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PAPER

Synthesis, characterization, dynamics and reactivity toward amination of η^3-allyl palladium complexes bearing mixed ancillary ligands. evaluation of the electronic characteristics of the ligands from kinetic data†

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On the basis of an original protocol, we have synthesized several complexes of the type $[Pd(\eta^3\text{-}C_3H_3R_2)(LL')]ClO_4$ (R = H, Me; L, L′ = PPh_3, $P(OEt)_3$, 2,6-dimethylphenylisocyanide, *t*-butylisocyanide, 1,3-dimesitylimidazolidine, 1,3-dimesitylimidazol-2-ylidene). The complexes, some of which are completely new species, were fully characterized and their behaviour in solution was studied by means of ^{1}H NMR. The reactions of the complexes bearing the symmetric allyl moiety $[Pd(\eta^3\text{-}C_3H_5)(LL')]ClO_4$ with piperidine in the presence of the olefin dimethylfumarate were followed under kinetically controlled conditions. Formation of allyl-amine and of the palladium(0) derivatives $[Pd(\eta^2\text{-dmfu})(LL']$ was observed. The reaction rates k_2 proved to be strongly dependent on the ancillary ligand nature and allowed a direct comparison among the electronic characteristics of the ligands. The reactivity trend determined appears to be mainly influenced by the capability of the ancillary ligands in transferring electron density to the metal centre and consequently on the allyl fragment.

Introduction

Phosphines and phosphites are efficient spectator ligands which historically have represented a suitable choice when the stabilization of complexes of the platinum group metals was the synthetic aim. Within this class of ligands it is now appropriate to take into consideration the carbene derivatives NHC. Since Arduengo and co-workers synthesized the first stable NHC derivatives,[1] carbene complexes of transition metals have acquired an increasing importance in the field of metal catalyzed reactions[2] and the carbene derivatives of palladium were often employed as useful substitutes of phosphine or phosphite complexes.[2l,3] This is mainly due to their low toxicity, their stability toward heat, moisture and air[4] and the easy modulation of the substituents at the imidazolic nitrogen [5] which renders these compounds interesting alternatives among ligands that can stabilize the catalysts. It is well known that the chemical character of metal complexes is markedly influenced by the ability of the ligands in transferring or removing electronic density to or from the metal centre.

Quite recently, the allyl amination of isostructural phosphino-pyrazole (P–N) and phosphino-carbene (P–C) allyl Pd(II) complexes was studied in detail in order to determine how the *trans*-effect/influence of different atoms may affect the reactivity of the complexes.[5a] It was apparent that the phosphino-carbene derivative is far less reactive than its P–N analogue. The electronic withdrawal from palladium to the allyl fragment induced by the almost pure σ-donor carbene[6,7] disfavors nucleophilic attack by the amine on the terminal carbons of the allyl fragment. Thus, it was proved that carbene carbon represents a better donating atom than the pyrazole nitrogen. Such an experimental outcome indicates the valuable opportunity of extending this kinetic approach to comparing the donor/acceptor properties of the ancillary ligands. With this goal in mind, we have chosen to synthesize several allyl complexes of the type $[Pd(\eta^3\text{-}C_3H_3R_2)(LL')$ (R = H, Me; L, L′ = NHC, phosphine, phosphite and isocyanide, Scheme 1) and to determine the reactivity toward amination of the allyl group by piperidine (Scheme 2). Incidentally, the appropriate rate and easy monitoring of the reaction progress render such methodology suitable for our purpose.[8]

It is well known that attack of the amine on the allyl fragment in a palladium(II) complex takes place on the allyl face opposite to the metal, therefore reducing the steric involvement of the ancillary ligands.[9] Furthermore, when a symmetric allyl moiety is employed, no complication due to the regiochemical nature of the attack will arise.[10] Thus, we surmise that in the allyl amination by the scarcely hindered piperidine (Scheme 2), the overall reactivity will be mainly modulated by the electronic status of the allyl fragment which will be influenced only by the electron density on the palladium centre, thereby providing a valuable direct comparison among the electronic characteristics of all the ligands taken into consideration.

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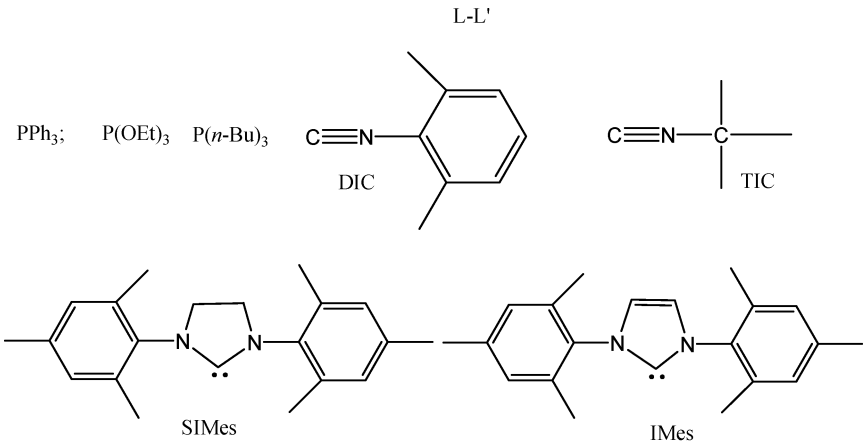

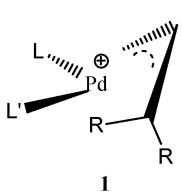

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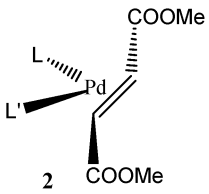
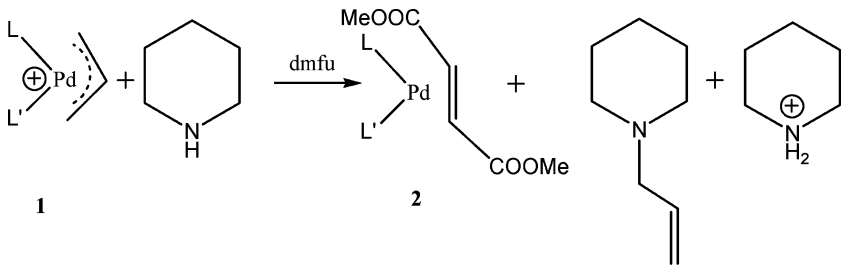


2

R = H
L= L' = PPh_3;
L= L' = $P(OEt)_3$
L= L' = DIC
L= L' = TIC
L= PPh_3, L' = DIC
L= PPh_3, L' = TIC
L= PPh_3, L' = SIMes
L= PPh_3, L' = IMes
L= $P(OEt)_3$, L' = SIMes
L= $P(OEt)_3$, L' = IMes
L= DIC, L' = SIMes
L= DIC, L' = IMes
L= DIC, L' = $P(n\text{-}Bu)_3$
L= TIC, L' = SIMes
L= TIC, L' = IMes

R = CH_3
L = PPh_3, L' = SIMes
L = PPh_3, L' = IMes
L = $P(OEt)_3$, L' = SIMes
L = $P(OEt)_3$, L' = IMes
L = DIC, L' = SIMes
L = DIC, L' = IMes

Scheme 1



1 2

dmfu = Dimethylfumarate

Scheme 2

This study is based on the comparison of the reactivity of allyl complexes bearing four different classes of *neutral* ligands with marked σ-donating and different π-electron withdrawing character.[11] The complexes of the type $[Pd(\eta^3\text{-allyl})(NHC)L]^+$ (L = CNR, $P(OEt)_3$) represent a completely new class of derivatives while similar carbene-phosphine derivatives $[Pd(\eta^3\text{-allyl})(NHC)(PR_3)]^+$ have been recently synthesized by Cavell and co-workers.[12] The isocyanide derivatives have been inserted in this study owing to the well recognized σ-donating ability of the isocyanides themselves and the scarcity of data available in the literature when the latter are used as ancillary ligands toward allyl derivatives.[13]

Table 1 Selected ^{1}H and ^{13}C NMR data for complexes $[Pd(\eta^3\text{-}C_3H_5)(NHC)(L)]^+$ at 298 K (NHC = SIMes, IMes; L = DIC, TIC, PPh_3, $P(OEt)_3$)

	σ(^{1}H) allyl					σ(^{13}C) allyl			
	trans L		*trans* NHC						
	H_{syn}	H_{anti}	H_{syn}	H_{anti}	$H_{central}$	C_{transL}	$C_{transNHC}$	$C_{central}$	σ(^{13}C) carbenic
$[Pd(\eta^3\text{-}C_3H_5)(SIMes)(DIC)]^+$	3.97	2.08	4.28[a]	2.68	5.04	63.5	68.0	120.9	204.0
$[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$	3.85	2.13	4.39	2.83	5.01	63.9	68.1	121.0	175.7
$[Pd(\eta^3\text{-}C_3H_5)(SIMes)(TIC)]^+$	3.80	2.05	4.16[a]	2.53	4.91	62.1	67.9	120.2	205.3
$[Pd(\eta^3\text{-}C_3H_5)(IMes)(TIC)]^+$	3.78	2.08	4.27	2.68	5.01	62.5	67.9	120.3	176.5
$[Pd(\eta^3\text{-}C_3H_5)(SIMes)(PPh_3)]^+$	4.35	2.39	3.04	2.02	4.94	69.9	72.4	119.8	209.0
$[Pd(\eta^3\text{-}C_3H_5)(IMes)(PPh_3)]^+$	4.18[b]	2.15[a,b]	3.15[b]	2.40[a,b]	5.08[b]	70.2	71.9	120.2	179.2
$[Pd(\eta^3\text{-}C_3H_5)(SIMes)(P(OEt)_3)]^+$	4.47	2.41	3.78	2.22	5.08	71.3	61.2	121.5	207.0
$[Pd(\eta^3\text{-}C_3H_5)(IMes)(P(OEt)_3)]^+$	4.33	2.36	3.88	2.15	5.20	71.5	61.2	121.8	177.9

[a] From ^{1}H-2D COSY spectrum. [b] From low temperature (253 K) spectrum.

Results and discussion

Synthesis of palladium allyl and 1,1- dimethyl allyl complexes bearing NHC-L′ ligands (NHC = SIMes, IMes; L′ = DIC, TIC, PPh_3, $P(OEt)_3$)

The transmetalation reaction between the palladium allyl dimers $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_3R_2)]_2$ (R = H, Me) and the silver carbenic complexes NHC-Ag-Cl (NHC = SIMes, IMes)[14] carried out at RT in CH_2Cl_2 yields the complexes $[Pd(\eta^3\text{-}C_3H_3R_2)(NHC)Cl]$, which have been obtained by Nolan and co-workers by an alternative procedure.[15] Probably, owing to the considerable steric hindrance of the carbenic ligand used in our case, at variance with Cavell's findings[12] no formation of di-carbenic species has been observed with our synthetic procedure. Dechlorination by $NaClO_4$ in mixed solvent (CH_2Cl_2/CH_3OH; 3/1) of the complexes $[Pd(\eta^3\text{-}C_3H_3R_2)(NHC)Cl]$ and addition of the appropriate ligand L′ (L′ = DIC, TIC, $P(OEt)_3$ and PPh_3) yields the allyl derivatives $[Pd(\eta^3\text{-}C_3H_3R_2)(NHC)(L')]^+$. Apart from the complexes $[Pd(\eta^3\text{-}allyl)(NHC)(PR_3)]^+$ (where NHC represents the little hindered tmiy and dipdmiy) obtained by Cavell[16] the species described in this paper represent to the best of our knowledge a new class of mixed ligand palladium allyl compounds.

Characterization of palladium allyl complexes bearing NHC-L′ ligands (NHC = SIMes, IMes; L′ = DIC, TIC, PPh_3, $P(OEt)_3$)

The ^{1}H and ^{13}C NMR spectra, recorded at RT, of the complexes bearing carbenic and isocyanide ligands display the signals of the terminal allyl protons and carbons resonating at different frequencies owing to the asymmetry arising from two different ancillary ligands. According to previous findings,[5a] an easy assignment of the allyl signals can be obtained on the basis of the intense cross-peak related to the carbenic carbon and the *anti* allyl proton *trans* to it in the 2D HMBC spectra. These complexes display the allyl protons and carbons *trans* to carbenes resonating at lower field than those *trans* to isocyanides (See Table 1). Notably, the signals ascribable to the central allyl proton and carbon and the terminal allyl protons *trans* to isocyanides resonate at significantly higher field than those of the homoleptic symmetric derivative $[Pd(\eta^3\text{-}C_3H_5)(CNR)_2]^+$ (CNR = DIC, TIC) (*See Experimental*). These high-field shifts can be traced back to the high electron density on the metal centre induced by the strong σ-donor NHC ligands although some electronic shielding exerted by the carbenic mesityl substituents on the allyl termini has to be invoked.[16] Eventually, a significant and not unprecedented difference between the chemical shifts of the carbenic carbons in SIMes and IMes derivatives is noticed also in these complexes ($\Delta\delta \cong 30$ ppm).[14a,17] In the case of complexes $[Pd(\eta^3\text{-}C_3H_5)(NHC)(POEt_3)]^+$ (NHC = SIMes, IMes) the terminal allyl protons and carbons again display different chemical shifts. The structural investigation in solution is favoured by the easily observable coupling of the terminal allyl protons and carbons with the phosphorus *trans* to them in the ^{1}H and $^{13}C\{^{1}H\}$NMR spectra, respectively[5a,12] and by the previously cited HMBC cross-peak between the carbenic carbon and the *anti* allyl proton *trans* to it.[5a] These complexes, at variance with the case discussed previously, display the allyl protons and carbons *trans* to carbenes resonating at higher field than those *trans* to phosphite. The reduced electron back-donation of the phosphite when compared with that of isocyanide ligands probably offsets the shielding brought about by the NHC substituents. The complexes $[Pd(\eta^3\text{-}C_3H_5)(NHC)(PPh_3)]^+$ (NHC = SIMes, IMes) display a spectrometric behaviour very similar to that of the phosphite derivatives. The signals of the allyl protons and carbons *trans* to the carbenes still resonate at higher field than those ascribable to the allyl protons *trans* to phosphite although the difference of chemical shifts $\Delta\delta$ in this latter case is smaller than that previously described. Remarkably, the difference between chemical shifts of the carbenic carbons of the complexes bearing SIMes and IMes is also confirmed in the case of the co-ligands PPh_3 and $P(OEt)_3$.[14a,18]

Generally speaking, the chemical shifts of the carbenic carbons of the ligands SIMes and IMes are scarcely influenced by the nature of the co-ligand and in any case these carbons resonate within a narrow interval (4-5 ppm). Notably, the allyl complexes bearing the NHC ligands tmiy and dipdmiy and a variety of phosphines display a similar behaviour.[12] (See Table 1).

Solution dynamics of the palladium allyl complexes bearing NHC-CNR ligands (NHC = SIMes, IMes; CNR = DIC, TIC)

As observed elsewhere,[12] the coordinated allyl fragment does not undergo $\eta^3\text{-}\eta^1\text{-}\eta^3$ isomerization since no negative-phase cross-peaks among terminal allyl protons are observed in the NOESY

experiments. The signals ascribable to the terminal and central protons are sharp and distinct and no related cross-peaks are detectable by NOESY experiments. This fact probably depends on the strong σ-donor capability of the ligands coupled with the poor coordinative nature of the solvent used which are not able to trigger a fluxional mechanism analogous to that recently proposed by Pregosin and co-workers.[7]

At variance with the allyl fragment, an unequivocal rotational rearrangement of the imidazolic aromatic substituents is detectable at RT in the case of the complexes $[Pd(\eta^3\text{-}C_3H_5)(NHC)(CNR)]^+$ (NHC = SIMes, IMes; CNR = DIC, TIC). The signals ascribable to the *ortho* methyl groups in *ortho* position of the phenyl substituents of carbenic ligands generate two independent singlets integrating 6 H each owing to their mutual position with respect to the main coordination plane. Similarly, the aromatic protons (b, b′ and e,e′; Fig. 1) resonate as two singlets at different chemical shifts. Conversely, the methyl groups in *para* position are isochronous and this fact is probably due to their long distance from the asymmetric centre of the complex.

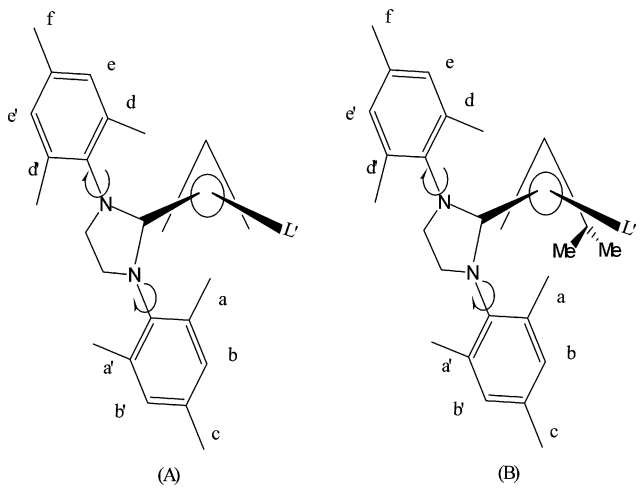


Fig. 1 Spatial representation of the complexes $[Pd(\eta^3\text{-}C_3H_5)(NHC)(L')]^+$ (A) and $[Pd(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)(NHC)(L')]^+$ (B).

Solution dynamics of the palladium allyl complexes bearing NHC-L′ ligands (NHC = SIMes, IMes; L′ = PPh_3, $P(OEt)_3$)

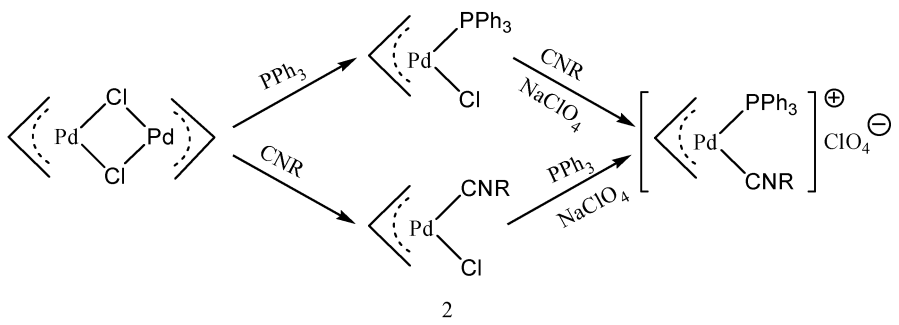
In the case of complexes $[Pd(\eta^3\text{-}C_3H_5)(NHC)(L')]^+$ (NHC = SIMes, IMes; L′ = PPh_3, $P(OEt)_3$) a complete or partially hindered rotation of one phenyl substituent of carbene is observed. Thus, the complex $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(PPh_3)]^+$ displays six distinct groups of signals at RT integrating 3 H each ascribable to the methyl protons of the phenyl substituent since the shielding effect exerted by the phosphine PPh_3 probably renders the *para* methyl protons different enough to be independently detected. Accordingly, the signals of the aromatic protons (b, b′ and e, e′) are detectable as four distinct singlets. Conversely, the complex $[Pd(\eta^3\text{-}C_3H_5)(IMes)(PPh_3)]^+$ displays a more extensive fluxionality which however can be easily "frozen" at 253 K. The ensuing ^1H NMR spectrum at reduced temperature becomes perfectly comparable with that of complex $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(PPh_3)]^+$ recorded at RT.

The RT solution behaviour of the complexes $[Pd(\eta^3\text{-}C_3H_5)(NHC)(P(OEt)_3)]^+$ (NHC = SIMes, IMes) can be traced back to that of the corresponding phosphine complexes. Thus, complex $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(P(OEt)_3)]^+$ displays three singlets integrating 3 H each related to three distinct *ortho* methyl protons and one singlet (integrating 9 H) which is comprehensive of the *para* and *ortho* methyl groups (c, f) resonating at almost the same chemical shift. The aromatic protons (b, b′ and e, e′) resonate as two singlets of 1 : 3 relative intensity.

The RT spectrum of complex $[Pd(\eta^3\text{-}C_3H_5)(IMes)(P(OEt)_3)]^+$ still displays a generalized fluxionality and the three distinct signals of the *ortho* methyl groups detected in the case of complex $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(P(OEt)_3)]^+$ resonate in this case as a broad singlet.

Synthesis, characterization and dynamics of palladium allyl complexes bearing PPh_3-CNR ligands (CNR = DIC, TIC)

The complexes of the type $[Pd(\eta^3\text{-}C_3H_5)(CNR)(PPh_3)]^+$ (CNR = DIC, TIC) are synthesized by adding to a solution of the palladium allyl dimer $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ the stoichiometric amount of PPh_3 followed by addition of the appropriate isocyanide in the presence of $NaClO_4$ or alternatively by adding the isocyanide followed by PPh_3 again in the presence of $NaClO_4$ (Scheme 3).



CNR = DIC, TIC

Scheme 3

Remarkably, both the intermediates (namely [Pd(η^3-C_3H_5)-(PPh_3)Cl] and [Pd(η^3-C_3H_5)(CNR)Cl]) can be separated from the reaction mixture and reacted with the adequate ligand in the presence of $NaClO_4$ to give the final reaction product and NaCl.

The ^{1}H and ^{13}C NMR spectra of the complexes [Pd(η^3-C_3H_5)(DIC)(PPh_3)]$^+$ and [Pd(η^3-C_3H_5)(TIC)(PPh_3)]$^+$ show no hint of η^3-η^1-η^3 allyl isomerization and are promptly interpreted on the basis of the coupling between the phosphorus atom with the protons (J^3_{PH}) and carbon (J^2_{PC}) of the allyl termini *trans* to it. In the case of the complex [Pd(η^3-C_3H_5)(DIC)(PPh_3)]$^+$ the coupling between the phosphorus and the allyl carbon *cis* to it is also detectable. However, the coupling constant in this case is considerably smaller (J^2_{PCcis} = 2.6 Hz, $J^2_{PCtrans}$ = 25.7 Hz). Irrespective of the complexes [Pd(η^3-C_3H_5)(DIC)(PPh_3)]$^+$ or [Pd(η^3-C_3H_5)(TIC)(PPh_3)]$^+$, the carbon of the allyl termini *trans* to phosphine displays the same chemical shift whereas the chemical shift of the carbon *trans* to isocyanide is influenced by the nature of the isocyanide itself. In this respect, the allyl carbon *trans* to TIC (complex [Pd(η^3-C_3H_5)(TIC)(PPh_3)]$^+$) resonates at higher field (~2 ppm) than that *trans* to DIC (complex [Pd(η^3-C_3H_5)(DIC)(PPh_3)]$^+$). Apparently, the alkyl substituent renders the *t*-butyl-isocyanide (TIC) a stronger electron donating species than di-methylphenylisocyanide (DIC) thereby inducing an increasing electron density on palladium and consequently on the allyl termini *trans* to it (this effect might be invoked in order to explain the difference in reactivity between the complexes [Pd(η^3-C_3H_5)(DIC)(PPh_3)]$^+$ and [Pd(η^3-C_3H_5)(TIC)(PPh_3)]$^+$, *Vide post*).

Characterization of palladium 1,1-dimethyl allyl complexes bearing NHC-L′ ligands (NHC = SIMes, IMes; L′ = DIC, TIC, PPh_3, $P(OEt)_3$)

Also in the case of the title complexes no η^3-η^1-η^3 isomerisation of the allyl fragment is observable. Furthermore, the allyl asymmetry allows an unequivocal structural investigation.

Remarkably, only the geometric isomer bearing the dimethyl substituted allyl termini *trans* to NHC ligands is detectable in solution (Fig. 1(B)). This fact is clearly confirmed by the ensuing cross-peak (J^4) between the carbenic carbon and the allyl protons of the *syn* and *anti* methyl groups *trans* to it. Moreover, in the cases of the complexes bearing PPh_3 and $P(OEt)_3$ the coupling between the phosphorus and the *syn* and *anti* protons of the allyl termini *trans* to it is clearly detectable.

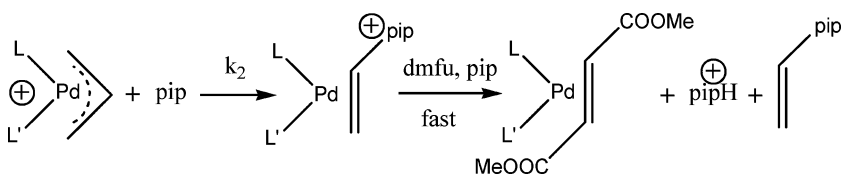
Solution dynamics of palladium 1,1-dimethyl allyl complexes bearing NHC-L′ ligands (NHC = SIMes, IMes; L′ = DIC, PPh_3, $P(OEt)_3$)

The phosphino and phosphito carbenic derivatives ([Pd(η^3-1,1-$Me_2C_3H_3$)(SIMes)(PPh_3)]$^+$, [Pd(η^3-1,1-$Me_2C_3H_3$)(IMes)(PPh_3)]$^+$, [Pd(η^3-1,1-$Me_2C_3H_3$)(SIMes)($P(OEt)_3$)]$^+$, [Pd(η^3-1,1-$Me_2C_3H_3$)-(IMes)($P(OEt)_3$)]$^+$) in solution behave similarly to their analogues bearing the symmetric allyl group. No rotation of the mesityl substituents at the imidazole nitrogens is detected at RT and therefore six distinct groups of signals integrating 3 H each related to the *ortho* and *para* methyl protons are detectable in the ^{1}H NMR spectra. Sometimes, in the most favourable cases the four signals integrating 1 H related to the b, b′,e, e′ aromatic protons are also detectable (Fig. 1(B)). On the contrary, the phenyl substituents of the ligands NHC in the carbene-DIC derivatives ([Pd(η^3-1,1-$Me_2C_3H_3$)(SIMes)(DIC)]$^+$, [Pd(η^3-1,1-$Me_2C_3H_3$)(IMes)(DIC)]$^+$) rotate freely and therefore two distinct signals integrating 6 H each ascribable to the methyl groups *ortho* to the phenyl substituents of imidazole nitrogens and one signal integrating 6 H related to the isochronous methyl groups in *para* position are detectable. Accordingly, two different signals for the aromatic protons b, b′-e, e′ integrating 2 H each are also observable.

Kinetic studies

The reaction in Scheme 2 was preliminarily studied in $CDCl_3$ at 25 °C by ^{1}H NMR techniques. The allyl amine [8] and the palladium(0) complexes were easily identified among the reaction products. The signals ascribable to the olefinic methoxy group and those of the protons of the coordinated dmfu of the latter resonate up-field and down-field respectively with respect to the signals of the uncoordinated olefin.[19] Moreover, the spectral features strongly depend on the ancillary ligands. Thus, the presence of ligands with a phophorus atom strongly influence the coupling constant of the olefin proton *trans* to it ($J_{PHtrans} > J_{PHcis}$). In these cases, the reaction progress can be easily followed by ^{31}P NMR technique by monitoring the disappearance of the phosphorus signal of the allyl complex and the concomitant appearance of that of the olefin complex which resonates down-field (3–5 ppm in the case of phosphine and ~20 ppm in the case of phosphite complexes). A table summarizing some selected characteristic ^{1}H and ^{31}P NMR signals of the complexes [Pd(η^2-dmfu)(LL′)] is reported in the Experimental section. Then the kinetics were carried out under *pseudo*-first order conditions by adding appropriate concentrations of piperidine to a chloroform solution of the complex under study in a thermostatted cell of a UV-Vis spectrophotometer in the presence of an adequate concentration of dimethylfumarate (dmfu) which stabilizes the ensuing derivatives [Pd(η^2-dmfu)(L)(L′)]. It is noteworthy that the dmfu concentration does not influence the overall reaction rate since such olefin quickly displaces the allylamine from its palladium(0) derivative[8,9] (Scheme 4).

In the cases of the carbenic complexes ([Pd(η^3-C_3H_5)(SIMes)(TIC)]$^+$ and [Pd(η^3-C_3H_5)(IMes)(TIC)]$^+$ the slow reactions were followed by means of ^{1}H NMR technique since the high concentrations ensure a shortened reaction time.



Scheme 4

Table 2 Rate constants k_2 for the allyl amination reaction (Scheme 2) determined in $CHCl_3$ at 25 °C measured by UV/Vis or ^1H NMR techniques

Complex	k_2 ($mol^{-1}dm^3s^{-1}$)	Complex	k_2 ($mol^{-1}dm^3s^{-1}$)
$[Pd(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+$	50 ± 3	$[Pd(\eta^3\text{-}C_3H_5)(SIMes)(P(OEt)_3)]^+$	$(7.8 \pm 0.1) \times 10^{-2}$
$[Pd(\eta^3\text{-}C_3H_5)(P(OEt)_3)_2]^+$	9.8 ± 0.4	$[Pd(\eta^3\text{-}C_3H_5)(IMes)(P(OEt)_3)]^+$	$(7.4 \pm 0.2) \times 10^{-2}$
$[Pd(\eta^3\text{-}C_3H_5)(DIC)_2)]^+$	61 ± 4	$[Pd(\eta^3\text{-}C_3H_5)(SIMes)(DIC)]^+$	$(7.3 \pm 0.3) \times 10^{-2}$
$[Pd(\eta^3\text{-}C_3H_5)(TIC)_2]^+$	9.7 ± 0.3	$[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$	$(5.7 \pm 0.1) \times 10^{-2}$
$[Pd(\eta^3\text{-}C_3H_5)(DIC)(PPh_3)]^+$	56 ± 3	$[Pd(\eta^3\text{-}C_3H_5)(SIMes)(TIC)]^+$	$(8.3 \pm 0.4) \times 10^{-3}$ [a]
$[Pd(\eta^3\text{-}C_3H_5)(TIC)(PPh_3)]^+$	20 ± 1	$[Pd(\eta^3\text{-}C_3H_5)(IMes)(TIC)]^+$	$(5.5 \pm 0.2) \times 10^{-3}$ [a]
$[Pd(\eta^3\text{-}C_3H_5)(SIMes)(PPh_3)]^+$	$(1.58 \pm 0.05) \times 10^{-1}$	$[Pd(\eta^3\text{-}C_3H_5)(DIC)(P(n\text{-}Bu)_3)]^+$	5.0 ± 0.3
$[Pd(\eta^3\text{-}C_3H_5)(IMes)(PPh_3)]^+$	$(1.84 \pm 0.09) \times 10^{-1}$		

[a] Reactions carried out by ^1H NMR experiments in $CDCl_3$ at 298 K.

All the studied reactions went smoothly to completion and follow the rate law:

$$-\frac{d[Complex]}{dt} = k_2[Pip]_0[Complex]$$

Each k_{obs} was evaluated by means of a non-linear regression analysis of the observed mono-exponential dependence of the absorbance (or concentration) of the reaction mixture (or of the starting allyl complex) as a function of time. The k_2 values were determined by unweighted linear regression of the calculated k_{obs} *vs*. piperidine concentration $[Pip]_0$ and are reported in Table 2. No statistically significant intercept was detectable in any linear regression analysis.[20]

We surmise that the allyl amination represents a valuable test in determining the *electronic influence* of the ligands on the metal centre and hence on the coordinated organic substrates. Steric hindrance of the ancillary ligand could hardly influence the reaction rate as can be deduced from the following observations and subsequent related experimental evidence:

i) It is well known that the piperidine attacks the allyl fragment at the face opposite to the metal.[9]

ii) The steric hindrance of the ligands IMes, SIMes and PPh_3 is very similar as can be deduced from the buried volume of the ligands themselves (26, 27, 27% respectively).[21] and refs. therein

iii) The buried volumes of the triethylphosphites and of n-butylphosphine are not available. It is however known that $P(OEt)_3$ and $P(n\text{–}Bu)_3$ display a reduced cone angle with respect to PPh_3 ($\Theta/\theta_{P(OEt)3} = 109°$; $\Theta/\theta_{P(n\text{-}Bu)3} = 132$; $\Theta/\theta_{PPh3} = 145°$) [22] and therefore they are less bulky ligands than the phosphine itself.

iv) The isocyanide ligands exert a reduced hindrance if compared with the other ligands described in the present paper. As a matter of fact isocyanides have a unique substituent R which is in addition separated by the coordinating carbon by one spacing nitrogen atom. This conclusion might also be supported by the structure of the complex $[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$ reported in this paper.

v) The DIC isocyanide displays a global unfavourable fan angle which is remarkably wider but only slightly narrower than TIC. (Fan angle $1_{DIC} = 106$, Fan angle $1_{TIC} = 70$; Fan angle $2_{DIC} = 53$, Fan angle $2_{TIC} = 68$).[23]

From these considerations it is apparent that the steric bulk of the ligands obey the following order:

$$PPh_3 \cong SIMes \cong IMes > P(n\text{-}Bu)_3 > P(OEt)_3 > DIC \geq TIC$$

whereas, from the experimental kinetic data reported in Table 2 it is apparent that the complexes display the following reactivity:

$$[Pd(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+ \gg [Pd(\eta^3\text{-}C_3H_5)(SIMes)(PPh_3)]^+ \cong [Pd(\eta^3\text{-}C_3H_5)(IMes)(PPh_3)]^+$$

$$[Pd(\eta^3\text{-}C_3H_5)(P(OEt)_3)_2]^+ \gg [Pd(\eta^3\text{-}C_3H_5)(SIMes)(P(OEt)_3)]^+ \cong [Pd(\eta^3\text{-}C_3H_5)(IMes)(P(OEt)_3)]^+$$

$$[Pd(\eta^3\text{-}C_3H_5)(DIC)(PPh_3)]^+ \cong [Pd(\eta^3\text{-}C_3H_5)(DIC)_2]^+ \gg [Pd(\eta^3\text{-}C_3H_5)(SIMes)(DIC)]^+ \cong [Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$$

This confirms that the bulkiness of the ligands does not affect the reactivity of the related derivatives, the latter being modulated by the electronic properties of the ligands only.

As a matter of fact:

a) The NHC ligands (SIMes, IMes) impart an almost indistinguishable reactivity to their derivatives bearing the same co-ligand (cfr. the reactivity of the couples $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(PPh_3)]^+$ -$[Pd(\eta^3\text{-}C_3H_5)(IMes)(PPh_3)]^+$, $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(P(OEt)_3)]^+$ -$[Pd(\eta^3\text{-}C_3H_5)(IMes)(P(OEt)_3)]^+$, $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(DIC)]^+$- $[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$ and $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(TIC)]^+$- $[Pd(\eta^3\text{-}C_3H_5)(IMes)(TIC)]^+$). This fact can be traced back to their very similar TEP.[22]

b) The Tolman Electronic Parameters would explain also the reactivity of the complexes bearing DIC isocyanides and the co-ligands PPh_3, $P(n\text{-}Bu)_3$, SIMes and IMes. The ensuing reactivity $[Pd(\eta^3\text{-}C_3H_5)(DIC)(PPh_3)]^+ > [Pd(\eta^3\text{-}C_3H_5)(DIC)(P(n\text{-}Bu)_3)]^+ \gg [Pd(\eta^3\text{-}C_3H_5)(SIMes)(DIC)]^+ \cong [Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$ parallels the tabulated TEP values of PPh_3 (2068.9 cm^{-1}), $P(n\text{-}Bu)_3$ (2060.3 cm^{-1}), SIMes (2051.5 cm^{-1}) and IMes (2050.7 cm^{-1}). A similar reactivity trend is noticed also in the case of isocyanide TIC.

c) The smallest rate constant values are observed in the case of the complexes of the type $[Pd(\eta^3\text{-}C_3H_5)(NHC)(TIC)]$ (NHC = SIMes, IMes). In these cases the strong donating ability of the carbene NHC is coupled with that of the isocyanide TIC bearing the electron donating butyl substituents.

d) The complexes $[Pd(\eta^3\text{-}C_3H_5)(TIC)(L')]^+$ (L′ = NHC, TIC, PPh_3) are always less reactive than the corresponding species $[Pd(\eta^3\text{-}C_3H_5)(DIC)(L')]^+$ (L′ = NHC, DIC, PPh_3). This observation is in agreement with the electronic donor properties of the isocyanides themselves.

e) When the complexes $[Pd(\eta^3\text{-}C_3H_5)(P(OEt)_3)_2]^+$, $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(P(OEt)_3)]^+$ and $[Pd(\eta^3\text{-}C_3H_5)(IMes)(P(OEt)_3)]^+$ are considered, it is apparent that their reactivity again fits their specific TEP values ($TEP_{P(OEt)3} = 2076.3$ cm^{-1}). As a matter of fact $[Pd(\eta^3\text{-}C_3H_5)(SIMes)(P(OEt)_3)]^+$ and $[Pd(\eta^3\text{-}C_3H_5)(IMes)(P(OEt)_3)]^+$ react slower than bis-phosphite species.

Table 3 Selected ^{1}H and ^{31}P NMR signals of the palladium(0) olefin complexes in $CDCl_3$ at 298 K

Complex	Olefinic protons	O-CH_3	^{31}P resonance
[Pd(η^2-dmfu)(SIMes)(DIC)]	3.42 d (9.7[a]); 2.93 (9.7)[a]	3.40 s; 3.24 s	
[Pd(η^2-dmfu)(IMes)(DIC)]	3.52 d (9.7[a]); 2.93 (9.7)[a]	3.35 s; 3.30 s	
[Pd(η^2-dmfu)(SIMes)(TIC)]	3.25 d (9.7[a]); 2.82 (9.7)[a]	3.39 s; 3.24 s	
[Pd(η^2-dmfu)(IMes)(TIC)]	3.31 d (9.6[a]); 2.80 (9.6)[a]	3.34 s; 3.31 s	
[Pd(η^2-dmfu)(SIMes)(PPh_3)]	3.35 dd (9.5[a]; 9.5[b]); 2.64 dd (9.5[a]; 4.6[c]);	3.23 s; 2.75 s	27.0
[Pd(η^2-dmfu)(IMes)(PPh_3)]	3.35 dd (9.5[a]; 9.5[b]); 2.79 dd (9.5[a]; 4.6[c]);	3.23 s; 2.78 s	27.4
[Pd(η^2-dmfu)(SIMes)($P(OEt)_3$)]	3.17[d] (9.6[a]; 3.6[c]); 3.10[d] (9.6[a]; 13[b]);	3.30 s; 3.24 s	151.3
[Pd(η^2-dmfu)(IMes)($P(OEt)_3$)]	3.26[d] (9.4[a]; 5.0[c]); 3.13[d] (9.4[a]; 14[b]);	3.29 s; 3.28 s	151.0
[Pd(η^2-dmfu)(DIC)(PPh_3)]	4.43 dd (9.8[a]; 9.8[b]); 4.15 dd (9.8[a]; 3.2[c]);	3.65 s; 2.96 s	27.5
[Pd(η^2-dmfu)(TIC)(PPh_3)]	4.27 dd (9.9[a]; 9.9[b]); 4.03 dd (9.9[a]; 3.1[c]);	3.66 s; 2.97 s	28.0
[Pd(η^2-dmfu)(DIC)($P(n\text{-}Bu)_3$)]	4.12 dd (9.9[a]; 9.9[b]); 4.03 dd (9.9[a]; 3.3[c]);	3.61 s; 3.58 s	9.07
[Pd(η^2-dmfu)($DIC)_2$)]	4.27 s	3.64 s	
[Pd(η^2-dmfu)($TIC)_2$)]	3.97 s	3.63 s	
[Pd(η^2-dmfu ($PPh_3)_2$]	4.14 m[e]	2.99	27.4
[Pd(η^2-dmfu)($P(OEt)_3)_2$]	4.07 m[e]	3.59	148.6

[a] J_{HH}, Hz. [b] J_{PH}, Hz (*trans* position). [c] J_{PH}, Hz (*cis* position). [d] AB part of an ABX system. [e] A_2 part of an A_2X_2 system.

f) At variance with the preceding observation, it is apparent that phosphite derivatives display a reduced reactivity with respect to the phosphine analogues despite their TEP values and bulkiness, which would suggest an opposite result. In this respect it is noteworthy that the reactivity of the complexes bearing phosphine ligands is always higher than that of their phosphite analogues ([Pd(η^3-C_3H_5)($PPh_3)_2$]$^+$> [Pd(η^3-C_3H_5)($P(OEt)_3)_2$]$^+$, [Pd(η^3-C_3H_5)(SIMes)(PPh_3)]$^+$ >[Pd(η^3-C_3H_5)(SIMes)($P(OEt)_3$)]$^+$, [Pd(η^3-C_3H_5)(IMes)(PPh_3)]$^+$ >[Pd(η^3-C_3H_5)(IMes)($P(OEt)_3$)]$^+$). Notably, the correlation between the electronic parameters determined by the spectral features and the reactivity of the complexes is not always feasible, especially when comparison among different metals is considered and the differences between parameters are not particularly high (TEP_{PPh3} = 2068.9, $TEP_{P(OEt)3}$ = 2076.3 cm^{-1}).[24]

g) The complexes of the type [Pd(η^3-C_3H_5)(NHC)(L)] (NHC = SIMes, IMes; L = PPh_3, DIC) react similarly although the phosphino-species [Pd(η^3-C_3H_5)(SIMes)(PPh_3)]$^+$ and [Pd(η^3-C_3H_5)(IMes)(PPh_3)]$^+$ display a slightly enhanced reactivity with respect to that of DIC derivatives [Pd(η^3-C_3H_5)(SIMes)(DIC)]$^+$ and [Pd(η^3-C_3H_5)(IMes)(DIC)]$^+$, while the homoleptic compounds [Pd(η^3-C_3H_5)($PPh_3)_2$]$^+$ and [Pd(η^3-C_3H_5)($DIC)_2$]$^+$ display similar rate constants.

Thus, the following order that can be traced back to the net capabilities of the ligands in transferring electron density to the metal and then to the allyl fragment can be proposed:

$$IMes \sim SIMes \gg P(n\text{-}Bu)_3 > TIC \cong P(OEt)_3 > DIC \cong PPh_3$$

Remarkably, when similar ligands are taken into consideration, this order turns out to be coincident with that proposed by Cavell and co-workers.[25]

X-ray crystal structures

The crystal structures of the complexes [Pd(η^3-C_3H_5)(IMes)(DIC)]$^+$ and [Pd(η^3-1,1-$Me_2C_3H_3$)(IMes)(PPh_3)]$^+$are shown in Fig. 2 and the main crystallographic data and bond lengths and angles are listed in Table 3, Table 4 and Table 5, respectively. In the CCDC[26] database only 15 entries show a Pd with an environment of 5 carbon atoms.[27–29] Complex

Table 4 Selected bond lengths (Å) and angles (deg) for the complex cation [Pd(η^3-C_3H_5)(IMes)(DIC)](ClO_4)

Bond lengths			
Pd–C(1)	2.046	C(1)–N(1)	1.359
Pd–C(22)	2.190	C(1)–N(2)	1.353
Pd–C(23)	2.166	C(25)–N(3)	1.148
Pd–C(24)	2.133	C(22)–C(23)	1.389
Pd–C(25)	1.999	C(23)–C(24)	1.397
Bond angles			
C(1)–Pd–C(22)	163.2	C(24)–Pd–C(25)	168.7
C(1)–Pd–C(24)	96.1	Pd–C(1)–N(1)	128.7
C(1)–Pd–C(25)	94.4	Pd–C(1)–N(2)	126.7
C(1)–Pd–C(23)	129.9	N(1)–C(1)–N(2)	104.6
C(22)–Pd–C(23)	37.2	Pd–C(25)–N(3)	174.4
C(22)–Pd–C(24)	67.7	Pd–C(22)–C(23)	70.4
C(22)–Pd–C(25)	101.5	Pd–C(23)–C(24)	69.8
C(23)–Pd–C(24)	37.9	Pd–C(23)–C(22)	72.4
C(23)–Pd–C(25)	133.7	Pd–C(24)–C(23)	72.3

[Pd(η^3-C_3H_5)(IMes)(DIC)]$^+$ appears to be, to the best of our knowledge, among the so far rare examples[27k,29] of a mononuclear Pd complex surrounded only by C donor atoms and showing both a carbene and an isocyanide ligand.

In [Pd(η^3-C_3H_5)(IMes)(DIC)]$^+$ the allyl anion binds the metal centre in the η^3 mode and the environment about the metal can be viewed as distorted square planar. In this description, the main coordination plane, beside Pd, is defined by the atoms C(1), C(22), C(24) and C(25), which are coplanar within 0.03 Å, while Pd is off by 0.06 Å.

We performed a search in the CCDC database looking for mononuclear Pd complexes showing a metal environment closely resembling that of the present complex (at least four donor C atoms and at least an η^3-bound allyl/allyl-like ligand).[15,27b,d,e,g,k,30]

By limiting the comparison to carbene complexes and considering Pd–C distances involving the peripheral carbon atoms of the ligand, it can be noted that in complexes reported there is a trend, on the average, towards bonds *ca.* 0.02 Å longer than those found in the present study (2.210 *vs.* 2.190(2) Å, 2.132 *vs.* 2.133(2) Å, respectively). The opposite is true for the central Pd–C bond, which in this study has been found to be about 0.03 Å longer than the reported mean (2.133 *vs.* 2.166(2) Å). The Pd–C(23) distance found here is the longest

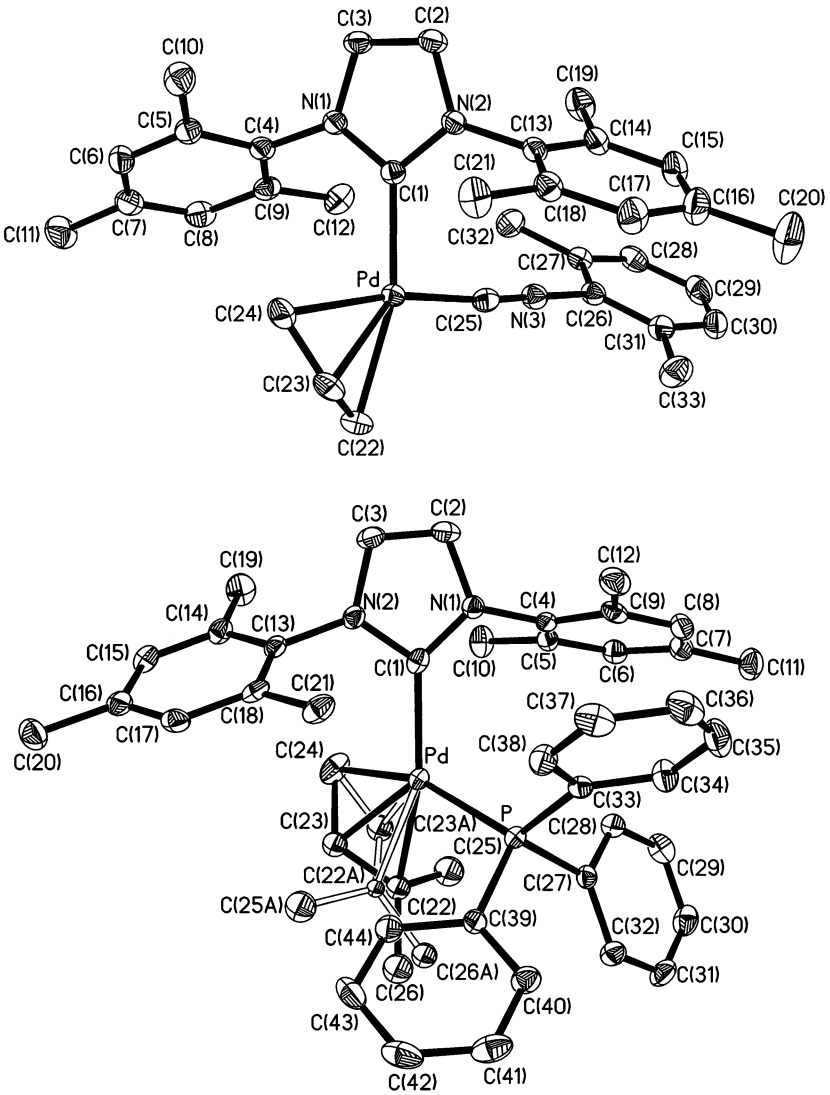


Fig. 2 ORTEP[33] view of the two complex cations $[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$ (top) and $[Pd(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)(IMes)(PPh_3)]^+$ (bottom), showing also the numbering scheme used. Thermal ellipsoids are at the 40% probability level. The hydrogen atoms and the perchlorate anions have been omitted. In the view of complex $[Pd(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)(IMes)(PPh_3)]^+$, the position of the 1,1,-dimethylallyl moiety with refined site occupancy = 0.23 has been drawn with white bonds.

one reported so far for Pd carbene complexes, and it ranks second longest after the one (2.170 Å) found in the cation *t*-butylisocyanido-(acetyl(triphenylphosphonio)methyl)-(η^3-2-methylallyl)-palladium(II),[27k] where Pd is also cooordinated by a neutral isocyanide ligand.

As for the other Pd–C distances, the one involving the carbene ligand, 2.046(2) Å, falls very close to the mean value found in the seventeen structures mentioned above (2.049 Å); the one involving the isocyanide ligand, 1.999(2) Å, fits in the restricted range of known data (1.979–2.038 Å) and ranks as second longest. On trying an overall comparison of the structural parameters in the coordination sphere, compounds most resembling our complex are (η^3-allyl)-chloro-(N,N′-dimesitylimidazol-2-ylidene)-palladium(0), (η^3-allyl)-chloro-(N,N′-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene)-palladium(0)[15] and chloro-(N,N′-bis(2,6-di-isopropylphenyl)imidazol-2-ylidene)-(η^3-1-phenylallyl)-palladium(II).[30c]

The overall arrangement of complex $[Pd(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)(IMes)(PPh_3)]^+$ does not appear too different from that of $[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$, except for the replacement of the isocyanide ligand with the triphenylphosphine group. Remarkably, the dimethyl *bis*-substituted allyl terminus is *trans* to NHC ligand as observed in solution by ^{1}H NMR technique. The metal environment is almost regular square planar, as the dihedral angle between the planes defined by the atoms C(22), Pd, C(24) and P, Pd, C(1) is 9.4°, and that between the planes defined by the atoms P, Pd, C(1) and C(22A), Pd, C(24) is 4.8°. In both cases, the sum of the bond angles about Pd equals almost exactly 360°. The 1,1-dimethylallyl residue again binds Pd in the η^3 mode and the atoms in the coordination sphere, that is, P, C(1), C(22) and C(24), deviate from the best mean plane by 0.06, 0,10, 0.12 and 0.11 Å, respectively (Pd off by 0.05 Å). In the alternate arrangement with C(22A) in place of C(22) all the atoms, including Pd, are coplanar within 0.06 Å.

Table 5 Selected bond lengths (Å) and angles (deg) for the complex cation $[Pd(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)(IMes)(PPh_3)]\ (ClO_4)$[a]

Bond lengths			
Pd–C(1)	2.070(3)	C(1)–N(1)	1.361(3)
Pd–C(22)	2.353(4)	C(1)–N(2)	1.370(3)
Pd–C(22A)	2.28(1)	P–C_{Ph}*	1.828(3)
Pd–C(23)	2.173(4)	C(22)–C(23)	1.401(6)
Pd–C(23A)	2.09(1)	C(22)–C(23A)	1.37(2)
Pd–C(24)	2.133(3)	C(23)–C(24)	1.437(5)
Pd–P	2.358(1)	C(23A)–C(24)	1.40(1)
Bond angles			
C(1)–Pd–C(22)	156.2(1)	C(24)–Pd–P	160.3(1)
C(1)–Pd–C(22A)	155.6(4)	Pd–C(1)–N(1)	130.4(2)
C(1)–Pd–C(24)	91.6(1)	Pd–C(1)–N(2)	125.5(2)
C(1)–Pd–P	108.1(1)	N(1)–C(1)–N(2)	103.8(2)
C(1)–Pd–C(23)	127.6(1)	Pd–P–C_{Ph}*	115.2(9)
C(1)–Pd–C(23A)	124.7(4)	Pd–C(22)–C(23)	65.1(2)
C(22)–Pd–C(23)	35.8(2)	Pd–C(22A)–C(23)	64.5.(7)
C(22A)–Pd–C(23A)	36.1(5)	Pd–C(23)–C(24)	69.0(2)
C(22)–Pd–C(24)	66.4(1)	Pd–C(23A)–C(24)	72.2(6)
C(22A)–Pd–C(24)	64.4(4)	Pd–C(23)–C(22)	79.1(2)
C(22)–Pd–P	94.1(1)	Pd–C(23A)–C(22A)	79.4(8)
C(22A)–Pd–P	96.0(4)	Pd–C(24)–C(23)	72.0(2)
C(23)–Pd–C(24)	39.0(1)	Pd–C(24)–C(23A)	69.1(5)
C(23A)–Pd–C(24)	38.7(4)	C(22)–C(23)–C(24)	120.5(4)
C(23)–Pd–P	122.2(1)	C(22A)–C(23A)–C(24)	116.8(1)
C(23A)–Pd–P	123.4(4)		

[a] Atom labels with a final 'A' refer to the alternate arrangement of the disordered 1,1-dimethylallyl residue. *Average of the three P–C(phenyl) distances/angles.

To the best of our knowledge, compound $[Pd(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)(IMes)(PPh_3)]^+$ would be the second instance of a Pd complex showing this coordination environment. In known structures,[8c,31,32] the Pd–C bond distances of the allyl moiety span a rather wide range of 0.36 Å (2.075–2.430 Å); the values found for the two arrangements of the allyl moiety in $[Pd(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)(IMes)(PPh_3)]^+$ remain within this range and span an interval of about 0.26 Å.

As a general trend, in known η^3 dimethylallyl complexes[8c,31] the longest Pd–C distance is the one involving the peripheral carbon atom bearing the two methyl residues (mean value of 2.276 Å), whereas the other terminal C (mean value of 2.131 Å) makes the shortest one in about one half of the reported complexes. The same setting has been found in $[Pd(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)(IMes)(PPh_3)]^+$ for the allyl residue in the arrangement with larger site occupancy (2.353(4) and 2.133(3) Å). In the other arrangement, the shorter Pd–C distance (2.09(1) Å) is the one involving the central atom of the allyl, a situation found in the other half of reported compounds (the mean bond length for the central Pd–C distance in all reported complexes is 2.149 Å). In the structures of ref. 32 the situation is different, with average values indicating a reduced difference between central and terminal Pd–C distances and, in general, a central bond (2.154 Å) being *ca.* 0.01–0.02 Å shorter than the terminal ones (2.161, 2.176 Å).

With respect to C–C distances in the allyl, the bond length between the central C atom and the methyl-bearing carbon in both arrangements is 0.03–0.04 Å longer than the bond between the central and the other terminal C atom, opposite to what has been observed in $[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$, where the two distances are much closer (1.389(3) and 1.397(3) Å), a situation that has already been observed in the other known dimethylallyl Pd complexes[8c,30c,31a,b] as well as in the compounds described in ref. 32.

The Pd–C distance of the carbene ligand, 2.070(3) Å, is about 0.02 Å longer than the corresponding distance in $[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$ and also longer than the mean value found in the seventeen structures mentioned when discussing $[Pd(\eta^3\text{-}C_3H_5)(IMes)(DIC)]^+$ (2.049 Å), which is also the mean value for the complexes reported in ref. 32 (2.049 Å); however, excluding the coordination position held by the isocyanide or triphenylphosphine ligand in the two molecules, the distance setting around Pd looks similar, with a short Pd–C bond involving the carbene doublet and allyl ligand in which the Pd–C(22) bond is always longer than the Pd–C(23), Pd–C(24) ones. As for the Pd–P length, 2.358(1) Å, it is not too different from the average found for 933 Pd-PPh_3 fragments in the CCDC database (2.300 Å).

Conclusion

We have prepared, by means of original synthetic paths, several novel allyl complexes bearing mixed, strong coordinating ligands. The complexes were completely characterized in solution and in two cases we have determined the crystal structures of the related allyl complexes. On the basis of kinetic studies of the reaction of allyl amination we were able to compare the donor/acceptor properties of different spectator ligands. It was apparent that the NHC species induce the highest electron density on the metal among all the ligands considered.

Experimental

Solvents and reagents

CH_2Cl_2 was distilled over CaH_2 under inert atmosphere (Ar), $CHCl_3$ was distilled and stored on silver foil. All other chemicals were commercial grade and were used without further purification. $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$,[34] $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_3Me_2)]_2$,[35] $[Pd(\eta^3\text{-}C_3H_5)(PPh_3)_2](ClO_4)$,[36] $[Pd(\eta^3\text{-}C_3H_5)(DIC)_2](ClO_4)$[37] $[Pd(\eta^3\text{-}C_3H_5)(TIC)_2](ClO_4)$,[37] [IMesAgCl][14a] and [SIMesAgCl][14b] were prepared following literature procedures.

NMR, UV-Vis and IR measurements

1D- and 2D-NMR spectra were recorded using a Bruker 300 Avance spectrometer. Chemical shifts (ppm) are given relative to TMS (^1H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR).

Peaks are labelled as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). The proton and carbon assignment was carried out by ^1H-2D COSY, ^1H-2D NOESY, ^1H-^{13}C HMQC and HMBC experiments.

UV-Vis spectra were recorded on a Perkin-Elmer lambda 40 spectrophotometer equipped with a Perkin-Elmer PTP 6 (Peltier temperature programmer) apparatus.

IR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer.

Preliminary studies and kinetic measurements

All the reactions were firstly analyzed by ^1H NMR technique by dissolving the complex under study in 0.8 mL of CD_2Cl_2 ($[complex]_0 \approx 0.02$ mol dm^{-3}) in the presence of dimethyl-fumarate

([dmfu]$_0$ ≈ 0.025 mol dm^{-3}) as stabilizing olefin of the final Pd(0) complex. An appropriate aliquot of piperidine was added ([pip]$_0$ ≈ 0.12 mol dm^{-3}), and the reaction was followed to completion by monitoring the disappearance of the starting complex (**1**) and the concomitant appearance of the Pd(0) olefin complex (**2**).

An UV-Vis preliminary investigation was carried out in order to determine the wavelength of the highest absorbance change. Thus, 3 mL of freshly distilled $CHCl_3$ solution of the complex under study ([complex]$_0$ ≈ 1 × 10^{-4} mol dm^{-3}) in the presence of dimethylfumarate ([dmfu]$_0$ ≈ 3 × 10^{-4} mol dm^{-3}) was placed in a thermostatted (298 K) cell compartment of the UV-Vis spectrophotometer. Adequate aliquots of a concentrated solution of piperidine were then added ([pip]$_0$ ≥ 10 × [complex]$_0$) by means of a micropipette. The reactions were monitored by recording the UV-Vis spectra as a function of time corresponding to the largest absorbance change in the 260–400 nm wavelength interval. The kinetics of nucleophilic attack at a fixed wavelength were recorded under *pseudo*-first order conditions at 310 nm. The piperidine concentrations spanned within the 1 × 10^{-3}–1 × 10^{-2} mol dm^{-3} interval and were obtained by adding known aliquots of the mother solution of piperidine (0.1–0.3 mol dm^{-3}) to a solution of the complex under study dissolved in 3 mL of freshly distilled $CHCl_3$ ([complex]$_0$ ≈ 1 × 10^{-4} mol dm^{-3}) in the presence of dimethylfumarate ([dmfu]$_0$ ≈ 3 × 10^{-4} mol dm^{-3}). In the case of the complexes [Pd(η^3-C_3H_5)(TIC)(NHC)]ClO_4 (NHC = SIMes, IMes) the reactions under UV-Vis conditions were slow and with inadequate spectral change. The reactions were therefore followed by means of NMR technique by integration of the decreasing signal ascribable to the central allylic proton of the starting complex in $CDCl_3$ at 298 K ([complex]$_0$: [dmfu] : [pip]$_0$ = 0.02 : 0.025 : 0.1 (and 0.2) mol dm^{-3}).

Synthesis of the complexes

[Pd(η^3-C_3H_5)(DIC)(PPh_3)](ClO_4). To 0.082 g (0.224 mmol) of [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ dissolved in CH_2Cl_2 (8 mL), 0.059 g (0.448 mmol) of DIC, 0.118 g (0.448 mmol) of PPh_3 individually dissolved in CH_2Cl_2 (4 + 4 mL) and 0.126 g (0.896 mmol) of $NaClO_4·H_2O$ in CH_3OH (5 mL) were added. The decoloration of the solution and the concomitant precipitation of NaCl was soon noticed. The reaction mixture was filtered over a Millipore filter, stirred for 30 min, and the solvent was removed under reduced pressure. The resulting sticky solid was dissolved in 20 mL of CH_2Cl_2, treated with activated charcoal, and filtered off through Celite. The clear solution was concentrated under reduced pressure. Upon addition of diethyl ether the crude product was obtained as pale yellow residue. The resulting solid was filtered off, washed with diethyl ether (3 × 3 mL) and with *n*-pentane (2 × 3 mL) and eventually dried under vacuum. Yield: 0.240 g (97%).

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 2.12 (s, 6H, DIC CH_3), 3.45 (d, 1H, allyl H$_{anti}$ *trans* DIC, J = 13.5 Hz), 3.95 (dd, 1H, allyl H$_{anti}$ *trans* PPh_3, J_{HH} = 13.5 Hz, J_{PH} = 10 Hz), 4.01 (d, 1H, H$_{syn}$ *trans* DIC, J = 7 Hz), 5.28 (td, 1H, allyl H$_{syn}$ *trans* PPh_3, J = 6 Hz, J = 2 Hz), 5.95 (m, 1H, allyl H$_{central}$), 7.06 (d, 2H, DIC H^3 and H^5, J = 8 Hz), 7.23 (t, 1H, DIC H^4), 7.47–7.57 (m, 15H, P(C_6H_5)$_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 18.3 (DIC CH_3), 72.4 (allyl CH_2 *trans* DIC, J_{CP} = 2.6 Hz), 76.2 (allyl CH_2 *trans* PPh_3, J_{CP} = 25.7 Hz), 123.7 (allyl CH, J_{CP} = 5.6 Hz), 125.3 (DIC C^1), 128.1 (DIC C^3, C^5), 130.6 (DIC C^4), 135.7 (DIC C^2, C^6), 142.7 (DIC *C*NR).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 24.9.

IR (KBr pellet, cm^{-1}) ν 2170.8 (CN), 1094.7 (ClO_4). Anal. Calcd. for $C_{30}H_{29}ClNO_4PPd$: C, 56.26; H, 4.56; N, 2.19. Found C, 55.98; H, 4.41; N, 2.09.

The following complexes were synthesized following a similar procedure using the same starting complex and the appropriate ancillary ligands.

[Pd(η^3-C_3H_5)(TIC)(PPh_3)](ClO_4). Yield: 88%, pale yellow microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.60 (s, 9H, TIC CH_3), 3.24 (d, 1H, allyl H$_{anti}$ *trans* TIC, J = 13.5 Hz), 3.80 (dd, 1H, allyl H$_{anti}$ *trans* PPh_3, J_{HH} = 13.5 Hz, J_{PH} = 9.5 Hz), 3.93 (d, 1H, H$_{syn}$ *trans* TIC, J = 7 Hz), 5.21 (td, 1H, allyl H$_{syn}$ *trans* PPh_3, J = 7 Hz, J = 2 Hz), 5.79 (m, 1H, allyl H$_{central}$), 7.44-7.54 (m, 15H, P(C_6H_5)$_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 29.6 (TIC CH_3), 58.9 ($C(CH_3)_3$), 70.6 (allyl CH_2 *trans* TIC), 76.2 (allyl CH_2 *trans* PPh_3), 122.3 (allyl CH, J_{CP} = 5.4 Hz), 131.3 (TIC *C*NR).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 25.0.

IR (KBr pellet, cm^{-1}) ν 2220.4 (CN), 1091.0 (ClO_4). Anal. Calcd. for $C_{26}H_{29}ClNO_4PPd$: C, 52.72; H, 4.93; N, 2.36. Found C, 52.54; H, 4.88; N, 2.30.

[Pd(η^3-C_3H_5)(DIC)(P(*n*-Bu)$_3$)](ClO_4). After treatment with activated charcoal, the solvent removal under reduced pressure induces the precipitation of the crude product as a black oil which was washed with *n*-hexane. Yield: 88%.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 0.93 (t, 9H, $PCH_2CH_2CH_3$), 1.41–1.53 (m, 6H, $PCH_2CH_2CH_3$), 1.93-2.02 (m, 6H, $PCH_2CH_2CH_3$), 2.48 (s, 6H, DIC CH_3), 3.19 (d, 1H, allyl H$_{anti}$ *trans* DIC, J = 16 Hz), 3.66 (dd, 1H, allyl H$_{anti}$ *trans* PPh_3, J_{HH} = 14 Hz, J_{PH} = 9 Hz), 4.31 (d, 1H, H$_{syn}$ *trans* DIC, J = 7 Hz), 5.07 (td, 1H, allyl H$_{syn}$ *trans* PPh_3, J = 7 Hz, J = 2 Hz), 5.70 (m, 1H, allyl H$_{central}$), 7.20 (d, 2H, DIC H^3 and H^5, J = 8 Hz), 7.33 (t, 1H, DIC H^4).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 13.6 ($PCH_2CH_2CH_3$), 18.9 (DIC CH_3), 24.1 ($PCH_2CH_2CH_3$, J_{CP} = 25.1 Hz), 26.3 ($PCH_2CH_2CH_3$, J_{CP} = 13.8 Hz), 64.5 (allyl CH_2 *trans* DIC), 76.1 (allyl CH_2 *trans* P(*n*-Bu)$_3$), 122.7 (allyl CH, J_{CP} = 5.6 Hz), 125.6 (DIC C^1), 128.4 (DIC C^3, C^5), 130.6 (DIC C^4), 135.4 (DIC C^2, C^6), (DIC *C*NR not found).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 15.3.

IR (KBr pellet, cm^{-1}) ν 2174.6 (CN), 1088.4 (ClO_4).

Anal. Calcd. for $C_{19}H_{31}ClNO_4PPd$: C, 44.72; H, 6.12; N, 2.74. Found C, 44.69; H, 6.16; N, 2.68.

[Pd(η^3-C_3H_5)(P(OEt)$_3$)$_2$](ClO_4). Precipitated with 1 : 1 mixture of diethyl ether/*n*-hexane. Yield: 69%, grey microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.36 (t, 18H, OCH_2CH_3), 3.55 (m, 2H, allyl H$_{anti}$), 4.04–4.14 (m, 12H, OCH_2CH_3), 4.72 (dd, 2H, allyl H$_{syn}$, J = 12 Hz, J = 6.6 Hz), 5.77 (m, 1H, allyl H$_{central}$).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 15.9 (d, OCH_2CH_3, J = 20.8 Hz), 62.0 (OCH_2CH_3), 71.6 (allyl CH_2), 124.4 (allyl CH).

^{31}P NMR ($CDCl_3$, 298 K): δ 126.6.

Anal. Calcd. for $C_{15}H_{35}ClO_{10}P_2Pd$: C, 3.10; H, 6.09. Found C, 3.14; H, 6.03.

[Pd(η^3-C_3H_5)(IMes)Cl]. 0.08 g (0.219 mmol) of solid [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ was added to a 0.212 g (0.437 mmol) of IMesAgCl

dissolved in CH_2Cl_2 (20 mL). The cloudy solution was filtered over Millipore and the solvent removed under reduced pressure. The colorless product was treated with a 1 : 1 mixture of diethylether/*n*-hexane and filtered over a Gooch filter, washed with diethyl ether (3 × 3 mL) and with *n*-pentane (2 × 3 mL). The resulting white compound was dried under vacuum. Yield: 0.211 g (99%). ^{1}H NMR ($CDCl_3$, T = K, ppm): δ 2.21 (s, 6H, Mesityl CH_3), 2.23 (s, 6H, Mesityl CH_3), 2.34 (s, 6H, Mesityl CH_3), 1.81 (d, 1H, allyl H_{anti}, J = 11.7 Hz), 2.82 (d, 1H, allyl H_{anti}, J = 13.5 Hz), 3.21 (d, 1H, allyl H_{syn}, J = 5.4 Hz), 3.89 (dd, 1H, allyl H_{syn}, J = 9.0 Hz, J = 2.4 Hz), 4.87 (m, 1H, allyl $H_{central}$), 6.98 (s, 4H, Mesityl H), 7.10 (s, 2H, -*H*C═C*H*-).

The following complex was synthesized following a similar procedure using the same starting complex and appropriate ancillary ligands.

[Pd(η^3-C_3H_5)(SIMes)Cl]. Yield: 97%, white microcrystals.

^{1}H NMR ($CDCl_3$, T = K, ppm): δ 2.29 (s, 6H, Mesityl CH_3), 2.43 (s, 12H, Mesityl CH_3), 1.78 (d, 1H, allyl H_{anti}, J = 12.0 Hz), 2.75 (d, 1H, allyl H_{anti}, J = 13.2 Hz), 3.27 (bd, 1H, allyl H_{syn}, J = 6.3 Hz), 3.83 (dd, 1H, allyl H_{syn}, J = 7.5 Hz, J = 1.5 Hz), 3.99 (s, 4H, CH_2-CH_2), 4.79 (m, 1H, allyl $H_{central}$), 6.93 (s, 4H, Mesityl H).

[Pd(η^3-C_3H_5)(SIMes)(PPh$_3$)](ClO$_4$). To a solution of 0.082 g (0.168 mmol) of [Pd(η^3-C_3H_5)(SIMes)Cl] in CH_2Cl_2 (8 mL), 0.044 g (0.168 mmol) of PPh_3 dissolved in 4 mL of CH_2Cl_2 was added. Addition of 0.047 g (0.336 mmol) of $NaClO_4 \cdot H_2O$ dissolved in CH_3OH (4 mL) to the stirred mixture yielded the precipitation of NaCl which was filtered off over a Millipore filter. The reaction mixture was stirred for 30 min and the solvent removed under reduced pressure. The resulting sticky solid was dissolved in 20 mL of CH_2Cl_2, treated with activated charcoal, and filtered through Celite. The clear solution, concentrated under reduced pressure yielded the crude product upon addition of diethyl ether. The white residue was filtered off, washed with diethyl ether (3 × 3 mL) and *n*-pentane (2 × 3 mL) and dried under vacuum. Yield: 0.125 g (91%).

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.77 (s, 3H, Mesityl CH_3), 2.01 (s, 3H, Mesityl CH_3), 2.27 (s, 3H, Mesityl CH_3), 2.34 (s, 3H, Mesityl CH_3), 2.36 (s, 3H, Mesityl CH_3), 2.47 (Mesityl CH_3), 2.02 (d, allyl H_{anti} *trans* SIMes), 2.39 (d, 1H, allyl H_{anti} *trans* P), 3.04 (d, 1H, allyl H_{syn} *trans* SIMes, J = 6.9 Hz), 4.07-4.29 (m, 4H, CH_2-CH_2), 4.35 (t, 1H, allyl H_{syn} *trans* P, J = 6.0 Hz), 4.94 (m, 1H, allyl $H_{central}$), 6.53 (s, 1H, Mesityl H), 6.84 (s, 1H, Mesityl H), 6.89-6.96 (m, 6H, P(C_6H_5)$_3$), 6.97 (s, 1H, Mesityl H), 7.04 (s, 1H, Mesityl H), 7.27–7.49 (m, 9H, P(C_6H_5)$_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 18.3, 18.4, 18.5, 18.85, 20.9, 21.0 (Mesityl *C*H$_3$), 52.3, 52.6 (SIMes *C*H$_2$), 69.9 (d, allyl *C*H$_2$ *trans* P, J_{CP} = 28.5 Hz), 72.4 (allyl *C*H$_2$ *trans* SIMes), 119.8 (d, allyl *C*H, J_{CP} = 4.8 Hz), 129.5, 129.6 (Mesityl *C*H), 135.0, 135.2, 135.7, 135.9, 136.1 (Mesityl *C*CH$_3$), 138.4, 138.7 (Mesityl *C*N), 209.0 (d, carbenic carbon, J_{CP} = 62.1 Hz).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 22.1.

IR (KBr pellet, cm^{-1}) ν 2919.7 (CH), 1608.7 (CN), 1482.5, 1436.4 (CC), 1093.2 (ClO_4).

Anal. Calcd. for $C_{42}H_{46}ClN_2O_4PPd$: C, 61.84; H, 5.68; N, 3.43. Found C, 61.77; H, 5.61; N, 3.38.

The following complexes were synthesized following a similar procedure using the appropriate starting complexes and ancillary ligands.

[Pd(η^3-C_3H_5)(IMes)(PPh$_3$)](ClO$_4$). Yield: 97%, white microcrystals.

^{1}H NMR ($CDCl_3$, T = K, ppm): δ 1.68 (bs, 3H, Mesityl CH_3), 1.87 (bs, 3H, Mesityl CH_3), 2.13–2.22 (m, 7H, allyl H_{anti} *trans* IMes and Mesityl CH_3), 2.33-2.48 (m, 7H, allyl H_{anti} *trans* P and Mesityl CH_3), 3.18 (d, 1H, allyl H_{syn} *trans* IMes, J = 7.2 Hz), 4.22 (bt, 1H, allyl H_{syn} *trans* P), 5.11 (m, 1H, allyl $H_{central}$), 6.63 (bs, 1H, Mesityl H), 6.87–6.93 (m, 6H, P(C_6H_5)$_3$), 6.96–7.10 (m, 3H, Mesityl H), 7.38 (bs, 2H, -*H*C═C*H*-), 7.28–7.48 (m, 9H, P(C_6H_5)$_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, T = K, ppm): δ 18.5, 18.7, 21.0, (Mesityl *C*H$_3$), 70.2 (d, allyl *C*H$_2$ *trans* P, J_{CP} = 29.6 Hz), 71.9 (allyl *C*H$_2$ *trans* IMes), 120.2 (d, allyl *C*H, J_{CP} = 4.6 Hz), 125.2 (-H*C* = *C*H-), 129.5, 129.6 (Mesityl *C*H), 134.8 (Mesityl *C*CH$_3$), 139.5 (Mesityl quaternary *C*N), 179.2 (d, carbenic carbon, J_{CP} = 15.1 Hz).

^{31}P NMR ($CDCl_3$, T = K, ppm): δ 22.6.

IR (KBr pellet, cm^{-1}) ν 2918.7 (CH), 1608.7 (CN), 1483.6, 1436.5 (CC), 1093.1 (ClO_4).

Anal. Calcd. for $C_{42}H_{44}ClN_2O_4PPd$: C, 62.00; H, 5,45; N, 3.44. Found C, 62.11; H, 5,40; N, 3.49.

[Pd(η^3-C_3H_5)(SIMes)(P(OEt)$_3$)](ClO$_4$). Precipitated by addition of a 1 : 1 mixture of diethyl ether/*n*-hexane. Yield: 73%, grey microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.17 (t, 9H, OCH$_2$C*H*$_3$, J = 7 Hz), 2.22 (1H, allyl H_{anti} *trans* SIMes), 2.24 (s, 3H, Mesityl CH_3), 2.26 (s, 3H, Mesityl CH_3), 2.29 (s, 3H, Mesityl CH_3), 2.41 (bs, 10H, Mesityl CH_3, allyl H_{anti} *trans* P), 3.40-3.67 (m, 6H, OC*H*$_2$CH$_3$), 3.78 (d, 1H, allyl H_{syn} *trans* SIMes, J = 7.5 Hz), 4.05-4.29 (m, 4H, C*H*$_2$-C*H*$_2$), 4.47 (td, 1H, allyl H_{syn} *trans* P, J = 9 Hz, J = 2.4 Hz), 5.01-5.15 (m, 1H, allyl $H_{central}$), 6.91 (s, 2H, Mesityl H), 6.96 (s, 2H, Mesityl H).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 15.9 (d, OCH$_2$*C*H$_3$, J_{CP} = 6.3 Hz), 18.0, 18.1 20.8, 20.9 (Mesityl *C*H$_3$), 51.8, 52.1 (SIMes *C*H$_2$), 61.2 (allyl *C*H$_2$ *trans* SIMes), 61.2 (O*C*H$_2$CH$_3$), 71.3 (d, allyl *C*H$_2$ *trans* P, J_{CP} = 45.3 Hz), 121.5 (d, allyl *C*H, J_{CP} = 8.5 Hz), 129.4 (Mesityl *C*H), 134.7, 135.0, 135.4, 135.7, 136.0, 136.2 (Mesityl *C*CH$_3$), 138.5, 138.9 (Mesityl *C*N), 207.0 (d, carbenic carbon, J_{CP} = 23.5 Hz).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 129.0.

IR (KBr pellet, cm^{-1}) ν 2982.4, 2918.4 (CH), 1608.5 (CN), 1490.2, 1442.3 (CC), 1093.7 (ClO_4). Anal. Calcd. for $C_{30}H_{46}ClN_2O_7PPd$: C, 50.08; H, 6.44; N, 3.89. Found C, 50.01; H, 6.38; N, 3.81.

[Pd(η^3-C_3H_5)(IMes)(P(OEt)$_3$)](ClO$_4$). Precipitated by addition of a 1 : 1 mixture of diethyl ether/*n*-hexane. Yield: 91%, grey microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.14 (t, 9H, OCH$_2$C*H*$_3$, J = 7.8 Hz), 2.15 (bs, 13H, Mesityl C*H*$_3$, allyl H_{anti} *trans* IMes), 2.33 (s, 6H, Mesityl C*H*$_3$), 2.36 (dd, 1H, allyl H_{anti} *trans* P, partially obscured), 3.42-3.69 (m, 6H, OC*H*$_2$CH$_3$), 3.88 (d, 1H, allyl H_{syn} *trans* IMes, J = 7.2 Hz), 4.33 (td, 1H, allyl H_{syn} *trans* P, J = 8 Hz, J = 2 Hz), 5.13–5.27 (m, 1H, allyl $H_{central}$), 7.00 (s, 4H, Mesityl H), 7.33 (s, 2H, -*H*C═C*H*-).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 16.0 (d, OCH$_2$*C*H$_3$, J_{CP} = 6.8 Hz), 17.9, 18.1, 20.9 (Mesityl *C*H$_3$), 61.2 (allyl *C*H$_2$ *trans* IMes), 61.2 (O*C*H$_2$CH$_3$), 71.5 (d, allyl *C*H$_2$ *trans* P, J_{CP} = 47 Hz), 121.8 (d, allyl *C*H, J_{CP} = 8.8 Hz), 125.1 (-H*C* = *C*H-), 129.3, 129.4 (Mesityl *C*H), 134.7, 134.8 (Mesityl *C*CH$_3$), 139.7 (Mesityl *C*N), 177.9 (d, carbenic carbon, J_{CP} = 26.3 Hz).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 128.8.

IR (KBr pellet, cm^{-1}) ν 2980.5, 2921.5 (CH), 1609.6 (CN), 1488.4 (CC), 1090.3 (ClO_4).

Anal. Calcd. for $C_{30}H_{44}ClN_2O_7PPd$: C, 50.22; H, 6.18; N, 3.90. Found C, 50.15; H, 6.11; N, 3.87.

[Pd(η^3-C_3H_5)(SIMes)(DIC)](ClO$_4$). Yield: 90%, white microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 2.23 (s, 6H, DIC CH_3), 2.28 (s, 6H, Mesityl CH_3), 2.32 (s, 6H, Mesityl CH_3), 2.33 (s, 6H, Mesityl CH_3), 2.08 (d, 1H, allyl H_{anti} *trans* DIC, J = 13.2 Hz), 2.68 (d, 1H, allyl H_{anti} *trans* SIMes, J = 13.5 Hz), 3.97 (d, 1H, allyl H_{syn} *trans* DIC, J = 7.2 Hz), 4.23-4.28 (m, 5H, CH_2-CH_2 and allyl H_{syn} *trans* SIMes), 5.04 (m, 1H, allyl $H_{central}$), 6.84 (s, 2H, Mesityl H), 6.90 (s, 2H, Mesityl H), 7.20 (d, 2H, DIC H^3 and H^5, J = 7.8 Hz), 7.34 (t, 1H, DIC H^4).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 17.8, 18.0, 20.9 (Mesityl CH_3), 18.5 (DIC CH_3), 52.0 (SIMes CH_2), 63.5 (allyl CH_2 *trans* DIC), 68.0 (allyl CH_2 *trans* SIMes), 120.9 (allyl *C*H), 120.9 (DIC C^1), 128.4 (DIC C^3, C^5), 130.5 (DIC C^4), 135.2 (DIC C^2, C^6), 129.5, 129.7 (Mesityl *C*H), 134.3, 134.6, 134.7 (Mesityl *C*CH_3), 138.7 (Mesityl *C*N), 146.6 (DIC *C*N*R*), 204.0 (carbenic carbon).

IR (KBr pellet, cm^{-1}) ν 2921.5 (CH), 2162.6 (CN), 1608.6 (CN), 1492.2, 1454.3 (CC), 1093.3 (ClO_4).

Anal. Calcd. for $C_{33}H_{40}ClN_3O_4Pd$: C, 57.90; H, 5.89; N, 6.14. Found C, 57.85; H, 5.80; N, 6.07.

[Pd(η^3-C_3H_5)(IMes)(DIC)](ClO$_4$). Yield: 92%, white microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 2.08 (s, 6H, DIC CH_3), 2.13 (s, 6H, Mesityl CH_3), 2.19 (s, 6H, Mesityl CH_3), 2.31 (s, 6H, Mesityl CH_3), 2.13 (d, 1H, allyl H_{anti} *trans* DIC, J = 13.1 Hz), 2.83 (d, 1H, allyl H_{anti} *trans* IMes, J = 13.8 Hz), 3.85 (d, 1H, allyl H_{syn} *trans* DIC, J = 7.2 Hz), 4.39 (dd, 1H, allyl H_{syn} *trans* IMes, J = 7 Hz, J = 2 Hz), 5.01 (m, 1H, allyl $H_{central}$), 6.91 (s, 2H, Mesityl H), 6.98 (s, 2H, Mesityl H), 7.19 (d, 2H, DIC H^3 and H^5, J = 7.5 Hz), 7.30 (t, 1H, DIC H^4), 7.39 (s, 2H, -*H*C═C*H*-). ^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 17.8 (Mesityl CH_3), 17.9 (Mesityl CH_3), 18.4 (DIC CH_3), 21.0 (Mesityl CH_3), 63.9 (allyl CH_2 *trans* DIC), 68.1 (allyl CH_2 *trans* IMes), 121.0 (allyl *C*H), 124.5 (-H*C* = *C*H-), 125.3 (DIC C^1), 128.3 (DIC C^3, C^5), 130.4 (DIC C^4), 135.2 (DIC C^2, C^6), 129.3, 129.6 (Mesityl *C*H), 134.3, 134.6, 134.7 (Mesityl *C*CH_3), 140.0 (Mesityl *C*N), DIC *C*N*R* obscured, 175.7 (carbenic carbon).

IR (KBr pellet, cm^{-1}) ν 2918.7 (CH), 2175.4 (CN), 1608.7 (CN), 1487.6 (CC), 1093.2 (ClO_4).

Anal. Calcd. for $C_{33}H_{38}ClN_3O_4Pd$: C, 58.07; H, 5.61; N, 6.16. Found C, 58.14; H, 5.54; N, 6.09.

[Pd(η^3-C_3H_5)(SIMes)(TIC)](ClO$_4$). Yield: 93%, white microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.53 (s, 9H, TIC CH_3), 2.30 (s, 6H, Mesityl CH_3), 2.31 (s, 6H, Mesityl CH_3), 2.36 (s, 6H, Mesityl CH_3), 2.05 (d, 1H, allyl H_{anti} *trans* TIC, J = 13.2 Hz), 2.53 (d, 1H, allyl H_{anti} *trans* SIMes, J = 13.5 Hz), 3.90 (d, 1H, allyl H_{syn} *trans* TIC, J = 7 Hz), 4.14-4.20 (m, 5H, CH_2-CH_2 and allyl H_{syn} *trans* SIMes), 4.91 (m, 1H, allyl $H_{central}$), 6.94 (s, 4H, Mesityl H).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 17.9, 18.0, 20.9 (Mesityl CH_3), 30.0 (TIC CH_3), 51.9 (SIMes CH_2), 58.9 ($C(CH_3)_3$), 62.1 (allyl CH_2 *trans* TIC), 67.9 (allyl CH_2 *trans* SIMes), 120.2 (allyl CH), 129.5, 129.7 (Mesityl *C*H), 134.9, 135.2, 135.3 (Mesityl *C*CH_3), 138.7 (Mesityl *C*N), 150.2 (TIC *C*N*R*), 205.3 (carbenic carbon).

IR (KBr pellet, cm^{-1}): ν 2985.5, 2921.5 (CH), 2199.3 (CN), 1609.6 (CN), 1493.2, 1455.3 (CC), 1090.4 (ClO_4).

Anal. Calcd. for $C_{29}H_{40}ClN_3O_4Pd$: C, 54.72; H, 6.33; N, 6.60. Found C, 54.65; H, 6.27; N, 6.56.

[Pd(η^3-C_3H_5)(IMes)(TIC)](ClO$_4$). Yield: 94%, white microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.63 (s, 9H, TIC CH_3), 2.11 (s, 6H, Mesityl CH_3), 2.12 (s, 6H, Mesityl CH_3), 2.36 (s, 6H, Mesityl CH_3), 2.08 (d, 1H, allyl H_{anti} *trans* TIC), 2.68 (d, 1H, allyl H_{anti} *trans* IMes, J = 13.8 Hz), 3.78 (d, 1H, allyl H_{syn} *trans* TIC, J = 7 Hz), 4.27 (dd, 1H, allyl H_{syn} *trans* IMes, J = 7.5 Hz, J = 2.4 Hz), 5.01 (m, 1H, allyl $H_{central}$), 7.03 (s, 4H, Mesityl H), 7.34 (s, 2H, -*H*C═C*H*-).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 17.8, 18.0, 21.0 (Mesityl CH_3), 29.9 (TIC CH_3), 58.9 ($C(CH_3)_3$), 62.5 (allyl CH_2 *trans* TIC), 67.9 (allyl CH_2 *trans* IMes), 120.3 (allyl CH), 124.4 (-H*C* = *C*H-), 129.4, 129.6 (Mesityl *C*H), 134.2, 134.4, 135.0 (Mesityl *C*CH_3), 139.7 (Mesityl *C*N), TIC *C*N*R* not observed, 176.5 (carbenic carbon).

IR (KBr pellet, cm^{-1}): ν 2980.6, 2922.6 (CH), 2199.2 (CN), 1608.6 (CN), 1488.4, 1460.5 (CC), 1093.4 (ClO_4).

Anal. Calcd. for $C_{29}H_{38}ClN_3O_4Pd$: C, 54.90; H, 6.04; N, 6.62. Found C, 54.91; H, 6.09; N, 6.58.

[Pd(η^3-1,1-$Me_2C_3H_3$)(SIMes)Cl]. 0.174 g (0.412 mmol) of solid $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_3Me_2)]_2$ was added to 0.400 g (0.823 mmol) SIMesAgCl dissolved in CH_2Cl_2 (40 mL). The cloudy solution was filtered over a Millipore filter and the solvent removed under reduced pressure. The colorless product was treated with a 1 : 1 mixture of diethylether/*n*-hexane and filtered over a Gooch filter, washed with diethyl ether (3 × 3 mL), *n*-pentane (2 × 3 mL) and dried under vacuum. Yield: 0.405 g (95%).

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 0.63 (s, 3H, allyl $CH_{3\,anti}$), 1.43 (s, 3H, allyl $CH_{3\,syn}$), 1.71 (dd, 1H, allyl H_{anti}, J = 12 Hz, J = 1.8 Hz), 2.28 (s, 6H, Mesityl CH_3), 2.43 (s, 6H, Mesityl CH_3), 2.44 (s, 6H, Mesityl CH_3), 2.84 (dd, 1H, allyl H_{syn}, J = 7.2 Hz, J = 1.9 Hz), 3.99 (s, 4H, CH_2-CH_2), 4.37 (dd, 1H, allyl $H_{central}$, J = 12 Hz, J = 7.2 Hz), 6.93 (s, 4H, Mesityl H).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 18.3, 18.4, 20.9 (Mesityl CH_3), 19.1 (allyl $CH_{3\,anti}$), 25.4 (allyl $CH_{3\,syn}$), 40.1 (allyl CH_2), 50.9 (SIMes CH_2), 106.1 (allyl *C*H), 107.5 (allyl $C(CH_3)_2$), 129.1 (Mesityl *C*H carbons), 136.2, 136.4, 137.7 (Mesityl *C*CH_3), Mesityl *C*N not observed, 212.7 (carbenic carbon).

IR (KBr pellet, cm^{-1}) ν 2915.6 (CH), 1608.7 (CN), 1488.3, 1452.5 (CC).

Anal. Calcd. for $C_{26}H_{35}ClN_2Pd$: C, 60.35; H, 6.82; N, 5.41. Found C, 60.27; H, 6.77; N, 5.38.

The following complex was synthesized following a similar procedure using the same starting complex and IMesAgCl.

[Pd(η^3-1,1-$Me_2C_3H_3$)(IMes)Cl]. Yield: 87%, white microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 0.72 (s, 3H, allyl $CH_{3\,anti}$), 1.48 (s, 3H, allyl $CH_{3\,syn}$), 1.73 (dd, 1H, allyl H_{anti}, J = 12 Hz, J = 1.4 Hz), 2.21 (s, 6H, Mesityl CH_3), 2.24 (s, 6H, Mesityl CH_3), 2.33

(s, 6H, Mesityl CH_3), 2.81 (dd, 1H, allyl H_{syn}, J = 7.2 Hz, J = 2.1 Hz), 4.44 (dd, 1H, allyl $H_{central}$, J = 12 Hz, J = 7.2 Hz), 6.97 (s, 4H, Mesityl H), 7.10 (s, 2H, -*H*C═C*H*-).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 18.1, 18.3, 21.0 (Mesityl *C*H_3), 19.3 (allyl *C*$H_{3\,anti}$), 25.5 (allyl *C*$H_{3\,syn}$), 39.9 (allyl *C*H_2), 105.9 (allyl *C*H), 106.3 (allyl *C*$(CH_3)_2$), 122.6 (IMes -*H*C═C*H*-), 128.8 (Mesityl *C*H), 135.5, 135.6, 136.1 (Mesityl *C*CH_3), 137.4 (Mesityl *C*N), 185.2 (carbenic carbon).

IR (KBr pellet, cm^{-1}) ν 2916.5 (CH), 1608.6 (CN), 1485.4, 1444.5 (CC). Anal. Calcd. for $C_{26}H_{33}ClN_2Pd$: C, 60.59; H, 6.45; N, 5.43. Found C, 60.51; H, 6.38; N, 5.40.

[Pd(η³-1,1-$Me_2C_3H_3$)(SIMes)(PPh_3)](ClO_4). To a solution of [Pd(η³-$C_3H_3Me_2$)(SIMes)Cl] (0.080 g, 0.144 mmol) in CH_2Cl_2 (8 mL), 0.041 g (0.156 mmol) of PPh_3 dissolved in CH_2Cl_2 (4 mL) was added. Addition under stirring of 0.043 g (0.308 mmol) $NaClO_4 \cdot H_2O$ dissolved in CH_3OH (4 mL) to the resulting solution induced the precipitation of NaCl which was filtered off on a Millipore filter. The reaction mixture was stirred for 30 min and the solvent removed under reduced pressure. The resulting sticky solid was dissolved in 20 mL of CH_2Cl_2, treated with activated charcoal, and filtered through celite. The clear solution concentrated under reduced pressure yielded the crude product upon addition of diethyl ether. The white residue was filtered off, washed with diethyl ether (3 × 3 mL), *n*-pentane (2 × 3 mL) and dried under vacuum. Yield: 0.110 g (87%).

^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 0.23 (d, 3H, allyl $CH_{3\,anti}$, J_{PH} = 3.6 Hz), 0.71 (d, 3H, allyl $CH_{3\,syn}$, J_{PH} = 5.4 Hz), (allyl H_{anti} *trans* P obscured by methyl signals), 1.79 (s, 3H, Mesityl CH_3), 1.96 (s, 3H, Mesityl CH_3), 2.26 (s, 3H, Mesityl CH_3), 2.39 (s, 3H, Mesityl CH_3), 2.43 (s, 3H, Mesityl CH_3), 2.46 (s, 3H, Mesityl CH_3), 3.62 (t, 1H, allyl H_{syn} *trans* P, J = 2.4 Hz), 4.15–4.24 (m, 4H, C*H*$_2$-C*H*$_2$), 4.63 (dd, 1H, allyl $H_{central}$, J = 12.5 Hz, J = 8.3 Hz), 6.55 (s, 1H, Mesityl H), 6.84 (s, 1H, Mesityl H), 6.90-6.96 (m, 7H, Mesityl H and P(C_6H_5)$_3$), 7.06 (s, 1H, Mesityl H), 7.31–7.49 (m, 9H, P(C_6H_5)$_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 17.3, 18.3, 18.7, 18.5, 19.5, 20.9 (Mesityl *C*H_3), 19.8 (allyl *C*$H_{3\,anti}$), 25.5 (allyl $CH_{3\,syn}$), 52.3 (SIMes *C*H_2), 54.5 (d, allyl *C*H_2, J_{CP} = 30.7 Hz), 110.7 (allyl *C*$(CH_3)_2$), 111.9 (allyl *C*H), 129.3, 129.5, 129.7 (Mesityl *C*H), 134.7, 134.9, 135.5, 135.9, 136.2, 136.6 (Mesityl *C*CH_3), 138.47, 138.7 (Mesityl *C*N), 209.6 (carbenic carbon).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 22.0.

IR (KBr pellet, cm^{-1}) ν 2918.7 (CH), 1608.7 (CN), 1482.5, 1435.5 (CC), 1090.3 (ClO_4).

Anal. Calcd. for $C_{44}H_{50}ClN_2O_4PPd$: C, 62.64; H, 5.97; N, 3.32. Found C, 62.58; H, 5.89; N, 3.27.

The following complexes were prepared under similar conditions using the appropriate ligands and precursors.

[Pd(η³-1,1-$Me_2C_3H_3$)(IMes)(PPh_3)](ClO_4). Yield: 85%, white microcrystals.

^1H NMR ($CDCl_3$, T = K, ppm): δ 0.31 (bd, 3H, allyl $CH_{3\,anti}$, J_{PH} = 3.3 Hz), 0.80 (bd, 3H, allyl $CH_{3\,syn}$, J_{PH} = 3.0 Hz), (allyl H_{anti} *trans* P obscured by methyl signals), 1.62 (bs, 3H, Mesityl CH_3), 1.93 (bs, 3H, Mesityl CH_3), 2.17 (bs, 3H, Mesityl CH_3), 2.20 (bs, 3H, Mesityl CH_3), 2.31 (bs, 3H, Mesityl CH_3), 2.45 (bs, 3H, Mesityl CH_3), 3.52 (bt, 1H, allyl H_{syn} *trans* P), 4.79 (bt, 1H, allyl $H_{central}$, J = 10.8 Hz), 6.68 (s, 1H, Mesityl H), 6.90–6.96 (m, 5H, P(C_6H_5)$_3$), 7.01 (bs, 1H, Mesityl H), 7.14 (bs, 1H, Mesityl H), HC═CH- obscured, 7.29–7.48 (m, 10H, P(C_6H_5)$_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = K, ppm): δ 17.1, 17.3, (Mesityl *C*H_3), 21.0 (allyl *C*H_{3anti}), 25.5 (allyl *C*H_{3syn}), 54.7 (allyl *C*H_2), allyl *C* $(CH_3)_2$ and allyl *C*H not observed, 125.1 (-H*C* = *C*H-) 129.8 (Mesityl *C*H), 134.3 (Mesityl *C*CH_3), 139.2 (Mesityl *C*N), 177.0 (d, carbenic carbon, J_{CP} = 10.9 Hz).

^{31}P NMR ($CDCl_3$, T = K, ppm): δ 22.4.

IR (KBr pellet, cm^{-1}) ν 2918.8 (CH), 1608.8 (CN), 1485.6, 1436.6 (CC), 1093.2 (ClO_4). Anal. Calcd. for $C_{44}H_{48}ClN_2O_4PPd$: C, 62.79; H, 5.75; N, 3.33. Found C, 62.83; H, 5.70; N, 3.29.

[Pd(η³-1,1-$Me_2C_3H_3$)(SIMes)(P(OEt)$_3$)](ClO_4). Precipitated by addition of a 1 : 1 mixture of diethyl ether/*n*-hexane. Yield: 65%, grey microcrystals

^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 0.65 (d, 3H, allyl $CH_{3\,anti}$, J_{PH} = 8.4 Hz), 1.22 (t, 9H, OCH_2CH_3, J = 7 Hz), 1.66 (d, 3H, allyl $CH_{3\,syn}$, J_{PH} = 10.8 Hz), 2.13 (dd, 1H, allyl H_{anti} *trans* P, J = 14.9 Hz, J = 1.5 Hz), 2.24 (s, 3H, Mesityl CH_3), 2.27 (s, 3H, Mesityl CH_3), 2.29 (s, 3H, Mesityl CH_3), 2.40 (s, 3H, Mesityl CH_3), 2.43 (s, 3H, Mesityl CH_3), 2.45 (s, 3H, Mesityl CH_3), 3.44–3.75 (m, 6H, OCH_2CH_3), 3.77 (dd, 1H, allyl H_{syn} *trans* P, J = 7.8 Hz, J = 2 Hz), 4.22–4.32 (m, 4H, C*H*$_2$-C*H*$_2$), 4.74 (dd, 1H, allyl $H_{central}$, J = 13.5 Hz, J = 7.8 Hz), 6.91 (s, 1H, Mesityl H), 6.93 (s, 1H, Mesityl H), 6.95 (s, 1H, Mesityl H), 6.98 (s, 1H, Mesityl H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 16.0 (d, OCH_2CH_3, J_{CP} = 6.9 Hz), 18.1, 18.3, 18.4, 20.7, 20.8 (Mesityl *C*H_3), 19.2 (allyl *C*$H_{3\,anti}$), 26.3 (allyl $CH_{3\,syn}$), 51.5, 52.3 (SIMes *C*H_2), 57.7 (d, allyl *C*H_2 *trans* P, J_{CP} = 48.7 Hz), 61.5 (d, OCH_2CH_3, J_{CP} = 3.7 Hz), 102.6 (d, allyl *C*$(CH_3)_2$, J_{CP} = 6.7 Hz), 113.1 (d, allyl *C*H, J_{CP} = 9.8 Hz), 129.2, 129.3, 129.5 (Mesityl *C*H), 135.0, 135.4, 135.6, 135.8, 136.0, 136.5 (Mesityl *C*CH_3), 138.3, 138.8 (Mesityl *C*N), 208.3 (d, carbenic carbon, J_{CP} = 26.9 Hz).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 122.9.

IR (KBr pellet, cm^{-1}) ν 2983.3, 2918.4 (CH), 1630.5, 1608.5 (CN), 1489.8, 1441.2 (CC), 1093.1 (ClO_4).

Anal. Calcd. for $C_{32}H_{50}ClN_2O_7PPd$: C, 51.41; H, 6.74; N, 3.75. Found C, 51.26; H, 6.68; N, 3.79.

[Pd(η³-1,1-$Me_2C_3H_3$)(IMes)(P(OEt)$_3$)](ClO_4). Precipitated by addition of a 1 : 1 mixture of diethyl ether/*n*-hexane. Yield: 81%, grey microcrystals.

^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 0.75 (d, 3H, allyl $CH_{3\,anti}$, J_{PH} = 8.4 Hz), 1.19 (t, 9H, OCH_2CH_3, J = 7 Hz), 1.74 (m, 4H, allyl $CH_{3\,syn}$,, allyl H_{anti} *trans* P), 2.08 (s, 3H, Mesityl CH_3), 2.14 (s, 3H, Mesityl CH_3), 2.21 (s, 3H, Mesityl CH_3), 2.24 (s, 3H, Mesityl CH_3), 2.33 (s, 3H, Mesityl CH_3), 2.34 (s, 3H, Mesityl CH_3), 3.46–3.73 (m, 7H, allyl H_{syn} *trans* P, OCH_2CH_3), 4.86 (ddd, 1H, allyl $H_{central}$, J = 13.5 Hz, J = 7.8 Hz, J = 1.2 Hz), 7.02 (s, 4H, Mesityl H), 7.34 (s, 2H, -*H*C═C*H*-).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 16.0 (d, OCH_2CH_3, J_{CP} = 6.7 Hz), 18.0, 18.1, 18.3, 18.5, 20.8, 20.9 (Mesityl *C*H_3), 19.4 (allyl *C*$H_{3\,anti}$), 26.4 (allyl $CH_{3\,syn}$), 57.8 (d, allyl *C*H_2 *trans* P, J_{CP} = 50.1 Hz), 61.5 (d, OCH_2CH_3, J_{CP} = 3.0 Hz), 102.0 (d, allyl *C*$(CH_3)_2$ J_{CP} = 6.9 Hz), 113.4 (d, allyl *C*H, J_{CP} = 9.7 Hz), 124.0, 125.3 (-H*C* = *C*H-), 129.1, 129.3, 129.5, 129.7 (Mesityl *C*H), 134.6, 134.9, 135.4, 135.5 (Mesityl *C*CH_3), 139.4, 139.7 (Mesityl *C*N), 179.1 (d, carbenic carbon, J_{CP} = 30.6 Hz).

^{31}P NMR ($CDCl_3$, T = 298 K, ppm): δ 122.3.

IR (KBr pellet, cm^{-1}) ν 2983.6, 2918.6 (CH), 1608.5 (CN), 1488.5, 1446.6 (CC), 1093.1 (ClO_4). Anal. Calcd. for $C_{32}H_{48}ClN_2O_7PPd$: C, 51.55; H, 6.49; N, 3.76. Found C, 51.61; H, 6.43; N, 3.69.

[Pd(η³-1,1-$Me_2C_3H_3$)(SIMes)(DIC)][ClO_4]. Yield: 95%, white microcrystals

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 0.91 (s, 3H, allyl $CH_{3\,anti}$), 1.81 (s, 3H, allyl $CH_{3\,syn}$), 1.93 (dd, 1H, allyl H_{anti}, J = 13.8 Hz, J = 2.4 Hz), 2.19 (6H, DIC CH_3), 2.27 (s, 6H, Mesityl CH_3), 2.30 (s, 6H, Mesityl CH_3), 2.32 (s, 6H, Mesityl CH_3), 3.35 (dd, 1H, allyl H_{syn}, J = 7.8 Hz, J = 2 Hz), 4.17–4.25 (m, 4H, CH_2-CH_2), 4.75 (dd, 1H, allyl $H_{central}$, J = 12.9 Hz, J = 7.8 Hz), 6.82 (s, 2H, Mesityl H), 6.92 (s, 2H, Mesityl H), 7.20 (d, 2H, DIC H^3 and H^5, J = 7.5 Hz), 7.35 (t, 1H, DIC H^4).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 17.8, 18.1, 20.5 (Mesityl CH_3), 18.3 (DIC CH_3), 20.9 (allyl $CH_{3\,anti}$), 27.3 (allyl $CH_{3\,syn}$), 51.8 (SIMes CH_2), 52.0 (allyl CH_2), 106.6 (allyl $C(CH_3)_2$), 112.0 (allyl CH), 125.2 (DIC C^1), 128.4 (DIC C^3, C^5), 130.4 (DIC C^4), 135.4 (DIC C^2, C^6), 129.3, 129.6 (Mesityl CH), 134.7, 135.5, 135.7 (Mesityl CCH_3), 138.6 (Mesityl CN), 150.7 (DIC CNR), 205.3 (carbenic carbon).

IR (KBr pellet, cm^{-1}) ν 2946.5, 2919.5 (CH), 2168.2 (CN), 1630.6, 1608.6 (CN), 1490.1, 1454.3 (CC), 1090.2 (ClO_4).

Anal. Calcd. for $C_{35}H_{44}ClN_3O_4Pd$: C, 58.99; H, 6.22; N, 5.90. Found C, 58.89; H, 6.26; N, 5.98.

[Pd(η³-1,1-$Me_2C_3H_3$)(IMes)(DIC)][ClO_4]. Yield: 95%, white microcrystals.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.06 (s, 3H, allyl $CH_{3\,anti}$), 1.87 (s, 3H, allyl $CH_{3\,syn}$), 1.91 (dd, 1H, allyl H_{anti}, J = 13.4 Hz, J = 2.7 Hz), 2.07 (s, 6H, Mesityl CH_3), 2.14 (s, 6H, Mesityl CH_3), 2.17 (6H, DIC CH_3), 2.32 (s, 6H, Mesityl CH_3), 3.27 (dd, 1H, allyl H_{syn}, J = 7.8 Hz, J = 2.6 Hz), 4.87 (dd, 1H, allyl $H_{central}$, J = 13.2 Hz, J = 7.8 Hz), 6.88 (s, 2H, Mesityl H), 7.00 (s, 2H, Mesityl H), 7.20 (d, 2H, DIC H^3 and H^5, J = 7.5 Hz), 7.35 (t, 1H, DIC H^4), 7.37 (s, 2H, -HC═CH-).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm): δ 17.8, 17.9, 21.0 (Mesityl CH_3), 18.3 (DIC CH_3), 21.0 (allyl $CH_{3\,anti}$), 27.4 (allyl $CH_{3\,syn}$), 52.2 (allyl CH_2), 106.7 (allyl $C_{quaternary}$), 112.1 (allyl CH), 124.3 (IMes -HC═CH-), (DIC C^1 not found), 128.4 (DIC C^3, C^5), 130.4 (DIC C^4), 135.4 (DIC C^2, C^6), 129.2 129.5 (Mesityl CH), 134.4, 134.5, 134.8 (Mesityl quaternary CCH_3), 136.9(Mesityl quaternary CN), 150.6 (DIC CNR), 177.1 (carbenic carbon).

IR (KBr pellet, cm^{-1}) ν 2952.6, 2920.5 (CH), 2168.1 (CN), 1630.2, 1608.6 (CN), 1486.4, 1448.5 (CC), 1090.5 (ClO_4).

Anal. Calcd. for $C_{35}H_{42}ClN_3O_4Pd$: C, 59.16; H, 5.96; N, 5.91. Found C, 59.25; H, 5.88; N, 5.87.

Characterization of the complexes [Pd(η²-dmfu)(L)(L′)]

In Table 3 the characterization of the complexes [Pd(η²-dmfu)(L)(L′)] based on some selected ^{1}H and ^{31}P NMR signals is reported.

X-ray analysis

Single crystals of the complexes [Pd(η³-C_3H_5)(IMes)(DIC)](ClO_4) and [Pd(η³-1,1-$Me_2C_3H_3$)(IMes)(PPh_3)](ClO_4) of X-ray quality were grown by slow diffusion of diethyl ether into a dichloromethane solution. The selected specimens were fastened on the top of a Lindemann glass capillary and centered on the four-circle kappa goniometer head of an Oxford Diffraction Gemini E diffractometer, equipped with a 2 K × 2 K EOS CCD area detector and sealed-tube Enhance (Mo) and (Cu) X-ray sources, under a cold nitrogen stream provided by an Oxford Instruments CryojetXL sample chiller. The diffraction data collection (ω scan technique) was carried out at T = 150.0(1) K, by using graphite–monochromated Mo Kα radiation (λ = 0.71073 Å), in a 1024 × 1024 pixel mode, using 2 × 2 pixel binning.

A total of 825 frames in eleven runs and 794 frames in thirteen runs for [Pd(η³-C_3H_5)(IMes)(DIC)](ClO_4) and [Pd(η³-1,1-$Me_2C_3H_3$)(IMes)(PPh_3)](ClO_4)respectively, were measured with a step of 1°. The diffraction intensities were corrected for Lorentz and polarization effects and were also optimized with respect to absorption. Empirical multi-scan absorption corrections using equivalent reflections were performed with the scaling algorithm *SCALE3 ABSPACK*. Data collection, data reduction and finalization were carried out through the CrysAlis Pro software.[38] Accurate unit-cell parameters were determined during the whole data collection by least–squares refinement of all reflection positions. Crystal stability was checked by measuring in both cases two reference frames every 50 frames; no sign of systematic changes was noticed either in peak positions or in intensities.

The structures were solved by means of the heavy-atom methods using SHELXTL-NT[39] and refined by full-matrix least-squares methods based on F_o^2 with SHELXL-97.[40] In the late stage of refinement for [Pd(η³-1,1-$Me_2C_3H_3$)(IMes)(PPh_3)](ClO_4), some peaks appeared in positions compatible with a second chemically reasonable arrangement of the allyl group. At the end of the refinement, the C(22), C(23), C(25) and C(26) atoms of the allyl ligand were found to be disordered over two sites. The two alternate arrangements were refined isotropically, with partial occupancies of 0.77 and 0.23, respectively. With the exception of disordered atoms, all non-H atoms were allowed to vibrate anisotropically in the last cycles of refinement. H atoms were placed in calculated positions and refined as "riding model". The U_{iso} values of hydrogen atoms were set at 1.2 (1.5 for methyl group) times U_{eq} of the pertinent carrier carbon atom.

The main crystallographic data are listed in Table 1SI† (Supplementary Information); selected bond lengths and angles are listed in Table 4. Full listings of atomic coordinates, bond lengths and angles, and anisotropic thermal parameters are available as supporting information (see below).

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