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Half-Sandwich Benzylidene Ruthenium Complexes Bearing Phosphanyl-Pyridine Ligands: Reactivity towards Nucleophiles and Electrophiles

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The chelating hemilabile phosphanyl-pyridines P*i*Pr$_2$XC$_5$H$_4$N (X = NH, the previously described diisopropylphosphanyl-pyrid-2-ylamine, **1a**; X = S, the novel diisopropylphosphanylmercaptopyridine, **1b**) have been prepared to be used as ligands in the synthesis of the new half-sandwich chloro complexes [Ru(η^5-C$_5$Me$_5$)(κ^2-*P,N*-P*i*Pr$_2$XC$_5$H$_4$N)Cl] (X = NH, **2a**; S, **2b**). These versatile starting compounds react with phenyldiazomethane to yield the novel carbene ruthenium complexes [Ru(η^5-C$_5$Me$_5$)(κ^2-*P,N*-P*i*Pr$_2$XC$_5$H$_4$N)(=CHC$_6$H$_5$)][BAr′$_4$] (Ar′ = 3,5-C$_6$H$_3$(CF$_3$)$_2$; X = NH, **3a**; S **3b**); **3a** has been characterized by X-ray crystallography. Compound **3a** reacts as a Brønsted base with an excess amount of triflic acid to give [Ru(η^5-C$_5$Me$_5$)(κ^2-*P,N*-P*i*Pr$_2$NHC$_5$H$_4$N)(η^2-CH$_2$C$_6$H$_5$)][CF$_3$SO$_3$]$_2$ (**4a**), the first example of a structurally characterized η^2-benzylruthenium complex. The benzylidene complex **3a** can also be deprotonated by bases, KO*t*Bu or KN(SiMe$_3$)$_2$, thereby yielding neutral complex [Ru(η^5-C$_5$Me$_5$)(κ^2-*P,N*-P*i*Pr$_2$NC$_5$H$_4$N)(=CHC$_6$H$_5$)] (**5a**). The cationic complex [Ru(η^5-C$_5$Me$_5$)(κ^2-*P,N*-P*i*Pr$_2$NHC$_5$H$_4$N)(PMe$_3$)][BAr′$_4$] (**6a**) has been prepared from **3a** by straightforward and quick reaction with trimethylphosphane. Compound **3a** also shows characteristic carbene reactivity against nucleophiles like NaBH$_4$/CH$_3$OH to afford alkyl compound [Ru(η^5-C$_5$Me$_5$)(κ^2-*P,N*-P*i*Pr$_2$NHC$_5$H$_4$N)(η^1-CH$_2$C$_6$H$_5$)] (**7a**). The reaction of carbene complex **3b** with LiCH$_3$ yields the neutral alkyl complex [Ru(η^5-C$_5$Me$_5$)(κ^2-*P,N*-P*i*Pr$_2$SC$_5$H$_4$N)(η^1-CH$_2$CH$_2$C$_6$H$_5$)] (**8b**), which contains a β hydrogen atom.

Introduction

Transition-metal chemistry can be greatly expanded by the use of polydentate ligands that contain significantly different chemical functionalities (hybrid ligands).[1] Among these compounds, phosphanyl-pyridines[2,3] have emerged as one powerful alternative to P,P or N,N ligands; 2-(diphenylphosphanyl)pyridine is the most studied member of this family.[4] This ligand can be used to stabilize binuclear complexes, especially heterobinuclear ones. However, the short bite angle makes its mononuclear chemistry somewhat limited. To override this disadvantage, spacer groups can be introduced between phosphanyl and pyridyl groups. In our case, the selected spacer groups were amino[5–10] and sulfur, with consequent changes in steric and electronic donor properties of the ligands.

Carbene complexes offer a wide variety of useful organic transformations.[11–14] Usually their chemical behaviour is summarized in Schrock and Fischer types, according to metal class and nature of the substituents on the carbenic atom. Often it is not possible to classify a carbene complex with regards to its electrophilicity or nucleophilicity. There is a broad range of reactivities in which Schrock and Fischer types are only particular cases.[15]

Ruthenium carbene complexes have been thoroughly studied for their potential ability to catalyse olefin metathesis, as shown by Grubbs carbene complexes.[15] In spite of these works, there are few reported examples of half-sandwich ruthenium carbene complexes with non-Fischer-type carbene ligands.[16] In this context, it seems reasonable that the presence of functionalized phosphanylpyridine ligands can stabilize carbene moieties and extend their reactivity.

In this work, new ruthenium chloro complexes that contain phosphanyl-pyridine ligands are reported, and their ability to form carbene complexes is studied. Additionally, several derivatives produced by electrophilic or nucleophilic attack on the carbene complex [Ru(η^5-C$_5$Me$_5$)(κ^2-*P,N*-P*i*Pr$_2$NHC$_5$H$_4$N)(=CHC$_6$H$_5$)]$^+$ are also studied.

Results and Discussion

Despite several existing reports[17–19] that describe the synthesis of P*i*Pr$_2$NHC$_5$H$_4$N, (diisopropylphosphanyl)-(pyrid-2-yl)amine (**1a**), we have used a previously undescribed preparation that involves the well-known lithiation of 2-aminopyridine and subsequent reaction with P*i*Pr$_2$Cl to create the P–N bond.[20] An analogous procedure with 2-mercaptopyridine has been used in the synthesis of the

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previously unreported P*i*Pr$_2$SC$_5$H$_4$N, 2-(diisopropylphosphanyl)mercaptopyridine (**1b**). This compound has been obtained as a yellow viscous oil.

The direct reaction of [{(η^5-C$_5$Me$_5$)RuCl}$_4$] with phosphanyl pyridines **1a** and **1b** gives neutral half-sandwich complexes [Ru(η^5-C$_5$Me$_5$)(κ^2-*P*,*N*-P*i*Pr$_2$NHC$_5$H$_4$N)Cl] (**2a**) and [Ru(η^5-C$_5$Me$_5$)(κ^2-*P*,*N*-P*i*Pr$_2$SC$_5$H$_4$N)Cl] (**2b**), which have been isolated as orange and reddish-orange microcrystalline solids, respectively. Compound **2a** is almost insoluble in nonpolar solvents and moderately soluble in polar solvents like dichloromethane or acetone. The most remarkable feature in its NMR spectra is the dependence of N*H* resonance on solvent. Accordingly, in CD_2Cl_2 it appears at 5.7 ppm as a wide singlet, whereas in CD_3COCD_3 it shows a doublet ($J_{P,H}$ = 5 Hz) at 7.5 ppm.

In the same way, compound **2b** is almost insoluble in nonpolar solvents, but it is a bit more soluble than **2a** in polar solvents like dichloromethane or acetone. Suitable single crystals of **2b** for X-ray diffraction analysis were obtained by slow diffusion of petroleum ether into a saturated dichloromethane solution of the complex. An ORTEP view of **2b** is displayed in Figure 1.

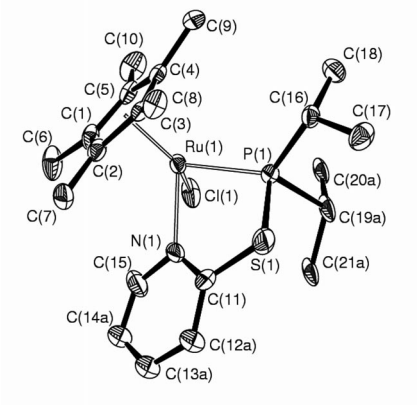


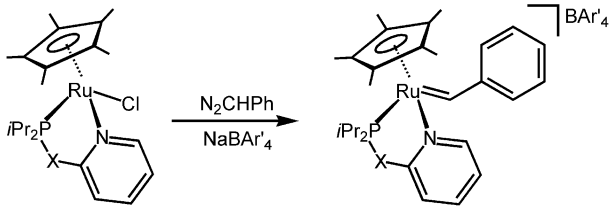
Figure 1. Molecular structure of **2b**. Thermal ellipsoids are drawn at the 50% probability level. Atoms that correspond to disordered groups in minor orientations and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Ru(1)–cyclopentadienyl(centroid) 1.818(5), Ru(1)–Cl(1) 2.444(1), Ru(1)–P(1) 2.269(2), Ru(1)–N(1) 2.111(5), S(1)–P(1) 2.157(2), S(1)–C(11) 1.756(7); Cl(1)–Ru(1)–P(1) 97.74(5), Cl(1)–Ru(1)–N(1) 85.44(15), P(1)–Ru(1)–N(1) 82.08(14), P(1)–S(1)–C(11) 96.6(3).

It shows a "three-legged piano stool" geometry, analogous to that found in related half-sandwich chlororuthenium complexes that contain P and N as donor centres.[21–23] Ru–P and Ru–Cl bond lengths are comparable to those found for [Ru(Ph-ind-ptpy)(PPh$_3$)Cl] {Ph-ptpy-ind = η^5-κN-3-phenyl-1-[2-(2-pyridyl)-4-tolyl]indenyl}.[23] Regarding this complex, the most distinctive features are shorter Ru–ring centroid distance [1.818(5) vs. 1.849(3) Å], Ru–N bond length [2.111(5) vs. 2.169(3) Å], and a smaller P–Ru–N angle [82.08(14) vs. 95.88(7)°], due to a large extent to the bulkiness of the ligands in [Ru(Ph-ind-ptpy)(PPh$_3$)Cl] and the P–N connection in **2b**.

The NMR spectra are very similar to those of **2a**, except for the absence of an N*H* signal. Both $^{31}P\{^1H\}$ spectra display notable downfield shifts, 124.4 (**2a**) and 129.9 ppm (**2b**), in relation to the values found for **1a** and **1b**, as expected for metal-bonded P atoms. However, in terms of the differences among related complexes,[7,8] there are no significant changes in the chemical shifts of protons in the pyridine ring.

There are scarce examples of carbene complexes with formula [Ru(C$_5$R$_5$)(=CR′R′′)(**L**)(**L**′)] (R = H, CH$_3$; R′, R′′ = H, alkyl, aryl; **L**, **L**′ = Cl, phosphanes, stibanes). The preparation of complex [Ru(η^5-C$_5$H$_5$)(=CPh$_2$)(PPh$_3$)Cl] requires strong conditions (an excess of diazo compound and relatively high temperatures).[24] Alternatively, a multistep synthetic sequence that involves the formation of labile compounds [Ru(C$_5$H$_5$)Cl(C$_2$H$_4$)(PPh$_3$)][25] or [Ru(C$_5$H$_5$)(κ^2-CH$_3$CO$_2$)(PPh$_3$)][26] is feasible. Complexes [Ru(C$_5$H$_5$)Cl(=CHPh)(PPh$_3$)] and [Ru(C$_5$Me$_5$)Cl(=CHPh)(PPh$_3$)] have been already prepared by using their respective labile ethylene complexes as precursors.[25] In the same way, similar compounds that contain rhodium[27] or iridium[28] have been synthesized. Nevertheless, the related osmium compound [Os(C$_5$H$_5$)Cl(P*i*Pr$_3$)(=CHPh)] has been obtained by direct reaction between [Os(C$_5$H$_5$)Cl(P*i*Pr$_3$)$_2$] and phenyldiazomethane.[29]

In our case, the reaction between [Ru(C$_5$Me$_5$)Cl(P*i*Pr$_2$NHC$_5$H$_4$N)] and phenyldiazomethane has been carried out in the presence of NaBAr′$_4$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] to avoid some disadvantages of this straightforward method, especially low yields and scant reproducibility. It is likely that the formation of a highly reactive 16e$^-$ intermediate promotes the immediate reaction with phenyldiazomethane, thereby releasing N$_2$(g). A change of colour occurs in the solution from the initial orange to greyish-blue. After workup, the benzylidene ruthenium complex [Ru(η^5-C$_5$Me$_5$)(κ^2-*P*,*N*-P*i*Pr$_2$NHC$_5$H$_4$N)(=CHC$_6$H$_5$)][BAr′$_4$] (**3a**) was obtained as a greenish-grey microcrystalline powder in 95% yield (Scheme 1).



Scheme 1. Preparation of benzylidene complexes.

Recrystallization in fluorobenzene/petroleum ether provides green crystals suitable for single-crystal X-ray diffraction. The structure of the cation in **3a** is shown in Figure 2.

The molecule has a "three-legged piano stool" geometry, where the ruthenium atom is formally six-coordinated. The Ru=C bond-length value of 1.916(7) Å is similar to those

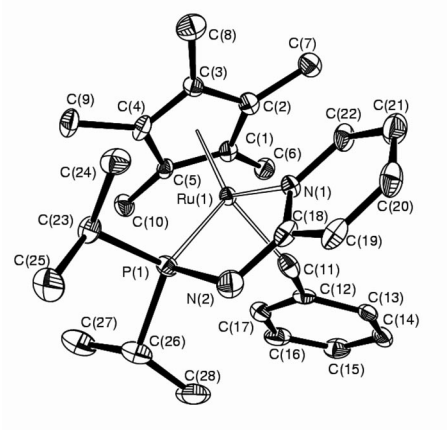


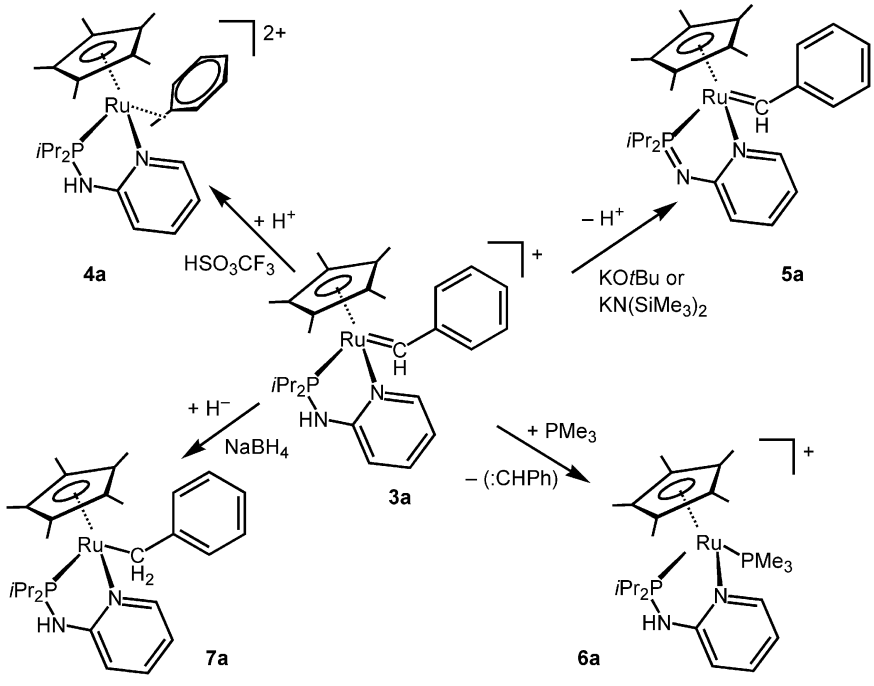
Figure 2. ORTEP view of cation complex $[Ru(\eta^5\text{-}C_5Me_5)(\kappa^2\text{-}P,N\text{-}PiPr_2NHC_5H_4N)(=CHC_6H_5)]^+$ in **3a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Ru(1)–cyclopentadienyl(centroid) 1.933(6), Ru(1)–P(1) 2.294(2), Ru(1)–N(1) 2.124(5), Ru(1)–C(11) 1.916(7), P(1)–N(2) 1.712(6), N(2)–C(18) 1.379(9); P(1)–Ru(1)–N(1) 78.9(2), P(1)–Ru(1)–C(11) 91.8(2), N(1)–Ru(1)–N(1) 82.9(3), P(1)–N(2)–C(18) 117.7(5).

found in related complexes like $[Ru(C_5H_5)Cl(PPh_3)(=CPh_2)]$ (1.916 Å)[30] and $[Ru(C_5H_5)(CO)(PPh_3)(=CPh_2)][PF_6]$ [1.973(4) Å][25] or in other heteroatom-substituted alkylidene complexes like $[Ru(C_5H_5)Cl(PPh_3)(=C(COPh)Ph)]$ (1.933 Å)[25] and $[CpRu(PMe_3)(=CPhNHpy)]$ (1.959 Å; Cp = cyclopentadienyl).[31] As expected, this Ru=C value is longer than those found for pentacoordinate "Grubbs catalysts": $[RuCl_2(PCy_3)_2(=CHPh)]$ [1.838(2) Å; Cy = cyclohexyl],[15] $[RuCl_2(PCy_3)(SIMes)(=CHPh)]$ [1.836 Å; SIMes = 1,3-bis(mesityl)imidazolidin-2-ylidene][32] and $[RuCl_2(PCy_3)(IMes)(=CHPh)]$ [1.840 Å; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene].[33]

The benzylidene compound **3b** of formula $[Ru(\eta^5\text{-}C_5Me_5)(\kappa^2\text{-}P,N\text{-}PiPr_2SC_5H_4N)(=CHC_6H_5)][BAr'_4]$ has been prepared in the same way. Both compounds present similar spectroscopic data. The $^{31}P\{^1H\}$ NMR spectra of compounds **3a** and **3b** in CD_2Cl_2 displayed one singlet at room temperature that showed the lack of appreciable restrictions in rotation around the Ru=C bond under these conditions. In the ^1H NMR spectra, the most noteworthy feature is the appearance of highly deshielded carbenic proton signals at 16.26 ppm for **3a** and 17.14 ppm for **3b**, respectively. These chemical shifts are similar to those described for related compounds, 17.25 ppm for $[Ru(C_5H_5)Cl(PPh_3)(=CHPh)]$ and 17.28 ppm for $[Ru(C_5Me_5)Cl(PPh_3)(=CHPh)]$.[25] In the $^{13}C\{^1H\}$ NMR spectra, carbenic carbon signals appear as doublets at δ = 305.8 ppm for **3a** and 316.1 ppm for **3b**, with coupling constants $^2J_{P,C}$ = 16 Hz in both cases. These data are in agreement with those reported for other related benzylidene complexes, δ = 327.5 ppm ($^2J_{P,C}$ = 16 Hz) for $[Ru(C_5H_5)Cl(PPh_3)(=CHPh)]$ and δ = 317.2 ppm ($^2J_{P,C}$ = 13 Hz) for $[Ru(C_5Me_5)Cl(PPh_3)(=CHPh)]$.[25]

Some acid–base reactions of complex **3a** were studied. The summary is shown in Scheme 2.

Alkylidene complexes are susceptible to protonation processes. In this way, the addition of an excess of trifluoromethanesulfonic acid to complex **3a** and further crystallization from acetone leads to an acetone adduct of compound $[Ru(\eta^5\text{-}C_5Me_5)(\kappa^2\text{-}P,N\text{-}PiPr_2NHC_5H_4N)(\eta^2\text{-}$



Scheme 2. Chemical reactivity of **3a**.

$CH_2C_6H_5)][CF_3SO_3]_2$ (**4a**) as red needle crystals. The structure of **4a**·Me_2CO has been elucidated by means of single-crystal X-ray analysis. The structure of the cation in **4a** is shown in Figure 3.

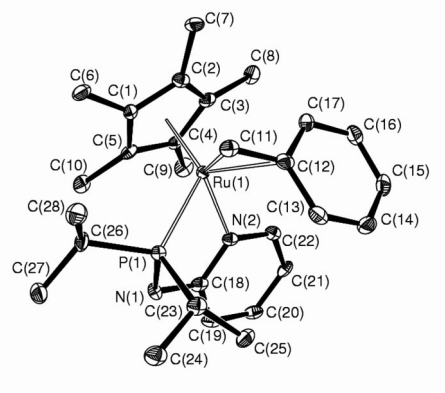


Figure 3. ORTEP view of cation complex $[Ru(\eta^5\text{-}C_5Me_5)(\kappa^2\text{-}P,N\text{-}PiPr_2NHC_5H_4N)(\eta^2\text{-}CH_2C_6H_5)]^{2+}$ in **4a**·Me_2CO. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Ru(1)–cyclopentadienyl(centroid) 1.922(4), Ru(1)–P(1) 2.334(1), Ru(1)–N(2) 2.111(3), Ru(1)–C(11) 2.163(4), Ru(1)–C(12) 2.332(4), P(1)–N(1) 1.711(3), N(1)–C(18) 1.379(5), C(11)–C(12) 1.445(6); P(1)–Ru(1)–N(2) 76.81(10), P(1)–Ru(1)–C(11) 84.76(12), P(1)–Ru(1)–C(12) 99.94(12), N(2)–Ru(1)–C(11) 128.33(15), N(2)–Ru(1)–C(12) 99.21(15), C(11)–Ru(1)–C(12) 37.26(16), Ru(1)–C(11)–C(12) 77.7(2), Ru(1)–C(12)–C(11) 1 65.0(2).

The crystallographic study reveals a dicationic complex $[Ru(\eta^5\text{-}C_5Me_5)(\kappa^2\text{-}P,N\text{-}PiPr_2NHC_5H_4N)(\eta^2\text{-}CH_2C_6H_5)]^{2+}$, which represents a protonated form of complex $[Ru(\eta^5\text{-}C_5Me_5)(\kappa^2\text{-}P,N\text{-}PiPr_2NHC_5H_4N)(=CHC_6H_5)]^{+}$ in **3a**. Bond lengths and angles are in agreement with the η^2 coordination of the benzyl ligand. The angle $Ru–C_{benzylic}–C_{ipso}$ of 77.7(2)° is much lower than the tetrahedral value expected for a η^1-alkyl coordination. Also, the η^2 instead of η^3 interaction is shown by the bond lengths [$Ru–C_{benzylic}$ = 2.163(4) Å, $Ru–C_{ipso}$ = 2.332(4) Å] and much longer $Ru–C_{ortho}$ distances: Ru(1)–C(17) 2.717(4) Å and Ru(1)–C(13) 3.214(5) Å. These data are quite different from those reported for $[Ru(PMe_3)_3\{\eta^4\text{-}OC(O)C_6H_4CH_2\}]$ in which a η^3-benzyl ligand shows a much shorter $Ru–C_{ortho}$ bond length, 2.411(2) Å.[34] The bond length C(11)–C(12) [1.445(6) Å] is shorter than a single C–C bond, likely due to some π delocalization from the phenyl ring and to the fact that it is not very different from a metal-activated double bond. However, these data do not exactly match those of an activated π olefin, and some σ-alkyl interaction of the benzyl ligand is indicated by the asymmetric η^2 coordination that was found. Other η^2-benzyl complexes have been previously reported, usually containing an early transition metal,[35–41] but, as far as we are aware, this is the first structurally characterized example of a ruthenium complex that contains a η^2-benzyl ligand. In our case, in contrast to complexes $[(C_5H_5)_2Zr(CH_2\text{-}Ar)]^{+}$,[42] η^2 coordination does not require the contribution of one solvent molecule as coligand.

The NMR spectroscopic data are in agreement with those reported for other transition-metal complexes that contain η^2-benzyl ligands. Methylene protons are diastereotopic and appear as two multiplets: one at δ = 2.71 ppm and the other as a double doublet at δ = 5.00 ppm. In particular, this last value shows a clear difference from an alkyl hydrogen and is closer to a olefin hydrogen. However, the methylene carbon appears at δ = 49.1 ppm, which is clearly out of range for alkyl carbon atoms (20–30 ppm) or for free olefin carbon atoms (around 120 ppm). In the ^1H NMR spectrum, the five phenyl hydrogen atoms are inequivalent, and the same occurs in the $^{13}C\{^1H\}$ NMR spectrum for the six carbon atoms. Equivalence on the NMR spectroscopic scale can be introduced in η^2- and η^3-benzyl complexes by fluxionality: in the case of $[Mo(C_5H_5)(NO)(\eta^2\text{-}CH_2Ph)Cl]$, a change in hapticity (η^2–η^1–η^2) and the rotation of the phenyl ring were invoked to account for the observed equivalence at room temperature.[40] In $[Ni(\eta^3\text{-}CH_2C_6H_5)Cl(PMe_3)]$ and $[Ni(\eta^1\text{-}CH_2C_6H_5)Cl(PMe_3)_2]$, the equivalence was explained by fast exchange of phosphane and fast suprafacial rearrangement.[43] Unfortunately, although ^1H and $^{13}C\{^1H\}$ NMR spectroscopic benzylic chemical shifts disregard a η^1-benzyl ligand, our NMR spectroscopic data do not allow us to discern between metal-bonded η^2- and η^3-benzyl in solution.

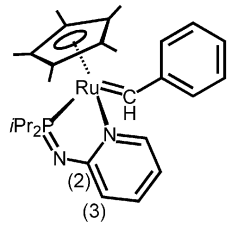
Several examples of reactions of phenylcarbene complexes with Brønsted acids have been reported.[27,28,44] They lead to η^1-benzyl (alkyl) or η^3-benzyl products depending on the nature of the anion present in the acid. For instance, treatment of the osmium complex $[Os(C_5H_5)Cl(PiPr_3)(=CHPh)]$ with HBF_4 affords η^3-benzyl complex $[Os(C_5H_5)Cl(PiPr_3)(\eta^3\text{-}C_6H_5CH_2)][BF_4]$.[29]

Regarding the mechanism that operates in these transformations, Werner pointed out two routes. In the first one, the nucleophilic carbenic atom can suffer a straightforward addition of H^+, followed by the coordination of benzyl ligand. Alternatively, the second possibility consists of the electrophilic attack on the rich metal centre and further transfer to the α-carbon atom. In our case, transient hydride species were detected through in situ NMR spectroscopic experiments that gave support to the second possibility. However, there were other unknown intermediates detected, which suggests that the real operating mechanism can be quite complex. We have been unable to find any evidence about NH participation, but this issue cannot be disregarded.

The analogous reaction with carbene **3b** gives unclear results. A reaction monitored by in situ NMR spectroscopy showed some differences from the previously discussed reaction of carbene **3a**. Several intermediates, metastable hydride species in higher concentration than for **3a** etc. were detected. They evolved to a complex mixture of products.

Deprotonation of carbene complexes has been observed in both nucleophilic and electrophilic compounds. The presence of a chelating phosphanyl-pyridine ligand offers alternative possibilities for the reaction with bases. Treatment of a solution of **3a** in THF with an excess of base, potassium

tert-butoxide or potassium bis(trimethylsilyl)amide, produced [Ru(η^5-C_5Me_5)(P*i*Pr$_2$NC_5H_4N)(=CHC_6H_5)] (**5a**; Scheme 3). It has been obtained as a green-coloured powder that is quite soluble in nonpolar solvents like petroleum ether and benzene. The most relevant feature in its NMR spectra is the presence of characteristic carbenic low-field resonances for both ^{1}H (16.22 ppm) and ^{13}C (288.0 ppm). These data, together with the absence of a signal attributable to the NH proton, suggest that deprotonation takes place on NH and thus the carbene moiety remains intact. Moreover, the rest of the spectroscopic data shows no change of connectivity between atoms, thereby keeping the chelating ligand in a κ^2-*P*,*N* mode of coordination. However, some noticeable changes in pyridyl-ring signals reveal an alteration in the electronic structure, especially the displacement of the pyridyl carbon atom (2) signal to lower field as expected (156.9 ppm) and the unusually high coupling constant of the pyridyl carbon atom (3) ($^3J_{P,C}$ = 23 Hz).



Scheme 3. Proposed structure of **5a**.

Deprotonation of carbene **3b** cannot be carried out by using THF as solvent because an immediate reaction with this solvent occurs even at room temperature. Reactivity of THF towards metal complexes can proceed through radical C–H activation or double dehydrogenation of an α-methylene compound to form an oxacyclocarbene complex.[45] Unfortunately, after some in situ NMR spectroscopic experiments, we could not establish the nature of this process. Attempts to deprotonate carbene **3b** in diethyl ether were unsuccessful. This compound proved to be unreactive towards NaH. The use of potassium bis(trimethylsilyl)amide leads to the disappearance of carbene signals and the formation of a mixture that contains several unidentified compounds.

Although nucleophilic addition on the carbenic atom is a well-known reaction of Fischer carbenes, in our case, reactivity studies of carbene complexes towards nucleophiles present several difficulties on account of the existence of competitive reactions. Casey tested the electrophilic nature of the carbenic atom in [Re(C_5H_5)(CO)$_2$-{=C$HCH_2CH_2C(CH_3)_3$}] by means of the reaction with P$(CH_3)_3$ to afford the zwitterionic compound [Re(C_5H_5)(CO)$_2${=CH[P$(CH_3)_3$]C$H_2CH_2C(CH_3)_3$}].[46] In contrast to this rhenium carbene complex, **3a** reacts with P$(CH_3)_3$ to afford quantitatively and immediately a yellow compound characterized as [Ru(η^5-C_5Me_5){P$(CH_3)_3$}-(P*i*Pr$_2$NC_5H_4N)][BAr′$_4$] (**6a**), the result of nucleophilic substitution of the benzylidene ligand at the metal centre by the phosphane, as indicated by the ^{31}P{^{1}H} NMR spectrum, which displays a strongly coupled double doublet ($^2J_{P,P'}$ = 42 Hz). This unexpected outcome is due mainly to the severe steric congestion around the carbenic atom. Steric congestion in **3a** at Cα is also illustrated by the lack of reactivity towards Grignard reagent CH_3MgCl. The substitution of carbene by phosphane is favoured by the relative weakness of Ru=C in ambivalent carbenes. In accord with theoretical studies, complexes with characteristics between Schrock and Fischer types present weakened bonds by the energy used in matching the multiplicities of metallic and carbene fragments.[47] The use of harder and unhindered nucleophiles like hydride partially solved these inconveniences, but they could not completely eliminate undesired reactions. When NaH is used as the hydride-transfer agent, the deprotonated compound was the major product. On the other hand, the reaction of **3a** with weaker hydride-tranference reagents like $LiHBEt_3$ or $NaBH_4$/CH_3OH afforded η^1-benzyl complex [Ru(η^5-C_5Me_5)(P*i*Pr$_2$NH-C_5H_4N)(η^1-CH_2Ph)] (**7a**). Complex [Ru(η^5-C_5Me_5)(P*i*Pr$_2$-NHPy)H] was also detected, likely formed as a minor subproduct by the nucleophilic substitution of the carbene ligand by hydride. This compound will be properly reported in the near future.

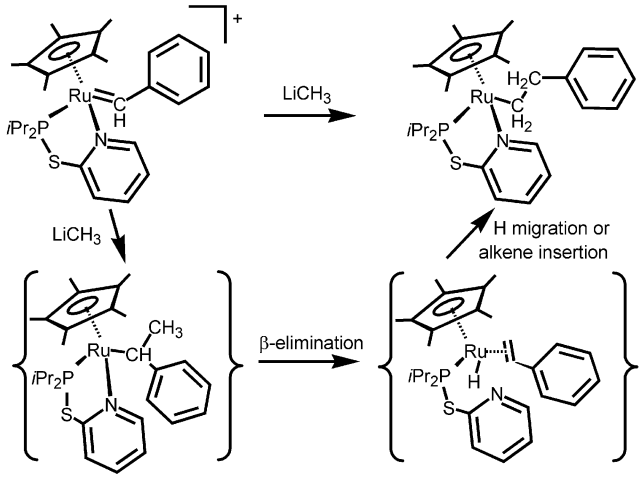
Compound **7a** was obtained as an oily orange solid, soluble in petroleum ether and nonpolar solvents, unlike its parent compound. Unambiguous characterization was provided by NMR spectra: ^{1}H NMR spectroscopy showed two resonances at δ = 2.46 and 3.10 ppm that corresponded to nonchemically equivalent CH_2 protons of the benzyl ligand. The first of them appears as a virtual triplet ($^2J_{H,P}$ = 9 Hz) and the second one, better resolved, as a double doublet ($^2J_{H,P}$ = 9 Hz, $J_{H,H}$ = 2 Hz). The ^{13}C{^{1}H} NMR spectrum displays the benzylic carbon as a doublet at δ = 12.1 ppm ($^2J_{P,C}$ = 11 Hz). ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC spectroscopy have properly correlated these signals.

Our results are in good agreement with other examples of η^1-benzyl ruthenium complexes.[48,49] In this context, Bianchini and co-workers have isolated and characterized *mer*-[(PNP)RuCl(CO)(η^1-CH_2Ph)] as an intermediate in C–C bond-cleavage reactions of terminal alkynes by water and mediated by Ru compounds.[50] Whereas NMR spectroscopy has not allowed us to distinguish between η^2 and η^3 coordination for **4a** in solution, in the case of **7a**, η^1 benzyl coordination has been unambiguously characterized by the chemical shift of the α-carbon atom being in the range of an alkyl, and the aromatic nuclei, which remain almost unaltered in relation to a nonbonded phenyl ring.

An analogous reaction of hydrides with carbene **3b** proceeded with the formation of a complex mixture of several compounds that contained the η^1 benzyl complex [Ru(η^5-C_5Me_5)(P*i*Pr$_2$SC_5H_4N)(η^1-CH_2Ph)] (analogous to **7a**), two hydride complexes and other unidentified compounds. In this case, the presumably greater stability of hydride intermediates from **3b** with respect to **3a** results in no clear reactions.

Treatment of a solution of carbene complex **3b** in ethyl ether with methyllithium gave a pink solution and microcrystalline solid. Extensive analysis, particularly by ^{1}H and

$^{13}C\{^1H\}$ NMR spectroscopy, gCOSY, DEPT, gHSQC and gHMBC allows its unequivocal characterization as [Ru(η^5-C_5Me_5)(P*i*Pr$_2$SC_5H_4N)(–$CH_2CH_2C_6H_5$)] (**8b**). ^{1}H NMR spectroscopy shows two pairs of protons at 1.38/1.83 and 1.89/1.92 ppm and does not display any hydride or carbene signal. These protons correlated with corresponding doublet carbon signals at δ = 15.0 and 40.9 ppm. Quite different results have been previously reported for reactions of similar carbene complexes with methyllithium. Indeed, they afforded hydride–olefin complexes, this being the result rationalized by a β elimination on a 16-electron alkylmetal intermediate. To explain our result in relation to earlier literature data, we postulate the mechanism shown in Scheme 4.



Scheme 4. Proposed mechanism for reaction of **3b** with $LiCH_3$.

In the first step, a branched alkyl complex is formed by direct nucleophilic attack on the carbenic atom, although an attack on the metal centre, as previously suggested,[16] cannot be disregarded. For the subsequent β elimination, the creation of a vacant site, likely by decoordination of a pyridyl group, is essential. In the η^2-alkene-hydride intermediate, a hydride transfer results in a formal alkene insertion to afford the final phenylethyl complex stable towards β elimination. Some other 2-phenyl-ethyl ruthenium complexes have already been reported, [TpRu(CO)(NCCH$_3$)(CH$_2$CH$_2$Ph)],[51] [{(C_5Me_5)Ru(μ_2-S*i*Pr-*S*,*S*)(CH$_2$CH$_2$Ph)}$_2$][52] and [Br(CH$_2$CH$_2$Ph){(C_5Me_5)Ru(μ_2-S*i*Pr-*S*,*S*)}$_2$],[53] all of them obtained by reaction with the corresponding halide or Grignard reagent containing CH_2CH_2Ph.

Conclusion

In summary, the syntheses of a new phosphanyl-pyridine ligand, P*i*Pr$_2$SC_5H_4N, two half-sandwich chloro complexes of ruthenium that contain P*i*Pr$_2$NHC_5H_4N or P*i*Pr$_2$SC_5H_4N and their respective benzylidene complexes are reported. The ambiphilic carbene character of [Ru(η^5-C_5Me_5)(κ^2-*P*,*N*-P*i*Pr$_2$XC_5H_4N)(=CHC_6H_5)]$^+$ versus nucleophiles and electrophiles has been studied. Its nucleophilic behaviour has been shown by reaction with H^+ to yield a η^2-benzyl ligand. There are some previously described examples of this coordination mode for early transition-metal benzylidene complexes, but it represents the first one in the case of ruthenium complexes. The electrophilic behaviour of [Ru(η^5-C_5Me_5)(κ^2-*P*,*N*-P*i*Pr$_2$XC_5H_4N)(=CHC_6H_5)]$^+$ has been shown by reaction with H^-, thereby giving rise to a η^1-benzyl complex. Normally, NMR spectroscopic studies allow for the unambiguous characterization of the η^1 coordination of a benzyl ligand. However, especially for late transition-metal complexes, the distinction between the usually disregarded η^2, and the generally considered η^3 mode has been revealed to be difficult. We propose, from this study, that the presence of a η^2-benzyl ligand in metal complexes should not be ruled out only based on their NMR spectra. Reaction of [Ru(η^5-C_5Me_5)(κ^2-*P*,*N*-P*i*Pr$_2$SC_5H_4N)(=CHC_6H_5)]$^+$ with $LiCH_3$ gives a 2-phenylethyl ruthenium complex stable towards β elimination, which is likely formed through β elimination on an intermediate 1-phenylethyl complex followed by hydride migration or, formally, alkene insertion.

Experimental Section

General Procedures: All synthetic operations were performed under a dry dinitrogen or argon atmosphere by following conventional Schlenk techniques. Tetrahydrofuran, diethyl ether and petroleum ether (boiling range 40–60 °C) were obtained oxygen- and water-free with an Innovative Technology Inc. solvent purification apparatus. Dichloromethane, toluene, acetone and fluorobenzene were of anhydrous quality and used as received. All solvents were deoxygenated immediately before use. Phenyldiazomethane (in toluene)[54] and NaBAr′$_4$[55] were prepared according to the reported procedures.

IR spectra were recorded in Nujol mulls with a Perkin–Elmer FTIR Spectrum 1000 spectrophotometer. NMR spectra were taken with Varian Inova 400 MHz, Varian Inova 600 MHz or Varian Gemini 300 MHz equipment. Chemical shifts are given in ppm from $SiMe_4$ (^{1}H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$). ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic signal assignments were confirmed by ^{1}H-gCOSY, 135-DEPT and gHSQC (^{1}H-^{13}C) experiments when required. Chemical-shift NMR spectra obtained for BAr′$_4^-$ and $CF_3SO_3^-$ are coincident with those found in their respective salts and they will not be listed. Microanalyses were performed with a LECO CHNS-932 elemental analyzer at the Servicio Central de Ciencia y Tecnología, Universidad de Cádiz.

Syntheses of P*i*Pr$_2$XC_5H_4N (X = NH, 1a; S, 1b): 2-Aminopyridine (or 2-mercaptopyridine) was suspended in ethyl ether and cooled to 0 °C. A stoichiometric amount of BuLi was added dropwise to the suspension and it was stirred for 1 h at room temperature. The solution was then cooled again to 0 °C and a stoichiometric amount of P*i*Pr$_2$Cl was added dropwise. After addition, the solution was stirred at room temperature and filtered to eliminate LiCl. The solvent was removed under vacuum. Compound **1a** was isolated as a white solid, whereas **1b** was obtained as a yellow viscous oil.

Compound 1a: Yield 6.96 g (92%). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, 298 K): δ = 49.61 (s) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.01–1.08 (m, 12 H, C*H*$_3$-*i*Pr), 1.76 (m, 2 H, C*H*-*i*Pr), 4.64 (d, $J_{H,P}$ = 11 Hz, N*H*), 6.62 (m, 1 H, 5), 7.06 (d, $J_{H,H}$ = 8 Hz,

1 H, 3), 7.42 (t, $J_{H,H}$ = 8 Hz, 1 H, 4), 8.01 (d, $J_{H,H}$ = 5 Hz, 1 H, 6) ppm. $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 298 K): δ = 17.1 (d, $J_{P,C}$ = 8 Hz, *C*H$_3$-*i*Pr), 18.6 (d, $J_{P,C}$ = 20 Hz, *C*H$_3$-*i*Pr), 26.3 (d, $J_{P,C}$ = 11 Hz, *C*H-*i*Pr), 108.6 (d, $J_{P,C}$ = 18 Hz, 3), 114.1 (s, 4), 137.5 (d, $J_{P,C}$ = 2 Hz, 4), 147.8 (s, 6), 160.8 (d, $J_{P,C}$ = 19 Hz, 2) ppm. IR (Nujol): $\tilde{\nu}$ = 3201 [ν(N–H)], 1602 [ν(C=N)], 908 [ν(P–N)] cm^{-1}. $C_{11}H_{19}N_2P$ (210.26): calcd. C 62.84, H 9.11, N 13.32; found C 62.88, H 9.15, N 13.27.

Compound 1b: Yield 1.36 g (75%). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, 298 K): δ = 58.7 (s) ppm. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.08–1.16 (m, 12 H, C*H*$_3$-*i*Pr), 2.03 (m, 2 H, C*H*-*i*Pr), 6.94 (t, $J_{H,H}$ = 5 Hz, 1 H, 5), 7.42 (t, $J_{H,H}$ = 8 Hz, 1 H, 4), 7.55 (d, $J_{H,H}$ = 8 Hz, 1 H, 3), 8.34 (d, $J_{H,H}$ = 5 Hz, 1 H, 6) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$, 298 K): δ = 18.7 (d, $J_{P,C}$ = 8 Hz, *C*H$_3$-*i*Pr), 19.4 (d, $J_{P,C}$ = 19 Hz, *C*H$_3$-*i*Pr), 25.4 (d, $J_{P,C}$ = 20 Hz, *C*H-*i*Pr), 119.9 (s, 5), 124.0 (d, $J_{P,C}$ = 12 Hz, 3), 136.2 (s, 4), 149.3 (s, 6), 160.0 (d, $J_{P,C}$ = 14 Hz, 2) ppm. IR (Nujol): $\tilde{\nu}$ = 1572 [ν(C=N)] cm^{-1}. $C_{11}H_{18}NPS$ (227.30): calcd. C 58.13, H 7.98, N 6.16; found C 58.17, H 8.01, N 6.10.

Syntheses of [Ru(η^5-C$_5$Me$_5$)(P*i*Pr$_2$XC$_5$H$_4$N)Cl] (X = NH, 2a; S, 2b): To prepare compound **2a**, [(η^5-C$_5$Me$_5$)RuCl]$_4$ (1 g) and a stoichiometric amount of **1a** were dissolved in petroleum ether (30 mL) and stirred at room temperature for 45 min. The resulting orange suspension was filtered and the recovered solid was washed with cold petroleum ether (10 mL) and dried. An orange powder was obtained. Compound **2b** was prepared in the same way but by using **1b** instead of **1a**. It was isolated as a reddish-orange powder.

Compound 2a: Yield 1.60 g (90%). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_3COCD_3, 298 K): δ = 124.4 (s) ppm. ^1H NMR (400 MHz, CD_3COCD_3, 298 K): δ = 1.24–1.33 (m, 12 H, C*H*$_3$-*i*Pr), 1.64 [d, $J_{P,H}$ = 2 Hz, 15 H, C$_5$(C*H*$_3$)$_5$], 2.49 (m, 1 H, C*H*-*i*Pr), 2.95 (m, 1 H, C*H*-*i*Pr), 6.48 (m, 1 H, 5), 6.82 (d, $J_{H,H}$ = 8 Hz, 1 H, 3), 7.23 (t, $J_{H,H}$ = 8 Hz, 1 H, 4), 7.52 (d, $J_{H,H}$ = 5 Hz, 1 H, N*H*), 8.37 (d, $J_{H,H}$ = 6 Hz, 1 H, 6) ppm. $^{13}C\{^1H\}$ NMR (75.45 MHz, CD_2Cl_2, 298 K): δ = 10.8 [s, C$_5$(*C*H$_3$)$_5$], 17.9 (s, *C*H$_3$-*i*Pr), 18.1 (s, *C*H$_3$-*i*Pr), 18.7 (s, *C*H$_3$-*i*Pr), 19.0 (d, $J_{P,C}$ = 7 Hz, *C*H$_3$-*i*Pr), 29.1 (d, $J_{P,C}$ = 21 Hz, *C*H-*i*Pr), 30.0 (d, $J_{P,C}$ = 21 Hz, *C*H-*i*Pr), 83.6 [s, *C*$_5$(CH$_3$)$_5$], 108.2 (s, 2), 114.6 (s, 5), 136.0 (s, 4), 153.9 (s, 6), 162.1 (d, $J_{P,C}$ = 7 Hz, 2) ppm. IR (Nujol): $\tilde{\nu}$ = 3386 (wide) [ν(N–H)], 1604 [ν(C=N)] cm^{-1}. $C_{21}H_{34}ClN_2PRu$ (482.01): calcd. C 52.35, H 7.10, N 5.83; found C 52.9, H 7.05, N 5.71.

Compound 2b: Yield 1.51 g (82%). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, 298 K): δ = 129.9 (s) ppm. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.10–1.41 (m, 12 H, C*H*$_3$-*i*Pr), 1.48 [d, $J_{P,H}$ = 1.5 Hz, 15 H, C$_5$(C*H*$_3$)$_5$], 2.62 (m, 1 H, C*H*-*i*Pr), 2.66 (m, 1 H, C*H*-*i*Pr), 6.80 (t, $J_{H,H}$ = 6 Hz, 1 H, 5), 7.22 (t, $J_{H,H}$ = 8 Hz, 1 H, 4), 7.38 (d, $J_{H,H}$ = 8 Hz, 1 H, 3), 8.83 (d, $J_{H,H}$ = 6 Hz, 1 H, 6) ppm. $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 298 K): δ = 9.9 [s, C$_5$(*C*H$_3$)$_5$], 19.1 (d, $J_{P,C}$ = 2 Hz, *C*H$_3$-*i*Pr), 19.4 (d, $J_{P,C}$ = 3 Hz, *C*H$_3$-*i*Pr), 19.7 (d, $J_{P,C}$ = 2 Hz, *C*H$_3$-*i*Pr), 20.2 (d, $J_{P,C}$ = 2 Hz, *C*H$_3$-*i*Pr), 30.3 (d, $J_{P,C}$ = 14 Hz, *C*H-*i*Pr), 31.3 (d, $J_{P,C}$ = 5 Hz, *C*H-*i*Pr), 84.3 [d, $J_{P,C}$ = 3 Hz, *C*$_5$(CH$_3$)$_5$], 119.7 (s, 5), 120.9 (d, $J_{P,C}$ = 3 Hz, 3), 133.6 (s, 4), 155.3 (d, $J_{P,C}$ = 3 Hz, 6), 166.2 (d, $J_{P,C}$ = 9 Hz, 6) ppm. IR (Nujol): $\tilde{\nu}$ = 1574 [ν(C=N)] cm^{-1}. $C_{21}H_{33}ClNPRuS$ (499.06): calcd. C 50.54, H 6.66, N 2.81; found C 50.59, H 6.69, N 2.80.

Synthesis of [Ru(η^5-C$_5$Me$_5$)(P*i*Pr$_2$NHC$_5$H$_4$N)(=CHC$_6$H$_5$)][BAr′$_4$] (3a): Freshly prepared phenyldiazomethane (3 mmol in toluene) was added to a solution of NaBAr′$_4$ in fluorobenzene (0.5 mmol in 5 mL). Complex **2a** (0.5 mmol) was immediately added to the resulting orange-red solution. The solution became deep blue-green with abundant N_2(g) evolution and was stirred for 5 min and filtered through Na_2SO_4. After filtration, the solvent was removed under vacuum. The resulting residue was washed with petroleum ether (2 × 10 mL), thereby affording a greenish-blue solid.

Compound 3a: Yield 0.67 g (95%). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_2Cl_2, 298 K): δ = 137.3 (s) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 0.65, 0.97, 1.24 (m, 12 H, C*H*$_3$-*i*Pr), 1.70 [d, $J_{P,H}$ = 1 Hz, 15 H, C$_5$(C*H*$_3$)$_5$], 2.23 (m, 1 H, C*H*-*i*Pr), 2.48 (m, 1 H, C*H*-*i*Pr), 5.67 (d, $J_{P,H}$ = 3 Hz, 1 H, N*H*), 6.64 (t, 1 H), 7.00 (d, $J_{H,H}$ = 8 Hz, 1 H), 7.20–7.30, 7.49 (d, 2 H), 16.26 (s, 1 H, Ru=C*H*) ppm. ^{13}C NMR (75.45 MHz, CD_2Cl_2, 298 K): δ = 10.8 [s, C$_5$(*C*H$_3$)$_5$], 16.5 (d, $J_{P,C}$ = 8 Hz, *C*H$_3$- *i*Pr), 16.9 (m, *C*H$_3$-*i*Pr), 28.6 (d, $J_{P,C}$ = 19 Hz, *C*H-*i*Pr), 30.7 (d, $J_{P,C}$ = 34 Hz, *C*H-*i*Pr), 101.7 [s, *C*$_5$(CH$_3$)$_5$], 110.4 (d, $J_{P,C}$ = 6 Hz, 3), 117.4 (s, 5), 126.8–131.5, (s, C$_6$H$_5$), 139.5 (s, 4), 155.6 (s, 6), 162.4 (s, 2), 305.8 (d, $^2J_{P,C}$ = 16 Hz, Ru=*C*) ppm. $C_{60}H_{52}BF_{24}N_2PRu$ (1399.90): calcd. C 51.48, H 3.74, N 2.00; found C 51.75, H 3.80, N 1.96.

Synthesis of [Ru(η^5-C$_5$Me$_5$)(P*i*Pr$_2$SC$_5$H$_4$N)(=CHC$_6$H$_5$)][BAr′$_4$] (3b): Freshly prepared phenyldiazomethane (3 mmol in toluene) was added to a solution of complex **2b in** fluorobenzene (0.25 g, 0.5 mmol). A solution of NaBAr′$_4$ in fluorobenzene (0.5 mmol in 5 mL) was immediately added. The orange-red solution thus obtained became dark green with abundant N_2(g) evolution. It was stirred for 5 min and filtered through anhydrous Na_2SO_4. After filtration the solvent was removed under vacuum. The resulting residue was washed with petroleum ether (4 × 10 mL), thereby affording a dark green solid.

Compound 3b: Yield 0.60 g (84.6%) $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_2Cl_2, 298 K): δ = 131.3 (s) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 0.79–0.94, 1.26–1.39 (m, 12 H, CH$_3$-*i*Pr), 1.56 [d, $J_{H,P}$ = 1 Hz, 15 H, C$_5$(C*H*$_3$)$_5$], 2.55 (m, 2 H, C*H*-*i*Pr), 7.12 (t, $J_{H,H}$ = 7 Hz, 1 H), 7.58 (m), 7.73 (d, $J_{H,H}$ = 8 Hz), 7.40 (m), 7.50 (d, $J_{H,H}$ = 8 Hz), 8.05 (m), 8.22 (d, $J_{H,H}$ = 6 Hz), 17.14 (s, Ru=C*H*) ppm. $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2, 298 K): δ = 10.3 [s, C$_5$(*C*H$_3$)$_5$], 18.4, 18.5 (s, *C*H$_3$-*i*Pr), 19.0 (d, $J_{P,C}$ = 3 Hz, *C*H$_3$-*i*Pr), 19.9 (s, $J_{P,C}$ = 4 Hz, *C*H$_3$-*i*Pr), 29.7 (d, $J_{P,C}$ = 16 Hz, *C*H-*i*Pr), 33.1 (d, $J_{P,C}$ = 16 Hz, *C*H-*i*Pr), 100.9 [d, $J_{P,C}$ = 2 Hz, *C*$_5$(CH$_3$)$_5$], 118.0 (d, $^3J_{P,C}$ = 4 Hz, 3), 123.9 (d, $J_{P,C}$ = 4 Hz), 126.5, 126.9, 128.6, 128.6, 129.0–129.9 (s, *C*$_6$H$_5$), 167.3 (d, $^2J_{P,C}$ = 6 Hz, 2), 316.1 (d, $^2J_{P,C}$ = 16 Hz, Ru=*C*) ppm. $C_{60}H_{51}BF_{24}NPRuS$ (1416.95): calcd. C 50.85, H 3.63, N 0.99; found C 50.90, H 3.69, N 0.96.

Synthesis of [Ru(η^5-C$_5$Me$_5$)(P*i*Pr$_2$NHC$_5$H$_4$N)(η^2-CH$_2$C$_6$H$_5$)][CF$_3$SO$_3$]$_2$ (4a): A solution of compound **3a** (0.7 g, 0.5 mmol) in dichloromethane was treated with an excess amount of trifluoromethanesulfonic acid. Immediately the reaction mixture became red and was stirred over 30 min at room temperature. The solution was then filtered through sodium sulfate and the solvent was removed under vacuum. Addition of acetone to the resulting oil caused the precipitation of red crystals, which were washed with petroleum ether and diethyl ether. The compound was obtained as an acetone adduct.

Compound 4a·CH$_3$COCH$_3$: Yield 0.45 g (66.7%). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_2Cl_2, 298 K): δ = 122.7 (s) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 0.75 (m, 3 H, CH$_3$-*i*Pr), 1.47–1.62 (m, 9 H, CH$_3$-*i*Pr), 1.85 [s, 15 H, C$_5$(C*H*$_3$)$_5$], 2.11 (s, C*H*$_3$COC*H*$_3$), 2.55 (m, 2 H, C*H*-*i*Pr), 3.28 (m, 1 H, Ru-C*H*), 5.00 (dd, $J_{H,H}$ = 11 Hz, $J_{H,P}$ = 4 Hz, Ru-C*H*), 6.07 (d, $J_{H,H}$ = 8 Hz, 1 H), 6.78 (t, $J_{H,H}$ = 8 Hz, 1 H), 6.81 (d, $J_{H,H}$ = 8 Hz, 1 H), 7.21 (t, $J_{H,H}$ = 8 Hz, 1 H), 7.31 (t, $J_{H,H}$ = 8 Hz, 1 H), 7.35 (d, $J_{H,H}$ = 8 Hz, 1 H), 7.52 (t, $J_{H,H}$ = 7 Hz, 1 H), 7.76 (t, $J_{H,H}$ = 7 Hz, 1 H), 7.86 (d, $J_{H,H}$ = 8 Hz, 1 H), 8.80 (s, N*H*) ppm. ^{13}C NMR (75.45 MHz, CD_3COCD_3, 298 K): δ = 10.5 [s, C$_5$(*C*H$_3$)$_5$], 17.1 (d, $J_{P,C}$ = 2 Hz, *C*H$_3$-*i*Pr), 18.2 (d, $J_{P,C}$ = 4 Hz, *C*H$_3$-*i*Pr), 18.7 (d, $J_{P,C}$ = 4 Hz, *C*H$_3$-*i*Pr), 19.1 (d, $J_{P,C}$ = 2 Hz, *C*H$_3$-*i*Pr) (methinic carbon atoms from isopropyl

groups overlap with those from acetone), 49.1 (d, $J_{P,C}$ = 4 Hz, Ru-CH_2), 103.4 [s, $C_5(CH_3)_5$], 110.5 (s), 113.6 (d, $J_{P,C}$ = 7 Hz), 120.9 (s), 129.0 (s), 134.2 (s), 136.2 (s), 142.3 (s), 143.1 (s), 153.1 (s), 162.0 (d, $^2J_{P,C}$ = 7 Hz, 2) ppm. IR (Nujol): $\tilde{\nu}$ = 3399 [ν(N–H)], 1613 [ν(C=N)] cm^{-1}. $C_{33}H_{47}F_6N_2O_7PRuS_2$ (893.90): calcd. C 44.34, H 5.30, N 3.13; found C 44.53, H 5.39, N 3.08.

Synthesis of [Ru(η⁵-C_5Me_5)(P*i*$Pr_2NC_5H_4N$)(=CHC_6H_5)] (5a): Complex **3a** (0.7 g, 0.5 mmol) was dissolved in tetrahydrofuran (8 mL). An excess amount of base, potassium *tert*-butoxide or potassium bis(trimethylsilyl)amide (1 mmol), was added to this solution. The solution was then stirred at room temperature over 5 min. The solvent was removed and the residue was extracted with petroleum ether (2 × 10 mL). The resulting green solution was filtered through sodium sulfate and cooled, thereby affording green microcrystals.

Compound 5a: Yield 0.11 g (41.1%). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6, 298 K): δ = 132.5 (s) ppm. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 0.76 (m, 3 H, CH_3-*i*Pr), 0.88 (m, 3 H, CH_3-*i*Pr), 1.04 (m, 3 H, CH_3-*i*Pr), 1.26 (m, 3 H, CH_3-*i*Pr), 1.45 [d, $J_{H,P}$ = 1 Hz, 15 H, $C_5(CH_3)_5$], 1.81 (m, 1 H, C*H*-*i*Pr), 2.42 (m, 1 H, C*H*-*i*Pr), 5.70 (m, 1 H, 4), 6.88 (m, 1 H, 4), 7.01 (m, 3 H, Ph + 6), 7.12 (m, 2 H, Ph + 3), 7.45 (m, 2 H, Ph), 16.27 (br. s, 1 H, Ru=C*H*) ppm. ^{13}C NMR (100.6 MHz, C_6D_6, 298 K): δ = 10.6 [s, $C_5(CH_3)_5$], 16.8 (d, $J_{P,C}$ = 6 Hz, *C*H$_3$-*i*Pr), 17.2 (s, *C*H$_3$-*i*Pr), 17.4 (d, $J_{P,C}$ = 3 Hz, *C*H$_3$-*i*Pr), 19.3 (d, $J_{P,C}$ = 1 Hz, *C*H$_3$-*i*Pr), 29.0 (d, $J_{P,C}$ = 30 Hz, *C*H-*i*Pr), 31.4 (d, $J_{P,C}$ = 43 Hz, *C*H-*i*Pr), 99.4 [d, $J_{P,C}$ = 1 Hz, $C_5(CH_3)_5$], 106.7 (s, 5), 114.1 (d, $J_{P,C}$ = 23 Hz, 3), 126.7–128.9 (Ph), 135.3 (d, $J_{P,C}$ = 3 Hz, 4), 152.4 (d, $J_{P,C}$ = 3 Hz, 6), 156.9 (s, *ipso*-Ph), 175.6 (s, 2), 288.0 (d, $J_{P,C}$ = 10 Hz, C_α) ppm. $C_{28}H_{39}N_2P_1Ru$ (535.67): calcd. C 62.78, H 7.34, N 5.23; found C 62.85, H 7.66, N 5.02.

Synthesis of [Ru(η⁵-C_5Me_5)(P*i*$Pr_2NHC_5H_4N$)(PMe_3)][BAr′$_4$] (6a): Compound **3a** (0.7 g, 0.5 mmol) was dissolved in dichloromethane (8 mL). An excess amount of PMe_3 was added. Immediately the bluish reaction mixture became orange. The solution was stirred over 20 min at room temperature and the solvent was removed. The remaining solid residue was washed with petroleum ether (3 × 10 mL) and dried under vacuum to afford a pale yellow microcrystalline solid.

Compound 6a: Yield 0.61 g (88%). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_2Cl_2, 298 K): δ = 130.4 (d, $J_{P,P}$ = 42 Hz, *Pi*$Pr_2NHC_5H_4N$), 4.6 (d, $J_{P,P}$ = 42 Hz, *P*Me_3) ppm. ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 0.93 (m, 3 H, CH_3-*i*Pr), 1.07 [d, $J_{H,P}$ = 8 Hz, P(CH_3)$_3$], 1.27–1.53 (m, 9 H, CH_3-*i*Pr), 1.69 [t, $J_{H,P}$ = 1.5 Hz, 15 H, $C_5(CH_3)_5$], 2.23 (m, 1 H, C*H*-*i*Pr), 2.44 (m, 1 H, C*H*-*i*Pr), 6.54 (dt, $J_{H,H}$ = 6.5 H, 1 Hz, 4), 7.19–7.53 (m) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2, 298 K): δ = 7.5 [d, $^1J_{P,C}$ = 56 Hz, P(*C*H$_3$)$_3$], 9.9 [s, $C_5(CH_3)_5$], 15.4 (d, $J_{P,C}$ = 8 Hz, *C*H$_3$-*i*Pr), 16.4 (d, $J_{P,C}$ = 8 Hz, *C*H$_3$-*i*Pr), 17.6 (s, *C*H$_3$-*i*Pr), 18.0 (d, $J_{P,C}$ = 8 Hz, *C*H$_3$-*i*Pr), 29.6 (d, $J_{P,C}$ = 19 Hz, *C*H-*i*Pr), 30.5 (d, $J_{P,C}$ = 50 Hz, *C*H-*i*Pr), 90.4 [s, $C_5(CH_3)_5$], 109.4 (d, $J_{P,C}$ = 6 Hz, 3), 115.1 (s, 5), 136.4 (s, 4), 151.6 (s, 6), 162.1 (d, $^2J_{P,C}$ = 11 Hz, 2) ppm. IR (Nujol): $\tilde{\nu}$ = 3402 [ν(N–H)], 1606 [ν(C=N)] cm^{-1}. $C_{56}H_{55}BF_{24}N_2P_2Ru$ (1385.86): calcd. C 48.53, H 4.01, N 2.02; found C 49.02, H 4.11, N 1.96.

Synthesis of [Ru(η⁵-C_5Me_5)(P*i*$Pr_2NHC_5H_4N$)(η¹-$CH_2C_6H_5$)] (7a): Complex **3a** (1.05 g, 0.75 mmol) and $NaBH_4$ (1.5 mmol) were dissolved in tetrahydrofuran (8 mL) and methanol (2 mL) was added. The reaction mixture became orange-red during treatment with bubbling H_2. It was then stirred over 20 min at room temperature and the solvent was removed. The remaining residue was extracted with petroleum ether (4 × 20 mL). The resulting solution was filtered through sodium sulfate. After filtration, petroleum ether was removed to afford an orange oil.

Compound 7a: Yield 0.081 g (20%). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6, 298 K): δ = 136.7 (s) ppm. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 1.03 (m, 3 H, CH_3-*i*Pr), 1.13 (m, 3 H, CH_3-*i*Pr), 1.24 (m, 3 H, CH_3-*i*Pr), 1.38 (m, 3 H, CH_3-*i*Pr), 1.86 [d, *J* = 1 Hz, 15 H, $C_5(CH_3)_5$], 2.10 (m, 1 H, C*H*-*i*Pr), 2.46 (vt, *J* = 9 Hz, 1 H, Ru-C*H*), 2.82 (m, 1 H, C*H*-*i*Pr), 3.10 (dd, $J_{H,H}$ = 9 Hz, $J_{H,P}$ = 2 Hz, 1 H, Ru-C*H*), 5.94 (d, *J* = 8 Hz, 3), 6.10 (m, 5), 7.0–7.5 (Ph), 7.77 (d, *J* = 6 Hz, 6), 7.84 (br. s, N*H*), 8.55 (t, unresolved, 4) ppm. ^{13}C NMR (75.45 MHz, C_6D_6, 298 K): δ = 11.3 [s, $C_5(CH_3)_5$], 12.1 (d, *J* = 11 Hz, Ru-*C*H$_2$), 17.8 (d, $J_{P,C}$ = 3 Hz, *C*H$_3$-*i*Pr), 17.8 (d, $J_{P,C}$ = 4 Hz, *C*H$_3$-*i*Pr), 18.5 (d, $J_{P,C}$ = 7 Hz, *C*H$_3$-*i*Pr), 19.1 (d, $J_{P,C}$ = 9 Hz, *C*H$_3$-*i*Pr), 28.1 (d, $J_{P,C}$ = 24 Hz, *C*H-*i*Pr), 32.0 (d, $J_{P,C}$ = 15 Hz, *C*H-*i*Pr), 86.6 [d, $J_{P,C}$ = 4 Hz, $C_5(CH_3)_5$], 106.2 (d, $J_{P,C}$ = 6 Hz, 3), 114.2 (s, 5), 126.1–131.1 (Ph), 137.8 (s, 4), 154.5 (d, $J_{P,C}$ = 2 Hz, 6), 161.0 (d, $J_{P,C}$ = 13 Hz, 2) ppm. $C_{28}H_{41}N_2PRu$ (539.66): calcd. C 62.53, H 7.70, N 5.21; found C 62.65, H 7.29, N 5.10.

Synthesis of [Ru(η⁵-C_5Me_5)(P*i*$Pr_2SC_5H_4N$)(–$CH_2CH_2C_6H_5$)] (8b): A green solution of carbene complex **3b** (0.25 g, 0.17 mmol) was treated with methyllithium (0.2 mL, 0.3 mmol, 1.6 M in diethyl ether). The reaction mixture became red. After 10 min of reaction at room temperature, the solvent was removed until dryness and the resultant oil was extracted in petroleum ether and filtered through anhydrous sodium sulfate. Then, the pink solution was concentrated to 5 mL and cooled to –20 °C, thereby affording after several days tiny pink microcrystals. They were separated by decantation.

Compound 8b: Yield 0.035 g (35%). $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6, 298 K): δ = 151.0 (s) ppm. ^1H NMR (600 MHz, C_6D_6, 298 K): δ = 1.06–1.16 (m, 12 H, CH_3-*i*Pr), 1.38 (m, 1 H, Ru-CH_2), 1.69 [d, *J* = 1 Hz, 15 H, $C_5(CH_3)_5$], 1.73 (m, 1 H, Ru-CH_2), 1.89 (m, 1 H, Ru-CH$_2$-CH_2), 2.14 (m, 1 H, C*H*-*i*Pr), 2.52–2.60 (m, 2 H, C*H*-*i*Pr, Ru-CH$_2$-CH_2), 6.06 (t, $J_{H,H}$ = 7 Hz, 1 H, 5), 6.43 (t, $J_{H,H}$ = 8 Hz, 1 H, 4), 7.03 (t, $J_{H,H}$ = 7 Hz, 1 H, *p*-Ph), 7.12 (d, $J_{H,H}$ = 8 Hz, 1 H, 3), 7.20 (t, $J_{H,H}$ = 7 Hz, 2 H, *m*-Ph), 7.24 (d, $J_{H,H}$ = 8 Hz, 2 H, *o*-Ph), 8.35 (d, $J_{H,H}$ = 7 Hz, 1 H, 6) ppm. ^{13}C NMR (100.5 MHz, C_6D_6, 298 K): δ = 10.7 [s, $C_5(CH_3)_5$], 15.0 (d, $J_{P,C}$ = 13 Hz, Ru-*C*H$_2$), 17.5 (d, $J_{P,C}$ = 4 Hz, *C*H$_3$-*i*Pr), 19.3 (d, $J_{P,C}$ = 3 Hz, *C*H$_3$-*i*Pr), 19.5 (vt, $J_{P,C}$ = 3 Hz, *C*H$_3$-*i*Pr), 30.3 (d, $J_{P,C}$ = 18 Hz, *C*H-*i*Pr), 31.8 (d, $J_{P,C}$ = 9 Hz, *C*H-*i*Pr), 40.9 (d, $J_{P,C}$ = 3 Hz, Ru-CH$_2$-*C*H$_2$), 88.8 [d, $J_{P,C}$ = 4 Hz, $C_5(CH_3)_5$], 118.8 (s, 3), 121.1 (d, $J_{P,C}$ = 4 Hz, 3), 124.3 (s, *p*-Ph), 128.1 (s, *o*-Ph), 128.2 (s, *m*-Ph), 129.4 (s, 4), 150.6 (d, $J_{P,C}$ = 1 Hz, *i*-Ph), 154.7 (d, $J_{P,C}$ = 4 Hz, 6), 165.0 (d, $^2J_{P,C}$ = 9 Hz, 2) ppm. $C_{29}H_{42}NPRuS$ (568.76): calcd. C 61.24, H 7.44, N 2.46; found C 61.25, H 7.46, N 2.45.

Crystal Structure Analysis: Suitable single crystals of **2b**, **3a** and **4a** were obtained. Each crystal was mounted on a glass fibre and then transferred to the cold nitrogen gas stream of a Bruker Smart APEX CCD three-circle diffractometer (*T* = 100 K) with a sealed-tube source and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz. Crystal data and experimental details are given in Table 1. In each case, four sets of frames were recorded over a hemisphere of the reciprocal space by omega scan with δ(ω) 0.30° and exposure of 10 s per frame. Correction for absorption was applied by scans of equivalents using the SADABS program.[56] An insignificant crystal decay correction was also applied. The structures were solved by direct (**2b**, **4a**·Me_2CO) or Patterson (**3a**) methods, completed by subsequent difference Fourier syntheses and refined on F^2 by full-matrix least-squares procedures using the programs contained in the SHELXTL package.[57] Some disorder was found in **2b** for the pyridyl ring and one isopropyl group. The disorder was modelled by splitting several atoms in two positions. Most non-hydrogen atoms were refined with anisotropic displace-

Table 1. Crystal data and experimental details.

	2b	**3a**	**4a**·Me_2CO
Formula	$C_{21}H_{33}ClNPRuS$	$C_{60}H_{52}BF_{24}N_2PRu$	$C_{33}H_{47}F_6N_2O_7PRuS_2$
Formula weight	499.03	1399.89	893.89
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$ (no.14)	$P2_1/c$ (no.14)	$P\bar{1}$ (no.2)
a [Å]	17.229(3)	13.210(3)	11.196(2)
b [Å]	8.979(2)	27.972(6)	12.754(3)
c [Å]	15.953(3)	16.697(3)	14.847(3)
α [°]	90.00	90.00	67.11(3)
β [°]	111.68(3)	105.41(3)	84.96(3)
γ [°]	90.00	90.00	81.58(3)
V [Å^3]	2293.(8)	5948(2)	1931.0(7)
Z	4	4	2
$D_{calcd.}$ [g cm^{-3}]	1.445	1.563	1.537
μ (Mo-K_α) [mm^{-1}]	0.967	0.407	0.632
F(000)	1032	2824	920
Crystal size [mm]	0.27 × 0.09 × 0.09	0.37 × 0.17 × 0.05	0.26 × 0.09 × 0.08
T [K]	100(2)	100(2)	100(2)
λ [Å] (Mo-K_α)	0.71073	0.71073	0.71073
Absorption correction (T_{max}, T_{min})	1.000, 0.718	1.000, 0.869	1.000, 0749
$\theta_{min} - \theta_{max}$ [°]	1.3, 25.0	1.8, 23.8	1.8, 25.0
Dataset (h,k,l limits)	–20:20; –10:10; –18:18	–13:14; –31:31; –18:18	–13:13; –15:14; –15:17
Total, unique data, R(int)	15356, 4025, 0.0544	36735, 9049, 0.065	10195, 6700, 0.039
Observed data [$I > 2\sigma(I)$]	3704	8243	5970
Number of reflections, parameters	4025, 239	9049, 811	6700, 480
R, wR_2 [$I > 2\sigma(I)$]	0.0567, 0.1073	0.0785, 0.1789	0.0542, 0.1033
R, wR_2 (all)	0.0641, 0.1108	0.0900, 0.1877	0.0633, 0.1080
w	$1/[\sigma^2(F_o^2) + (0.160P)^2 + 12.2948P]$[a]	$1/[\sigma^2(F_o^2) + (0.0839P)^2 + 66.0316P]$[a]	$1/[\sigma^2(F_o^2) + (0.0309P)^2 + 4.2884P]$[a]
GOF	1.084	0.943	1.047
Max., average shift/error	0.001, 0.000	0.001, 0.000	0.001, 0.000
Min., max. residual density [e Å^{-3}]	–0.812, 1.003	–1.240, 0.707	–0.569, 0.940

[a] In which $P = (F_o^2 + 2F_c^2)/3$.

ment parameters, and the SHELX riding model was employed in the refinement of the hydrogen atoms.[57] The ORTEP-3 program was used for plotting.[58]

CCDC-729403 (for **2b**), -729404 (for **3a**) and -729405 (for **4a**·Me_2CO) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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