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Straightforward Synthesis of Donor-Stabilised Phosphenium Adducts from Imidazolium-2-carboxylate and Their Electronic Properties

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Cationic imidazolium-2-phosphanes were obtained by the addition of a chlorophosphane (R_2PCl, R = Ph, *i*Pr or Cy) to 1,3-dimethylimidazolium-2-carboxylate without the need for a purification step. An additional anion exchange reaction with KPF_6 led to the corresponding halide-free ligands in excellent yields. The molecular structure of one of them was examined both in the solid state and in solution. The lone pair of electrons on the phosphorus atom is not delocalised to the imidazolium fragment and thus remains available for further metal coordination. As such compounds can be described as phosphenium cations stabilised by a N-heterocarbene donor base, the electronic properties of the Lewis acceptor phosphorus centre was evaluated upon nickel tricarbonyl coordination, and the properties are surprisingly similar to those found for phosphites. The stronger π-acceptor character of these imidazolium-2-phosphanes relative to that of neutral tertiary phosphanes can thus explain the higher catalytic activities observed with the corresponding rhodium complexes in styrene hydroformylation reactions. Additionally, a preliminary study of platinum coordination chemistry indicated that the steric demand of 1,3-dimethylimidazolium-2-phosphanes is comparable to mixed arylalkylphosphanes.

Introduction

Imidazolium-functionalised phosphanes, when compared to neutral phosphane ligands, represent an interesting opportunity to decrease strongly the metal leaching in homogeneous polyphasic catalysis, especially with the use of an ionic liquid phase.[1–3] However, if the C-2 position of the imidazolium ring is unprotected, this type of cationic ligand can sometimes decrease the activity of the catalyst and/or the enantioselectivity of the reaction because of the production of zerovalent metals[4,5] induced by the formation of the corresponding chelating N-heterocarbene phosphane.[6] To overcome such a limitation, we thus focused our investigations on imidazolium-2-phosphanes. Moreover, these particular structures represent rare examples of "base donor, P acceptor complexes" involving an electron rich P^{III} centre as the Lewis acceptor.[7] It is also noteworthy that a simple change in the substituent on the nitrogen atom can easily tune their electronic and steric properties.

There are few examples of imidazolium-2-phosphanes in the literature.[8] They are obtained either by selective N alkylation of the corresponding free[9] or metal-coordinated[10] neutral imidazolyl-2-phosphane or by the addition of chlorodiphenylphosphane to isolated[11] or in situ generated imidazol-2-ylidenes from the related imidazolium salts in the presence of a strong base.[1] However, all these preparations require several steps, most of which are quite difficult due to the air-sensitive phosphorus intermediates or the use of strong alkyllithium bases. Thus, we developed a short and easy synthetic method allowing the obtention of the expected products on a large scale. Our synthetic approach is thus based on the use of 1,3-dimethylimidazolium-2-carboxylate (**1**) as a N heterocarbene source,[12] as it was reported in the preparation of N heterocarbene metal complexes[13,14] or ionic liquids,[15,16] as well as in the study of its reactivity towards several chlorophosphanes.

Results and Discussion

Synthesis and Characterisation of Imidazolium-2-phosphanes

The chlorophosphanes Ph_2PCl and iPr_2PCl react smoothly with **1** to afford pure imidazolium-2-phosphanes **2a** and **2b**, respectively (see Experimental Section) after 4 h (Scheme 1). When the more sterically hindered chloroalkylphosphane Cy_2PCl was used, complete conversion leading to cationic ligand **2c** was achieved after a longer period (ca. 8 h), which also favoured the formation of small amounts of 1,3-dimethylimidazolium chloride [MMIM]Cl as a result of the competitive hydrolysis of the chlorophosphane by trace amounts of water in the solution and the subsequent protonation–decarboxylation of **1** with HCl.[15,16] This side reaction is, however, inhibited by the addition of molecular

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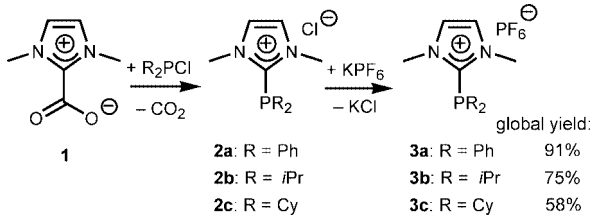
sieves. It is noteworthy that the bulky chlorodialkylphosphane tBu$_2$PCl does not react with imidazolium-2-carboxylate at room temperature even after 24 h.



Scheme 1.

An anion exchange reaction of **2a**–**c** with KPF_6 in CH_2Cl_2, which can be done in a one-pot synthesis, led to the corresponding halide free ligands **3a**–**c** in excellent yields. Compounds **3a** and **3c** could be crystallised from dichloromethane/pentane as white plates in poor quality and as a white crystalline powder, respectively, which were therefore unsuitable for crystallographic studies. However, suitable crystals for X-ray structure determination were obtained for compound **3b** (Figure 1) from the same mixture of solvents.

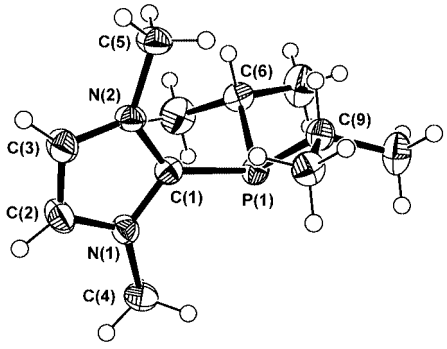


Figure 1. Molecular structure of **3b** with thermal ellipsoids presented at the 50% probability level. The PF_6^- anion is omitted for clarity.

The ORTEP view shows that the P(1)–C(1) bond length of 1.840(3) Å (Table 1) is similar to that found in the 1,3-diisopropyl-4,5-dimethylimidazolium-2-phosphane analogue (1.813 Å)[11] obtained from the reaction of Ph_2PCl and the corresponding imidazol-2-ylidene.

Table 1. Selected bond lengths [Å] and bond angles [°] for **3b**.

P(1)–C(1)	1.840(3)	P(1)–C(6)	1.859(3)
P(1)–C(9)	1.855(3)	C(1)–N(1)	1.344(4)
C(1)–N(2)	1.354(4)	C(4)–N(1)	1.476(4)
C(5)–N(2)	1.474(4)	C(2)–C(3)	1.341(5)
N(1)–C(1)–N(2)	105.6(3)	N(1)–C(1)–P(1)	121.3(2)
N(2)–C(1)–P(1)	133.0(2)	C(1)–P(1)–C(9)	102.47(15)
C(1)–P(1)–C(6)	98.96(15)	C(9)–P(1)–C(6)	105.58(16)
C(9)–P(1)–C(1)–N(2)	51.8(4)	C(6)–P(1)–C(1)–N(2)	–56.5(4)

The imidazolium heterocycle is in the bisector plan of the C(9)–P(1)–C(6) angle [dihedral angles C(6,9)–P(1)–C(1)–N(2), Table 1], analogously to the structure of the above-mentioned cationic compound, possibly because of the strong steric hindrance of the methyl groups in the solid state. In $CDCl_3$ solution, we observed two different signals for the C(6,9)–CH_3 methyl groups. To obtain more information, an additional 1D-NMR NOE experiment was recorded at 298 K. Figure 2 shows a strong Overhauser effect of 2.5% between the irradiated N–Me groups and the C(6,9)H protons. This effect decreases from 1 to <0.2% for the C(6,9)Me$_{endo}$ and C(6,9)Me$_{exo}$ methyl groups, respectively. Such a difference in the Overhauser effect observed for the latter fragments proves that the spatial organisation of the isopropyl groups observed in the solid state is maintained in solution. However, the unique signals obtained at

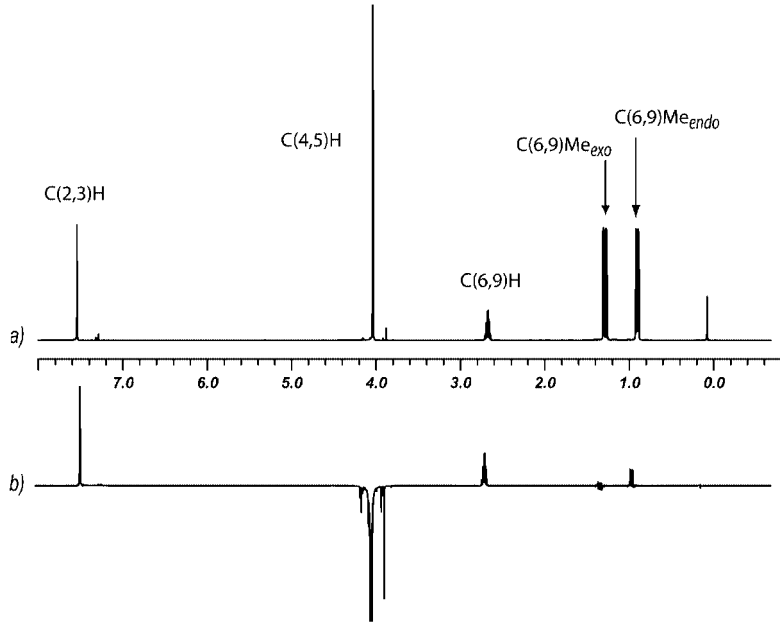
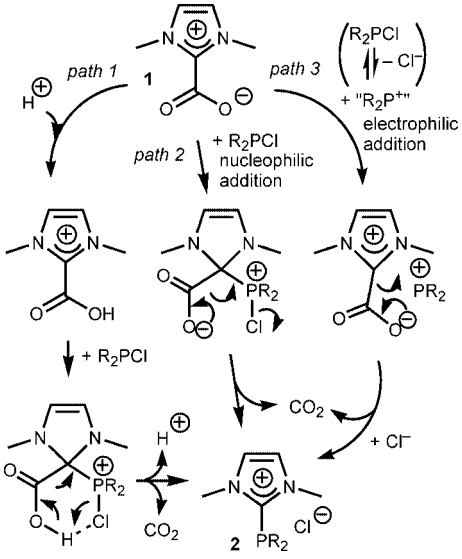


Figure 2. (a) ^{1}H NMR spectrum and (b) NOE difference spectrum of **3b** in $CDCl_3$ at room temperature.

298 K for the N–Me group and for the olefinic CH moiety of compound **2** in the ^{1}H and ^{13}C NMR spectra (for example Figure 2, spectrum a) seemed to indicate free rotation of the imidazolium ring. Indeed, VT-NMR spectroscopic experiments in CD_2Cl_2 solutions were investigated at lower temperature and differentiation between the two N–Me signals and between the two olefinic CH was found at 193 K in the ^{1}H and ^{13}C NMR for **2a**, whereas the same phenomena was observed at 273 K for **2b**. These observations show unambiguously that the cationic fragment rotates around the P(1)–C(1) bond at room temperature, whereas the isopropyl groups do not rotate around the P–C(6,9) bonds. In addition, and in line with previous calculations,[7] this easy rotation of the imidazolium ring confirms that the lone pair of electrons on the P centre remains selectively localised on the phosphorus atom, which thus makes it available for further metal coordination.

Mechanistic Aspects in the Formation of Imidazolium-2-phosphane

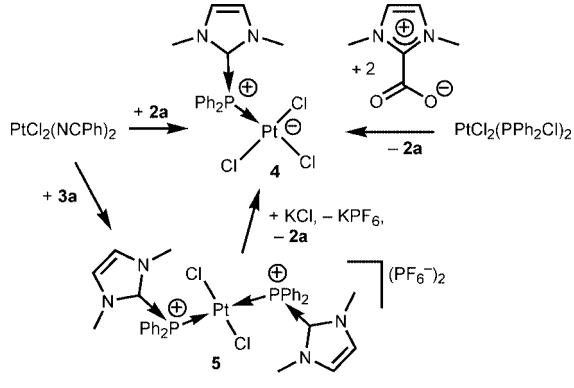
As our phosphorylation reaction contrasts other preparations of imidazolium-2-phosphanes because it does not involve the use of additional alkyllithium for the formation of the N heterocyclic carbene intermediate, different mechanistic pathways can reasonably be proposed to explain the formation of **2** (Scheme 2).



Scheme 2. Possible phosphorylation mechanisms of the imidazolium-2-carboxylate.

A first kinetic experiment in CH_2Cl_2 solution with Ph_2PCl showed that the addition of a stoichiometric amount of K_2CO_3 did not prevent the formation of **2a**, although an increased reaction time from 4 to 14 h was needed to reach complete conversion. This observation is more consistent with the strong stabilizing interaction observed in our laboratory between **1** and alkali metals[17] rather than with an acid-catalysed mechanism. A second experiment based on the direct addition of Ph_2PCl to the pure carboxylic acid form [MMIM-2-CO_2H](BF_4)[15,17] of **1** in a CH_2Cl_2/C_6D_6 mixture did not proceed even after 18 h at room temperature. Both observations exclude the possibility of an acid-catalysed phosphorylation reaction.

Notably, a mechanism involving the formation of a P–O bond followed by P migration to the N–C–N carbon atom can also be excluded, as no adduct was observed after the addition of tBu$_2$PCl to the imidazolium-2-carboxylate. Therefore, two alternative mechanisms both involving the direct addition of R_2PCl were examined (Scheme 2, paths 2 and 3); these mechanisms differ in their nucleophilic and electrophilic nature. To distinguish between them, we envisioned the use of a chlorophosphane reagent in which the nucleophilic character would be masked by metal coordination. The reactivity of imidazolium-2-carboxylate towards *cis*-$PtCl_2(PPh_2Cl)_2$ was then investigated in CD_2Cl_2 solution. ^{31}P NMR spectroscopic analysis of the crude product performed after 2 d showed the absence of a signal at δ = 71.4 ppm, which is due to the platinum starting material, and the presence of two new peaks at δ = –26.9 and 2.2 ppm; the latter peak showed a $^1J_{Pt,P}$ value of 3420 Hz. This spectrum indicates that the *cis*-$PtCl_2(PPh_2Cl)_2$ complex had totally disappeared while free ligand **2a** and a new monophosphane platinum complex were formed. The latter complex was assigned to the [$PtCl_3$(**2a**)] complex **4**, which was independently prepared by treating [$PtCl_2(NCPh)_2$] with one equivalent of compound **2a** (Scheme 3), and by using reaction conditions similar to those described for a platinum analogue complex.[18] Because the imidazolium-2-phosphane was formed in the above experiment in spite of the platinum coordination, which masks the lone pair of electrons on the phosphorus atom in chlorodiphenylphosphane, we can suggest that PR_2Cl likely reacts as an electrophilic reagent[19] toward imidazolium-2-carboxylate (Scheme 2, path 3). This assumption is supported by the lack of reactivity when the less electron rich carboxylic acid [MMIM-2-CO_2H](BF_4) is used under the conditions described for imidazolium-2-carboxylate (Scheme 2, path 1). Nevertheless, the presence of free ligand **2a** could also be the result of the direct addition of imidazolium-2-carboxylate to free PPh_2Cl, which thus illustrates the electrophilic character of compound **1**. However, the release of Ph_2PCl



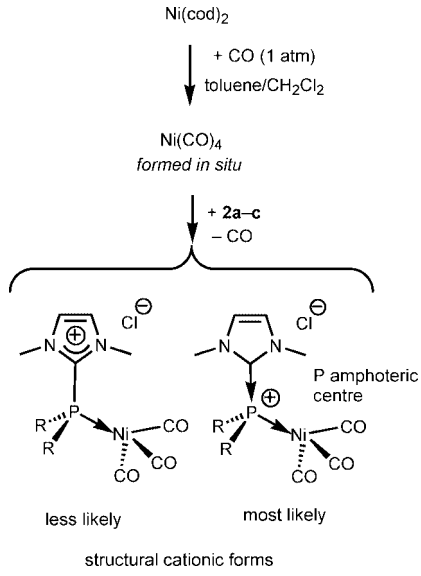
Scheme 3.

from *cis*-$PtCl_2(PPh_2Cl)_2$ is unlikely at room temperature, as the reaction would then induce *cis*/*trans*-$PtCl_2(PPh_2Cl)_2$ isomerisation, which was shown to require higher temperatures.[20] Therefore, in our case the presence of free ligand **2a** in solution seems to be the consequence of imidazolium-2-phosphane displacement by a chloride anion, which leads to more stable complex **4**.

Electronic Properties of the Ligands and Catalytic Properties

As mentioned in the introduction, there is only one report of the use of imidazolium-2-phosphanes in homogeneous catalysis.[1] In that paper, the authors observed that the presence of a *para*-phenylene spacer between the phosphorus atom and the imidazolium fragment decreased the TOF from 552 to 51 h^{-1} for rhodium catalysts in hydroformylation reactions of 1-octene and also decreased the *n:i* aldehyde ratio.[1] Besides, terminal alkenes are hydroformylated at higher rates when bulky phosphites[21] or arylphosphanes containing electron-withdrawing substituents[22] are used instead of triphenylphosphane. All results agree with the fact that the nature of the phosphorus ligand plays an important role in the stabilisation of the active species in hydroformylation reactions and the associated kinetic behaviour (alkene coordination vs. hydrogenolysis step), which drastically modify the conversion rate and selectivity in the catalytic reaction.[23] However, recent calculations performed on imidazolium-2-phosphanes describe these compounds as nonmetal complexes with a coordination bond between the electron rich N–C–N carbon and the P acceptor centre instead of a P–C covalent bond.[7] Therefore, we thought that the different hydroformylation experiments performed with an imidazolium-2-phosphane could be correlated with its specific σ-donor/π-acceptor character, which should certainly be different to those of the unmodified PPh_3, although the lone pair of electrons on the phosphorus atom is not delocalised (see above). The electronic/donor properties of the P atom was then evaluated by measurement of the A_1 symmetric stretching frequency of nickel complexes prepared in situ by replacement of a CO group in $[Ni(CO)]_4$ by phosphane **2a**. Although less-toxic compounds than $Ni(CO)_4$ {prepared in situ from $[Ni(cod)_2]$} are now more commonly used to characterise the electronic properties of phosphanes {for example, the $[Rh(CO)_2Cl]_2$ dimer}, we opted to prepare a nickel–carbonyl complex to compare easily the imidazolium-2-phosphane complex parameters directly with the large database tabulated by Tolman for adducts of the $Ni(CO)_3$ moiety.[24] We thus reacted **2a** with an equimolar amount of $Ni(CO)_4$ to afford [$Ni(CO)_3$(**2a**)] (Scheme 4).

The new nickel complex was not isolated but was recognised by its characteristic $\nu_{CO}(A_1)$ carbonyl stretching mode in the infrared spectrum of the crude mixture, which was found at 2082 cm^{-1} in a toluene/CH_2Cl_2 solution. This value classifies **2a** as less electron-donating than the common arylphosphanes [$\nu_{CO}(A_1)$ = 2069 cm^{-1} with PPh_3]. The



Scheme 4.

replacement of the aryl groups by isopropyl or cyclohexyl substituents in imidazolium-2-phophanes **2b** and **2c** led to new stretching frequencies at 2075 and 2078 cm^{-1}, respectively, in the infrared spectra for the corresponding phosphane–nickel tricarbonyl complexes. The latter values are slightly shifted to lower frequencies owing to the presence of better electron-donating alkyl groups. Nevertheless, the electronic parameters of compounds **2a**–**c** are wedged in the range of strong π-acceptor ligands such as phosphites, from $P(OiPr)_3$ [with $\nu_{CO}(A_1)$ = 2076 cm^{-1}] and $P(OPh)_3$ ligands [with $\nu_{CO}(A_1)$ = 2085 cm^{-1}][24] and clearly illustrate the strong acceptor properties of a donor-stabilised phosphenium cation reinforced by the presence of its positive charge (Scheme 4).

In addition to the above electronic properties studied, a preliminary determination of the steric demands of imidazolium-2-phosphanes was investigated in platinum dichloride complexes with the smallest ligand. So, the addition of one (or two) equivalent(s) of ligand **2a** to $PtCl_2(NCPh)_2$ in CH_2Cl_2 solution at room temperature led selectively to the formation of [$PtCl_3$(**2a**)] complex **4**. When the same reaction was performed under similar conditions with two equivalents of related halide-free ligand **3a**, the selective formation of new [$PtCl_2$(**3a**)$_2$] complex **5** was observed with a typical $^1J_{Pt,P}$ value of 2785 Hz for a P *trans* geometry around the metal centre (Scheme 3). Additionally, the $^{31}P\{^1H\}$ NMR spectrum of **5** recorded in CH_2Cl_2/C_6D_6 after introduction of KCl in a 1:1 ratio showed the presence of complex **4** and free ligand **2a**. This observation confirms the higher stability of the latter platinum trichloride complex **4**, and noteworthy is the phosphane decoordination from the platinum centre by halide addition (Scheme 3).

It is interesting to note that the nature of the counter anion perfectly controls the metal/ligand ratio in the metal–imidazoliumphosphane complexes. Nevertheless, the latter reaction contrasts those with other tertiary phosphanes Ph_2PR (R = Ph, Cl, OMe or NEt_2[20]), which selectively

lead, under similar mild conditions, to the corresponding *cis*-[$PtCl_2(Ph_2PR)_2$] isomers. The results seem to indicate that compound **2a** behaves as a bulky phosphane like the mixed arylalkylphosphanes. Other investigations on the electronic and steric properties of the cationic imidazolium-2-phosphanes, as well as their catalytic properties, are currently in progress.

Conclusions

In this paper, we report that imidazolium-2-carboxylate is an interesting starting material in the simple and straightforward synthesis of imidazolium-2-phosphanes, and the reaction could easily be extended to large-scale preparation. The synthesis of other base-stabilised phosphenium cation complexes, in addition to their optically pure forms, are currently in progress in our laboratory. Moreover, the measurements of the A_1 symmetric stretching frequency of related $Ni(CO)_3$(imidazolium-2-phosphane) complexes have shown that such compounds behave as stronger π-acceptor ligands like phosphites. The result seems to be the consequence of the C→P bond present in imidazolium-2-phosphanes, which displaces the positive charge from the imidazolium ring to the phosphorus centre. This electronic property combined with the ionic nature of the compounds renders these ligands very promising in the development of new continuous-flow catalytic processes that are currently being investigated.

Experimental Section

General Procedures: All reactions were performed in Schlenk-type flasks under an argon atmosphere. Solvents were purified and dried by conventional methods and distilled under an argon atmosphere. With the exception of compound **1** and the *trans*-$PtCl_2$(**3a**)$_2$ complex, all ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker Avance 300 instrument at 298 K. Complete assignment was achieved by COSY, DEPT and HMQC experiments. All chemical shifts are reported relative to $SiMe_4$ (^1H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR) and are given in ppm. Electrospray spectra were performed with a Bruker micrOTOF-Q instrument. The IR instrument was calibrated with solutions of $Ni(CO)_3(PPh_3)$, for which the A_1 ν_{CO} stretching band was reported to be 2068.9 cm^{-1}.[24] Elemental analyses were performed with a Fisons EA 1108 apparatus at the ICMUB in Dijon. The chlorophosphanes Ph_2PCl, *i*Pr_2PCl and Cy_2PCl were commercial products from Aldrich and Ni(1,5-cod)$_2$ was a commercial product from Strem, and all were used as received. 1,3-Dimethylimidazolium-2-carboxylate (**1**) and the $PtCl_2(NCPh)_2$ complex were prepared according to the literature.[15,17,25] Nickel tetracarbonyl $Ni(CO)_4$ was prepared from Ni(1,5-cod)$_2$ and CO according to the literature;[26] however, owing to its highly toxic nature, this preparation was handled with extreme care in a dedicated facility (CECUB, Université de Bourgogne).

Compound 2a: To a mixture of **1** (0.164 g, 1.17 mmol) and Ph_2PCl (0.258 g, 1.17 mmol) was added CH_2Cl_2 (5 mL). The mixture was stirred for 4 h at room temp. The solvent was then removed under vacuum to afford a white powder (359 mg, 97%) that was dried for 3 h under vacuum. M.p. 200 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.46 (s, 2 H, CH=), 7.42–7.23 (m, 10 H, aromatics), 3.78 (d, $J_{P,H}$ = 7.2 Hz, 6 H, NCH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 142.24 (d, $J_{P,C}$ = 52.1 Hz, 1 C, NCN), 132.74–130.95 (m, 12 C, aromatics), 128.52 (s, 2 C, CH=), 37.71 (d, $^3J_{P,C}$ = 9.1 Hz, 2 C, NCH_3) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –27.31 (s) ppm. $C_{17}H_{18}N_2PCl$ (316.76): calcd. C 64.46, H 5.73, N 8.84; found C 64.23, H 5.78, N 8.84.

Compound 2b: Prepared in an analogous manner to **2a** and obtained as white powder (250 mg, 86%). M.p. 133 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.50 (s, 2 H, CH=), 4.18 (s, 6 H, NCH_3), 2.62 (hept., $^3J_{H,H}$ = 6.6 Hz, 2 H, PCH), 1.23 (dd, $^3J_{H,H}$ = 6.6 Hz, $^3J_{P,H}$ = 12.6 Hz, 6 H, CCH_3 *exo*), 0.83 (dd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{P,H}$ = 7.2 Hz, 6 H, CCH_3 *endo*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 145.07 (d, $J_{P,C}$ = 60.4 Hz, 1 C, NCN), 127.17 (s, 2 C, CH=), 37.86 (d, $^3J_{P,C}$ = 9.1 Hz, 2 C, NCH_3), 24.07 (d, $^3J_{P,C}$ = 10.6 Hz, 2 C, PCH), 21.33 (d, $^3J_{P,C}$ = 27.2 Hz, 4 C, CH_3 *exo*), 20.75 (d, $^3J_{P,C}$ = 9.1 Hz, 4 C, CH_3 *endo*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –9.44 (s) ppm. $C_{11}H_{22}N_2PCl$ (248.73): calcd. C 53.12, H 8.91, N 11.26; found C 53.05, H 8.71, N 11.70.

Compound 2c: Prepared in an analogous manner to **2a** over molecular sieves and obtained as a white powder (277 mg, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.61 (s, 2 H, CH=), 4.14 (s, 6 H, NCH_3), 2.33 (m, 1 H, PCH), 1.77 (m, 8 H, CH_2), 1.24 (m, 10 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 144.5 (d, $J_{P,C}$ = 60.4 Hz, 1 C, NCN), 127.4 (s, 2 C, CH=), 37.79 (s, 2 C, NCH_3), 33.99 (d, $J_{P,C}$ = 11.3 Hz, 2 C, PCH), 31.85 (d, $^2J_{P,C}$ = 24.2 Hz, 2 C, CH_2), 30.39 (d, $^2J_{P,C}$ = 6.0 Hz, 2 C, CH_2), 26.33 (d, $^3J_{P,C}$ = 8.3 Hz, 2 C, CH_2), 26.08 (d, $^3J_{P,C}$ = 15.1 Hz, 2 C, CH_2), 25.51 (s, 2 C, CH_2) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –19.77 (s) ppm. $C_{17}H_{30}N_2PCl$ (328.86): No satisfactory elemental analysis was obtained for **2a** owing to its strong hygroscopic character.

Compound 3a: To a solution of **2a** (0.380 g, 1.20 mmol) in acetone (5 mL) was added KPF_6 (0.277 g, 1.50 mmol), and the resulting suspension was stirred for 2 d at room temp. The solvent was removed under vacuum at 50 °C for 2 h. The residue was dissolved in CH_2Cl_2 (5 mL), and the resulting solution was filtered. Evaporation of solvent under vacuum afforded compound **3a**, which was crystallised from CH_2Cl_2/pentane as white plates (481 mg, 94%). M.p. 176 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49 (s, 2 H, CH=), 7.45–7.24 (m, 10 H, aromatics), 3.57 (s, 6 H, NCH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 143.08 (d, $J_{P,C}$ = 54.3 Hz, 1 C, NCN), 133.06–130.07 (m, 12 C, aromatics), 127.00 (s, 2 C, CH=), 37.65 (d, $^3J_{P,C}$ = 7.6 Hz, 2 C, NCH_3) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –25.89 (s, $P_{phosphane}$), –144.14 (hept., $J_{P,F}$ = 712 Hz, PF_6^-) ppm. $C_{17}H_{18}N_2P_2F_6$ (426.27): calcd. C 47.90, H 4.25, N 6.57; found C 47.80, H 4.08, N 6.49.

Compound 3b: Prepared in an analogous manner to **3a** and obtained as white solid (374 mg, 87%). M.p. 154 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (s, 2 H, CH=), 3.96 (s, 6 H, NCH_3), 2.60 (hept., $^3J_{H,H}$ = 6.9 Hz, 2 H, PCH), 1.20 (dd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{P,H}$ = 12.3 Hz, 6 H, CCH_3 *exo*), 0.82 (dd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{P,H}$ = 7.20 Hz, 6 H, CCH_3 *endo*) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 145.89 (d, $J_{P,C}$ = 62.4 Hz, 1 C, NCN), 126.14 (s, 2 C, CH=), 37.35 (d, $^3J_{P,C}$ = 9.8 Hz, 2C, NCH_3), 23.88 (d, $J_{C,P}$ = 10.5 Hz, 2 C, PCH), 21.16 (d, $^3J_{P,C}$ = 27.2 Hz, 4 C, CH_3 *exo*), 20.46 (d, $^3J_{P,C}$ = 9.8 Hz, 4 C, CH_3 *endo*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –8.57 (s, $P_{phosphane}$), –144.40 (hept., $J_{P,F}$ = 712 Hz, PF_6^-) ppm. $C_{11}H_{22}N_2P_2F_6$ (358.24): calcd. C 36.88, H 6.19, N 7.82; found C 36.39, H 6.08, N 7.54.

Compound 3c: Prepared in an analogous manner to **3a** and obtained as white solid (421 mg; 80%). M.p. 193 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (s, 2 H, CH=), 3.95 (s, 6 H, NCH_3), 2.37 (m, 2 H, PCH), 1.75 (m, 8 H, CH_2), 1.23 (m, 10 H, CH_2) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 144.53 (d, $J_{P,C}$ = 62.6 Hz, 1 C, NCN), 125.6 (s, 2 C, CH=), 36.57 (s, 2 C, NCH_3), 32.86 (d, $J_{P,C}$ = 11.3 Hz, 2 C, PCH), 30.87 (d, $^2J_{P,C}$ = 24.2 Hz, 2 C, CH_2), 29.33 (d, $^2J_{P,C}$ = 6.8 Hz, 2 C, CH_2), 25.22 (d, $^3J_{P,C}$ = 8.3 Hz, 2 C, CH_2), 25.02 (d, $^3J_{P,C}$ = 15.1 Hz, 2 C, CH_2), 24.56 (s, 2 C, CH_2) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = –18.89 (s, $P_{phosphane}$), –144.33 (hept., $J_{P,F}$ = 712 Hz, PF_6^-) ppm. $C_{17}H_{30}N_2P_2F_6$ (438.37): calcd. C 46.58, H 6.90, N 6.39; found C 44.99, H 7.54, N 6.05.

Formation of [Ni(CO)$_3$(2a–c)]: $Ni(CO)_4$ was prepared by treating a solution of [Ni(1,5-cod)$_2$] (50.1 mg, 0.182 mmol) in toluene (1 mL) with CO at 0 °C for 5 min, followed by the addition of **2a** (0.0545 mg, 0.172 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred for 15 min. A light-green solution was obtained, which was analysed by infrared spectroscopy. IR (toluene/CH_2Cl_2): ν_{CO} = 2082 (A_1), 2013 cm^{-1} (E). The formation of the analogous [Ni(CO)$_3$(**2b**)] and [Ni(CO)$_3$(**2c**)] complexes was performed under similar conditions. IR (toluene/CH_2Cl_2): ν_{CO} = 2075 (A_1), 2051 cm^{-1}(E) for [Ni(CO)$_3$(**2b**)] and ν_{CO} = 2078 (A_1), 2005 cm^{-1} (E) for [Ni(CO)$_3$(**2c**)].

Platinum Complex 4: To a mixture of **2a** (60.1 mg, 0.19 mmol) was added $PtCl_2(PhCN)_2$ (86.6 mg, 0.19 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred for 7 h. A yellow suspension was obtained. The suspension was filtered off, and the yellow solid was washed with diethyl ether and dried under vacuum to afford $PtCl_3$(**2a**) (94 mg, 85%). M.p. >200 °C (dec.). ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 7.56–7.78 (m, 12 H, aromatics and CH=), 2.03 (s, 6 H, NCH_3) ppm. ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone): δ = 2.24 (s, $J_{Pt,P}$ = 3425 Hz, $P_{phosphane}$) ppm. MS: *m*/*z* = 510.060 [M – Cl – HCl]$^+$. $C_{17}H_{18}Cl_3N_2PPt$ (582.76): calcd. C 35.04, H 3.11, N 4.81; found C 35.51, H 2.78, N 4.26.

Platinum Complex 5: To a mixture of **3a** (0.0396 mg, 0.093 mmol) was added $PtCl_2(PhCN)_2$ (0.0224 mg, 0.049 mmol) in CH_2Cl_2 (1.5 mL), and the mixture was stirred for 12 h. A yellow suspension was obtained. The suspension was filtered off, and the yellow solid was dried under vacuum to afford *trans*-$PtCl_2$(**3a**)$_2$ (100 mg, 95%). M.p. 216 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 8.43–7.80 (m, 20 H, aromatics), 7.97 (s, 4 H, CH=), 3.75 (s, 12 H, NCH_3) ppm. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone): δ = 141.64 (d, $J_{P,C}$ = 7.5 Hz, 2 C, NCN), 139.51–127.09 (m, 24 C, aromatics), 126.68 (s, 4 C, CH=), 44.04 (s, 4 C, NCH_3) ppm. ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone): δ = 17.83 (s, $J_{Pt,P}$ = 2785 Hz, $P_{phosphane}$), –139.08 (hept, $J_{P,F}$ = 712 Hz, PF_6^-) ppm. $C_{34}H_{48}Cl_2F_{12}N_4P_4Pt$ (1130.64): calcd. C 36.12, H 4.28, N 4.96; found C 36.30, H 3.86, N 4.66.

Crystal Structure Determination for 3b: Crystal data and refinement figures are reported in Table 2. The data set was collected with an Enraf–Nonius Kappa CCD diffractometer at 110 K with Mo-K_α radiation. The structure was solved by direct methods and refined with full-matrix least-squares methods[27] based on $|F^2|$ with the aid of the WINGX program.[28] All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms were either calculated or located on final Fourier difference maps and refined, after idealization, with a riding model. CCDC-649689 contains 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.

Table 2. Crystallographic and refinement data for complex **3b**.

Formula	$C_{11}H_{22}F_6N_2P_2$
M	358.25
T [K]	110(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	12.5537(4)
b [Å]	11.1571(4)
c [Å]	13.0473(6)
$\alpha = \gamma$ [°]	90
β [°]	112.897(1)
V [Å^3]	1683.45(11)
Z	4
F(000)	744
$D_{calcd.}$ [g cm^{-3}]	1.413
Diffractometer	Enraf–Nonius KappaCCD
Scan type	mixture: ϕ rotations and ω scans
λ [Å]	0.71073
μ [mm^{-1}]	0.311
Crystal size [mm]	$0.25 \times 0.07 \times 0.01$
$\sin(\theta)/\lambda$ max [Å^{-1}]	0.65
Index ranges	*h* –16; 16 *k* –14; 9 *l* –16; 16
RC = refl. collected	5899
IRC = independent RC	3831 [*R*(int) = 0.0414]
IRCGT = IRC and [$I > 2\sigma(I)$]	2580
Refinement method	full-matrix L.S. on F^2
Data/restraints/parameters	3831/0/192
R for IRCGT	R_1[a] = 0.064, wR_2[b] = 0.137
R for IRC	R_1[a] = 0.105, wR_2[b] = 0.159
Goodness-of-fit[c]	1.024
Largest diff. peak and hole [e Å^{-3}]	0.758 and –0.446

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2)+(0.049P)^2+3.10P]$ where $P = [\max(F_o^2,0) + 2\cdot F_c^2]/3$. [c] Goodness of fit = $[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

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[1] D. J. Brauer, K. W. Kottsieper, C. Liek, O. Stelzer, H. Waffenschmidt, P. Wasserscheid, *J. Organomet. Chem.* **2001**, *630*, 177–184.
[2] S.-G. Lee, Y. J. Zhang, J. Y. Piao, C. E. Song, J. H. Choi, J. Hong, *Chem. Commun.* **2003**, 2624–2625.
[3] R. P. J. Bronger, S. M. Silva, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Dalton Trans.* **2004**, 1590–1596.
[4] C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247–2273.
[5] L. Magna, Y. Chauvin, P. G. Niccolai, J.-M. Basset, *Organometallics* **2003**, *22*, 4418–4425.
[6] L. D. Field, B. A. Messerle, K. Q. Vuong, P. Turner, *Organometallics* **2005**, *24*, 4241–4250.
[7] B. D. Ellis, P. J. Ragogna, C. L. B. Macdonald, *Inorg. Chem.* **2004**, *43*, 7857–7867.
[8] N. Burford, P. J. Ragogna, *J. Chem. Soc. Dalton Trans.* **2002**, 4307–4315.
[9] A. A. Tolmachev, A. A. Yurchenko, A. S. Merculov, M. G. Semenova, E. V. Zarudnitskii, V. V. Ivanov, A. M. Pinchuk, *Heteroat. Chem.* **1999**, *10*, 585–597.

[10] I. V. Komarov, M. Y. Kornilov, *Tetrahedron* **1995**, *51*, 11271–11280.
[11] N. Kuhn, J. Fahl, D. Bläser, R. Boese, *Z. Anorg. Allg. Chem.* **1999**, *625*, 729–734.
[12] J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R. D. Rogers, *Chem. Commun.* **2003**, 28–29.
[13] A. M. Voutchkova, L. N. Appelhans, A. R. Chianese, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 17624–17625.
[14] A. Tudose, A. Demonceau, L. Delaude, *J. Organomet. Chem.* **2006**, *691*, 5356–5365.
[15] M. Picquet, D. Poinsot, S. Stutzmann, I. Tkatchenko, I. Tommasi, P. Wasserscheid, J. Zimmermann, *Top. Catal.* **2004**, *29*, 139–143.
[16] M. Smiglak, J. D. Holbrey, S. T. Griffin, W. M. Reichert, R. P. Swatloski, A. R. Katritzky, H. Yang, D. Zhang, K. Kirichenko, R. D. Rogers, *Green Chem.* **2007**, *9*, 90–98.
[17] E. Bouajila, *Thèse de doctorat*, Université de Bourgogne, France, **2004**.
[18] N. Kuhn, M. Goëhner, G. Henkel, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1415–1416.
[19] J. Andrieu, P. Braunstein, A. Tiripicchio, F. Ugozzoli, *Inorg. Chem.* **1996**, *35*, 5975–5985.
[20] P. W. Dyer, J. Fawcett, M. J. Hanton, R. D. W. Kemmitt, R. Padda, N. Singh, *Dalton Trans.* **2003**, 104–113.
[21] A. van Rooy, J. N. H. de Bruijn, F. K. Roobeek, C. J. Kamer, P. W. N. M. van Leeuwen, *J. Organomet. Chem.* **1996**, *507*, 69–73.
[22] D. R. Palo, C. Erkey, *Organometallics* **2000**, *19*, 81–86.
[23] *Rhodium Catalyzed Hydroformylation* (Eds.: P. W. N. M. van Leeuwen, C. Claver), Kluwer, Dordrecht, **2000**, vol. 22.
[24] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
[25] P. Braunstein, R. Bender, J.-M. Jud, *Inorg. Synth.* **1989**, *26*, 341–350.
[26] P. W. Jolly, G. Wilke, *The Organic Chemistry of Nickel*, Academic Press, New York, London, **1974**, vol. 1.
[27] G. M. Sheldrick, *SHELX97: Programs for Crystal Structure Analysis (Includes SHELXS97 and SHELXL97)*, Release 97–2, University of Göttingen, Göttingen, Germany, **1998**.
[28] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

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