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# Cyclometallated derivatives of rhodium(III). Activation of $C(sp^3)$–H *vs.* $C(sp^2)$–H bonds

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The reaction of $RhCl_3 \cdot 3H_2O$ with a series of 6-substituted-2,2′-bipyridines HL ($N_2C_{10}H_7R$, R = $CH_2Ph$, $HL^b$; $C(CH_3)_2Ph$, $HL^{dm}$; $CH(CH_3)_2$, $HL^{ip}$; $C(CH_3)_3$, $HL^{tb}$; or $CH_2C(CH_3)_3$, $HL^{np}$) in refluxing water–acetonitrile gave cyclometallated species, either neutral, $[Rh(L)(CH_3CN)Cl_2]$, or cationic, $[Rh(L)(CH_3CN)_2Cl]^+$, resulting from direct activation of $C(sp^2)$–H or $C(sp^3)$–H bonds. Surprisingly, in the case of R = $C(CH_3)_2Ph$ metallation involved one of the methyls rather than the phenyl group. The crystal structure of $[Rh(L^b)(CH_3CN)Cl_2]$ has been determined by X-ray diffraction. Adducts $[Rh(HL)(CH_3CN)Cl_3]$, likely to be intermediates in the synthesis of the metallated species, have been isolated and characterized. Some aspects of the reactivity of the adducts and of the cyclometallated species are also reported.

## Introduction

The intramolecular activation of C–H bonds by means of transition metal ions, an important topic in organometallic chemistry, has received considerable and developing interest in recent years[1] owing to the wide range of potential applications. In this context much work has been done in our and other laboratories on the behaviour of 2-substituted pyridines and 6-substituted 2,2′-bipyridines towards metal ions such as $Pt^{II}$,[2–4] $Pd^{II}$[2,3,5] and $Au^{III}$,[3,6] the focus of the attention being the activation of C–H bonds to give cyclometallated N,C rings. In the case of rhodium(III) a number of five-membered cyclometallated complexes containing a pyridine N and a $C(sp^2)$ atom are known:[5a,7] less common are six-membered rings.[8]

As far as we know with 6-substituted 2,2′-bipyridines, only two N,N,C cyclometallated systems have been reported (R = $C_6H_5$ or $C_4H_3S$).[3,9] In this paper we describe the results of an investigation on the reaction of $RhCl_3$ with five 6-substituted 2,2′-bipyridines (see Chart 1). The nature of the substituent obviously plays an important role in the behaviour of these ligands towards metallation, both electronic and steric factors being active. We have observed previously[10] that in several cases the behaviour of these ligands is hardly predictable, subtle factors often driving the reactions towards unexpected results. In this study the substituents, benzyl and alkyl groups, were chosen in order to compare both the stability of five- *vs.* six-membered rings and the facility of $C(sp^3)$–H *vs.* $C(sp^2)$–H bond activation.

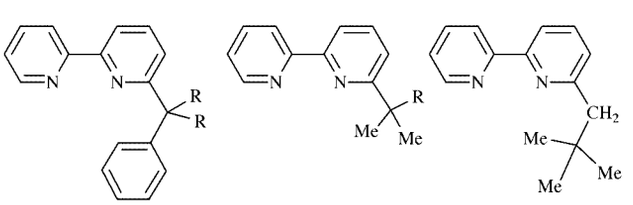



**Chart 1**

A series of rhodium(III) complexes containing an N,N,C sequence of donor atoms has been obtained by activation of $C(sp^2)$–H or $C(sp^3)$–H bonds. Noteworthy is the behaviour of the ligand $HL^{dm}$ (R = Me) which is reminiscent of that of $HL^{tb}$ (R = Me) and $HL^{ip}$ (R = H) in contrast to the behaviour of $HL^b$ (R = H). In the cases of $HL^{dm}$ and $HL^{ip}$ activation of a methyl group generates an asymmetric carbon in the cyclometallated C,N ring β to the metal atom. With the ligands $HL^b$, $HL^{ip}$ and $HL^{np}$ neutral adducts, $[Rh(HL)(CH_3CN)Cl_3]$, have been isolated and fully characterized.

## Results and discussion

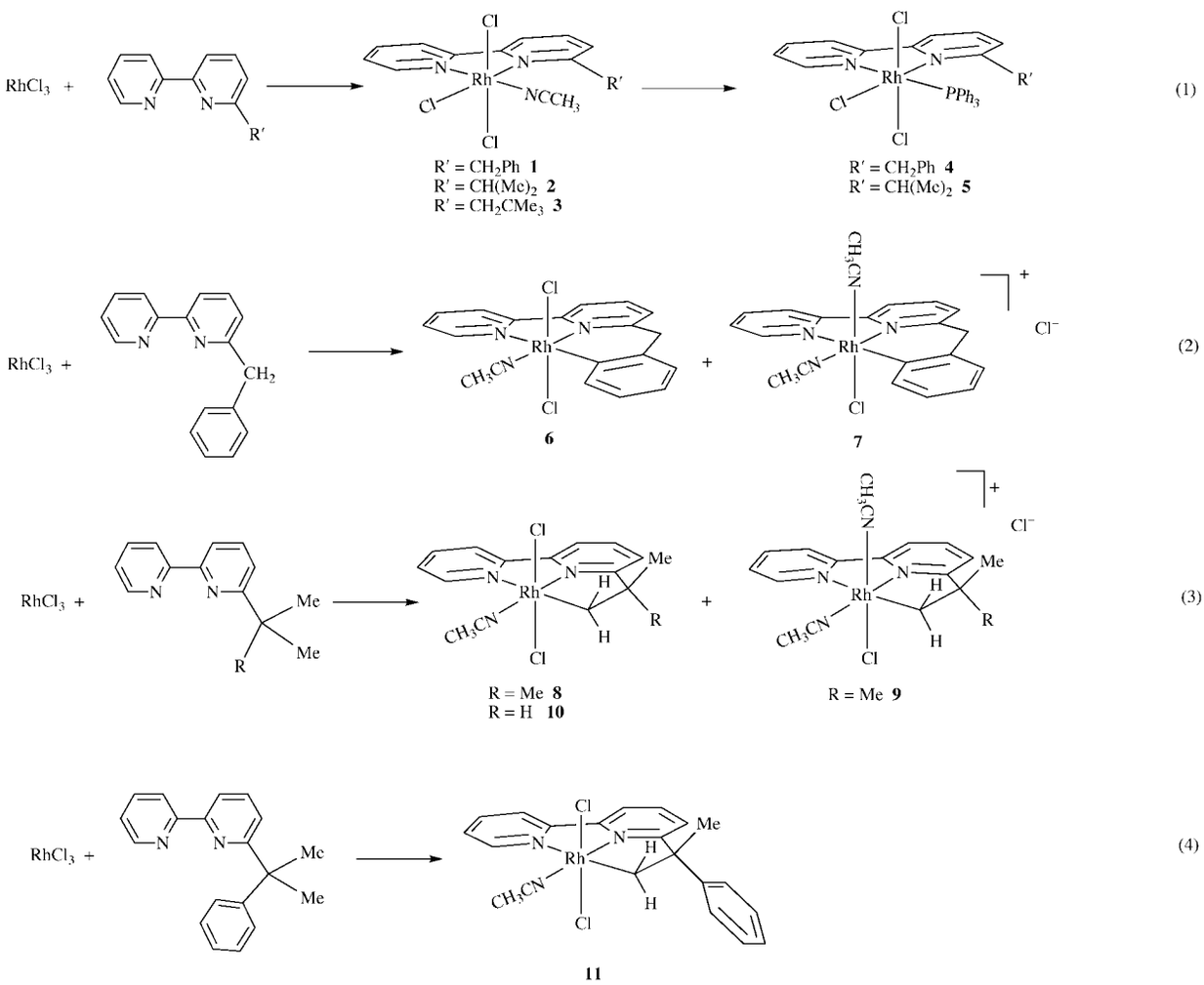
The ligands HL were prepared as previously described.[11] Reaction of $RhCl_3 \cdot 3H_2O$ in refluxing aqueous acetonitrile (1:1) afforded cyclometallated species or adducts (see Scheme 1) depending on the ligand and the experimental conditions. Pure 1:1 adducts $[Rh(HL)(CH_3CN)Cl_3]$ **1**–**3** have been obtained with the ligands $HL^b$, $HL^{ip}$ and $HL^{np}$, respectively. They have been characterized mainly on the basis of microanalyses and $^1H$ NMR spectra. In the $^1H$ NMR spectra a considerable shift of the H(6′) as well as of the aliphatic CH and $CH_2$ resonances to low field with respect to the "free" ligand (see Tables 1 and 3) is observed.

The co-ordinated $CH_3CN$ molecule is easily displaced by $PPh_3$: reaction of **1** and **2** with $PPh_3$, under mild conditions, gave compounds $[Rh(HL^b)(PPh_3)Cl_3]$ **4** and $[Rh(HL^{ip})(PPh_3)Cl_3]$ **5**, respectively, in good yields. The $^{31}P$ NMR spectra of **4** and **5** show a doublet ($\delta$ 18.4, $^1J_{Rh\text{-}P}$ = 107, **4**; 18.7, $^1J_{Rh\text{-}P}$ = 108 Hz, **5**): the $^1J_{Rh\text{-}P}$ values are consistent with a phosphorus *trans* to a ligand having a moderate *trans* influence.[12] In the $^1H$ NMR spectra the H(6′) protons, at very low field, appear as triplets due to coupling with the $^{31}P$ nucleus ($^4J_{H\text{-}P}$ = 4.6, **4**; 4.4 Hz, **5**) supporting co-ordination of the $PPh_3$ ligand *trans* to the nitrogen atom of the unsubstituted pyridine. This formulation was supported by NOE difference experiments on complex **5** ($CD_2Cl_2$ solution). Irradiation of the methyl groups signal at $\delta$ 0.65 gives enhancement of the bipyridine H(3) proton ($\delta$ 7.22), of the H(*ortho*) protons of the co-ordinated $PPh_3$ ($\delta$ 7.89) and

**Table 1** The $^{1}H$ and $^{31}P$ NMR data [a]

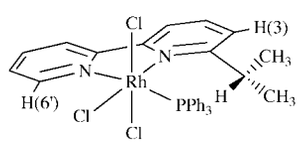
| Compound | $CH_3CN$ | $CH_3$ | $CH_2$ | CH | H(6′) | Other aromatics | $^{31}P$ |
|---|---|---|---|---|---|---|---|
| **1** $[Rh(HL^{b})(CH_3CN)Cl_3]$ | 1.90 (s) | | 4.98 (s) | | 10.09 (dd) | 7.25–8.10 | |
| **2** $[Rh(HL^{ip})(CH_3CN)Cl_3]$ | 2.63 (s) | 1.48 (d) | | 4.35 (m) | 10.07 (dd) | 7.55–8.05 | |
| **3** $[Rh(HL^{np})(CH_3CN)Cl_3]$ | 2.59 (s) | 1.11 (s) | 3.64 (s) | | 10.01 (dd) | 7.55–8.05 | |
| **4** $[Rh(HL^{b})(PPh_3)Cl_3]$ | | | 4.22 (s) | | 10.11 (td) [b] | 6.68–8.16 | 18.4 (d) [107] |
| **5** $[Rh(HL^{ip})(PPh_3)Cl_3]$ | | 0.65 (d) (6.3) | | 3.35 (m) (6.3) | 10.07 (td) [b] | 7.20–8.16 | 18.7 (d) [108] |
| **6** $[Rh(L^{b})(CH_3CN)Cl_2]$ [c] | 2.68 (s) | | 4.84 (s) [2 H] | | 9.36 (ddd) | 7.06–8.31 | |
| **7** $[Rh(L^{b})(CH_3CN)_2Cl]Cl$ | 2.40 (s) | | 4.49 [1 H] (16.0) | | 9.81 (dd) | 7.15–8.37 | |
| | 2.97 (s) | | 4.89 [1 H] (16.0) | | | | |
| **8** $[Rh(L^{tb})(CH_3CN)Cl_2]$ | 2.45 (s) | 1.62 (s) | 4.03 (d) [2.4] | | 9.22 (ddd) | 7.2–8.2 | |
| **9** $[Rh(L^{tb})(CH_3CN)_2Cl]Cl$ | 2.43 (s) | 1.54 (s) | 3.72 (8.4) [2.4] | | 9.30 (dd) | 7.38–8.42 | |
| | 2.68 (s) | 1.63 (s) | 4.06 (8.4) [2.4] | | | | |
| **9a** $[Rh(L^{tb})(CH_3CN)_2Cl]BF_4$ | 2.31 (s) | 1.49 (s) | 3.69 (8.4) [2.1] | | 9.50 (dd) | 7.31–8.23 | |
| | 2.59 (s) | 1.62 (s) | 4.09 (8.4) [2.5] | | | | |
| **10** $[Rh(L^{ip})(CH_3CN)Cl_2]$ | 2.47 (s) | 1.61 (d) (6.6) | 4.06 (m) [d] | 4.06 (m) [d] | 9.25 (dd) | 7.26–8.18 | |
| **11** $[Rh(L^{dm})(CH_3CN)Cl_2]$ | 2.42 (s) | 2.04 (s) | 4.10 (8.0) [2.6] | | 9.35 (ddd) | 6.7–8.2 | |
| | | | 4.72 (8.0) [2.7] | | | | |
| **12** $[Rh(L^{tb})(PPh_3)Cl_2]$ | | 1.48 (s) | 3.34 (t) [e] [2.3] | | 8.56 (dd) | 7.10–8.18 | 28.2 (d) [123] |

[a] Solvent $CDCl_3$ unless otherwise indicated, room temperature, coupling constants in Hz, $J_{HH}$ in parentheses, $J_{Rh\text{-}H}$ and $J_{Rh\text{-}P}$ in square brackets, chemical shifts in ppm from internal TMS ($^{1}H$) and external 85% $H_3PO_4$ ($^{31}P$). [b] $^{4}J_{P\text{-}H}$ = 4.6 (**4**) and 4.4 Hz (**5**). [c] Solvent $CD_2Cl_2$. [d] Signals overlapping, 3H ($CH + CH_2$). [e] $^{3}J_{P\text{-}H}$ = 2.3 Hz.




**Scheme 1**

of the aliphatic CH proton at $\delta$ 3.35; irradiation of the latter signal results in enhancement of the methyl groups and the *ortho* protons of $PPh_3$, but not of the H(3) proton. It seems therefore that, on the NMR timescale, rotation around the $C(sp^2)$–$CHMe_2$ bond is hindered, with the methyl groups above and under the pyridine plane and the C–H proton being held in the vicinity of the co-ordinated $PPh_3$.




**5**

**Table 2** Aromatic $^1$H and selected $^{13}$C NMR data for compounds **6**, **8**, **9**, **10** and **11** [a]

| | | 6 | 8 | 9 | 10 | 11 [b] |
|---|---|---|---|---|---|---|
| $^1$H | | | | | | |
| | H(6′) | 9.36 (ddd) | 9.22 (ddd) | 9.30 (dd) | 9.25 (dd) | 9.35 (ddd) |
| | H(5′) | 7.78 (ddd) | 7.63 (ddd) | 7.87 (ddd) | 7.64 (ddd) | 7.66 (ddd) |
| | H(4′) | 8.19 (td) | 7.99 (td) | 8.21 (td) | 8.00 (td) | 8.02 (td) |
| | H(3′) | 8.29 (dt) | 8.06 (dt) | 8.40 (dt) | 8.14 (dd) | 8.15 (ddd) |
| | H(3) | 8.10 (dd) | 7.84 (dd) | 8.16 (dd) | 7.85 (dd) | 7.84 (dd) |
| | H(4) | 7.94 (t) | 7.74 (t) | 8.02 (t) | 7.76 (t) | 7.59 (t) |
| | H(5) | 7.51 (dd) | 7.24 (dd) | 7.40 (dd) | 7.30 (dd) | 6.79 (dd) |
| | H(2″) | | | | | 7.69 (m) (2H, *o*-H) |
| | H(3″) | 7.71 (dd) | | | | 7.33 (m) (2H, *m*-H) |
| | H(4″) | 7.11 (m) [c] | | | | 7.25 (m) (1H, *p*-H) |
| | H(5″) | 7.11 (m) [c] | | | | |
| | H(6″) | 7.25 (dd) | | | | |
| $^{13}$C | | | | | | |
| | CH | | | | 48.4 | |
| | $CH_2$ | 48.8 | | | | |
| | $CH_3$ | | 32.4 | 31.6, 32.7 | 19.9 | 29.6 |
| | $CH_2Rh$ | | 35.1 (19.5) | 36.5 (19.1) | 29.4 (18.9) | 37.1 (19.6) |
| | C(6′) | 148.8 | 149.9 | 150.9 | 150.0 | 150.0 |

[a] Solvent $CDCl_3$ unless otherwise indicated, room temperature, chemical shifts in ppm from internal TMS, $^1J_{Rh\text{-}C}$ in Hz (in parentheses). [b] $^{13}$C NMR spectrum in $CD_2Cl_2$. [c] Signals overlapping.

Compounds **1**–**3** can exist in different isomeric forms, the position of the co-ordinated $CH_3CN$ being uncertain. Difference NOE spectra did not resolve this case: in the absence of structural data we tentatively propose, mainly on the basis of NMR data, a structure similar to that of compounds **4** and **5**, with the $CH_3CN$ in place of $PPh_3$. The adducts **1**–**3** can be isolated as pure products after a short time of reaction: *e.g.* **1** after 1 h in refluxing water–acetonitrile. On prolonged heating (*ca*. 20–25 h, depending on the ligand) mixtures of products are found that cannot easily be separated.

### Cyclometallated species

**(a) Activation of C(sp$^2$)–H bonds.** From the reaction of $RhCl_3$ with $HL^b$, besides the adduct **1**, other species are formed, two of which were isolated and characterized as a neutral, $[Rh(L^b)(CH_3CN)Cl_2]$ **6**, and a cationic, $[Rh(L^b)(CH_3CN)_2Cl]Cl$ **7**, cyclometallated complex (see Scheme 1). Also adduct **1** can be converted into **6** (yield *ca.* 50%) on prolonged heating in water–acetonitrile.

For compound **6** the absence in the IR spectrum (Nujol mull) of a band around 700 cm$^{-1}$, typical of a monosubstituted benzene,[13] and the absence of a proton of the phenyl substituent in the $^1$H NMR spectrum indicate *ortho*-metallation of the aromatic ring: the downfield shift of the H(6′) proton (Table 2: $\delta$ 9.36, ddd, **6**; 8.67, ddd, $HL^b$) confirms the co-ordination of the external pyridine ring. The assignment of the resonances in the $^1$H NMR spectrum has been accomplished by a two dimensional $^1$H correlation spectrum (COSY-90) allowing us to confirm the *ortho*-metallation. In the $^1$H NMR spectrum at room temperature a singlet due to the $CH_2$ protons ($\delta$ 4.84, s) is consistent with a fluxional behaviour of the six-membered ring in a boat-like conformation. A similar behaviour was reported by Hiraki *et al.*[8] for the derivative $[Rh(L^*)(PR_3)_2Cl_2]$ ($HL^*$ = 2-benzylpyridine), which was however described as containing a planar six-membered ring. On lowering the temperature to −90 °C the $^1$H spectrum shows no significant difference. On the whole the spectroscopic evidence suggests an apical co-ordination of the two chloride ions with the $CH_3CN$ ligand in the bipyridine plane. This environment has been confirmed by an X-ray diffraction study.

The structure consists of the packing of $[Rh(L^b)(CH_3CN)Cl_2]$ and $CH_2Cl_2$ molecules in the molar ratio 1:1 with no unusual van der Waals contacts. Selected bond lengths and angles are reported in Table 4 and an ORTEP[14] view of the complex molecule is shown in Fig. 1. The rhodium atom displays an octahedral co-ordination with the two chlorine atoms *trans* to each other and the N,N and C atoms of the terdentate L ligand in *mer* position. The Rh–C(13), Rh–N(2), and Rh–N(3) bond lengths, 2.018(3), 2.016(3), and 2.019(3) Å, respectively, are equal within one e.s.d. and can be compared with the Rh–C and Rh–N(*cis*) distances, 1.992(3) and 2.039(2) Å, found in the octahedral cation $[Rh(L^*)_2(2,2'\text{-bipy})]^+$,[15] **13** ($HL^*$ = 2-phenylpyridine). The present Rh–N(1) bond, 2.154(3) Å, is elongated by the *trans* influence of the aryl carbon atom, and a similar elongation is observed in **13**: Rh–N(*trans*) 2.142(2) Å. The Rh–N(2)–C(10)–C(11)–C(12)–C(13) metallacycle is in a boat conformation with the N(2), C(10), C(12) and C(13) atoms essentially coplanar, maximum deviations from their best plane being +0.017(4) Å for C(12) and −0.018(4) Å for C(10); the Rh and C(11) atoms lie 0.378(1) and 0.522(4) Å above this best plane, respectively. The $CH_3CN$ ligand is approximately linear [Rh–N(3)–C(18) angle 175.7 and N(3)–C(18)–C(19) 178.3°].

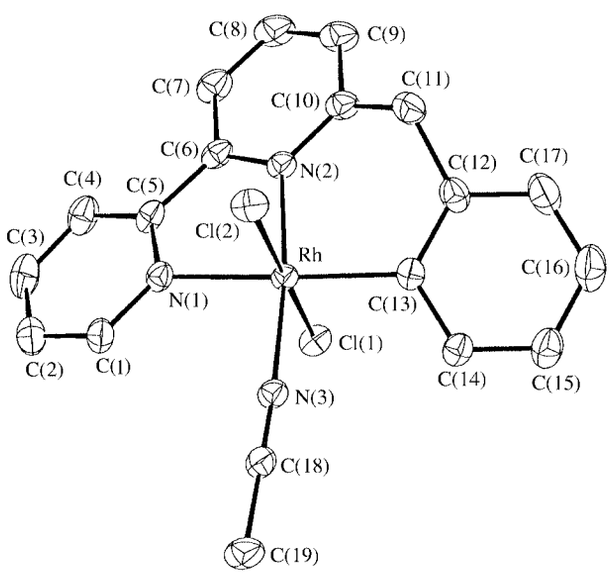



**Fig. 1** An ORTEP view of compound **6**. Ellipsoids are drawn at the 30% probability level.

**Table 3** Proton and selected $^{13}C$ NMR data for the ligands[a]

| | | HL[b] | HL[dm] | HL[ip] | HL[tb] | HL[np] |
|---|---|---|---|---|---|---|
| $^1H$ | $CH_3$ | | 1.83 (s) | 1.35 (d) | 1.43 (s) | 1.05 (s) |
| | $CH_2$ | 4.25 (s) | | | | 2.80 (s) |
| | CH | | | 3.10 (m) | | |
| | H(6′) | 8.67 (ddd) | 8.66 (ddd) | 8.65 (ddd) | 8.66 (ddd) | 8.66 (ddd) |
| | H(5′) | *ca.* 7.3[b] | *ca.* 7.3[b] | 7.26 (ddd) | 7.29 (ddd) | 7.27 (ddd) |
| | H(4′) | 7.81 (td) | 7.81 (td) | 7.78 (td) | 7.81 (ddd) | 7.79 (ddd) |
| | H(3′) | 8.45 (dt) | 8.54 (dt) | 8.50 (dt) | 8.55 (dt) | 8.42 (dt) |
| | H(3) | 8.21 (dd) | 8.22 (dd) | 8.20 (dd) | 8.21 (dd) | 8.22 (dd) |
| | H(4) | 7.69 (t) | 7.64 (t) | 7.71 (t) | 7.74 (t) | 7.69 (t) |
| | H(5) | 7.10 (dd) | 7.04 (dd) | 7.17 (dd) | 7.35 (dd) | 7.11 (d) |
| | *o*-H + *m*-H | 7.27–7.35 (m) | 7.25–7.35 (m) | | | |
| | *p*-H | 7.25 (m) | 7.19 (m) | | | |
| $^{13}C$ | $CH_3$ | | 29.5 | 22.6 | 30.1 | 29.6 |
| | $CH_2$ | 44.7 | | | | 51.8 |
| | CH | | | 33.3 | | |
| | $C(CH_3)_n$ | | 45.7 | | 37.5 | 31.9 |
| | C(6′) | 149.0 | 148.9 | 148.9 | 148.8 | 148.9 |

[a] Solvent $CDCl_3$, room temperature, chemical shifts in ppm from internal TMS. [b] Signals overlapping with the *ortho* and *meta* protons.

The cationic species **7** can be isolated, albeit in low yield (*ca.* 10%), from the mixture of products soluble in the reaction medium. Analytical and spectroscopic data indicate an ionic formulation $[Rh(L^b)(CH_3CN)_2Cl]Cl$, confirmed by conductivity measurements and FAB mass spectrum ($[M]^+$ *m*/*z* 465). In the $^1H$ NMR spectrum two resonances for the $CH_3CN$ molecules and an AB system for the benzylic protons ($\delta$ 4.49, 4.89, $J_{AB}$ = 16.0 Hz) are indicative either of a rigid system or of an asymmetric situation. Assuming by analogy with complex **6** a fluxional behaviour, as suggested by the persistence of the AB system up to +55 °C, an asymmetric co-ordination environment can be inferred with one $CH_3CN$ in apical position, and the other one in the plane of the bipyridine (see Scheme 1).

**(b) Activation of C(sp$^3$)–H bonds.** Although it is generally agreed that activation of aromatic C–H bonds is more facile than that of aliphatic bonds,[16] besides $HL^b$ we studied the behaviour of $HL^{tb}$, $HL^{ip}$ and $HL^{np}$ with the aim of obtaining C(sp$^3$)–Rh metallated systems. The reaction of $RhCl_3 \cdot 3H_2O$ with $HL^{tb}$ (Scheme 1, reaction 3) gave two cyclometallated species, as observed for $HL^b$, a neutral and a cationic complex, $[Rh(L^{tb})(CH_3CN)Cl_2]$ **8** (yield 15%) and $[Rh(L^{tb})(CH_3CN)_2Cl]Cl$ **9** (yield 80%). Surprisingly, metallation occurs easier than with $HL^b$, even at room temperature. Tentatively, a rationale can be found taking account that five-membered rings are considered more favoured than six-membered ones, or that, in the case of the *t*-butyl substituent, metallation can involve one among many (nine) C–H bonds. Evidence for a metallated $CH_2$ group in compounds **8** and **9** is provided by $^1H$ and $^{13}C$-{$^1H$} NMR spectra (see Tables 1 and 2): in particular in the $^{13}C$ NMR spectra a carbon atom directly bonded to the metal is clearly seen ($\delta$ 35.1, d, $^1J_{Rh\text{-}C}$ = 19.5 Hz, **8**; 36.5, d, $^1J_{Rh\text{-}C}$ = 19.1 Hz, **9**).

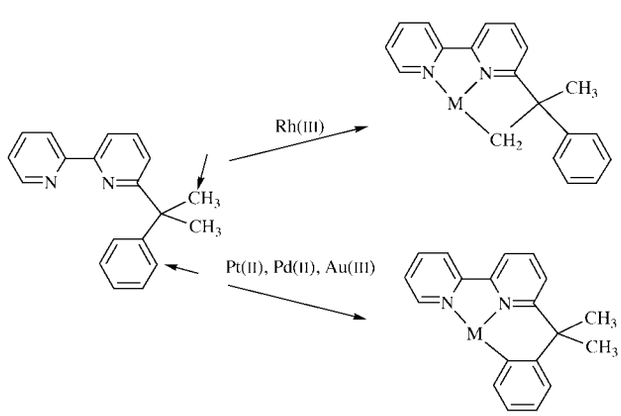
The $^1H$ NMR spectrum of complex **8** shows the equivalence of the $CH_2$ protons ($\delta$ 4.03, d, $J_{Rh\text{-}H}$ = 2.4 Hz), as well as of the two $CH_3$ groups, and is almost unaffected on lowering the temperature from +20 to −90 °C, indicating that the five-membered ring is fluxional on the NMR timescale and the chloride ligands are in apical position, as in **6**. The cationic species **9** is less symmetric: in the $^1H$ NMR spectrum the two methyls are not equivalent ($\delta$ 1.54, s; 1.63, s) and the $RhCH_2$ protons give the AB part of an ABX system ($\delta_A$ 3.72, $^2J_{Rh\text{-}H}$ = 2.4 Hz; $\delta_B$ 4.06, $^2J_{Rh\text{-}H}$ = 2.4; $^2J_{H\text{-}H}$ = 8.4 Hz). Two different co-ordinated $CH_3CN$ are present ($\delta$ 2.43, s; 2.68, s) as in complex **7**. The spectrum is consistent with one $CH_3CN$ molecule in apical position and the other in the co-ordination plane of the bipyridine. Also in the case of complex **8** a 2-D COSY spectrum helped us in the assignment of the aromatic resonances in the $^1H$ spectrum.

The chloride counter ion in complex **9** can easily be replaced by $BF_4^-$ to give complex **9a** $[Rh(L^{tb})(CH_3CN)_2Cl]BF_4$.

The activation of a C–H bond in $HL^{ip}$ and $HL^{np}$ is more difficult. In the case of $HL^{ip}$ we were able to isolate a metallated species $[Rh(L^{ip})(CH_3CN)Cl_2]$ **10**, although in very low yield and only with prolonged reaction times (*ca.* 60 h). Its formulation rests mainly on NMR data ($^1H$ and $^{13}C$). The fraction soluble in the reaction medium contains a complex mixture of different and unidentified species. With $HL^{np}$ only the adduct **3** was isolated.

It is worth mentioning that metallation of a Me substituent in $HL^{tb}$ has been previously reported in palladium(II)[2f] and platinum(II)[2f,4e] chemistry as well as in a gold(III) species, $[Au(L^{tb})Cl]^+$.[6e]

**(c) Aliphatic *vs.* aromatic activation.** Having proved that both aliphatic and aromatic C–H activation is possible we studied the reaction of $HL^{dm}$ with $RhCl_3$. Ligand $HL^{dm}$ is particularly interesting: both activation of an aromatic C(sp$^2$)–H bond, to give a six-membered ring, as with ligand $HL^b$, or of an aliphatic C(sp$^3$)–H bond, with the formation of a five-membered ring, as for $HL^{tb}$, are possible. In this case, therefore, we have to consider not only C–H aromatic *vs.* aliphatic activation but also six- *vs.* five-membered ring formation. In our laboratory we have recently studied the behaviour of $HL^{dm}$ with $d^8$ ions ($Au^{III}$,[6e] $Pd^{II}$ [17] and $Pt^{II}$ [17]): as yet, in all cases we have observed only activation of an aromatic C–H bond (see Scheme 2).

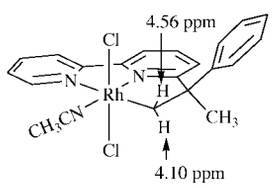



**Scheme 2**

**Table 4** Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for compound **6**

| | | | |
|---|---|---|---|
| Rh–Cl(1) | 2.349(1) | Rh–Cl(2) | 2.363(1) |
| Rh–N(1) | 2.154(3) | Rh–N(2) | 2.016(3) |
| Rh–N(3) | 2.019(3) | Rh–C(13) | 2.018(3) |
| Cl(1)–Rh–Cl(2) | 178.86(3) | Cl(1)–Rh–N(1) | 84.66(8) |
| Cl(1)–Rh–N(2) | 88.67(8) | Cl(1)–Rh–N(3) | 91.67(8) |
| Cl(1)–Rh–C(13) | 88.0(1) | Cl(2)–Rh–N(1) | 94.60(8) |
| Cl(2)–Rh–N(2) | 90.34(8) | Cl(2)–Rh–N(3) | 89.25(8) |
| Cl(2)–Rh–C(13) | 92.7(1) | N(1)–Rh–N(2) | 79.2(1) |
| N(1)–Rh–N(3) | 94.3(1) | N(1)–Rh–C(13) | 170.8(1) |
| N(2)–Rh–N(3) | 173.4(1) | N(2)–Rh–C(13) | 95.1(1) |
| N(3)–Rh–C(13) | 91.5(1) | | |

With $RhCl_3$ (reaction 4, Scheme 1) a product identified as $[Rh(L^{dm})(CH_3CN)Cl_2]$ **11** was isolated. The presence, in the IR spectrum, of a band at 706 $cm^{-1}$ and, in the $^1H$ NMR spectrum, of a $CH_2$ coupled to Rh ($\delta_A$ 4.10, $^2J_{Rh\text{-}H}$ = 2.6 Hz; $\delta_B$ 4.72, $^2J_{Rh\text{-}H}$ = 2.7; $^2J_{H\text{-}H}$ = 8.0 Hz) as well as twelve aromatic protons, indicate the activation of a C–H bond of one methyl group. To help in the assignments a series of NOE difference experiments ($CD_2Cl_2$) were carried out. The data show that the proton which resonates at $\delta$ 4.10 is on the same side of the methyl group and the other one, $\delta$ 4.56, on the side of the phenyl group, probably experiencing anisotropic effects from the adjacent phenyl ring. No contacts were observed for the acetonitrile $CH_3$ protons.




**11**

Compound **11** can exist in different isomeric forms. Overall the NMR data are consistent with the same structure as that of **6**, characterized in the solid state by X-ray diffraction.

In the case of $d^8$ square-planar complexes, the six-membered ring arising from the activation of a C($sp^2$)–H bond usually adopts a boat conformation: this implies that one of the substituents on the benzylic carbon is in a pseudo axial position pointing towards the metal atom. In the rhodium(III) derivative the boat conformation is hampered by the octahedral geometry and the less sterically demanding five-membered ring, arising from C($sp^3$)–H activation, is likely to be favoured. At variance, the weak M–H interactions, often observed in the crystal structures of boat-like six-membered cyclometallated $d^8$ complexes,[6d,e,18] may play a role in favouring C($sp^2$)–H activation. Actually, many subtle factors can drive the reaction toward C($sp^3$)–H or C($sp^2$)–H activation, as shown, for example, in the case of the cyclopalladation of *N*-mesitylbenzylideneamines [19] where both C($sp^2$)–M and C($sp^3$)–M bonds were formed in the same solvent at different temperatures.

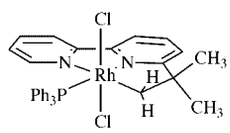
Finally it is worth noting that in complexes **10** and **11** metallation gives rise to a stereogenic carbon atom, a result not unprecedented, but still rare.[20]

The reactivity of the cyclometallated compounds **6**–**9** towards $PPh_3$ (molar ratio $PPh_3$ : Rh 1 : 1) was tested. At variance with the adducts, at room temperature the metallated species do not react. In refluxing chloroform the cationic complex **9** reacts slowly with $PPh_3$ giving compounds $[Rh(L^{tb})(PPh_3)Cl_2]$ **12** and **8**, eqn. (5). The presence of the latter species as a product led us to study the behaviour of **9** in refluxing chloroform. Under these conditions it was found that **9** converts into the neutral species **8**, eqn. (6).

$$\underset{\mathbf{9}}{[Rh(L^{tb})(CH_3CN)_2Cl]Cl} + PPh_3 \xrightarrow{heat} \underset{\mathbf{12}}{[Rh(L^{tb})(PPh_3)Cl_2]} + \underset{\mathbf{8}}{[Rh(L^{tb})(CH_3CN)Cl_2]} + CH_3CN \quad (5)$$

$$\underset{\mathbf{9}}{[Rh(L^{tb})(CH_3CN)_2Cl]Cl} \xrightarrow{heat} \underset{\mathbf{8}}{[Rh(L^{tb})(CH_3CN)Cl_2]} + CH_3CN \quad (6)$$

The proposed formulation for **12**, shown below, is based on the equivalence, in the $^1H$ NMR spectrum, of the protons of the $CH_2$ bonded to the metal and of the two methyl groups, supporting a symmetric environment above and below the plane of the N,N,C system. The $^1H$ NMR spectrum shows also a strong upfield shielding of the H(6′) and of the $CH_2$ protons with respect to complex **8** (see Table 1) due to the shielding effect of the phenyl substituents on the phosphorus atom.




**12**

## Experimental

The ligands were prepared according to literature methods.[11] The compound $RhCl_3 \cdot 3H_2O$ (39.51% Rh) was obtained from Engelhard. All the solvents were purified before use according to standard methods.

Elemental analyses were performed with a Perkin-Elmer Elemental Analyzer 240B by Mr A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. Infrared spectra were recorded with a Perkin-Elmer 983 spectrometer using Nujol mulls or in $CH_2Cl_2$ solution, $^1H$, $^{13}C$-{$^1H$} and $^{31}P$-{$^1H$} NMR spectra with a Varian VXR 300 spectrometer operating at 299.9, 75.4 and 121.4 MHz respectively. Chemical shifts are given in ppm relative to internal TMS ($^1H$, $^{13}C$) and external 85% $H_3PO_4$ ($^{31}P$). The 2-D experiments and the NOE difference spectra were performed by means of standard pulse sequences. Mass spectra were obtained with a VG 7070EQ instrument operating under FAB conditions with 3-nitrobenzyl alcohol as supporting matrix.

### Preparations

**$[Rh(HL^b)(CH_3CN)Cl_3]$ 1.** To a solution of $RhCl_3 \cdot 3H_2O$ (0.054 g, 0.21 mmol) in water (2.5 $cm^3$) was added under vigorous stirring a solution of 6-benzyl-2,2′-bipyridine ($HL^b$, 0.052 g, 0.21 mmol) in $CH_3CN$ (2.5 $cm^3$). The red solution was refluxed and stirred for 1 h in a water-bath at 90 °C. The orange precipitate was collected and washed with EtOH and $Et_2O$ to give the analytical sample, yield 42%, mp >280 °C (Found: C, 45.30; H, 3.52; N, 8.48. Calc. for $C_{19}H_{17}Cl_3N_3Rh \cdot 0.5H_2O$: C, 45.13; H, 3.59; N, 8.31%). IR (Nujol), $\tilde{\nu}_{max}$/$cm^{-1}$: 2322vw, 2298vw, 1601m, 1566m, 702m, 352m, 343m and 328w.

**$[Rh(HL^{ip})(CH_3CN)Cl_3]$ 2.** To a solution of $RhCl_3 \cdot 3H_2O$ (0.294 g, 1.13 mmol) in water (15 $cm^3$) was added under vigorous stirring a solution of 6-(isopropyl)-2,2′-bipyridine ($HL^{ip}$, 0.224 g, 1.13 mmol) in $CH_3CN$ (15 $cm^3$). The red solution was refluxed and stirred for 12 h in a water-bath at 90 °C. The orange product was collected and washed with $Et_2O$ to give the analytical sample, yield 43%, mp 280 °C (decomp.) (Found: C, 39.37; H, 3.84; N, 8.87. Calc. for $C_{15}H_{17}Cl_3N_3Rh \cdot H_2O$: C, 38.61;

H, 4.10; N, 9.01%). IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$: 2326vw, 2302vw, 1626m, 1597m and 332s (br). FAB mass spectrum: *m/z* 412 (M − Cl), 376 (M − Cl − HCl) and 336 (M − 2Cl − $CH_3CN$).

**[Rh(HL$^{np}$)(CH$_3$CN)Cl$_3$] 3.** To a solution of $RhCl_3 \cdot 3H_2O$ (0.200 g, 0.768 mmol) in water (10 $cm^3$) was added under vigorous stirring a solution of 6-(neopentyl)-2,2′-pyridine (HL$^{np}$, 0.1738 g, 0.768 mmol) in $CH_3CN$ (10 $cm^3$). The mixture was refluxed for 11 h in a water-bath at 90 °C, then concentrated to small volume. The precipitate was filtered off, washed with water, EtOH and $Et_2O$ to give the analytical sample. Yield 95%, mp 240 °C (decomp.) (Found: C, 42.83; H, 4.58; N, 8.43. Calc. for $C_{17}H_{21}Cl_3N_3Rh$: C, 42.84; H, 4.44; N, 8.82%). IR (Nujol): $\tilde{\nu}_{max}/cm^{-1}$: 2335vw, 2309vw, 1635m, 1601m and 350m.

**[Rh(HL$^{b}$)(PPh$_3$)Cl$_3$] 4.** To a solution of complex **1** (0.040 g, 0.08 mmol) in $CH_2Cl_2$ (20 ml) was added under vigorous stirring 0.022 g of $PPh_3$ (0.08 mmol). The solution was stirred at room temperature for 3 h, then concentrated to small volume. Addition of diethyl ether gave a yellow precipitate which was filtered off and washed with diethyl ether to give the analytical sample. Yield 90%, mp 215 °C (decomp.) (Found: C, 58.59; H, 4.33; N, 3.58. Calc. for $C_{35}H_{29}Cl_3N_2PRh$: C, 58.56; H, 4.07; N, 3.90%). IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$: 1595m, 1568w, 1122m, 698m, 346m and 327m.

**[Rh(HL$^{ip}$)(PPh$_3$)Cl$_3$] 5.** To a solution of complex **2** (0.052 g, 0.11 mmol) in $CH_2Cl_2$ (20 $cm^3$) was added under vigorous stirring 0.035 g of $PPh_3$ (0.13 mmol). The solution was stirred for 5 h, then concentrated to small volume. Addition of diethyl ether gave a yellow precipitate which was filtered off and washed with diethyl ether to give the analytical sample, yield 90%, mp 210 °C (decomp.) (Found: C, 54.95; H, 4.78; N, 4.13. Calc. for $C_{31}H_{29}Cl_3N_3PRh$: C, 55.59; H, 4.36; N, 4.18%). IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$: 1601m, 1567m, 1118m, 701s, 352m and 328m.

**[Rh(L$^{b}$)(CH$_3$CN)Cl$_2$] 6.** To a solution of $RhCl_3 \cdot 3H_2O$ (0.503 g, 1.93 mmol) in water (25 $cm^3$) was added a solution of 6-benzyl-2,2′-bipyridine (HL$^{b}$, 0.480 g, 1.95 mmol) in $CH_3CN$ (20 $cm^3$). The mixture was refluxed for 60 h in a water-bath at 90 °C. The yellow precipitate formed was collected, washed with water, EtOH, $Et_2O$ to give the analytical sample, yield 32%, mp 290 °C (Found: C, 47.64; H, 3.64; N, 8.40. Calc. for $C_{19}H_{16}Cl_2N_3Rh \cdot H_2O$: C, 47.72; H, 3.79; N, 8.79%). IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$: 2324vw, 2297vw, 1595s, 1568s and 343s. FAB mass spectrum: *m/z* 477 ($M^+ + H_2O$), 459 ($M^+$), 418 (M − $CH_3CN$), 383 (M − $CH_3CN$ − Cl) and 348 (M − $CH_3CN$ − 2Cl). $^{13}C$-{$^1H$} NMR ($CDCl_3$): $\delta$ 4.9, 48.8, 121.2, 122.9, 124.0, 125.6, 125.9, 126.5, 127.0, 138.9, 139.2, 139.7, 141.6, 148.8 and 155.5.

**[Rh(L$^{b}$)(CH$_3$CN)$_2$Cl]Cl 7.** To a solution of $RhCl_3 \cdot 3H_2O$ (0.396 g, 1.52 mmol) in water (20 $cm^3$) was added a solution of 6-(benzyl)-2,2′-bipyridine (HL$^{b}$, 0.374 g, 1.52 mmol) in $CH_3CN$. The mixture was refluxed for 14 h in a water-bath at 90 °C. The yellow precipitate was filtered off and washed with water, EtOH, $Et_2O$ to give a first sample (0.239 g) which resulted in a mixture of compounds **1** and **6** (molar ratio 4:3, NMR criterion). The filtered solution was evaporated to dryness, taken up with water, filtered, evaporated to dryness and recrystallized from $CH_3CN$ and $Et_2O$ to give complex **7** as a yellow solid, yield 11%, mp 282 °C (decomp.) (Found: C, 44.58; H, 4.48; N, 9.35. Calc. for $C_{21}H_{19}Cl_2N_4Rh \cdot 4H_2O$: C, 44.00; H, 4.75; N, 9.77%). $\Lambda_M$ ($5 \times 10^{-4}$ M, $CH_3CN$) = 84 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$: 2326w, 2297w, 1595s, 1567s and 342vs (br). FAB mass spectrum: *m/z* 465 ([M]$^+$), 424 ([M − $CH_3CN$]$^+$), 383 (M − 2$CH_3CN$) and 348 (M − 2$CH_3$-$CN$ − Cl).

**[Rh(L$^{tb}$)(CH$_3$CN)Cl$_2$] 8 and [Rh(L$^{tb}$)(CH$_3$CN)$_2$Cl]Cl 9.** To a solution of $RhCl_3 \cdot 3H_2O$ (0.393 g, 1.51 mmol) in water (20 $cm^3$) was added under vigorous stirring a solution of 6-(*tert*-butyl)-2,2′-bipyridine (HL$^{tb}$, 0.321 g, 1.51 mmol) in $CH_3CN$ (20 $cm^3$). The red solution obtained was refluxed in a water-bath at 90 °C for 15 h, then concentrated to small volume. The yellow precipitate was collected and washed with water, EtOH, $Et_2O$ to give complex **8** as a yellow solid. The filtered solution was evaporated to dryness and recrystallized from $CH_3CN$ and diethyl ether to give **9** as a yellow solid. Compound **8**: yield 15%, mp 270 °C (decomp.) (Found: C, 43.65; H, 4.36; N, 9.20. Calc. for $C_{16}H_{18}Cl_2N_3Rh \cdot H_2O$: C, 43.27; H, 4.54; N, 9.46%); IR (Nujol) $\tilde{\nu}_{max}/cm^{-1}$ 2320w, 2295w, 1595m, 1567m, 349s and 331s; FAB mass spectrum *m/z* 390 ([M − Cl]$^+$); $^{13}C$-{$^1H$} NMR ($CDCl_3$): $\delta$ 4.6, 32.4, 35.1 ($^1J_{Rh\text{-}C}$ = 19.5 Hz), 120.2, 122.7, 123.2, 124.8, 137.0, 138.2, 149.9, 154.2, 155.0 and 179.1. Compound **9**: yield 80%, mp 130 °C (Found: C, 40.75; H, 5.18; N, 10.80. Calc. for $C_{18}H_{21}Cl_2N_4Rh \cdot 3H_2O$: C, 41.48; H, 5.22; N, 10.75%), $\Lambda_M$ ($5 \times 10^{-4}$ M, $CH_3CN$) = 104 $\Omega^{-1}$ $cm^2$ $mol^{-1}$; IR (Nujol); $\tilde{\nu}_{max}/cm^{-1}$ 2318vw, 1594s, 1556s, 349s and 341s $cm^{-1}$; FAB mass spectrum: *m/z* 431 ([M]$^+$) and 390 ([M − $CH_3CN$]); $^{13}C$-{$^1H$} NMR ($CDCl_3$): $\delta$ 5.2, 31.6, 32.7, 36.5 ($^1J_{Rh\text{-}C}$ = 19.1 Hz), 121.5, 123.3, 124.0, 128.0, 139.1, 139.6, 150.9, 154.4, 154.6 and 178.3.

**Conversion of complex 9 into 8.** A solution of complex **9** (0.100 g, 0.214 mmol) in $CHCl_3$ (20 $cm^3$) was refluxed for 40 h, then filtered and concentrated to small volume. Addition of diethyl ether gave a yellow precipitate that was filtered off and washed with diethyl ether to give **8**. Yield 89%.

**[Rh(L$^{tb}$)(CH$_3$CN)$_2$Cl][BF$_4$] 9a.** To a solution of complex **9** (0.100 g, 0.214 mmol) in $CH_3CN$ (15 $cm^3$) was added under vigorous stirring a solution of $NaBF_4$ (0.073 g, 0.665 mmol) in water (8 $cm^3$). The yellow solution was stirred at room temperature for 9 h, then evaporated to dryness. The residue was dissolved with $CH_2Cl_2$ and concentrated to small volume. Addition of diethyl ether gave a yellow product that was collected and washed with $Et_2O$ to give the analytical sample, yield 69%, mp 200 °C (decomp.) (Found: C, 40.23; H, 4.26; N, 10.50. Calc. for $C_{18}H_{21}BClF_4N_4Rh \cdot H_2O$: C, 40.29; H, 4.32; N, 10.44%); $\Lambda_M$ ($5 \times 10^{-4}$ M, $CH_3CN$) = 134 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$: 2299w, 2328vw, 1595m, 1567m, 1065 (br) m, 332s (br) and 320m.

**[Rh(L$^{ip}$)(CH$_3$CN)Cl$_2$] 10.** To a solution of $RhCl_3 \cdot 3H_2O$ (0.260 g, 1.00 mmol) in water (10 $cm^3$) was added under vigorous stirring a solution of 6-isopropyl-2,2′-bipyridine (HL$^{ip}$, 0.198 g, 1.00 mmol) in $CH_3CN$ (10 $cm^3$). The mixture was refluxed for 60 h in a water-bath at 90 °C, then cooled. The yellow precipitate formed was collected, washed with water, EtOH, $Et_2O$ to give the analytical sample. Yield 5%, mp >280 °C (Found: C, 41.43; H, 3.88; N, 9.51. Calc. for $C_{15}H_{16}Cl_2N_3Rh \cdot H_2O$: C, 41.88; H, 4.22; N, 9.77%). IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$: 2319vw, 1591s, 1566m and 331s. $^{13}C$-{$^1H$} NMR ($CDCl_3$): $\delta$ 4.4, 19.9, 29.4 ($^1J_{Rh\text{-}C}$ = 18.9 Hz), 48.4, 119.5, 122.2, 122.3, 126.4, 136.6, 137.7, 150.0, 154.6, 154.7 and 174.0.

**[Rh(L$^{dm}$)(CH$_3$CN)Cl$_2$] 11.** To a solution of $RhCl_3 \cdot 3H_2O$ (0.196 g, 0.752 mmol) in water (10 $cm^3$) was added a solution of 6-(1,1-dimethylbenzyl)-2,2′-bipyridine (HL$^{dm}$, 0.203 g, 0.752 mmol) in $CH_3CN$ (10 $cm^3$). The mixture was refluxed for 45 h in a water-bath at 90 °C. The yellow precipitate was collected, washed with water, EtOH, $Et_2O$ to give the analytical sample. Yield 42%, mp >280 °C (Found: C, 50.41; H, 4.03; N, 8.40. Calc. for $C_{21}H_{20}Cl_2N_3Rh \cdot 0.5H_2O$: C, 50.73; H, 4.26; N, 8.45%). IR (Nujol), $\tilde{\nu}_{max}/cm^{-1}$: 2324vw, 1590s, 1565m, 1556m, 706m, 406s, 338s and 312s. FAB mass spectrum: *m/z* 487 ([M]$^+$), 452 (M − Cl), 446 (M − $CH_3CN$) and 411 (M − Cl − $CH_3CN$).

**[Rh(L$^{tb}$)(PPh$_3$)Cl$_2$] 12.** To a solution of complex **9** (0.100 g, 0.214 mmol) in $CHCl_3$ (20 ml) was added 0.0616 g of $PPh_3$ (0.235 mmol). The solution was refluxed for 40 h, then concentrated to small volume. The yellow precipitate formed by add-

**Table 5** Crystallographic data for compound **6**·$CH_2Cl_2$

| | |
|---|---|
| Formula | $C_{20}H_{18}Cl_4N_3Rh$ |
| $M$ | 545.1 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ (no. 14) |
| $a$/Å | 9.855(1) |
| $b$/Å | 13.814(2) |
| $c$/Å | 16.236(2) |
| $\beta$/° | 97.13(1) |
| $U$/Å$^3$ | 2193.2(5) |
| $Z$ | 4 |
| $T$/K | 298 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 12.7 |
| Measured reflections (total, independent) | 24966; 5544 |
| $R_{int}$ | 0.025 |
| Unique observed reflections with $I > 3\sigma(I)$ | 3923 |
| Final $R$ and $R'$ | 0.034, 0.049 |

ition of $Et_2O$ was filtered off and washed with $Et_2O$. The crude product (90.0 mg) was a mixture of compounds **8** and **12** (NMR criterion, molar ratio 3:2) which were separated by chromatography on a column of silica gel (60 mesh) using benzene–acetone (2:1) as eluent. Complex **12**: yield 15%, mp 252–254 °C (Found: C, 59.16; H, 4.98; N, 4.06. Calc. for $C_{32}H_{30}Cl_2N_2PRh$: C, 59.37; H, 4.67; N, 4.33%); IR (Nujol), $\tilde{\nu}_{max}$/cm$^{-1}$ 1594m, 1085m, 697s and 325m; FAB mass spectrum: $m/z$ 646 ([M]$^+$), 611 (M − Cl) and 576 (M − 2Cl).

### X-Ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 5. The diffraction experiment was carried out on a Siemens SMART CCD area-detector diffractometer at room temperature. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares. The hydrogen atoms of the $CH_3CN$ ligand were detected in the final Fourier maps and refined with fixed thermal parameters. All other hydrogen atoms were placed in ideal positions and not refined.

CCDC reference number 186/1602.

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