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ARTICLE

Ruthenium(III) complexes containing bi- and tridentate phosphorus–nitrogen ligands

Dona C. Mudalige, Erin S.F. Ma, Steven J. Rettig, Brian O. Patrick, and Brian R. James

Abstract: Air-stable Ru^{III} complexes containing a bidentate aminophosphine ligand (*PN*) of the type *mer*-$RuCl_3$(*PN*)(PR_3) are made from the precursors $RuCl_3(PR_3)_2$(DMA)·DMA (*PN* = *o*-diphenylphosphino-*N*,*N*′-dimethylaniline (P–N) and (*R*)-*N*,*N*′-dimethyl-1-[*o*-diphenylphosphinophenyl]ethylamine ((*R*)-AMPHOS); R = Ph, *p*-tolyl; DMA = *N*,*N*′-dimethylacetamide). With the tridentate bis[*o*-(*N*,*N*′-dimethylamino)phenyl]phenylphosphine (BNP), the product is *mer*-$RuCl_3$(BNP) (**3**), while tris[*o*-(*N*,*N*′-dimethylaminophenyl)phosphine (TNP) is unreactive toward the precursor. Crystal structures of *mer*-$RuCl_3$(*PN*)(PPh_3), where *PN* is P–N (**2a**), (*R*)-AMPHOS (**4a**), and **3**·$CHCl_3$ are reported as well as those of (*R*)-AMPHOS, BNP, and TNP. The Ru^{III}–aminophosphine complexes are the first monomeric Ru^{III} species to be formed via the useful, easily synthesized, air-stable Ru^{III} precursors $RuCl_3(PR_3)_2$(DMA)·DMA (**1a** and **1b**); complex **2a** is formed also via reaction of HCl with *trans*-$RuCl_2$(P–N)(PPh_3). A crystal structure of *mer*,*cis*-$RuCl_3(DMA)_2(PPh_3)$·DMA (**1c**), a side-product from the synthesis of the Ru^{III} precursor, is also presented and is the first-reported complex of DMA with Ru^{III}. Preliminary data show that the Ru^{III}–aminophosphine complexes in DMA (a proton-accepting solvent) are reduced by H_2 to Ru^{II} species that can react further to form an η^2-H_2 adduct and then a Ru^{II}-hydridochloro species.

Key words: Ru(III) complexes, phosphorus–nitrogen ligands, *N*,*N*′-dimethylacetamide complex, HCl as oxidant, crystallography.

Résumé : Les complexes de l'ion Ru^{III} du type *mer*-$RuCl_3$(*PN*)(PR_3), comportant un ligand bidentate aminophosphine (*PN*), sont synthétisés à partir des précurseurs $RuCl_3(PR_3)_2$(DMA)·DMA (*PN* = *o*-diphénylphosphino-*N*,*N*′-diméthylaniline (ligand P–N) et (*R*)-*N*,*N*′-diméthyl-1-[*o*-diphénylphosphinophényl]éthylamine ((*R*)-AMPHOS); R = Ph, *p*-tolyl; DMA = *N*,*N*′-diméthylacétamide). Avec le tridentate bis[*o*-(*N*,*N*′-diméthylamino)phényl]phénylphosphine (BNP), le produit obtenu est un *mer*-$RuCl_3$(BNP) (**3**), alors que tris[*o*-(*N*,*N*′-diméthylamino)phényl]phosphine (TNP) ne montre aucune réactivité avec le précurseur. Les structures cristallines des ligands *mer*-$RuCl_3$(*PN*)(PPh_3), où *PN* représente le ligand P–N (**2a**) et (*R*)-AMPHOS (**4a**), et **3**·$CHCl_3$ ainsi que celles des ligands (*R*)-AMPHOS, BNP et TNP sont décrites dans le présent article. Les complexes Ru^{III}–aminophosphine sont les premières espèces monomériques à être produites à l'aide des précurseurs du Ru^{III}, utiles, facilement synthétisables et stable à l'air, de formule $RuCl_3(PR_3)_2$(DMA)·DMA (**1a** et **1b**). Le complexe **2a** est produit par la réaction du HCl avec *trans*-$RuCl_2$(P–N)(PPh_3). La structure cristalline du complexe *mer*,*cis*-$RuCl_3(DMA)_2(PPh_3)$·DMA (**1c**), sous-produit de la synthèse du précruseur du Ru^{III}, est également présent dans le présent article. Il s'agit du premier complexe jamais observé formé à partir du DMA et du Ru^{III}. Des données préliminaires montrent que que les complexes de Ru^{III}–aminophosphine dans le DMA (solvant accepteur de protons) sont réduits pas H_2 pour former des complexes du Ru^{II} pouvant réagir à leur tour et produire un adduit de formule η^2-H_2 puis des complexes Ru^{II}-hydridochloro. [Traduit par la Rédaction]

Mots-clés : complexes du Ru(III), ligands phosphore–azote, complexe *N*,*N*′-diméthylacétamide, HCl comme oxydant, cristallographie.

Introduction

Ruthenium phosphine chemistry has been an ongoing interest in our group for almost 50 years,[1] a shorter time than one of us (B.R.J.) has known Barry Lever! Of note, the first report on asymmetric hydrogenation of olefinic substrates using Ru^{II}-chiral phosphine species appeared from our group in 1975,[2] and a readily observed problem with using such precursor catalyst species is their sensitivity to O_2 (with concomitant formation of phosphine oxides[3]); thus, air-stable Ru^{III}–phosphine complexes were synthesized[4] because these could be readily reduced in situ by H_2 to Ru^{II}, the required oxidation state for catalytic hydrogenation.[4a–4d] We have used previously the air-stable complexes $Ru^{III}Cl_3(PR_3)_2$(DMA)·DMA, R = Ph (**1a**) or *p*-tolyl (**1b**), which contain both a coordinated and solvate *N*,*N*′-dimethylacetamide molecule as a convenient source of Ru^{II}.[4c,4d] The syntheses of these complexes from reaction of $RuCl_3·3H_2O$ with a twofold excess of PR_3 in DMA at room temperature have been briefly described,[4c] and further details on these syntheses, and one of a $RuCl_3(DMA)_2(PPh_3)$·DMA (**1c**) side-product, are presented in this current paper. More importantly, we report here on the reactions of **1a** and 1**b** with four known aminophosphines, one of which is chiral (Scheme 1), to form air-stable Ru^{III} complexes; some data are also presented on the reactivity of the Ru^{III} products toward H_2. The first three aminophosphines were first reported by Venanzi's group[5] and the chiral one by Tsuji's group[6] with Payne and Stephan later providing synthesis and characterization details;[7] crystal structures of BNP, TNP, and (*R*)-AMPHOS (referred to hereafter as AMPHOS) are also reported here in our paper.

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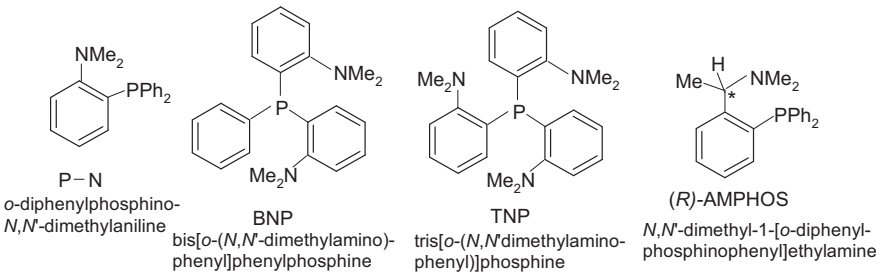
This article, based on Ru(III) chemistry, is dedicated to Professor A.B.P. (Barry) Lever in recognition of his contributions (particularly in ruthenium chemistry) to the development of Canadian chemistry.

Scheme 1. The aminophosphines used in the studies.



Experimental section

General procedures

All manipulations were carried out under an O_2-free argon atmosphere at room temperature (r.t.) (~22 °C) using standard Schlenk techniques. Analytical-grade solvents and $CDCl_3$ from Cambridge Isotope Laboratories were purified and stored using standard methods;[8] DMA was stirred over CaH_2 for at least 24 h, vacuum distilled at 35–40 °C, and stored under argon in the dark. Purified argon (H.P.) and H_2 (Research, extra dry) were Union Carbide Canada products, and anhydrous HCl was obtained from the Matheson Gas Co.; the argon was dried by passage through $CaSO_4$ columns, and H_2 was passed through an Engelhard Deoxo catalytic hydrogen purifier to remove trace O_2. The aminophosphines P–N,[5] bis[*o*-(*N*,*N*′-dimethylamino)phenyl]phenylphosphine (BNP),[5] TNP,[5] and AMPHOS[7] were synthesized by the reported methods; X-ray-quality crystals of BNP and TNP were obtained by recrystallization from their ethanol solutions, and crystals of AMPHOS were acquired by slow evaporation of a benzene solution of the compound. The $RuCl_3{\cdot}3H_2O$ was donated by Colonial Metals Inc., and *trans*-$RuCl_2$(P–N)(PPh_3) was made as reported.[9] Proton sponge (PS = 1,8-bis(dimethylamino)naphthalene) was obtained from Aldrich. NMR spectra were recorded at r.t. on Varian XL300 (300.0 MHz for ^1H and 121.4 MHz for ^{31}P) or Bruker AMX500 (500.0 MHz for ^1H and 202.5 MHz for ^{31}P) instruments. Residual deuterated solvent protons (relative to external $SiMe_4$) and external 85% H_3PO_4 were used as references. Infrared data were recorded on a Bomem Michelson 100 FTIR instrument and are reported in cm^{-1}. The magnetic susceptibilities of the Ru^{III}–*PN* complexes were determined at 20 °C by either the Evans' method (for the P(*p*-tolyl)$_3$-containing species) using $CDCl_3$ solutions containing ~2% *t*-butanol and the complex[10] or the Gouy method (for the less soluble PPh_3-containing species) using a Johnson–Matthey Magnetic Susceptibility Balance, diamagnetic contributions from Ru^{III} and ligands being calculated from Pascal's constants.[11] Microanalyses were performed in this department on a Carlo Erba 1106 instrument; chloride was measured gravimetrically using $AgNO_3$.

$RuCl_3(PPh_3)_2$(DMA)·DMA (1a) and mer,cis-$RuCl_3$(DMA)$_2$(PPh_3)·DMA (1c)

Solid PPh_3 (4.0 g, 15.3 mmol) was added to a dark brown solution of $RuCl_3{\cdot}3H_2O$ (2.0 g, 7.6 mmol) in DMA (60 mL) and the mixture was stirred at r.t. for 24 h. The air-stable, green precipitate was filtered off, washed with DMA (2 × 5 mL) and hexanes (3 × 5 mL), and dried under vacuum. Yield of **1a**: 5.2 g, 75%. Anal. calcd. $C_{44}H_{48}N_2O_2Cl_3P_2Ru$: C 58.32, H 5.34, N 3.09, Cl 11.76; found: C 58.2, H 5.2, N 3.0, Cl 11.8. IR (Nujol): $\nu_{C=O}$ 1632 (free DMA) and 1590 (coordinated DMA), ν_{Ru-Cl} 335 and 319. μ_{eff} = 1.84 BM. After ~4 weeks, dark red crystals precipitated from the DMA filtrate, their identity being established first by X-ray analysis. Yield of **1c**: ~0.5 g, 9%. Anal. calcd. $C_{30}H_{42}N_3O_3Cl_3PRu$: C 49.29, H 5.79, N 5.75; found: C 49.1, H 5.9, N 5.8. IR (Nujol): $\nu_{C=O}$ 1635 (free DMA), 1593 and 1572 (coordinated DMA).

$RuCl_3(P(p\text{-}tolyl_3))_2$(DMA)·DMA (1b)

The synthesis was the same as described for **1a** but using a twofold excess of P(*p*-tolyl)$_3$ (4.7 g, 15.3 mmol). Yield: 4.0 g, 53%. Anal. calcd. $C_{50}H_{60}N_2O_2Cl_3P_2Ru$: C 60.64, H 6.06, N 2.83, Cl 10.76; found: C 60.5, H 6.1, N 2.9, Cl 10.6. IR (Nujol): $\nu_{C=O}$ 1646 (free DMA) and 1598 (coordinated DMA).

mer-$RuCl_3$(P–N)(PPh_3) (2a)

(*a*) A suspension of **1a** (1.0 g, 1.10 mmol) and P–N (0.34 g, 1.10 mmol) in 100 mL of hexanes was refluxed for 24 h and then cooled to r.t., when a red solid precipitated. This was collected and washed with hexanes (4 × 15 mL), dissolved in CH_2Cl_2, and reprecipitated by addition of hexanes. Yield: 0.77 g, 90%. Anal. calcd. $C_{38}H_{35}NCl_3P_2Ru$: C 58.89, H 4.55, N 1.81; found: C 58.7, H 4.7, N 1.8; μ_{eff} = 2.0 BM. X-ray-quality crystals of **2a** were obtained by layering hexanes onto a CH_2Cl_2 solution of the complex.

(*b*) In an NMR-scale reaction, 1 atm of anhydrous HCl was bubbled at r.t. through a dark green C_6D_6 solution of *trans*-$RuCl_2$(P-N)(PPh_3) (~10^{-2} mol L^{-1}). The colour immediately became deep red, and the $^{31}P\{^1H\}$ AX doublets of the Ru^{II} reactant (δ 83.69 and 48,87, $^2J_{PP}$ = 36.5 Hz)[9] disappeared; some red crystals deposited on slow evaporation of the solvent, and an X-ray structure revealed the compound to be **2a**. Anal. found: C 58.7, H 4.6, N 1.8.

mer-$RuCl_3$(P–N)(P(p-tolyl$_3$)) (2b)

The complex was prepared as described for **2a** but using **1b** as precursor (1.0 g, 1.01 mmol). Yield: 0.73 g, 88%. Anal. calcd. $C_{41}H_{41}NCl_3P_2Ru$: C 60.26, H 5.06, N 1.71, Cl 13.02; found: C 60.4, H 5.2, N 1.6, Cl 13.3. μ_{eff} = 1.73 BM.

mer-$RuCl_3$(BNP) (3)

A solution of BNP (38.0 mg, 0.11 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **1a** (100.0 mg, 0.11 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 2.5 h during which time an orange solution formed. The solution volume was then reduced to 3 mL, and hexanes (10 mL) were added to precipitate a dark orange solid that was collected and washed with hexanes (2 × 10 mL). Yield: 55 mg, 90%. Satisfactory elemental analysis was not obtained even after three reprecipitations with CH_2Cl_2–hexanes. μ_{eff} = 1.5 BM. Orange crystals of **3**·$CHCl_3$ were obtained by slow evaporation from a $CHCl_3$ solution of the complex.

mer-$RuCl_3$(AMPHOS)(PPh_3) (4a)

The complex was prepared as described for **2a** but using AMPHOS as the aminophosphine (0.37 g, 1.10 mmol); the product was bright red. Yield: 0.71 g, 80%. Anal. calcd. $C_{40}H_{39}NCl_3P_2Ru$: C 59.82, H 4.89, N 1.74; found: C 59.7, H 5.0, N, 1.7. μ_{eff} = 1.5 BM. X-ray-quality crystals of **4a** were obtained by layering hexanes onto a CH_2Cl_2 solution of the complex.

Table 1. Crystallographic data for the aminophosphine ligands.

Crystal	BNP	TNP	(*R*)-AMPHOS
Formula	$C_{22}H_{25}N_2P$	$C_{24}H_{30}N_3P$	$C_{23}H_{24}NP$
Formula weight	348.41	391.48	333.41
Crystal colour, habit	Colourless, plate	Colourless, irregular	Colourless, prism
Crystal size (mm)	0.04×0.25×0.30	0.40×0.40×0.30	0.25×0.35×0.40
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*Cc*(#9)	*P*1 (#2)	*P*1(#1)
a (Å)	9.026(1)	7.582(1)	10.484(2)
b (Å)	14.859(2)	9.098(1)	12.486(2)
c (Å)	15.677(1)	16.969(4)	8.582(1)
α (°)	90	83.859(7)	96.09(2)
β (°)	106.119(7)	87.340(3)	103.74(1)
γ (°)	90	65.63(1)	114.79(1)
V (Å^3)	2019.9(4)	1060.1(3)	963.3(3)
Z	4	2	2
D_c (g cm^{-3})	1.146	1.226	1.149
μ (cm^{-1})	12.3	1.44	1.40
Total no. of reflections	2271	9643	4663
No. of unique reflections	2168 (R_{int} = 0.024)	4789 (R_{int} = 0.044)	4418 (R_{int} = 0.017)
No. of variables	231	259	431
R_1	0.069 ($I > 2\sigma(I)$)	0.041 ($I > 2\sigma(I)$)	0.033 ($I > 3\sigma(I)$)
wR_2	0.240 ($I > 2\sigma(I)$)	0.103 ($I > 2\sigma(I)$)	0.032 ($I > 3\sigma(I)$)
Goodness-of-fit	1.12	0.96	1.85
Max. diff. (e Å^{-3})	0.23	0.23	0.12
Min. diff. (e Å^{-3})	−0.32	−0.46	−0.16

Table 2. Crystallographic data for the Ru^{III} complexes.

Crystal	**2a**	**3**·$CHCl_3$	**4a**	**1c**
Formula	$C_{38}H_{35}NCl_3P_2Ru$	$C_{23}H_{26}N_2Cl_6PRu$	$C_{40}H_{39}NCl_3P_2Ru$	$C_{30}H_{42}N_3O_3Cl_3PRu$
Formula weight	775.08	675.25	803.13	731.08
Crystal colour, habit	Red, prism	Orange, plate	Red, prism	Red, unavailable[a]
Crystal size (mm)	0.30×0.40×0.45	0.03×0.25×0.25	0.12×0.25×0.25	Unavailable[a]
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*Pna*2$_1$(#33)	*P*2$_1$/n(#14)	*P*2$_1$2$_1$2$_1$(#19)	*P*2$_1$2$_1$2$_1$(#19)
a (Å)	19.615(3)	13.027(3)	13.311(3)	9.839(3)
b (Å)	17.538(2)	10.470(2)	20.649(3)	10.252(2)
c (Å)	10.152(1)	21.221(3)	13.187(4)	33.568(7)
α, β, γ (°)	90, 90, 90	90, 106.92, 90	90, 90, 90	90, 90, 90
V (Å^3)	3492.4(7)	2769.1(9)	3624(1)	3386(5)
Z	4	4	4	4
D_c (g cm^{-3})	1.474	1.620	1.472	1.43
μ (mm^{-1})	7.9	105.8	7.63	7.72
Total no. of reflections	8466	6028	3601	Unavailable[a]
No. of unique reflections	8040 (R_{int} = 0.057)	5414 (R_{int} = 0.033)	2356 ($I > 3\sigma(I)$)	3861 ($I > 3\sigma(I)$)
No. of variables	409	302	424	388
R_1	0.030 ($I > 2\sigma(I)$)	0.056 ($I > 2\sigma(I)$)	0.030 ($I > 3\sigma(I)$)	0.034 ($I > 3\sigma(I)$)
wR_2	0.078 ($I > 2\sigma$(I))	0.153 ($I > 2\sigma$(I))	0.030	0.043
Goodness-of-fit	0.97	1.05	1.25	1.54
Max. diff. (e Å^{-3})	0.52	1.13	0.26	0.78
Min. diff. (e Å^{-3})	−1.08	−1.20	−0.32	Unavailable[a]

[a]See Appendix C (supplementary material).

***mer*-$RuCl_3$(AMPHOS)(P(*p*-tolyl$_3$)) (4b)**

The complex was prepared as described for **2a** but using **1b** as precursor (1.0 g, 1.01 mmol) and an equimolar amount of AMPHOS (0.34 g, 1.01 mmol). A yield of 0.66 g (77%) of the bright red product was obtained. Anal. calcd. $C_{43}H_{45}NCl_3P_2Ru$: C 61.11, H 5.37, N 1.66, Cl 12.58; found: C 61.4, H 5.6, N 1.7, Cl 12.4. μ_{eff} = 1.87 BM.

X-ray crystallographic analyses

The structural measurements for the aminophosphines and the four Ru^{III} complexes were carried out on Rigaku instruments (AFC6S or ADSC area detector). Graphite monochromated MoKα radiation (0.71069 Å) was used for TNP, AMPHOS, **2a**, and **4a**; CuKα radiation (1.54178 Å) was used for BNP and **3**·$CHCl_3$. Data were collected at 21 ± 1 °C, except for the TNP structure when –93 ± 1 °C was used. Tables 1 and 2 list some crystallographic data for the aminophosphines and complexes, respectively. Full details for data collection, data reduction, structure solution and refinement, and the relevant references for the procedures used are given in the "Supplementary material" section, which contains crystallographic data in CIF format for BNP, TNP, **2a**, and **3**·$CHCl_3$ (CCDC Nos. 962715–962718, respectively) and Appendices A, B, and C for the structures of AMPHOS, **4a**, and **1c**, respectively, in non-CIF format.

Results and discussion

Structures of the aminophosphines

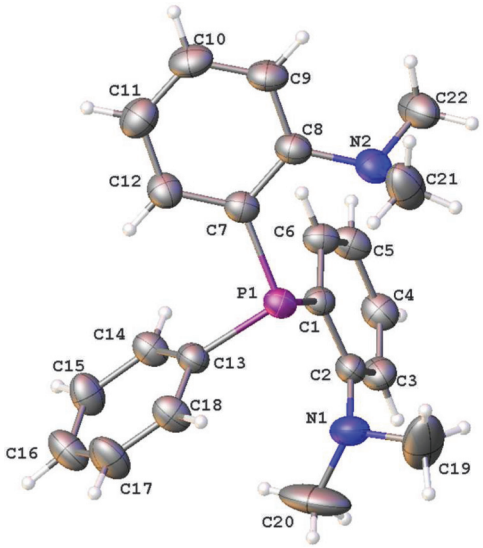
Although the four aminophosphines shown in Scheme 1 have been known for at least 30 years, only the crystal structure of P–N has been reported;[12] this paper also gives a survey of the early

Table 3. Selected bond lengths and angles for BNP, TNP, and (*R*)-AMPHOS, with estimated standard deviations in parentheses.

	Bond	Length (Å)	Bond	Angle (°)
BNP	C(1)–P(1)	1.836 (7)	C(1)–P(1)–C(7)	103.6 (3)
	C(7)–P(1)	1.841 (8)	C(1)–P(1)–C(13)	98.3 (3)
	C(13)–P(1)	1.847 (8)	C(7)–P(1)–C(13)	102.1 (4)
TNP	C(1)–P(1)	1.8470 (15)	C(1)–P(1)–C(9)	101.30 (7)
	C(9)–P(1)	1.8534 (16)	C(1)–P(1)–C(17)	99.46 (6)
	C(17)–P(1)	1.8526 (14)	C(9)–P(1)–C(17)	101.01 (7)
(*R*)-AMPHOS[a]	C(1)–P(1)	1.840 (6)	C(1)–P(1)–C(7)	100.9 (2)
	C(7)–P(1)	1.837 (5)	C(1)–P(1)–C(13)	102.8 (3)
	C(13)–P(1)	1.835 (5)	C(7)–P(1)–C(13)	101.6 (2)

[a]Data for one of two independent molecules in the asymmetric unit.

Fig. 1. ORTEP diagram of BNP with 33% probability thermal ellipsoids.



work on metal–*PN* ligand systems in homogeneous catalysis. Thus, crystals of BNP, TNP, and AMPHOS were subjected to X-ray analysis. Table 3 lists selected bond lengths and angles for these three aminophosphines.

BNP contains one more dimethylamino group than P–N and has three potential binding sites. As expected, the ORTEP diagram (Fig. 1) reveals trigonal pyramidal geometry about the phosphorus atom; the average P–C bond length of 1.84 Å is basically the same as that of PPh_3 (1.83 Å), while the C(1)–P(1)–C(7) (103.6°), C(7)–P(1)–C(13) (102.1°), and C(1)–P(1)–C(13) (98.3°) bond angles differ slightly from the average C–P–C angle of 103° in PPh_3,[13] the difference presumably arising because of the steric effects of the NMe_2 groups. The dihedral angles for the P(1)–C(1)–C(2)–N(1) and P(1)–C(7)–C(8)–N(2) planes are –1.2(7)° and 3.7(8)°, respectively, indicating that the NMe_2 groups and the phosphorus atom lone pair point essentially in the same direction.

TNP with three NMe_2 groups has four potential binding sites and, like BNP, the structure (Fig. 2) shows that the phosphorus atom and the amino groups point in the same direction as indicated by the small dihedral angles of –2.4(2)°, –10.9(2)°, and 4.4(2)° for the three relevant P–C–C–N planes. The P–C bond lengths and C–P–C angles are in the ranges 1.84–1.85 Å and 99.4°–101.3°, respectively.

The AMPHOS structure, which confirms the (*R*)-configuration, is shown in Fig. 3; there are two independent molecules in the asymmetric unit (one is shown), and these are related by a pseudo-centre of symmetry with only the chiral amine portion of the structure breaking the pseudo-inversion symmetry. The P–C bond lengths and C–P–C angles of both molecules are "standard", being, respectively, 1.83–1.84 Å and 101.6°–102.8°.

Fig. 2. ORTEP diagram of TNP with 33% probability thermal ellipsoids.

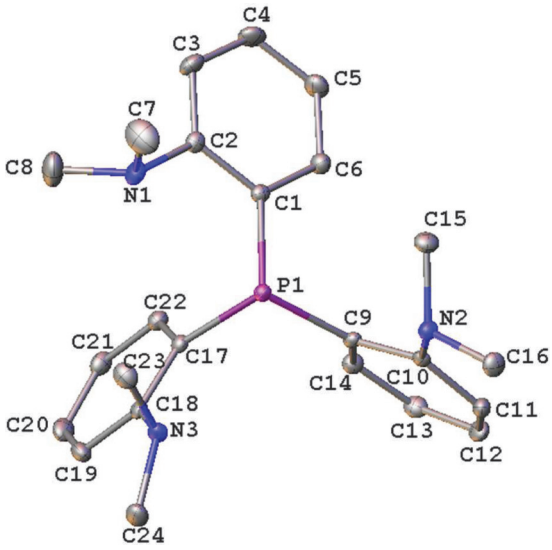
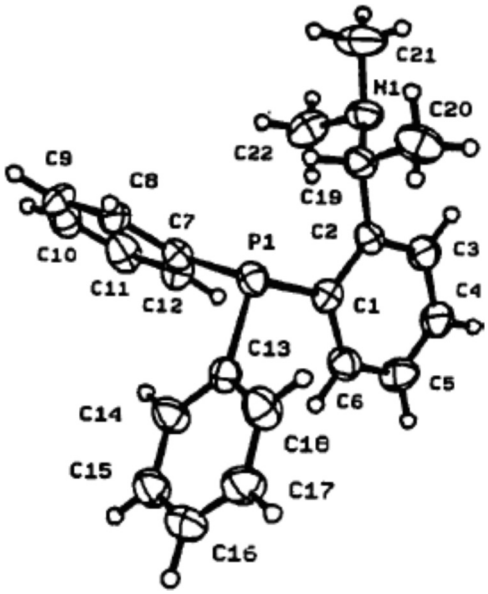


Fig. 3. ORTEP diagram of (*R*)-AMPHOS with 50% probability thermal ellipsoids; one of two independent molecules in the asymmetric unit.



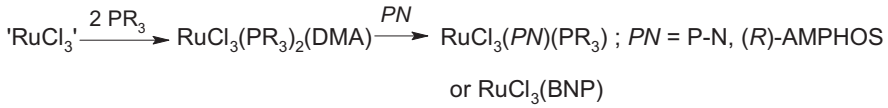
In all three aminophosphines, the N–C bond lengths and C–N–C angles are in the ranges of 1.41–1.48 Å and 108–116°, respectively, and are again standard values.

Ruthenium(III)–aminophosphine complexes

On the 1:1 reactions of the Ru^{III} precursors **1a** and **1b** with each of P–N, BNP, and AMPHOS, PR_3 and DMA ligands are substituted, and air-stable Ru^{III}–*PN* complexes are generated: P–N forms the *mer*-$RuCl_3$(P-N)(PR_3) complexes **2a** (R = Ph) and **2b** (R = *p*-tolyl), BNP forms *mer*-$RuCl_3$(BNP) (**3**), and (*R*)-AMPHOS gives the *mer*-$RuCl_3$-(AMPHOS)(PR_3) species **4a** (R = Ph) and **4b** (R = *p*-tolyl). The chemistry is summarized in Scheme 2.

TNP did not react with **1a** or **1b**, under the conditions used for the three other *PN* ligands, presumably due to mutual repulsion of the sterically demanding PR_3 and TNP ligands; TNP was reported at the time of its synthesis to form four-coordinate, square planar complexes of the type MX_2(*P*,*N*-TNP), where M = Pd^{II} and Pt^{II} and X = halide,[5b] and catalysts based on Pd-TNP species have been used for ethylene oligomerization and polymerization of a substituted

Scheme 2. Synthetic route to the Ru^{III}–aminophosphine complexes.



thiophene.[14] Cobalt(II) and nickel(II) complexes containing TNP are also known.[5a]

The structures of **2a** (Fig. 4), **3**·$CHCl_3$ (Fig. 5), and **4a** (Fig. 6) all show distorted octahedral geometry, with *mer*-chloride ligands. In **2a** and **4a**, the nitrogen atom is *trans* to the monodentate phosphine; in **3**, the BNP ligand is also bonded in a *mer*-configuration. Selected bond lengths and angles are given in Tables 4 and 5, respectively, and they are essentially as expected. In **2a**, the major distortions from the octahedral geometry involve the P1 atom of the P–N ligand, which shows distortion from orthoganolity up to ~12° and ~10° from linearity within the *trans*-Cl ligands; in **4a**, the corresponding distortions are both ~10°, and the *trans*-Cl–Ru–Cl angle is 171.6°, which is ~5° more than for **2a**; in **3**, the departure from orthogonality is only ~8°, although the *mer*-coordination of BNP leads to a restricted *trans*-N–Ru–N angle of only 160°. The aminophosphine ligand in **2a** and **4a** subtends angles at the ruthenium atom of about 79° and 90°, respectively, and in **3**, the two such angles are about 85° and 82°. The C–P–C and C–N–C bond angles at the coordinated phosphorus and nitrogen atoms are within ~6° of the tetrahedral angle, while those involving coordination to ruthenium (i.e., C–P–Ru and C–N–Ru) are always greater than the tetrahedral angle (up to ~20°).

The bond lengths are similar to those found within examples of other Ru^{III} complexes containing phosphorus, nitrogen, or chloride donor ligands,[15] including a related *mer*-$RuCl_3$-*PN*-ligand species where *PN* is diphenyl(2-pyridyl)phosphine,[15e] but interesting features are evident. The Ru–P and Ru–N bond lengths in **3** are at least 0.15 Å shorter than the average values of these bond lengths in **2a** and **4a**, presumably because of the rigidly bonded *mer*-BNP. In **3** also, two chloride ligands, Cl(2) and Cl(3), are weakly hydrogen bonded to the hydrogen atom of the $CHCl_3$ solvate with Cl···H distances of 2.68 and 2.83 Å (Fig. 5) and, as a result, the two associated Ru–Cl bonds are longer by up to ~0.16 Å than the Ru–Cl(1) bond, although some lengthening of the Ru–Cl(3) bond results from the strong *trans*-influence of the phosphorus atom of the BNP ligand. The same *trans* influence is seen in the structures of **2a** and **4a**, where the relevant Ru–Cl bond is 0.07–0.08 Å longer than the other two Ru–Cl bonds (Table 4). Finally, the average values of the *trans*-Ru–Cl bond lengths in **2a** and **4a** are ~0.05 Å shorter than the corresponding value found for the Ru^{II} analogue, *trans*-$RuCl_2$(P–N)(P(*p*-tolyl$_3$)),[9b] which seems reasonable in terms of the difference in oxidation states.

The magnetic moments of complexes **2–4** (1.5 to 2.0 BM) are consistent with high-spin Ru^{III} species. Of note, the reported complex $RuCl_3$(NO)(P–N) appears analogous to **2a** and **2b**, but in fact is a $Ru^{II}(NO^+)$ species;[16] other Ru^{II}(P–N)-containing complexes have been reported.[17]

Ruthenium(III) precursor complexes

The Ru^{III}–aminophosphine complexes discussed above are the first monomeric Ru^{III} species to be formed via the useful, easily synthesized, air-stable Ru^{III} precursors, $RuCl_3(PR_3)_2$(DMA)·DMA (**1a** and **1b**). We have previously used these precursors with phosphine ligands for formation of monomeric and dimeric Ru^{II} complexes and dimeric Ru^{II}/Ru^{III} mixed-valence complexes;[4b–4d] and a species that we initially formulated as a Ru^{III}_2 species, $RuH(PR_3)_2(\mu\text{-}Cl)_2(\mu\text{-}H)Ru(H)_2(PR_3)_2$,[4b] was later shown (by us) to be the first structurally characterized dimeric species to contain a molecular H_2 ligand, and so, it is, in fact, formally a Ru^{II}_2 complex.[18] Of interest, when **1a** and **1b** are reacted with chelating bidentate P–P ligands under the identical conditions used for the

Fig. 4. ORTEP diagram of *mer*-$RuCl_3$(P–N)(PPh_3) (**2a**) with 33% probability thermal ellipsoids.

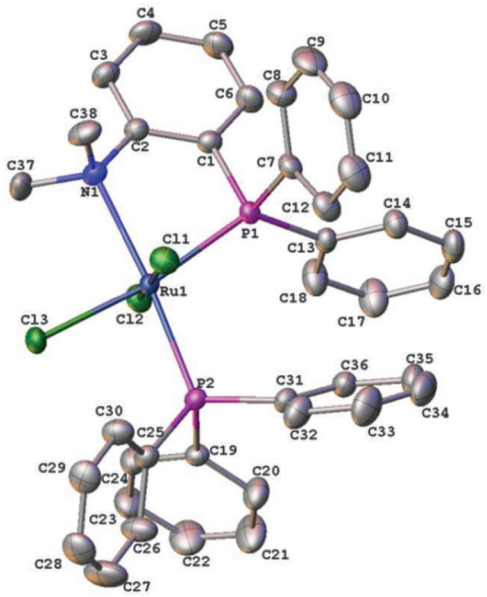
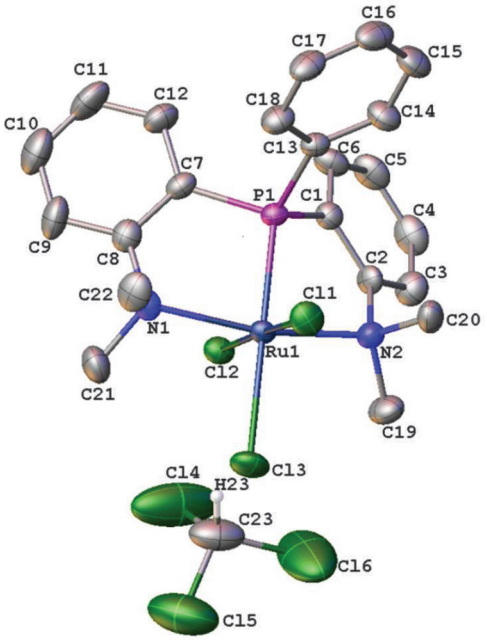


Fig. 5. ORTEP diagram of *mer*-$RuCl_3$(BNP) (**3**)·$CHCl_3$ with 33% probability thermal ellipsoids.



PN ligands, the products are the mixed-valence, triply chloride-bridged species Ru_2Cl_5(P-P)$_2$ and the OPR_3 oxide, the reduction process being caused by the presence of trace water.[19] The difference in reactivity of the *PN* and P–P ligands is attributed to the σ-donor ability of the amine function that better stabilizes the Ru^{III} oxidation state. Complexes **1a** and **1b** are much superior Ru^{III}

Fig. 6. ORTEP diagram of *mer*-$RuCl_3$(AMPHOS)(PPh_3) (**4a**) with 50% probability thermal ellipsoids.

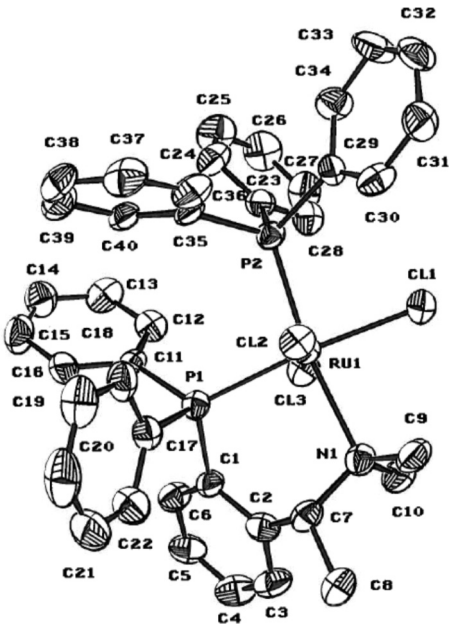


Table 4. Selected bond lengths for the *mer*-complexes $RuCl_3$(P–N)(PPh_3) (**2a**), $RuCl_3$(BNP) (**3**), $RuCl_3$(AMPHOS)(PPh_3) (**4a**), and $RuCl_3(PPh_3)(DMA)_2$·DMA (**1c**), with estimated standard deviations in parentheses.

Bond	Length (Å)	Bond	Length (Å)
Complex 2a			
Ru–Cl(1)	2.3272 (9)	Ru–P(1)	2.3666 (9)
Ru–Cl(2)	2.3331 (9)	Ru–P(2)	2.3497 (8)
Ru–Cl(3)	2.3980 (8)	Ru–N(1)	2.350 (3)
Complex 3·$CHCl_3$			
Ru–Cl(1)	2.3182 (15)	Ru–P(1)	2.1995 (13)
Ru–Cl(2)	2.3577 (14)	Ru–N(1)	2.204 (5)
Ru–Cl(3)	2.4847 (15)	Ru–N(2)	2.210 (5)
Cl(2)···H(23)	2.68	Cl(3)···H(23)	2.83
Complex 4a			
Ru–Cl(1)	2.398 (2)	Ru–P(1)	2.401 (2)
Ru–Cl(2)	2.319 (2)	Ru–P(2)	2.374 (2)
Ru–Cl(3)	2.356 (2)	Ru–N(1)	2.355 (6)
Complex 1c			
Ru–Cl(1)	2.345 (1)	Ru–O(1)	2.064 (3)
Ru–Cl(2)	2.350 (1)	Ru–O(2)	2.200 (3)
Ru–Cl(3)	2.311(1)	Ru–P	2.273(1)

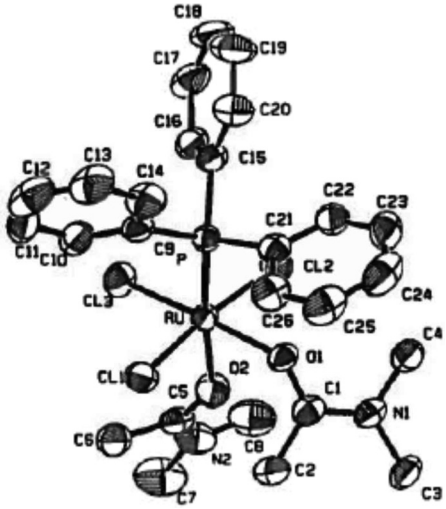
precursors than the commercially variable $RuCl_3·3H_2O$, which is a mixture of Ru^{III} and Ru^{IV} compounds.[20]

To the best of our knowledge, only one other group has used **1a** and **1b** as synthetic precursors, the products again being Ru^{II}[21] or Ru^{II}–Ru^{III} species.[22] Worth noting is the accidental isolation of crystals of *mer*,*cis*-$RuCl_3(DMA)_2(PPh_3)$·DMA (**1c**) that precipitates from the filtrate obtained from the synthesis of **1a**; one PPh_3 ligand of **1a** has been replaced by DMA. Attempts to make **1c** on purpose by using a 1:1 $PPh_3/RuCl_3·3H_2O$ reaction in DMA were surprisingly unsuccessful. The basic octahedral structure of **1c** (Fig. 7), which is less distorted than those of **2a** and **4a**, reveals *cis*-O-bonded DMA ligands and, we believe, is the first reported for a Ru^{III}–DMA complex. There are structures reported for the Ru^{II} complexes *trans*,*trans*-$RuCl_2(PPh_3)_2(CO)(DMA)$[21] and *trans*,*trans*-$RuCl_2(PCy_3)_2(H_2)(DMA)$[23] in which the Ru–O bond lengths are 2.149 Å (*trans* to CO) and 2.323 Å (*trans* to H_2), respectively. The Ru–O bond lengths in **1c** are 2.064 and 2.200 Å and are respectively *trans* to a chlorine and a phosphorus atom, the significantly longer

Table 5. Selected bond angles for the *mer*-complexes $RuCl_3$(P–N)(PPh_3) **(2a)**, $RuCl_3$(BNP) (**3**), $RuCl_3$(AMPHOS)(PPh_3) (**4a**), and $RuCl_3(PPh_3)(DMA)_2$·DMA (**1c**), with estimated standard deviations in parentheses.

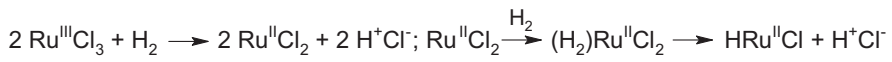
Bond	Angle (°)	Bond	Angle (°)
Complex 2a			
Cl(1)–Ru–Cl(2)	175.00 (3)	P(2)–Ru–Cl(3)	84.22 (3)
Cl(1)–Ru–Cl(3)	92.37 (3)	P(2)–Ru–Cl(2)	94.64 (3)
Cl(1)–Ru–P(1)	90.15 (3)	P(2)–Ru–N	175.38 (8)
Cl(1)–Ru–P(2)	88.67 (3)	P(2)–Ru–P(1)	105.02 (3)
Cl(1)–Ru–N	93.77 (8)	Cl(3)–Ru–Cl(2)	91.69 (3)
Cl(2)–Ru–P(1)	85.37 (3)	Cl(3)–Ru–N	91.75 (8)
Cl(2)–Ru–N	83.18 (8)	Cl(3)–Ru–P(1)	170.47 (3)
		N–Ru–P(1)	78.91 (8)
Complex 3·$CHCl_3$			
Cl(1)–Ru–Cl(2)	177.63(6)	Cl(2)–Ru–N(2)	82.95 (14)
Cl(1)–Ru–Cl(3)	87.77 (6)	Cl(3)–Ru–P	179.91 (7)
Cl(2)–Ru–Cl(3)	90.00 (6)	Cl(3)–Ru–N(1)	95.51 (14)
Cl(1)–Ru–P	92.13 (6)	Cl(3)–Ru–N(2)	98.28 (13)
Cl(1)–Ru–N(1)	98.40 (14)	P(1)–Ru–N(1)	84.50 (14)
Cl(1)–Ru–N(2)	96.57 (14)	P(1)–Ru–N(2)	81.74 (13)
Cl(2)–Ru–P	90.09 (5)	N(1)–Ru–N(2)	159.99 (18)
Cl(2)–Ru–N(1)	82.61 (14)		
Complex 4a			
Cl(1)–Ru–Cl(2)	99.15 (7)	Cl(2)–Ru–N	87.2 (1)
Cl(1)–Ru–P(1)	170.08 (7)	Cl(3)–Ru–P(1)	82.24 (7)
Cl(1)–Ru–P(2)	85.73 (7)	Cl(3)–Ru–P(2)	98.01 (7)
Cl(1)–Ru–N	86.5 (2)	Cl(3)–Ru–N	90.0 (1)
Cl(1)–Ru–Cl(3)	88.53 (7)	P(1)–Ru–P(2)	99.09 (7)
Cl(2)–Ru–Cl(3)	171.61 (8)	P(1)–Ru–N	89.9 (2)
Cl(2)–Ru–P(1)	89.87 (7)	P(2)–Ru–N	168.7 (2)
Cl(2)–Ru–P(2)	86.00 (7)		
Complex 1c			
O(1)–Ru–P	90.91 (8)	O(1)–Ru–O(2)	85.9 (1)
O(1)–Ru–Cl(3)	175.15 (9)	P–Ru–Cl(3)	93.69 (4)
O(1)–Ru–Cl(1)	88.5 (1)	P–Ru–Cl(1)	90.09 (5)
O(1)–Ru–Cl(2)	84.7 (1)	P–Ru–Cl(2)	90.43 (5)
O(2)–Ru–P	173.9 (1)	Cl(3)–Ru–Cl(1)	93.01 (5)
O(2)–Ru–Cl(3)	89.3 (1)	Cl(3)–Ru–Cl(2)	93.73 (5)
O(2)–Ru–Cl(1)	95.1 (1)	Cl(1)–Ru–Cl(2)	173.19 (5)
O(2)–Ru–Cl(2)	84.1 (1)		

Fig. 7. ORTEP diagram of *mer*,*cis*-$RuCl_3(DMA)_2(PPh_3)$·DMA (**1c**) with 50% probability thermal ellipsoids.



bond resulting from the *trans* influence of the phosphine ligand. The geometries of the coordinated DMA in all three structures are essentially the same and correspond to that found in other transition metal – DMA complexes.[24]

Scheme 3. Formation of Ru^{II}-hydridochloro species from a Ru^{III} precursor; ancillary ligands omitted.



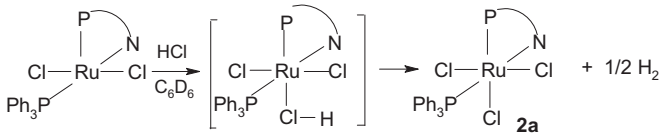
Reactivity of the *mer*-$RuCl_3$(P–N)(PR_3) complexes (2a and 2b)

No reactions were observed on exposure of CH_2Cl_2 solutions of the Ru^{III}–aminophosphine complexes (at ~10^{-2} mol L^{-1}) to 1 atm H_2 at r.t.; however, in DMA solution, the initially dark red colour of **2a** (or **2b**) rapidly becomes orange–red. The reaction with **2b**, for example, generates a solution whose $^{31}P\{^1H\}$ spectrum shows just two species in a ratio of ~2:1 that are considered to be $RuCl_2$(P–N)(P(*p*-tolyl)$_3$)(DMA) (**5**) and (η^2-H_2)$RuCl_2$(P–N)(P(*p*-tolyl)$_3$) (**6**), with respective AX doublet patterns at δ 56.6 and 72.4 ($^2J_{PP}$ = 39.9 Hz) and δ 53.5 and 59.1 ($^2J_{PP}$ = 25.5 Hz). The spectrum for **5** is the same as that seen on dissolution of the known complex $RuCl_2$(P–N)(P(*p*-tolyl)$_3$)[9b] in DMA under argon, and exposure of this solution to H_2 generates essentially the same 2:1 spectrum noted above; such reactivity with H_2 in CH_2Cl_2, $CHCl_3$, and acetone solutions, is known to generate the molecular H_2 derivative.[9b,25] Further, when DMA solutions of **2a** or **2b** are similarly reacted with H_2 in the presence of six equivalents of PS, only one in situ product is seen in the $^{31}P\{^1H\}$ spectrum, and this is considered to be the hydridochloro species Ru(H)Cl(P–N)(PR_3), which have been isolated via reactions of PS with the $RuCl_2$(P–N)(PR_3) complexes in benzene solution;[9b,25] the $^{31}P\{^1H\}$ spectra for both of these complexes in DMA (doublets at δ ~ 86 and ~70 with $^2J_{PP}$ ~ 35 Hz) are very similar to those seen in the in situ PS reactions. Use of two to four equivalents of PS in the H_2/DMA reaction generates a mixture of the η^2-H_2 and hydridochloro species, the relative amounts of the latter increasing with greater PS concentration.

The presence of a base such as DMA[26] or PS is required for the reduction of the Ru^{III} to Ru^{II}; this oxidation state allows for formation of the η^2-H_2 complex that, in the presence of PS (a stronger base than DMA), gives the hydridochloro species The relevant chemistry is outlined in Scheme 3, in which both the initial and final steps require base to react with the HCl coproduct. The net chemistry has been well established within chloro-phosphine systems,[4b,18] but only in the case of the chloro-aminophosphine systems is there direct evidence for the monomeric η^2-H_2 complex,[9b,25] although an η^2-H_2 moiety within dimeric Ru-(chloro)-phosphine species is well known.[18,27] Of note, the Ru^{II} species mentioned in this section (Scheme 3) are all O_2 sensitive, and the in situ synthesis via H_2 reduction of Ru^{III} provides a convenient way for their preparation.

Of significant interest, after our extensive studies on reactions of the five-coordinate *trans*-$RuCl_2$(P–N)(PR_3) complexes with small molecules (H_2S and thiols,[3a] H_2,[9b,25] N_2,[9b] N_2O,[28] H_2O and alcohols,[29] and CO and NH_3[30]), which all form (at least initially) six-coordinate 1:1 adducts, gaseous HCl was also tested. The red, crystalline solid isolated from the r.t. reaction of anhydrous HCl gas with the dark green C_6D_6 solution of $RuCl_2$(P–N)(PPh_3) was surprisingly *mer*-$RuCl_3$(P–N)(PPh_3) (**2a**), as discovered via what turned out to be a duplicate X-ray analysis and then elemental analysis! We had hoped optimistically for a structure showing a metal-coordinated HCl, which has yet to be reported, although Sellman's group has isolated a Ru^{II}(ClH)(PPh_3)("S_4") complex, where "S_4" is a dianionic, tetradentate dithiolate ligand, with spectroscopic evidence suggesting that the HCl is coordinated as a chloride ligand with the H^+ hydrogen bonded to both the chloride and a thiolate.[31] Noted also in this paper is a reaction where this Ru^{II} species is converted under N_2 to $Ru^{III}Cl(PPh_3)$("S_4"), with the speculation that the H^+ might be the oxidant. In our reaction, written speculatively as proceeding via an intermediate with coordinated HCl (Scheme 4), the proton must be the oxidant; unfortunately, the required H_2 coproduct was not detected (δ ~ 4.5) because its concentration is low and the solution contains paramagnetic Ru^{III}. The observations imply that the reaction steps in

Scheme 4. Plausible steps for the HCl/$RuCl_2$(P–N)(PPh_3) reaction to give **2a**; P–N is shown in Scheme 1.



Scheme 4 are reversible and that the production of H_2 would require two Ru^{II} (or a Ru^{II}_2) species. More studies are needed on this reaction, particularly at low temperature, to confirm the stoichiometry and elucidate mechanistic details. Relevant also is a report that gives a crystal structure of a Pt^{II} complex formulated [$PtCl_2$·HCl]Cl, where L is the *P*,*N*-coordinated aminophosphine $Ph_2P(CH_2)_2N(H)^tBu$; however, the HCl is present as the proton in an $-N(H)_2{}^tBu^+$ moiety and an associated chloride anion;[32] a related, reversible, solid-state reaction of two equivalents of HCl with $CuCl_2L_2$ (L = 3-chloropyridine) has been shown to give $[HL^+]_2CuCl_4{}^{2-}$.[33] Such protonation in our system would generate a $Ru^{II}Cl_3$(P–NH^+)(PPh_3) intermediate, but we consider this less likely to result in a redox process to give $Ru^{III}Cl_3$(P–N)(PPh_3). There is certainly one paper that reports a one-electron oxidation of a transition metal ($Ni^I \rightarrow Ni^{II}$) with coproduction of H_2, and kinetic data were interpreted in terms of a mechanism essentially involving initial protonation to form $Ni^{III}H$ followed by bimolecular decomposition of this to Ni^{II} and H_2.[34] Processes involving two-electron oxidative addition of HCl are well known;[35] such an initial step in our Ru^{II} system would involve formation of a Ru^{IV}–hydride intermediate, with the Ru^{III} product being formed via a subsequent bimolecular process. A reviewer suggests that a species with coordinated Cl···HCl moiety is also a feasible intermediate for the reaction of Scheme 4, but we prefer reactivity involving the vacant site.

Preliminary studies on the other Ru^{III} complexes **3** and **4a** and **4b** with H_2 suggest behaviour similar to that of **2a** and **2b**. The systems are active for catalytic hydrogenation of selected olefinic substrates and imines in C_6H_6/MeOH mixed solvents at ~10 atm H_2; up to 100% conversions can be achieved, but asymmetric induction using **4a** and **4b**, the chiral AMPHOS species, is minimal (<10%).[36]

Conclusions

Synthetic routes to air-stable aminophosphine complexes of Ru^{III} via easily made Ru^{III} precursors are described; earlier work has shown that use of phosphine ligands generates Ru^{II} or dimeric Ru^{II}/Ru^{III} mixed-valence complexes. Reported here are X-ray structures of three known aminophosphine ligands, three Ru^{III} complexes containing aminophosphine ligands, and a precursor-type Ru^{III}–DMA complex, which is the first structurally reported *N*,*N*′-dimethylactamide complex of Ru^{III}. The aminophosphine complexes can be reduced in situ by H_2 to air-sensitive Ru^{II} species, this providing a convenient route to the usual +2 oxidation state of catalytic ruthenium species. The formation of *mer*-$RuCl_3$-(P–N)(PPh_3) by reaction of $RuCl_2$(P–N)(PPh_3) with gaseous HCl provides a rare example of this reagent acting as an overall one-electron oxidant.

Supplementary material

Supplementary material is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0539. This provides crystal data for (*R*)-AMPHOS,

and complexes **4a** and **1c**, in non-CIF form; the CCDC reference numbers for BNP, TNP, and complexes **2a** and **3**·$CHCl_3$ are 962715–962718, respectively.

Acknowledgements

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