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Rhodium vinylidene and alkyne complexes containing a pendant uracil group

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ABSTRACT

Reaction of HC≡CUr (Ur = uracil) with [RhCl(P*i*Pr$_3$)$_2$] results in the formation of the vinylidene complex [RhCl(P*i*Pr$_3$)$_2$(=C=C{H}Ur)]. In the solid state this complex forms a hydrogen bonded network which consists of complementary interactions between uracil groups on neighbouring rhodium complexes and with the methanol of crystallisation. The η^2-alkyne complexes [RhCl(P*i*Pr$_3$)$_2$(η^2-PhC≡CUr)] and [Rh(η^5-C$_5$H$_5$)(P*i*Pr$_3$)(η^2-PhC≡CUr)] have also been prepared. In contrast to the behaviour of [Rh(η^5-C$_5$H$_5$)(P*i*Pr$_3$)(η^2-PhC≡CUr)], [RhCl(P*i*Pr$_3$)$_2$(η^2-PhC≡CUr)] shows little evidence for the formation of hydrogen bonded aggregates in solution. The difference in behaviour between the two species is rationalised on the basis of steric effects.

1. Introduction

The synthesis of metal complexes which contain functional groups in their secondary coordination sphere that are capable of engaging in hydrogen bonding is an area of considerable current interest [1]. For example, the use of functional groups which may engage in self-complementary hydrogen bonding has been used to dictate the assembly of inorganic complexes in the solid state [2]. In addition, functional groups such as amino-pyridines [3] and modified barbituates [4] have been used to develop novel anion sensors [5] and complexes containing pendant nucleobase units have been developed as biological probes [6] and novel therapeutic agents [7].

We have previously demonstrated that the incorporation of pendant uracil groups into metal complexes may be employed to direct self assembly in the solid state and solution [8]. For example, reaction of [RuCl(η^5-C$_5$H$_5$)(PPh$_3$)$_2$] with the uracil-substituted alkyne HC≡CUr in the presence of a suitable halide scavenger results in the formation of [Ru(η^5-C$_5$H$_5$)(=C=C{H}Ur)(PPh$_3$)$_2$]$^+$. This reaction is highly selective and we reasoned that the soft metal–substrate reacts selectively with the C≡C functionality of the alkyne rather than the hard N and O donor atoms of the uracil. By virtue of hydrogen bonds between the uracil groups, [Ru(η^5-C$_5$H$_5$)(=C=C{H}Ur)(PPh$_3$)$_2$]$^+$ self-assembles in the solid state to give hexagonal arrays containing six ruthenium cations [9]. This vinylidene complex acts as a precursor to a range of uracil-substituted complexes containing carbene [Ru(η^5-C$_5$H$_5$)(=C{OMe}CH$_2$-Ur)(PPh$_3$)$_2$]$^+$, alkynyl [Ru(η^5-C$_5$H$_5$)(−C≡CUr)(PPh$_3$)$_2$] and phosphonio-alkenyl [Ru(η^5-C$_5$H$_5$)(−C{H}=C{PPh$_3$}Ur)(PPh$_3$)$_2$]$^+$ ligands [10,11]. All of these complexes show evidence of aggregation in solution and the solid state structures of the carbene and phosphonio-alkenyl complexes show a dimeric arrangement of the uracil groups. In addition, we have prepared a gold complex containing a uracil-substituted phosphine, viz. [AuCl(PPh$_2$Ur)] [12]. In this case the uracil groups form a hydrogen bonded tape structure utilising both N–H and C=O functional groups of the nucleobase. The tape structures pack in such a manner as to create a cavity of dimensions 11.720 and 11.4547 Å which is occupied by THF molecules of crystallisation.

As there are many possible applications of metal complexes containing pendant nucelobase groups, the development of versatile synthetic routes to these species is an important goal. As part of our programme utilising substituted alkynes to achieve the facile incorporation of uracil groups into the periphery of different metal-containing compounds, the series of rhodium complexes based on the RhCl(PR$_3$)$_2$ motif pioneered by Werner and co-workers were targeted as possible supports for the nucleobase [13]. Using terminal alkynes a series of complexes containing alkyne, **A**, alkynyl hydride **AH**, and vinylidene, **V**, ligands have been prepared (Fig. 1) and their mechanism of interconversion has been probed in recent theoretical [14–16] and experimental studies [17–19]. These results demonstrate that the conversion from **A** to **AH** and **V** occurs in a unimolecular fashion and the formation of the vinylidene complexes is essentially irreversible. The use of internal alkynes such as PhC≡CPh prohibits the formation of alkynyl hydride and vinylidene complexes and the resulting π-alkyne species [RhCl(P*i*Pr$_3$)$_2$(η^2-PhC≡CPh)] may prepared which, on reaction

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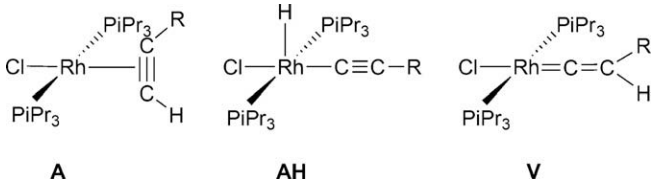


Fig. 1. Structures of rhodium alkyne (**A**), alkynyl hydride (**AH**) and vinylidene (**V**) complexes.

with NaCp, may be converted into the corresponding half sandwich complexes [RhCl(η^5-C_5H_5)(P*i*Pr$_3$)(η^2-PhC≡CPh)] [20].

We now report the reaction of the uracil-substituted alkynes HC≡CUr and PhC≡CUr with the RhCl(PR$_3$)$_2$-system to give vinylidene [RhCl(P*i*Pr$_3$)$_2$(=C=C{H}Ur)] and alkyne complexes [RhCl(P*i*Pr$_3$)$_2$(η^2-PhC≡CUr)], respectively. The latter was also shown to react with NaC_5H_5 to afford [RhCl(η^5-C_5H_5)(P*i*Pr$_3$)(η^2-PhC≡CUr)].

2. Results and discussion

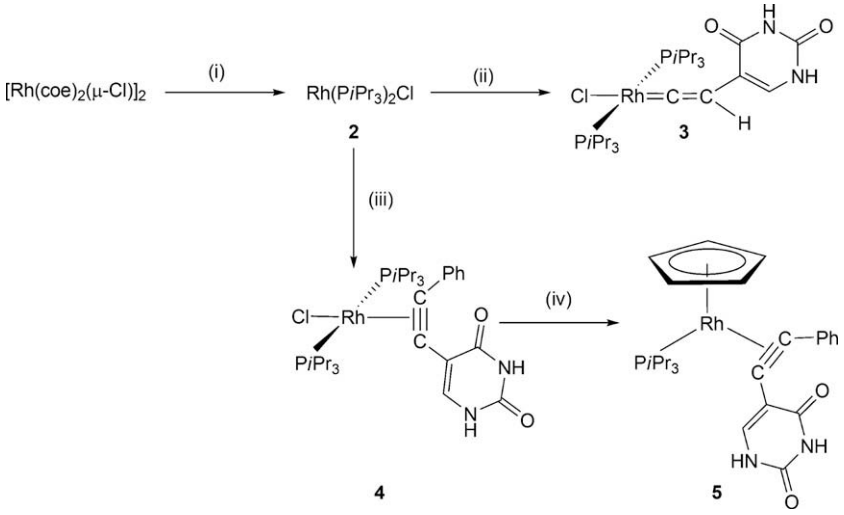
The synthetic routes employed to prepare all of the complexes reported in this study are shown in Scheme 1. The compounds were characterised principally by multinuclear NMR spectroscopy, IR spectroscopy and mass spectrometry: the structure of [RhCl(P*i*Pr$_3$)$_2$(=C=C{H}Ur)] was also determined by single crystal X-ray diffraction.

2.1. Synthesis and structure of [RhCl(P*i*Pr$_3$)$_2$(=C=C{H}Ur)], 3

Reaction of HC≡CUr, **1**, with [RhCl(P*i*Pr$_3$)$_2$], **2**, (prepared *in situ* from the reaction of [Rh(coe)$_2$(μ-Cl)]$_2$and excess P*i*Pr$_3$, coe = cyclooctene), in THF solution resulted in an immediate colour change from dark violet to bright orange: over the course of 30 min a final colour change to violet/dark green was observed. After 16 h, the reaction mixture was subjected to a work-up procedure to afford a blue/green precipitate of [RhCl(P*i*Pr$_3$)$_2$(=C=C{H}Ur)], **3**. The presence of the vinylidene ligand in **3** was confirmed by resonances in the $^{13}C\{^1H\}$ NMR spectrum at δ 295.50 (dt, $^1J_{CRh}$ = 58.3 Hz, $^2J_{CP}$ = 15.8 Hz) and 99.71 (dt, $^2J_{CRh}$ = 15.9 Hz, $^2J_{CP}$ = 6.3 Hz) for the α- and β-carbons, respectively. A triplet resonance was observed at δ 1.30 (t, $^4J_{HP}$ = 3.0 Hz) in the ^1H NMR spectrum for the proton attached to the β-carbon of the vinylidene ligand. These resonances are typical for vinylidene ligands supported by the RhClL_2 motif [13b,18]. In addition, a series of resonances for the uracil substituent were observed in the ^1H NMR spectrum notably resonances for the two N–H protons of the uracil group were observed at δ = 10.16 and 9.56 as well as a peak for the C–H(5) proton at δ 7.06 (d, $^3J_{HH}$ = 5.2 Hz): a series of resonances for this group were also observed in the $^{13}C\{^1H\}$ NMR spectrum.

Recrystallisation of **3** from methanol at −20 °C resulted in the formation of crystals of the complex suitable for study by single crystal X-ray diffraction. The resulting structural determination demonstrated that **3** crystallised as a MeOH solvate in the orthorhombic space group *Pbca*: an ORTEP diagram of the asymmetric unit of **3**·MeOH is shown in Fig. 2. Complex **3** adopts a square planar geometry with mutually *trans* phosphine ligands. The bond lengths and angles within the vinylidene ligands are typical with short Rh(1)–C(1) (1.791(3) Å) and C(1)–C(2) (1.319(4) Å) distances and an essentially linear vinylidene geometry (Rh(1)–C(1)–C(2) 179.5(3)°). The uracil and hydrogen atom attached to the vinylidene ligand lie in a plane which is perpendicular to the square plane containing the rhodium. Indeed, the structural metrics and topology of **3** are essentially identical to [RhCl(P*i*Pr$_3$)$_2$(=C=C{H}Me)] reported by Werner [13b]. The bond lengths and angles within the uracil group are also typical: H(1) and H(2A) were located in the electron difference map and refined as part of the structural solution.

As is the case in all the uracil-containing complexes we have prepared to date, the solid state structure of **3** exhibits a series of intermolecular hydrogen bonding interactions. The uracil groups on neighbouring molecules of **3** engage in a complementary hydrogen bonding interaction between C=O(2) and N(2)–H(2A) (N(2)–H(2A)···O(2) 2.786(3) Å), Fig. 3a. This type of hydrogen bonding interaction between uracil groups has been observed as part of a larger construct in the case of AuCl(PPh$_2$Ur) [12]. In organometallic complexes, dimeric arrays based on complementary hydrogen bonds between C=O(4) and N(2)–H(2a) have been observed in several cases, although in these instances the complexes are cationic with the anion being involved in hydrogen bonding to N–H(1) [9–11]. In the case of complex **3**, each uracil group is involved in hydrogen bonding to two molecules of MeOH:N–H(1) acts as a hydrogen bond donor to the oxygen atom, O(3), of the MeOH (N(1)–H(1)···O(3) 2.732(3) Å), whereas C=O(4) acts as hydrogen bond acceptor with the hydroxyl proton of a second methanol molecule (O(3)–H(3)···O(1) 2.730(3) Å).



Scheme 1. (i) + Excess P*i*Pr$_3$; (ii) + **1**, THF; (iii) + PhC≡CUr, THF; and (iv) + NaCp.

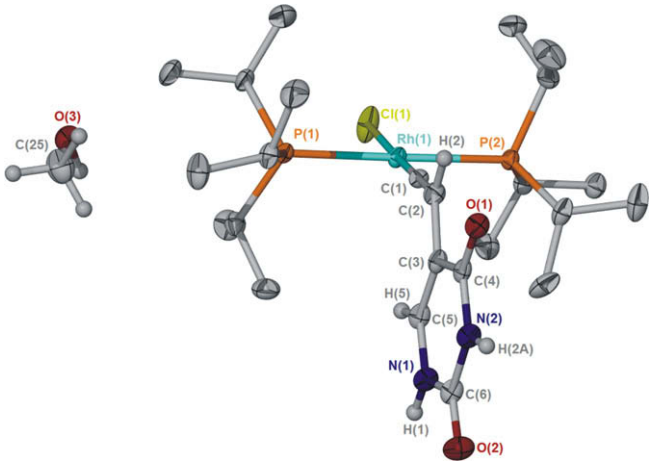


Fig. 2. ORTEP representation of **3**·MeOH, thermal ellipsoids shown at the 50% probability level and selected hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Rh(1) 1.791(3), P(1)–Rh(1) 2.3598(7), P(2)–Rh(1) 2.3624(7), Cl(1)–Rh(1) 2.3735(7) C(1)–C(2) 1.319(4), C(2)–C(3) 1.464(4),C(3)–C(5) 1.350(4), C(3)–C(4) 1.464(4), C(4)–O(1) 1.221(3),C(4)–N(2) 1.382(3), C(5)–N(1) 1.375(3), C(6)–O(2) 1.234(3) C(6)–N(1) 1.352(3), C(6)–N(2) 1.376(4), N(1)–H(1) 0.9030, N(2)–H(2A) 0.8890. C(1)–Rh(1)–P(1) 89.94(8), C(1)–Rh(1)–P(2) 90.00(8), P(1)–Rh(1)–P(2) 178.93(3), C(1)–Rh(1)–Cl(1) 177.43(9), P(1)–Rh(1)–Cl(1) 89.45(2), P(2)–Rh(1)–Cl(1) 90.57(2), C(1)–C(2)–C(3) 124.4(3), C(5)–C(3)–C(4) 117.4(2), C(5)–C(3)–C(2) 124.8(2), C(4)–C(3)–C(2) 117.8(2), O(1)–C(4)–N(2) 120.2(2), O(1)–C(4)–C(3) 124.9(3), N(2)–C(4)–C(3) 114.9(2), C(3)–C(5)–N(1) 123.3(2), O(2)–C(6)–N(1) 122.4(3), O(2)–C(6)–N(2) 122.5(2), N(1)–C(6)–N(2) 115.1(2), C(6)–N(2)–H(2A) 112.9, C(4)–N(2)–H(2A) 120.1.

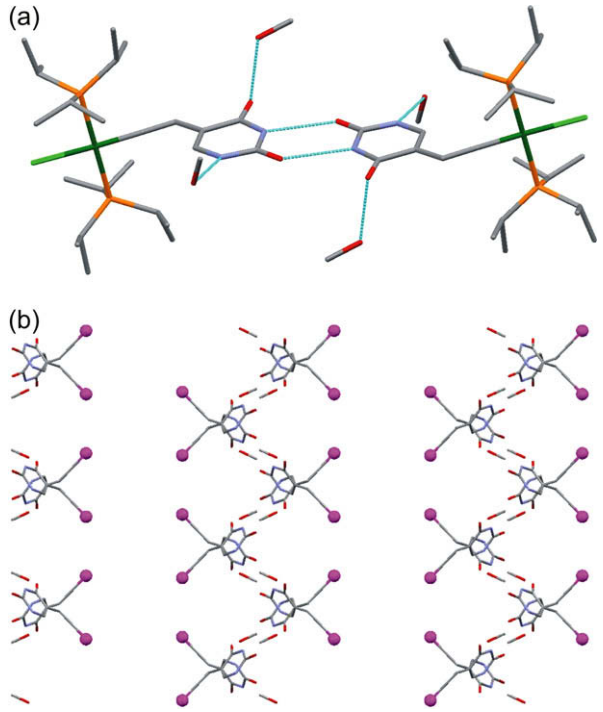


Fig. 3. (a) Hydrogen bonding interactions between **3** and MeOH. (b) Extended hydrogen bonding motif in **3**.MeOH viewed down the *b*-axis of the unit cell. For clarity, the RhCl($PiPr_3$)$_2$ unit is represented by purple spheres.

An extended view of the structure (Fig. 3b) demonstrates that a series of domains are present. One series of domains contains the non-polar regions of the rhodium complexes, whereas the others contain the polar uracil and methanol molecules. The clustering of polar and non-polar regions is common in structures containing pendant uracil groups [8,12]. Within the polar domain a two dimensional array of uracil and methanol groups is present. The uracil groups are present in two distinct planes (Fig. 3b): in each plane uracil groups are present that are engaged in complementary hydrogen bonding. The angle between the planes is *ca.* 64° and uracil groups in the respective planes are bridged by the methanol of crystallisation which acts as a both a hydrogen bond donor and acceptor to two different uracil groups. One important facet of this structure is that both of the uracil hydrogen bond donor and both acceptor groups are employed in the creation of the network. This ensures that the maximum number of hydrogen bonding interactions are present, which is consistent with our results which show that, within the confines of steric hindrance, this is tends to be the case.

2.2. Synthesis and solution state behaviour of [RhCl($PiPr_3$)$_2$(η^2-PhC≡CUr)], ***4***

Reaction of *in situ*-prepared **2** with PhC≡CUr in THF solution resulted in the formation of [RhCl($PiPr_3$)$_2$(η^2-PhC≡CUr)], **4**, in good yield. This method is analogous to that employed by Werner for the formation of [RhCl($PiPr_3$)$_2$(η^2-PhC≡CPh)] [20], although this latter case the reaction was performed in pentane – which is precluded in this instance due to the insolubility of PhC≡CUr in this solvent. The ^{1}H NMR spectrum of **4** recorded in d_8-THF solution exhibited the expected series of resonances. Notably, the N–H resonances of the uracil group were observed at δ 10.33 (d, br, $^3J_{HH}$ = 5.43 Hz, NH(1)) and 10.31 (s, br, NH(3)): the assignment of these resonances was confirmed with the aid of a ^{1}H–^{1}H COSY experiment which demonstrated that the peak at δ 10.33 was coupled to the proton in the 5-position of the uracil group (δ 8.44, d, $^3J_{HH}$ = 5.43 Hz). The presence of the η^2-alkyne ligand was confirmed by resonances in the ^{13}C{^{1}H} NMR spectrum at δ 81.07 (dt, $^1J_{CRh}$ = 14.8 Hz, $^2J_{CP}$ = 2.4 Hz) and 68.76 (dt, $^1J_{CRh}$ = 16.2 Hz, $^2J_{CP}$ = 2.3 Hz). As in the case of complex **3**, the NMR data for **4** closely match those observed for the aryl-substituted analogues indicating that the incorporation of the uracil group does not significantly alter either the structure of the complex or the nature of the bonding between the organic ligand and the metal.

Despite repeated attempts, we have been unable to grow a crystal of **4** suitable for study by single crystal X-ray diffraction. Therefore, in order to probe any aggregation effects induced by the uracil group a series of ^{1}H NMR spectra of **4** were recorded at a range of concentrations in d_8-THF solution (Fig. 4a). Considering dimeric structures alone, there are six possible interaction by which the uracil group may become engaged in complementary N–H···O=C hydrogen bonding (Fig. 5). Hydrogen bonded dimers with structures **A**, **B** and **C** have been observed by low temperature NMR experiments on substituted uracil and 1-methylthymine [21]. The experiments indicate that there is little difference in energy between the three motifs which is supported by theoretical calculations on the self-aggregation of 1-methylthymine which indicate only a 0.1 kcal mol^{-1} difference in energy between the three forms [22]. In addition, NMR studies performed on 1-cyclohexyluracil have demonstrated that both C=O(2) and C=O(4) may act as hydrogen bond acceptors [23]. Furthermore, calculations on the hydrogen bonding between uracil and water illustrate that there is a similar difference in energy between the binding of water to N–H(1) or N–H(3) [22]. These data indicate that, in principle, the formation of hydrogen bonded dimers may occur by any of the six modes **A**–**F** in Fig. 5.

Our previous studies on ruthenium complexes containing pendant uracil groups had demonstrated that the N–H protons of the uracil groups were a useful probe of aggregation processes occurring in solution [9–11]. By examining the changes in chemical shift of the N–H protons of the uracil group we have obtained evidence for all six modes being present in the various ruthenium complexes we have studied [9–11]. In the case of complex **4** it is evident that

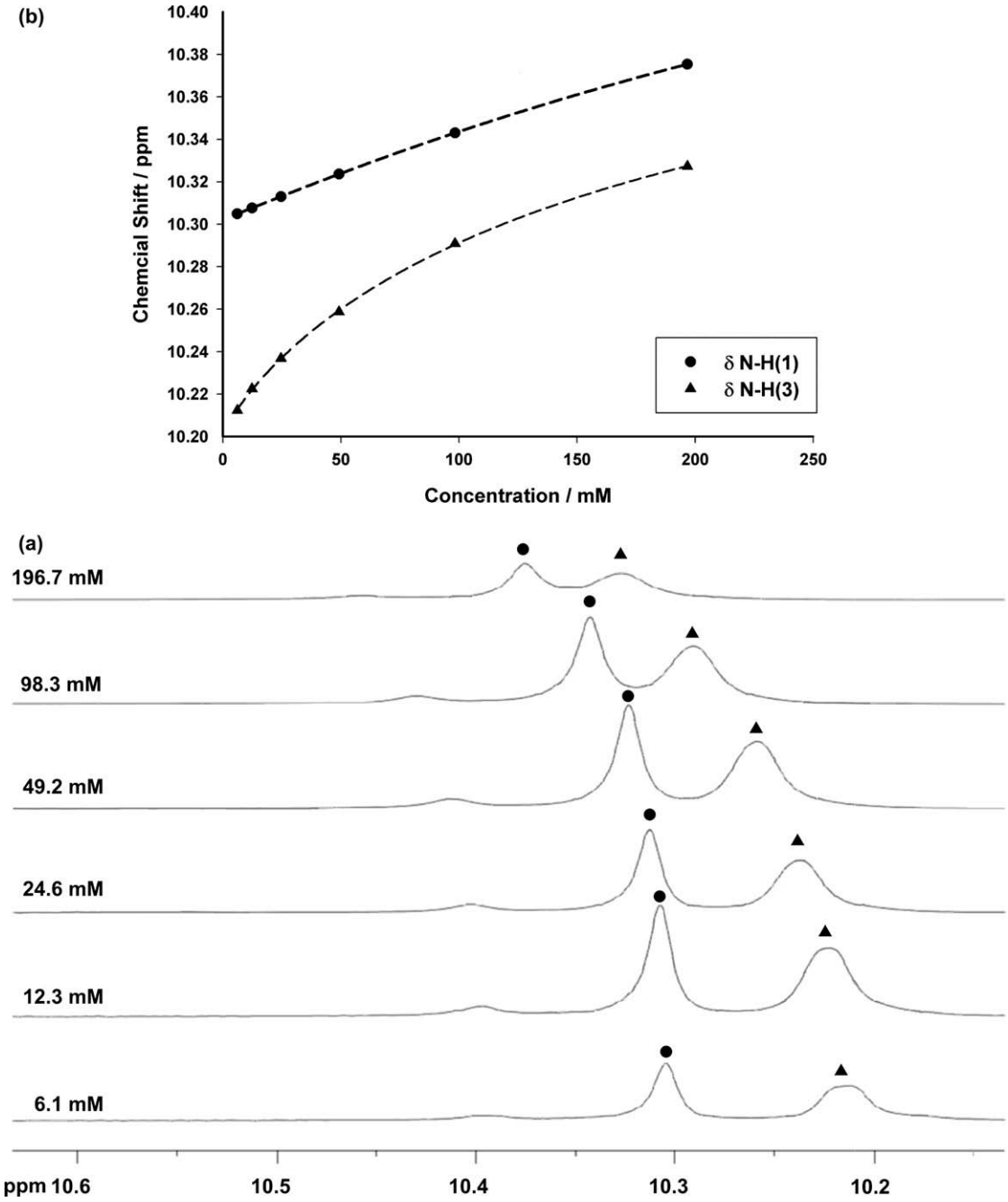


Fig. 4. (a) NH region of the ^{1}H NMR spectrum of **4** recorded at a range of concentrations in d_8-THF solution. (b) Graph of chemical shift of N–H resonances versus concentration.

the changes in chemical shift of the two N–H protons on increasing the concentration are small. Indeed, between the least (6.1 mM) and most (196.7 mM) concentrated solutions the proton for N–H(1) exhibited a downfield shift from δ 10.30 to 10.37 (0.07 ppm): for N–H(3) the corresponding shift is from δ 10.21 to 10.32 (0.11 ppm). Although the resonances for N–H(3) shows greater changes in chemical shift at lower concentrations (Fig. 4b) it must be emphasised that they are extremely small particularly when compared to the ruthenium complexes, albeit typically recorded in CD_2Cl_2 solution, where changes in chemical shift of 1 ppm are typical even when smaller concentrations ranges are employed. Unfortunately, the poor solubility of **5** in CH_2Cl_2 precluded any direct comparison of the ruthenium- and rhodium-containing systems. These data therefore appear to indicate that the extent of aggregation exhibited by **4** is limited in THF solution, and given that the changes in chemical shift for both NH protons are similar over the concentration range studied aggregation may be occurring by any, or indeed all, of the binding modes in Fig. 5.

2.3. Synthesis and solution state behaviour of [Rh(η^5-C_5H_5)(PiPr$_3$)(η^2-PhC≡CUr)], ***5***

The cyclopentadienyl-containing complex [Rh(η^5-C_5H_5)(P*i*Pr$_3$)-(η^2-PhC≡CUr)], **5**, was prepared from the reaction of a THF solution of **4** with 2 equiv. of NaC_5H_5 in an analogous manner to that reported by Werner et al. [20]. After stirring for 10 h the solvent was removed *in vacuo* and the resulting solid washed with hexane. Complex **5** was obtained as a yellow solid by precipitation from THF solution of the complex with hexane and characterised by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

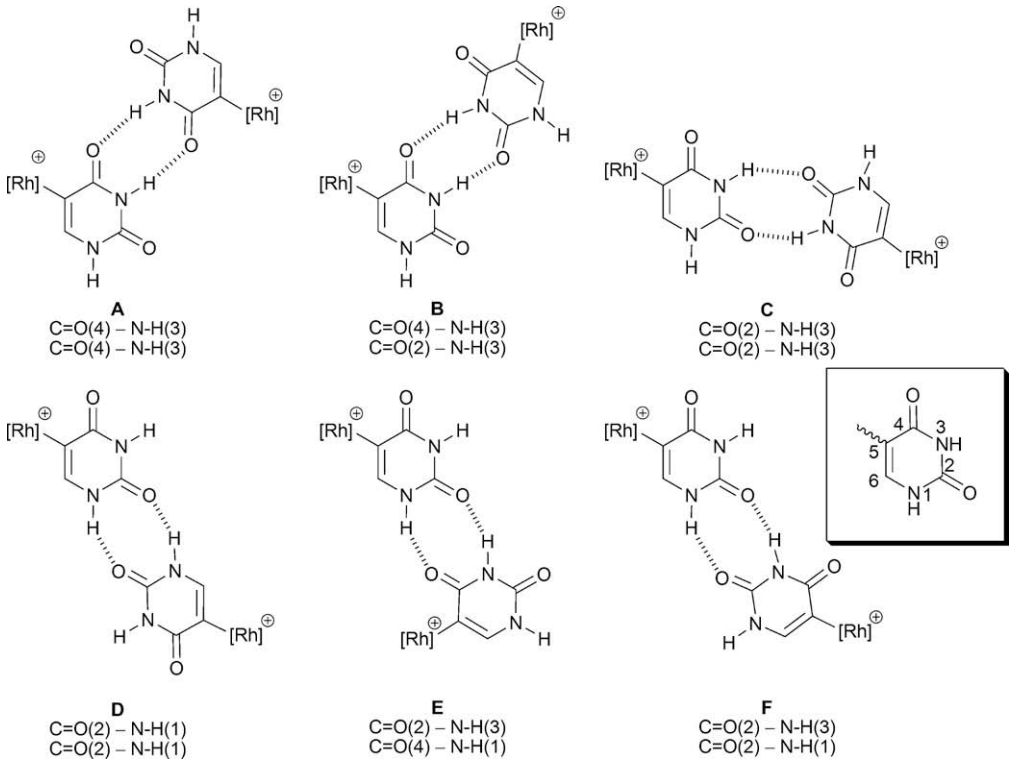


Fig. 5. Possible dimeric hydrogen bonding arrangements for complexes with pendant uracil groups. [Rh] = RhCl(P*i*Pr$_3$)$_2$(=C=C{H}), **3**, [RhCl(P*i*Pr$_3$)$_2$(η^2-PhC≡C–)], **4**, [Rh(η^5-C$_5$H$_5$)(P*i*Pr$_3$)(η^2-PhC≡C–)], **5**.

In contrast to **4**, the NMR spectra of **5** exhibited the effects of intermolecular hydrogen bonding. The NMR spectra of **5** recorded in d$_4$-methanol solution were sharp. For example, the ^{31}P{^{1}H} NMR spectrum exhibited a resonance at δ 72.63 ($^1J_{PRh}$ = 203.7 Hz), Fig. 6a. In addition, the ^{1}H NMR spectrum confirmed the presence of the pertinent structural features in **5**. For example, a singlet resonance due to the cyclopentadienyl group was observed at δ 5.31, as were resonances for the two N–H groups at 8.42 and 7.90 and the resonance for the C–H(5) group at δ 8.10 (d, $^3J_{HH}$ = 7.9 Hz). In contrast recording the ^{31}P{^{1}H} and ^{1}H NMR spectra in d$_8$-THF solution resulted in an extremely broad series of resonances. For example, the ^{31}P{^{1}H} NMR spectrum of **5** exhibited an extremely broad resonance at δ 73.08 ($^1J_{PRh}$ = 211.3 Hz), Fig. 6b. The ^{1}H NMR spectrum was similarly broad.

We have interpreted these data in the following manner. In MeOH solution the uracil group is able to engage in hydrogen bonding to the solvent, as has been demonstrated in the structure of complex **3**, MeOH is able to act as both hydrogen bond acceptor and donor to this functional group. Therefore, little aggregation between uracil groups on different molecules is observed. In contrast, in THF solution, the solvent is not able to participate in significant interaction with the uracil and hence the structure in solution is dominated by hydrogen bonding between uracil groups. As this hydrogen bond may occur *via* several different modes and, in principle, aggregates with different nuclearity may also be present, broadening of the ^{31}P{^{1}H} NMR spectra occurs. We have observed almost identical effects in the NMR spectra of the alkynyl complex [Ru(–C≡CUr)(η^5-C$_5$H$_5$)(PPh$_3$)$_2$] [11].

It is interesting to compare the aggregation behaviour exhibited by **4** and **5** in THF solution. In the case of the former little evidence for hydrogen bonding was obtained whilst the opposite is true of the latter. As discussed above, our previous studies have indicated that, within steric constraints, the uracil group strives to employ all of its N–H and C=O groups in hydrogen bonding in both the solid state and solution. Therefore, we propose that in the case of **4** the fact that the uracil group will sit in a plane between two sterically demanding P*i*Pr$_3$ groups inhibits aggregation. In the case of **5**, one of the P*i*Pr$_3$ groups has been removed and the uracil group is now orientated away from this ligand and as such may more freely engage in hydrogen bonding.

3. Conclusions

In this manuscript we have demonstrated that the reactions of uracil-substituted alkynes with the low valent, electron-rich rhodium precursor **2** exhibit few differences when compared to simple aryl- and alkyl-substituted analogues. The crystal structure of **3** demonstrates that non-covalent interactions may play an important role in the assembly of organometallic complexes in the solid state. It is also evident that steric effects have an important role in determining the modes of assembly in complexes such as this. When the uracil group is remote from the metal (as in **3**) then all of the functional groups may be utilised in hydrogen bonding. The same effects appear to occur in solution, in more hindered situations such as **4** aggregation appears to be very limited, whereas in **5** more pronounced intermolecular interactions are present.

4. Experimental

4.1. General considerations

All experimental procedures were performed under an atmosphere of dinitrogen or argon using standard Schlenk line and glove box techniques. Solvents were purified by distillation under argon prior to use from appropriate drying agents (MeOH from Mg/I$_2$, THF and hexane from Na wire). The d$_8$-THF used for NMR experiments was dried over potassium metal and degassed with three freeze-pump-thaw cycles. The compounds HC≡CUr, **1** [24], and [Rh(μ-Cl)(coe)$_2$]$_2$ [25] were prepared according to published

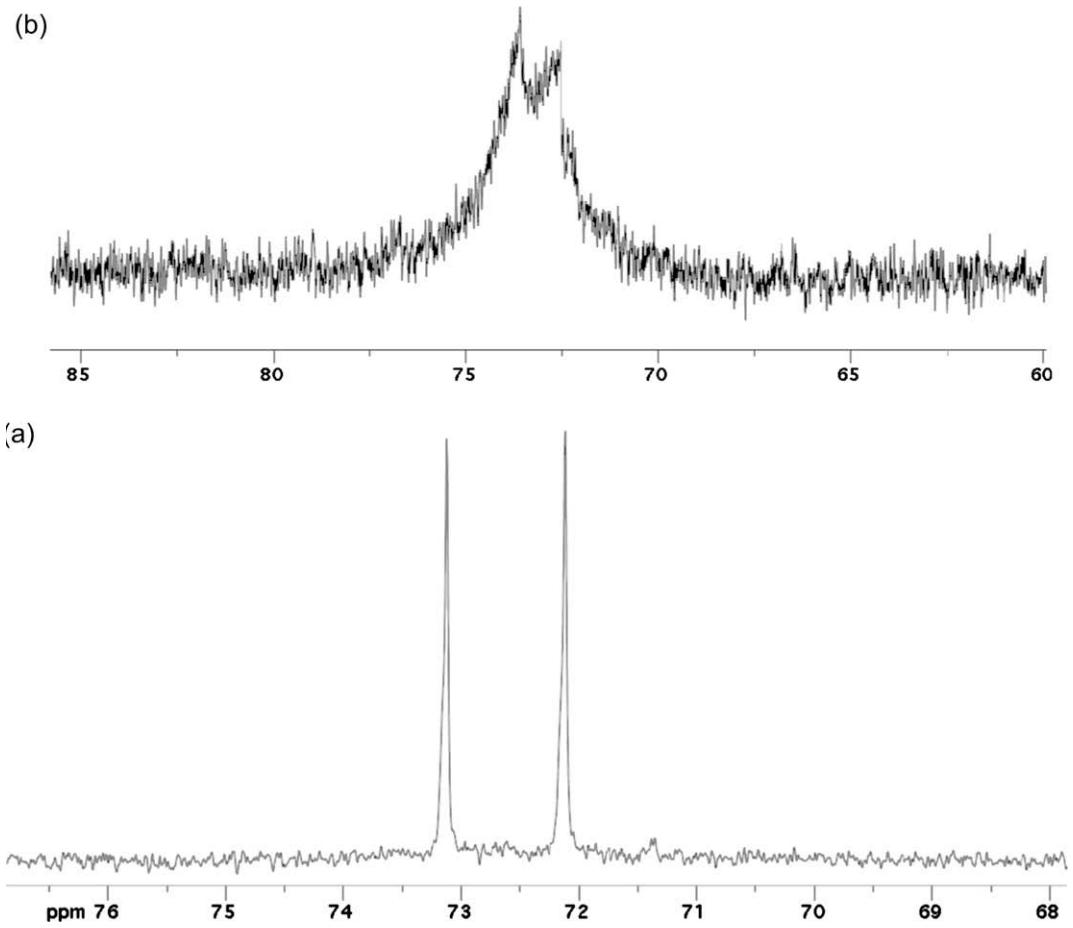


Fig. 6. (a) $^{31}P\{^{1}H\}$ NMR spectrum of **5** in MeOD. (b) $^{31}P\{^{1}H\}$ NMR spectrum of **5** in d_8-THF.

procedures, PhC≡CUr was provided by Dr Benjamin Moulton and was obtained from the Sonogashira reaction of PhC≡CH with IUr. NMR spectra were acquired on a Bruker AV 500 spectrometer (Operating Frequencies ^{1}H 500.13 MHz, ^{31}P 202.47 MHz) or a Bruker Avance 700 Spectrometer (Operating Frequencies ^{1}H 700.13 MHz, ^{31}P 283.46 MHz). Solution state NMR studies were performed using standard d_8-THF or d_4-methanol solutions of **4** and **5** made to the appropriate concentrations by using serial dilution. IR spectra were acquired using a Mattson Research Series FTIR spectrometer using solution state cells. Mass spectrometry measurements were performed on Bruker MicroTOF instrument and data for the peak at highest *m/z* are reported. Attempts to obtain satisfactory combustion analyses were unsuccessful.

4.2. Synthesis of [RhCl(PiPr$_3$)$_2$(=C=\{H\}Ur)], **3**

[Rh(μ-Cl)(coe)$_2$]$_2$ (250 mg, 0.35 mmol) was placed in a Schlenk tube and suspended in THF. P*i*Pr$_3$ (0.5 mL, 2.5 mmol) was added rapidly to the solution, whereupon the solution underwent a colour change from orange to dark violet. After stirring for 10 min, 2 equiv. HC≡CUr (95 mg, 0.7 mmol) were added to the solution, which turned orange immediately, turning dark green/purple after 30 min. After stirring for 16 h, the solution was filtered and the solvent removed *in vacuo*. The oily residue was washed with hexane (2 × 10 mL) and then redissolved in THF (20 mL). The THF solution was triturated with hexane to give a blue/green precipitate. The solid was isolated by filtration and washed with hexane (3 × 10 mL), then dried under vacuum. The complex was crystallized by preparing a saturated solution in methanol, filtering off the solid and storing the filtrate at −20 °C for several days. Yield 194 mg, 64%.

^{1}H NMR: (d_8-THF, 300 K) δ = 10.16 (s, 1H, N***H***), 9.56 (s, 1H, N***H***), 7.06 (d, $^{3}J_{HH}$ = 5.2 Hz, 1H, uracil C$_5$***H***), 2.77 (m, 6H, PC***H***CH$_3$), 1.35 (dd, $^{3}J_{HP}$ = 13.7 Hz, $^{3}J_{HH}$ = 6.8, 36 H, PCHC***H***$_3$), 1.30 (t, $^{4}J_{HP}$ = 3.0 Hz, 1H, Rh=C=C(***H***)Ur). $^{31}P\{^{1}H\}$ NMR: (d_8-THF, 300 K) δ = 42.51 (d, $^{1}J_{RhP}$ = 134.2 Hz, ***P***iPr_3). $^{13}C\{^{1}H\}$ NMR: (d_8-THF, 300 K) δ = 295.50 (dt, $^{1}J_{CRh}$ = 58.3 Hz, $^{2}J_{CP}$ = 15.8 Hz, Rh=C), 161.25 (s, C=O), 150.20 (s, C=O), 132.72 (s, Ur ***C***$_5$H), 99.71 (dt, $^{2}J_{CRh}$ = 15.9 Hz, $^{2}J_{CP}$ = 6.3 Hz, Rh=C=C), 96.18 (s, Ur C_1), 23.48 (vt, *J* = 10 Hz, P***C***), 19.63 (s, PCH***C***H$_3$). IR: (THF) 2962 cm^{-1}, 2906 cm^{-1} (NH); 1703 cm^{-1}, 1647 cm^{-1}(CO); 1622 cm^{-1} (C=C). ESI mass spectrum: (MeOH, positive mode) *m/z* = 559.2093 (Calc. for $C_{24}H_{46}N_2O_2P_2Rh$ [M−Cl$^-$] 559.2084).

4.3. Synthesis of [RhCl(PiPr$_3$)$_2$(η^2-PhC≡CUr)], **4**

[Rh(μ-Cl)(coe)$_2$]$_2$ (250 mg, 0.35 mmol) was placed in a Schlenk tube and suspended in THF (20 mL). P*i*Pr$_3$ (0.5 mL, 2.5 mmol) was added rapidly to the solution, whereupon the solution underwent a colour change from orange to dark violet. After stirring for 10 min, 2 equiv. PhC≡CUr (148 mg, 0.7 mmol) was added to the solution, which turned orange immediately. After stirring for 16 h, the solution was filtered and the solvent removed *in vacuo*. The oily residue was washed with hexane (2 × 10 mL) and then redissolved in THF (20 mL). The product was precipitated from the resulting THF solution by addition of hexane and isolated by filtration. The yellow solid was washed with hexane (3 × 10 mL), then dried under vacuum. Yield 364 mg, 77%.

^{1}H NMR: (d_8-THF , 300 K) δ = 10.33 (d, br, $^3J_{HH}$ = 5.43 Hz, N***H***(1)), 10.31 (s, br, N***H***(3)), 8.51 (d, $^3J_{HH}$ = 7.7 Hz, 2H ortho-Ph), 8.44 (d, $^3J_{HH}$ = 5.43 Hz, 1H, Ur C_5***H***), 7.21 (t, $^3J_{HH}$ = 7.6 Hz, 2H, meta-Ph), 7.11 (t, $^3J_{HH}$ = 7.3 Hz, 1H, para-Ph), 2.26 (m, 6H PC***H***), 1.23 (dvt, 36 H, PCH(C***H***$_3$)$_2$). ^{31}P{^{1}H} NMR: (d_8-THF, 300 K) δ = 29.13 (d, $^2J_{PRh}$ = 116.5 Hz, P*i*Pr$_3$). ^{13}C{^{1}H} NMR: (d_8-THF, 300 K) δ = 161.04 (s, C═O), 151.20 (s, C═O), 143.52 (s, Ur ***C***$_5$H), 133.36 (s, ortho-Ph), 131.14 (Ph ***C***$_1$), 127.76 (s, meta-Ph), 126.73 (s, para-Ph), 105.99 (Ur ***C***$_1$), 81.07 (dt, $^1J_{CRh}$ = 14.8 Hz, $^2J_{CP}$ = 2.4 Hz, C≡C), 68.76 (dt, $^1J_{CRh}$ = 16.2 Hz, $^2J_{CP}$ = 2.3 Hz, C≡C), 25.07 (s. P***C***), 21.08 (d, $^2J_{CP}$ = 8.07 Hz, PCH(***C***H$_3$)$_2$). IR: (THF) 3056 cm^{-1}, 2929 cm^{-1} (NH), 1881 cm^{-1}, 1867 cm^{-1} (C═C), 1715 cm^{-1}, 1690 cm^{-1} (C═O), 1662 cm^{-1} (C═C). ESI mass spectrum: (MeOH, positive mode) *m*/*z* = 635.2403 (Calc. for $C_{30}H_{50}N_2O_2P_2Rh$ [M−Cl$^-$] 635.2397).

4.4. Synthesis of [Rh(η^5-C_5H_5)(P*i*Pr$_3$)(η^2-PhC≡CUr)], **5**

[RhCl(P*i*Pr$_3$)$_2$(η^2-PhC≡CUr)] (70 mg, 0.104 mmol) was dissolved in THF (15 mL). NaCp (0.1 mL of a 2 M solution in THF, 2 equiv, 0.200 mmol) was added to the stirred solution. The orange solution was stirred for 10 h during which time it became darker in colour. The solvent was removed *in vacuo* and the solid residue was washed with hexane (3 × 10 mL). The orange solid remaining was extracted with THF. The product was precipitated from the resulting THF solution by addition of hexane and isolated by filtration.

^{1}H NMR: (d_4-MeOH, 300 K) δ = 8.42 (s, NH), 8.10 (d, $^3J_{HH}$ = 7.9 Hz, Ur C_5***H***), 7.90 (s, NH), 7.45 (d, J = 7.8 Hz, 1H, Ph), 7.30–7.22 (m, 2H, Ph), 7.16 (t, *J* = 7.3 Hz, 1H, Ph), 6.99 (t, *J* = 7.0 Hz, 1H, Ph), 5.31 (d, $^2J_{HRh}$ = 9.7 Hz, C_5***H***$_5$), 1.85 (m, 3H, PC***H***(CH$_3$)$_2$) 1.03 (dq, *J* = 21.2 Hz, 7.16 Hz, 9H, PCH(C***H***$_3$)$_2$). ^{31}P{^{1}H} (d_4-MeOH, 300 K) δ = 72.63 ($^1J_{PRh}$ = 203.7 Hz). IR: (THF) 1726 cm^{-1} (br, C═O). ESI mass spectrum: (MeOH, positive ion mode) *m*/*z* = 541.1504 (Calc. for $C_{26}H_{35}N_2O_2PRh$ [M+H$^+$] 541.1486).

4.5. Details of X-ray diffraction experiment

Diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo Kα radiation (λ = 0.71073 Å) using a SMART CCD camera. Diffractometer control, data collection and initial unit cell determination was performed using "SMART" [26]. Frame integration and unit cell refinement software was carried out with "SAINT+" [27]. Absorption corrections were applied by SADABS (v2.03, SHELDRICK). Structures were solved by direct methods using SHELXS-97 [28] and refined by full-matrix least-squares using SHELXL-97 [29]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions.

Empirical formula $C_{25}H_{50}ClN_2O_3P_2Rh$, formula weight 626.97, temperature 110(2) K, λ = 0.71073 Å, crystal system orthorhombic, space group *Pbca*, *a* = 9.8959(5) Å, *b* = 15.7711(7) Å, *c* = 40.0113(19) Å. *V* = 6244.5(5) Å^3, *Z* = 8, D_{calc} = 1.334 mg/m^3, absorption coefficient 0.761 mm^{-1}, *F*(0 0 0) = 2640, crystal size 0.16 × 0.12 × 0.05 mm^3, theta range for data collection 1.02–28.28°, index ranges $-13 \leqslant h \leqslant 13$, $-20 \leqslant k \leqslant 20$, $-53 \leqslant l \leqslant 53$, reflections collected 61 314, independent reflections 7733 (R_{int} = 0.0650), completeness to φ 28.28° = 99.9%, absorption correction: semi-empirical from equivalents, max and min transmission = 0.963 and 0.856, refinement method: full-matrix least-squares on F^2, data/ restraints/parameters 7733/0/323, goodness-of-fit (GOF) on F^2 1.063, final *R* indices [$I > 2\sigma(I)$] R_1 = 0.0369, wR_2 = 0.0787, *R* indices (all data) R_1 = 0.0623, wR_2 = 0.0928, largest difference in peak and hole = 0.879 and −0.845 e Å^{-1}.

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Appendix A. Supplementary material

CCDC 734602 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.020.

References

[1] (a) D.B. Grotjahn, Chem. Eur. J. 11 (2005) 7146;
(b) K. Severin, Chem. Commun. (2006) 3859.
[2] (a) A.D. Burrows, C.-W. Chan, M.M. Chowdhry, J.E. McGrady, D.M.P. Mingos, Chem. Soc. Rev. 24 (1995) 329;
(b) D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375;
(c) A.M. Beatty, Coord. Chem. Rev. 246 (2003) 131;
(d) L. Brammer, Chem. Soc. Rev. 33 (2004) 476;
(e) D. Braga, M. Polito, F. Grepioni, Cryst. Growth Des. 4 (2004) 769;
(f) M. Oh, G.B. Carpenter, D.A. Sweigart, Acc. Chem. Res. 37 (2004) 1;
(g) S.U. Son, J.A. Reingold, G.B. Carpenter, D.A. Sweigart, Chem. Commun. (2006) 708;
(h) J.A. Reingold, S.U. Son, S.B. Kim, C.A. Dullaghan, M. Oh, C. Frake, G.B. Carpenter, D.A. Sweigart, Dalton Trans. (2006) 2385.
[3] (a) K.J. Wallace, R. Daari, W.J. Belcher, L.O. Abouderbala, M.G. Boutelle, J.W. Steed, J. Organometal. Chem. 666 (2003) 63;
(b) S.J. Dickson, S.C.G. Biagini, J.W. Steed, Chem. Commun. (2007) 4955.
[4] (a) J.-L. Fillaut, J. Andriès, L. Toupet, J.-P. Desvergne, Chem. Commun. (2005) 2924;
(b) J.-L. Fillaut, J. Andriès, J. Perruchon, J.-P. Desvergne, L. Toupet, L. Fadel, B. Zouchoune, J.-Y. Saillard, Inorg. Chem. 46 (2007) 5922.
[5] P.D. Beer, P.A. Gale, Angew. Chem., Int. Ed. 40 (2001) 486.
[6] [a] D.J. Hurley, Y. Tor, J. Am. Chem. Soc. 120 (1998) 2194;
(b) S.I. Khan, A.E. Beilstein, G.D. Smith, M. Sykora, M.W. Grinstaff, Inorg. Chem. 38 (1999) 2411;
(c) S.I. Khan, A.E. Beilstein, M.W. Grinstaff, Inorg. Chem. 38 (1999) 418;
(d) S.I. Khan, A.E. Beilstein, M.T. Tierney, M. Sykora, M.W. Grinstaff, Inorg. Chem. 38 (1999) 5999;
(e) C.J. Yu, H. Wang, Y. Wan, H. Yowanto, J.C. Kim, L.H. Donilon, C.L. Tao, M. Strong, Y. Chong, J. Org. Chem. 66 (2001) 2937;
(f) M. Hocek Štěpnička, J. Ludvík, I. Císařová, I. Votruba, D. Řeha, P. Hobza, Chem. Eur. J. 10 (2004) 2058;
(g) A.R. Pike, L.C. Ryder, B.R. Horrocks, W. Clegg, B.A. Connolly, A. Houlton, Chem. Eur. J. 11 (2005) 344;
(h) H. Song, X. Li, Y. Long, G. Schatte, H.-B. Kraatz, Dalton Trans. (2006) 4696;
(i) M. Vrábel, M. Hocek, L. Havran, M. Fojta, I. Votruba, B. Klepetářová, R. Pohl, L. Rulíšek, L. Zendlová, P. Hobza, I. Shih, E. Mabery, M. Rackman, Eur. J. Inorg. Chem. (2007) 1752.
[7] (a) N. Esho, B. Davies, J. Lee, R. Dembinski, Chem. Commun. (2002) 332;
(b) M. Etheve-Quelquejeu, J.-P. Trachier, F. Rose-Munch, E. Rose, L. Naesens, E. De Clercq, Organometallics 26 (2007) 5727;
(c) C.D. Sergeant, I. Ott, A. Sniady, S. Meneni, R. Gust, A.L. Rheingold, R. Dembinski, Org. Biomol. Chem. 6 (2008) 73.
[8] J.M. Lynam, Dalton Trans. (2008) 4067.
[9] M.J. Cowley, J.M. Lynam, A.C. Whitwood, Dalton Trans. (2007) 4427.
[10] H. Hamidov, J.C. Jeffery, J.M. Lynam, Chem. Commun. (2004) 1364.
[11] M.J. Cowley, J.M. Lynam, R.S. Moneypenny, A.C. Whitwood, A.R. Wilson, Dalton Trans., in press, doi:10.1039/B912855G.
[12] T.D. Nixon, L.D. Dingwall, J.M. Lynam, Adrian C. Whitwood, Chem. Commun. (2009) 2890.
[13] (a) J. Wolf, H. Werner, O. Serhadli, M.L. Ziegler, Angew. Chem., Int. Ed. Engl. 22 (1983) 414;
(b) F.J.G. Alonso, A. Höhn, J. Wolf, H. Otto, H. Werner, Angew. Chem., Int. Ed. Engl. 24 (1985) 406;
(c) H. Werner, J. Wolf, F.J.G. Alonso, M.L. Ziegler, O. Serbadli, J. Organometal. Chem. 336 (1987) 397;
(d) H. Werner, F.J.G. Alonso, J. Otto, J. Wolf, Z. Naturforsch. B 43 (1988) 722;
(e) H. Werner, U. Brekau, Z. Naturforsch. B 44 (1989) 1439;
(f) T. Rappert, O. Nürnberg, N. Mahr, J. Wolf, H. Werner, Organometallics 11 (1992) 4156;
(g) H. Werner, T. Rappert, M. Baum, A. Stark, J. Organometal. Chem. 459 (1993) 319;

(h) H. Werner, M. Baum, D. Schneider, B. Windmüller, Organometallics 13 (1994) 1089.
[14] C.H. Suresh, N. Koga, J. Theor. Comput. Chem. 4 (2005) 59.
[15] F. De Angelis, A. Sgamellotti, N. Re, Organometallics 26 (2007) 5285.
[16] B.A. Vastine, M.B. Hall, Organometallics 27 (2008) 4325.
[17] D.B. Grotjahn, X. Zeng, A.L. Coosky, J. Am. Chem. Soc. 128 (2006) 2798.
[18] D.B. Grotjahn, X. Zeng, A.L. Cooksy, W.S. Kassel, A.G. DiPasquale, L.N. Zakharov, A.L. Rheingold, Organometallics 26 (2007) 3385.
[19] M.J. Cowley, J.M. Lynam, J.M. Slattery, Dalton Trans. (2008) 4552.
[20] H. Werner, J. Wolf, U. Schubert, K. Ackermann, J. Organometal. Chem. 243 (1983) C63.
[21] A. Dunger, H.H. Limbach, K. Weiss, Chem. Eur. J. 4 (1998) 621.
[22] J. Pranata, S.G. Wierschke, W.L. Jorgensen, J. Am. Chem. Soc. 113 (1991) 2810.
[23] H. Iwahashia, Y. Kyogoku, J. Am. Chem. Soc. 99 (1977) 7761.
[24] J.W.B. Cooke, R. Bright, M.J. Coleman, K.P. Jenkins, Org. Proc. Res. Develop. 5 (2001) 383.
[25] A. Van der Ent, A.L. Onderdelinden, Inorg. Synth. 14 (1973) 94.
[26] Smart Diffractometer Control Software (v5.625), Bruker AXS, Bruker AXS GmbH, Karlsruhe, Germany.
[27] SAINT+ (v6.22), Bruker AXS, Bruker AXS GmbH, Karlsruhe, Germany.
[28] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, 1997.
[29] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen, 1997.