (hept., J(P,F) = 710.6 Hz); IR (KBr): $\tilde{\nu}$ = 3051, 2960, 2922, 1656, 1564, 1496, 1482, 1435, 1405, 1389, 1314, 1267, 1189, 1159, 1095, 1052, 1027, 999, 918, 836, 747, 693, 611, 558, 521, 493 cm^{-1}; MS (ESI-pos.): m/z: 767.3 [M^+-PF_6]; elemental analysis calcd (%) for: C 54.02, H 4.64, N 12.50; found: C 54.12, H 4.58, N 12.57.

Compound 28a (X = O): yellow solid (110 mg, 30%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.68–7.58 (m, 7H), 7.54–7.47 (m, 12H), 7.44–7.39 (m, 12H), 7.20–7.15 (m, 2H), 6.84–6.81 (m, 2H), 3.18 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 207.5 (C), 153.2 (C), 134.3 (t, J(C,P) = 5.8 Hz, CH), 132.2 (CH), 130.2 (CH), 129.3 (t, J(C,P) = 5.3 Hz, CH), 128.5 (C), 128.1 (CH), 120.4 (CH), 44.5 (CH_3), 38.8 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 21.4, −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3057, 1598, 1574, 1482, 1435, 1347, 1308, 1266, 1226, 1156, 1095, 1026, 999, 841, 770, 751, 694, 606, 558, 521, 496 cm^{-1}; MS (ESI-

pos.): m/z: 814.1 [M^+-PF_6], 553.9 [$M^+-PF_6-PPh_3$]; elemental analysis calcd (%) for: C 56.27, H 4.30, N 1.46; found: C 56.16, H 4.12, N 1.36.

Compound 28b (X=S): colorless solid (116 mg, 24%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.69–7.48 (m, 31H), 7.30–7.25 (m, 4H), 3.41 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ=230.3 (C), 140.4 (C), 134.7 (CH), 134.5 (CH), 132.1 (CH), 131.8 (CH), 130.4 (CH), 129.1 (t, J(C,P)=5.3 Hz, CH), 128.4 (C), 44.9 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ=19.9, −143.9 (hept., J(P,F)=711 Hz); IR (KBr): $\tilde{\nu}$=3058, 1616, 1586, 1574, 1532, 1481, 1435, 1404, 1391, 1322, 1308, 1267, 1225, 1191, 1133, 1095, 1071, 1027, 999, 924, 897, 877, 838, 745, 735, 694, 617, 557, 520, 495 cm^{-1}; MS (ESI-pos.): m/z: 830.2 [M^+-PF_6], 570.1 [$M^+-PF_6-PPh_3$]; elemental analysis calcd (%) for: C 55.34, H 4.23, N 1.43; found: C 55.37, H 4.21, N 1.38.

Compound 33: yellow solid (151 mg, 43%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.50–7.46 (m, 4H), 7.40–7.36 (m, 3H), 7.27–7.23 (m, 6H), 7.20–7.11 (m, 17H), 6.84–6.81 (m, 2H), 6.62 (br, 2H), 5.79–5.74 (m, 1H), 4.15–4.11 (m, 1H), 3.90 (s, 3H), 2.03 (d, J=6.6 Hz, 3H), 1.59 (d, J=6.7 Hz, 3H), 1.07 (d, J=6.9 Hz, 3H), 0.94 (d, J=7.0 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ=235.1 (C), 161.4 (C), 135.9 (d, J(C,P)=3.0 Hz, C), 134.8 (d, J(C,P)=10.7 Hz, CH), 134.6 (d, J(C,P)=10.4 Hz, CH), 134.0 (d, J(C,P)=12.1 Hz, C), 132.3 (d, J(C,P)=2.7 Hz, CH), 130.9 (d, J(C,P)=2.4 Hz, CH), 130.3 (d, J(C,P)=50.2 Hz, C), 129.2 (d J(C,P)=11.2 Hz, CH), 128.4 (d, J(C,P)=10.3 Hz, CH), 127.3 (CH), 113.2 (CH), 71.0 (CH_3), 57.0 (CH), 55.8 (CH), 25.2 (CH_3), 21.8 (CH_3), 21.1 (CH_3), 20.3 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ=29.0 (d, J=37.2 Hz), 22.7 (d, J=37.3 Hz), −143.9 (hept., J(P,F)=711 Hz); IR (KBr): $\tilde{\nu}$=3057, 2987, 2939, 2845, 1600, 1572, 1503, 1481, 1438, 1392, 1376, 1368, 1310, 1284, 1256, 1209, 1179, 1160, 1143, 1096, 1026, 997, 875, 839, 742, 693, 629, 594, 557, 530, 519, 507 cm^{-1}; MS (ESI-pos.): m/z: 884.2 [M^+-PF_6], 622.1 [$M^+-PF_6-PPh_3$], 586.1 [$M^+-PF_6-PPh_3-Cl$]; elemental analysis calcd (%) for: C 58.26, H 4.99, N 1.36; found: C 58.33, H 5.08, N 1.32.

Compound 35: yellow solid (71 mg, 22%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.63–7.38 (m, 30H), 6.84–6.82 (m, 2H), 6.64–6.61 (m, 2H), 4.34 (t, J=5.8 Hz, 2H), 3.81 (s, 3H), 2.91 (t, J=5.3 Hz, 2H), 1.63–1.62 (m, 2H), 1.55–1.51 (m, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ=226.5 (C), 162.9 (C), 140.4 (C), 135.9 (d, J(C,P)=3.0 Hz, C), 134.6 (t, J(C,P)=6.2 Hz, CH), 131.9 (CH), 131.1 (CH), 129.1 (t, J=5.3 Hz, CH), 114.1 (CH), 63.4 (CH_2), 56.6 (CH_2), 56.0 (CH_3), 26.0 (CH_2), 24.8 (CH_2), 22.9 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ=23.9, −143.9 (hept., J(P,F)=711 Hz); IR (KBr): $\tilde{\nu}$=3060, 2954, 2863, 2677, 2580, 1599, 1541, 1505, 1482, 1436, 1310, 1265, 1232, 1172, 1109, 1095, 1072, 1024, 999, 931, 839, 747, 725, 692, 645, 604, 558, 520, 494 cm^{-1}; MS (ESI-pos.): m/z: 868.2 [M^+-PF_6], 608.2 [$M^+-PF_6-PPh_3$]; elemental analysis calcd (%) for: C 58.00, H 4.67, N 1.38; found: C 57.92, H 4.58, N 1.34.

Compound 9b (X=PF$_6$)

Method A: A suspension of the imidazolium salt **6b** (X=PF_6, 100 mg, 0.27 mmol) and [$Pd(PPh_3)_4$] (312 mg, 0.27 mmol, 1 equiv) in CH_2Cl_2 (18 mL) was refluxed under argon for 2 h. For work up, the solvent was removed in vacuo, the waxy residue was suspended in pentane and stirred for 1 h at RT to form a fine powder. The pentane was discarded and the residue was extracted with pentane to remove the remaining PPh_3. The crude product was then recrystallized from CH_2Cl_2 to precipitate impurities. After filtration, crystallization of the product was induced by slowly diffusing pentane into the CH_2Cl_2 solution affording the desired product **9b** as a pale yellow solid (110 mg, 41%).

Method B: $AgPF_6$ (35 mg, 0.14 mmol) was added to a solution of the corresponding chloride complex **9a** (X=Cl, 125 mg, 0.14 mmol) in CH_2Cl_2 (1 mL) and the resulting suspension was stirred for 1 h under argon. The mixture was filtered and the solvent was evaporated to give the desired product as a pale yellow solid (99 mg, 71%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.71–7.66 (m, 5H), 7.60–7.50 (m, 13H), 7.44–7.34 (m, 12H), 7.26–7.17 (m, 5H), 3.67–3.57 (m, 1H), 3.44–3.30 (m, 2H), 3.06 (t, J=10.7 Hz, 1H), 2.88–2.86 (m, 1H), 1.94–1.90 (m, 1H), 1.75–1.72 (m, 2H), 0.62 (t, J=9.7 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=190.0 (C), 139.2 (C), 134.4 (t, J(C,P)=6.2 Hz, CH), 132.1 (CH), 131.9 (CH), 129.5 (C), 129.1 (dt, J(C,P)=13.0, 5.3 Hz, CH), 126.3 (CH), 118.7 (CH), 63.9 (CH), 54.7 (CH_2), 46.4 (CH_2), 29.8 (CH_2), 26.1 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ=22.8, −143.4 (hept., J(P,F)=711 Hz); IR (KBr): $\tilde{\nu}$=3058, 2954, 2918, 2881, 2850, 1598, 1586, 1574, 1521, 1494, 1482, 1471, 1458, 1436, 1413, 1370, 1325, 1301, 1259, 1185, 1119, 1094, 1072, 1028, 998, 922, 877, 840, 757, 746, 734, 697, 625, 594, 558, 542, 517, 497 cm^{-1}; MS (ESI-pos.): m/z: 853.3 [M^+-PF_6]; elemental analysis calcd (%) for: C 57.79, H 4.45, N 2.81; found: C 57.86, H 4.37, N 2.72.

Representative procedure for the preparation of palladium carbene complexes by oxidative insertion into amidinium chloride salts—Compound 13: A solution of the imidazolium salt **8a** (X=Cl) (150 mg, 0.47 mmol) and [$Pd(PPh_3)_4$] (543 mg, 0.47 mmol) in CH_2Cl_2 (30 mL) was stirred under argon for 16 h at ambient temperature. The solvent was removed in vacuo, the waxy residue was suspended in pentane and stirred for 1 h at ambient temperature to form a fine powder. The pentane was discarded and the residue was extracted with pentane to remove the remaining PPh_3. The crude product was then recrystallized from CH_2Cl_2 to precipitate impurities. After filtration, the crystallization of the product was induced by slowly diffusing pentane into the CH_2Cl_2 solution, affording product **13** as a yellow solid (230 mg, 70%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.80–7.74 (m, 5H), 7.59–7.52 (m, 3H), 7.50–7.44 (m, 8H), 7.38–7.35 (m, 3H), 7.30–7.23 (m, 4H), 6.49–6.47 (m, 2H), 4.54 (d, J=11.6 Hz, 1H), 4.01 (d, J=11.6 Hz, 1H), 3.20 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=195.0 (C), 136.4 (C), 135.5 (C), 134.7 (d, J(C,P)=11.4 Hz, CH), 131.5 (d, J(C,P)=2.4 Hz, CH), 131.0 (d, J(C,P)=52.3 Hz, C), 130.7 (CH), 129.9 (CH), 129.4 (CH), 129.1 (CH), 128.8 (d, J(C,P)=11.0 Hz, CH), 128.1 (CH), 127.3 (CH), 78.3 (CH), 75.7 (CH), 36.5 (CH_3), 35.5 (CH_3); ^{31}P NMR (162 MHz, CD_2Cl_2): δ=27.90; IR (KBr): $\tilde{\nu}$=3050, 2963, 2909, 1702, 1650, 1586, 1571, 1525, 1492, 1481, 1455, 1436, 1407, 1393, 1262, 1194, 1158, 1096, 1027, 999, 942, 923, 803, 747, 721, 703, 693, 653, 619, 585, 533, 508 cm^{-1}; MS (ESI-pos., CH_2Cl_2): m/z: 653.2 [M^+-Cl]; elemental analysis calcd (%) for: C 60.93, H 4.82, N 4.06; found: C 61.05, H 4.76, N 4.03.

The following complexes were prepared analogously:

Compound 9a (X=Cl): Colorless solid (458 mg, 67%). In solution, this product exists as an equilibrium mixture of the cationic form **9a**, the neutral form and PPh_3 (1:0.28:0.46). ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.80–7.51 (m, 3H), 7.70–7.66 (m, 4H), 7.62–7.51 (m, 10H), 7.47–7.05 (m, 52H), 4.99–4.93 (m, 1H), 3.74–3.44 (m, 5H), 3.39–3.29 (m, 2H), 3.15–3.09 (m, 1H), 3.01–2.92 (m, 1H), 2.29–2.09 (m, 2H), 2.03–1.72 (m, 4H), 1.57–1.47 (m, 1H), 0.71–0.60 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=193.2 (C), 193.1 (C), 139.8 (C), 139.2 (C), 137.5 (d, J(C,P)=21.1 Hz, C, PPh_3), 134.5 (d, J(C,P)=11.5 Hz, CH), 134.3 (t, J(C,P)=6.1 Hz, CH), 133.8 (d, J(C,P)=19.7 Hz, PPh_3), 132.1 (CH), 132.0 (CH), 131.9 (CH), 131.1 (d, J(C,P)=2.4 Hz, CH), 130.1 (d, J(C,P)=54.5 Hz, C), 129.5 (s, C), 129.1 (t, J(C,P)=13.3 Hz, CH), 128.8 (CH, PPh_3), 128.6 (d, J(C,P)=6.9 Hz, CH, PPh_3), 128.2 (d, J(C,P)=11.2 Hz, CH), 126.8 (CH), 126.3 (CH), 120.6 (CH), 118.9 (CH), 64.3 (CH), 63.1 (CH), 55.0 (CH_2), 54.3 (CH_2), 47.4 (CH_2), 46.4 (CH_2), 30.4 (CH_2), 30.0 (CH_2), 26.1 (CH_2), 24.4 (CH_2); ^{31}P NMR (162 MHz, CD_2Cl_2): δ=27.5 (neutral), 23.1 (cationic), −4.3 (PPh_3); IR (KBr): $\tilde{\nu}$=3051, 2961, 2927, 2876, 1597, 1585, 1514, 1495, 1481, 1467, 1434, 1409, 1371, 1320, 1286, 1257, 1158, 1118, 1093, 1027, 997, 804, 746, 721, 694, 624, 542, 517, 497, 470 cm^{-1}; MS (ESI-pos.): m/z: 851.2 (cationic form, [M^+-Cl]), 589.1 (neutral form, [M^+-Cl]); elemental analysis calcd (%) for the cationic complex: C 64.91, H 4.99, N 3.15; found: C 64.72, H 5.15, N 3.08.

Complex 11 (X=Cl): colorless foam (85%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ=7.76–7.71 (m, 6H), 7.52–7.47 (m, 3H), 7.44–7.39 (m, 6H), 4.03 (dt, J=13.2, 4.7 Hz, 1H), 3.90 (dt, J=13.4, 4.4 Hz, 1H), 3.43 (dt, J=13.1, 4.8 Hz), 3.01 (dt, J=13.1, 4.7 Hz, 1H), 2.95–2.88 (m, 1H), 2.01–1.93 (m, 2H), 1.92–1.83 (m, 2H), 1.82–1.69 (m, 3H), 1.37–0.98 (m, 6H), 0.93 (s, 9H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ=194.5, 134.9 ($|^2J_{P,C}+{}^4J_{P,C}|$=11.2 Hz), 131.3 (J=2.7 Hz), 130.9 ($|^1J_{P,C}+{}^3J_{P,C}|$=52.9 Hz), 128.5 ($|^3J_{P,C}+{}^5J_{P,C}|$=11.0 Hz), 67.8, 67.2, 45.9, 45.3, 42.2, 39.9, 29.8, 29.7, 29.1, 28.9, 28.0, 24.0, 23.8; ^{31}P NMR (162 Hz, CD_2Cl_2): δ=27.5; IR (KBr): $\tilde{\nu}$=3054, 2952, 2865, 1587, 1573, 1483, 1450, 1436, 1394, 1365, 1354, 1325, 1307, 1251, 1236, 1191, 1162, 1095, 1064, 1028, 999, 967, 911, 842, 749, 695, 662, 641, 616, 533, 513, 494; MS (ESI-pos) m/z: 695.25 [M^+-Cl]; elemental analysis calcd (%) for C 60.70, H 7.02, N 3.83; found: C 60.45, H 7.12, N 3.69.

Compound 16a (X = Cl): pale yellow solid (278 mg, 62 %). In solution, this product exists as an equilibrium mixture of the cationic form, the neutral form, and PPh_3 (neutral/cationic/PPh_3 0.37:1:0.34). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.80–7.68 (m, 15H), 7.59–7.47 (m, 24H), 7.45–7.47 (m, 6H), 7.32–7.27 (m, 15H), 3.51 (s, 6H), 3.33 (s, 6H), 2.96–2.91 (m, 2H), 2.49 (ddd, J = 12.7, 7.8, 4.8 Hz, 2H), 2.31 (t, J = 6.0 Hz, 4H), 1.68–1.65 (m, 1H), 1.31–1.24 (m, 1H), 0.93 (quint., J = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 187.4 (C), 186.0 (C), 137.2 (C, PPh_3), 134.5 (d, J(C,P) = 11.4 Hz, CH), 134.4 (t, J(C,P) = 6.4 Hz, CH), 133.7 (d, J(C,P) = 19.6 Hz, CH, PPh_3), 131.9 (CH), 131.3 (d, J(C,P) = 2.6 Hz, CH), 130.6 (d, J(C,P) = 52.4 Hz, C), 129.4 (d, J(C,P) = 25.1 Hz, C), 129.1 (t, J(C,P) = 5.2 Hz, CH), 128.8 (CH, PPh_3), 128.51 (d, J(C,P) = 6.3 Hz, CH, PPh_3), 128.47 (d, J(C,P) = 11.1 Hz, CH), 46.5 (CH_2), 46.2 (CH_3), 45.93 (CH_2), 45.90 (CH_3), 19.5 (CH_2), 18.1 (CH_2); ^{31}P NMR (162 MHz, CD_2Cl_2); δ = 26.5 (neutral), 22.2 (cationic), −4.6 (PPh_3); IR (KBr): $\tilde{\nu}$ = 3049, 2916, 2850, 1697, 1629, 1575, 1522, 1629, 1575, 1522, 1493, 1480, 1434, 1402, 1359, 1318, 1240, 1217, 1185, 1159, 1094, 1025, 998, 856, 748, 695, 619, 599, 521, 495 cm^{-1}; MS (ESI-pos., CH_2Cl_2): m/z: 777.2 (cationic complex, [M^+−Cl]); elemental analysis calcd (%) for the cationic complex: C 61.97, H 5.20, N 3.44; found C 62.10, H 5.12, N 3.38.

Compound 22: colorless solid (124 mg, 40 %). In solution, this product exists as an equilibrium mixture of the cationic form, the neutral form, and PPh_3 (neutral/cationic/PPh_3 0.64:1:0.86). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.73–7.66 (m, 15H), 7.59–7.47 (m, 24H), 7.46–7.40 (m, 6H), 7.32–7.27 (m, 15H), 3.45 (s, 6H), 3.00 (s, 6H), 2.73 (s, 6H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 201.3 (C), 201.2 (C), 137.5 (d, J(C,P) = 20.1 Hz, C, PPh_3), 134.6 (d, J(C,P) = 11.1 Hz, CH), 134.4 (t, J(C,P) = 6.3 Hz, CH), 133.7 (d, J(C,P) = 19.6 Hz, CH, PPh_3), 131.9 (s, CH), 131.3 (d, J(C,P) = 2.2 Hz, CH), 130.9 (d, J(C,P) = 51.3 Hz, C), 129.6 (d, J(C,P) = 25.6 Hz, C), 129.3 (t, J(C,P) = 5.3 Hz, CH), 128.8 (CH, PPh_3), 128.6 (d, J(C,P) = 11.2 Hz, CH), 128.5 (CH, PPh_3), 47.1 (CH_3), 43.3 (CH_3); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 27.5 (neutral), 22.8 (cationic), −4.6 (PPh_3); IR (KBr): ν = 3050, 2955, 2916, 2849, 2674, 1617, 1563, 1480, 1434, 1404, 1382, 1309, 1265, 1185, 1158, 1094, 1052, 1026, 997, 917, 868, 747, 694, 612, 521, 495 cm^{-1}; MS (ESI-pos.): m/z: 505.0 (neutral complex, [M^+−Cl]), 767.2 (cationic complex, [M^+−Cl]; elemental analysis calcd (%) for the neutral complex: C 51.18, H 5.04, N 5.19; found: C 51.08, H 5.11, N 5.08.

Compound 27a (X = O): clorless solid (190 mg, 35 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.50–7.46 (m, 3H), 7.40–7.20 (m, 17H), 3.80 (s, 3H), 3.01 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 204.8 (d, J = 6.2 Hz, C), 154.1 (C), 134.3 (d, J(C,P) = 11.2 Hz, CH), 131.4 (d, J(C,P) = 2.7 Hz, CH), 129.6 (CH), 128.5 (d, J(C,P) = 11.2 Hz, CH), 126.9 (C), 122.2 (CH), 115.7 (CH), 44.7 (CH_3), 38.7 (CH_3); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 26.17; IR (KBr): $\tilde{\nu}$ = 3052, 2984, 2923, 1622, 1599, 1577, 1483, 1455, 1435, 1412, 1355, 1310, 1275, 1246, 1187, 1147, 1096, 1071, 1026, 999, 820, 759, 693, 609, 534, 510, 498 cm^{-1}; MS (ESI-pos.): m/z: 552.1 [M^+−Cl]; elemental analysis calcd (%) for: C 55.08, H 4.45, N 2.38, found: C 54.95, H 4.49, N 2.43.

Compound 27b (X = S): colorless solid (166 mg, 64 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.95–7.93 (m, 2H), 7.65–7.60 (m, 3H), 7.49–7.43 (m, 7H), 7.35–7.27 (m, 19H), 3.94 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 228.7 (C), 136.0 (CH), 134.5 (C), 132.1 (CH), 131.3 (d, J(C,P) = 2.6 Hz, CH), 130.8 (CH), 129.7 (CH), 129.2 (CH), 128.4 (d, J(C,P) = 11.1 Hz, CH), 44.7 (CH_3); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 25.9; IR (KBr): $\tilde{\nu}$ = 3142, 3052, 2962, 2919, 2854, 2673, 1667, 1585, 1572, 1545, 1480, 1435, 1403, 1310, 1263, 1228, 1186, 1157, 1117, 1094, 1070, 1026, 998, 923, 900, 857, 803, 746, 721, 693, 617, 557, 533, 512, 495 cm^{-1}; MS (ESI-pos.): m/z: 832.1 [M^+−Cl], 570.0 [M^+−Cl−PPh_3]; elemental analysis calcd (%) for: C 62.33, H 4.77, N 1.62; found: C 62.26, H 4.83, N 1.65.

Complex 32: yellow solid (124 mg, 56 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.50–7.34 (m, 15H), 6.67–6.58 (m, 4H), 6.16 (hept., J = 6.6 Hz, 1H), 4.07 (hept., J = 7.0 Hz, 1H), 3.81 (s, 3H), 1.86 (d, J = 6.6 Hz, 3H), 1.44 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 232.4 (d, J = 8.2 Hz, C), 160.4 (C), 134.8 (d, J(C,P) = 11.2 Hz, CH), 133.9 (d, J = 2.9 Hz, C), 131.04 (d, J(C,P) = 52.5 Hz, C), 131.03 (d, J(C,P) = 2.5 Hz, CH), 128.4 (d, J(C,P) = 10.9 Hz, CH), 126.9 (CH), 112.7 (CH), 69.6 (CH_3), 55.8 (CH), 55.5 (CH), 20.8 (CH_3), 20.6 (CH_3); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 26.1; IR (KBr): $\tilde{\nu}$ = 3053, 2973, 2934, 2875, 2836, 1601, 1563, 1502, 1481, 1454, 1435, 1390, 1373, 1308, 1291, 1253, 1220, 1177, 1163, 1142, 1096, 1072, 1026, 1000, 838, 782, 747, 730, 693, 629, 595, 530, 510, 496, 456 cm^{-1}; MS (ESI-pos.): m/z: 624.1 [M^+−Cl], 586.1 [M^+−2 Cl], 218.2 [M^+−2Cl−PPh_3−Pd]; elemental analysis calcd (%) for: C 58.33, H 5.51, N 2.13; found: C 58.24, H 5.59, N 2.16.

Compound 34: pale yellow solid (116 mg, 50 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.50–7.26 (m, 15H), 6.71–6.70 (m, 4H), 5.52–5.45 (m, 1H), 4.06–3.99 (m, 1H), 3.81 (s, 3H), 3.10–3.04 (m, 1H), 2.54–2.48 (m, 1H), 1.92–1.85 (m, 2H), 1.68–1.50 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 226.4 (d, J(C,P) = 6.6 Hz, C), 161.1 (C), 134.6 (d, J(C,P) = 11.4 Hz, CH), 133.7 (d, J = 19.7 Hz, C), 131.1 (d, J(C,P) = 2.7 Hz, CH), 130.5 (d, J(C,P) = 52.5 Hz, C), 129.0 (CH), 128.4 (d, J(C,P) = 10.9 Hz, CH), 113.4 (CH), 63.7 (CH_2), 55.6 (CH_3), 55.1 (CH_2), 26.6 (CH_2), 25.7 (CH_2), 23.7 (CH_2); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 26.0; IR (KBr): $\tilde{\nu}$ = 3053, 2942, 2861, 2677, 1600, 1570, 1505, 1481, 1435, 1352, 1300, 1278, 1256, 1234, 1176, 1136, 1096, 1072, 1026, 999, 951, 858, 836, 804, 777, 746, 694, 606, 568, 532, 511, 498 cm^{-1}; MS (ESI-pos.): m/z: 868.2 [M^+−Cl], 608.1 [M^+−Cl−PPh_3]; elemental analysis calcd (%) for: C 57.92, H 5.02, N 2.18; found: C 57.84, H 5.10, N 2.21.

Representative procedure for the formation of nickel complexes by oxidative addition—Compound 37: [Ni(cod)$_2$] (99 mg, 0.36 mmol) was added to a solution of PPh_3 (189 mg, 0.72 mmol) in anhydrous THF (10 mL) and the dark red mixture was stirred for 15 min under argon. The imidazolium salt **1a** (100 mg, 0.36 mmol) was then introduced and the resulting brown-yellow suspension was stirred for 3 h at ambient temperature causing the precipitation of a yellow solid. This precipitate was allowed to settle, the supernatant solution was siphoned off, and the solid was dried in vacuo to give product **37** as a yellow solid (267 mg, 86 %). Crystals suitable for X-ray structure analysis were formed by slowly diffusing pentane into a CH_2Cl_2 solution of the complex. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.75–7.71 (m, 12H), 7.61–7.50 (m, 18H), 3.13 (s, 6H), 2.49 (s, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 197.1 (C), 134.3 (t, J(C,P) = 5.6 Hz, CH), 131.9 (CH), 129.1 (d, J(C,P) = 48.2 Hz, C), 129.0 (d, J(C,P) = 5.5 Hz, CH), 51.0 (CH_2), 36.8 (CH_3); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 21.6, −143.9 (hept., J(P,F) = 710.6 Hz); IR (KBr): $\tilde{\nu}$ = 3057, 2957, 2924, 2884, 1646, 1587, 1572, 1543, 1516, 1482, 1435, 1402, 1323, 1287, 1208, 1190, 1095, 1028, 999, 838, 745, 695, 620, 558, 524, 513, 494 cm^{-1}; MS (ESI-pos.): m/z: 453.0 [M^+−PF_6−PPh_3]; elemental analysis calcd (%) for: 57.14, H 4.68, N 3.25; found: C 56.98, H 4.78, N 3.21.

The following complexes were analogously prepared:

Complex 38: yellow solid (223 mg, 62 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.73–7.72 (m, 12H), 7.59–7.52 (m, 18H), 3.13 (s, 6H), 2.50 (s, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 197.0 (C), 134.3 (t, J(C,P) = 5.1 Hz, CH), 131.9 (CH), 129.1 (d, J(C,P) = 48.3 Hz, C), 129.0 (J(C,P) = 5.1 Hz, CH), 51.0 (CH_2), 36.8 (CH_3); ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 21.8; IR (KBr): $\tilde{\nu}$ = 3053, 2951, 2869, 2678, 1670, 1585, 1571, 1543, 1517, 1481, 1436, 1400, 1323, 1287, 1207, 1184, 1163, 1092, 1055, 998, 901, 805, 751, 698, 621, 522, 494 cm^{-1}; MS (ESI-pos.): m/z: 715.2 [M^+−BF_4], 453.1 [M^+−BF_4−PPh_3]; elemental analysis calcd (%) for: C 61.27, H 5.02, N 3.49; found: C 61.20, H 5.12, N 3.41.

Complex 39: yellow solid (160 mg, 77 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 3.66 (t, J = 1.3 Hz, 4H), 3.52 (s, 6H), 1.70–1.62 (m, 12H), 1.21 (quint., J = 7.9 Hz, 18H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 198.3 (J(C,P) = 31.3 Hz, C), 51.6 (CH_2), 37.4 (CH_3), 15.0 (J(C,P) = 13.9 Hz, CH_3), 8.4 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 17.4, −143.9 (hept., J(P,F) = 710.6 Hz); IR (KBr): ν = 2971, 2942, 2882, 2801, 1537, 1517, 1483, 1458, 1435, 1407, 1380, 1325, 1292, 1260, 1210, 1101, 1038, 1014, 929, 876, 839, 756, 739, 725, 701, 631, 557 cm^{-1}; MS (ESI-pos.): m/z: 427.2 [M^+-PF_6], 309.1 [M^+-PF_6-PEt_3]; elemental analysis calcd (%) for: C 35.60, H 7.03, N 4.88; found: C 35.84, H 6.89, N 4.81.

Compound 40: yellow solid (193 mg, 41 %); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.68–7.32 (m, 30H), 4.82 (m, 3H), 3.57 (m, 2H), 2.10 (m, 3H), 1.53–1.16 (m, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 196.2 (C), 134.4 (CH), 131.7 (CH), 129.1 (t, J(C,P) = 4.8 Hz, CH), 128.6 (C), 57.0 (CH_2), 25.2 (CH_2), 23.3 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 21.8,

−143.8 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3057, 2944, 2860, 1639, 1585, 1535, 1481, 1436, 1409, 1346, 1322, 1283, 1260, 1244, 1187, 1162, 1129, 1093, 1068, 1023, 999, 877, 839, 793, 748, 701, 610, 557, 520, 496 cm^{-1}; MS (ESI-pos.): m/z: 535.2 [M^+−PF_6−PPh_3]; elemental analysis calcd (%) for: C 59.80, H 5.34, N 2.97; found: C 59.88, H 5.26, N 3.06.

Compound 41: yellow solid (135 mg, 50%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.69–7.50 (m, 30H), 4.47 (m, 4H), 2.76 (m, 4H), 1.43–1.35 (m, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 191.5 (C), 134.4 (CH), 131.8 (CH), 129.5 (C), 129.1 (t, J(C,P) = 4.9 Hz, CH), 56.8 (CH_2), 51.4 (CH_2), 25.7 (CH_2), 24.0 (CH_2); ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 18.6, −143.9 (hept., J(P,F) = 711 Hz); IR (KBr): $\tilde{\nu}$ = 3058, 2975, 2949, 2876, 1684, 1586, 1573, 1521, 1482, 1436, 1374, 1321, 1295, 1267, 1232, 1187, 1161, 1092, 1073, 1028, 999, 920, 839, 747, 698, 617, 558, 518, 494 cm^{-1}; MS (ESI-pos.): m/z: 769.1 [M^+−PF_6], 507.2 [M^+−PF_6−PPh_3]; elemental analysis calcd (%) for: C 59.01, H 5.06, N 3.06; found: C 58.96, H 5.07, N 3.11.

Compound 42: yellow solid (203 mg, 64%); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.73–7.51 (m, 30H), 4.02 (s, 6H), 1.96 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 199.9 (C), 134.3 (CH), 131.8 (CH), 129.6 (C), 129.2 (t, J(C,P) = 4.9 Hz, CH), 47.7 (CH_3), 42.0 (CH_3). ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 19.9, −143.9 (hept., J(P,F) = 710.6 Hz); IR (KBr): $\tilde{\nu}$ = 3058, 2965, 2869, 1556, 1481, 1470, 1436, 1406, 1388, 1380, 1315, 1270, 1188, 1154, 1093, 1064, 1028, 1000, 837, 747, 697, 619, 558, 522, 493 cm^{-1}; MS (ESI-pos.): m/z: 717.1 [M^+−PF_6], 455.1 [M^+−PF_6−PPh_3]; elemental analysis calcd (%) for: C 57.01, H 4.90, N 3.24; found: C 57.11, H 5.01, N 3.21.

Representative procedure for the Heck reaction: A mixture of the aryl halide (1.5 mmol, 1 equiv), butyl acrylate (1.65 mmol, 1.1 equiv), the Pd complex (1 mol%) and Cs_2CO_3 (3 mmol, 2 equiv) in NMP (1 mL) was stirred for 16 h at 120°C under argon. After cooling, the mixture was diluted with water, the aqueous phase was repeatedly extracted with CH_2Cl_2, the combined organic layers were dried (Na_2SO_4), the solvent was evaporated and the residue was purified by flash chromatography to give butyl cinnamate, the analytical and spectroscopic data of which were identical to those of an authentic sample.

Representative procedure for the Suzuki reaction: A mixture of phenylboronic acid (1.1 mmol, 1 equiv), 4-haloacetophenone (0.9 mmol, 1 equiv), the Pd-complex (1 mol%) and K_2CO_3 (2.5 mmol, 2.8 equiv) in THF (15 mL) was refluxed for 16 h under argon. After cooling, the mixture was diluted with water, the aqueous phase was repeatedly extracted with ethyl acetate, the combined organic layers were dried (Na_2SO_4), the solvent was evaporated and the residue was purified by flash chromatography (hexane/ethyl acetate 30:1) to give 4-phenyl-acetophenone, the analytical and spectroscopic data of which were identical to those of an authentic sample.[58]

Representative procedure for the Kumada reaction: A suspension of the aryl halide (0.5 mmol, 1 equiv) and the nickel complex (3 mol%) in THF (0.5 mL) was stirred for 5 min at ambient temperature. After dropwise addition of Grignard reagent (0.75 mmol, 1.5 equiv) the reaction mixture was stirred for 18 h at RT under argon. The reaction was quenched with MeOH, the mixture was diluted with water, the aqueous phase was repeatedly extracted with ethyl acetate, the combined organic layers were dried (Na_2SO_4), the solvent was evaporated and the residue was purified by flash chromatography.

2-(4-Methoxyphenyl)-pyridine (48): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66–8.64 (m, 1H), 7.96–7.93 (m, 2H), 7.72–7.64 (m, 2H), 7.18–7.15 (m, 1H), 7.01–6.98 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8 (C), 157.4 (C), 149.7 (CH), 137.1 (CH), 132.2 (C), 128.5 (CH), 121.7 (CH), 120.2 (CH), 116.5 (CH), 115.0 (CH), 114.5 (CH), 55.6 (CH_3); IR (KBr): $\tilde{\nu}$ = 3051, 2998, 2960, 2937, 2836, 1608, 1588, 1563, 1515, 1465, 1435, 1307, 1272, 1248, 1178, 1152, 1112, 1037, 1023, 988, 839, 806, 780, 737, 718, 638, 580, 556, 487 cm^{-1}; MS (EI): m/z (%): 185 (100) [M^+], 170 (29), 154 (4), 142 (36), 141 (18), 127 (2), 115 (7), 89 (5), 78 (3), 63 (5), 51 (4), 39 (3); HRMS: calcd for $C_{12}H_{11}NO$: 185.0841, found: 185.0840.

Representative procedure for the Hartwig–Buchwald reaction: A mixture of the aryl halide (1 mmol, 1 equiv), morpholine (1.2 mmol, 1.2 equiv), the Pd complex (1 mol%) and NaO*t*Bu (2 mmol, 2 equiv) in DME (1 mL) was stirred for 5 h at ambient temperature or 70°C under argon. The reaction was monitored by GC and after complete consumption of aryl halide the mixture was adsorbed onto silica gel and purified by flash chromatography.

Compound 52: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.19 (m, 1H), 7.51–7.47 (m, 1H), 6.67–6.62 (m, 2H), 3.82 (t, J = 4.8 Hz, 4H), 3.49 (t, J = 4.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9 (C), 148.2 (CH), 137.9 (CH), 114.1 (CH), 107.3 (CH), 67.1 (CH_2), 46.0 (CH_2); IR (KAP): $\tilde{\nu}$ = 3051, 3004, 2962, 2892, 2852, 2689, 1725, 1593, 1565, 1481, 1436, 1376, 1333, 1312, 1242, 1216, 1160, 1121, 1070, 1056, 981, 943, 857, 775, 733, 645, 620, 532, 456 cm^{-1}; MS (EI): m/z (%): 164 (69) [M^+], 163 (42), 134 (13), 133 (67), 119 (25), 107 (47), 106 (16), 86 (10), 80 (10), 79 (100), 78 (30), 67 (10), 52 (11), 51 (15); HRMS: calcd for $C_9H_{12}N_2O$: 164.0950, found: 164.0950.

Crystallographic data

Complex *trans*-2a: Empirical formula $C_{42}H_{41}Cl_4F_6N_2P_3Pd$, colorless, M_r = 1028.88, crystal size = 0.20 × 0.17 × 0.16 mm, monoclinic, space group $P2_1/c$, a = 11.98900(10), b = 23.8189(2), c = 15.80730(10) Å, β = 102.85°, V = 4400.96(6) Å^3, Z = 4, ρ_{calcd} = 1.553 Mg m^{-3}, μ = 0.832 mm^{-1}, θ range for data collection = 2.12 to 32.56°, 110920 reflections, 15970 independent reflections, 14349 observed reflections [$I > 2\sigma(I)$], 523 parameters, S = 1.291, R_1 = 0.0374 (observed data), wR^2 = 0.1586 (all data), largest diff. peak/hole = 1.061/−3.049 e Å^{-3}; CCDC-249509.

Thiourea 5: Empirical formula $C_{12}H_{14}N_2S$, colorless, M_r = 218.31, crystal size = 0.18 × 0.13 × 0.10 mm, monoclinic, space group $P2_1$, a = 5.30140(10), b = 12.9538(3), c = 8.2297(2) Å, β = 107.7120(10)°, V = 538.37(2) Å^3, Z = 2, ρ_{calcd} = 1.347 Mg m^{-3}, μ = 0.267 mm^{-1}, θ range for data collection = 2.60 to 30.97°, 14969 reflections, 3421 independent, 3224 observed reflections [$I > 2\sigma(I)$], 192 parameters, S = 1.036, R_1 = 0.0286 (observed data), wR^2 = 0.0717 (all data), largest diff. peak/hole = 0.261/−0.157 e Å^3; CCDC-249510.

Complex 9a: Empirical formula $C_{49}H_{46}Cl_4N_2P_2Pd$, colorless, M_r = 973.02, crystal size = 0.15 × 0.10 × 0.06 mm, orthorhombic, space group $P2_12_12_1$, a = 14.99730(10), b = 15.29630(10), c = 19.02290(10) Å, V = 4363.91(5) Å^3, Z = 4, ρ_{calcd} = 1.481 Mg m^{-3}, μ = 0.781 mm^{-1}, θ range for data collection = 2.92 to 31.50°, 63808 reflections, 14486 independent reflections, 12438 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 523 parameters, S = 1.012, R_1 = 0.0366 (observed data), wR^2 = 0.0769 (all data), absolute structure parameter = −0.016(16), largest diff. peak/hole = 1.375/−0.785 e Å^{-3}; CCDC-249514.

Complex 9b: Empirical formula $C_{49}H_{46}Cl_3F_6N_2P_3Pd$, colorless, M_r = 1082.54, crystal size = 0.28 × 0.20 × 0.05 mm, orthorhombic, space group $P2_12_12_1$, a = 14.80630(10), b = 16.43080(10), c = 19.2805(2) Å, V = 4690.55(6) Å^3, Z = 4, ρ_{calcd} = 1.533 Mg m^{-3}, μ = 0.730 mm^{-1}, θ range for data collection = 4.11 to 31.07°, 70574 reflections, 14999 independent reflections, 14084 observed reflections [$I > 2\sigma(I)$], Gaussian absorption correction ($T_{min/max}$ = 0.82/0.96), 577 parameter, S = 1.015, R_1 = 0.0295 (observed data), wR^2 = 0.0683 (all data), absolute structure parameter = −0.016(11), largest diff. peak/hole = 0.468/−0.413 e Å^{-3}; CCDC-249513.

Complex 11: Empirical formula $C_{37}H_{51}Cl_2N_2PPd$, colorless, M_r = 732.07, crystal size = 0.15 × 0.12 × 0.05 mm, orthorhombic, space group $P2_12_12_1$, a = 10.92080(10), b = 14.09380(10), c = 24.0674(3) Å, V = 3704.35(6) Å^3, Z = 4, ρ_{calcd} = 1.313 Mg m^{-3}, μ = 0.715 mm^{-1}, θ range for data collection = 2.92 to 30.99°, 50077 reflections, 11796 independent reflections, 10146 observed reflections [$I > 2\sigma(I)$], Gaussian absorption correction ($T_{min/max}$ = 0.91/0.96), 388 parameters, S = 0.847, R_1 = 0.0406 (observed data), wR^2 = 0.1200 (all data), largest diff. peak/hole = 0.554/−0.471 e Å^{-3}; CCDC-249517.

Complex 12: Empirical formula $C_{53}H_{48}ClF_6N_2P_3Pd \times 2CH_2Cl_2$, colorless, M_r = 1231.55, crystal size = 0.20 × 0.13 × 0.06 mm, triclinic, space group $P\bar{1}$, a = 11.78560(10), b = 12.0961(2), c = 12.2016(2) Å, α = 92.1710(10), β = 116.9250(10), γ = 114.2700(10)°, V = 1359.07(3) Å^3, Z = 1, ρ_{calcd} = 1.505 Mg m^{-3}, μ = 0.735 mm^{-1}, θ range for data collection = 3.09 to 33.21°, 34742 reflections, 18690 independent reflections, 16740 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 649 parameters, S = 0.929, R_1 = 0.0492 (observed data), wR^2 = 0.1474 (all data), absolute structure parameter = −0.014(18), largest diff. peak/hole = 1.257/−1.079 e Å^{-3}; CCDC-249523.

Complex 13: Empirical formula $C_{35}H_{33}Cl_2N_2PPd$, pale yellow, M_r = 689.90, crystal size = 0.08 × 0.08 × 0.06 mm, orthorhombic, space group $P2_12_12_1$, a = 10.58720(10), b = 16.3433(2), c = 18.2229(2) Å, V = 3153.10(6) Å^3, Z = 4, ρ_{calcd} = 1.453 Mg m^{-3}, μ = 0.836 mm^{-1}, θ range for data collection = 2.95 to 33.15°, 58136 reflections, 11978 independent reflections, 9814 observed reflections [$I > 2\sigma(I)$], Gaussian absorption correction ($T_{min/max}$ = 0.94/0.96), 372 parameters, S = 1.001, R_1 = 0.0404 (observed data), wR^2 = 0.0726 (all data), absolute structure parameter = −0.021(17), largest diff. peak/hole = 0.462/−0.592 e Å^{-3}; CCDC-249512.

Complex 16a: Empirical formula $C_{43}H_{48}Cl_4N_2O_2P_2Pd$, colorless, M_r = 934.97, crystal size = 0.22 × 0.16 × 0.12 mm, hexagonal, space group $P6_3/m$, a = 22.24080(10), b = 22.24080(10), c = 14.698 Å, V = 6296.45(4) Å^3, Z = 6, ρ_{calcd} = 1.479 Mg m^{-3}, μ = 0.812 mm^{-1}, θ range for data collection = 4.21 to 32.03°, 130892 reflections, 7538 independent reflections, 6382 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 278 parameters, S = 1.099, R_1 = 0.0318 (observed data) = wR^2 = 0.0886 (all data), largest diff. peak/hole = 1.623/−1.092 e Å^{-3}; CCDC-249520.

Complex 16b: Empirical formula $C_{43}H_{44}Cl_3F_6N_2P_3Pd$, pale yellow, M_r = 1008.46, crystal size = 0.46 × 0.14 × 0.14 mm, monoclinic, space group $P2_1/m$, a = 9.57680(10), b = 22.7126(2), c = 19.9983(2) Å, β = 93.62°, V = 4341.22(7) Å^3, Z = 4, ρ_{calcd} = 1.543 Mg m^{-3}, μ = 0.783 mm^{-1}, θ range for data collection = 3.73 to 30.53°, 61540 reflections, 13550 independent reflections, 12027 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 649 parameters, S = 1.144, R_1 = 0.0471 (observed data), wR^2 = 0.1144 (all data), largest diff. peak/hole = 1.344/−1.041 e Å^{-3}; CCDC-249521.

Complex 19: Empirical formula $C_{48}H_{52}ClF_6N_2P_3Pd_3$, colorless, M_r = 1218.48, crystal size = 0.25 × 0.10 × 0.05 mm, monoclinic, space group $P2_1/n$, a = 16.00390(10), b = 11.25450(10), c = 26.6487(2) Å, β = 92.96°, V = 4793.43(6) Å^3, Z = 4, ρ_{calcd} = 1.688 Mg m^{-3}, μ = 1.329 mm^{-1}, θ range for data collection = 4.16 to 30.57°, 98616 reflections, 14635 independent reflections, 12245 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 565 parameters, S = 1.085, R_1 = 0.0633 (observed data), wR^2 = 0.1612 (all data), largest diff. peak/hole = 2.535/−1.599 e Å^{-3}; CCDC-249515.

Complex 22: Empirical formula $C_{24}H_{29}Cl_4N_2PPd$, colorless, M_r = 624.66, crystal size = 0.20 × 0.17 × 0.10 mm, triclinic, space group $P\bar{1}$, a = 10.83190(10), b = 10.86860(10), c = 11.44660(10 Å, α = 100.76, β = 91.15, γ = 90.98°, V = 1323.30(2) Å^3, Z = 2, ρ_{calcd} = 1.568 Mg m^{-3}, μ = 1.181 mm^{-1}, θ range for data collection = 4.12 to 33.17°, 42141 reflections, 10085 independent reflections, 9236 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 293 parameters, S = 0.994, R_1 = 0.0258 (observed data), wR^2 = 0.0740 (all data), largest diff. peak/hole = 1.693/−1.450 e Å^{-3}; CCDC-249519.

Complex 23: Empirical formula $C_{41}H_{42}ClN_2P_3F_6Pd\cdot 2CH_2Cl_2$, colorless, M_r = 1081.38, crystal size = 0.19 × 0.17 × 0.02 mm, monoclinic, space group $P2_1/c$, a = 11.5234(2), b = 27.8267(6), c = 15.3671(3) Å, β = 110.2350(10)°, V = 4623.46(16) Å^3, Z = 4, ρ_{calcd} = 1.554 Mg m^{-3}, μ = 0.852 mm^{-1}, θ range for data collection = 4.12 to 30.45°, 15643 reflections, 11335 independent reflections, 7624 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 541 parameters, S = 1.084, R_1 = 0.0726 (observed data), wR^2 = 0.1571 (all data), largest diff. peak/hole = 1.404/−1.002 e Å^{-3}; CCDC-249518.

Complex 27a: Empirical formula $C_{27}H_{26}Cl_2NOPPd$, colorless, M_r = 588.76, crystal size = 0.33 × 0.22 × 0.07 mm, monoclinic, space group $P2_1/n$, a = 9.6858(1), b = 16.8205(1), c = 15.2823(1) Å, β = 91.30°, V = 2489.15(3) Å^3, Z = 4, ρ_{calcd} = 1.571 Mg m^{-3}, μ = 1.045 mm^{-1}, θ range for data collection = 3.21 to 31.51°, 65806 reflections, 8279 independent reflections, 7930 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 300 parameters, S = 1.088, R_1 = 0.0200 (observed data), wR^2 = 0.0493 (all data), largest diff. peak/hole = 0.629/−0.684 e Å^{-3}; CCDC-249532.

Complex 27b: Empirical formula $C_{28}H_{28}Cl_4NPPdS$, colorless, M_r = 689.74, crystal size = 0.06 × 0.03 × 0.02 mm, triclinic, space group $P\bar{1}$, a = 9.5008(3), b = 13.3533(5), c = 14.6947(6) Å, α = 65.3260(10), β = 83.911(2), γ = 69.611(2)°, V = 1586.23(10) Å^3, Z = 2, ρ_{calcd} = 1.444 Mg m^{-3}, μ = 1.056 mm^{-1}, θ range for data collection = 2.29 to 25.00°, 22092 reflections, 5575 independent reflections, 4803 observed reflections [$I > 2\sigma(I)$], 348 parameters, S = 1.066, R_1 = 0.0433 (observed data), wR^2 = 0.1285 (all data), largest diff. peak/hole = 1.607/−0.998 e Å^{-3}; CCDC-249530.

Complex 28b: Empirical formula $C_{46}H_{43}Cl_3F_6NP_3PdS$, colorless, M_r = 1061.53, crystal size = 0.06 × 0.04 × 0.04 mm, monoclinic, space group $P2_1/c$, a = 19.2454(4), b = 13.9966(3), c = 17.0816(2) Å, β = 97.2090(10)°, V = 4564.90(15) Å^3, Z = 4, ρ_{calcd} = 1.545 Mg m^{-3}, μ = 0.792 mm^{-1}, θ range for data collection = 2.91 to 30.98°, 77600 reflections, 14509 independent reflections, 10033 observed reflections [$I > 2\sigma(I)$], Gaussian absorption correction ($T_{min/max}$ = 0.96/0.98), 552 parameters, S = 1.000, R_1 = 0.0491 (observed data), wR^2 = 0.1053 (all data), largest diff. peak/hole = 1.338/−1.368 e Å^{-3}; CCDC-249531.

Complex 32: Empirical formula $C_{32}H_{36}Cl_2NOPPd$, pale yellow, M_r = 658.89, crystal size = 0.24 × 0.24 × 0.08 mm, monoclinic, space group $P2_1/n$, a = 10.49190(10), b = 17.3034(2), c = 16.0856(2) Å, β = 94.22°, V = 2912.36(6) Å^3, Z = 4, ρ_{calcd} = 1.503 Mg m^{-3}, μ = 0.902 mm^{-1}, θ range for data collection = 3.06 to 30.99°, 49601 reflections, 9247 independent reflections, 8441 observed reflections [$I > 2\sigma(I)$], gaussian absorption correction ($T_{min/max}$ = 0.88/0.95), 487 parameters, S = 1.006, R_1 = 0.0234 (observed data), wR^2 = 0.0585 (all data), largest diff. peak/hole = 0.459/−0.599 e Å^{-3}; CCDC-249526.

Complex 33: Empirical formula $C_{51}H_{53}Cl_3F_6NOP_3Pd$, yellow, M_r = 1115.60, crystal size = 0.25 × 0.19 × 0.07 mm, triclinic, space group $P\bar{1}$, a = 10.95160(10), b = 14.63970(10), c = 16.5360(2) Å, α = 84.09, β = 87.9010(10), γ = 71.4710(10)°, V = 2500.36(4) Å^3, Z = 2, ρ_{calcd} = 1.482 Mg m^{-3}, μ = 0.688 mm^{-1}, θ range for data collection = 2.95 to 30.99°, 60449 reflections, 15859 independent reflections, 14246 observed reflections [$I > 2\sigma(I)$], gaussian absorption correction ($T_{min/max}$ = 0.84/0.96), 597 parameters, S = 1.060, R_1 = 0.0558 (observed data), wR^2 = 0.1616 (all data), largest diff. peak/hole = 1.120/−2.750 e Å^{-3}; CCDC-249528.

Complex 34: Empirical formula $C_{31.50}H_{32}Cl_{3.25}NOPPd$, colorless, M_r = 693.16, crystal size = 0.08 × 0.05 × 0.04 mm, orthorhombic, space group $Pbcn$, a = 21.6007(2), b = 16.6871(2), c = 16.9748(2) Å, V = 6118.62(12) Å^3, Z = 8, ρ_{calcd} = 1.505 Mg m^{-3},μ = 0.969 mm^{-1}, θ range for data collection = 3.05 to 31.50°, 90112 reflections, 10168 independent reflections, 8229 observed reflections [$I > 2\sigma(I)$], 389 parameters, S = 1.032, R_1 = 0.0384 (observed data), wR^2 = 0.1406 (all data), largest diff. peak/hole = 1.059/−1.217 e Å^{-3}; CCDC-249529.

Nickelate complex 36: Empirical formula $C_{10}H_{20}Cl_6N_4Ni$, blue, M_r = 467.71, crystal size = 0.16 × 0.15 × 0.14 mm, monoclinic, space group $P2_1/c$, a = 14.9304(2), b = 8.85360(10), c = 14.9304(2) Å, β = 103.67°, V = 1917.69(4) Å^3, Z = 4, ρ_{calcd} = 1.620 Mg m^{-3}, μ = 1.845 mm^{-1}, θ range for data collection = 6.60 to 32.94°, 26795 reflections, 6688 independent reflections, 5216 observed reflections [$I > 2\sigma(I)$], Gaussian absorption correction ($T_{min/max}$ = 0.84/0.94), 194 parameters, S = 1.116, R_1 = 0.0355 (observed data), wR^2 = 0.0660 (all data), largest diff. peak/hole = 0.523/−0.442 e Å^{-3}; CCDC-249516.

Complex 37: Empirical formula $C_{42}H_{42}Cl_3F_6N_2NiP_3$, yellow, M_r = 946.75, crystal size = 0.20 × 0.19 × 0.05 mm, triclinic, space group $P\bar{1}$, a = 12.58330(10), b = 18.08800(10), c = 20.55670(10) Å, α = 108.14, β = 96.15, γ = 100.60°, V = 4302.09(5) Å^3, Z = 4, ρ_{calcd} = 1.462 Mg m^{-3}, μ = 0.808 mm^{-1}, θ range for data collection = 4.10 to 33.11°, 135076 reflections, 32612 independent reflections, 26339 observed reflections [$I > 2\sigma(I)$], Gaussian absorption correction ($T_{min/max}$ = 0.86/0.96), 1031 parameters, S = 1.063, R_1 = 0.0488 (observed data), wR^2 = 0.1355 (all data), largest diff. peak/hole = 0.960/−0.898 e Å^{-3}; CCDC-249524.

Complex 38: Empirical formula $C_{43}H_{44}BCl_5F_4N_2NiP_2$, yellow, M_r = 973.51, crystal size = 0.22 × 0.18 × 0.08 mm, monoclinic, space group $P2_1$, a = 9.18310(10), b = 20.86120(10), c = 11.61080(10) Å, β = 91.75°, V = 2223.24(3) Å^3, Z = 2, ρ_{calcd} = 1.454 Mg m^{-3}, μ = 0.859 mm^{-1}, θ range for data collection = 2.95 to 31.03°, 57225 reflections, 14113 independent reflections, 13455 observed reflections [$I > 2\sigma(I)$], empirical absorption correction (multiscan method), 535 parameters, S = 1.004, R_1 = 0.0268 (observed data), wR^2 = 0.0655 (all data), absolute structure parameter = 0.009(5), largest diff. peak/hole = 0.539/−0.378 e Å^{-3}; CCDC-249525.

Complex 42: Empirical formula $C_{42}H_{44}Cl_3F_6N_2NiP_3$, yellow-orange, M_r = 948.76, crystal size = 0.12 × 0.09 × 0.04 mm, triclinic, space group $P\bar{1}$, a =

12.18140(10), $b=17.50240(10)$, $c=21.3701(2)$ Å, $\alpha=71.21$, $\beta=82.00$, $\gamma=89.91°$, $V=4266.78(6)$ Å^3, $Z=4$, $\rho_{calcd}=1.477$ Mg m^{-3}, $\mu=0.815$ mm^{-1}, θ range for data collection $=2.92$ to $27.50°$, 95991 reflections, 19569 independent reflections, 15204 observed reflections [$I>2\sigma(I)$], Gaussian absorption correction ($T_{min/max}=0.91/0.98$), 1037 parameters, $S=1.013$, $R_1=0.0521$ (observed data), $wR^2=0.1290$ (all data), largest diff. peak and hole $=2.198$ and -1.151 e Å^{-3}; CCDC 249527.

The CCDC data contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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