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The dominant steric effect in the synthesis of ammine hydrido- and chlorido-Ru(II)-*N*,*N*-dimethylhydrazine and mixed alkyl–aryl phosphine complexes: Novel methyldiazene reduction intermediates

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ABSTRACT

Novel cationic hydrido complexes [RuH(1,5-cod)(NH_3)(NH_2NMe_2)$_2$](X) (X = PF_6, BPh_4) and chlorido-ammine complexes [RuCl(1,5-cod)(NH_3)$_2$(NH_2NMe_2)](X) (X = PF_6, BPh_4), were isolated from the reaction of the polymeric [$RuCl_2$(1,5-cod)]$_x$ with NH_2NMe_2. Reaction of the hydrido complexes with the phosphine ligands PMe_3, PMe_2Ph, $P(OMe)_2Ph$ resulted in the formation of monohydrido-phosphine complexes, whereas reaction with the bulkier $PMePh_2$ ligand gave dihydrido-phosphine complexes. Similar reactions of the chlorido-ammine complexes with the phosphine ligands PMe_3, PMe_2Ph, $P(OMe)_2Ph$, and $PMePh_2$ all sequentially substituted the NH_2NMe_2 and the 1,5-cod ligands to give the chlorido-ammine phosphine complexes. All complexes were fully characterised and the single crystal X-ray structures were determined for [RuH{$P(OMe)_2Ph$}$_5$](BPh_4), [RuH_2($PMePh_2$)$_4$], [{Ru(PMe_2Ph)$_3$}$_2$(μ-F)$_3$](PF_6), *fac*-[RuCl(NH_3)$_2$(PMe_2Ph)$_3$](PF_6), and [RuCl(NH_3)(PMe_2Ph)$_4$](PF_6). Intramolecular strain between coordinated σ-donor ligands in the Ru(II)-NH_2NMe_2 precursor complexes as well as the relative steric bulk of incoming σ-donor ligands were found to be chemically directing in the formation of monohydrido-, bishydrido-, mono-ammine, and bis-ammine ruthenium(II) complexes.

1. Introduction

Synthetic routes to complexes of Ru(II) containing hydrazine and other partially reduced dinitrogen ligands are still of great importance, as their products are shown to be useful intermediates in the numerous synthetic, organic functionalisation, catalytic, and industrial processes, as well as in biologically important nitrogenase and nitrogen fixation processes [1–5]. Numerous recent reports deal with Ru(II)-hydrazine complexes and their role as nitrogenase-relevant molecules whereby the isolation of hydrazine intermediates in the enzyme turnover is of great importance [5a,6–11]. Ruthenium(II) counterparts of the unstable and reactive iron intermediates are generally more stable, which allows the isolation of intermediate species [1b,5b,10,12,13].

An extensive range of stable cationic and neutral ruthenium(II) species containing the hydrazine ligands NH_2NHR (R = H, Me) have been reported, and primarily includes complexes with carbonyl [1e,6b], phosphine and phosphite [1e,2a,6,14,10,15,16a], 1,5-cyclooctadiene [2b,16], cyclopentadienyl [17d,18], and p-cymene ancillary ligands [6a]. The pioneering work of Singleton et al. throughout 1977–1987, who reported the synthetic and catalytically active complexes [CpRuX(cod)] (X = H, Cl, Br) [18c] and the first metallacyclopentatriene complex [CpRu($C_4Ph_2H_2$)] [18a,18b], all emanated from the use of the Ru(II) complexes of [RuH(1,5-cod)(NH_2NHR)$_3$](X) (R = H, Me; X = PF_6, BPh_4) as precursors [16,17d,19]. These catalytically important Ru–H complexes were found to be reactive precursors to a range of allyl- and cyclooctadiene ruthenium(II) species which has significance in hydride transfer reactions [16,17,20–21].

In light of the well-documented N–N fission reactions of Ru(II)-NH_2NH_2 complexes to form Ru(II)-NH_3 complexes, along with their important application in DNA binding studies [2c,22], reports on the use of the Ru(II)-hydrazine complexes as precursors in these studies remain limited [2a,10,15,23]. Furthermore, reports of *in-situ* decomposition of NH_2NMe_2 to form NH_3 as a by-product are to the best of our knowledge non-existent.

These NH_2NMe_2- and NH_3-ruthenium(II) complexes are stabilised by neutral ancillary phosphine and phosphite ligands, to form isolable intermediates for the conversion of dinitrogen to ammonia [1b,23–24]. Extensive research by Sellman et al. showed that the phosphine-containing [Ru(P^iPr_3)('$N_2Me_2S_2$')] complex fragment is capable of binding N_2H_2, N_2H_4, NH_3, and H_2, all nitrogenase-relevant molecules [6,7b,25]. The latter fragment

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containing only the bulky PPh_3 and PCy_3 phosphine ligands allowed for the nitrogenase-relevant molecules L = N_2, N_2H_4, NH_3, and CO to coordinate, forming the species [Ru(L)(PR_3)('$N_2Me_2S_2$')] [6b].

We report four novel Ru(II)-NH_2NMe_2 complexes, all of which contain the *in-situ* generated ammine ligands produced from the combined effect of nitrogenase-mimicking and NH_4PF_6 hydrolysis. These complexes were isolated during the reinvestigation of the known reaction of $[RuCl_2(1,5\text{-cod})]_x$ with NH_2NMe_2. The reactivity and ligand-competing behaviour of these complexes are also demonstrated in the reactions with selected phosphine and phosphonite ligands to produce a range of novel monohydrido-, bishydrido-, mono-ammine, and bis-ammine Ru(II) complexes.

2. Material and methods

2.1. General

All experiments were carried out under an Ar atmosphere using standard Schlenk techniques. Solvents were dried using standard techniques. The compound $[RuCl_2(1,5\text{-cod})]_x$ was prepared using the literature procedure [26]. All other chemicals were purchased from Sigma–Aldrich and used without further purification. ^1H (400 MHz), $^{13}C\{H\}$ (101 MHz), $^{31}P\{H\}$ (162 MHz) and ^{15}N–^1H HMBC NMR spectra were recorded on a Bruker Avance III Ultrashield 400 MHz spectrometer fitted with a B-ACS 60 auto-sampler using either $CDCl_3$, CD_2Cl_2 or $(CD_3)_2CO$ solutions. All measurements were performed at ambient temperature (~296 K), unless otherwise noted. Chemical shifts were referenced to the internal residual *protio* impurities in the solvent (δ_H 7.24, 5.32, or 2.04 ppm in $CDCl_3$, CD_2Cl_2, or $(CD_3)_2CO$ respectively) or carbon signals (δ_H 77.0, 53.8, or 29.8 and 206.3 ppm in $CDCl_3$, CD_2Cl_2, or $(CD_3)_2CO$ respectively). Solid state FT-IR experiments were carried out on a Bruker Tensor 27 FT-IR as pressed KBr pellets in air. Melting points were performed in air on a Stuart SMP10 and are uncorrected. Microanalytical analyses (%CHNS) were performed at Rhodes University (RSA) using an Elementar Vario Micro cube instrument with a TCD detector. In cases where %Cl was required, the analyses were performed externally at Galbraith Laboratories (USA).

2.2. Syntheses of [RuH(1,5-cod)(NH_3)(NH_2NMe_2)$_2$](PF_6) **3** and [RuCl(1,5-cod)(NH_3)$_2$(NH_2NMe_2)](PF_6) **5**

A suspension of $[RuCl_2(1,5\text{-cod})]_x$ (0.497 g, 1.77 mmol) in MeOH (8.0 mL) with NH_2NMe_2 (3.0 mL, 39.4 mmol) and H_2O (0.75 mL) was heated under reflux for 30 min, after which a filtered solution of NH_4PF_6 (0.597 g, 3.7 mmol) in H_2O (3.0 mL) was added. The reaction mixture was concentrated *in vacuo*, filtered, and washed with EtOH/Et_2O from which an off-white microcrystalline solid (0.218 g) was isolated. The crude product was extracted with $CHCl_3$ (~15 mL), followed separately by CH_2Cl_2 (~15 mL), after which the residue was extracted with acetone (~15 mL). Concentration of each extracted fraction led to the isolation of the known [RuH(1,5-cod)(NH_2NH_3)$_3$](PF_6) **1** ($CHCl_3$ fraction, light brown microcrystals, 62 mg, 26%), **3** (CH_2Cl_2 fraction, brown microcrystals, 47 mg, 22%), and **5** (acetone fraction, beige powder, 74 mg, 34%). Characterisation for **1** is in agreement with literature [16f]. **3**: m.p.: >147 °C (decomposition without melt). IR (ν, cm^{-1}): 3375 (w); 3237 (ν(NH), w); 3066 (ν(NH), w); 2958 (ν(=CH), w); 2873 (ν(NH), w); 2836 (ν(–CH), m); 2789 (m); 2036 (ν(RuH), w); 1607 (δ(NH), asym, m); 1459 (δ(–CH), sym, m); 1406 (δ(–CH), asym, w); 1168 (δ(NH), sym, m); 1151 (δ(NH), sym, m); 1022 (ν(CN), m); 985 (δ(=CH), m); 918 (ν(NN), m); 830 (ν(PF), s); 556 (δ(PF), s). ^1H NMR (ppm) (400 MHz, $CDCl_3$, δ_H) −5.58 (s, Ru*H*, 1H); 1.23 (s, NH_3, 3H); 1.56 (s, H_2O); 1.67 (t, $^3J_{HH}$ = 11 Hz, CH_2 of cod, 2H); 2.26 (m, CH_2 of cod, 4H); 2.44 (s, NCH_3 *trans* to cod, 6H); 2.73 (s, NCH_3 *cis* to cod, 3H); 3.06 (s, CH_2 of cod, 2H); 4.56 (d, $^3J_{HH}$ = 10 Hz, =C*H* of cod, 2H); 4.99 (d, $^3J_{HH}$ = 10 Hz, =C*H* of cod, 2H); 6.08 (br s, NH_2, 2H). $^{13}C\{^1H\}$ NMR (ppm) (101 MHz, $(CD_3)_2CO$, δ_C) 27.7 (s, CH_2 of cod); 47.1 (s, NCH_3 *cis* to cod); 48.8 (s, NCH_3 *trans* to cod); 78.6 (s, =C*H* of cod); 81.1 (s, =C*H* of cod); 88.6 (s, =C*H* of cod); 91.3 (s, =C*H* of cod). $^{31}P\{^1H\}$ NMR (ppm) (162 MHz, CD_2Cl_2, δ_P) −144.3 (sp, $^1J_{PF}$ = 716 Hz, PF_6). CHN (%): [RuH(1,5-cod)(NH_3)(NH_2NMe_2)$_2$](PF_6).H_2O: C, 27.99 (28.23); H, 6.65 (6.71); N, 13.82 (13.72). **5**: m.p.: >165 °C (decomposition without melt). IR (ν, cm^{-1}): 3295 (ν(NH), w); 3066 (ν(NH), w); 2918 (ν(=CH), w); 2877 (ν(NH), w); 2846 (ν(–CH), m); 2158 (m); 1629 (δ(NH), asym, w); 1571 (δ(NH), asym, m); 1467 (δ(–CH), sym, m); 1408 (δ(–CH), asym, m); 1363 (m); 1317 (m); (m); 1179 (δ(NH), sym, w); 1163 (δ(NH), sym, m); 1024 (ν(CN), m); 978 (δ(=CH), m); 904 (ν(NN), m); 830 (ν(PF), s); 556 (δ(PF), s). ^1H NMR (ppm) (400 MHz, $(CD_3)_2CO$, δ_H) 1.89 (br s, NH_3, 2H); 2.30 (d, $^3J_{HH}$ = 7 Hz, CH_2 of cod); 2.41–2.53 (m, CH_2 of cod, 3H); 2.58–2.65 (m, CH_2 of cod, 1H); 2.78 (s, NCH_3, 6H); 3.33 (br s, NH_3, 2H); 3.52 (d, $^3J_{HH}$ = 4 Hz, CH_2 of cod, 1H); 3.84 (s, 1H); 4.07 (d, $^3J_{HH}$ = 7 Hz, CH_2 and =C*H* of cod, 4H); 5.94 (d, $^3J_{HH}$ = 11 Hz, =C*H* of cod, 1H); 6.82 (d, $^3J_{HH}$ = 12 Hz, =C*H* of cod, 1H). $^{13}C\{^1H\}$ NMR (ppm) (101 MHz, $(CD_3)_2CO$, δ_C) 27.6 (s, CH_2 of cod); 47.2 (s); 48.8 (s, NCH_3); 78.4 (s, =C*H* of cod); 81.3 (s, =C*H* of cod); 88.6 (s, =C*H* of cod); 91.3 (s, =C*H* of cod). $^{31}P\{^1H\}$ NMR (ppm) (162 MHz, $(CD_3)_2CO$, δ_P) −144.3 (sp, $^1J_{PF}$ = 708 Hz, PF_6). CHN (%): [RuCl(1,5-cod)(NH_3)$_2$(NH_2NMe_2)](PF_6): C, 24.64 (24.82); H, 5.31 (5.42); N, 11.18 (11.58); Cl 7.54 (7.33).

2.3. Synthesis of [RuH(1,5-cod)(NH_3)(NH_2NMe_2)$_2$](BPh_4) **4**, and [RuCl(1,5-cod)(NH_3)$_2$(NH_2NMe_2)](BPh_4) **6**

Similar to the syntheses of **1**, **3**, and **5**, employing $NaBPh_4$ instead of NH_4PF_6. Concentration of each extracted fraction gave [RuH(1,5-cod)(NH_2NMe_2)$_3$](BPh_4) **2**, from the (CH_2Cl_2 fraction, light brown powder, 135 mg, 43%), **4** ($CHCl_3$ fraction, brown powder, 83 mg, 28%), and **6** (acetone fraction, beige powder, 39 mg, 13%). Characterisation data for **2** agrees with literature [16f]. **4**: m.p.: >142 °C (decomposition without melt). IR (ν, cm^{-1}): 3127 (ν(NH), m); 3054 (ν(NH), m); 3002 (ν(=CH), w); 2870 (ν(NH), w); 2831 (ν(–CH), w); 2039 (ν(RuH), w); 1602 (δ(NH), asym, w); 1579 (δ(NH), asym, w); 1453 (δ(–CH), sym, m); 1401 (δ(–CH), asym, s); 1387 (s); 1157 (δ(NH), sym, w); 1095 (δ(NH), sym, w); 1022 (ν(CN), m); 974 (δ(=CH), w); 916 (ν(NN), w); 735 (ν(BC), m); 706 (ν(BC), m); 609 (m). ^1H NMR (ppm) (400 MHz, $CDCl_3$, δ_H) −5.72 (s, Ru*H*, 1H); 1.67 (m, H_2O, 2H); 1.94 (d, $^3J_{HH}$ = 14 Hz, CH_2 of cod, 1H); 2.07 (br s, NH_3, 3H); 2.24 (t, $^3J_{HH}$ = 15 Hz, NCH_3 *trans* to cod, 6H); 2.41 (s, NCH_3 *cis* to cod, 6H); 2.47 (s, CH_2 of cod, 2H); 2.55 (d, $^3J_{HH}$ = 24 Hz, CH_2 of cod, 2H); 2.96 (s, CH_2 of cod, 1H); 3.53 (s, =C*H* of cod, 0.5H); 3.73 (s, =C*H* of cod, 0.5H); 4.05 (dd, $^3J_{HH}$ = 9 and 43 Hz, =C*H* of cod, 1H); 4.71 (dd, $^3J_{HH}$ = 10 and 44 Hz, =C*H* of cod, 1H); 5.12 (d, $^3J_{HH}$ = 10 Hz, =C*H* of cod, 0.5H); 5.27 (d, $^3J_{HH}$ = 10 Hz, =C*H* of cod, 0.5H); 5.81 (d, $^3J_{HH}$ = 10 Hz, NH_2, 2H); 6.90 (t, $^3J_{HH}$ = 7 Hz, C_6H_5, 4H); 7.04 (t, $^3J_{HH}$ = 7 Hz, C_6H_5, 8H); 7.41 (s, C_6H_5, 8H). $^{13}C\{^1H\}$ NMR (ppm) (75 MHz, CD_2Cl_2, δ_C) 26.2 (s, CH_2 of cod); 28.5 (d, $^3J_{CC}$ = 34 Hz, CH_2 of cod); 31.0 (s, CH_2 of cod); 33.1 (s, CH_2 of cod); 48.8 (s, NCH_3 *trans* to cod); 49.9 (s, NCH_3 *cis* to cod); 88.1 (s, =C*H* of cod); 91.5 (s, =C*H* of cod); 122.4 (s, C_6H_5); 126.2 (d, $^3J_{CC}$ = 3 Hz, C_6H_5); 136.3 (s, C_6H_5), 164.4 (m, C_6H_5). ^{15}N NMR (ppm) (51 MHz, $(CD_3)_2CO$, δ_N) 58 (s, NH_3); 86 (s, NMe_2); 106 (s, NMe_2); 132 (s, NH_2). CHN (%): [RuH(1,5-cod)(NH_3)(NH_2NMe_2)$_2$](BPh_4).3H_2O: C, 60.13 (59.99); H, 7.76 (8.11); N, 9.44 (9.72). **6**: m.p.: 142–144 °C. IR (ν, cm^{-1}): 3127 (ν(NH), m); 3054 (ν(NH), m); 3027 (ν(=CH), w); 2867 (ν(NH), w); 2845 (ν(–CH), w); 1627 (δ(NH), asym, w); 1596 (w); 1562 (δ(NH),

asym, w); 1456 (δ(–CH), sym, m); 1400 (δ(–CH), asym, s); 1385 (s); 1152 (δ(NH), sym, w); 1091 (δ(NH), sym, w); 1030 (ν(CN), m); 972 (δ(=CH), w); 908 (ν(NN), w); 802 (m); 736 (ν(BC), m); 709 (ν(BC), m); 606 (m). ^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$, δ_H) 1.79 (q, $^3J_{HH}$ = 8 Hz, CH_2 of cod); 1.92 (s, NH_3, 1H); 2.25 (d, $^3J_{HH}$ = 12 Hz, CH_2 of cod, 1H); 2.31 (s, CH_2 of cod, 2H); 2.49 (t, $^3J_{HH}$ = 8 Hz, CH_2 of cod, 2H); 2.60 (s, NCH_3, 6H); 3.04 (m, CH_2 of cod, 1H); 3.83 (s, =C*H* of cod, 1H); 4.01 (t, $^3J_{HH}$ = 7 Hz, =C*H* of cod, 2H); 4.12 (s, =C*H* of cod, 1H); 4.46 (br s, NH_3, 2H); 5.56 (d, $^3J_{HH}$ = 11 Hz, 1H); 5.99 (m, NH_2, 1H); 6.77 (t, $^3J_{HH}$ = 7 Hz, C_6H_5, 4H); 6.92 (t, $^3J_{HH}$ = 7 Hz, C_6H_5, 8H); 7.33 (s, C_6H_5, 8H). ^{13}C{^{1}H} NMR (ppm) (101 MHz, CD_2Cl_2, δ_C) 28.7 (s, CH_2 of cod); 33.2 (s, CH_2 of cod); 48.8 (s, NCH_3 *trans* to cod); 64.7 (s, =C*H* of cod); 70.3 (s, =C*H* of cod); 122.2 (s, C_6H_5); 126.0 (q, $^3J_{CC}$ = 2 Hz, C_6H_5); 136.4 (s, C_6H_5); 164.5 (m, C_6H_5). ^{15}N NMR (ppm) (51 MHz, $(CD_3)_2CO$, δ_N) −18 (s, NH_3); 57 (s, NMe_2); 69 (s, NMe_2); 116 (s, NH_2); 344 (s). CHN (%): [RuCl(1,5-cod)$(NH_3)_2(NH_2NMe_2)$](BPh_4).H_2O: C, 60.39 (60.40); H, 7.44 (7.16); N, 9.49 (9.29).

2.4. Synthesis of [{Ru(PMe$_2$Ph)$_3$}$_2$(μ-F)$_3$](PF$_6$) (**10**)

To a dark yellow solution of *cis*- and *trans*-[$RuH_2(PMe_2Ph)_4$] (PF_6) [30] (2.856 g, 4.4 mmol) in EtOH (60 mL) was added $PMePh_2$ (0.6 mL, 4.2 mmol) and HPF_6 (0.8 mL, 9.0 mmol) and the resulting reaction mixture was heated under reflux for 2 h. After cooling, the clear light yellow solution was filtered using vacuum filtration, and washed with EtOH (5 mL) and Et_2O (10 mL) to give a light yellow powder. This was recrystallized as light yellow needles using CH_2Cl_2/EtOH (2.314 g, 43%). m.p.: 212–214 °C. IR (ν, cm^{-1}): 3137 (ν(=CH), m); 3057 (ν(=CH), w); 3001 (ν(–CH), m); 1619 (ν(C=C), w); 1486 (m); 1432 (δ(–CH), sym, s); 1402 (δ(–CH), asym, s); 1296 (δ(=CH), m); 1277 (δ(=CH), m); 1100 (s); 938 (δ(=CH), s); 903 (δ(*para* =CH), s); 839 (ν(PF), s); 747 (δ(*ortho* =CH), s); 702 (δ(–CH), s); 676 (δ(*meta* =CH), s); 557 (δ(PF), s). ^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$, δ_H) 1.49 (br s, P(CH_3), 36H); 7.55 (m, P(C_6H_5), 18H); 8.28 (m, P(C_6H_5), 12H). ^{13}C{^{1}H} NMR (ppm) (101 MHz, $CDCl_3$, δ_C) 17.7 (s, P(CH_3)); 18.4 (s, P(CH_3)); 128.6 (t, $^2J_{CC}$ = 140 Hz, P(C_6H_5)); 129.5 (d, $^2J_{CC}$ = 27 Hz, P(C_6H_5)); 131.1 (s, P(C_6H_5)). ^{31}P{^{1}H} NMR (ppm) (162 MHz, $CDCl_3$, δ_P) −144.3 (sp, $^1J_{PF}$ = 713 Hz, *P*F_6); 33.9 (ddd, $^1J_{PP}$ = 171 Hz and $^2J_{PP}$ = 36 and 88 Hz, *P*Me_2Ph). CHN (%): [{Ru($PMe_2Ph)_3$}$_2$(μ-F)$_3$](PF_6): C, 46.87 (46.76); H, 5.40 (5.40); N, 0.00 (0.00).

2.5. Synthesis of [RuCl(NH$_3$)$_2$(PMe$_3$)$_3$](PF$_6$) (**11**)

To a brown solution of [RuCl(1,5-cod)$(NH_3)_2(NH_2NMe_2)$](PF_6) (**5**) (1.057 g, 2.2 mmol) in EtOH (30 mL) was added PMe_3 (0.8 mL, 7.8 mmol) and the resulting reaction mixture was heated under reflux for 1 h. The dark brown solution was concentrated, filtered, and washed with EtOH (10 mL) and Et_2O (10 mL) from which a blue–green precipitate was isolated. Recrystallisation using acetone/EtOH gave a dark blue powder (0.456 g, 38%). m.p.: >300 °C (decomposition without melt). IR (ν, cm^{-1}): 3367 (ν(NH), w); 3303 (ν(NH), w); 2981 (ν(–CH), w); 2924 (ν(–CH), w); 1626 (δ(NH), asym, m); 1435 (δ(–CH), sym, m); 1311 (m); 1298 (m); 1130 (δ(NH), sym, w); 947 (m); 828 (ν(PF), s); 739 (m); 672 (δ(–CH), m); 556 (δ(PF), s). ^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$, δ_H) 1.56 (m, P(CH_3)$_3$, 27H); 2.08 (br s, NH_3, 2H); 3.30 (br s, NH_3, 2H). ^{13}C{^{1}H} NMR (ppm) (101 MHz, $(CD_3)_2CO$, δ_C) 20.1 (t, $^3J_{CC}$ = 20 Hz, P(CH_3)$_3$); 49.6 (s). ^{31}P{^{1}H} NMR (ppm)(162 MHz, $(CD_3)_2CO$, δ_P) −144.3 (sp, $^1J_{PF}$ = 708 Hz, *P*F_6); 20.8 (s, *P*Me_3); 22.4 ppm (d, $^2J_{PP}$ = 24 Hz, *P*Me_3). CHN (%): [RuCl$(NH_3)_2(PMe_3)_3$](PF_6): C, 19.98 (19.88); H, 5.90 (6.12); N, 4.95 (5.15).

2.6. Synthesis of fac-[RuCl(NH$_3$)$_2$(PMe$_2$Ph)$_3$](PF$_6$) (**12**)

To a brown solution of [RuCl(1,5-cod)$(NH_3)_2(NH_2NMe_2)$](PF_6) (**5**) (2.367 g, 4.9 mmol) in MeOH (40 mL) was added PMe_2Ph (2.4 mL, 16.9 mmol) and the resulting reaction mixture was heated under reflux for 1 h. After cooling the yellow crystalline product was filtered and washed with EtOH (5 mL) and Et_2O (5 mL) from which the title compound was isolated as deep yellow cuboid crystals (1.289 g, 36%). m.p.: 156–158 °C. IR (ν, cm^{-1}): 3371 (ν(NH), m); 3346 (ν(NH), w); 3060 (ν(=CH), w); 2987 (ν(–CH), m); 2924 (w); 1829 (w); 1617 (δ(NH), asym, s); 1482 (m); 1433 (δ(–CH), sym, s); 1405 (δ(–CH), asym, s); 1288 (s); 1262 (s); 1222 (δ(=CH), s); 1100 (δ(NH), sym, m); 1051 (m); 1000 (δ(=CH), w); 945 (s); 904 (s); 869 (δ(*para* =CH), s); 839 (ν(PF), s); 749 (δ(*ortho* =CH), s); 703 (s); 677 (δ(*meta* =CH), s); 556 (δ(PF), s). ^{1}H NMR (ppm) (400 MHz, $(CD_3)_2CO$, δ_H) 1.11 (t, J_{HH} = 7 Hz, CH_3CH_2OH, 1H); 1.73 (d, J_{HH} = 8 Hz, P(CH_3)$_2$, 6H); 1.75 (s, NH_3, 3H); 1.96 (t, J_{HH} = 4 Hz, P(CH_3)$_2$, 6H); 2.01 (d, J_{HH} = 4 Hz, P(CH_3)$_2$, 3H); 2.08 (s, P(CH_3)$_2$, 3H); 3.30 (s, NH_3, 3H); 3.55 (s, CH_3OH, 1H); 7.27–7.35 (m, P(C_6H_5), 4H); 7.46 (d, J_{HH} = 7 Hz, P(C_6H_5), 6H); 7.62 (s, P(C_6H_5), 5H). ^{13}C{^{1}H} NMR (ppm) (101 MHz, $CDCl_3$, δ_C) 17.9 (s, P(CH_3)$_2$); 18.2 (s, P(CH_3)$_2$); 18.4 (s, P(CH_3)$_2$); 18.7 (m, P(CH_3)$_2$); 128.9 (t, $^3J_{CC}$ = 4 Hz, P(C_6H_5)); 129.2 (t, $^3J_{CC}$ = 4 Hz, P(C_6H_5)); 129.4 (d, $^3J_{CC}$ = 9 Hz, P(C_6H_5)); 129.8 (s, P(C_6H_5)); 129.9 (s, P(C_6H_5)); 136.6 (d, $^3J_{CC}$ = 45 Hz, P(C_6H_5)). ^{31}P{^{1}H} NMR (ppm) (162 MHz, $(CD_3)_2CO$, δ_P) −144.2 (sp, $^1J_{PF}$ = 708 Hz, *P*F_6); 19.2 (d, $^2J_{PP}$ = 34 Hz, *P*Me_2Ph *cis* to equatorial NH_3); 25.9 (t, $^2J_{PP}$ = 32 Hz, *P*Me_2Ph *trans* to equatorial NH_3). ^{15}N NMR (ppm) (51 MHz, $CDCl_3$, δ_N) −8 (s, NH_3). CHN (%): [RuCl$(NH_3)_2(PMe_2Ph)_3$](PF_6).0.5EtOH: C, 39.26 (39.87); H, 6.70 (5.62); N, 3.37 (3.72).

2.7. Synthesis of [RuCl(NH$_3$)(PMe$_2$Ph)$_4$](PF$_6$) (**13**)

To a brown solution of [RuCl(1,5-cod)$(NH_3)_2(NH_2NMe_2)$](PF_6) (**5**) (2.228 g, 4.6 mmol) in MeOH (50 mL) was added PMe_2Ph (3.0 mL, 21.1 mmol) and heated under reflux for 1 h. After cooling, yellow crystals formed from the clear reddish-brown solution and was filtered, washed with MeOH (10 mL) and Et_2O (10 mL) to give light yellow cuboid crystals (1.641 g, 42%). m.p.: 175–177 °C. IR (ν, cm^{-1}): 3365 (ν(NH), w); 3056 (ν(=CH), w); 2988 (ν(–CH), w); 1608 (δ(NH), asym, m); 1595 (ν(C=C), w); 1484 (m); 1436 (δ(–CH), sym, m); 1412 (δ(–CH), asym, m); 1317 (m); 1239 (δ(=CH), m); 1095 (δ(NH), sym, w); 943 (m); 897 (δ(*para* =CH), s); 831 (ν(PF), s); 760 (m); 744 (δ(*ortho* =CH), s); 725 (m); 703 (δ(–CH), s); 676 (δ(*meta* =CH), s); 556 (δ(PF), s). ^{1}H NMR (ppm) (400 MHz, CD_2Cl_2, δ_H) 0.32 (br s, NH_3, 3H); 1.19 (s, P(CH_3)$_2$ *trans* to Cl, 6H); 1.93 (s, P(CH_3)$_2$ *cis* to Cl, 9H); 1.98 (q, $^3J_{HH}$ = 8 Hz, P(CH_3)$_2$ *cis* to Cl, 9H); 7.20 (m, P(C_6H_5), 2H); 7.32 (s, P(C_6H_5), 10H); 7.47 (s, P(C_6H_5), 3H); 7.55–7.65 (m, P(C_6H_5), 5H). ^{13}C{^{1}H} NMR (ppm) (101 MHz, $CDCl_3$, δ_C) 16.0 (t, $^2J_{CC}$ = 29 Hz, P(CH_3)$_2$ *cis* to Cl); 21.6 (d, $^2J_{CC}$ = 30 - Hz, P(CH_3)$_2$ *cis* to Cl); 23.5 (s, P(CH_3)$_2$ *trans* to Cl); 129.5 (s, P(C_6H_5)); 129.7 (m, P(C_6H_5)); 130.5 (d, $^3J_{CC}$ = 23 Hz, P(C_6H_5)); 130.8 (d, $^3J_{CC}$ = 20 Hz, P(C_6H_5)). ^{31}P{^{1}H} NMR (ppm) (162 MHz, CD_2Cl_2, δ_P) −144.5 (sp, $^1J_{PF}$ = 711 Hz, *P*F_6); −1.2 (t, $^2J_{PP}$ = 30 Hz, *P*Me_2Ph *trans* to NH_3); 11.7 (q, $^2J_{PP}$ = 32 Hz, *P*Me_2Ph *cis* to NH_3); 15.3 (q, $^2J_{PP}$ = 28 Hz, *P*Me_2Ph *trans* to Cl). ^{15}N NMR (ppm) (51 MHz, $CDCl_3$, δ_N) −7 (s, NH_3). CHN (%): [RuCl$(NH_3)(PMe_2Ph)_4$](PF_6): C, 45.04 (45.16); H, 5.73 (5.57); N, 1.64 (1.65).

2.8. X-ray crystallography of compounds **8**, **9**, **10**, **12**, and **13**

Single crystals of compounds **8**, **9**, **10**, **12**, and **13** were mounted on a fine glass rod and diffracted with graphite-monochromated Mo Kα radiation (k = 0.71069 Å) using a Bruker APEX-II CCD area-detector diffractometer. X-ray diffraction measurements were made at 293(2) K (**8**), 293(2) K (**9**), 100(1) K (**10**), 150(2) K (**12**),

and 293(2) K (**13**). Absorption corrections were carried out using SADABS [27]. All structures were solved by direct methods with SHELXS-97 [28] using the OLEX2 [29] interface. All H atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms. Crystal data and experimental parameters for complexes **8**, **9**, **10**, **12**, and **13** are given in Table 1.

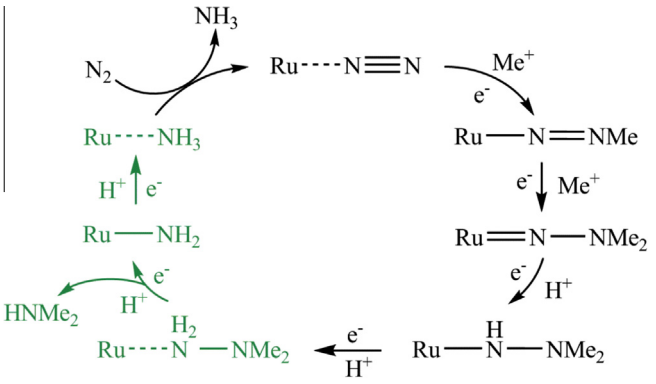
3. Results and discussion

3.1. Synthesis of hydrido- and chlorido-ammine-Ru(II) complexes

Due to the interest in the highly reactive synthetic precursor $[RuH(1,5\text{-cod})(NH_2NMe_2)_3](PF_6)$ during the years of 1977–1986, a number of by-products in the preparative reactions of the latter complex were missed or simply not further investigated [16]. The complex $[RuH(1,5\text{-cod})(NH_2NMe_2)_3](PF_6)$ was mainly employed as a synthon to a vast range of catalytically active Ru (II) and Ru(IV) complexes, for which access to vacant coordination sites at the metal centre is readily obtained through NH_2NMe_2 and/or 1,5-cod ligand dissociation [16–18]. However, the formation of Ru(II)-ammine species from reactions involving Ru(II)-NH_2NMe_2 and NH_4PF_6/$NaBPh_4$ salts in our laboratories lead us to reinvestigate the known reaction of the polymeric $[RuCl_2(1,5\text{-cod})]_x$ and NH_2NMe_2, and the synthetic and catalytic properties that these novel Ru(II)-ammine complexes may exhibit.

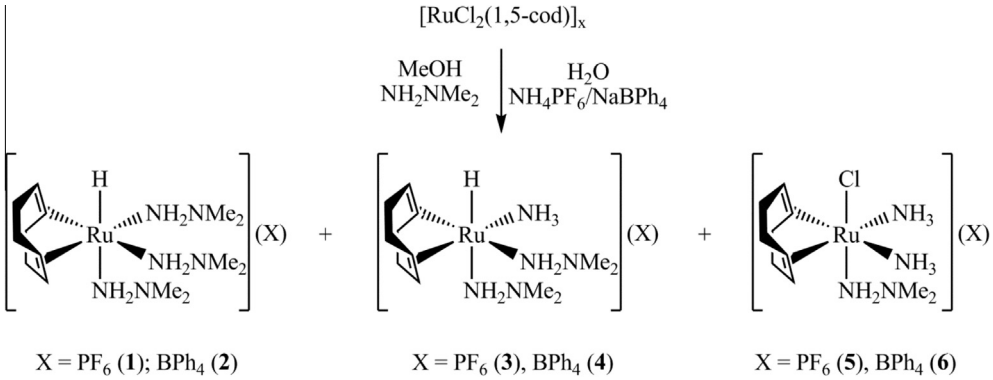
The known [16f] reaction involves heating a methanol slurry of the polymer with 6 equivalents of NH_2NMe_2 in the presence of H_2O for 30 min, after which anion exchange with NH_4PF_6 (in H_2O) or $NaBPh_4$ (in MeOH) occurs. Concentration of the resulting solutions gave beige microcrystalline precipitates, from which in both cases three products were isolated (Scheme 1). Extraction of both the PF_6- and BPh_4-salts with $CHCl_3$ followed by CH_2Cl_2, and finally acetone gave the following complexes respectively: *fac*-$[RuH(1,5\text{-cod})(NH_2NMe_2)_3](PF_6)$ (**1**) (known), $[RuH(1,5\text{-cod})(NH_3)(NH_2NMe_2)_2](PF_6)$ (**3**) (novel), and $[RuCl(1,5\text{-cod})(NH_3)_2(NH_2NMe_2)](PF_6)$ (**5**) (novel); and the complexes $[RuH(1,5\text{-cod})(NH_3)(NH_2NMe_2)_2](BPh_4)$ (**4**) (novel), *fac*-$[RuH(1,5\text{-cod})(NH_2NMe_2)_3](BPh_4)$ (**2**) (known), and $[RuCl(1,5\text{-cod})(NH_3)_2(NH_2NMe_2)](BPh_4)$ (**6**) (novel).

To the best of our knowledge, complexes **5** and **6** are the first reported chloro-cyclooctadiene bis-ammine ruthenium(II) complexes. The appearance of NH_3 as a coordinated ligand in these reactions from $[RuCl_2(1,5\text{-cod})]_x$ and NH_2NMe_2 is proposed to have two sources. The first is the catalytic decomposition, or nitrogenase [24b,30], of a molecule of NH_2NMe_2 to form NH_3 and $HNMe_2$ as by-products (Scheme 2). The catalysed decomposition of NH_2NH_2 in particular is well-documented, and only one report on the decomposition of phenylhydrazine as a substituted hydrazine has been reported [1e,24b,30]. This is the first reported instance of the catalytic decomposition of NH_2NMe_2 by Ru(II), and forms some of the first examples where NH_2NMe_2 Ru(II)-ammine intermediate complexes are isolated in the N_2 and methyldiazene activation routes [15]. Another source for the formed NH_3 is the conjugated acid-base pairs NH_3 and HPF_6 from the aqueous NH_4PF_6 salt employed. The *in situ* formation of NH_3 as ligand specifically in Ru(II) systems are rather common, as cited in reports involving the use of NH_4PF_6, where it is used in the activation of ammonia and the formation of alkynylamine [4a,14,31]. The complexes $[RuH(1,5\text{-cod})(NH_3)(NH_2NMe_2)_2](BPh_4)$ (**2**) and $[RuCl(1,5\text{-cod})(NH_3)_2(NH_2NMe_2)](BPh_4)$ (**6**) were isolated, albeit in low yields, in the absence of any external source of NH_3 which indicates NH_2NMe_2 decomposition. Complexes $[RuH(1,5\text{-cod})(NH_3)(NH_2NMe_2)_2](PF_6)$ (**3**) and $[RuCl(1,5\text{-cod})(NH_3)_2(NH_2NMe_2)](PF_6)$ (**5**) were isolated in higher yields due to the combined effect of NH_2NMe_2 decomposition and the conjugated base pair formation from NH_4PF_6. We found that when >1.8 M equivalents of NH_4PF_6 is used, an increase in the formation of **3** and **5** is observed, suggesting the NH_4PF_6 salt does play a major role in the *in situ* formation of NH_3.



Scheme 2. The Chatt cycle [5a] derived for methyldiazene and *N,N*-dimethylhydrazine counterparts in the N_2 reduction process.

The steric requirements of a coordinated chloride-ion together with three relatively bulky NH_2NMe_2 ligands may drive the molecule to react either by conversion to the smaller hydride ligand through an intermolecular hydride formation mechanism using MeOH, or through a catalytic decomposition of a NH_2NMe_2 ligand to form NH_3. Attempts to convert the chlorido-ammine complexes **5** and **6** into the hydrido-ammine complexes **3** and **4** respectively by the reactions of excess NH_2NMe_2 in MeOH failed. However, upon heating reaction mixtures containing **3** and **4** with an excess of NH_2NMe_2 in MeOH, complexes **1** and **2** are eventually obtained, albeit in low yields (~30%).



Scheme 1. Synthesis of NH_2NMe_2–Ru(II) complexes from the polymeric $[RuCl_2(1,5\text{-cod})]_x$.

The ^{1}H NMR spectrum of **3** contains a singlet assigned to the Ru–H at δ_H −5.58, signals for NH_2NMe_2 in a 1:1 ratio at δ_H 2.44 (NMe *trans* to 1,5-cod) and 2.73 (NMe *cis* to 1,5-cod) ppm respectively, and a broad singlet at δ_H 1.23 for the NH_3 proton. The ^{1}H NMR spectrum of **5** showed two broad singlets at δ_H 1.89 and 3.33 for the protons of two NH_3 in chemically different environments. The ^{1}H- and ^{13}C{^{1}H} NMR spectra for the BPh_4-anion analogues (**2**, **4**, and **6**) were generally comparable to the PF_6-anion analogues.

3.2. Reactions of [RuH(1,5-cod)(NH_2NMe_2)$_3$](A) (A = PF_6, **1**; BPh_4, **2**)

The majority of the following reactions described in this section are known reactions that lead to methyldiazene activation intermediates that have not been identified or fully characterised before. The reaction of the complexes [RuH(1,5-cod)(NH_2NMe_2)$_3$](X) (X = PF_6, **1**; BPh_4, **2**) with 5.2 equivalents of $P(OMe)_2Ph$ in boiling MeOH under a N_2 atmosphere gave the known complexes [RuH{$P(OMe)_2Ph$}$_5$](X) (X = PF_6, **7**; BPh_4, **8**) in high yields (86% for **7**, 88% for **8**). Upon employing the slightly larger PMe_2Ph ligand the known complexes [RuH(1,5-cod)(PMe_2Ph)$_3$](PF_6) and [RuH(PMe_2Ph)$_5$](PF_6) were isolated under similar reaction conditions [16a,d].

The unknown molecular structure of complex **8** shows a slightly distorted octahedron of the cation with five coordinated $P(OMe)_2$-Ph ligands, four in the same equatorial plane, and the fifth in the apical position, *trans* to the hydride ligand (Fig. 1). With the hydride ligand in the apical position, a structural *trans*-influence of the hydride ligand on the *trans*-coordinated P13 ligand is expected although the Ru1–P13 bond (2.3408(2) Å), is only the second longest Ru-P bond observed. The bond angles of P11–Ru1–P14 = 177.067(2)°, and P12–Ru1–P15 = 159.174(1)° are indicative of the inherent distortion (Table 2). The ligands P12 and P15 show a degree of folding towards the smaller hydride ligand, as indicated by the P12–Ru1–P15 bond angle as well as the bond angles P12–Ru1–H1 = 80.221(1)° and P15–Ru1–H1 = 78.977(1)°.

The reaction of [RuH(1,5-cod)(NH_2NMe_2)$_3$](X) (**1**) or [RuH(1,5-cod)(NH_3)(NH_2NMe_2)$_2$](PF_6) (**2**) with excess $PMePh_2$ in EtOH, gave light yellow crystals of the known complex *cis*-[$RuH_2(PMePh_2)_4$] (**9**), whose molecular structure is unknown. As the intraligand repulsion of the bulkier phosphine ligands is increased, the tendency for halide ligand substitution by hydride ligands increases, and therefore suggests a steric-controlled outcome in these reactions (Scheme 3) [32].

The molecular structure of **9** shows three phosphine ligands (P1, P2, P4) coordinated to the ruthenium atom in the same (equatorial) plane, with the fourth phosphine ligand (P3) occupying the apical position *trans* to one apical hydride ligand (H1b) (Fig. 2). The equatorial plane itself is disordered, with P1–Ru1–P2 = 146.41(2)°, and H1a–Ru1–P4 = 172.33(2)°, both deviating from the ideal 180° expected (Table 2). Significant folding in of P1 and P2 towards the smaller hydrido atom is observed with angles H1a–Ru1–P1 = 80.34(2)°, and H1a–Ru1–P2 = 77.90(2)°. H1a is coordinated in an equatorial plane with three phosphine ligands, resulting in a shorter Ru–H bond length (Ru1–H1a = 1.5943(4) Å), as compared to H1b (Ru1–H1b 1.6479(5) Å).

In an attempt to convert the dihydrido complexes [$RuH_2(L)_4$] (L = PMe_2Ph, $PMePh_2$) into the monohydrido complexes [RuH$(L)_5$](PF_6), the complex [$RuH_2(PMe_2Ph)_4$] [32a] was reacted with 2 equivalents each of both HPF_6 and PMe_2Ph under reflux. The known dimeric triply fluoro-bridged complex, [{Ru(PMe_2Ph)$_3$}$_2$(μ-F)$_3$](PF_6) (**10**), was isolated in moderate yields (43%). The labilization of fluoride ions from a PF_6^- source to form triply-bridged fluoride dimers is not uncommon, and has been reported for the reactions of [RuH(1,5-cod)(NH_2NMe_2)$_3$](A) (A = PF_6, BPh_4) with PMe_2Ph in acetone/methanol mixtures in the presence of H_2O, H_2S, HSMe, or HF to give [{Ru(PMe_2Ph)$_3$}$_2$(μ-X)$_3$](A) (A = PF_6, BPh_4, X = OH, F, SH, SMe) [16g,33a]. These reactions occur due to the minimisation of intraligand strain, and the overall stabilization of ruthenium(II) complexes by anionic-bridges [33].

The ^{31}P NMR of **10** shows a single multiplet at δ_P 33.9 (ddd, $^1J_{PP}$ = 171 Hz and $^2J_{PP}$ = 36 and 88 Hz) for symmetrical arrangement

Table 1
Crystal data and experimental parameters for complexes **8**, **9**, **10**, **12**, and **13**.

Complex	**8**	**9**	**10**	**12**	**13**
Emp. formula	$C_{128}H_{152}B_2O_{20}P_{10}Ru_2$	$C_{52}H_{54}P_4Ru$	$C_{48}H_{66}F_9P_7Ru_2$	$C_{25}H_{42}ClF_6N_2O_{0.5}P_4Ru$	$C_{32}H_{47}ClF_6NP_5Ru$
Formula weight (g mol^{-1})	2543.95	903.90	1232.93	753.00	851.07
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Pca2$_1$*	*P2$_1$/n*	*C2/c*	*P2$_1$/c*	*P2$_1$/n*
Crystal descr.	Brown prism	Yellow cuboid	Yellow needle	Orange needle	Yellow cuboid
Crystal size (mm)	0.331 × 0.162 × 0.08	0.342 × 0.216 × 0.179	0.365 × 0.080 × 0.074	0.385 × 0.24 × 0.182	0.223 × 0.129 × 0.126
a (Å)	28.469(4)	9.903(1)	31.3480(2)	10.1732(1)	16.367(3)
b (Å)	11.957(3)	38.116(2)	16.3711(8)	19.072(2)	12.042(5)
c (Å)	36.635(5)	11.667(1)	28.4795(2)	17.343(2)	20.301(0)
α (°)	90.000	90.000	90.000	90.000	90.000
β (°)	90.000	90.702(5)	121.8850(1)	105.483(5)	113.035(1)
γ (°)	90.000	90.000	90.000	90.000	90.000
V (Å^3)	12,471(4)	4404.3(6)	12410.3(1)	3242.8(7)	3682(2)
Z	4	4	8	4	4
D_{calc} (mg m^{-3})	1.355	1.363	1.320	1.542	1.535
Abs. coefficient (m mm^{-1})	0.437	0.537	0.844	0.819	0.771
F(000)	5312.0	1880.0	5024.0	1540.0	1744.0
2*θ* range (°)	4.312–41.66	2.136–56.98	1.68–56.76	4.672–67.566	2.73–50.086
Independent reflections	28,752	11,092	15,481	7465	6398
Index ranges	$-37 \leqslant h \leqslant 37$	$-13 \leqslant h \leqslant 13$	$-41 \leqslant h \leqslant 41$	$-13 \leqslant h \leqslant 13$	$-15 \leqslant h \leqslant 19$
	$-15 \leqslant k \leqslant 15$	$-50 \leqslant k \leqslant 50$	$-21 \leqslant k \leqslant 21$	$-24 \leqslant k \leqslant 24$	$-13 \leqslant k \leqslant 14$
	$-47 \leqslant l \leqslant 47$	$-15 \leqslant l \leqslant 15$	$-38 \leqslant l \leqslant 37$	$-22 \leqslant l \leqslant 22$	$-24 \leqslant l \leqslant 24$
Completeness (%)	99.7	99.3	99.5	99.9	98.0
Abs. corr. method	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Data/restraints/parameter	13,027/1/1487	11,092/0/526	15,481/0/607	12,982/0/398	6398/0/433
Goodness-of-fit (GOF) on F^2	1.050	1.097	1.008	1.080	1.060
Final R_1 indices	0.0278	0.0292	0.0410	0.0302	0.0259
wR_2 indices (all data)	0.0619	0.0719	0.1096	0.0787	0.0585
Largest difference in peak and hole (e Å^{-3})	0.53 and −0.24	0.42 and −0.39	0.67 and −0.75	1.11 and −0.69	0.35 and −0.47

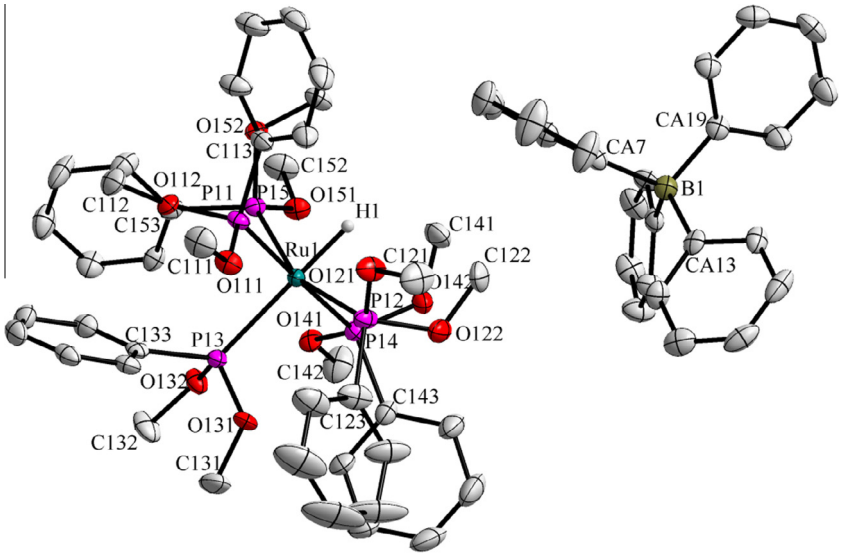


Fig. 1. (a) Molecular diagram of $[RuH\{P(OMe)_2Ph\}_5](BPh_4)$ (**8**), with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms (apart from the hydride ligand) are omitted for clarity.

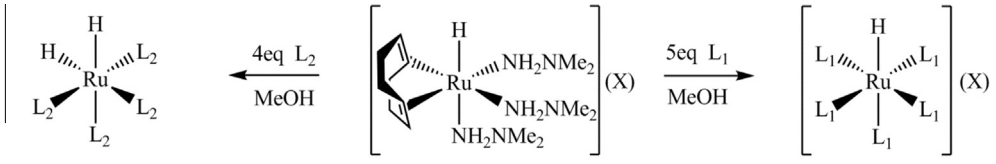
of the PMe_2Ph ligands around each ruthenium centre. The Ru1–Ru2 interatomic distance of 3.1097(4) Å is slightly longer than that reported for $[\{Ru(PMe_2Ph)_3\}_2(\mu\text{-}OH)_3](BPh_4)$ (3.08 Å), but compares well with the complex $[\{Ru(PEt)_3\}_2(\mu\text{-}F)_3](CF_3SO_3)$ [3.1081 (4) Å] (Table 2) [33a]. Three equivalent PMe_2Ph ligands are *fac*-coordinated to each ruthenium centre, with typical Ru–P bond lengths varying between 2.2413(9)–2.2474(8) Å, which is slightly shorter than the reported Ru-P bond lengths for the similar $[\{Ru(PEt)_3\}_2(\mu\text{-}F)_3](CF_3SO_3)$ complex (Fig. 3) [33a].

3.3. Reactions of $[RuCl(1,5\text{-}cod)(NH_3)_2(NH_2NMe_2)](PF_6)$ (**5**)

Contrasting to the reactions of **1**–**4** bearing hydride moieties that are known, reactions of the novel chlorido-Ru(II)–ammine complexes results in the isolation of novel chloride methyldiazene and ammine intermediates. Reaction of $[RuCl(1,5\text{-}cod)(NH_3)_2(NH_2NMe_2)_3](PF_6)$ (**5**) with 3.5 equivalents of PMe_3 in boiling MeOH gave $[RuCl(NH_3)_2(PMe_3)_3](PF_6)$ (**11**) and the known dimeric complex $[\{Ru(PMe_3)_3\}_2(\mu\text{-}Cl)_3]$. Recrystallization of the mixture

Table 2
Selected bond distances (Å) and angles (°) for complexes **8**, **9**, and **10**.

8		**9**		**10**	
Ru1–P11	2.3258(2)	Ru1–P1	2.3038(8)	Ru1–Ru2	3.1097(4)
Ru1–P12	2.3111(1)	Ru1–P2	2.3050(7)	Ru1–P11	2.2425(8)
Ru1–P13	2.3409(9)	Ru1–P3	2.3675(9)	Ru1–P12	2.2460(8)
Ru1–P14	2.3427(1)	Ru1–P4	2.3390(7)	Ru1–P13	2.2432(8)
Ru1–P15	2.3142(9)	Ru1–H1a	1.5943(4)	Ru2–P21	2.2413(9)
Ru1–H1	1.4987(2)	Ru1–H1b	1.6479(5)	Ru2–P22	2.2430(8)
B1–CA1	1.648(5)	H1a–Ru1–H1b	87.31(2)	Ru2–P23	2.2474(8)
B1–CA7	1.649(6)	H1a–Ru1–P1	80.34(2)	Ru1–F1	2.1345(2)
P11–Ru1–P12	91.27(4)	H1a–Ru1–P2	77.90(2)	Ru1–F2	2.1372(2)
P11–Ru1–P13	90.84(3)	H1a–Ru1–P3	87.59(2)	Ru1–F3	2.1528(2)
P11–Ru1–P14	177.08(4)	H1b–Ru1–P1	72.24(2)	Ru1–F1–Ru2	93.30(6)
P12–Ru1–P15	159.14(3)	H1b–Ru1–P4	86.46(2)	Ru1–F2–Ru2	93.58(7)
P14–Ru1–P15	89.76(3)	P1–Ru1–P2	146.41(2)	Ru1–F3–Ru2	92.87(6)
H1–Ru1–P12	80.22(5)	P1–Ru1–P3	106.83(3)	P11–Ru1–P12	95.67(3)
H1–Ru1–P13	179.46(5)	P1–Ru1–P4	101.97(3)	P11–Ru1–P13	93.77(3)
H1–Ru1–P15	78.98(5)	P2–Ru1–P3	97.52(3)	P12–Ru1–P13	93.44(3)
Ru1–P13–O131	108.70(1)	P2–Ru1–P4	96.72(3)	P21–Ru2–P22	95.73(3)
Ru1–P13–O132	113.20(1)	P3–Ru1–P4	98.62(3)	P21–Ru2–P23	93.49(3)



$L_2 = PMe_2Ph$, $PMePh_2$ (**9**)

$L_1 = P(OMe)_2Ph$;
$X = PF_6$ (**7**), BPh_4 (**8**)

Scheme 3. Syntheses of $[RuHL_1](X)$ and $[RuH_2(L_2)_4]$ species using different $L_1 = PMe_3$, PMe_2Ph, $P(OMe)_2Ph$, and $L_2 = PMe_2Ph$, $PMePh_2$ phosphines.

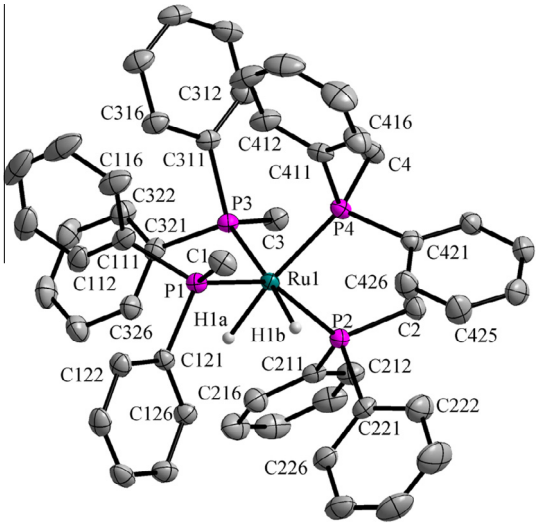


Fig. 2. (a) Molecular diagram of *cis*-[$RuH_2(PMePh_2)_4$] (**9**), with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms (apart from the hydride ligands) are omitted for clarity.

yielded **11** as a dark blue powder in low yield (38%), which was difficult to analyse. It is concluded that dimerization is a secondary reaction occurring after the formation of **11**, possibly due to the stabilization effect brought about by the halogen bridges. The ^1H NMR spectrum shows two unique broad singlets for the *cis* NH_3 ligands at δ_H 2.08 and 3.30 ppm. The presence of the PMe_3 ligands in two unique chemical environments are shown in the NMR spectra of **11**: a multiplet at δ_H 1.56 in the ^1H NMR spectrum; two signals at δ_C 20.1 (t, $^3J_{CC}$ = 20 Hz) and 49.6 (s) in the ^{13}C NMR spectrum; and two resonances at δ_P 20.8 (s) and 22.4 (d, $^2J_{PP}$ = 24 - Hz) in the ^{31}P NMR spectrum.

Upon reacting **5** with 3 equivalents of PMe_2Ph in MeOH, *fac*-[$RuCl(NH_3)_2(PMe_2Ph)_3$](PF_6) (**12**) was isolated as deep yellow crystals. Both NH_3 ligands remained coordinated to the ruthenium centre, similar to the analogous [$RuCl(NH_3)_2(PMe_3)_3$](PF_6) (**11**). In the reaction of [RuCl(1,5-cod)$(NH_3)_2(NH_2NMe_2)_3$](PF_6) (**5**) with 4 equivalents of PMe_2Ph, one molecule of NH_3 dissociates (in addition to NH_2NMe_2 and 1,5-cod) to give [$RuCl(NH_3)(PMe_2Ph)_4$](PF_6) (**13**) (Scheme 4). It has been found that **12** may be converted to **13** by reaction of an additional equivalent of PMe_2Ph. The ^1H NMR spectrum of **12** exhibits two distinct NH_3 singlets at δ_H 1.75 and 3.30, indicating that each of these ligands occupies a different chemical environment, whereas a single broad singlet at δ_H 0.32 was observed for the NH_3 ligand in **13**. The ^{15}N–^1H HMBC NMR spectra of **4** and **6** both showed similar signals for the non-equivalent ammine ligands at δ_N 58 (**4**) and −18 (**6**). Other typical ^{15}N resonances observed included those of the NH_2NMe_2 ligands, which were similar for all the complexes around δ_N 57–69 (NMe_2), 86–106 (NMe_2) and 116–132 (NH_2). The ammine signals shifted in the phosphine-substituted complexes **12** and **13**, with signals resonating at δ_N −8 (two doublets for non-equivalent NH_3 ligands) (**12**), and δ_N −7 (one doublet for a single NH_3 ligand) (**13**).

Addition of a few drops of D_2O to $(CD_3)_2CO$ solutions of both **5** and **13** bearing NH_3 moieties resulted in the disappearance of the NH_3 proton signals. Both 2D COSY ^1H–^1H and ^{15}N–^1H HMBC spectra also showed no coupling between the D_2O and NH_3 signals, which indicate spontaneous exchange of the Ru-NH_3 and Ru-OD_2 species, as opposed to Ru–NH_3 and Ru–ND_3 exchange. The ^{31}P NMR spectrum of **12** revealed three PMe_2Ph ligands in two chemically unique environments: δ_P 19.2 (d, $^2J_{PP}$ = 34 Hz) and 25.9 (t, $^2J_{PP}$ = 32 Hz); whereas for **13** signals for four PMe_2Ph in three chemically different environments were observed: δ_P −1.2 (t, $^2J_{PP}$ = 30 Hz, PMe_2Ph *trans* to NH_3); 11.7 (q, $^2J_{PP}$ = 32 Hz, PMe_2Ph *cis* to NH_3); 15.3 (q, $^2J_{PP}$ = 28 Hz, PMe_2Ph *trans* to Cl).

The complex [$RuCl(NH_3)(PMe_2Ph)_4$](PF_6) (**13**), exhibits only one NH_3 ligand in the equatorial position, along with three PMe_2Ph ligands in the same plane. In both **12** and **13** the chlorido-ligand is coordinated *cis* to the equatorial NH_3 ligand, along with two other PMe_2Ph ligands (Figs. 4 and 5). In **12**, the bond angles N1–Ru1–P2 (170.40(5)°), Cl1–Ru1–P1 (170.28(2)°), and N2–Ru1–P3 (169.85(6)°) all show distortion along the apical plane (Table 3). The relative degree of steric strain in the equatorial plane of the complex brought about by phosphines P1 and P3 is illustrated in the increased P1–Ru1–P3 bonding angle of 96.25(2)°, together with

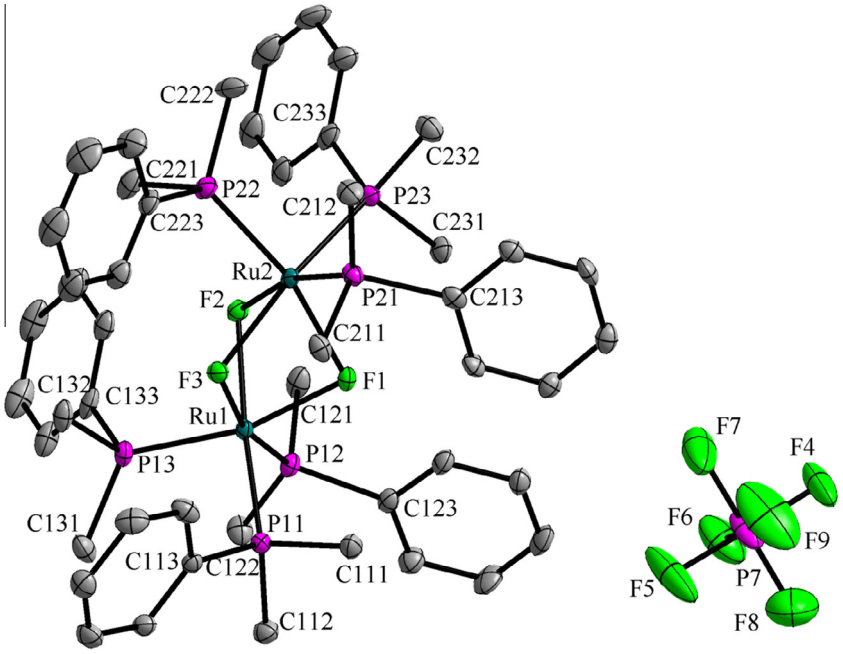
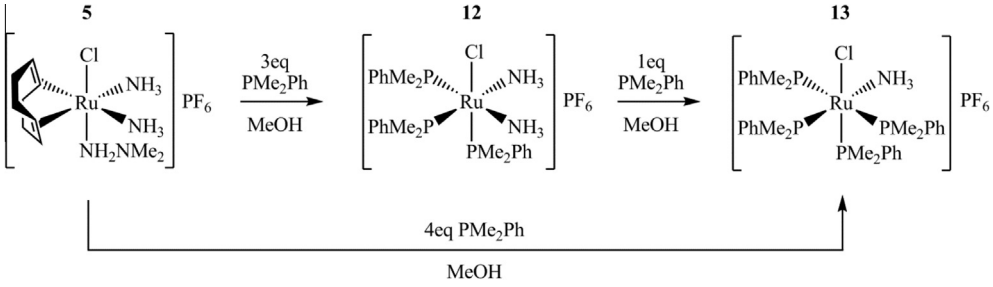


Fig. 3. Molecular diagram of [{$Ru(PMePh_2)_3$}$_2$(μ-F)$_3$](PF_6) (**10**), with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.



Scheme 4. Syntheses of mono- and bis-ammine Ru(II)-PMe_2Ph complexes.

the smaller Cl1–Ru1–P3 and P1–Ru1–N2 angles of 91.61(2)° and 92.82(6)° respectively. The folding in of Cl and N2 due to the presence of P1 and P3 results in the significantly smaller Cl1–Ru1–N2 bonding angle of 78.92(6)°. The degree of resulting intraligand repulsion increased in **13** due to an additional PMe_2Ph ligand. This was evident in the equatorial plane, where the reduced Cl1–Ru1–P1 and Cl1–Ru1–P4 bond angles of 84.41(3)° and 80.82(3)°, respectively were observed. The folding in of the substituents of P1 and P4 towards Cl1 resulted directly in the increased P1–Ru1–P3 and P3–Ru1–P4 bond angles of 92.91(3)° and 101.18(3)°, respectively.

3.4. ^1H NMR spectrometry of successive PMe_3 additions

In light of the reactions of complexes **1**–**4** with phosphines and phosphonites to form the cationic $[RuH(P)_5]^+$ and related species, we were interested in the ligand substitution route followed and how it agrees with our steric-controlled reaction outcomes. Firstly, it is known that the complexes $[RuH(1,5\text{-cod})(NH_2NMe_2)_3](X)$ (X = PF_6, **1**; BPh_4, **2**) reacts with 3 equivalents of phosphines (P = $P(OMe)_3$, PMe_3, PMe_2Ph, $PMePh_2$) to form the complexes $[RuH(1,5\text{-cod})(P)_3](X)$ (X = PF_6, BPh_4). These complexes react further with excess phosphine to substitute the diene ligand to produce the complexes $[RuH(P)_5](X)$ (X = PF_6, BPh_4). An acetone-d_6 solution of $[RuH(1,5\text{-cod})(NH_2NMe_2)_3](BPh_4)$ (**2**) shows a hydride

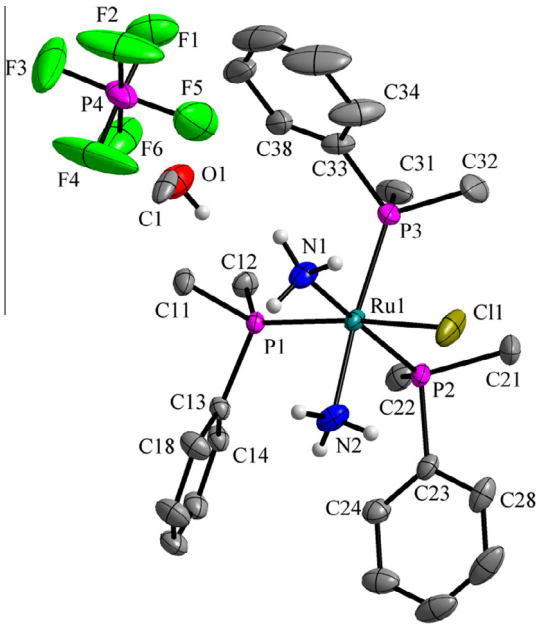


Fig. 4. Molecular diagram of *fac*-$[RuCl(NH_3)_2(PMePh_2)_3](PF_6)\cdot 0.5EtOH$ (**12**·0.5EtOH). Thermal ellipsoids were drawn at 50% probability level, and hydrogen atoms (apart from the NH_3 and OH functionalities) are omitted for clarity.

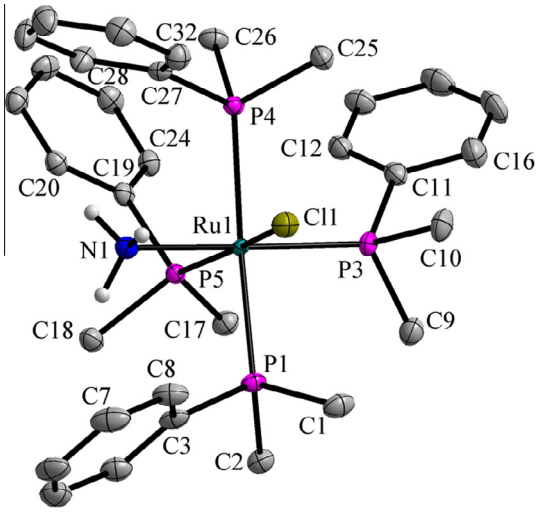
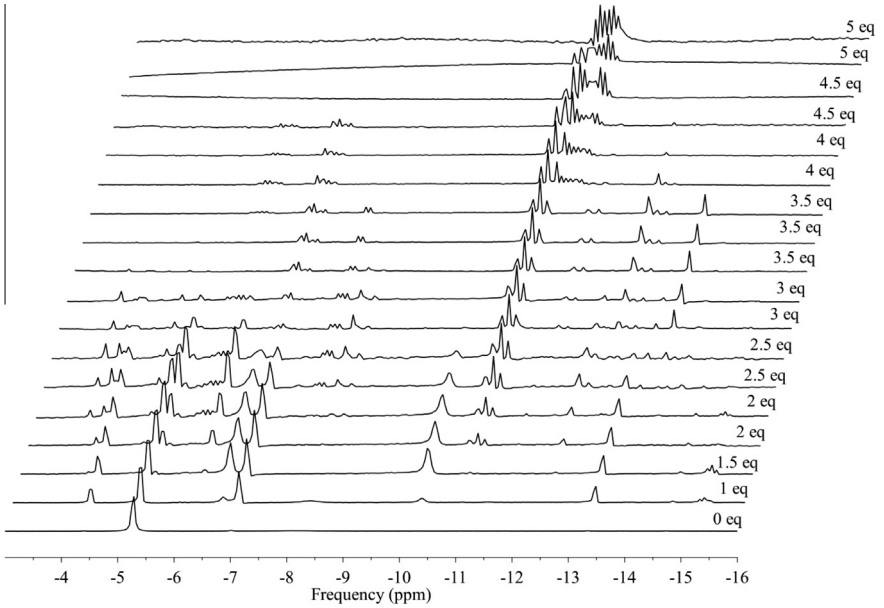


Fig. 5. Molecular diagram of $[RuCl(NH_3)(PMePh_2)_4](PF_6)$ (**13**). Thermal ellipsoids were drawn at 50% probability level, and hydrogen atoms (apart from the NH_3 ligand) are omitted for clarity.

signal in the ^1H NMR spectrum at −5.28 ppm, which upon addition of 1 M equivalent of PMe_3 resolves to 6 different hydride singlets of variable intensities (Scheme 5). This is ascribed to a mixture of complexes resulting from the mono-substitution of PMe_3 at two different coordination positions (equatorial and apical). In addition, the *in situ* substitution of NH_2NMe_2 by $(CD_3)_2CO$ as a competing ligand in high concentration readily occurs. This solution behaviour was not observed in a $CDCl_3$ solution of **2**. Further

Table 3
Selected bond distances (Å) and angles (°) for complexes **12** and **13**.

12		**13**	
Ru1–P1	2.2875(5)	Ru1–P1	2.3847(7)
Ru1–P2	2.2886(6)	Ru1–P2	2.3110(8)
Ru1–P3	2.2962(6)	Ru1–P3	2.3263(7)
Ru1–Cl1	2.4654(6)	Ru1–P4	2.4110(7)
Ru1–N1	2.1907(2)	Ru1–Cl1	2.4948(9)
Ru1–N2	2.1973(2)	Ru1–N1	2.2038(2)
P1–Ru1–P2	96.80(2)	P5–F1	1.5987(2)
P1–Ru1–P3	96.25(2)	P1–Ru1–P2	90.96(3)
P2–Ru1–P3	93.06(2)	P1–Ru1–P3	92.91(3)
P1–Ru1–Cl1	170.28(2)	P1–Ru1–P4	165.086(2)
P1–Ru1–N1	91.68(5)	P2–Ru1–P3	99.09(2)
P2–Ru1–N1	170.40(5)	P2–Ru1–P4	91.63(3)
P3–Ru1–N1	90.47(6)	P3–Ru1–P4	101.18(3)
Cl1–Ru1–N1	82.52(5)	P1–Ru1–Cl1	84.41(3)
N2–Ru1–N1	84.73(7)	P3–Ru1–Cl1	168.50(2)
N2–Ru1–Cl1	78.92(6)	P4–Ru1–Cl1	80.82(3)
N2–Ru1–P3	169.85(6)	N1–Ru1–Cl1	80.18(5)
P3–Ru1–Cl1	91.61(2)	N1–Ru1–P2	172.32(5)



Scheme 5. Stacked ^{1}H NMR spectrum of the sequential PMe_3 addition to $[RuH(1,5\text{-cod})(NH_2NMe_2)_3](BPh_4)$ (**2**).

addition to a total of 2 equivalents PMe_3 reveals a triplet at −10.98 ppm ($^{2}J_{HP}$ = 55 Hz) which is ascribed to the coupling of the hydride ligand with two different phosphorous nuclei. The concentration of this complex increases, where signals for the complex $[RuH(1,5\text{-cod})(PMe)_3](BPh_4)$ appears. Addition of 4 M equivalents of PMe_3 results in direct substitution of the 1,5-cod ligand to give $[RuH(PMe_3)_4(L)](BPh_4)$ (L = NH_2NMe_2, $(CD_3)_2CO$) and finally $[RuH(PMe_3)_5](BPh_4)$. It is unclear at this stage if direct substitution of the 1,5-cod ligand by two molecules of PMe_3 is concerted at the relative high concentrations of PMe_3. The prevalence of the PMe_3 ligand to coordinate over the $(CD_3)_2CO$ ligand at high PMe_3 concentrations, however, is evident.

A doublet of pentets are expected for the complex $[RuH(PMe_3)_5](BPh_4)$, but only a partially resolved doublet of pentets is observed for the final *in situ* product, even after prolonged exposure to excess PMe_3. The ^{1}H NMR spectra obtained for isolated complexes **7** and **8** in $CDCl_3$, shows an overlapping doublet of pentets for the hydride ligand at δ_H −8.78 (dp, $^{2}J_{HP}$ = 19 and 88 Hz) and −8.90 (dp, $^{2}J_{HP}$ = 19 and 89 Hz), respectively. The ^{31}P NMR spectra of the latter complexes corresponds to the equivalence of the phosphines through the appearance of singlets observed at δ_P 20.3 (**7**) and 20.9 ppm (**8**) for the $P(OMe)_2Ph$ moieties.

These results demonstrate how the bulkier NH_2NMe_2 ligands is readily substituted by smaller ligands (such as NH_3), especially in the presence of the much larger chlorido-anion as opposed to the small hydrido-ligand. The coupling provided by the hydride and phosphorous nuclei acted as a probe to identify at which stage each ligand is substituted in complexes that form intermediates which are extremely difficult to isolate or identify otherwise.

4. Conclusions

Through the synergistic effect of nitrogenase-type activity and NH_4PF_6 hydrolysis, the novel ammine hydrido- and chlorido-ruthenium(II) complexes $[RuH(1,5\text{-cod})(NH_3)(NH_2NMe_2)_2]X$ (X = PF_6, BPh_4) and $[RuCl(1,5\text{-cod})(NH_3)_2(NH_2NMe_2)]X$ (X = PF_6, BPh_4) were synthesised as products in a mixture containing the known complexes $[RuH(1,5\text{-cod})(NH_2NMe_2)_3]X$ (X = PF_6, BPh_4). All of these complexes served as reactive precursors to a range of neutral and cationic ruthenium(II)-ammine complexes from the reactions with tertiary phosphines and phosphonites. These complexes were stable, isolable intermediates of the N_2 and methyldiazene activation processes, which allows for further catalytic and synthetic investigations. Intramolecular strain of the precursor complexes, as well as the steric bulk and electronic properties of the incoming σ-donating ligands was found to be two determining factors to the selective formation of monohydrido-, bishydrido-, as well as mono-ammine, and bis-ammine ruthenium(II) complexes.

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Appendix A. Supplementary material

CCDC 997437, 997438, 997675, 997674 and 997676 contains the supplementary crystallographic data for **8**, **9**, **10**, **12** and **13**, respectively. 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 http://dx.doi.org/10.1016/j.ica.2015.08.019.

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