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Synthesis and characterization of cationic rhodium(I) dicarbonyl complexes

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ABSTRACT

Treatment of $Rh(acac)(CO)_2$ (acac = acetoacetonate) with perchloric acid followed by addition of an α-diimine (α-diimine = 1,4-bis(Ar)-2,3-dimethyl-1,4-diaza-1,3-butadiene, Ar = 3,5-dimethylphenyl, **1**; 3,5-di-*tert*-butylphenyl, **2**; and 3,4,5-trimethoxyphenyl, **3**; phenyl, **4**; and 4-chlorophenyl, **5**) generates a series of complexes of the type $[Rh(\alpha\text{-diimine})(CO)_2][ClO_4]$ **6**–**10** with varying electronic properties of the supporting diimine ligand. X-ray crystal structures have been determined for the α-diimine ligands **1**–**5**, and complexes **6**, **8**, and **10**.

1. Introduction

Rhodium carbonyl coordination complexes play an important role in organic transformations, with two of the largest and most important being hydroformylation [1–6] and the carbonylation of methanol to acetic acid with $[Rh(CO)_2I_2]^-$ by Monsanto [3,7–9]. Efforts to improve Monsanto's acetic acid synthesis are ongoing, with a considerable number of these catalysts being rhodium carbonyl complexes [10–17]. Additionally, rhodium complexes with carbonyl ligands show catalytic activity towards carbonylative hydrosilylation [18], reductive amination [19], isomerization [20–22] polymerization [23,24], and reduction [25,26]. C–H activation of alkanes by the photodissociation of a CO ligand of the rhodium carbonyl complexes $Rh(Cp)(CO)_2$ and $Rh(Tp')(CO)_2$ ($Cp = \eta^5\text{-}C_5H_5$, Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate) are well understood [27–31] and the reactive fragments: [Rh(Cp)(CO)] [32–39] [Rh(Tp′)(CO)] [40], and $[Rh(\eta^5\text{-}C_4H_4P)(CO)]$ [41] have been investigated by theoreticians. Extending the utility of C–H activation, Shul'pin et al. showed how the rhodium carbonyl cluster $Rh_6(CO)_{16}$ (and to a lesser extent $Rh_2Cp_2(CO)_3$ and $Rh_3(CpMe)_3(CO)_3$) could C–H activate and functionalize benzene to phenol with hydrogen peroxide [42].

2. Results and discussion

2.1. General/synthesis

Oro synthesized $[Rh(bipym)(CO)_2][ClO_4]$ (bipym = 2,2′-bipyrimidine) by protonation of the acac ligand of $Rh(acac)(CO)_2$ (acac = acetylacetonate) with perchloric acid in acetone generating $[Rh(acetone)_2(CO)_2][ClO_4]$ *in situ*, and then addition of bipym to displace the acetone ligands [43]. Similarly, we found that protonation of the acac ligand of $Rh(acac)(CO)_2$ with perchloric acid followed by coordination the chelating diimines **1**–**5** (Fig. 1), led to the formation of **6**–**10**.

While these syntheses are similar, there are subtle but significant differences that should be observed to ensure a clean product. Specifically, the details of the order of addition, reaction time, stoichiometry, and work-up procedures detailed in the experimental section are very important to generate the pure complexes. For instance, longer reaction times did not necessarily increase yield, but often decreased purity. Workup procedures also differed: evaporating the crude reaction solution to dryness, then washing with non-polar solvents was sufficient to purify **7** and **9**. This was not the case for **8**, which required a second purification step (crystallization) after the non-polar solvent wash. Non-polar solvent washing was not an appropriate purification method for **6** and **10**; both required crystallization by layering the crude reaction solution with diethyl ether at −20 °C.

2.2. X-ray Crystallography

The α-diimine ligands **1**–**5** were synthesized as described in the Section 4. Evaporation of acetone or ethanol solutions produced crystals suitable for structure determination. The data parameters for these compounds are summarized in Table 1, with thermal ellipsoid representations shown in Fig. 2. Average bond lengths for **1**–**5** are typical, with N1–C1 = 1.28 Å, N1–C3 = 1.42 Å, C1–C1A = 1.50 Å, and C1–C2 = 1.50 Å, and all molecules crystallize with an *anti* conformation about the C1–C1A bond (Table 2). Rhodium complexes $\mathbf{6{\cdot}CDCl_3}$, $\mathbf{8{\cdot}CDCl_3}$, and **10** crystallized by layering a

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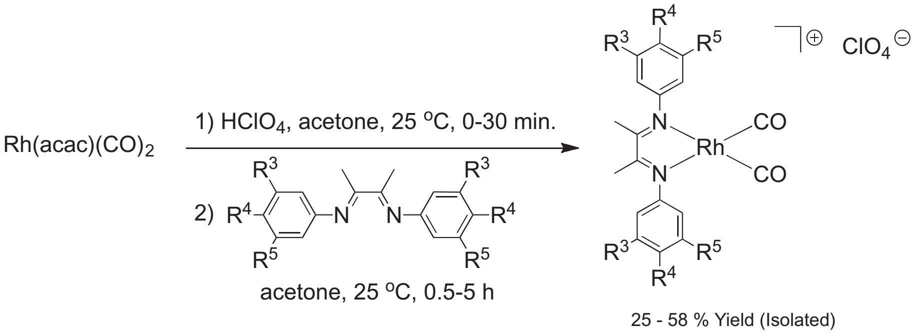

6, $R^3 = R^5 = CH_3$, $R^4 = H$
7, $R^3 = R^5 = C(CH_3)_3$, $R^4 = H$
8, $R^3 = R^4 = R^5 = OCH_3$
9, $R^3 = R^4 = R^5 = H$
10, $R^3 = R^5 = H$, $R^4 = Cl$

Fig. 1. Syntheses of **6–10**.

Table 1
X-ray data parameter table of **1–5**, **6·$CDCl_3$**, **8·$CDCl_3$**, **8·C_3H_6O**, and **10**.

Parameter	1	2	3	4	5	6·$CDCl_3$	8·$CDCl_3$	8·C_3H_6O	10
Empirical formula	$C_{20}H_{24}N_2$	$C_{32}H_{48}N_2$	$C_{22}H_{28}N_2O_6$	$C_{16}H_{16}N_2$	$C_{16}H_{14}Cl_2N_2$	$C_{23}H_{24}Cl_4DN_2O_6Rh$	$C_{25}H_{28}Cl_4DN_2O_{12}Rh$	$C_{27}H_{34}ClN_2O_{13}Rh$	$C_{18}H_{14}Cl_3N_2O_6Rh$
Formula weight	292.41	460.72	416.46	236.31	305.19	671.17	795.22	732.92	563.57
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_1/n$	$C2/c$	$C2/c$	$Pbca$	$P2_1/n$	$Pbca$	$Cmc2_1$	$Cmc2_1$	$Cmcm$
a (Å)	5.2793(3)	35.129(4)	32.0431(19)	5.4366(4)	5.6857(4)	16.158(3)	20.932(2)	20.776(2)	22.210(5)
b (Å)	11.2707(6)	5.8999(7)	4.6033(3)	8.6026(6)	8.6145(6)	12.6924(19)	13.2850(13)	13.2576(16)	13.152(3)
c (Å)	14.1803(8)	15.3407(19)	14.2004(8)	27.3962(18)	15.6359(12)	27.519(4)	11.5186(11)	11.3548(13)	7.4991(16)
α (°)	90	90	90	90	90	90	90	90	90
β (°)	96.294(1)	114.873(2)	95.807(1)	90	97.887(1)	90	90	90	90
γ (°)	90	90	90	90	90	90	90	90	90
V (Å^3)	838.66(8)	2884.6(6)	2083.9(2)	1281.29(15)	758.59(10)	5643.7(15)	3203.0(5)	3127.6(6)	2190.5(8)
Z	2	4	4	4	2	8	4	4	4
Goodness-of-fit (GOF) on F^2	1.047	1.04	1.05	1.035	1.051	1.009	1.053	1.048	1.11
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0418$ $wR2 = 0.1192$	$R1 = 0.0403$ $wR2 = 0.1133$	$R1 = 0.0357$ $wR2 = 0.1037$	$R1 = 0.0410$ $wR2 = 0.1098$	$R1 = 0.0385$ $wR2 = 0.1054$	$R1 = 0.0533$ $wR2 = 0.0980$	$R1 = 0.0322$ $wR2 = 0.0645$	$R1 = 0.0336$ $wR2 = 0.0724$	$R1 = 0.0436$ $wR2 = 0.0740$
R indices (all data)	$R1 = 0.0493$ $wR2 = 0.1263$	$R1 = 0.0473$ $wR2 = 0.1198$	$R1 = 0.0394$ $wR2 = 0.1078$	$R1 = 0.0490$ $wR2 = 0.1154$	$R1 = 0.0538$ $wR2 = 0.1152$	$R1 = 0.1131$ $wR2 = 0.1170$	$R1 = 0.0403$ $wR2 = 0.0675$	$R1 = 0.0429$ $wR2 = 0.0767$	$R1 = 0.1126$ $wR2 = 0.0936$

concentrated chloroform solution of the complex with pentane and a second crystallization method was discovered for **8** by layering an acetone solution with pentane crystallizing as **8·C_3H_6O**. The data parameters for these compounds are summarized in Tables 1 and 3, with thermal ellipsoid representations shown in Fig. 3. The average Rh–CO bond length is 1.87 ± 0.01 Å and the average Rh–N bond length is 2.06 ± 0.01 Å. When comparing the free diimine ligands **1**, **3**, **5** to the coordinated diimine complexes **6·$CDCl_3$**, **8·$CDCl_3$**, **8·C_3H_6O**, and **10**, there is little elongation of the N=C bond[1]or elongation of the backbone C(sp^2)–C(sp^2) bond[2] observed.

2.3. Other characterization

Compounds **1** and **6–10** show ^{1}H NMR spectra that indicate purity. Combustion analyses for **1**, **6**, and **10** also indicate the isolation of analytically pure compounds. Combustion analyses for **7**, **8**, and **9** are consistent with complexes in the form of monohydrates **7·H_2O**, **8·H_2O**, and **9·H_2O**, respectively. It is difficult to provide direct evidence for these monohydrate complexes explicitly; however hydrogen bonding of water to these oxygen rich complexes is not unreasonable. It should be noted that **8** crystallizes with either chloroform-d_1 or acetone as **8·$CDCl_3$** or **8·C_3H_6O**, respectively, forming solvent channels throughout the crystal lattice. These solvent channels for both crystal systems are of similar size, and exhibit similar behavior. Upon removal from the mother liquor, both crystallization systems very readily lose solvent from the lattice, thus destroying the integrity of the crystal for analysis by X-ray diffraction. It is proposed that upon removal of organic solvent in the workup steps for **7**, **8**, and **9**, water may be incorporated forming the respective monohydrates.

3. Conclusion

We have outlined the synthesis and characterization of a series of cationic rhodium(I) dicarbonyl complexes with a variety of diimine ligands. Further investigation of the reactivity of these complexes is underway.

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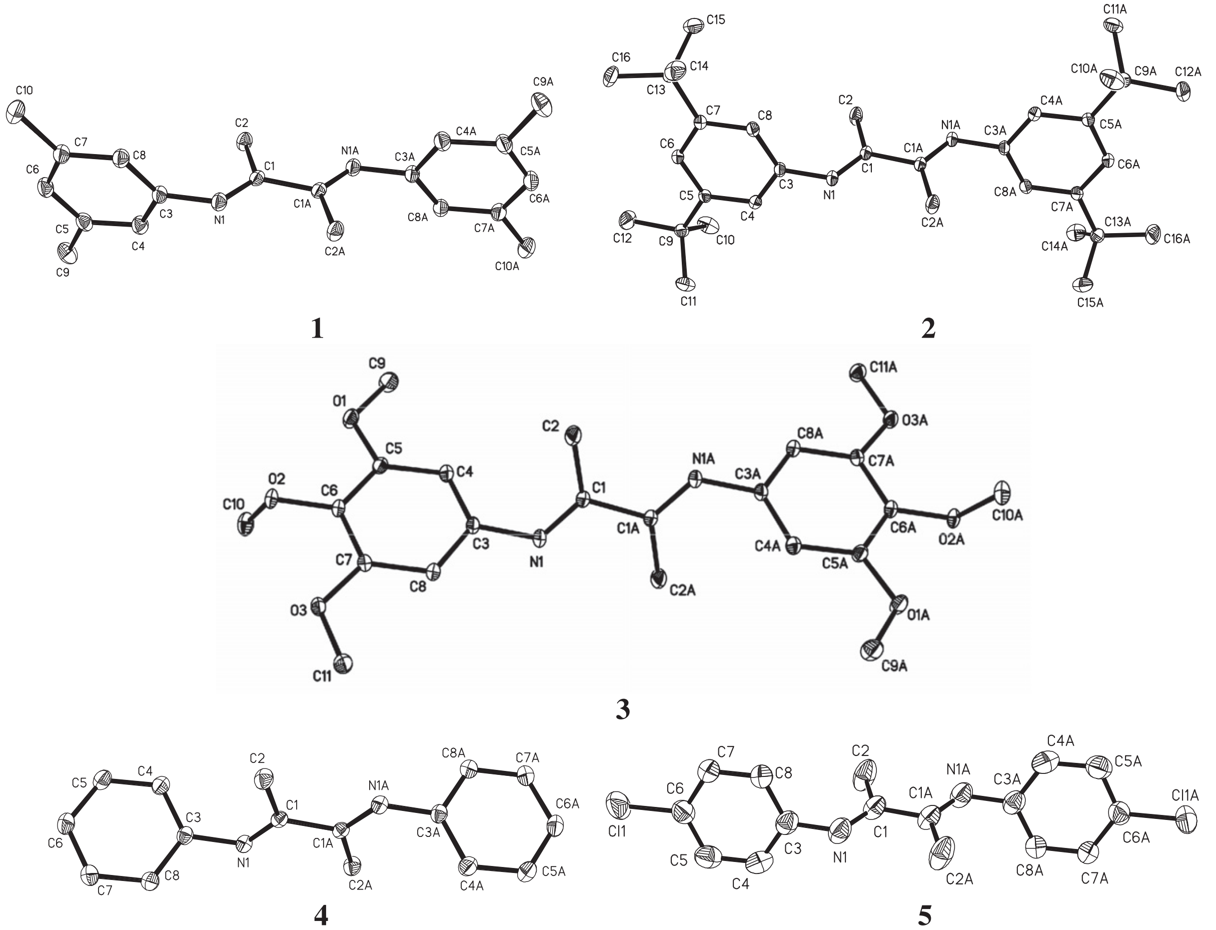
[1] Elongation of the N=C bond for **6**·$CDCl_3$ = 0.001(1) and 0.004(4) Å, **8**·CDCl3 = 0.005(4) Å, **8**·C_3H_6O = 0.007(3) Å, and 10 = 0.004(4) Å.

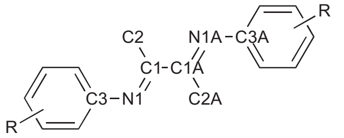
[2] Elongation of the backbone C(sp^2)–C(sp^2) bond for **6**·$CDCl_3$ = 0.007(5) Å, **8**·$CDCl_3$ = 0.017(5) Å, **8**·C_3H_6O = 0.010(7) Å, and 10 = 0.008(8) Å.



1 2 3 4 5

Fig. 2. Molecular structures of **1**–**5**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were omitted for clarity. All molecules exhibit a crystallographic inversion center at the midpoint of the C1–C1A bond.

Table 2
Selected bond lengths (Å) and torsion angles (°) of **1**–**5**.



·	**1**	**2**	**3**	**4**	**5**
N1–C1	1.2814(9)	1.2807(9)	1.2807(9)	1.2811(10)	1.2782(16)
N1–C3	1.4212(9)	1.4236(8)	1.4203(8)	1.4224(10)	1.4158(15)
C1–C1A	1.5028(13)	1.5028(12)	1.4987(13)	1.5032(15)	1.502(2)
C1–C2	1.5030(10)	1.4997(10)	1.5035(10)	1.5027(11)	1.4970(16)
C3–N1–C1–C1A	175.82(7)	179.30(7)	177.64(7)	179.11(8)	178.41(13)

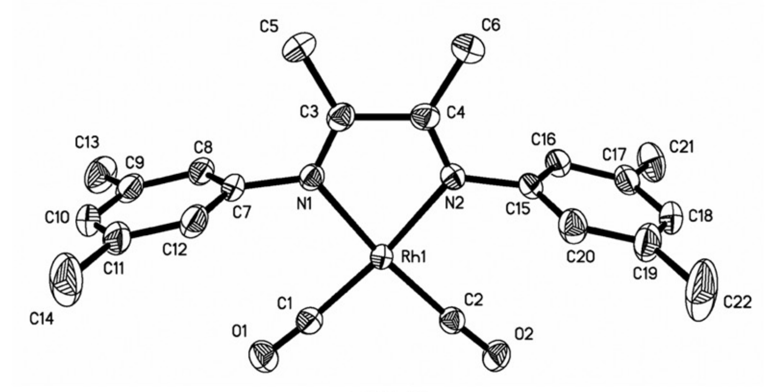
4. Experimental

4.1. General considerations

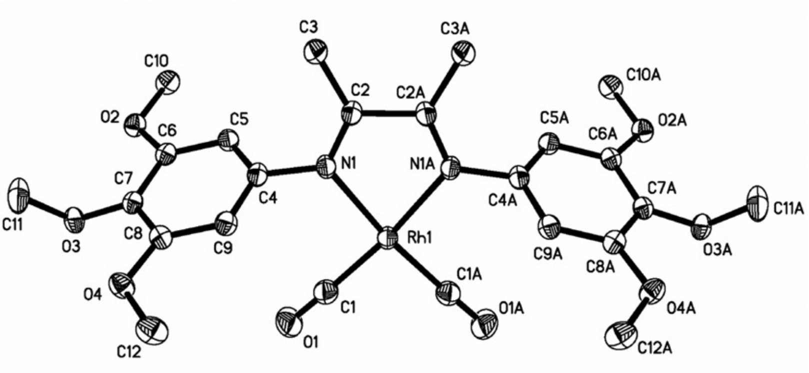
Rhodium(acetylacetonate)$(CO)_2$ (Strem), formic acid (J.T. Baker, 90.5%). 2,3-butanedione (Alfa Aesar, 99%), 3,4,5-trimethoxyaniline (Acros, 97%), 4-chloroaniline (Eastman) were used as received. Acetone, aniline, hexane, and methanol were purchased from Mallinckrodt and used as received. Perchloric acid (70%), diethyl ether, and pentane were purchased from Fisher and used as received. 3,5-Dimethylaniline (98%) and 3,5-di-*tert*-butylaniline (98%) were purchased from Aldrich and used as received. $CDCl_3$ with 1% (vol:vol) tetramethylsilane was purchased from Cambridge Isotope Laboratories, Inc. and used as received. NMR spectra were recorded on a Bruker 500 MHz or 400 MHz spectrometer. ^{13}C NMR spectral assignments were determined by comparing the $^{13}C\{^1H\}$ spectrum to the corresponding ^{13}C and ^1H–^{13}C HSQC spectra. C, H, N analysis was obtained from the CENTC Elemental Analysis Facility at the University of Rochester. Infrared spectra were obtained on a Shimadzu 8400S FTIR using an ATR attachment.

4.2. Synthesis of 1,4-bis(3,5-dimethylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene, *1*

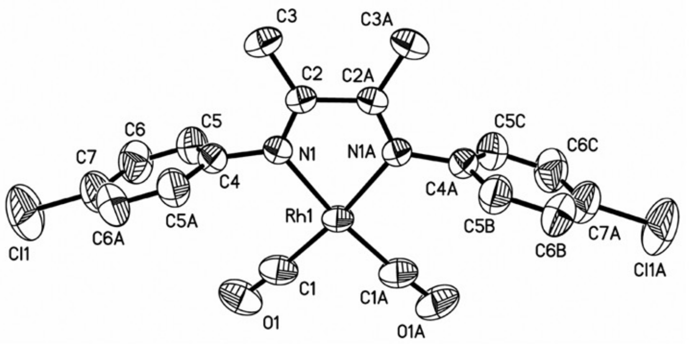
A 100 mL round bottom flask was loaded with 3,5-dimethyaniline (5.936 g, 48.01 mmol), 2,3-butanedione (2.004 g, 23.04 mmol),



6•CDCl$_3$



8•CDCl$_3$



10

Fig. 3. Molecular structures of **6·CDCl$_3$**, **8·CDCl$_3$**, and **10**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, perchlorate ions, and solvent molecules were omitted for clarity.

and methanol (50 mL). Formic acid (0.4 mL) was added and the reaction mixture was stirred at room temperature for 23 h. The yellow precipitate was separated by filtration and then washed with −30 °C MeOH (3 × 30 mL). Recrystallization from boiling EtOH, washing with cold EtOH (0 °C, 3 × 30 mL), then cold pentane (0 °C, 1 × 30 mL), and drying under vacuum afforded yellow crystals (1.876 g, 28%, mp 141–142 °C). Crystals suitable for structure determination were grown by evaporation of an acetone solution. *Anal.* Calc. for $C_{16}H_{16}N_2$: C, 82.14; H, 8.27; N, 9.58. Found: C, 82.18; H, 8.30; N, 9.86%. IR (ATR) $\nu_{C{=}N}$ 1633 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ 6.76 (s, 2H, H_{AR}), 6.42 (s, 4H, H_{AR}), 2.34 (s, 12H, CH_3), 2.15 (s, 6H, CH_3). ^{13}C{^{1}H}NMR (125 MHz, CDCl$_3$, 25 °C): δ 167.9 (s, *C*), 151.0 (s, *C*), 138.6 (s, *C*), 125.3 (s, *C*H), 116.3 (s, *C*H), 21.3 (s, *C*H$_3$), 15.3 (s, *C*H$_3$).

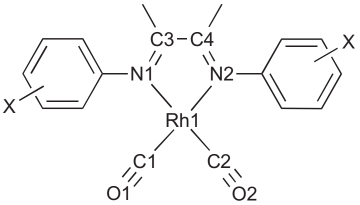
4.3. Synthesis of 1,4-bis(3,5-di-tert-butylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene, ***2***

Prepared according to the literature [44]. Crystals suitable for structure determination were grown by evaporation of an acetone solution.

4.4. Synthesis of 1,4-bis(3,4,5-trimethoxyphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene, ***3***

Prepared according to the literature [44]. Crystals suitable for structure determination were grown by evaporation of an acetone solution.

Table 3
Selected bond lengths (Å) and angles (°) of **6·$CDCl_3$**, **8·$CDCl_3$**, **8·C_3H_6O**, and **10**. Note: the below drawing is provided for comparison purposes and may or may not correspond to the actual atom numbering in the respective ORTEP diagrams.



	6·$CDCl_3$	8·$CDCl_3$	8·C_3H_6O	10
Rh1–C1	1.874(3)	1.872(3)	1.8648(17)	1.859(5)
Rh1–C2	1.879(3)	1.872(3)	1.8649(17)	1.859(5)
Rh1–N1	2.058(2)	2.062(2)	2.0663(13)	2.055(3)
Rh1–N2	2.062(2)	2.062(2)	2.0663(13)	2.055(3)
N1–C3	1.278(4)	1.286(3)	1.288(2)	1.280(5)
N2–C4	1.284(4)	1.286(3)	1.288(2)	1.280(5)
C3–C4	1.510(4)	1.516(4)	1.510(3)	1.508(8)
C1–O1	1.130(4)	1.129(3)	1.135(2)	1.133(6)
C2–O2	1.129(3)	1.129(3)	1.135(2)	1.133(6)
C1–Rh1–C2	92.08(13)	88.95(16)	88.31(10)	91.7(3)
N1–Rh1–N2	77.35(10)	77.39(11)	77.17(7)	76.96(19)

*4.5. Synthesis of 1,4-diphenyl-2,3-dimethyl-1,4-diaza-1,3-butadiene, **4***

Prepared by a modified literature procedure [45]. Crystals suitable for structure determination were grown by evaporation of an acetone solution.

*4.6. Synthesis of 1,4-bis(4-chlorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene, **5***

Prepared by a modified literature procedure [46]. Crystals suitable for structure determination were grown dissolving in boiling ethanol and cooling to 25 °C.

*4.7. Synthesis of [Rh(1,4-bis(3,5-dimethylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene)$(CO)_2$][ClO_4], **6***

A 50 mL round bottom flask was loaded with, in this order: Rh(acac)$(CO)_2$ (50.0 mg, 0.194 mmol), acetone (12 mL), $HClO_4$ (16 μL, 0.186 mmol), solid 1,4-bis(3,5-dimethylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene (56.8 mg, 0.194 mmol), and stirred vigorously for 30 min at 25 °C. Diethyl ether (35 mL) was added to the resulting red solution, and cooled to −20 °C overnight to crystallize. The product was separated by filtration, washed with diethyl ether (3 × 10 mL), and dried under vacuum affording red needles (33.7 mg, 33%). Crystals suitable for structure determination were grown by layering a $CDCl_3$ solution of **6** with pentane at 25 °C crystallizing as **6·$CDCl_3$**. *Anal.* Calc. for $C_{22}H_{24}ClN_2O_6Rh$: C, 47.97; H, 4.39; N, 5.08. Found: C, 47.76; H, 4.32; N, 5.04%. IR (ATR) $\nu_{C{=}O}$ 2093, 2040 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.98 (s, 2H, C*H*), 6.92 (s, 4H, C*H*), 2.38 (s, 6H, CH_3), 2.37 (s, 12H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 182.6 (s, *C*), 181.7 (d, $^1J_{C-Rh}$ = 70 Hz, *C*O), 148.9 (s, *C*), 140.3 (s, *C*), 130.1 (s, *C*H), 117.7 (s, *C*H), 21.3 (s, *C*H_3), 20.6 (s, *C*H_3).

*4.8. Synthesis of [Rh(1,4-bis(3,5-di-tert-butylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene)$(CO)_2$][ClO_4], **7***

A 100 mL round bottom flask was loaded with, in this order: Rh(acac)$(CO)_2$ (49.9 mg, 0.193 mmol), acetone (6 mL), $HClO_4$ (17 μL, 0.197 mmol), solid 1,4-bis(3,5-di-*tert*-butylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene (89.1 mg, 0.193 mmol), and stirred vigorously for 5 h at 25 °C. The red solution was evaporated to dryness and the resulting red solid was washed with hexane (3 × 15 mL), pentane (3 × 15 mL), and diethyl ether (3 × 20 mL), then dried under vacuum affording a red-orange solid (34.7 mg, 25%). *Anal.* Calc. for $C_{34}H_{48}ClN_2O_6Rh{\cdot}H_2O$: C, 55.40; H, 6.84; N, 3.80. Found: C, 55.82; H, 7.08; N, 3.80%. IR (ATR) $\nu_{C{=}O}$ 2100, 2051 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.38 (s, 2H, H_{AR}), 7.17 (s, 4H, H_{AR}), 2.43 (s, 6H, –CH_3), 1.35 (s, 36H, –C(CH_3)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 182.4 (s, *C*), 181.8 (d, $^1J_{C-Rh}$ = 70 Hz, *C*O), 153.4 (s, *C*), 148.6 (s, *C*), 122.1 (s, *C*H_{AR}), 114.9 (s, *C*H_{AR}), 35.3 (s, *C*(CH_3)$_3$), 31.2 (s, C(*C*H_3)$_3$), 20.6 (s, *C*H_3).

*4.9. Synthesis of [Rh(1,4-bis(3,4,5-trimethoxyphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene)$(CO)_2$][ClO_4], **8***

A 100 mL round bottom flask was loaded with, in this order: Rh(acac)$(CO)_2$ (50.3 mg, 0.195 mmol), acetone (6 mL), $HClO_4$ (17 μL, 0.197 mmol), solid 1,4-bis(3,4,5-trimethoxyphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene (81.1 mg, 0.195 mmol), and stirred vigorously for 4.5 h at 25 °C. The red solution was evaporated to dryness and the resulting red solid was washed with hexane (3 × 15 mL), pentane (3 × 15 mL), and diethyl ether (3 × 20 mL), then dried under vacuum affording a red solid (92.2 mg, 70% (crude)). The complex was further purified by dissolving in acetone (6 mL), layering with diethyl ether (15 mL), and cooling to −20 °C forming red needles (42.2 mg, 32% (purified)). Crystals suitable for structure determination were grown by layering a $CDCl_3$ solution of **8** with pentane at 25 °C forming **8·$CDCl_3$**, or by layering an acetone solution with pentane at 25 °C forming **8·C_3H_6O**. *Anal.* Calc. for $C_{24}H_{28}ClN_2O_{12}Rh{\cdot}H_2O$: C, 41.60; H, 4.36; N, 4.04. Found: C, 41.33; H, 4.52; N, 4.06%. IR (ATR) $\nu_{C{=}O}$ 2091, 2034 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 6.61 (s, 4H, H_{ARYL}), 3.91 (s, 12H, –OCH_3), 3.88 (s, 6H, –OCH_3), 2.43 (s, 6H, –CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 182.8 (s, *C*), 181.6 (d, J_{C-Rh} = 70 Hz, Rh–*C*O), 154.4 (s, *C*), 144.6, (s, *C*), 137.5 (s, *C*), 97.6 (s, *C*H), 61.1 (s, O*C*H_3), 56.6 (s, O*C*H_3), 20.7 (s, *C*H_3).

*4.10. Synthesis of [Rh(1,4-diphenyl-2,3-dimethyl-1,4-diaza-1,3-butadiene)$(CO)_2$][ClO_4], **9***

A 25 mL round bottom flask was loaded with, in this order: Rh(acac)$(CO)_2$ (49.9 mg, 0.193 mmol), acetone (10 mL), and $HClO_4$ (20 μL, 0.232 mmol), and stirred vigorously for 30 min at 25 °C. 1,4-Diphenyl-2,3-dimethyl-1,4-diaza-1,3-butadiene (45.9 mg, 0.194 mmol) dissolved in acetone (6 mL) was added and stirred vigorously for 3 h at 25 °C. The dark red solution was evaporated to dryness and the resulting dark red solid was washed with hexane (5 × 15 mL) and pentane (5 × 15 mL), then dried under vacuum affording a dark red (maroon) solid (55.5 mg, 58%). *Anal.* Calc. for $C_{18}H_{16}ClN_2O_6Rh{\cdot}H_2O$: C, 42.17; H, 3.54; N, 5.46. Found: C, 41.74; H, 3.17; N, 5.57%. IR (ATR) $\nu_{C{=}O}$ 2086, 2040 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.44 (t, *J* = 8 Hz, 4H), 7.38 (d, *J* = 8 Hz, 4H), 7.32 (t, *J* = 7 Hz, 2H), 2.37 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ 183.5 (s, *C*), 181.8 (d, J_{C-Rh} = 70 Hz, Rh–*C*O), 149.1 (s, *C*), 130.0 (s,*C*H), 128.3 (s, *C*H), 120.6 (s, *C*H), 20.5 (s, *C*H_3).

*4.11. Synthesis of [Rh(1,4-bis(4-chlorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene)$(CO)_2$][ClO_4], **10***

A 100 mL round bottom flask was loaded with, in this order: Rh(acac)$(CO)_2$ (50.1 mg, 0.194 mmol), acetone (6 mL), $HClO_4$ (17 μL, 0.197 mmol), solid 1,4-bis(4-chlorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene (59.4 mg, 0.195 mmol), and stirred vigorously for 30 min at 25 °C. Diethyl ether (50 mL) was added to the resulting red solution, and cooled to −20 °C overnight. The precipitate was separated by filtration, washed with diethyl ether (3 × 20 mL), and dried under vacuum affording a red solid (39.5 mg, 36%). Crystals suitable for structure determination were grown by layering a $CDCl_3$ solution with pentane at 25 °C. *Anal.* Calc. for $C_{18}H_{14}Cl_3N_2O_6Rh$: C, 38.36; H, 2.50; N, 4.97. Found: C, 37.98; H, 2.53; N, 4.95%. IR (ATR) $\nu_{C=O}$ 2094, 2046 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.49 (d, *J* = 8 Hz, 4H), 7.33 (d, *J* = 8 Hz, 4H), 2.38 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 183.9 (s, *C*), 181.5 (d, J_{C-Rh} = 69 Hz, Rh–*C*O), 147.3 (s, *C*), 134.3 (s, *C*), 130.2 (s, *C*H), 122.3 (s, *C*H), 20.6 (s, *C*H_3).

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Appendix A. Supplementary material

CCDC 799909–799917 contain the supplementary crystallographic data for **1–5**, **6·$CDCl_3$**, **8·$CDCl_3$**, **8·C_3H_6 O**, and **10**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.005.

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