

## A series of new fluororhodium(I) complexes†

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The reaction of  $[\text{Rh}\{\eta^2\text{-O}_2\text{S}(\text{O})\text{CF}_3\}(\text{PPr}^i_3)_2]$  **1** with terminal alkynes  $\text{RC}\equiv\text{CH}$  ( $\text{R} = \text{Ph}$  or  $\text{Bu}^t$ ) led to the formation of the vinylidene compounds  $\text{trans-}[\text{Rh}\{\eta^1\text{-OS}(\text{O})_2\text{CF}_3\}(\text{C}=\text{CHR})(\text{PPr}^i_3)_2]$  **2a, 2b**, which on treatment with tetrabutylammonium fluoride hydrate or KF gave the fluororhodium(I) complexes  $\text{trans-}[\text{RhF}(\text{C}=\text{CHR})(\text{PPr}^i_3)_2]$  **3a, 3b** in ca. 70% yield. An alternative route for the preparation of **3a** ( $\text{R} = \text{Ph}$ ) is based on the reaction of phenylacetylene with the dimer  $[\{\text{Rh}(\mu\text{-F})(\text{PPr}^i_3)_2\}_2]$  **4**, the latter being obtained from **1** and  $[\text{NBu}_4]\text{F}$  hydrate as starting materials. Compound **4** reacts smoothly with  $\text{L}' = \text{CO}$ ,  $\text{CNC}_6\text{H}_3\text{Me}_2\text{-2,6}$ ,  $\text{C}_2\text{Ph}_2$  and  $\text{C}_2\text{H}_4$  to afford the mononuclear complexes  $\text{trans-}[\text{RhF}(\text{L}')(\text{PPr}^i_3)_2]$ , of which that with  $\text{L}' = \text{C}_2\text{H}_4$  was characterized by X-ray crystallography. In contrast to the hydroxo compound  $\text{trans-}[\text{Rh}(\text{OH})(\text{C}=\text{CHPh})(\text{PPr}^i_3)_2]$ , which on treatment with acids  $\text{HX}$  ( $\text{X} = \text{CF}_3\text{SO}_3$ ,  $\text{CH}_3\text{CO}_2$ ,  $\text{PhO}$  or  $\text{PhC}\equiv\text{C}$ ) gave  $\text{trans-}[\text{RhX}(\text{C}=\text{CHPh})(\text{PPr}^i_3)_2]$ , the fluoro derivative **3a** reacts only with  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{PhC}\equiv\text{CH}$  by ligand substitution to yield the corresponding compounds. Acetic acid and phenol interact with **3a** via  $\text{XH}\cdots\text{FRh}$  hydrogen bridges to form 1 : 1 adducts, of which that with  $\text{X} = \text{CH}_3\text{CO}_2$  rearranges to give  $\text{trans-}[\text{Rh}(\text{O}_2\text{CMe})(\text{C}=\text{CHPh})(\text{PPr}^i_3)_2]$  and probably  $\text{trans-}[\text{Rh}(\text{FHF})(\text{C}=\text{CHPh})(\text{PPr}^i_3)_2]$ .

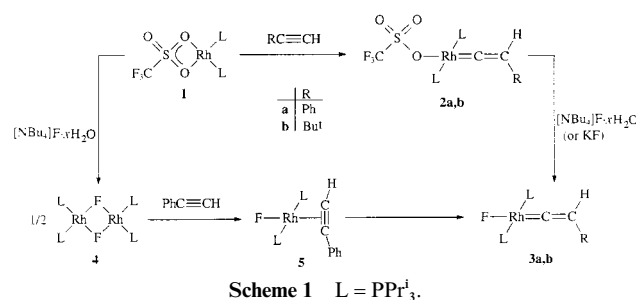
In contrast to the abundance of electron-rich transition metal complexes containing chloride, bromide and iodide as ligands, only a small number of compounds with covalent metal-fluorine bonds have been reported.<sup>1</sup> The reason for this could be first the dearth of anhydrous fluoride-transfer reagents which are soluble in organic solvents,<sup>2</sup> and second the argument (based on the hard/soft acid/base, HSAB, concept)<sup>3</sup> that the bond between an electron-rich transition metal and fluorine should be intrinsically weak. However, in contrast to this hypothesis some recent observations indicate that fluorometal complexes of d<sup>8</sup> metal systems are not particularly unstable and, in anhydrous dichloromethane or chloroform as solvent, the affinity of, e.g., rhodium(I) and palladium(II) to halide ligands decreases in the order  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ .<sup>4,5</sup> Moreover, it has also been shown that the chemistry of fluorometal compounds is substantially different from that of analogous chloro-, bromo- or iodo-metal derivatives,<sup>1,6</sup> and that complexes containing M–F bonds could play an important role in homogeneous catalysis.<sup>1,7</sup>

Recently, we described the preparation of allenylidene- and vinylidene-rhodium(I) compounds with a hydroxo ligand and illustrated by several examples that the Rh–OH linkage can easily be cleaved by Brønsted acids.<sup>8,9</sup> We also showed that reactions of square-planar hydroxorhodium complexes with substituted diynes  $\text{R}_3\text{EC}\equiv\text{CC}\equiv\text{CER}_3$  ( $\text{R}_3\text{E} = \text{Me}_3\text{Si}$  or  $\text{Ph}_3\text{Sn}$ ) lead to the formation of binuclear rhodium complexes in which the two rhodium centers are connected by a naked  $\text{C}_4$  bridge.<sup>9,10</sup> In the present paper we report the synthesis and characterization of a series of fluororhodium(I) complexes with  $\text{Rh}(\text{PPr}^i_3)_2$  as a building block and discuss the reactivity of the corresponding vinylidene complex  $\text{trans-}[\text{RhF}(\text{C}=\text{CHPh})(\text{PPr}^i_3)_2]$  towards Brønsted acids.

## Results and discussion

## Synthesis of four-co-ordinate fluororhodium(I) complexes

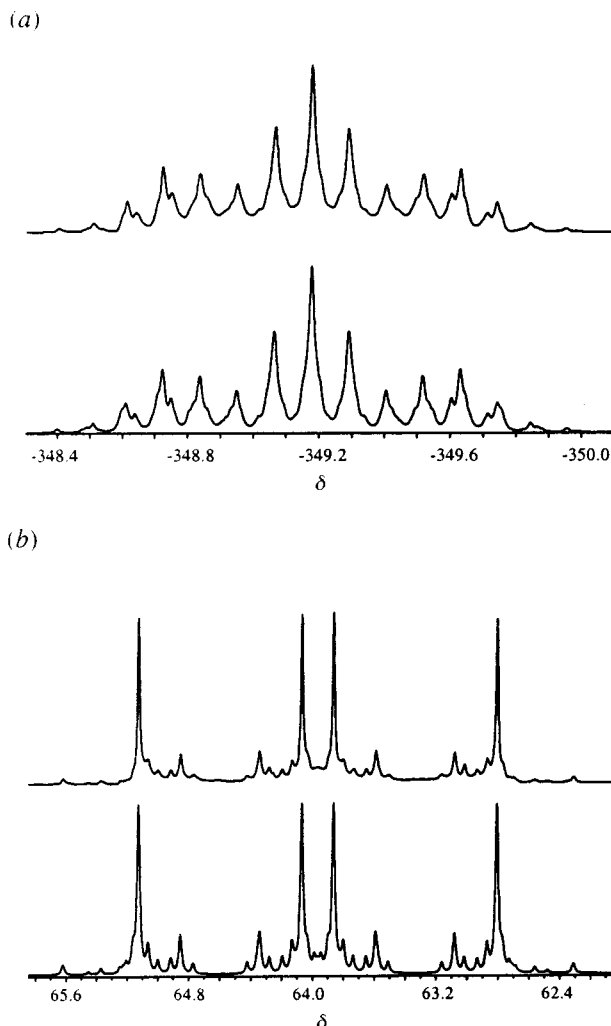
The preparation of the triflate(vinylidene)rhodium(I) complexes **2a, 2b** follows the procedure which we recently used to obtain the analogous tosylatometal derivatives.<sup>11</sup> Treatment of compound **1** with an equimolar amount of the terminal alkyne  $\text{RC}\equiv\text{CH}$  in acetone at room temperature leads to a partial cleavage of the chelate bond and gives the vinylidene complexes **2a, 2b** (see Scheme 1) in nearly quantitative yield. The green-



blue or violet solids have been characterized by elemental analysis, mass spectra, IR and NMR spectroscopic techniques. The most typical features are the doublet of triplets at  $\delta$  1.51 (**2a**) or  $-0.22$  (**2b**) for the  $=\text{CHR}$  proton in the  $^1\text{H}$  NMR and the low-field resonance (also a doublet of triplets) at  $\delta$  301.6 (**2a**) or 295.7 (**2b**) for the  $\alpha$ -carbon atom of the vinylidene unit in the  $^{13}\text{C}$  NMR spectra.

The new fluoro(vinylidene)rhodium(I) complexes **3a, 3b** can be prepared by two different routes, using either **2a, 2b** or the fluoro-bridged dimer **4** as the starting material. The triflates **2a, 2b** react with potassium fluoride in acetone or with tetrabutylammonium fluoride hydrate in benzene by ligand exchange to afford the fluoro derivatives **3a, 3b** in about 70% yield. These complexes are red-violet, air-sensitive solids which can be stored at room temperature under argon for days and

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**Fig. 1** The  $^{19}\text{F}$  (a) and  $^{31}\text{P}\{-^1\text{H}\}$  (b) NMR spectra of complex **4**; observed (up) and simulated (down) using the following coupling constants (Hz):  $^1J(\text{RhP}) = -204.7$ ,  $^1J(\text{RhF}) = -42$ ,  $^2J(\text{FP})_{\text{trans}} = +168.7$ ,  $^2J(\text{FP})_{\text{cis}} = +2.6$ ,  $^2J(\text{FF}) = +70.3$ ,  $^2J(\text{PP}) = -54.0$ ,  $^2J(\text{RhRh}) = 0$ ,  $^3J(\text{RhP}) = -0.2$ ,  $^4J(\text{PP}) = +0.8$  and  $+0.6$ .

do not decompose in solution (*e.g.* in benzene). Attempts to prepare compound **3a** from the related chloro complex *trans*- $[\text{RhCl}(\text{C}=\text{CHPh})(\text{PPr}^i_3)_2]$  and potassium fluoride in acetone failed. Even after prolonged stirring no halide exchange took place. When it was treated with an excess of tetrabutylammonium fluoride hydrate in benzene only partial substitution was observed. With regard to the  $^{13}\text{C}$  NMR data of the fluoro(vinylidene) complexes **3a,3b** it should be mentioned that the characteristic resonances for the vinylidene ligand at  $\delta$  *ca.* 300 ( $\alpha$ -C) and 115 ( $\beta$ -C) show a strong  $^{19}\text{F}$ - $^{13}\text{C}$  coupling of 89–96 and 14–15 Hz, respectively, in addition to the  $^{103}\text{Rh}$ - $^{13}\text{C}$  and  $^{31}\text{P}$ - $^{13}\text{C}$  couplings which are also observed for the chloro derivatives *trans*- $[\text{RhCl}(\text{C}=\text{CHR})(\text{PPr}^i_3)_2]$ .<sup>12</sup>

The phenylvinylidene complex **3a** is not only formed from **2a** by ligand exchange but also upon treatment of the dinuclear complex **4** with the terminal alkyne. As outlined in Scheme 1, the formerly unknown compound **4** was obtained from triflate **1** and tetrabutylammonium fluoride hydrate in benzene. The isolated yield of the orange-red, very air-sensitive solid was 74%. We note that the chloro counterpart of **4** with the composition  $[\{\text{Rh}(\mu\text{-Cl})(\text{PPr}^i_3)_2\}_2]$ , which was isolated in our laboratory<sup>13</sup> and recently structurally characterized by Binger *et al.*,<sup>14</sup> is not an appropriate starting material for the synthesis of **4**. All attempts to replace the chloride in  $[\{\text{Rh}(\mu\text{-Cl})(\text{PPr}^i_3)_2\}_2]$  by fluoride using  $[\text{NBu}_4]\text{F}$  hydrate or TIF as the substrate failed.

In contrast to the  $^{31}\text{P}$  NMR spectrum of the monomeric species  $[\text{RhF}(\text{PCy}_3)_2]$ , which displays a doublet of doublets,<sup>15</sup>

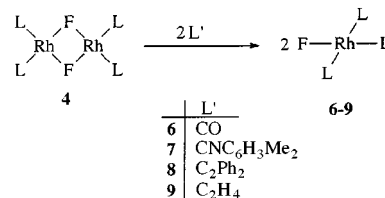
**Table 1** Coupling constants (Hz)<sup>a</sup> for complexes  $[\{\text{RhX}(\text{L})_2\}_n]$

| Compound   | $^1J(\text{RhP})$ | $^2J(\text{PP})$ | $^2J(\text{PF})$ | Ref.      |
|--|-------------------|------------------|------------------|-----------|
| $[\{\text{Rh}(\mu\text{-F})(\text{PPr}^i_3)_2\}_2]$ <b>4</b> | -204.7            | -54.0            | +168.7           | This work |
| $[\{\text{Rh}(\mu\text{-Cl})(\text{PPr}^i_3)_2\}_2]$         | 198               | 55               | —                | 16        |
| $[\{\text{Rh}(\mu\text{-Cl})(\text{PMe}_3)_2\}_2]$           | 191.3             | 60               | —                | 16        |
| $[\{\text{Rh}(\mu\text{-Cl})(\text{PCy}_3)_2\}_2]$           | 195.3             | —                | —                | 16        |
| $[\text{RhF}(\text{PCy}_3)_2]$                               | 206.0             | —                | 165.0            | 15        |
| $[\text{RhCl}(\text{PCy}_3)_2]$                              | 210               | —                | —                | 16        |

<sup>a</sup> Absolute values are given unless a sign is explicitly included.

the  $^{31}\text{P}$  and also the  $^{19}\text{F}$  NMR spectrum of **4** is rather complicated. The complexity of the spectra, as illustrated in Fig. 1, originates from the dimeric structure which causes the magnetic non-equivalence of the  $^{19}\text{F}$ ,  $^{31}\text{P}$  and  $^{103}\text{Rh}$  nuclei in the molecule. The computer simulation for an  $\text{AA}'\text{A}''\text{A}'''\text{MM}'\text{XX}'$ -spin system, where  $\text{A} = ^{31}\text{P}$ ,  $\text{M} = ^{103}\text{Rh}$  and  $\text{X} = ^{19}\text{F}$ , gives an excellent fitting between the experimental and the calculated data. The values of  $^1J(\text{RhP})$  and  $^2J(\text{PF})$  (see Table 1) are similar to those found in  $[\text{RhF}(\text{PCy}_3)_2]$ .<sup>15</sup> Moreover, the coupling constant  $^2J(\text{PP})$  of **4** is in excellent agreement with that of related dimers such as  $[\{\text{Rh}(\mu\text{-Cl})(\text{PPr}^i_3)_2\}_2]$  and  $[\{\text{Rh}(\mu\text{-Cl})(\text{PMe}_3)_2\}_2]$ .<sup>16</sup> In this context we note that also for the fluoro-bridged complexes  $[\{\text{Rh}(\mu\text{-F})(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\}_2]$  ( $n = 2$  or  $3$ )<sup>17</sup> complicated NMR spectra have been observed. However, in this case the  $^{31}\text{P}$  NMR spectroscopic data were not discussed in detail and no  $^{19}\text{F}$  NMR data were given.

Similar to  $[\{\text{Rh}(\mu\text{-Cl})(\text{PPr}^i_3)_2\}_2]$ , the corresponding fluoro complex **4** is also an excellent starting material for the preparation of square-planar rhodium(i) compounds of the general type *trans*- $[\text{RhF}(\text{L})(\text{PPr}^i_3)_2]$ . The reactions of **4** with CO, 2,6-dimethylphenyl isocyanide, diphenylacetylene and ethene afford the mononuclear complexes **6–9** in good yields (Scheme 2). Compounds **6–9** are yellow solids, which can be handled in



**Scheme 2**  $\text{L} = \text{PPr}^i_3$ .

air for a short period of time and are stable in  $\text{C}_6\text{D}_6$  solution for several days.

Selected IR and NMR spectroscopic data of the four-coordinate complexes **3a,3b** and **6–9** are listed in Table 2. In all cases, the  $^{31}\text{P}$  NMR spectra display one doublet of doublets with a  $^{103}\text{Rh}$ - $^{31}\text{P}$  coupling constant that seems to be characteristic for this type of molecule. The  $^{19}\text{F}$  NMR spectra of **3a** and **6–9** display a doublet of triplets except for the diphenylacetylene derivative **8**, for which a broadened doublet is observed. Since besides the  $^{103}\text{Rh}$ - $^{19}\text{F}$  coupling observed in the  $^{19}\text{F}$  NMR also the corresponding signal in the  $^{31}\text{P}$  NMR spectrum of **8** shows a coupling to the  $^{19}\text{F}$  nuclei, we assume that the broadening is due to a dynamic process which does not involve the cleavage of the  $\text{Rh-F}$  bond. Upon addition of anhydrous  $\text{Na}_2\text{CO}_3$  to a solution of **8** in  $\text{C}_6\text{D}_6$  the  $^{19}\text{F}$  NMR spectrum displays the expected doublet of triplets with the  $^{103}\text{Rh}$ - $^{19}\text{F}$  and  $^{31}\text{P}$ - $^{19}\text{F}$  coupling constants shown in Table 2. From this experiment we conclude that in the absence of  $\text{Na}_2\text{CO}_3$  the fluoro ligand of compound **8** may interact *via* a hydrogen bridge with traces of a species containing acidic hydrogen. The interaction with water could be discarded since the addition of some drops of it to a solution of **8** which was treated previously with sodium carbonate did not lead to a broadening of the  $^{19}\text{F}$  NMR resonance.

**Table 2** Selected IR and NMR data for complexes *trans*-[RhF(L)(PPr<sup>i</sup><sub>3</sub>)<sub>2</sub>] ( $\nu$  in cm<sup>-1</sup>;  $\delta$  in ppm;  $J$  in Hz)

| Complex   | L  | $\nu(\text{RhF})$ | $\delta(^{19}\text{F})$ | $^1J(\text{RhF})$ | $^2J(\text{PF})$ | $\delta(^{31}\text{P})$ | $^1J(\text{RhP})$ |
|-----------|--|-------------------|-------------------------|-------------------|------------------|-------------------------|-------------------|
| <b>3a</b> | C=CHPh   | 469               | -216.6                  | 13.4              | 19.0             | 45.6                    | 144.0             |
| <b>3b</b> | C=CHBu <sup>t</sup> <sup>a</sup>                 | 453               | -222.7                  | 17.2              | 17.2             | 44.8                    | 146.6             |
| <b>6</b>  | CO   | 465               | -269.3                  | 49.6              | 19.7             | 51.8                    | 130.6             |
| <b>7</b>  | C≡NC <sub>6</sub> H <sub>3</sub> Me <sub>2</sub> | 458               | -280.7                  | 47.5              | 20.1             | 50.3                    | 137.1             |
| <b>8</b>  | PhC≡CPh <sup>a</sup>                             | 452               | -258.1                  | 79.3              | 16.6             | 32.5                    | 125.5             |
| <b>9</b>  | H <sub>2</sub> C=CH <sub>2</sub>                 | 426               | -248.2                  | 76.3              | 18.7             | 36.4                    | 129.8             |

<sup>a</sup> In the presence of Na<sub>2</sub>CO<sub>3</sub>.

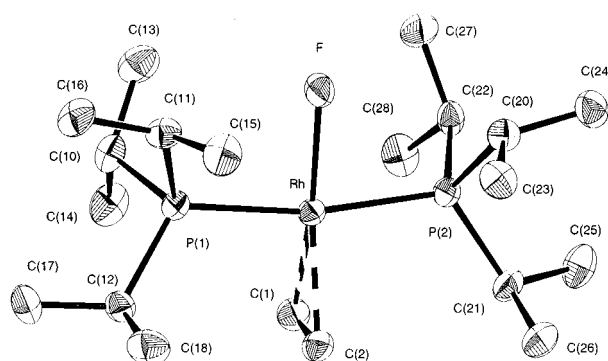
A comparison of the NMR data of the four-co-ordinate complexes **3a,3b** and **6–9** reveals that the values of the <sup>103</sup>Rh–<sup>19</sup>F coupling constants increase as a function of L in the order C=CHPh < C=CHBu<sup>t</sup> < CNC<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> < CO < H<sub>2</sub>C=CH<sub>2</sub> < PhC≡CPh (Table 2). In contrast, there is an increase of the <sup>103</sup>Rh–<sup>31</sup>P coupling constants in the reverse order. Since it has been observed both by van Gaal and McFarlane and co-workers<sup>18</sup> that in square-planar rhodium(i) compounds having two tertiary phosphines in *trans* disposition the increase in the effective electronegativity at the metal leads to an increase in the size of  $J(\text{RhP})$ , the decrease of the <sup>103</sup>Rh–<sup>31</sup>P coupling constants in the spectra of **3a,3b** and **6–9** may be due to a decrease of the  $\pi$ -acceptor ability of the ligands L' by going from the left to the right in the above-mentioned series. Recent electrochemical measurements suggest that in complexes of the type *trans*-[RhCl(L')(PPr<sup>i</sup><sub>3</sub>)<sub>2</sub>] the  $\pi$ -acceptor ability decreases in the order CO > C≡CPh<sub>2</sub> > C<sub>2</sub>H<sub>4</sub>,<sup>19</sup> whereas with respect to carbon monoxide and vinylidene both UV photoelectron spectra and DV-X $\alpha$  calculations point to a higher  $\pi$ -acceptor ability for C=CH<sub>2</sub> than for CO.<sup>20</sup>

The IR spectra of complexes **3a,3b** and **6–9** exhibit one band between 425 and 470 cm<sup>-1</sup> with medium intensity which is assigned to the Rh–F stretching frequency. The band lies in the same region as that of other fluororhodium complexes such as *trans*-[RhF(CO)(PCy<sub>3</sub>)<sub>2</sub>] (470 cm<sup>-1</sup>), *trans*-[RhF(C<sub>2</sub>H<sub>4</sub>)(PCy<sub>3</sub>)<sub>2</sub>] (421 cm<sup>-1</sup>) and *trans*-[RhF(PhC≡CPh)(PCy<sub>3</sub>)<sub>2</sub>] (462 cm<sup>-1</sup>).<sup>15</sup>

Since we assumed that the remarkable stability of complexes **3a,3b** and **6–9** could be due to the favorable *trans* arrangement of a strong  $\pi$  acceptor (in particular CO, CNR and vinylidene) and fluoride as a good  $\pi$ -donor ligand,<sup>1,21</sup> we became interested to know whether the combination of fluoride and a very weak  $\pi$  acceptor such as pyridine or acetonitrile in *trans* disposition could also be realized. However, these experiments failed. While compound **4** did not react with a 10-fold excess of pyridine in C<sub>6</sub>D<sub>6</sub> at room temperature, upon warming the solution at 50 °C for 5 h a partial reaction was observed. Besides the resonances of the starting material three new signals appeared in the <sup>31</sup>P NMR spectrum, of which one was due to free triisopropylphosphine and one [a doublet of doublets at  $\delta$  37.0 with  $^2J(\text{PF}) = 17.8$  and  $^1J(\text{RhP}) = 157.6$  Hz] possibly to *cis*-[RhF-(py)<sub>2</sub>(PPr<sup>i</sup><sub>3</sub>)<sub>2</sub>].<sup>22</sup> The third signal [a doublet at  $\delta$  55.9 with  $^1J(\text{RhP}) = 114.5$  Hz] could not be assigned. Treatment of **4** with piperidine or acetonitrile gave a mixture of products which we were unable to separate by fractional crystallization or chromatographic techniques.

### Molecular structure of the ethenerhodium(i) complex **9**

The molecular structure of complex **9** was determined by single-crystal X-ray crystallography. The ORTEP<sup>23</sup> plot (Fig. 2) reveals that the ligand sphere around the metal centre is slightly distorted square-planar with moderate bending of the phosphine ligands toward the fluoride. The structure is thus quite similar to that of the carbonyl complex *trans*-[RhF(CO)(PPh<sub>3</sub>)<sub>2</sub>] for which also a non-linear P–Rh–P axis exists.<sup>24</sup> The Rh–F bond length of **9** [2.060(3) Å] (Table 3) is nearly identical to that of the before-mentioned carbonyl compound [2.046(2) Å] but significantly shorter than the distances in the tetramer [RhF(C<sub>2</sub>H<sub>4</sub>)(C<sub>2</sub>F<sub>4</sub>)<sub>4</sub>], which contains  $\mu_3$ -bridging fluorides.<sup>25</sup>

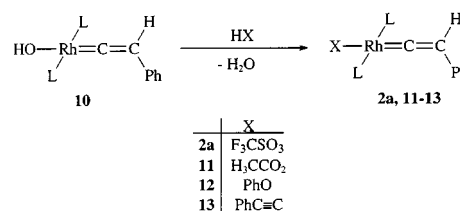
**Fig. 2** An ORTEP plot of complex **9**.**Table 3** Selected bond lengths (Å) and angles (°) for complex **9**

|              |          |              |           |
|--------------|----------|--------------|-----------|
| Rh–F         | 2.060(3) | Rh–P(1)      | 2.326(2)  |
| Rh–C(1)      | 2.096(5) | Rh–P(2)      | 2.328(2)  |
| Rh–C(2)      | 2.103(5) | C(1)–C(2)    | 1.380(8)  |
| F–Rh–C(1)    | 160.4(2) | C(2)–Rh–P(1) | 95.6(2)   |
| F–Rh–C(2)    | 161.2(2) | C(2)–Rh–P(2) | 94.8(2)   |
| F–Rh–P(1)    | 85.71(9) | C(1)–Rh–C(2) | 38.4(2)   |
| F–Rh–P(2)    | 84.71(9) | C(1)–C(2)–Rh | 70.5(3)   |
| C(1)–Rh–P(1) | 93.8(2)  | C(2)–C(1)–Rh | 71.1(3)   |
| C(1)–Rh–P(2) | 93.8(2)  | P(1)–Rh–P(2) | 169.53(5) |

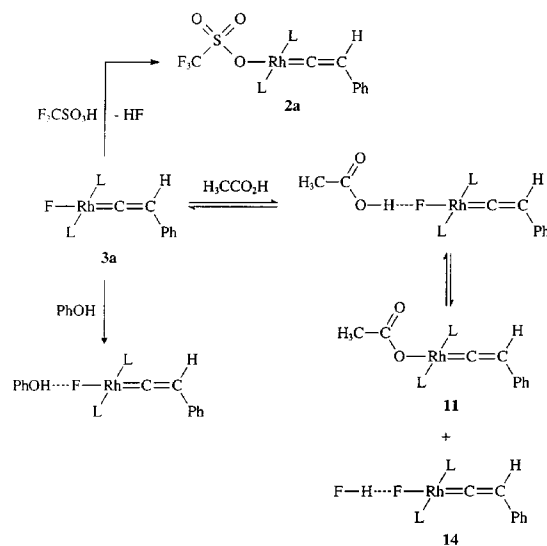
There is a minor difference between the Rh–C bond lengths of **9** [2.096(5) and 2.103(5) Å] and of the analogous chloro complex *trans*-[RhCl(C<sub>2</sub>H<sub>4</sub>)(PPr<sup>i</sup><sub>3</sub>)<sub>2</sub>] [2.116(2) and 2.128(2) Å],<sup>26</sup> which indicates that in the fluoro compound the bond between ethene and the metal is somewhat stronger. A larger difference exists between the C–C distance of the ethene ligand in **9** [1.380(8) Å] and of the chloro counterpart [1.319(4) Å] which we contribute to a higher degree of back bonding from rhodium to the olefin in **9**. The co-ordinated fluoride is obviously a better  $\pi$  donor than chloride and permits a stronger push-pull effect to the  $\pi^*$  orbital of ethene.

### Acid–base reactions of the fluoro(vinylidene) complex **3a**

In order to compare the basic character of the hydroxo and fluoro ligands in the vinylidene complexes *trans*-[RhX-(=C=CHPh)(PPr<sup>i</sup><sub>3</sub>)<sub>2</sub>], the reactions of **10** (X = OH) and **3a** (X = F) with Brønsted acids have been studied. The hydroxo derivative **10** reacts with CF<sub>3</sub>SO<sub>3</sub>H, CH<sub>3</sub>CO<sub>2</sub>H, PhOH and PhC≡CH in benzene to afford the substitution products **2a**, **11**,<sup>27</sup> **12**,<sup>9</sup> and **13**<sup>27</sup> in virtually quantitative yield (Scheme 3).

**Scheme 3** L = PPr<sup>i</sup><sub>3</sub>.

If in the same way a solution of complex **3a** in  $C_6D_6$  is treated with one equivalent of  $CF_3SO_3H$  compound **2a** is formed. However, treatment of **3a** with one equivalent of acetic acid does not lead to the formation of the corresponding acetato complex but yields a new species, the  $^1H$  and  $^{31}P$  NMR data (chemical shifts and coupling constants) of which lie between those of **3a** and **11**. There are two facts which indicate that on the NMR timescale a fast exchange is taking place: first, the  $^1H$  and  $^{31}P$  NMR spectra display a single set of signals regardless of the amount of added acetic acid (from 12 to 200% with respect to the quantity of **3a**), and second, no P–F or F–H couplings are observed in each case. In the  $^{19}F$  NMR spectrum a broad singlet appears at  $\delta -213.9$  at room temperature, which suggests that at least one of the species present in solution contains a fluoride bonded to rhodium. We assume that an exchange process as shown in Scheme 4 occurs. An acetic acid



Scheme 4  $L = PPt^i_3$ .

molecule possibly interacts with **3a** by forming a hydrogen bond to the fluoro ligand, the Rh–F bond subsequently breaks to give the acetato complex and HF, and the free HF molecule is finally added to the fluoro ligand of another molecule of **3a** to give a compound with a RhFHF unit. We note that recent studies by Grushin<sup>5</sup> as well as by Perutz, Parkin and co-workers<sup>28,29</sup> have confirmed that HF can indeed be trapped by a fluorometal complex to generate a co-ordinated bifluoride unit.

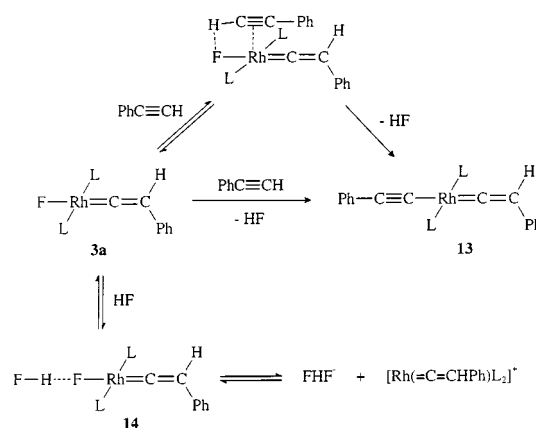
The fast exchange between the species in equilibrium (see Scheme 4), which may explain the absence of P–F and F–H couplings in the NMR spectra of the solution containing **3a** and acetic acid at 20 °C, could be slowed by decreasing the temperature. In the  $^{19}F$  NMR spectrum at –83 °C the broad resonance observed at room temperature decoalesces into three signals. The first is a doublet of doublets at  $\delta -179.1$  with coupling constants  $^1J(FH) = 418$  and  $^2J(FF) = 101$  Hz, which may be assigned to the terminal fluoride of the Rh–FHF ligand.<sup>30</sup> The second signal is a very broad multiplet at  $\delta -214.8$ , which probably corresponds to the fluoro ligand of **3a**. The third resonance is also a broad multiplet at  $\delta -228.7$  with approximately the same intensity as that of the doublet of doublets at  $\delta -179.1$ , which we tentatively assign to the rhodium-bound fluoride of the RhFHF unit. The  $^1J(FH)$  and  $^2J(FF)$  values of the signal for the terminal fluoride indicate that the interaction  $MF \cdots HF$  is significantly weaker than in the ruthenium complex  $[RuH(FHF)(dmpe)_2]$ <sup>28</sup> but similar to that in the eight-coordinate molybdenum compound  $[MoH_2F(FHF)(PMe_3)_4]$ .<sup>29</sup>

In the presence of one equivalent of PhOH the NMR spectra of complex **3a** undergo only slight changes indicating that hydrogen bonding between phenol and the fluoro ligand of **3a** is only weak. Therefore, we conclude that the Rh–F bond in **3a**

is a weaker Brønsted base than the Rh–OH bond in **10**, the fluoride ligand being completely displaced by  $CF_3SO_3H$ , partially displaced by  $CH_3CO_2H$  and not displaced by PhOH.

The behaviour of compound **3a** toward phenylacetylene deserves a special comment. As shown in Scheme 1, the reaction of dimer **4** with two equivalents of  $PhC\equiv CH$  gives, after a short period of time, an unstable  $\pi$ -alkyne intermediate **5** (not isolated) which smoothly isomerizes to the vinylidene complex **3a**. When more than two equivalents of the alkyne are added to a solution of **4** or when **3a** is treated with one equivalent of phenylacetylene, in the  $^1H$  and  $^{31}P$  NMR spectra of the reaction mixture signals corresponding to compound **13**<sup>27</sup> are observed. In  $C_6D_6$ , in the absence of a base, after two hours at room temperature about 80% of the fluororhodium(i) derivative remained. However, upon addition of  $Na_2CO_3$  to this solution the alkynyl(vinylidene) complex **13** is quantitatively formed. Compound **3a** thus behaves similarly to the acetato derivative **11** which also reacts with phenylacetylene in the presence of a base to give **13**.<sup>27</sup>

A mechanism that explains the reactivity of complex **3a** toward  $PhC\equiv CH$  is represented in Scheme 5. We assume that



Scheme 5  $L = PPt^i_3$ .

the initial step consists of the addition of the alkyne to rhodium forming a five-co-ordinate intermediate with an 18-electron configuration at the metal centre. Subsequently, the alkyne is deprotonated by the co-ordinated fluoride to give **13** and HF. In the absence of a base, the hydrogen fluoride formed at the beginning of the reaction could interact with the metal-bonded fluoride, thus decreasing its basicity and slowing the reaction. The assumption, that the addition of HF to RhF is a reversible process, is supported by the result that on treatment of a solution of 0.04 mmol of **3a** in 0.4 cm<sup>3</sup> of  $C_6D_6$  with 0.002 mmol of HF the  $^1H$  and  $^{31}P$  NMR spectra of the reaction mixture display no F–H or P–F couplings, the position of the signals being only slightly different to those of **3a**. It is conceivable that the interaction of HF with the co-ordinated fluoride weakens the Rh–F bond, therefore allowing the  $HF_2^-$  anion to dissociate. Exchange processes involving co-ordinated and free bifluoride moieties have been observed in  $[RuH(FHF)(dmpe)_2]$ <sup>28</sup> and  $[PdR(FHF)(PPh_3)_2]$  ( $R = Me$  or  $Ph$ ),<sup>5</sup> respectively.

## Conclusion

The work presented in this paper describes the preparation, structural characterization and reactivity of a series of four-co-ordinate fluororhodium(i) complexes including the first representatives with  $F-Rh-C\equiv C-CHR$  as a molecular chain. Despite the progress made during the last decade in developing synthetic routes to organometallic compounds with M–F bonds,<sup>1</sup> the number of those where  $M = Rh$  is still quite small. Previously, van Gaal and co-workers<sup>15,31</sup> reported the preparation of a family of three- and four-co-ordinate fluoro-



rhodium(I) complexes mainly with  $\text{PCy}_3$  as phosphine ligand by using  $[\{\text{RhF}(\text{C}_8\text{H}_{14})_2\}_n]$  as the starting material. The most extensively studied compound, however, is the Vaska-type derivative  $\text{trans}[\text{RhF}(\text{CO})(\text{PPh}_3)_2]$ , for which not only a high-resolution low-temperature crystal structure analysis has been carried out but also density functional theory applied.<sup>24</sup> These data together with those obtained from spectroscopic and electrochemical investigations suggest that in compounds of the general type  $\text{trans}[\text{RhX}(\text{CO})(\text{PPh}_3)_2]$  the electron density at the metal centre increases along the series  $\text{I} < \text{Br} < \text{Cl} < \text{F}$ .<sup>1</sup> The results presented in this paper are in agreement with these. With regard to the synthesis of the complexes **3a**, **3b** and **4** it should be noted that until recently the most common way to form a Rh–F bond was by chloride abstraction with silver fluoride or a silver salt of a weakly co-ordinating anion followed by treatment with a fluoride-donor reagent.<sup>1</sup> In this work we have illustrated that an alternative method for introducing a fluoro ligand in the co-ordination sphere of rhodium(I) consists of the displacement of triflate by fluoride, thereby using tetrabutylammonium fluoride hydrate or KF as the fluoride source. Work in progress in our laboratory reveals that this procedure can also be applied to the preparation of new organo-iridium and -ruthenium complexes containing M–F bonds and we will report about these studies in due course.

## Experimental

All reactions were carried out under an atmosphere of argon by using Schlenk techniques. The starting materials **1**<sup>11</sup> and **10**<sup>9</sup> were prepared by recently published methods. Tetrabutylammonium fluoride hydrate (98%) was purchased from Aldrich and used without drying. The NMR spectra were recorded at room temperature on Bruker AC 200 and AMX 400 instruments and the IR spectra on a Bruker IFS 25 spectrometer. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; vt, virtual triplet;  $N = {}^3J(\text{PH}) + {}^5J(\text{PH})$  or  ${}^1J(\text{PC}) + {}^3J(\text{PC})$ . The simulations of the NMR spectra were performed using the WIN-DAISY program. Melting points were determined by DTA. Electron impact mass spectra were measured on Finnigan and MAT 8200 instruments.

## Preparations

**trans-[Rh( $\eta^1\text{-OS}(\text{O})_2\text{CF}_3$ )(=C=CHPh)(PPR<sup>i</sup><sub>3</sub>)<sub>2</sub>] 2a.** A solution of compound **1** (0.484 g, 0.84 mmol) in acetone (15 cm<sup>3</sup>) was treated with phenylacetylene (0.092 cm<sup>3</sup>, 0.84 mmol) at  $-78^\circ\text{C}$ . The reaction mixture was slowly warmed to room temperature, stirred for 5 h and then brought to dryness *in vacuo*. The residue was dissolved in diethyl ether (3 cm<sup>3</sup>) and the solution stored at  $-20^\circ\text{C}$  for 3 d. A dark green-blue solid precipitated, which was washed three times with 2 cm<sup>3</sup> portions of diethyl ether ( $-20^\circ\text{C}$ ) and dried *in vacuo*: yield 0.466 g (82%); mp  $70^\circ\text{C}$  (decomp.) (Found: C, 47.82; H, 7.35; S, 4.91.  $\text{C}_{27}\text{H}_{48}\text{F}_3\text{O}_3\text{P}_2\text{RhS}$  requires C, 48.07; H, 7.17; S, 4.75%). IR (Nujol):  $\nu(\text{C}=\text{C})$  1654, 1629, 1594 cm<sup>-1</sup>. NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (200 MHz) 7.10–6.82 (5 H, m,  $\text{C}_6\text{H}_5$ ), 2.59 (6 H, m,  $\text{PCHCH}_3$ ), 1.51 [1 H, dt,  $J(\text{RhH})$  0.9,  $J(\text{PH})$  3.1,  $\text{Rh}=\text{C}=\text{CH}$ ] and 1.20 [36 H, dvt,  $J(\text{HH})$  7.1,  $N$  14.0 Hz,  $\text{PCHCH}_3$ ];  $\delta_{\text{C}}$  (50.3 MHz) 301.6 [dt,  $J(\text{RhC})$  64.4,  $J(\text{PC})$  16.6,  $\text{Rh}=\text{C}$ ], 128.7, 128.3, 125.9 (all s,  $\text{C}_6\text{H}_5$ ), 124.0 (br s, *ipso*-C of  $\text{C}_6\text{H}_5$ ), 111.9 [dt,  $J(\text{RhC})$  17.6,  $J(\text{PC})$  5.9 Hz,  $\text{Rh}=\text{C}=\text{C}$ ], 24.1 (vt,  $N$  20.2 Hz,  $\text{PCHCH}_3$ ), 20.2 (s,  $\text{PCHCH}_3$ ), signal of  $\text{CF}_3$  carbon atom obscured by other signals;  $\delta_{\text{F}}$  (188.3 MHz)  $-77.4$  (s,  $\text{CF}_3$ );  $\delta_{\text{P}}$  (81.0 MHz) 44.0 [d,  $J(\text{RhP})$  134.8 Hz]. EI MS (70 eV):  $m/z$  674 ( $\text{M}^+$ , 0.7), 572 ( $\text{M}^+ - \text{PhC}_2\text{H}$ , 1) and 422 ( $\text{M}^+ - \text{PhC}_2\text{H} - \text{CF}_3\text{SO}_3\text{H}$ , 0.4%).

**trans-[Rh( $\eta^1\text{-OS}(\text{O})_2\text{CF}_3$ )(=C=CHBu<sup>t</sup>)(PPR<sup>i</sup><sub>3</sub>)<sub>2</sub>] 2b.** This compound was prepared as described for **2a**, using **1** (0.657 g, 1.15 mmol) and 3,3-dimethyl-1-butyne (0.142 cm<sup>3</sup>, 1.15 mmol)

as starting materials. The acetone solution was brought to dryness *in vacuo*, the resulting violet solid washed three times with 4 cm<sup>3</sup> portions of pentane (*ca.*  $-10^\circ\text{C}$ ) and dried *in vacuo* at  $45^\circ\text{C}$ : yield 0.735 g (98%); mp  $89^\circ\text{C}$  (decomp.) (Found: C, 45.73; H, 8.15; S, 4.56.  $\text{C}_{25}\text{H}_{52}\text{F}_3\text{O}_3\text{P}_2\text{RhS}$  requires C, 45.87; H, 8.01; S, 4.90%). IR (Nujol):  $\nu(\text{C}=\text{C})$  1677, 1653 cm<sup>-1</sup>. NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (400 MHz) 2.66 (m, 6 H,  $\text{PCHCH}_3$ ), 1.25 [36 H, dvt,  $J(\text{HH})$  = 7.2,  $N$  13.8,  $\text{PCHCH}_3$ ], 0.86 [9 H, s,  $\text{C}(\text{CH}_3)_3$ ] and  $-0.22$  [1 H, dt,  $J(\text{RhH})$  0.8,  $J(\text{PH})$  3.1 Hz,  $\text{Rh}=\text{C}=\text{CH}$ ];  $\delta_{\text{C}}$  (100.6 MHz) 295.7 [dt,  $J(\text{RhC})$  64.7,  $J(\text{PC})$  17.3,  $\text{Rh}=\text{C}$ ], 120.7 [q,  $J(\text{CF})$  319.6,  $\text{CF}_3$ ], 116.8 [dt,  $J(\text{RhC})$  17.1,  $J(\text{PC})$  6.0 Hz,  $\text{Rh}=\text{C}=\text{C}$ ], 31.9 [s,  $\text{C}(\text{CH}_3)_3$ ], 26.4 [s,  $\text{C}(\text{CH}_3)_3$ ], 23.8 (vt,  $N$  19.9 Hz,  $\text{PCHCH}_3$ ) and 20.3 (s,  $\text{PCHCH}_3$ );  $\delta_{\text{F}}$  (376.4 MHz)  $-76.9$  (s,  $\text{CF}_3$ );  $\delta_{\text{P}}$  (162.0 MHz) 41.7 [d,  $J(\text{RhP})$  136.9 Hz]. EI MS (70 eV):  $m/z$  654 ( $\text{M}^+$ , 0.3), 572 ( $\text{M}^+ - \text{Bu}^t\text{C}_2\text{H}$ , 2), 504 ( $\text{M}^+ - \text{CF}_3\text{SO}_3\text{H}$ , 1) and 422 ( $\text{M}^+ - \text{Bu}^t\text{C}_2\text{H} - \text{CF}_3\text{SO}_3\text{H}$ , 1%).

**trans-[RhF(=C=CHPh)(PPR<sup>i</sup><sub>3</sub>)<sub>2</sub>] 3a.** A solution of compound **2a**, prepared from **1** (0.786 g, 1.37 mmol) and phenylacetylene (0.152 cm<sup>3</sup>, 1.39 mmol) in acetone (15 cm<sup>3</sup>), was treated with KF (0.200 g, 4.76 mmol). The mixture was stirred for 1 h at room temperature and then brought to dryness *in vacuo*. The residue was extracted three times with 15 cm<sup>3</sup> portions of pentane. The combined extracts were filtered through cotton, the filtrate was concentrated to *ca.* 4 cm<sup>3</sup> and then stored for 14 h at  $-60^\circ\text{C}$ . Red-violet crystals precipitated, which were washed three times with 3 cm<sup>3</sup> portions of pentane ( $-78^\circ\text{C}$ ) and dried *in vacuo*: yield 0.529 g (71%); mp  $52^\circ\text{C}$  (decomp.) (Found: C, 57.18; H, 9.05.  $\text{C}_{26}\text{H}_{48}\text{FP}_2\text{Rh}$  requires C, 57.35; H, 8.89%). IR (Nujol):  $\nu(\text{C}=\text{C})$  1643, 1623, 1595, 1570,  $\nu(\text{RhF})$  469 cm<sup>-1</sup>. NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (400 MHz) 7.21 [2 H, d,  $J(\text{HH})$  7.3, *ortho*-H of  $\text{C}_6\text{H}_5$ ], 7.10 [2 H, t,  $J(\text{HH})$  7.3, *meta*-H of  $\text{C}_6\text{H}_5$ ], 6.84 [1 H, t,  $J(\text{HH})$  7.3, *para*-H of  $\text{C}_6\text{H}_5$ ], 2.48 (6 H, m,  $\text{PCHCH}_3$ ), 1.68 (1 H, m,  $\text{Rh}=\text{C}=\text{CH}$ ), 1.28 [36 H, dvt,  $J(\text{HH})$  6.4,  $N$  13.6 Hz,  $\text{PCHCH}_3$ ];  $\delta_{\text{C}}$  (100.6 MHz) 301.6 [ddt,  $J(\text{FC})$  95.6,  $J(\text{RhC})$  52.3,  $J(\text{PC})$  15.5,  $\text{Rh}=\text{C}$ ], 128.5, 127.4, 124.8, 124.3 (all s,  $\text{C}_6\text{H}_5$ ), 112.1 [ddt,  $J(\text{FC}) = J(\text{RhC})$  15.1,  $J(\text{PC})$  5.7,  $\text{Rh}=\text{C}=\text{C}$ ], 23.3 (vt,  $N$  19.0 Hz,  $\text{PCHCH}_3$ ) and 20.2 (s,  $\text{PCHCH}_3$ );  $\delta_{\text{F}}$  (188.3 MHz)  $-216.6$  [dt,  $J(\text{RhF})$  13.4,  $J(\text{PF})$  19.0 Hz];  $\delta_{\text{P}}$  (81.0 MHz) 45.6 [dd,  $J(\text{RhP})$  144.0,  $J(\text{PF})$  19.0 Hz]. EI MS (70 eV):  $m/z$  544 ( $\text{M}^+$ , 6), 524 ( $\text{M}^+ - \text{HF}$ , 2), 442 ( $\text{M}^+ - \text{PhC}_2\text{H}$ , 14), 422 ( $\text{M}^+ - \text{HF} - \text{PhC}_2\text{H}$ , 7), 400 ( $\text{M}^+ - \text{PhC}_2\text{H} - \text{C}_3\text{H}_6$ , 12) and 380 ( $\text{M}^+ - \text{HF} - \text{PhC}_2\text{H} - \text{C}_3\text{H}_6$ , 10%).

Alternatively, compound **3a** was prepared on treatment of a solution of **4** (0.074 g, 0.084 mmol) in benzene (5 cm<sup>3</sup>) with phenylacetylene (0.019 cm<sup>3</sup>, 0.17 mmol). After the reaction mixture was stirred for 41 h at room temperature the <sup>31</sup>P NMR spectrum displayed two doublets corresponding to a *ca.* 3:2 mixture of **3a** and  $\text{trans}[\text{RhF}(\text{PhC}\equiv\text{CH})(\text{PPR}^i_3)_2]$  **5**. Upon heating the solution for 2.5 h at  $50^\circ\text{C}$  the spectroscopic data revealed that besides small amounts of free  $\text{PPR}^i_3$  and  $\text{OPPR}^i_3$ , only compound **3a** was present. The solution was then brought to dryness *in vacuo* and worked up as described above to give a red-violet solid: yield 0.052 g (57%). NMR data for **5** ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (200 MHz) 8.21 [2 H, d,  $J(\text{HH})$  7.7, *ortho*-H of  $\text{C}_6\text{H}_5$ ], 7.21–7.00 [3 H, m, *meta*- and *para*-H of  $\text{C}_6\text{H}_5$ ], 3.92 [1 H, d,  $J(\text{RhH})$  2.0,  $\text{C}\equiv\text{CH}$ ], 2.07 (6 H, m,  $\text{PCHCH}_3$ ), 1.29 [18 H, dvt,  $J(\text{HH})$  6.4,  $N$  13.2,  $\text{PCHCH}_3$ ] and 1.17 [18 H, dvt,  $J(\text{HH})$  6.3,  $N$  12.9 Hz,  $\text{PCHCH}_3$ ];  $\delta_{\text{P}}$  (81.0 MHz) 35.2 [d,  $J(\text{RhP})$  125.5 Hz].

**trans-[RhF(=C=CHBu<sup>t</sup>)(PPR<sup>i</sup><sub>3</sub>)<sub>2</sub>] 3b.** A solution of compound **2b**, prepared from **1** (0.258 g, 0.45 mmol) and 3,3-dimethyl-1-butyne (0.055 cm<sup>3</sup>, 0.45 mmol) in acetone (7 cm<sup>3</sup>), was treated with KF (0.078 g, 1.34 mmol) and stirred for 1.5 h at room temperature. The solvent was removed *in vacuo* and the residue extracted twice with 10 cm<sup>3</sup> portions of pentane. The combined extracts were filtered through cotton, the filtrate was concentrated to *ca.* 2 cm<sup>3</sup> and then stored for 24 h at  $-60^\circ\text{C}$ . Dark red-violet crystals precipitated which were washed twice with 2 cm<sup>3</sup>

portions of pentane ( $-78^{\circ}\text{C}$ ) and dried *in vacuo*: yield 0.155 g (66%); mp  $98^{\circ}\text{C}$  (Found: C, 54.61; H, 9.98.  $\text{C}_{24}\text{H}_{52}\text{FP}_2\text{Rh}$  requires C, 54.96; H, 9.99%). IR (Nujol):  $\nu(\text{C}=\text{C})$  1671, 1645,  $\nu(\text{RhF})$  453  $\text{cm}^{-1}$ . NMR ( $\text{C}_6\text{D}_6$ , 400 MHz)  $\delta_{\text{H}}$  (C $_6\text{D}_6$ , 400 MHz) 2.60 (6 H, m,  $\text{PCHCH}_3$ ), 1.35 [36 H, dvt,  $J(\text{HH})$  7.0,  $N$  13.5 Hz,  $\text{PCHCH}_3$ ], 1.04 [9 H, s,  $\text{C}(\text{CH}_3)_3$ ] and 0.08 (1 H, m,  $\text{Rh}=\text{C}=\text{CH}$ );  $\delta_{\text{C}}$  ( $\text{C}_6\text{D}_6$ , 100.6 MHz) 298.1 [ddt,  $J(\text{FC})$  89.0,  $J(\text{RhC})$  52.1,  $J(\text{PC})$  15.9,  $\text{Rh}=\text{C}$ ], 118.4 [ddt,  $J(\text{FC}) = J(\text{RhC})$  14.1,  $J(\text{PC})$  4.7,  $\text{Rh}=\text{C}=\text{C}$ ], 32.7 [s,  $\text{C}(\text{CH}_3)_3$ ], 24.8 [s,  $\text{C}(\text{CH}_3)_3$ ], 23.1 (vt,  $N$  17.6 Hz,  $\text{PCHCH}_3$ ) and 20.2 (s,  $\text{PCHCH}_3$ );  $\delta_{\text{F}}$  ( $d_8$ -toluene, 188.3 MHz)  $-222.5$  (br s);  $\delta_{\text{F}}$  (after treatment with anhydrous  $\text{Na}_2\text{CO}_3$ ,  $d_8$ -toluene, 188.3 MHz)  $-222.7$  [dt,  $J(\text{RhF}) = J(\text{PF})$  17.2 Hz];  $\delta_{\text{P}}$  ( $d_8$ -toluene, 81.0 MHz) 44.8 [dd,  $J(\text{RhP})$  146.6,  $J(\text{PF})$  17.2 Hz]. EI MS (70 eV):  $m/z$  524 ( $\text{M}^+$ , 4), 504 ( $\text{M}^+ - \text{HF}$ , 1), 442 ( $\text{M}^+ - \text{Bu}^t\text{C}_2\text{H}$ , 25), 422 ( $\text{M}^+ - \text{HF} - \text{Bu}^t\text{C}_2\text{H}$ , 10), 400 ( $\text{M}^+ - \text{Bu}^t\text{C}_2\text{H} - \text{C}_3\text{H}_6$ , 20) and 380 ( $\text{M}^+ - \text{HF} - \text{Bu}^t\text{C}_2\text{H} - \text{C}_3\text{H}_6$ , 16%).

**[Rh( $\mu$ -F)(PPR $_3$ ) $_2$ ] 4.** A solution of compound **1** (0.220 g, 0.38 mmol) in benzene (3  $\text{cm}^3$ ) was treated with tetrabutylammonium fluoride hydrate (solid, 98%, 0.120 g, 0.45 mmol) at room temperature. The mixture was stirred for 20 min and then pentane (30  $\text{cm}^3$ ) added. The suspension was stirred for 5 min and filtered using a cannula equipped with a cotton filter. The filtrate was brought to dryness *in vacuo*, the resulting orange-red solid washed twice with 2  $\text{cm}^3$  portions of pentane ( $-78^{\circ}\text{C}$ ) and dried: yield 0.126 g (74%); mp  $111^{\circ}\text{C}$  (decomp.) (Found: C, 48.61; H, 9.62.  $\text{C}_{36}\text{H}_{84}\text{F}_2\text{P}_4\text{Rh}_2$  requires C, 48.87; H, 9.57%). NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (400 MHz) 1.98 (12 H, m,  $\text{PCHCH}_3$ ) and 1.40 [72 H, dd,  $J(\text{HH})$  7.2,  $J(\text{PH})$  12.0 Hz,  $\text{PCHCH}_3$ ];  $\delta_{\text{C}}$  (100.6 MHz) 24.9 (m,  $\text{PCHCH}_3$ ) and 20.8 (s,  $\text{PCHCH}_3$ );  $\delta_{\text{F}}$  (376.5 MHz)  $-349.2$  (m, X part of the AA'A''A'''MM'XX' spectrum);  $\delta_{\text{P}}$  (162.0 MHz) 68.3 (m, A part of the AA'A''A'''MM'XX' spectrum).

**trans-[RhF(CO)(PPR $_3$ ) $_2$ ] 6.** A stream of CO was passed through a solution of compound **4** (0.208 g, 0.47 mmol) in pentane (20  $\text{cm}^3$ ) for 30 s at room temperature. A change from orange-red to pale yellow was observed. After the solution was stirred for 10 min at room temperature the solvent was removed *in vacuo*, the resulting yellow solid washed twice with 3  $\text{cm}^3$  portions of pentane ( $-20^{\circ}\text{C}$ ) and dried *in vacuo*: yield 0.165 mg (75%); mp  $154^{\circ}\text{C}$  (decomp.) (Found: C, 48.27; H, 8.72.  $\text{C}_{19}\text{H}_{42}\text{FOP}_2\text{Rh}$  requires C, 48.51; H, 9.00%). IR (Nujol):  $\nu(\text{CO})$  1934,  $\nu(\text{RhF})$  465  $\text{cm}^{-1}$ . NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (400 MHz) 2.32 (6 H, m,  $\text{PCHCH}_3$ ) and 1.29 [36 H, dvt,  $J(\text{HH})$  7.0,  $N$  13.8 Hz,  $\text{PCHCH}_3$ ];  $\delta_{\text{C}}$  (100.6 MHz) 192.9 [ddt,  $J(\text{FC})$  78.3,  $J(\text{RhC})$  68.1,  $J(\text{PC})$  15.3 Hz,  $\text{RhCO}$ ], 23.9 (vt,  $N$  19.3 Hz,  $\text{PCHCH}_3$ ) and 20.1 (s,  $\text{PCHCH}_3$ );  $\delta_{\text{F}}$  (376.5 MHz)  $-269.3$  [dt,  $J(\text{RhF})$  49.6,  $J(\text{PF})$  19.7 Hz];  $\delta_{\text{P}}$  (162.0 MHz) 51.8 [dd,  $J(\text{RhP})$  130.6,  $J(\text{PF})$  19.7 Hz]. EI MS (70 eV):  $m/z$  470 ( $\text{M}^+$ , 21), 442 ( $\text{M}^+ - \text{CO}$ , 4), 422 ( $\text{M}^+ - \text{CO} - \text{HF}$ , 9), 400 ( $\text{M}^+ - \text{CO} - \text{C}_3\text{H}_6$ , 13) and 380 ( $\text{M}^+ - \text{HF} - \text{CO} - \text{C}_3\text{H}_6$ , 10%).

**trans-[RhF(CNC $_6\text{H}_3\text{Me}_2$ -2,6)(PPR $_3$ ) $_2$ ] 7.** A solution of compound **4** (0.571 g, 0.64 mmol) in benzene (20  $\text{cm}^3$ ) was treated with 2,6-dimethylphenyl isocyanide (0.164 mg, 1.25 mmol) at room temperature. The solution was stirred for 1 h and then filtered through cotton. The filtrate was brought to dryness *in vacuo*, the resulting yellow solid washed three times with 5  $\text{cm}^3$  portions of hexane ( $0^{\circ}\text{C}$ ) and dried *in vacuo*. The mother-liquors were concentrated to ca. 4  $\text{cm}^3$  and stored for 5 d at  $-20^{\circ}\text{C}$  to give a second portion of the yellow solid: yield 0.585 mg (76%); mp  $48^{\circ}\text{C}$  (decomp.) (Found: C, 56.60; H, 8.62; N, 2.64.  $\text{C}_{27}\text{H}_{51}\text{FNP}_2\text{Rh}$  requires C, 56.53; H, 8.96; N, 2.45%). IR (Nujol):  $\nu(\text{C}=\text{N})$  2038, 2009,  $\nu(\text{RhF})$  458  $\text{cm}^{-1}$ ; NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (400 MHz) 6.76 [3 H, m,  $\text{C}_6\text{H}_3(\text{CH}_3)_2$ ], 2.37 [6 H, s,  $\text{C}_6\text{H}_3(\text{CH}_3)_2$ ], 2.35 (6 H, m,  $\text{PCHCH}_3$ ) and 1.37 [36 H, dvt,  $J(\text{HH})$  6.8,  $N$  13.2 Hz,  $\text{PCHCH}_3$ ];  $\delta_{\text{C}}$  (100.6 MHz) 133.1, 132.4, 128.0, 125.0 [all s,  $\text{C}_6\text{H}_3(\text{CH}_3)_2$ ], 23.9 (vt,  $N$  18.0 Hz,  $\text{PCHCH}_3$ ), 20.3 (s,  $\text{PCHCH}_3$ ) and 19.1 [s,  $\text{C}_6\text{H}_3(\text{CH}_3)_2$ ];  $\delta_{\text{F}}$  (188.3 MHz)

$-280.7$  [dt,  $J(\text{RhF})$  47.5,  $J(\text{PF})$  20.1 Hz];  $\delta_{\text{P}}$  (162.0 MHz) 50.3 [dd,  $J(\text{RhP})$  137.1,  $J(\text{PF})$  20.1 Hz]. EI MS (70 eV):  $m/z$  573 ( $\text{M}^+$ , 8) and 413 ( $\text{M}^+ - \text{PPR}_3$ , 3%).

**trans-[RhF(PhC $\equiv$ CPh)(PPR $_3$ ) $_2$ ] 8.** A solution of compound **4** (0.135 g, 0.15 mmol) in benzene (5  $\text{cm}^3$ ) was treated with diphenylacetylene (0.055 g, 0.31 mmol) at room temperature. The solution was stirred for 2 h and then brought to dryness *in vacuo*. The residue was extracted three times with 4  $\text{cm}^3$  portions of pentane. The combined extracts were filtered through cotton, the filtrate was concentrated to ca. 2  $\text{cm}^3$  and stored for 24 h at  $-20^{\circ}\text{C}$ . Yellow crystals precipitated which were washed three times with 2  $\text{cm}^3$  portions of pentane ( $-20^{\circ}\text{C}$ ) and dried *in vacuo*: yield 0.141 g (74%); mp  $94^{\circ}\text{C}$  (decomp.) (Found: C, 61.72; H, 8.74.  $\text{C}_{32}\text{H}_{52}\text{FP}_2\text{Rh}$  requires C, 61.93; H, 8.45%). IR (Nujol):  $\nu(\text{C}=\text{C})$  1870,  $\nu(\text{RhF})$  452  $\text{cm}^{-1}$ . NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (400 MHz) 8.37 [4 H, d,  $J(\text{HH})$  7.6, *ortho*-H of  $\text{C}_6\text{H}_5$ ], 7.27 [4 H, t,  $J(\text{HH})$  7.6, *meta*-H of  $\text{C}_6\text{H}_5$ ], 7.07 [2 H, t,  $J(\text{HH})$  7.6, *para*-H of  $\text{C}_6\text{H}_5$ ], 2.09 (6 H, m,  $\text{PCHCH}_3$ ) and 1.21 [36 H, dvt,  $J(\text{HH})$  6.7,  $N$  12.9 Hz,  $\text{PCHCH}_3$ ];  $\delta_{\text{C}}$  (100.6 MHz) 131.3, 130.8, 128.2, 126.4 (all s,  $\text{C}_6\text{H}_5$ ), 81.5 [dt,  $J(\text{RhC})$  16.2,  $J(\text{PC})$  2.9 Hz,  $\text{C}=\text{C}$ ], 23.0 (vt,  $N$  16.2 Hz,  $\text{PCHCH}_3$ ) and 20.2 (s,  $\text{PCHCH}_3$ );  $\delta_{\text{F}}$  (376.5 MHz)  $-257.8$  [br d,  $J(\text{RhF})$  80.1 Hz];  $\delta_{\text{F}}$  (after treatment with anhydrous  $\text{Na}_2\text{CO}_3$ ,  $d_8$ -toluene, 188.3 MHz)  $-258.1$  [dt,  $J(\text{RhF})$  79.3,  $J(\text{PF})$  16.6 Hz];  $\delta_{\text{P}}$  (81 MHz) 32.5 [dd,  $J(\text{RhP})$  125.5,  $J(\text{PF})$  16.6 Hz]. EI MS (70 eV):  $m/z$  620 ( $\text{M}^+$ , 0.03), 442 ( $[\text{RhF}(\text{PPR}_3)_2]^+$ , 0.02) and 178 ( $\text{Ph}_2\text{C}_2^+$ , 100%).

**trans-[RhF(C $_2\text{H}_4$ )(PPR $_3$ ) $_2$ ] 9.** A slow stream of ethylene was passed through a solution of compound **4** (0.210 g, 0.24 mmol) in pentane (15  $\text{cm}^3$ ) for 1 min at room temperature. A change from orange-red to yellow-orange occurred. After the solution was stirred for 15 min at room temperature, the solvent was removed *in vacuo*, the resulting yellow solid was washed three times with 2  $\text{cm}^3$  portions of pentane ( $-20^{\circ}\text{C}$ ) and dried *in vacuo*: yield 0.166 g (74%); mp  $95^{\circ}\text{C}$  (decomp.) (Found: C, 50.83; H, 9.43.  $\text{C}_{20}\text{H}_{46}\text{FP}_2\text{Rh}$  requires C, 51.06; H, 9.86%). IR (Nujol):  $\nu(\text{RhF})$  426  $\text{cm}^{-1}$ . NMR ( $\text{C}_6\text{D}_6$ ):  $\delta_{\text{H}}$  (400 MHz) 2.25 (4 H, br s,  $\text{C}_2\text{H}_4$ ), 2.08 (6 H, m,  $\text{PCHCH}_3$ ) and 1.27 [36 H, dvt,  $J(\text{HH})$  6.4,  $N$  12.8 Hz,  $\text{PCHCH}_3$ ];  $\delta_{\text{C}}$  (100.6 MHz) 33.8 [d,  $J(\text{RhC})$  15.3 Hz,  $\text{C}_2\text{H}_4$ ], 21.5 (vt,  $N$  16.3 Hz,  $\text{PCHCH}_3$ ) and 20.0 (s,  $\text{PCHCH}_3$ );  $\delta_{\text{F}}$  (188.3 MHz)  $-248.2$  [dt,  $J(\text{RhF})$  76.3,  $J(\text{PF})$  18.7 Hz];  $\delta_{\text{P}}$  (162.0 MHz) 36.4 [dd,  $J(\text{RhP})$  129.8,  $J(\text{PF})$  18.7 Hz]. EI MS (70 eV):  $m/z$  470 ( $\text{M}^+$ , 1), 442 ( $\text{M}^+ - \text{C}_2\text{H}_4$ , 3), 400 ( $\text{M}^+ - \text{C}_2\text{H}_4 - \text{C}_3\text{H}_6$ , 3) and 380 ( $\text{M}^+ - \text{C}_2\text{H}_4 - \text{C}_3\text{H}_6 - \text{HF}$ , 2%).

## Reactions of compound 10

**With trifluoromethanesulfonic acid.** In an NMR tube a solution of compound **10** (0.037 g, 0.068 mmol) in  $\text{C}_6\text{D}_6$  (0.4  $\text{cm}^3$ ) was treated with  $\text{CF}_3\text{SO}_3\text{H}$  (0.072  $\text{cm}^3$  of a 0.95 M solution in diethyl ether, 0.068 mmol) at room temperature. After 15 min the  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of the solution indicated a quantitative conversion into **2a**. In order to isolate compound **2a**, the solution was evaporated to dryness and pentane (15  $\text{cm}^3$ ) and anhydrous  $\text{Na}_2\text{CO}_3$  (0.5 g) were added to the residue. The mixture was stirred for 5 min, the solution was filtered through cotton and the filtrate brought to dryness *in vacuo*. The resulting blue-green solid was washed with pentane (2  $\text{cm}^3$ ,  $-78^{\circ}\text{C}$ ) and dried: yield 0.023 g (50%).

**With acetic acid.** In an NMR tube a solution of compound **10** (0.042 g, 0.077 mmol) in  $\text{C}_6\text{D}_6$  (0.4  $\text{cm}^3$ ) was treated with acetic acid (30  $\mu\text{L}$  of a 2.6 M solution in  $\text{C}_6\text{D}_6$ , 0.078 mmol) at room temperature. After 25 min, the  $^1\text{H}$  and  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of the solution indicated a quantitative conversion to compound **11**,<sup>27</sup> which was isolated in the same way as described for **2a**: yield 0.030 g (67%). The corresponding reactions of compound **10** with phenol and phenylacetylene have been reported.<sup>9</sup>



## Reactions of compound 3a

**With trifluoromethanesulfonic acid.** In an NMR tube a solution of compound **3a** (0.035 g, 0.064 mmol) in  $C_6D_6$  (0.4 cm<sup>3</sup>) was treated with  $CF_3SO_3H$  (0.067 cm<sup>3</sup> of a 0.95 M solution in diethyl ether, 0.064 mmol) at room temperature. An instant change from red-violet to dark violet was observed. The  $^1H$ ,  $^{19}F$  and  $^{31}P$ - $\{^1H\}$  NMR spectra of the solution indicated a quantitative conversion of **3a** into **2a**.

**With acetic acid.** In an NMR tube a solution of compound **3a** (0.043 g, 0.079 mmol) in  $C_6D_6$  (0.4 cm<sup>3</sup>) was treated with acetic acid (0.053 cm<sup>3</sup> of a 1.5 M solution in  $C_6D_6$ , 0.08 mmol) at room temperature. After 10 min the NMR spectra were recorded at room temperature:  $\delta_H$  (200 MHz) 11.3 (br s), 7.15–7.04 (4 H, m, *ortho*- and *meta*-H of  $C_6H_5$ ), 6.85 [1 H, t,  $J(HH)$  6.9, *para*-H of  $C_6H_5$ ], 2.45 (6 H, m,  $PCHCH_3$ ), 1.88 (3 H, s,  $CH_3CO_2$ ), 1.63 [1 H, dt,  $J(RhH)$  1.3,  $J(PH)$  3.1, C=CH] and 1.25 [36 H, dvt,  $J(HH)$  6.6,  $N$  13.9 Hz,  $PCHCH_3$ ];  $\delta_F$  (188.3 MHz) –213.9 (br s);  $\delta_P$  (81.0 MHz) 45.4 [d,  $J(RhP)$  140.0 Hz]. An analogous experiment was performed using  $d_6$ -toluene as solvent in order to measure the NMR spectra at low temperature:  $\delta_H$  (400 MHz, –70 °C) 13.9 (br s,  $CH_3CO_2H$ ), 12.0 [br d,  $J(FH)$  ca. 420 Hz,  $FHF-Rh$ ], 7.20–6.93 (5 H, m,  $C_6H_5$ ), 2.43 (6 H, br m,  $PCHCH_3$ ), 1.97 (3 H, br s,  $CH_3CO_2$ ), 1.68 (1 H, br m,  $Rh=C=CH$ ) and 1.25 (36 H, br m,  $PCHCH_3$ );  $\delta_F$  (376.5 MHz, –83 °C) –179.1 [br dd,  $J(FF)$  101,  $J(FH)$  418 Hz,  $FHF-Rh$ ], –214.8 (br m,  $F-Rh$ ) and –228.7 (br m,  $FHF-Rh$ );  $\delta_P$  (162.0 MHz, –83 °C) 44.4 [br d,  $J(RhP)$  139.0] and 41.2 [br d,  $J(RhP)$  137.3 Hz].

**With phenylacetylene.** A solution of compound **3a** (0.031 g, 0.057 mmol) in  $C_6D_6$  (0.4 cm<sup>3</sup>) was treated with phenylacetylene (0.052 cm<sup>3</sup> of a 1.1 M solution in  $C_6D_6$ , 0.057 mmol) and an excess of anhydrous  $Na_2CO_3$  (ca. 0.1 g) at room temperature. The mixture was stirred for 30 min at room temperature which led to a change from red-violet to green. The solution was then transferred to an NMR tube. The  $^1H$  and  $^{31}P$ - $\{^1H\}$  NMR spectra indicated a quantitative conversion of **3a** into **13**.<sup>27</sup>

## Crystallography

Single crystals of complex **9** were grown from pentane (–25 °C). Crystal data (from 25 reflections,  $10 < \theta < 15^\circ$ ): monoclinic, space group  $P2_1/c$  (no. 14);  $a = 19.401(9)$ ,  $b = 8.5915(9)$ ,  $c = 15.175(7)$  Å,  $\beta = 112.59(1)^\circ$ ,  $V = 2335(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.338$  g cm<sup>–3</sup>,  $\mu(Mo-K\alpha) = 0.868$  mm<sup>–1</sup>; crystal size  $0.12 \times 0.10 \times 0.03$  mm; Enraf-Nonius CAD4 diffractometer, graphite monochromator, zirconium filter (factor 16.5);  $T = 173(2)$  K,  $\omega$ – $\theta$  scans, maximum  $2\theta = 50^\circ$ ; 4191 reflections measured, 3875 independent, 2886 with  $I > 2\sigma(I)$ , 3869 used for refinement. Data reduction was performed with SDP.<sup>32</sup> Intensity data were corrected for Lorentz-polarization effects. Linear decay (loss of intensity 6.5%) and empirical absorption corrections ( $\psi$  scans) were applied (minimum transmission 94.34%).<sup>33</sup> The structure was solved by direct methods (SHELXS 86).<sup>34</sup> Atomic co-ordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms were refined anisotropically by full-matrix least squares on  $F^2$  (241 parameters; SHELXL 93).<sup>35</sup> The positions of H(1A), H(1B), H(2A), and H(2B) could be located in a final Fourier-difference synthesis and refined isotropically with fixed  $U_{eq}$ . The positions of the other hydrogen atoms were calculated according to ideal geometry using the riding method. Conventional  $R = 0.0405$  [for 2888 reflections with  $I > 2\sigma(I)$ ] and weighted  $wR2 = 0.1129$  for all 3869 data reflections; reflection-to-parameter ratio 16.05, residual electron density +0.673/–0.968.

CCDC reference number 186/1383.

See <http://www.rsc.org/suppdata/dt/1999/1437/> for crystallographic files in .cif format.

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Paper 9/00440H