Flexible coordination of bulky amidinates and guanidinates towards rhodium(I): conversion of kinetic to thermodymanic isomers†

Cameron Jones,*[a] David P. Mills[a,b] and Andreas Stasch[a]

Received 17th April 2008, Accepted 2nd June 2008
First published as an Advance Article on the web 21st July 2008
DOI: 10.1039/b806542j

Reactions of the bulky amidinate and guanidinate salts K[(ArN)$_2$CR] (R = Bu^t, NPr$^i_2$ or N(C$_6$H$_{11}$)$_2$; Ar = 2,6-diisopropylphenyl) with [{RhCl(η^4-COD)}$_2$] (COD = 1,5-cyclooctadiene) lead to KCl elimination and the formation of the complexes, [Rh{(η^5-ArN)(ArN)CR}(COD)], in which the anionic ligand coordinates the rhodium centre in an unprecedented η^5-cyclohexadienyl mode. The thermal conversions of these complexes to their N,N′-chelated isomers, [Rh{κ^2-*N*,*N*′-(ArN)$_2$CR}(COD)], were carried out and the kinetics of these processes have been shown to be first order. The rates of the isomerisations are inversely proportional to the size of the amidinate or guanidinate backbone substituent. Analogies between the ligating properties of the bulky amidinates and guanidinates used in the study, and those of β-diketiminates are discussed.

Introduction

The coordination of amidinates and guanidinates towards metals from all blocks of the periodic table has been extensively examined.[1] Throughout this work a variety of coordination modes have been identified for these ligands, the complexes of which have found many applications. In the past three years we have extended the field to the use of very bulky guanidinates and amidinates (*e.g.* [(ArN)$_2$CR]$^-$; R = N(C$_6$H$_{11}$)$_2$ (Giso$^-$), NPr$^i_2$ (Priso$^-$) or Bu^t (Piso$^-$); Ar = 2,6-diisopropylphenyl) for the stabilisation of novel low oxidation state s-, p-, d- and f-block metal complexes. These include highly reactive group 2,[2] 13,[3] 14[4] and 15[5] metal(I) heterocycles, and the first examples of planar 4-coordinate lanthanide(II) complexes.[6] Most recently, we have employed the Piso$^-$ ligand to stabilise an unprecedented example of a monomeric amidinato complex of a first row transition metal in the +1 oxidation state (*viz.* [Fe(κ^2-*N*,*N*′-Piso)(η^6-toluene)]).[7] The Fe(Piso) fragment of this compound has been shown to weakly activate dinitrogen.

Although second and third row transition metal(I) amidinate and guanidinate complexes have been previously reported,[1] we wished to examine the complexation of Piso$^-$, Priso$^-$ and Giso$^-$ with heavier transition metals, and compare the structural motifs adopted by the formed complexes with those of less hindered examples. The group 9 metals, rhodium and iridium, were seen as being of particular interest because of the widespread use of their complexes as, for example, catalysts for hydroformylation, olefin hydrogenation and C–H activation processes. Despite this, there are only two structurally characterised rhodium(I) complexes incorporating an N,N′-chelating amidinate ligand (*viz.* [Rh{(PhN)$_2$CPh}(COD)][8] and [Rh{(CyN)$_2$CFc}(CO)$_2$][9]; COD = 1,5-cyclooctadiene, Cy = cyclohexyl, Fc = ferrocenyl) described in the literature. Moreover, there are no crystallographically elucidated guanidinate complexes of either metal in the +1 oxidation state.

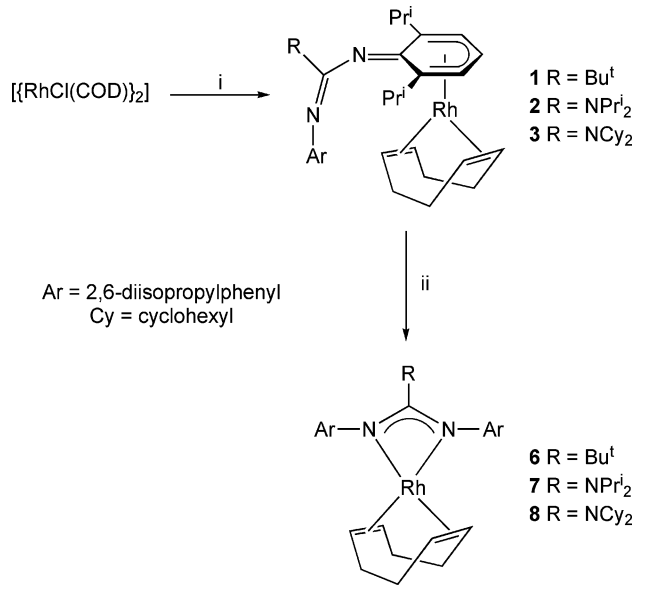
Over the course of our studies with bulky amidinates and guanidinates, it has become apparent that these ligands have similar stabilising properties to those of sterically hindered β-diketiminates, *e.g.* [(R^{1}NCR^2)$_2$CH]$^-$ (R^1 and R^2 = alkyl or aryl). These Nacnac$^-$ ligands, as they are sometimes known, have been extensively used for the preparation of low oxidation state metal complexes.[10] These include an array of rhodium(I) and iridium(I) examples in which the Nacnac$^-$ moiety acts as an N,N′-chelating ligand, *e.g.* [M{(RNCMe)$_2$CH}(COD)] (M = Rh, R = C$_6$H$_3$Me$_2$-2,6[11]; M = Ir, R = Ar[12]). In this study analogies between the Nacnac$^-$ ligand class and bulky amidinates and guanidinates are further highlighted.

Results and discussion

Oro *et al.* previously prepared the rhodium(I) amidinate complex, [Rh{κ^2-*N*,*N*′-(PhN)$_2$CPh}(COD)], *via* a salt elimination reaction between K[(PhN)$_2$CPh] and [{RhCl(η^4-COD)}$_2$].[8] It was envisaged that a similar synthetic methodology would successfully give N,N′-chelated complexes in this study. However, the treatment of [{RhCl(η^4-COD)}$_2$] with two equivalents of either [K(Piso)], [K(Priso)] or [K(Giso)] in toluene led, instead, to the unusual η^5-cyclohexadienyl complexes, **1–3**, in low to good isolated yields (Scheme 1). When the reactions were repeated in THF, **1–3** were formed in similar yields. It is of note that a low yield (<2%) by-product, [{Rh(η^4-COD)}$_4$(μ$_4$-O$_2$SiMe$_2$)$_2$], was isolated from the reaction involving K[Giso] and subsequently crystallographically characterised (see ESI†). Although the mechanism of formation of this compound is unknown, it almost certainly originates from contamination of the reaction mixture with a small amount of silicone grease. No attempt was made to rationally synthesise the compound in a higher yield, but it is worthy of mention that the

[a]*School of Chemistry, Monash University, PO Box 23, VIC, 3800, Australia*
[b]*School of Chemistry, Main Building, Cardiff University, Cardiff, UK CF10 3AT*

† Electronic supplementary information (ESI) available: Full crystallographic details for [{Rh(η^4-COD)}$_4$(μ$_4$-O$_2$SiMe$_2$)$_2$] and ORTEP diagrams for **1**, **2**, **6** and **7**. CCDC reference numbers 685416–685422. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b806542j



Scheme 1 (i) K[Piso], K[Priso] or K[Giso], toluene, −KCl; (ii) toluene, 80 °C, 5 h.

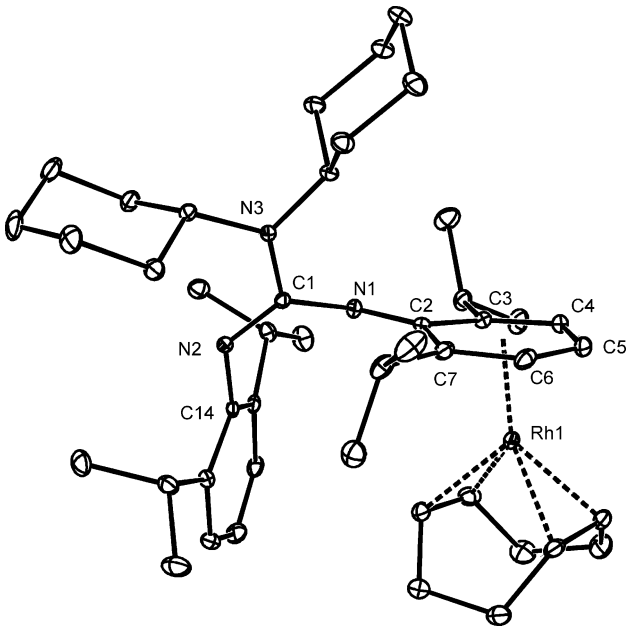


Fig. 1 Molecular structure of **3** (25% thermal ellipsoids are shown, hydrogen atoms are omitted for clarity).

abstraction of Me_2SiO_2 units from silicone grease in the presence of organometallic reagents has been observed on a number of previous occasions.[13]

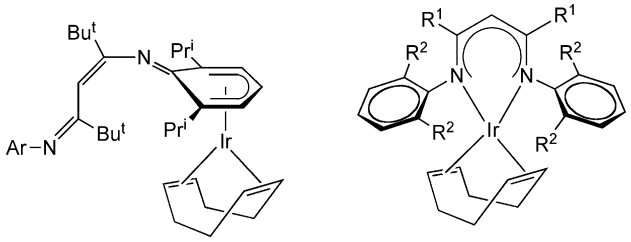
Less success was had with the reactions of [{IrCl(η⁴-COD)}₂] with two equivalents of either [K(Piso)], [K(Priso)] or [K(Giso)], which in each case resulted in an intractable mixture of products. Likewise, the treatment of [{RhCl(η²-COE)₂}₂] (COE = cyclooctene) with the amidinate or guanidinate salts resulted in the formation of complex product mixtures. Oro *et al.* have previously reported that treatment of the rhodium(I) amidinate complex [Rh{(PhN)₂CPh}(COD)] with CO affords the amidinate-bridged rhodium carbonyl dimer, [Rh₂{μ-(PhN)₂CPh}₂(CO)₄].[8] In contrast, exposure of toluene solutions of **1–3** to atmospheres of CO led to the formation of rhodium metal and the free amidine or guanidine, amongst other products. It is not known why these differences occur, but the unusual "aryl only" coordination mode of the amidinate or guanidinate ligands in **1–3** could be a factor in the ease of reduction of these complexes.

Compounds **1–3** were crystallographically characterised and found to have very similar structures in the solid state. As a result, only the molecular structure of **3** is depicted in Fig. 1, though relevant geometrical data for all complexes can be found in Table 1. In each compound the amidinate or guanidinate ligates the Rh(COD) fragment in what is best described as an η⁵-cyclohexadienyl fashion. Consistent with this are the distances from Rh(1) to the carbons of the coordinated aryl group, C(3)–C(7), (**1**: 2.207(2)–2.508(2) Å; **2**: 2.185(3)–2.478(3) Å; **3**: 2.213(3)–2.497(3) Å) which are significantly shorter than the Rh(1)–C(2) interactions. In addition, the C(2)–C(3) and C(2)–C(7) distances are close to those expected for single bonded interactions. These parameters are not dissimilar to those described for rhodium(I) and iridium(I) cyclohexadienyl complexes in the literature.[14] While there appears to be some delocalisation over the anionic ligands in the complexes, the geometric data strongly suggest a high degree of double bond character to the N(1)–C(2) and C(1)–N(2) attachments. There appears to be no significant inter- or intramolecular interactions between any of the N-centres, or the other aryl substituent, with the rhodium atoms of the complexes.

Although we have previously reported that the ligands used in this study can act as localised imino–amides that *N*,arene-chelate metal centres, *e.g.* Tl(I),[3] we believe that there have been no accounts of any amidinate or guanidinate coordinating a metal centre in an η⁵-cyclohexadienyl fashion. Saying this, a recent report[12] on the coordination of *N*-aryl substituted β-diketiminates to the Ir(COD) fragment has revealed that the very bulky ligand in **4** (Fig. 2) coordinates the metal centre in a strikingly similar fashion to the situation in **1–3**. Interestingly, the less bulky β-diketiminate ligands in **5** coordinate iridium in the more conventional N,N′-fashion. There was no mention in the report

Table 1 Selected bond lengths (Å) and angles (°) for **1–3**

	1	**2**	**3**		**1**	**2**	**3**
Rh(1)–C(3–7) centroid	1.876(3)	1.856(3)	1.865(3)	C(1)–N(2)	1.284(3)	1.294(3)	1.300(3)
Rh(1)···C(2)	2.600(2)	2.662(2)	2.569(2)	N(2)–C(14)	1.413(3)	1.408(3)	1.405(3)
Rh(1)–COD alkene centroid	2.024 (mean)	2.020 (mean)	2.014 (mean)	C(1)–N(3)	—	1.395(3)	1.390(3)
C(2)–C(3)	1.467(3)	1.483(4)	1.475(4)				
C(2)–C(7)	1.472(3)	1.472(3)	1.467(4)	C(2)–N(1)–C(1)	136.8(2)	131.6(2)	133.5(2)
C(2)–N(1)	1.306(3)	1.300(3)	1.310(3)	N(1)–C(1)–N(2)	125.9(2)	123.6(2)	124.8(2)
C(1)–N(1)	1.367(3)	1.381(3)	1.373(3)	C(1)–N(2)–C(14)	122.2(2)	119.7(2)	122.8(2)



4 **5** $R^1 = R^2 = Me$; $R^1 = Me$, $R^2 = Pr^i$; $R^1 = CF_3$, $R^2 = Pr^i$

Fig. 2 Iridium β-diketiminate complexes related to the rhodium amidinate and guanidinate complexes in this study (see ref. 12).

as to whether the β-diketiminate in **4** can change its coordination mode when heated, for example. What is clear, however, is that the structural similarities between **4** and **1–3** provide further support for the aforementioned proposed analogies connecting bulky β-diketiminate, amidinate and guanidinate ligands.

It is evident from the NMR spectra of **1–3** that they retain their solid state structures in solution. Most telling in their ^{1}H NMR spectra are the high field positions of the signals corresponding to the *para*- and *meta*-protons of the coordinated aryl substituent (*e.g.* 3.83 and 5.72 ppm respectively for **1**). In addition, the chemical shifts and $^1J_{RhC}$ couplings for the *ortho*-, *meta*- and *para*-carbons of that substituent in the $^{13}C\{^1H\}$ NMR spectra of the complexes (*e.g.* 115.5 ppm, $^1J_{RhC}$ = 2.3 Hz; 101.5 ppm, $^1J_{RhC}$ = 3.6 Hz; 74.5 ppm, $^1J_{RhC}$ = 5.2 Hz respectively for **1**) are consistent with a π-cyclohexadienyl coordination mode.

Considering the unusual amidinate or guanidinate coordination mode in the 18-electron complexes, **1–3**, it was proposed that they might undergo isomerisation to more normal 16-electron N,N′-chelated species, *cf.* [Rh{(PhN)$_2$CPh}(COD)], under the right conditions. A somewhat related isomerisation has been recently observed when the 18-electron tris(arylamido)stannate complex [Rh(COD){(η^6-Ar′NSiMe$_2$)Sn(Ar′NSiMe$_2$)$_2$SiMe}] (Ar′ = 3,5-xylyl) was treated with a series of nucleophiles, *e.g.* PPh$_3$. This effected a shift in the Rh(COD) fragment from being η^6-aryl coordinated to being η^1-coordinated by the tin lone pair and the added nucleophile, *e.g.* as in the 16-electron compound [Rh(COD)(PPh$_3$){η^1-Sn(Ar′NSiMe$_2$)$_3$SiMe}].[15] In contrast, when **1–3** were treated with PPh$_3$ in toluene, decomposition of the complexes to unidentifiable mixtures rapidly occurred. Alternatively, it was considered that the isomerisation of **1–3** might result from their irradiation with UV light. However, when toluene solutions of the complexes were irradiated (λ = 254 nm) for 3 h, no isomerisation was observed, as determined by NMR spectroscopy.

Finally, thermal isomerisations of the complexes were attempted by heating their toluene solutions at 80 °C for 5 h. In each case, the ^{1}H NMR spectrum of the reaction mixture revealed that near quantitative conversion to the 16-electron N,N′-chelated isomer (**6–8**, Scheme 1) had occurred. The isolated crystalline yields of the complexes were moderate to good. It is of note that the lowest molecular weight complex, **1**, can also be isomerised in high yield when it is sublimed under reduced pressure (140 °C, 5 × 10^{-6} Torr). These results suggest that complexes **1–3** are the kinetic products in the original salt elimination reactions that gave them, and that **6–8** are their thermodynamically more stable isomeric forms.

The X-ray crystal structures of the three monomeric complexes were obtained and found to be similar to each other and that of [Rh{(PhN)$_2$CPh}(COD)].[8] As a result, only the molecular structure of **8** is depicted in Fig. 3, though relevant metrical parameters for all complexes are given in Table 2. The rhodium centre in each compound has a distorted square planar geometry with Rh–C and Rh–N distances in the normal range.[16] An examination of the C–N distances within the amidinate or guanidinate ligand backbones suggested a significant degree of delocalisation over their CN$_2$ or CN$_3$ fragments. The NMR spectra of the complexes are symmetrical and fully consistent with them retaining their solid state structures in solution.

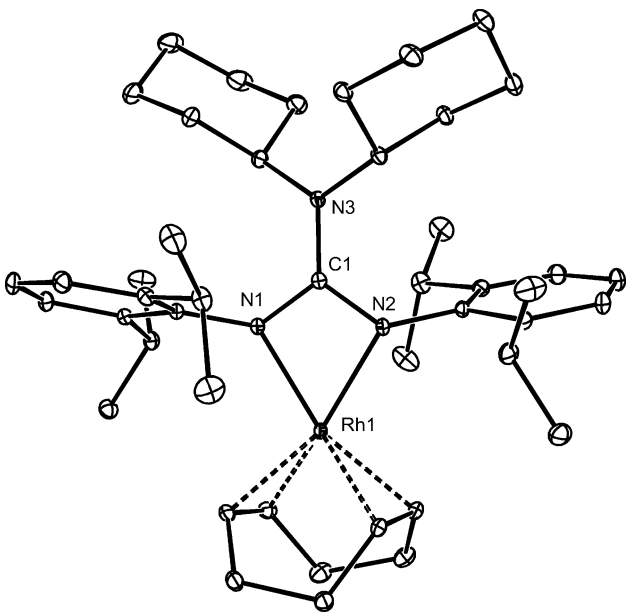


Fig. 3 Molecular structure of **8** (25% thermal ellipsoids are shown, hydrogen atoms are omitted for clarity).

Table 2 Selected bond lengths (Å) and angles (°) for **6–8**

	6	**7**	**8**
Rh(1)–N(1)	2.0926(18)	2.091(2)	2.0889(13)
Rh(1)–N(2)	2.0836(17)	2.087(2)	2.0939(13)
C(1)–N(1)	1.351(2)	1.337(3)	1.346(2)
C(1)–N(2)	1.332(3)	1.353(3)	1.350(2)
C(1)–N(3)	—	1.380(3)	1.378(2)
Rh(1)–COD alkene centroid	2.010 (mean)	2.002 (mean)	2.001 (mean)
N(1)–C(1)–N(2)	108.76(17)	109.7(2)	109.31(14)
N(1)–Rh(1)–N(2)	62.98(7)	63.54(8)	63.46(5)

As the thermal isomerisations (at 80 °C) of toluene solutions of **1–3** were effectively complete within 5 h, it was proposed to examine the kinetics of these processes using ^{1}H NMR spectroscopy. It was believed this would shed light on the effect the amidinate or guanidinate backbone substituent has on the rates of the isomerisations. To achieve this, solutions of the same concentration of **1–3** in C_6D_6 were prepared and an internal $SiMe_4$ standard added to each. The ^{1}H NMR spectra of the samples were obtained and they were subsequently heated to 80 °C. Their ^{1}H NMR spectra were then taken at 15 min intervals. Monitoring the integration of the *meta*-aryl (Rh coordinated) proton resonance, relative to that of the internal standard, allowed a determination of the change of absolute concentration of the complexes with time. The conversion of **1** to **6** was found to be complete within 15 min of heating, whilst the conversions of **2** to **7**, and **3** to **8** took *ca.* 3 and 5 h respectively. Considering the rapid conversion of **1**, only the natural logarithm of the concentrations of **2** and **3** could be accurately plotted against time (Fig. 4). Straight lines were fitted to both sets of data with excellent correlations ($R^2 = 0.992$ **2**, $R^2 = 0.972$ **3**), thus demonstrating that the thermal isomerisations are unimolecular processes following first order kinetics. The slopes of the lines yielded rate constants for the isomerisations (**2**: $k = 5.41 \times 10^{-4}$ s^{-1}, **3**: $k = 2.87 \times 10^{-4}$ s^{-1}) which, combined with the rapid isomerisation of **1**, indicate that there is an inverse correlation between the rates of the conversions and the size of the ligand backbone substituent. This is not surprising, as larger backbone substituents would be expected to hinder the rotation of the ligand ArN fragments about the C(1)–N bonds, and the migration of the Rh(COD) fragment, both of which are required for the isomerisations to occur.

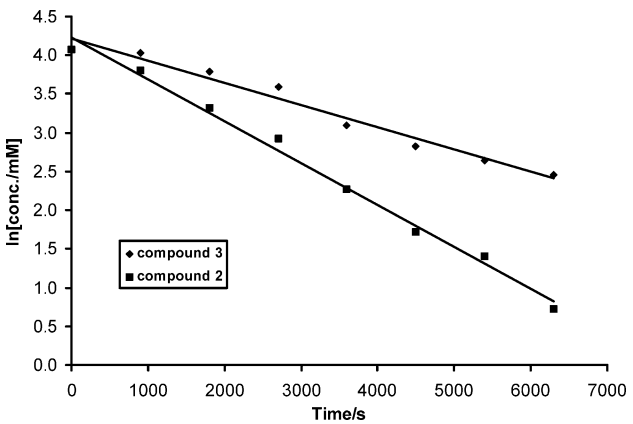


Fig. 4 Plot of ln [**2**] and ln [**3**] *vs* time for the thermal isomerisations of **2** and **3** in C_6D_6 at 80 °C.

Conclusion

In summary, the reactions of a series of aryl-substituted amidinate and guanidinate salts with [{RhCl(η^4-COD)}$_2$] have yielded complexes in which the ligand does not act as an N,N′-chelator, but instead coordinates the rhodium centre solely through an aryl substituent in an η^5-cyclohexadienyl mode. Thermal conversions of these complexes to their N,N′-chelated isomers have been carried out and the kinetics of these processes have been shown to be first order. The rates of the isomerisations are inversely proportional to the size of the amidinate or guanidinate backbone substituent. This study has identified further analogies between the ligating and stabilising properties of bulky amidinates and guanidinates, and those of β-diketiminates. We are currently examining the coordination of these ligands to other low oxidation state transition metal centres and will report on this work in due course.

Experimental section

Synthesis

General considerations. All manipulations were carried out using standard Schlenk and glove box techniques under atmospheres of high purity argon or dinitrogen. Hexane and toluene were distilled over molten potassium metal. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Mass spectra were recorded at the EPSRC National Mass Spectrometric Service at Swansea University. Microanalyses were obtained from the Campbell Microanalytical Laboratory, University of Otago. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either Bruker DPX 300 or AV 200 spectrometers and were referenced to the resonances of the solvent used. K[Piso], K[Priso], K[Giso][6] and [{RhCl(η^4-COD)}$_2$][17] were synthesised by variations of literature methods. All other reagents were used as received.

Preparation of [Rh{(η^5-ArN)(ArN)CBu^t}(COD)] 1. A suspension of [K(Piso)] (0.50 g, 1.09 mmol) in toluene (25 cm^3) was added to a solution of [{RhCl(η^4-COD)}$_2$] (0.27 g, 0.55 mmol) in toluene (15 cm^3) at −78 °C over 10 min. The reaction mixture was warmed to 20 °C over 2 h and stirred for a further hour to give a yellow solution. Volatiles were then removed *in vacuo* and the residue extracted into hexane (60 cm^3) and filtered. The filtrate was concentrated to *ca.* 20 cm^3 and stored at −30 °C overnight to give pale yellow blocks of **1**. A second crop was obtained (0.19 g, 28%). Mp 133–135 °C (decomp.); ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ 1.41 (2 × coincidental d, $^3J_{HH} = 6.6$ Hz, 12 H, $(CH_3)_2$CH), 1.60 (d, $^3J_{HH} = 6.7$ Hz, 6 H, $(CH_3)_2$CH), 1.61 (d, $^3J_{HH} = 6.9$ Hz, 6 H, $(CH_3)_2$CH), 1.64 (s, 9 H, $(CH_3)_3$C), 1.78 (m, 4 H, CH_2CH), 2.07 (m, 4 H, CH_2CH), 3.20 (sept, $^3J_{HH} = 6.8$ Hz, 2 H, $(CH_3)_2CH$), 3.27 (br. m, 4 H, CH_2CH), 3.65 (sept, $^3J_{HH} = 6.7$ Hz, 2 H, $(CH_3)_2CH$), 3.85 (t, $^3J_{HH} = 5.8$ Hz, 1 H, η^5-arene-*p*-Ar-*H*), 5.65 (d, $^3J_{HH} = 5.8$ Hz, 2 H, η^5-arene-*m*-Ar-*H*), 7.11 (t, $^3J_{HH} = 6.7$ Hz, 1 H, *p*-Ar-*H*), 7.30 (br. m, 2 H, *m*-Ar-*H*); ^{13}C{^{1}H} NMR (50.33 MHz, C_6D_6, 298 K): δ 21.6 ($(CH_3)_3$C), 23.9, 24.8, 25.4, 26.7 ($(CH_3)_2$CH), 29.1, 29.8 ($(CH_3)_2CH$), 31.7 (CH_2), 42.2 ($(CH_3)_3C$), 73.3 (br., CH_2CH), 74.5 (d, $^1J_{RhC} = 5.2$ Hz, η^5-arene-*p*-Ar-*C*), 101.5 (d, $^1J_{RhC} = 3.6$ Hz, η^5-arene-*m*-Ar-*C*), 115.5 (d, $^1J_{RhC} = 2.3$ Hz, η^5-arene-*o*-Ar-*C*), 121.4, 121.9, 138.8, 148.6 (Ar-*C*), 164.8 (CN_2); MS (EI 70 eV) *m*/*z* (%): 630 (MH$^+$, 13), 573 (MH$^+$ − Bu^t, 31), 522 (MH$^+$ − COD, 29), 420 ({[N(Ar)$_2$]CBu^t}H$^+$, 17); IR ν/cm^{-1} (Nujol): 1593 s, 1567 s, 1538 s, 1360 m, 1253 m, 1139 m, 910 m, 866 m, 842 m, 800 m; EI acc. mass on M$^+$: calc. for $C_{37}H_{55}N_2Rh$ 630.3415, found 630.3415; $C_{37}H_{55}N_2Rh$ requires C 70.46, H 8.79, N 4.44%; found C 70.46, H 8.53, N 4.45%.

Preparation of [Rh{(η^5-ArN)(ArN)CNPr$^i_2$}(COD)] 2. This compound was prepared by a similar procedure to that used for the synthesis of **1**. Yellow blocks (yield 42%). Mp 164–166 °C

(decomp.); ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ 1.50 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, $(CH_3)_2CHN$), 1.57–1.68 (overlapping d, $^3J_{HH}$ = *ca.* 6.8 Hz, 24 H, $(CH_3)_2CH$), 1.83 (m, 4 H, CH_2), 2.12 (m, 4 H, CH_2), 3.40 (br. m, 4 H, CH_2CH), 3.60 (sept, $^3J_{HH}$ = 6.9 Hz, 2 H, $(CH_3)_2CHN$), 3.83 (t, $^3J_{HH}$ = 5.8 Hz, 1 H, η^5-arene-*p*-Ar-*H*), 3.94 (overlapping sept, $^3J_{HH}$ = *ca.* 6.9 Hz, 4 H, $(CH_3)_2CH$), 5.72 (d, $^3J_{HH}$ = 5.8 Hz, 2 H, η^5-arene-*m*-Ar-*H*), 7.11 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, *p*-Ar-*H*), 7.22–7.36 (m, 2 H, Ar-*H*); ^{13}C{^{1}H} NMR (50.33 MHz, C_6D_6, 298 K): δ 21.9 ($(CH_3)_2CHN$), 24.4, 24.8, 26.0, 26.4 ($(CH_3)_2CH$), 29.1 (b, 2 × $(CH_3)_2CH$), 31.7 (CH_2), 47.0 ($(CH_3)_2CHN$), 72.1 (d, $^1J_{RhC}$ = 13.3 Hz, CH_2CH), 74.6 (d, $^1J_{RhC}$ = 5.4 Hz, η^5-arene-*p*-Ar-*C*), 101.1 (d, $^1J_{RhC}$ = 3.5 Hz, η^5-arene-*m*-Ar-*C*), 116.5 (d, $^1J_{RhC}$ = 2.3 Hz, η^5-arene-*o*-Ar-*C*), 120.5, 122.2, 140.0, 142.4, 147.0 (Ar-*C*), 175.7 (CN_3); MS (EI 70 eV) *m*/*z* (%): 673 (MH^+, 8), 630 ($MH^+ - Pr^i$, 16), 573 ($MH^+ - NPr^i_2$, 3), 565 ($MH^+ - COD$, 4), 462 ({[N(Ar)]$_2$CNPr$^i_2$}H$^+$, 3); IR ν/cm^{-1} (Nujol): 1555 s, 1537 s, 1366 m, 1311 m, 1279 m, 1260 m, 1218 m, 1134 m, 992 m, 848 m, 800 m; EI acc. mass on M^+: calc. for $C_{39}H_{60}N_3Rh$ 673.3837, found 673.3839; $C_{39}H_{60}N_3Rh$ requires C 69.52, H 8.98, N 6.24%; found C 69.50, H 8.93, N 6.28%.

Preparation of [Rh{(η^5-ArN)(ArN)CN(C_6H_{11})$_2$}(COD)] 3. This compound was prepared by a similar procedure to that used for the synthesis of **1**. Yellow blocks (yield 54%). Mp 169–171 °C (decomp.); ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ 1.45 (m_c, 12 H, Cy-CH_2), 1.54 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, $(CH_3)_2CH$), 1.58 (d, $^3J_{HH}$ = 7.0 Hz, 6 H, $(CH_3)_2CH$), 1.62 (d, $^3J_{HH}$ = 6.6 Hz, 6 H, $(CH_3)_2CH$), 1.70 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, $(CH_3)_2CH$), 1.84 (br. m, 8 H, Cy-CH_2), 2.12 (br. m, 8 H, COD-CH_2), 3.46 (br. m, 4 H, COD-CH), 3.57 (m, 2 H, Cy-CH), 3.59 (sept, $^3J_{HH}$ = 6.4 Hz, 2 H, $(CH_3)_2CH$), 3.91 (t, 1 H, $^3J_{HH}$ = 5.8 Hz, η^5-arene-*p*-Ar-*H*), 3.94 (sept, $^3J_{HH}$ = 7.0 Hz, 2 H, $(CH_3)_2CH$), 5.74 (d, $^3J_{HH}$ = 5.8 Hz, 2 H, η^5-arene-*m*-Ar-*H*), 7.13 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, *p*-Ar-*H*), 7.34 (m, 2 H, *m*-Ar-*H*); ^{13}C{^{1}H} NMR (75.48 MHz, C_6D_6, 298 K): δ 20.8, 23.5 (Cy-CH_2), 25.0, 25.2, 26.1, 26.3 (br., $(CH_3)_2CH$), 28.1, 29.5 ($(CH_3)_2CH$), 30.7 (COD-CH_2), 34.6 (Cy-CH_2), 57.0 (CHN), 73.5 (d, $^1J_{RhC}$ = 5.2 Hz, η^5-arene-*p*-Ar-*C*), 75.4 (d, $^1J_{RhC}$ = 13.0 Hz, COD-CH), 99.8 (d, $^1J_{RhC}$ = 3.6 Hz, η^5-arene-*m*-Ar-*C*), 119.1, 121.1, 122.6, 138.7, 144.0, 145.6 (br, Ar-*C*); MS (EI 70 eV) *m*/*z* (%): 753 (MH^+, 2), 710 ($MH^+ - Pr^i$, 1), 670 ($MH^+ - Cy$, 2), 645 ($MH^+ - COD$, 1), 542 ({[N(Ar)]$_2$CNCy$_2$}H$^+$, 12); IR ν/cm^{-1} (Nujol): 1563 s, 1520 s, 1352 m, 1283 m, 1235 m, 1206 m, 1170 m, 1127 m, 1007 m, 970 m, 932 m, 891 m, 848 m, 802 m; EI acc. mass on M^+: calc. for $C_{45}H_{68}N_3Rh$ 753.4467, found 753.4463; $C_{45}H_{68}N_3Rh$ requires C 71.69, H 9.09, N 5.57%; found C 70.21, H 9.15, N 5.31%.

N.B. a low yield (<2%) by-product, [{Rh(η^4-COD)}$_4$(μ_4-O_2SiMe_2)$_2$], was isolated from the reaction mixture and crystallographically characterised (see ESI†).

Preparation of [Rh{κ^2-*N*,*N*′-(ArN)$_2$CBu^t}(COD)] 6. A solution of **1** (0.10 g, 0.16 mmol) in toluene (10 cm^3) was heated at 80 °C for 5 h. Volatiles were removed from the resultant solution *in vacuo*, the residue extracted into hexane (10 cm^3) and filtered. The filtrate was concentrated to *ca.* 2 cm^3 and stored at −30 °C overnight to give pale yellow blocks of **6**. A second crop was obtained (0.06 g, 60%). Mp 133–135 °C (decomp.); ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ 1.10 (s, 9 H, $(CH_3)_3C$), 1.58 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $(CH_3)_2CH$), 1.59 (br. m, 4 H, CH_2), 1.76 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, $(CH_3)_2CH$), 2.43 (br. m, 4 H, CH_2), 3.83 (br. m, 4 H, CH_2CH), 4.14 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $(CH_3)_2CH$), 7.15–7.29 (m, 6 H, Ar-*H*); ^{13}C{^{1}H} NMR (50.33 MHz, C_6D_6, 298 K): δ 24.0 ($(CH_3)_3C$), 25.9, 28.2 ($(CH_3)_2CH$), 30.2 ($(CH_3)_2CH$), 30.7 (CH_2), 44.5 ($(CH_3)_3C$), 78.5 (d, $^1J_{RhC}$ = 13.7 Hz, CH_2CH), 123.8, 124.5, 143.0, 143.9 (Ar-*C*), 186.8 (d, $^2J_{RhC}$ = 5.0 Hz, CN_2C); MS (EI 70 eV) *m*/*z* (%): 630 (MH^+, 45), 573 ($MH^+ - Bu^t$, 78), 522 ($MH^+ - COD$, 92), 420 ({[N(Ar)$_2$]CBu^t}H$^+$, 21); IR ν/cm^{-1} (Nujol): 1315 m, 1241 m, 1170 m, 1098 m, 949 m, 800 m, 761 m; EI acc. mass on M^+: calc. for $C_{37}H_{55}N_2Rh$ 630.3415, found 630.3418; $C_{37}H_{55}N_2Rh$ requires C 70.46, H 8.79, N 4.44%; found C 70.19, H 8.91, N 4.45%.

Preparation of [Rh{κ^2-*N*,*N*′-(ArN)$_2$CNPr$^i_2$}(COD)] 7. This compound was prepared by a similar procedure to that used for the synthesis of **6**, except using **2** as the starting material. Yellow blocks (yield 56%). Mp 183–185 °C (decomp.); ^{1}H NMR (200.13 MHz, C_6D_6, 298 K): δ 0.91 (d, $^3J_{HH}$ = 7.0 Hz, 12 H, $(CH_3)_2CHN$), 1.54 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, $(CH_3)_2CH$), 1.61 (m, 4 H, CH_2), 1.94 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $(CH_3)_2CH$), 2.42 (m, 4 H, CH_2), 3.94 (br. m, 4 H, CH_2CH), 4.11 (2 × overlapping sept, $^3J_{HH}$ = *ca.* 6.9 Hz, 6 H, $(CH_3)_2CH$), 7.18–7.34 (m, 6 H, Ar-*H*); ^{13}C{^{1}H} NMR (50.33 MHz, C_6D_6, 298 K): δ 23.5 ($(CH_3)_2CHN$), 26.1, 26.2 ($(CH_3)_2CH$), 27.6 ($(CH_3)_2CH$), 30.9 (CH_2), 49.0 ($(CH_3)_2CHN$), 76.2 (d, $^1J_{RhC}$ = 14.0 Hz, CH_2CH), 123.8, 124.0, 143.8, 144.7 (Ar-*C*), 174.5 (d, $^2J_{RhC}$ = 5.7 Hz, CN_3); MS (EI 70 eV) *m*/*z* (%): 673 (MH^+, 50), 630 ($MH^+ - Pr^i$, 100), 573 ($MH^+ - NPr^i_2$, 13), 565 ($MH^+ - COD$, 18), 462 ({[N(Ar)]$_2$CNPr$^i_2$}H$^+$, 10); IR ν/cm^{-1} (Nujol): 1434 s, 1407 s, 1316 m, 1275 m, 1245 m, 1176 m, 1124 m, 1109 m, 952 m, 932 m, 871 m, 799 s, 757 s, 658 m; EI acc. mass on M^+: calc. for $C_{39}H_{60}N_3Rh$ 673.3837, found 673.3834; $C_{39}H_{60}N_3Rh$ requires C 69.52, H 8.98, N 6.24%; found C 69.82, H 9.00, N 6.35%.

Preparation of [Rh{κ^2-*N*,*N*′-(ArN)$_2$CN(C_6H_{11})$_2$}(COD)] 8. This compound was prepared by a similar procedure to that used for the synthesis of **6**, except using **3** as the starting material. Yellow blocks (yield 29%). Mp 164–166 °C (decomp.); ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 0.91–1.08 (m, 8 H, Cy-CH_2), 1.52 (m_c, 12 H, Cy-CH_2), 1.58 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $(CH_3)_2CH$), 1.59 (m, 4 H, COD-CH_2), 1.93 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $(CH_3)_2CH$), 2.32 (m, 4 H, COD-CH_2), 3.72 (m, 2 H, Cy-CH), 3.91 (br. m, 4 H, COD-CH), 3.95 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $(CH_3)_2CH$), 7.17 (tr, $^3J_{HH}$ = 6.4 Hz, 2 H, *p*-Ar-*H*), 7.26 (d, $^3J_{HH}$ = 6.8 Hz, 4 H, *m*-Ar-*H*); ^{13}C{^{1}H} NMR (50.33 MHz, C_6D_6, 298 K): δ 23.6 (Cy-CH_2), 26.1, 26.4 ($(CH_3)_2CH$), 26.9 (Cy-CH_2), 27.6 ($(CH_3)_2CH$), 31.1 (COD-CH_2), 35.8 (Cy-CH_2), 58.6 (Cy-CHN), 76.7 (d, $^1J_{RhC}$ = 13.0 Hz, COD-CH), 123.6, 123.8, 143.1, 145.1 (Ar-*C*), 174.1 (d, $^2J_{RhC}$ = 5.5 Hz, CN_3); MS (EI 70 eV) *m*/*z* (%): 753 (MH^+, 100), 710 ($MH^+ - Pr^i$, 51), 670 ($MH^+ - Cy$, 87), 645 ($MH^+ - COD$, 39), 560 ($MH^+ - COD - Cy$, 29), 542 ({[N(Ar)]$_2$CNCy$_2$}H$^+$, 47); IR ν/cm^{-1} (Nujol): 1434 s, 1393 s, 1323 s, 1279 s, 1243 s, 1096 m, 1020 s, 896 m, 866 m, 825 m, 791 s, 772 m, 750 s, 660 m; EI acc. mass on M^+: calc. for $C_{45}H_{68}N_3Rh$ 753.4463, found 753.4463; $C_{45}H_{68}N_3Rh$ requires C 71.69, H 9.09, N 5.57%; found C 71.88, H 9.36, N 5.67%.

X-Ray crystallography

Crystals of **1–3**, **6**, **7**, **8**·(hexane) and [{Rh(η^4-COD)}$_4$(μ_4-O_2SiMe_2)$_2$] suitable for X-ray structural determination were

Table 3 Crystal data for compounds **1–3** and **6**, **7** and **8**·(hexane)

Compound	**1**	**2**	**3**	**6**	**7**	**8**·(hexane)
Empirical formula	$C_{37}H_{55}N_2Rh$	$C_{39}H_{60}N_3Rh$	$C_{45}H_{68}N_3Rh$	$C_{37}H_{55}N_2Rh$	$C_{39}H_{60}N_3Rh$	$C_{51}H_{82}N_3Rh$
FW	630.74	673.81	753.93	630.74	673.81	840.11
Temp./K	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)
Cryst. syst.	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/n$
a/Å	12.178(2)	10.163(2)	11.3725(5)	18.725(4)	40.659(8)	12.1799(3)
b/Å	15.861(3)	10.502(2)	17.6352(7)	16.203(3)	11.960(2)	23.6855(4)
c/Å	16.978(3)	19.025(4)	20.1756(6)	11.480(2)	23.891(5)	16.3738(3)
α/°	90	102.33(3)	90	90	90	90
β/°	93.63(3)	109.60(1)	94.264(1)	106.75(3)	108.90(3)	101.444(1)
γ/°	90	108.69(3)	90	90	90	90
Vol./Å^3	3272.8(11)	6761(3)	4035.1(3)	3335.3(11)	10 991(4)	4629.72(16)
Z	4	2	4	4	12	4
Density (calcd)/Mg m^{-3}	1.280	1.226	1.241	1.256	1.222	1.205
μ(Mo-Kα)/mm^{-1}	0.549	0.497	0.457	0.538	0.495	0.405
F(000)	1344	720	1616	1344	4320	1816
No. of reflections collected	14 460	13 308	55 950	15 377	18 381	52 844
No. of independent reflns (R_{int})	7487 (0.0232)	7394 (0.0208)	11 843 (0.0650)	8034 (0.0223)	12 544 (0.0239)	10 698 (0.0278)
Final $R1$ ($I > 2\sigma(I)$) and w$R2$ indices (all data)	0.0353 and 0.0967	0.0402 and 0.1063	0.0489 and 0.1225	0.0329 and 0.0841	0.0432 and 0.1129	0.0295 and 0.0766

mounted in silicone oil. Crystallographic measurements were made using either a Nonius Kappa CCD or a Bruker X8 CCD diffractometer. The structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX-97)[18] using all unique data. Hydrogen atoms have been included in calculated positions (riding model) for all structures. The crystal structure of **7** contains 1.5 crystallographically independent molecules in the asymmetric unit. Only the metrical parameters of the full molecule are discussed in the text. Crystal data, details of data collections and refinement are given in Table 3.

Acknowledgements

We thank the Australian Research Council (fellowships for CJ and AS) and the EPSRC (studentship for DPM). The EPSRC Mass Spectrometry Service at Swansea University is also thanked.

References

1 For general references on the structure and reactivity of amidinate and guanidinate complexes see: (*a*) J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219; (*b*) F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403; (*c*) P. J. Bailey and S. Price, *Coord. Chem. Rev.*, 2001, **214**, 91; (*d*) M. P. Coles, *Dalton Trans.*, 2006, 985 and references therein.
2 S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754.
3 (*a*) C. Jones, P. C. Junk, J. A. Platts and A. Stasch, *J. Am. Chem. Soc.*, 2006, **128**, 2206; (*b*) C. Jones, P. C. Junk, J. A. Platts, D. Rathmann and A. Stasch, *Dalton Trans.*, 2005, 2497; (*c*) G. Jin, C. Jones, P. C. Junk, A. Stasch and W. D. Woodul, *New J. Chem.*, 2008, **32**, 835.
4 S. P. Green, C. Jones, P. C. Junk, K.-A. Lippert and A. Stasch, *Chem. Commun.*, 2006, 3978.
5 S. P. Green, C. Jones, G. Jin and A. Stasch, *Inorg. Chem.*, 2007, **46**, 8.
6 D. Heitmann, C. Jones, P. C. Junk, K.-A. Lippert and A. Stasch, *Dalton Trans.*, 2007, 187.
7 R. P. Rose, C. Jones, C. Schulten, S. Aldridge and A. Stasch, *Chem.–Eur. J.*, in press.
8 F. L. Lahoz, A. Tiripicchio, M. T. Camellini, L. A. Oro and M. T. Pinillos, *J. Chem. Soc., Dalton Trans.*, 1985, 1487.
9 J. R. Hagadorn and J. Arnold, *J. Organomet. Chem.*, 2001, **637–639**, 521.
10 L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.
11 P. H. M. Budzelaar, N. N. P. Moonen, R. de Gelder, J. M. M. Smits and A. W. Gal, *Eur. J. Inorg. Chem.*, 2000, 753.
12 W. H. Bernskoetter, E. Lobkovsky and P. J. Chirik, *Organometallics*, 2005, **24**, 6250.
13 I. Haiduc, *Organometallics*, 2004, **23**, 3 and references therein.
14 See for example: (*a*) L. Dahlenburg and N. Hock, *J. Organomet. Chem.*, 1985, **284**, 129; (*b*) M. Martin, E. Sola, S. Tejero, J. L. Andres and L. A. Oro, *Chem.–Eur. J.*, 2006, **12**, 4043.
15 M. Kilian, H. Wadepohl and L. H. Gade, *Organometallics*, 2007, **26**, 3076.
16 As determined by a survey of the Cambridge Crystallographic Database, March 2008.
17 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, 1990, **28**, 88.
18 G. M. Sheldrick, *SHELX-97*, University of Göttingen, Germany, 1997.

