# Mononuclear Rhodium(I) Complexes with Chelating *N*-Heterocyclic Carbene Ligands − Catalytic Activity for Intramolecular Hydroamination

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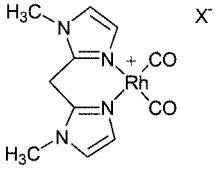
The mononuclear cationic $Rh^I$ complexes $[Rh(cod)(mdd)]^+X^-$ and $[Rh(CO)_2(mdd)]^+X^-$ (X = $BPh_4$, $PF_6$) containing the chelating bidentate *N*-heterocyclic carbene ligand 1,1′-methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene (mdd) have been synthesised and spectroscopically characterised. The complexes $[Rh(cod)(mdd)]^+BPh_4^-$ and $[Rh(CO)_2(mdd)]^+PF_6^-$ have also been characterised by X-ray crystallography. The dicarbonyl complexes catalyse the intramolecular hydroamination of 4-pentyn-1-amine to 2-methyl-1-pyrroline.



## Introduction

In 1991, Arduengo[1] synthesised and characterised the first crystalline carbene 1,3-di-1-adamantylimidazol-2-ylidene. Since then, there has been a resurgence of interest in metal complexes containing *N*-heterocyclic carbene ligands, fuelled by reports of their ability to increase catalyst activity in a range of catalytic reactions.[2,3] Our interest in Rh complexes with chelating *N*-heterocyclic carbene ligands stemmed from the synthesis of a successful hydroamination catalyst[4] $[Rh(bim)(CO)_2]^+BPh_4^-$ **1** [bim = bis(*N*-methylimidazol-2-yl)methane]; a carbene analogue might influence the catalytic activity.



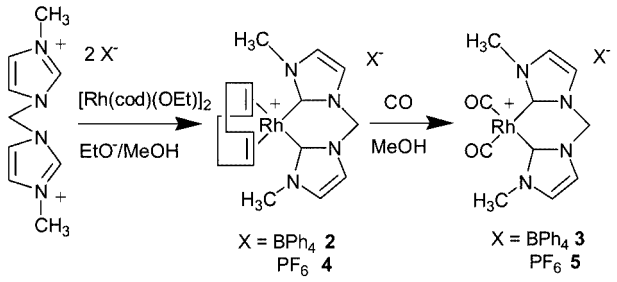
X = $BPh_4$ **1**
$PF_6$ **6**

Reactions of $Rh^I$ precursors such as $[RhCl(cod)]_2$ or $[Rh(OEt)(cod)]_2$ (cod = 1,5-cyclooctadiene) with bidentate *N*-heterocyclic carbenes (or their precursor imidazolium halide salts) have produced dinuclear complexes where two rhodium metals are bridged by the bidentate carbene ligand.[5,6] These reactions are probably driven by the inherent insolubility of the dinuclear products. Similar reactions in the presence of $OAc^-$ and $I^-$ gave the mononuclear complexes, although the rhodium metal was oxidised from $Rh^I$ to $Rh^{III}$ [7] and the mechanism for this oxidation is as yet unknown.

In this paper, we report the successful synthesis and characterisation of mononuclear $Rh^I$ complexes with chelating bidentate *N*-heterocyclic carbene ligands and initial studies into their activity as hydroamination catalysts.

## Results and Discussion

The mononuclear $Rh^I$ complexes were synthesised using a modification of the sodium ethoxide method introduced by Köcher et al.[6] (Scheme 1). $[RhCl(cod)]_2$ was treated with NaOEt and the product $[Rh(OEt)(cod)]_2$ was washed with methanol to remove residual chloride. The halide-free $[Rh(OEt)(cod)]_2$ was reacted with 1,1′-methylene-3,3′-dimethyldiimidazolium bis(tetraphenylborate) to form predominantly the mononuclear Rh carbene complex $[Rh(cod)(mdd)]^+BPh_4^-$ (**2**; mdd = 1,1′-methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene). The removal of all



X = $BPh_4$ **2**
$PF_6$ **4**

X = $BPh_4$ **3**
$PF_6$ **5**

Scheme 1

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halide from the reaction mixture is the simple and effective key to the formation of the mononuclear complex rather than the dinuclear complex containing bridging mdd ligands. The reaction, however, was complicated by the formation of an off-white, sparingly soluble by-product which was difficult to remove. The by-product was identified as the zwitterionic compound [Rh(cod)($\eta^6$-PhBPh$_3$)] by the four IR bands at 1478, 1458, 1426 and 1395 cm$^{-1}$ characteristic of coordinated tetraphenylborate.[8] Complex **2** was isolated as a microanalytically pure compound after careful recrystallisation from acetone. Further reaction of **2** with carbon monoxide gas formed the Rh dicarbonyl complex [Rh(CO)$_2$(mdd)]$^+$BPh$_4^-$ (**3**). The hexafluorophosphate analogues [Rh(cod)(mdd)]$^+$PF$_6^-$ (**4**) and [Rh(CO)$_2$(mdd)]$^+$PF$_6^-$ (**5**) were synthesised in similar reactions. In the synthesis of complex **4**, it is essential to use halide-free [Rh(OEt)(cod)]$_2$ to avoid the formation of the dinuclear complex.

The $^1$H NMR spectra of the cod complexes **2** and **4** show two separate resonances for the backbone methylene protons with a geminal splitting of 13.0 Hz, whilst the dicarbonyl complexes **3** and **5** show only a singlet for the corresponding protons. The magnetic inequivalence of the methylene protons in the cod complexes probably arises from rigidity of the non-planar metallacyclic ring imposed by the steric bulk of the cod ligand, whereas the methylene protons in the dicarbonyl complexes are more fluxional and exchange rapidly on the NMR timescale. The $^{13}$C{$^1$H} NMR spectra for cod complexes **2** and **4** show the carbene resonances at $\delta$ = 181 ppm with $^1J_{Rh,C}$ in the range 52−53 Hz. The cod resonances also exhibit coupling to Rh with coupling constant values of about 8 Hz. The carbene resonances for dicarbonyl complexes **3** and **5** appear at $\delta$ = 174 ppm with $^1J_{Rh,Carbene}$ of about 45 Hz, whilst the carbonyl carbons appear at $\delta$ = 189 ppm with $^1J_{Rh,CO}$ of 57 Hz. The assignment of the carbonyl resonances was confirmed when solutions of the complexes were placed under an atmosphere of $^{13}$C-labelled CO gas. There is exchange between bound and free CO and the carbonyl resonances increase in intensity relative to all resonances. The value of $^1J_{Rh,CO}$ (57 Hz) is somewhat smaller than that for the corresponding bim complexes and other related bidentate nitrogen-donor complexes where the one-bond coupling is typically in the range 66−69 Hz.[4,9] Two strong IR stretches for ν(CO) were observed for complexes **3** and **5** at 2071−2076 and 2014−2017 cm$^{-1}$, consistent with the *cis* geometry of the complexes.

### X-ray Crystallography

A single-crystal X-ray diffraction analysis of an orange tabular section excised under a polarising microscope from a contact twinned crystal mass (grown from a concentrated [D$_6$]acetone solution at 300 K), confirmed the structure of [Rh(cod)(mdd)]$^+$BPh$_4^-$ (**2**). An ORTEP[10,11] depiction of the cation is shown in Figure 1 and selected bond lengths and angles are listed in Table 1. The structure was modelled as a pseudo-centrosymmetric structure, with $P2_1/m$ symmetry broken by a lack of mirror symmetry in the cyclooctadiene ligand. The complex molecule is bisected by a (pseudo) mirror plane, with the Rh metal and methylene carbon C(12) located in that plane. The six-membered metallacyclic ring as defined by Rh(1), C(9), N(1), C(12), N(1*) and C(9*) is boat-like with Rh and methylene carbon deviations from the boat plane of 0.94 Å and 0.58 Å, respectively. The Rh-carbene bond length [2.025(3) Å] agrees well with that found in non-chelated Rh(cod)(carbene) complexes such as [RhCl(cod)(diy)] and [Rh(cod)(diy)$_2$]Cl (diy = 1,3-dimethylimidazoline-2-ylidene) [2.023(2)−2.059(8) Å].[5,12] The Rh-cod distances [2.171(6)−2.244(6) Å] are also similar to the corresponding distances in [RhCl(cod)(diy)] and [Rh(cod)(diy)$_2$]Cl [2.095(2)−2.205(2) Å].

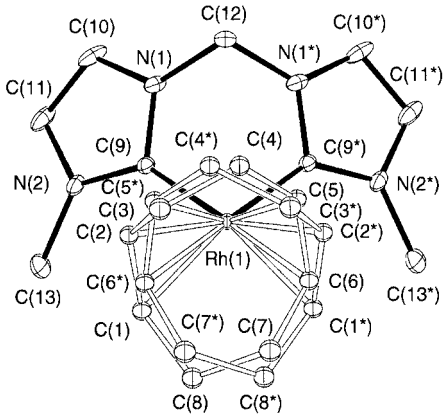



Figure 1. An ORTEP[10,11] depiction of the cation of [Rh(cod)(mdd)]$^+$BPh$_4^-$ (**2**) showing 20% displacement ellipsoids and cod ligand disorder about a (pseudo) mirror plane (see main text and Exp. Sect.); atoms labelled with an asterisk are generated from the unique sites by $x$, 3/2 − $y$, $z$

Single crystal X-ray diffraction analysis of an orange columnar-like crystal (grown from a methanol/diethyl ether solution) confirmed the structure of [Rh(CO)$_2$(mdd)]$^+$PF$_6^-$ (**5**). An ORTEP[10,11] depiction of the cation is shown in Figure 2 and selected bond lengths and angles are listed in Table 1. The asymmetric unit in the crystal structure of complex **5** contains the complex molecule and its hexafluorophosphate counterion, both of which are bisected by a mirror plane passing through Rh(1), C(5), P(1), F(3) and F(4). The complex has a boat-like metallacyclic ring as defined by Rh(1), C(2), N(1), C(5), N(1*) and C(2*) with Rh and methylene carbon deviations from the boat plane of 0.88 Å and 0.59 Å respectively. The Rh-carbene bond length [2.062(2) Å] is similar to that reported for [Rh(CO)(diy)$_2$Cl][13] [2.049(4) Å and 2.047(4) Å]. The Rh-carbonyl bond length [1.892(2) Å] is marginally longer than those in analogous Rh complexes with N-donor bidentate ligands [1.79(1)−1.868(7) Å].[9]

### Hydroamination Catalysts

Cationic Rh$^{I}$ complexes with chelating N-donor ligands are known to catalyse intramolecular hydroamination of aminoalkynes,[4] amino alcohols and amino carboxylic acids.[14] At a catalyst loading of 1.5%, both complexes

Table 1. Selected bond lengths (Å) and angles (°) for $[Rh(cod)(mdd)]^+BPh_4^-$ (**2**) and $[Rh(CO)_2(mdd)]^+PF_6^-$ (**5**)

| Atoms | Bond lengths (Å) | Atoms | Bond angles (°) |
|---|---|---|---|
| | | *[Rh(cod)(mdd)]$^+BPh_4^-$ 2* | |
| Rh(1)−C(9) | 2.025(3) | C(9)−Rh(1)−C(9*[a]) | 83.19(19) |
| Rh(1)−C(5) | 2.171(6) | N(1)−C(9)−N(2) | 103.0(3) |
| Rh(1)−C(6) | 2.221(6) | | |
| Rh(1)−C(1) | 2.243(7) | | |
| Rh(1)−C(2) | 2.244(6) | | |
| | | *[Rh(CO)$_2$(mdd)]$^+PF_6^-$ 5* | |
| Rh(1)−C(1) | 1.8924(17) | C(1)−Rh(1)−C(1*[b]) | 92.01(9) |
| Rh(1)−C(2) | 2.0619(16) | C(2)−Rh(1)−C(2*[b]) | 83.48(8) |
| O(1)−C(1) | 1.1373(19) | N(1)−C(2)−N(2) | 104.3(1) |

[a] $x$, 3/2 − $y$, $z$. [b] $x$, 1/2 − $y$, $z$.

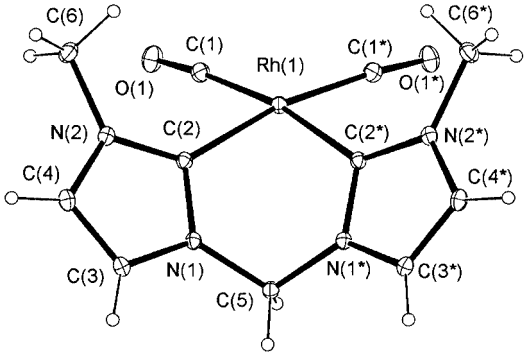
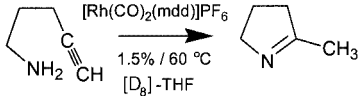



Figure 2. An ORTEP[10,11] depiction of the cation of $[Rh(CO)_2(mdd)]^+PF_6^-$ **5** showing 20% displacement ellipsoids. Atoms labelled with an asterisk are generated from the unique sites by $x$, 1/2 − $y$, $z$

$[Rh(CO)_2(mdd)]^+BPh_4^-$ (**3**) and $[Rh(CO)_2(mdd)]^+PF_6^-$ (**5**) catalyse the cyclisation of 4-pentyn-1-amine to 2-methyl-1-pyrroline (76% and 85% conversion, respectively, in 16 hours at 60 °C in $[D_8]$THF solution). Turnover rates[15] at 50% conversion of 6 $h^{-1}$ and 10 $h^{-1}$ were calculated for complexes **3** and **5** respectively (Scheme 2). The reaction rate for complex **3** was slower than that observed for the analogous bisimidazolylmethane complex $[Rh(bim)(CO)_2]^+BPh_4^-$ (**1**) (Figure 3), where conversion was complete after 12 hours (turnover rate 17 $h^{-1}$). In contrast, the reaction rate for complex **5** was significantly faster than that observed for $[Rh(bim)(CO)_2]^+PF_6^-$ (**6**) where the conversion was only 49% complete after 16 hours (turnover rate 2 $h^{-1}$) at the same catalyst loading under the same reaction conditions. Complex **6** is the $PF_6^-$ analogue of **1**. The synthesis of **6** is analogous to that reported for the synthesis of **1**.[4]

In comparing the two carbene complexes, the $PF_6^-$ complex **5** has a higher turnover rate for the conversion of 4-




Scheme 2

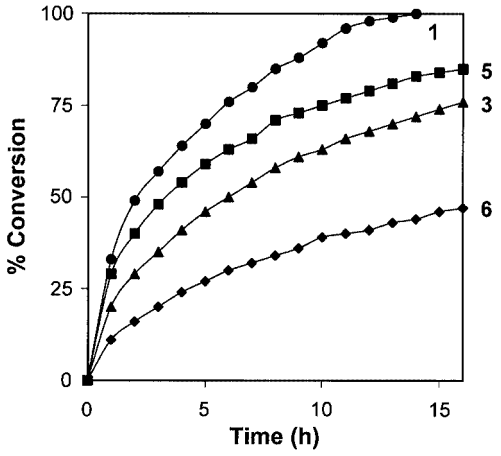



Figure 3. Comparative reaction rates for the metal-catalysed cyclisation of 4-pentyn-1-amine to 2-methyl-1-pyrroline using $[Rh(CO)_2(mdd)]^+BPh_4^-$ **3** (▲), $[Rh(CO)_2(mdd)]^+PF_6^-$ **5** (■), $[Rh(bim)(CO)_2]^+PF_6^-$ **6** (◆), and $[Rh(bim)(CO)_2]^+BPh_4^-$ **1** (●); catalyst loading 1.5% at 60 °C in $[D_8]$THF solution

pentyn-1-amine to 2-methyl-1-pyrroline than the corresponding $BPh_4^-$ complex **3**. The dependence of the turnover rate on the counterion has also been noted previously with related catalysts and this could be the result of significant ion pairing in solution.

## Conclusions

A synthetic route to mononuclear $Rh^I$ complexes containing the bidentate bis-carbene ligand 1,1′-methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene (mdd) has been developed. The complexes are robust and two Rh complexes containing the mdd ligand have been structurally characterised. Both complexes show the presence of a boat-like six-membered metallacycle containing two metal-carbon bonds. $[Rh(mdd)(CO)_2]^+$ is catalytically active for the intramolecular cyclisation of aminoalkynes and the turnover rate is similar to $[Rh(bim)(CO)_2]^+$ and other related catalysts for this conversion. Reaction conditions for this conversion are as yet unoptimised and these results demonstrate the future potential of rhodium carbenes in a range of catalytic applications.

## Experimental Section

All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk or vacuum techniques or in a Vacuum Atmospheres nitrogen-filled drybox. $RhCl_3 \cdot H_2O$ was purchased from Strem and used as received. $[RhCl(cod)]_2$ was prepared by the literature method.[16] 1,1′-Methylene-3,3′-dimethyldiimidazolium dibromide was synthesised by a modification of the literature procedure for the analogous diiodide salt.[17] All bulk compressed gases were obtained from BOC Gases. Nitrogen (> 99.5%) and carbon monoxide (> 99.5%) were used as supplied without further purification.

Tetrahydrofuran and diethyl ether were stored over sodium wire and distilled under nitrogen from sodium benzophenone ketyl. Methanol was distilled from magnesium methoxide under nitrogen. Acetone was distilled from calcium sulfate under nitrogen. Deuterated solvents for NMR purposes were obtained from Merck and Cambridge Isotopes. Solvents were dried over suitable drying agents, degassed using three consecutive freeze-pump-thaw cycles and vacuum distilled immediately prior to use.

Microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer. Infra-red spectra were obtained using a Perkin−Elmer 1600 Series F.T.I.R. spectrometer as KBr discs.

NMR spectra were recorded on Bruker Avance DPX 300 or DRX 400 spectrometers at 300 K. $^1H$ and $^{13}C$ NMR chemical shifts (δ/ppm) were referenced to internal solvent resonances. $^{31}P$ NMR chemical shifts were referenced to external neat trimethyl phosphite, taken to be at δ = 140.85 ppm. $^{19}F$ NMR chemical shifts were externally referenced to neat hexafluorobenzene, taken to be at δ = −163 ppm.

**Synthesis of $[mddH_2]^{2+}$ $2BPh_4^-$:** Sodium tetraphenylborate (2.0 g, 5.9 mmol) was added to a solution of 1,1′-methylene-3,3′-dimethyldiimidazolium dibromide (1.0 g, 3.0 mmol) in water (20 mL). The white precipitate formed was isolated by filtration and dried in vacuo overnight. 1,1′-Methylene-3,3′-dimethyldiimidazolium bis(tetraphenylborate) was recrystallised from acetone/diethyl ether as a white solid (1.4 g, 58%), m.p. 218 °C (dec). $C_{57}H_{54}B_2N_4$ (816.69): calcd. C 83.8, H 6.7, N 6.9; found C 83.7, H 6.8, N 6.9. $^1H$ NMR ([D$_6$]acetone, 400 MHz): δ = 8.75 (s, 2 H, NCHN), 7.75 (d, $^3J_{H,H}$ = 1.6 Hz, 2 H, NCH), 7.53 (d, $^3J_{H,H}$ = 1.6 Hz, 2 H, NCH), 7.48 (m, 16 H, *o*-H), 6.93 (t, $^3J_{H,H}$ = 7.3 Hz, 16 H, *m*-H), 6.77 (t, $^3J_{H,H}$ = 7.3 Hz, 8 H, *p*-H), 6.50 (s, 2 H, $NCH_2$), 3.81 (s, 6 H, $NCH_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 101 MHz): δ = 164.9 (q, $^1J_{C,B}$ = 49.3 Hz, *ipso*-C), 138.4 (NCHN), 136.9 (*o*-C), 126.1 (*m*-C), 126.0 (NCH), 122.9 (NCH), 122.3 (*p*-C), 59.8 ($NCH_2$), 37.1 ($NCH_3$) ppm.

**Synthesis of $[mddH_2]^{2+}$ $2PF_6^-$:** A solution of 1,1′-methylene-3,3′-dimethyldiimidazolium dibromide (2.6 g, 7.7 mmol) in water (15 mL) was added to a solution of potassium hexafluorophosphate (2.9 g, 15 mmol) in water (50 mL). The precipitate was isolated by filtration, washed with diethyl ether and dried in vacuo overnight to give 1,1′-methylene-3,3′-dimethyldiimidazolium bis(hexafluorophosphate) as a white solid (2.8 g, 77%), m.p. 200 °C. $C_9H_{14}F_{12}N_4P_2$ (468.24): calcd. C 23.1, H 3.0, N 12.0; found C 23.1, H 3.2, N 11.7. $^1H$ NMR ([D$_6$]acetone, 300 MHz): δ = 9.37 (s, 2 H, NCHN), 8.05 (s, 2 H, NCH), 7.84 (s, 2 H, NCH), 7.02 (s, 2 H, $NCH_2$), 4.10 (s, 6 H, $NCH_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 75 MHz): δ = 139.1 (NCHN), 126.0 (NCH), 123.2 (NCH), 60.1 ($NCH_2$), 37.2 ($NCH_3$) ppm. $^{19}F$ NMR ([D$_6$]acetone, 282 MHz): δ = −70.9 (d, $^1J_{P,F}$ = 708 Hz) ppm. $^{31}P$ NMR ([D$_6$]acetone, 121 MHz): δ = −146.4 (sep, $^1J_{P,F}$ = 708 Hz). Note: Spectroscopic data ($^1H$ and $^{31}P$ NMR) for this compound have been reported,[18] although no microanalytical data were included.

**Synthesis of $[Rh(OEt)(cod)]_2$:** $[RhCl(cod)]_2$ (100 mg, 0.20 mmol) in methanol (0.6 mL) was treated with NaOEt (0.44 mL of 1 M methanol solution, 0.44 mmol) under nitrogen. After stirring for 30 min, the yellow suspension was filtered. The yellow solid obtained was washed with methanol and dried. $[Rh(cod)(OEt)]_2$ (102 mg, 98%) was used directly without further purification.

**Synthesis of $[Rh(cod)(mdd)]^+$ $BPh_4^-$ (2):** Sodium ethoxide (0.40 mL of 1 M methanol solution, 0.40 mmol) and 1,1′-methylene-3,3′-dimethyldiimidazolium bis(tetraphenylborate) (290 mg, 0.36 mmol) were added to a suspension of $[Rh(cod)(OEt)]_2$ (92 mg, 0.18 mmol) in methanol (1 mL). The reaction mixture was heated at reflux for 15 minutes and then stirred at room temperature overnight, during which time the pale-yellow suspension changed to an orange suspension. The resulting precipitate was filtered and washed with methanol. (Cyclooctadiene)(1,1′-methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene)rhodium(I) tetraphenylborate was recrystallised from acetone as an orange crystalline solid (159 mg, 63%), m.p. 188 °C (dec). $C_{41}H_{44}BN_4Rh$ (706.52): calcd. C 69.7, H 6.3, N 7.9; found C 69.5, H 6.5, N 8.0. $^1H$ NMR ([D$_6$]acetone, 400 MHz): δ = 7.45 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, NCH), 7.34 (m, 8 H, *o*-H), 7.15 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, NCH), 6.92 (t, $^3J_{H,H}$ = 7.3 Hz, 8 H, *m*-H), 6.77 (t, $^3J_{H,H}$ = 7.3 Hz, 4 H, *p*-H), 6.59 (d, $^2J_{H,H}$ = 13.0 Hz, 1 H, $NCH_2$), 6.26 (d, $^2J_{H,H}$ = 13.0 Hz, 1 H, $NCH_2$), 5.05 [m, 2 H, CH(cod)], 4.87 [m, 2 H, CH(cod)], 3.84 (s, 6 H, $NCH_3$), 2.54 [m, 2 H, $CH_2$(cod)], 2.4−2.1 [m, 6 H, $CH_2$(cod)] ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 101 MHz): δ = 181.1 (d, $^1J_{Rh,C}$ = 52.7 Hz, NCN), 164.9 (q, $^1J_{C,B}$ = 49.6 Hz, *ipso*-C), 137.0 (*o*-C), 126.0 (*m*-C), 123.4 (NCH), 122.3 (*p*-C), 121.8 (NCH), 92.0 [d, $^1J_{Rh,C}$ = 7.8 Hz, CH(cod)], 87.8 [d, $^1J_{Rh,C}$ = 7.8 Hz, CH(cod)], 64.1 ($NCH_2$), 38.0 ($NCH_3$), 31.2 [$CH_2$(cod)], 31.0 [$CH_2$(cod)] ppm. MS (ES+, $CH_3CN$): *m/z* (%) = 387 (45) $[Rh(cod)(mdd)]^+$, 361 (25) $[Rh(mdd)(CH_3CN)_2]^+$, 320 (100) $[Rh(mdd)(CH_3CN)]^+$, 279 (35) $[Rh(mdd)]^+$.

**Synthesis of $[Rh(CO)_2(mdd)]^+$ $BPh_4^-$ (3):** $[Rh(cod)(mdd)]^+BPh_4^-$ (**2**; 50 mg, 71 μmol) was suspended in methanol (1 mL). The mixture was degassed using three freeze-pump-thaw cycles, flushed with carbon monoxide gas and stirred at room temperature overnight, during which time the orange suspension became a yellow suspension. The precipitate was isolated by filtration and washed with diethyl ether producing dicarbonyl(1,1′-methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene)rhodium(I) tetraphenylborate as a yellow solid (41 mg, 88%), m.p. 170 °C (dec). $C_{35}H_{32}BN_4O_2Rh$ (654.36): calcd. C 64.2, H 4.9, N 8.6; found C 64.2, H 4.7, N 8.7. $^1H$ NMR ([D$_6$]acetone, 400 MHz): δ = 7.56 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, NCH), 7.35 (m, 9 H, NCH and *o*-H), 6.91 (t, $^3J_{H,H}$ = 7.3 Hz, 8 H, *m*-H), 6.77 (t, $^3J_{H,H}$ = 7.3 Hz, 4 H, *p*-H), 6.21 (s, 2 H, $NCH_2$), 3.93 (s, 6 H, $NCH_3$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 101 MHz): δ = 189.0 (d, $^1J_{Rh,C}$ = 57.0 Hz, CO), 173.6 (d, $^1J_{Rh,C}$ = 45.2 Hz, NCN), 164.9 (q, $^1J_{C,B}$ = 49.3 Hz, *ipso*-C), 137.0 (*o*-C), 126.0 (*m*-C), 124.1 (NCH), 123.2 (NCH), 122.2 (*p*-C), 63.8 ($NCH_2$), 38.9 ($NCH_3$) ppm. MS (ES+, $CH_3CN$): *m/z* (%) = 361 (18) $[Rh(mdd)(CH_3CN)_2]^+$, 335 (26) $[Rh(CO)_2(mdd)]^+$, 320 (100) $[Rh(mdd)(CH_3CN)]^+$, 279 (53) $[Rh(mdd)]^+$. IR: $\tilde{\nu}$ = 2071s (νCO), 2014s (νCO) $cm^{-1}$.

**Synthesis of $[Rh(cod)(mdd)]^+$ $PF_6^-$ (4):** Sodium ethoxide (0.45 mL of 1 M methanol solution, 0.45 mmol) and 1,1′-methylene-3,3′-

dimethyldiimidazolium bis(hexafluorophosphate) (190 mg, 0.40 mmol) were added to a suspension of $[Rh(OEt)(cod)]_2$ (100 mg, 0.20 mmol) in methanol (1 mL). The reaction mixture was stirred at room temperature for three days, during which time the yellow suspension became an orange suspension. The resulting precipitate was filtered and washed with methanol. (Cyclooctadiene)(1,1′-methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene)rhodium(I) hexafluorophosphate was recrystallised from acetone as an orange-red crystalline solid (142 mg, 67%), m.p. 203 °C (dec). $C_{17}H_{24}F_6N_4PRh$ (532.28): calcd. C 38.4, H 4.5, N 10.5; found C 38.5, H 4.8, N 10.4. $^1$H NMR ([D$_6$]acetone, 300 MHz): δ = 7.50 (d, $^3J_{H,H}$ = 1.9 Hz, 2 H, $CH_2NCH$), 7.17 (d, $^3J_{H,H}$ = 1.9 Hz, 2 H, $CH_3NCH$), 6.61 (d, $^2J_{H,H}$ = 13.0 Hz, 1 H, $NCH_2$), 6.31 (d, $^2J_{H,H}$ = 13.0 Hz, 1 H, $NCH_2$), 5.05 [m, 2 H, CH(cod)], 4.88 [m, 2 H, CH(cod)], 3.86 (s, 6 H, $NCH_3$), 2.54 [m, 2 H, $CH_2$(cod)], 2.27 [m, 4 H, $CH_2$(cod)], 2.08 [m, 2 H, $CH_2$(cod)] ppm. $^{13}$C{$^1$H} NMR ([D$_6$]acetone, 75 MHz): δ = 181.1 (d, $^1J_{Rh,C}$ = 52.2 Hz, NCN), 123.4 ($CH_3NCH$), 121.9 ($CH_2NCH$), 92.0 [d, $^1J_{Rh,C}$ = 8.6 Hz, CH(cod)], 87.8 [d, $^1J_{Rh,C}$ = 7.8 Hz, CH(cod)], 64.1 ($NCH_2$), 38.0 ($NCH_3$), 31.2 [$CH_2$(cod)], 31.0 [$CH_2$(cod)] ppm. $^{19}$F NMR ([D$_6$]acetone, 282 MHz): δ = −71.0 (d, $^1J_{P,F}$ = 708 Hz) ppm. $^{31}$P NMR ([D$_6$]acetone, 121 MHz): δ = −146.3 (sep, $^1J_{P,F}$ = 708 Hz) ppm. MS (ES+, MeOH): *m*/*z* (%) = 387 (10) $[Rh(cod)(mdd)]^+$, 311 (100) $[Rh(mdd)(MeOH)]^+$, 279 (15) $[Rh(mdd)]^+$ ppm. MS (ES-, MeOH): *m*/*z* (%) = 145 (100) $[PF_6^-]$.

**Synthesis of $[Rh(CO)_2(mdd)]^+PF_6^-$ (5):** $[Rh(cod)(mdd)]^+PF_6^-$ (**4**; 70 mg, 0.13 mmol) was suspended in diethyl ether (1 mL) and methanol (1 mL). The suspension was degassed using three freeze-pump-thaw cycles, flushed with carbon monoxide gas and stirred at room temperature for 3 days, during which time the orange suspension became a yellow suspension. The precipitate was isolated by filtration and washed with diethyl ether producing dicarbonyl(1,1′-methylene-3,3′-dimethyldiimidazoline-2,2′-diylidene)-rhodium(I) hexafluorophosphate as a yellow solid (29 mg, 46%), m.p. 200 °C (dec). $C_{11}H_{12}F_6N_4O_2PRh$ (480.13): calcd. C 27.5, H 2.5, N 11.7; found C 27.7, H 2.8, N 11.6. $^1$H NMR ([D$_6$]acetone, 400 MHz): δ = 7.68 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, $CH_2NCH$), 7.46 (d, $^3J_{H,H}$ = 1.8 Hz, 2 H, $CH_3NCH$), 6.41 (s, 2 H, $NCH_2$), 4.01 (s, 6 H, $NCH_3$) ppm. $^{13}$C{$^1$H} NMR ([D$_6$]acetone, 101 MHz): δ = 189.0 (d, $^1J_{Rh,C}$ = 56.6 Hz, CO), 173.6 (d, $^1J_{Rh,C}$ = 45.4 Hz, NCN), 124.1 ($CH_3NCH$), 123.3 ($CH_2NCH$), 63.9 ($NCH_2$), 38.9 ($NCH_3$) ppm. $^{19}$F NMR ([D$_6$]acetone, 282 MHz): δ = −67.7 (d, $^1J_{P,F}$ = 710 Hz) ppm. $^{31}$P NMR ([D$_6$]acetone, 121 MHz): δ = −143.1 (sep, $^1J_{P,F}$ = 710 Hz) ppm. MS (ES+, MeOH): *m*/*z* (%) = 335 (100) $[Rh(CO)_2(mdd)]^+$. MS (ES-, MeOH): *m*/*z* (%) = 145 (100) $[PF_6^-]$. IR: $\tilde{\nu}$ = 2076s (νCO), 2017s (νCO) cm$^{-1}$.

**Synthesis of $[Rh(bim)(CO)_2]^+PF_6^-$ (6):** A solution of bis(*N*-methylimidazol-2-yl)methane (80 mg, 0.45 mmol) in methanol (5 mL) was added to a solution of $[RhCl(CO)_2]_2$ (88 mg, 0.22 mmol) in methanol (15 mL) at room temperature. The yellow precipitate that formed initially dissolved after the addition of the ligand was complete. The mixture was stirred for 30 minutes before adding an excess of potassium hexafluorophosphate (400 mg) in methanol (10 mL). The resulting precipitate was filtered and washed with methanol. [Bis(*N*-methylimidazol-2-yl)methane)dicarbonylrhodium(I) hexafluorophosphate was recrystallised from acetone as a dark pink solid (191 mg, 90%), m.p. 262 °C (dec). $C_{11}H_{12}F_6N_4O_2PRh$ (480.12): calcd. C 27.5, H 2.5, N 11.7; found C 27.6, H 2.2, N 11.4. $^1$H NMR ([D$_6$]acetone, 400 MHz): δ = 7.55 (d, $^3J_{H5,H4}$ = 1.4 Hz, 2 H, H5), 7.42 (d, 2 H, H4), 4.63 (s, 2 H, $CH_2$), 3.97 (s, 6 H, $NCH_3$) ppm. $^{13}$C{$^1$H} NMR ([D$_6$]acetone, 101 MHz): δ = 185.3 (d, $^1J_{Rh,C}$ = 68.2 Hz, CO), 143.9 (C2), 130.9 (C5), 124.3 (C4), 34.8 ($NCH_3$), 24.4 ($CH_2$) ppm. $^{19}$F NMR ([D$_6$]acetone, 376 MHz): δ = −67.5 (d, $^1J_{P,F}$ = 708 Hz) ppm. $^{31}$P{$^1$H} NMR ([D$_6$]acetone, 162 MHz): δ = −135 (sep, $^1J_{P,F}$ = 708 Hz) ppm. MS (ES+, THF): *m*/*z* (%) = 335 (100) $[Rh(bim)(CO)_2]^+$. IR: $\tilde{\nu}$ = 2084s (νCO), 2026s (νCO) cm$^{-1}$.

### X-ray Crystallography

Low-temperature single-crystal diffraction data were collected with a Bruker SMART 1000 diffractometer using graphite monochromated Mo-$K_\alpha$ radiation (λ = 0.71073 Å) from a sealed tube. Crystallographic details are given in Table 2. Data integration and reduction were undertaken with SAINT and XPREP[19] and sub-

Table 2. Crystallographic data for $[Rh(cod)(mdd)]^+BPh_4^-$ (**2**) and $[Rh(CO)_2(mdd)]^+PF_6^-$ (**5**)

| | **2** | **5** |
|---|---|---|
| Empirical formula | $C_{41}H_{44}BN_4Rh$ | $C_{11}H_{12}F_6N_4O_2PRh$ |
| Molecular weight (g mol$^{-1}$) | 706.52 | 480.13 |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/m$ (no. 11) | *Pnma* (no. 62) |
| *a* (Å) | 10.457(3) | 12.416(4) |
| *b* (Å) | 13.108(4) | 12.790(4) |
| *c* (Å) | 12.295(4) | 10.408(3) |
| β (°) | 95.731(5) | |
| *V* (Å$^3$) | 1676.9(9) | 1652.7(9) |
| *Z* | 2 | 4 |
| *T* (K) | 150(2) | 100(2) |
| μ Mo-$K_\alpha$ (mm$^{-1}$) | 0.546 | 1.207 |
| Crystal Size (mm) | 0.233 × 0.154 × 0.071 | 0.324 × 0.121 × 0.120 |
| $T$(Gaussian)$_{min,max}$ | 0.902, 0.962 | 0.820, 0.946 |
| $2\theta_{max}$ (°) | 56.50 | 56.60 |
| *hkl* range | −13 13, −17 16, −16 16 | −16 16, −17 17, −13 13 |
| *N* | 14318 | 16349 |
| $N_{ind}$ | 4005 ($R_{merge}$ 0.0310) | 2079 ($R_{merge}$ 0.0321) |
| $N_{obs}$ [$I > 2\sigma(I)$] | 3444 | 1888 |
| Goodness of fit (all data) | 1.499 | 1.316 |
| *R*1 [*F*, $I > 2\sigma(I)$] | 0.0492 | 0.0189 |
| *wR*2 ($F^2$, all data) | 0.1325 | 0.0549 |

sequent computations were carried out with the teXsan[20] and WinGX[21] graphical user interfaces. A Gaussian absorption correction was applied to the data.[19,22] The structures were solved by direct methods with SIR97[23] and extended and refined with SHELXL-97.[24] In general the non-hydrogen atoms were modelled with anisotropic displacement parameters, and a riding-atom model with group displacement parameters was used for the hydrogen atoms. The crystal structure of complex **2** was modelled as a disordered (pseudo)centrosymmetric structure in $P2_1/m$ (no. 11). An alternative model in $P2_1$ (no. 4) had significantly higher residuals at convergence [$R1(F) = 0.0591$ and $wR2(F^2) = 0.1656$], and high levels of correlation requiring extensive geometry and displacement restraints. The Flack parameter[25] in $P2_1$ refined to 0.49(8) suggesting either an inversion twin or a centrosymmetric structure. The disordered centrosymmetric model was adopted as the better model for the crystal structure. The asymmetric unit in $P2_1/m$ contains a complex molecule bisected by a (pseudo) mirror plane, with the metal ion and C(12) atoms located in that plane. A tetraphenylborate counterion also resides on a mirror plane, with the B(1), C(14), C(15), C(16), C(17), C(18), C(19), C(20) and C(23) atoms located in the mirror plane. Two of the phenyl residues of the counterion have orientational disorder about the boron to quaternary carbon axis. The $P2_1/m$ symmetry is broken by a lack of mirror symmetry in the cyclooctadiene ligand, which is disordered about the mirror plane. The fully occupied non-hydrogen sites were modelled with anisotropic displacement parameters, and isotropic displacement parameters were used for the partially occupied non-hydrogen sites and for the fully occupied boron site. The site occupancies were refined, and then fixed and rounded to the first decimal place.

CCDC-186563 (**2**) and -186564 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD2 1EZ, UK; Fax: (internat.) + 44-1233/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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