Chiral and Achiral Diphosphine Complexes of Ruthenium(II) Incorporating Labile Nitrile Ligands: Synthesis and Solution Chemistry of Mono- and Dinuclear Derivatives of $Ru_2Cl_4(PP)_2$ (PP = Chelating Diphosphine)

Deryn E. Fogg and Brian R. James*

Department of Chemistry, The University of British Columbia, Vancouver, BC V6T 1Z1, Canada

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A family of nitrile complexes has been prepared by reaction of $Ru_2Cl_4(PP)_2$ or $RuCl_2(PP)(PPh_3)$ (PP = $Ph_2P(CH_2)_4PPh_2$ (dppb), $Ph_2PCH_2CHOCMe_2OCHCH_2PPh_2$ (diop), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap)) with MeCN or PhCN, the product formed depending strongly on the reaction conditions. At high nitrile concentrations, the principal species present is $RuCl(PP)(RCN)_3^+X^-$ (X = Cl); the cation can generally be isolated (as the PF_6 salt) by abstraction of the chloride counterion with NH_4PF_6. Use of 2 equiv of NH_4PF_6 generates $Ru(PP)(RCN)_4^{2+}(PF_6^-)_2$ (PP = dppb). In the absence of a halide-abstracting agent, addition of hexanes or diethyl ether precipitates neutral $RuCl_2(PP)(RCN)_2$ species, which undergo further loss of nitrile in the solid state (R = Me) or in solution (R = Me, Ph). Redissolution of the neutral species in chlorocarbon solvents gives $Ru_2Cl_3(PP)_2(RCN)_2^+X^-$ (X = Cl) and, in benzene, $Ru_2Cl_4(PP)_2(RCN)$. The dinuclear cation (X = PF_6) is also accessible by reaction of $RuCl(PP)(RCN)_3^+PF_6^-$ with CH_2Cl_2 or $CDCl_3$, while the mononitrile can be obtained directly by reaction of $Ru_2Cl_4(PP)_2$ or $RuCl_2(PP)(PPh_3)$ with small amounts of nitrile in benzene.

Introduction

Utilization of Ru complexes in homogeneous catalysis appears to grow exponentially. The use of Ru catalysts containing chelating bis(tertiary phosphine) ligands (PP) for asymmetric hydrogenation was established about 20 years ago,[1,2] and there have been recent spectacular advances in the area for a wide range of unsaturated organics.[3] More generally, besides being active for the "more classic" catalytic organic reactions (such as hydrogenation, isomerization, hydrosilylation, decarbonylation, dehydration, H/D exchange, homologation of amines, etc.),[4] Ru phosphine complexes also find increasing utilization in a much wider range of catalytic reactions including, for example, C−H/olefin coupling,[5] oxidations,[6] aldol and Michael additions via C−H activation of nitriles,[7] and addition of carboxylic acids to alkynes.[8]

The use of nitriles as ancillary ligands in potential catalysts is attractive because of their general lability and ease of replacement,[9] for example by an organic moiety, and thus we and others[10−12] chose to study the interaction of dichlororuthenium(II) phosphine compexes with nitriles. While early studies in this area were directed principally at complexes of monodentate phosphines,[10] we were interested, for the purposes of asymmetric catalysis, in extending this chemistry to complexes of chelating chiral diphosphines. The susceptibility of the nitrile ligands themselves in such systems to H_2-hydrogenation has been examined in related work from this laboratory,[13,14] and a detailed assessment of the comparative catalytic activity toward imine hydrogenation of the nitrile complexes described herein has been reported.[15] The present work involved initially the optimized syntheses and solution behavior using the achiral diphosphine dppb ($Ph_2P(CH_2)_4PPh_2$) as a model for the later used chiral diphosphines diop and binap, which likewise form seven-membered chelate rings. Several of the dppb complexes of MeCN have been briefly described.[13,16,17] Routes to some of the mononuclear binap complexes, via thermolysis of $RuCl(arene)(binap)^+X^-$ or $Ru_2Cl_4(binap)_2(NEt_3)$ in the presence of nitriles, were reported by other groups during the course of this present work;[11,12] one of these papers[11] noted the variation of the catalytic activity and stereoselectivity of a Ru(binap) system with solvent composition, especially if MeCN was used as cosolvent. Together with improved routes to a range of nitrile-containing complexes with Ru(PP) moieties, also discussed here is their surprisingly intricate solution behavior

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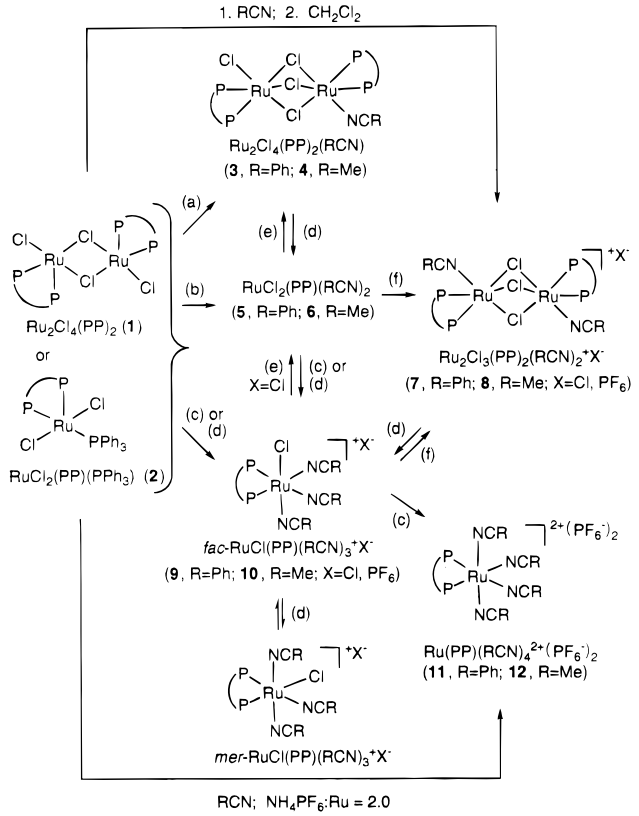
Scheme 1. Summary of Relationships between Nitrile Complexes (Stereochemistry Omitted; See eq 1 and Figures 1 and 2)[a]



[a] Conditions: (a) benzene, RCN:Ru_2 = 1.0; (b) RCN; (c) RCN, NH_4PF_6:Ru = 1.0; (d) RCN; (e) vacuum (R = Me) or benzene; (f) CH_2Cl_2 or $CDCl_3$. PP: In the text, **a**, **b**, and **c** refer to dppb, diop, and binap species, respectively; in one case (**10d**), **d** refers to a bis PPh_3 complex.

(Scheme 1), which can be exploited to gain access to any member of this network from virtually any other.

Experimental Section

Synthetic and spectroscopic work was performed under Ar at room temperature (room temperature, ~20 °C). Solvents were distilled from CaH_2 (CH_2Cl_2) or sodium−benzophenone (C_6H_6, ether, hexanes). Acetonitrile and benzonitrile were distilled prior to use and stored under Ar in the dark. NMR spectra were recorded on a Varian XL300 spectrometer, using the residual proton of the solvent (^{1}H) or free PPh_3 (^{31}P: C_6D_6, −5.06; $CDCl_3$, −5.46; CD_2Cl_2, −5.64; CD_3CN, −6.49 ppm with respect to 85% external H_3PO_4) as internal standards [s = singlet, dd = doublet of doublets, q = quartet, sept = septet; all J values are in Hz]. Infrared spectra (cm^{-1}) were measured as Nujol mulls between KBr plates on a Bomem Michelson 100 FT-IR spectrophotometer (w = weak). Elemental analyses were performed by Mr. P. Borda of the UBC Microanalytical Service; all new complexes gave satisfactory analyses (Table S1, Supporting Information) unless otherwise indicated. The Ru precursors $Ru_2Cl_4(PP)_2$ (**1a**−**c**),[2,16] $RuCl_2(PPh_3)_3$,[4] and $RuCl_2$-(PP)(PPh_3) (**2a**−**c**)[6,18,19] (PP: **a**, dppb; **b**, diop; **c**, binap) were prepared as previously described. We reported recently the syntheses of the Ru(dppb)$(RCN)_4^{2+}(PF_6^-)_2$ species (R = Ph, **11a**, or Me, **12a**), including the X-ray structure of the MeCN complex.[17]

The ^{31}P{^{1}H} NMR data are listed with the individual, synthesized complexes (see below); ^{1}H NMR data for **3a**−**c**, **4a**, **5a**−**c**, and **6a**, and the PF_6^- salts of **7a**, **8a**, **9a**,**b**, and **10a**,**d** are given in the Supporting Information, Table S2.

$Ru_2Cl_4(PP)_2$(PhCN). PP = dppb (3a). A suspension of **5a** (51 mg, 0.063 mmol) in C_6H_6 (10 mL) was stirred for 24 h. The solution was concentrated, and Et_2O was added to obtain an orange precipitate, which was filtered off, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 29 mg (71%). ^{31}P{^{1}H} NMR (C_6D_6): δ 54.7, 54.4 (ABq, J = 44.2); 52.4, 45.7 (ABq, J = 35.8). IR: ν(C≡N) 2230 (w).

PP = diop (3b). Precursor **2b** (108 mg, 0.115 mmol) was stirred in C_6H_6 (5 mL) with a small excess of PhCN (8 μL, 1.4 equiv per Ru_2) for 1 h. The solution was then concentrated to 0.25 mL and Et_2O added to precipitate the product, which was reprecipitated from C_6H_6−hexanes. Yield: 71 mg (85%). ^{31}P{^{1}H} NMR (C_6D_6): δ 47.1, 44.1 (ABq, J = 42.1); 44.7, 35.8 (ABq, J = 34.7); 44.6, 39.0 (ABq, J = 35.6); ~44−45 (concealed; inferred from integration). IR: ν(C≡N) 2232 (w).

PP = binap (3c). The complex was prepared from **5c** in 4 h, in the manner described for **3a**, but with a further reprecipitation from C_6H_6−hexanes (83% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 62.5, 56.3 (ABq, J = 42.0); 62.3, 58.4 (ABq, J = 41.0); 57.0, 51.2 (ABq, J = 33.5); 55.3, 53.8 (ABq, J = 35.1). IR: ν(C≡N) 2229 (w).

Ru_2Cl_4(dppb)$_2$(MeCN) (4a). The complex was prepared from **2a** in 92% yield in the manner described for **3b** but using 1:2 MeCN−C_6H_6. Alternatively, a suspension of **1a** (400 mg, 0.33 mmol) in MeCN (10 mL) was stirred for 2 h, and the solvent then removed under vacuum. The residue was dissolved in hot C_6H_6, and Et_2O was added to precipitate an orange solid, which was filtered off, washed with Et_2O (3 × 5 mL), and dried under vacuum. Yield: 0.29 g (71%). ^{31}P{^{1}H} NMR (C_6D_6): δ 53.5, 52.2 (ABq, J = 44.3); 51.0, 45.8 (ABq, J = 36.2); (CD_2Cl_2) δ 52.3 (s); 50.8, 46.5 (ABq, J = 36.4). IR: ν(C≡N) 2282 (w).

$RuCl_2$(PP)(PhCN)$_2$. PP = dppb (5a). Precursor **2a** (233 mg, 0.270 mmol) was stirred in a mixture of PhCN (0.5 mL) and C_6H_6 (8 mL) for 12 h. The yellow product was filtered off, washed with hexanes (3 × 10 mL), and dried under vacuum. Yield: 182 mg (83%). ^{31}P-{^{1}H} NMR (C_6D_6): δ 50.5 (s). IR: ν(C≡N) 2241 (w).

PP = diop (5b). The complex was prepared from **2b** in a manner similar to that given for **5a** but without the benzene cosolvent; the mixture was stirred for 15 min before precipitating the product with hexanes (77% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 49.7, 36.0 (dd, J = 38.2). IR: ν(C≡N) 2237 (w).

PP = binap (5c). The complex was prepared from **2c** in the same manner as **5a** (91% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 50.3 (s, immediate, *t*-**5c**); 55.3, 53.6 (ABq, J = 35.0, grows in rapidly, *c*,*c*,*c*-**5c**); (10:1 PhCN−C_6D_6) δ 50.1 (s, *t*-**5c**); 47.9, 44.3 (ABq, J = 35.0; *c*,*c*,*c*-**5c**). IR: ν(C≡N) 2232 (w). Slightly different ^{31}P{^{1}H} NMR parameters in neat PhCN were described for *t*- and *c*,*c*,*c*-**5c** in a report which appeared during the course of this present work[12] (see text).

$RuCl_2$(PP)(MeCN)$_2$. PP = dppb (6a). A solution of **1a** (74 mg, 0.060 mmol) in MeCN (10 mL) was stirred for 15 h and then concentrated to ~4 mL and treated with Et_2O to precipitate the yellow product (48 mg, 69% yield). Samples of the isolated product turned orange on drying under air or vacuum overnight and were identified by ^{31}P{^{1}H} NMR (C_6D_6) as a mixture of **6a** and **4a**. Loss of nitrile from isolated **6a** also occurred rapidly in benzene solution. Attempts to prepare **6a** in the same manner as its PhCN analog **5a** were unsuccessful. ^{31}P{^{1}H} NMR (C_6D_6): δ 50.3 (s).

PP = binap (6c). The complex was observed in situ. A sharp ^{31}P-{^{1}H} AB pattern assigned to an all-cis isomer of **6c**, as well as the broad resonances due to *fac*- and *mer*-RuCl(binap)$(CD_3CN)_3^+Cl^-$ (cf. **10c**-Cl), was evident in spectra of precursor **2c** dissolved in CD_3CN. A sample of **10c**-PF_6 in $CDCl_3$ showed immediately on dissolution only a singlet at δ 51.9 for a trans-nitrile isomer of **6c** (assigned by analogy to data for **5c**). Reprecipitation of RuCl(binap)$(MeCN)_3^+PF_6^-$ (**10c**-PF_6) from CH_2Cl_2−C_6H_6 gave a yellow product which on dissolving in C_6D_6 showed an AB pattern tentatively assigned to another all-cis isomer of **6c**; no PF_6 septet was evident. ^{31}P{^{1}H} NMR (CD_3CN): δ 46.9, 41.3 (ABq, J = 38.0; *c*,*c*,*c*-**6c**); ($CDCl_3$) δ 51.9 (s, *t*-**6c**; this gives way over 24 h to the AB pattern of **8c**-Cl and a singlet at δ 45.5 of uncertain identity); (C_6D_6) δ 47.7, 45.1 (ABq, J = 31.9; *c*,*c*,*c*-**6c**). These NMR data contrast with values reported for **6c** in a paper which appeared during the course of this work[11] (for details see text).

Ru_2Cl_3(PP)$_2$(PhCN)$_2^+X^-$. PP = dppb, X = Cl (7a-Cl). A solution of **5a** (44 mg, 0.046 mmol) in CH_2Cl_2 (0.5 mL) was stirred for 1 h and then treated with Et_2O (~2 mL) to precipitate a bright yellow powder, which was filtered off and dried overnight under vacuum. Yield: 26 mg (68%). The NMR data agree with those for the PF_6 salt.

X = PF_6 (7a-PF_6). A solution of **5a** (88 mg, 0.109 mmol) in CH_2Cl_2 (5 mL) was treated with a solution of NH_4PF_6 (8.9 mg, 0.054 mmol)

in acetone (2 × 1 mL). The mixture was stirred for 1 h and then filtered through Celite. The filtrate was concentrated to ~1 mL and Et_2O added to precipitate the yellow product, which was filtered off and dried overnight under vacuum. Yield: 69 mg (83%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 49.3, 46.0 (ABq, J = 36.2), −144.5 (sept, J = 713, PF_6). IR: ν(C≡N) 2234 (w).

PP = diop, X = Cl (7b-Cl). The complex was prepared in situ (from **5b**) as described for **7a**-Cl above. $^{31}P\{^1H\}$ NMR spectra obtained immediately showed only signals for **7b**-Cl; the phosphine shift positions were identical to those of **7b**-PF_6.

X = PF_6 (7b-PF_6). The complex was prepared in situ by reaction of **9b**-PF_6 with $CDCl_3$, stirring the solution for 10 h before measuring the NMR spectrum. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.5, 36.4 (ABq, J = 35.6), −144.3 (sept, J = 713, PF_6).

PP = binap, X = PF_6 (7c-PF_6). The complex was prepared in 68% yield (from **5c**) as described for **7a**-PF_6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 54.1, 52.0 (ABq, J = 35.0), −144.2 (sept, J = 713, PF_6).

$Ru_2Cl_3(PP)_2(MeCN)_2^+X^-$. PP = dppb, X = Cl (8a-Cl). A solution of **1a** (74 mg, 0.062 mmol) in MeCN (10 mL) was stirred for 10 h and then concentrated to ~2 mL and treated with Et_2O to precipitate a yellow product, which was washed well with Et_2O (4 × 5 mL) to remove MeCN. Reprecipitation from CH_2Cl_2−Et_2O gave yellow **8a**-Cl; yield 40 mg (51%). ^1H NMR and $^{31}P\{^1H\}$ NMR spectra agree with those for the PF_6 salt.

X = PF_6 (8a-PF_6). The complex was not prepared by the method we originally reported[13] but by in situ reaction of **10a**-PF_6 with CH_2Cl_2 in 90% yield (as described for **7b**-PF_6 from **9b**-PF_6). Alternatively, a solution of **2a** (151 mg, 0.175 mmol) in MeCN (5 mL) was treated with NH_4PF_6 (14.3 mg, 0.088 mmol) in MeCN (2 × 1 mL). The mixture was stirred for 2 h and then stripped of solvent. The residue was redissolved in CH_2Cl_2 (5 mL), filtered through Celite, and the filtrate concentrated to ~1 mL. The yellow product was precipitated with C_6H_6 and dried under vacuum; yield 107 mg (88%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 49.4, 46.6 (ABq, J = 37.2), −144.5 (sept, J = 712, PF_6). IR: ν(C≡N) 2275 (w).

PP = diop, X = PF_6 (8b-PF_6). The complex was prepared in situ from crude (undried) RuCl(diop)$(MeCN)_3^+PF_6^-$ (**10b**-PF_6) in $CDCl_3$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 43.8, 37.4 (ABq, J = 36.0), −144.5 (sept, J = 713, PF_6).

PP = binap, X = Cl (8c-Cl). The complex was observed by $^{31}P\{^1H\}$ NMR in spectra of crude RuCl(binap)$(MeCN)_3^+PF_6^-$ (**10c**-PF_6) in $CDCl_3$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 54.3, 53.0 (ABq, J = 36.1).

RuCl(PP)$(PhCN)_3^+PF_6^-$. PP = dppb (9a-PF_6). To a suspension of **2a** (121 mg, 0.141 mmol) in PhCN (2 mL) under Ar was added CH_2Cl_2 (5 mL), giving a yellow solution which was immediately subjected to vacuum for 10 min to remove CH_2Cl_2. The mixture was stirred for 2 h and then treated with a solution of NH_4PF_6 (22.9 mg, 0.141 mmol) in acetone (2 × 1 mL). The mixture was stirred for 8 h and then filtered through Celite; the filtrate was concentrated to a yellow oil, diluted with C_6H_6 (1 mL), and treated with Et_2O to precipitate the product. Yield: 102 mg (71%) after washing with Et_2O and C_6H_6 (3 × 5 mL each) and drying under vacuum. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 40.3 (s, *fac*); 41.7, 34.4 (ABq, J = 33.5, *mer*), −145.3 (sept, J = 706, PF_6). IR: ν(C≡N) 2236 (w).

PP = diop (9b-PF_6). To a solution of **2b** (78.5 mg, 0.0842 mmol) in PhCN (0.25 mL) was added a solution of NH_4PF_6 (13.7 mg, 0.0840 mmol) in acetone (2 × 1 mL). The mixture was immediately diluted with CH_2Cl_2 (2 mL) and filtered through Celite, and the filtrate was concentrated to ~0.25 mL. The pale yellow product precipitated by addition of Et_2O was filtered off, washed with hexanes (3 × 5 mL), and dried under vacuum. Yield: 76.3 mg (83%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.2, 28.2 (ABq, J = 39.3), −144.2 (sept, J = 713, PF_6). IR: ν(C≡N) 2265, 2247 (w).

PP = binap (9c-PF_6). The complex was prepared in a manner similar to that described for the diop analog but stirring the precursor **2c** in PhCN for 24 h before adding NH_4PF_6. The mixture was then stirred for 2 h, diluted with C_6H_6 (5 mL), and filtered through Celite. The filtrate was concentrated and treated with Et_2O to precipitate the yellow product, which was filtered off and washed with warm hexanes (4 × 2 mL). Yield: 47 mg (61%). The microanalytical data are in poor agreement with the proposed structure, probably owing to loss of PhCN in the solid state. $^{31}P\{^1H\}$ NMR (10:1 PhCN-$CDCl_3$): δ 46.0, 44.4 (ABq, J = 29.8); −144.4 (sept, J = 712, PF_6). IR: ν(C≡N) 2234 (w).

RuCl(PP)$(MeCN)_3^+X^-$. PP = dppb, X = Cl (10a-Cl). This species was stable only in the presence of MeCN; after its formation in situ by dissolving **2a** in CD_3CN, the NMR spectra for the cation were identical to those of the PF_6 salt.

X = PF_6 (10a-PF_6). The complex was prepared in 76% yield from precursor **2a** in MeCN, in a manner otherwise similar to that described for the PhCN analog. Alternatively, a solution of **1a** (154 mg, 0.129 mmol) in MeCN (5 mL) was treated with NH_4PF_6 (41.9 mg, 0.257 mmol) in acetone (2 × 1 mL). The solution was stirred for 5 h and then filtered through Celite. The filtrate was concentrated to ~1 mL and diluted slightly with CH_2Cl_2 (1 mL), and the product was precipitated by addition of Et_2O. Reprecipitation from a 1:1 mixture of MeCN and CH_2Cl_2 gave a fine yellow powder; in the absence of MeCN, clean products (free of **8a**-PF_6) could not be obtained. The precipitate was washed with Et_2O and hexanes and dried under vacuum. Yield: 158 mg (74%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.7 (s), −144.2 (sept, J = 713, PF_6); (CD_3CN) δ 40.6 (s, *fac*); 42.5, 35.7 (ABq, J = 34.4, *mer*), −145.3 (sept, J = 706, PF_6). IR: ν(C≡N) 2268 (w).

PP = diop, X = Cl (10b-Cl). The complex was prepared in situ by dissolving **1b** in CD_3CN. The $^{31}P\{^1H\}$ NMR parameters agree with those for the PF_6 salt in CD_3CN.

X = PF_6 (10b-PF_6). Attempts to prepare this complex from **2b** in the manner described for the dppb analog gave a yellow precipitate (73% yield). Although this material showed the expected $^{31}P\{^1H\}$ NMR pattern, loss of MeCN occurred on exposure to vacuum: a color change to white and then pink was observed on drying overnight, and a complex series of NMR peaks was apparent on dissolving the pink solid in C_6D_6. Addition of MeCN (~0.2 mL) to the NMR sample regenerated the original spectrum. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 37.1, 30.5 (ABq, J = 40.2); −145.1 (sept, J = 707, PF_6).

PP = binap, X = Cl (10c-Cl). The complex was prepared in situ by dissolving **1c** in CD_3CN. The $^{31}P\{^1H\}$ NMR parameters agree with those for the PF_6 salt.

X = PF_6 (10c-PF_6). A solution of **2c** (108 mg, 0.102 mmol) in MeCN (5 mL) was treated with NH_4PF_6 (16.9 mg, 0.104 mmol) and stirred for 48 h. The solution was filtered through Celite, the filtrate stripped to a yellow oil, and C_6H_6 added to the residue, giving a yellow precipitate which was filtered off and washed with benzene (4 × 1 mL). Yield after drying under vacuum: 74 mg (70%). Microanalysis indicated a low nitrogen content and deteriorated further when a sample was reprecipitated from MeCN−C_6H_6. $^{31}P\{^1H\}$ NMR (CD_3CN): δ 47.5, 45.5 (br ABq, J unobservable); 47.5, 44.6 (ABq, J = 40.2); −145.1 (sept, J = 706, PF_6). IR: ν(C≡N) 2280 (w).

PP = 2PPh_3, X = PF_6 (10d-PF_6). A solution of $RuCl_2(PPh_3)_3$ (252 mg, 0.263 mmol) in MeCN (5 mL) was treated with NH_4PF_6 (42.9 mg, 0.263 mmol) and stirred for 48 h. The mixture was filtered through Celite, the filtrate concentrated to ~1 mL, and a pale yellow powder precipitated with Et_2O. The product was filtered off, washed with C_6H_6 (3 × 5 mL), and dried under vacuum. Yield: 175 mg (72%). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 43.8 (m), 40.4 (m), −145.3 (sept, J = 706, PF_6). IR: ν(C≡N) 2279 (w).

Results and Discussion

The doubly chloride-bridged dimer $[RuCl_2(dppb)]_2$ (**1a**) reacts with a wide range of two-electron donor ligands to give monosubstituted products of the type RuCl(dppb)$(\mu$-Cl$)_3$Ru(dppb)(L), eq 1; such species are readily detected by the

1 (1)

appearance of two AB quartet patterns in the $^{31}P\{^1H\}$ NMR spectra.[2,15] The corresponding L = nitrile derivatives **3** and **4** can be isolated (see below), but nitrile ligands can also easily cleave the chloride bridges to generate mononuclear RuCl(PP)$(RCN)_3^+Cl^-$ (R = Ph, Me), probably via the neutral

species $RuCl_2(PP)(RCN)_2$. Scheme 1 summarizes this chemistry and the related conversions to be discussed here. The five-coordinate complexes $RuCl_2(PP)(PPh_3)$ (**2**; PP = dppb, diop, binap), which in $CDCl_3$ or C_6H_6 provide an in situ source of $Ru_2Cl_4(PP)_2$ (**1**),[2,18] also act as direct precursors to the cationic species by displacement of PPh_3 and chloride. The mildness of these reaction conditions (room temperature, nitrile solvent), possible because of the high substitutional lability of the Ru precursors, is notable in view of the high temperatures typically employed in synthetic and catalytic chemistry of Ru−phosphine species.[10−12] Use of the mixed-phosphine complexes **2a**−**c**, accessible in two steps and quantitative yield from commercially available $RuCl_3$,[2,18] provides a particularly attractive route to nitrile derivatives.

The simultaneous presence in $RuCl(PP)(RCN)_3^+Cl^-$ of a labile nitrile ligand and the potentially coordinating Cl^- anion results in a product of low stability, and isolation of the cationic product requires removal of the counterion with, for example, NH_4^+. The stoichiometry of this reaction is critical; any excess of NH_4PF_6 leads to dicationic $Ru(PP)(RCN)_4^{2+}(PF_6^-)_2$, which has been crystallographically characterized (PP = dppb, R = Me).[17] Synthesis of the corresponding binap complex (**11c**) has also been reported.[11] Interestingly, the monocationic complex $RuCl(PP)(PhCN)_3^+PF_6^-$ (**9c**-PF_6) could not be isolated in a pure state, as earlier found for the MeCN analog.[11] Nitrile loss from such binap species may be facilitated by steric pressures exerted by the bulky and rigid diphosphine ligand; a high degree of lability or fluxionality was found in the present work to be characteristic of the binap complexes.

The dppb species **9a** and **10a** exist as the *fac* isomer in C_6D_6 or chlorocarbon solvents, as judged by the presence of a $^{31}P\{^1H\}$ NMR singlet (though reaction to give other products via loss of nitrile occurs, as discussed below). An accompanying AB quartet of variable intensity in neat or C_6D_6-spiked nitrile is attributed to isomerization to the *mer* species; the intensity of this signal increases over time. Measurements were made in CD_3CN for the PhCN species **9a** as well as **10a**; displacement of PhCN by CD_3CN did not interfere if measurements were made soon after dissolution because the nitrile exchange process is rather slow, being ca. 50% complete after 24 h.

For the diop and binap complexes, disruption of molecular symmetry by the chirality of the phosphine ligands should give rise to an AB pattern for each isomer; assignment as *fac* or *mer* is therefore made only by extrapolation from the dppb chemistry. Interestingly, neither **9b** nor **9c** exhibits more than one AB quartet in PhCN, probably owing to increased steric pressure at the axial positions exerted by the greater rigidity and/or bulk of the diphosphine ligand, relative to dppb. This tends to support identification of the species present as the *fac* isomer, for which interaction of the phosphine phenyl rings with the comparatively bulky nitrile ligand is minimized. Both isomers of the binap complex **10c** are formed in CD_3CN, though further assignment cannot be made with certainty. Two AB quartets are observed, the downfield halves of which (centered at δ 47.5) overlap; the upfield peaks, though broad, are distinguishable (δ 45.5, 44.6). Also initially present is an AB quartet due to all-*cis*-**6c** (see discussion below and Table 2). Only one AB pattern was reported for **10c** in a study of the binap−MeCN chemistry which appeared during the course of this work (1:1 MeCN−$CDCl_3$, −30 °C: δ 47.7, 44.9, J = 32).[11] The absence of signals for the second isomer may be due to any of a number of factors: Duration of time in solution is probably a key factor, but temperature or (given the usual absence of isomerization in C_6D_6 or halogenated solvents) the concentration of MeCN may also be significant. Rather surprisingly, only one isomer was observed for the diop analog **10b** in the present work, even on prolonged exposure to CD_3CN at room temperature. As this species proved unexpectedly susceptible to decomposition with loss of nitrile, it was not investigated in detail.

Table 1. $^{31}P\{^1H\}$ NMR Data Outlining the Solution Behavior of $RuCl_2(binap)(PhCN)_2$ (**5c**)

solvent	precursor	chem shift (J_{AB})[a]	assgnt
C_6D_6	isolated **5c**	50.3	*t*-**5c**
		55.3, 53.6 (35)	*c*,*c*,*c*-**5c**
1:7 PhCN−C_6D_6	**3c**	50.3	*t*-**5c**
		48.4, 44.2 (35)	*c*,*c*,*c*-**5c**
10:1 PhCN−C_6D_6	isolated **5c**	50.1	*t*-**5c**
		47.9, 44.3 (35)	*c*,*c*,*c*-**5c**
10:1 PhCN−$CDCl_3$	**2c**	54.1, 52.0 (35)	**7c**-Cl
		50.1	*t*-**5c**
		47.1, 43.9 (35)	*c*,*c*,*c*-**5c**
		46.0, 44.4 (30)	**9c**-Cl

[a] J values in Hz.

Attack of the chloride counterion on the Ru center, with displacement of a nitrile ligand, occurs during attempts to isolate solid $RuCl(PP)(RCN)_3^+Cl^-$, and the neutral $RuCl_2(PP)(RCN)_2$ complexes (**5**, R = Ph; **6**, R = Me) precipitate instead. In the case of the MeCN species **6a**, the neutral complex in turn undergoes loss of MeCN on drying under vacuum and gives orange $Ru_2Cl_4(dppb)_2(MeCN)$ (**4a**). The benzonitrile complexes **5a**−**c** are less susceptible to nitrile loss under vacuum, owing to the lower volatility of the aromatic nitrile, and the PhCN derivatives were therefore investigated in greater detail. In the solid state, **5a**−**c** probably exist as the *trans*-nitrile isomer, as judged from the single ν(C≡N) in the infrared. The dppb species **5a** retains this geometry in solution (though loss of nitrile is promoted in the absence of RCN, as discussed below); the diop and binap complexes, in contrast, appear to undergo facile isomerization. The $^{31}P\{^1H\}$ NMR spectrum of the diop derivative **5b**, obtained within 30 min of dissolution in C_6D_6, consists solely of a pair of doublets assigned to an all-cis isomer; the expected singlet for the trans isomer is not observed. For the binap species, a singlet at δ 50.3 observed immediately on dissolution of isolated, analytically pure **5c** in C_6D_6 is assigned to *trans*-**5c**. The solution behavior of **5c** is complex (Table 1): While an AB quartet (δ 55.3, 53.6; J = 35) grows in rapidly in neat C_6D_6, a different AB pattern (δ 48.4, 44.2; J = 35) is found in 1:7 PhCN−C_6D_6. The latter signal is shifted slightly upfield as the proportion of PhCN is increased and is then accompanied by that due to cationic **9c**-Cl. The location of the upfield AB quartet is in reasonable agreement with values found in neat PhCN by other workers (δ 47.0, 43.3; J = 35) and assigned to all-*cis* **5c**; this group recorded also a singlet at δ 48.6 for *trans*-**5c**.[12]

Two distinct cis isomers of **5c** can in fact be formed, owing to the chirality of the binap ligand; while the chemical shift difference between the two AB sets of signals described above seems large for this apparently subtle difference in structural form, precedent exists for such a distinction.[20] More perplexing is the implied diastereoselectivity of isomerization in a particular solvent mixture: In no case are both AB patterns observed simultaneously. An alternative possibility for assignment of the downfield AB pattern is the doubly chloride-bridged structure $[RuCl(PP)(PhCN)]_2(\mu\text{-}Cl)_2$. No evidence for such a species is

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Table 2. $^{31}P\{^1H\}$ NMR Data Outlining the Solution Behavior of $RuCl_2(binap)(MeCN)_2$ (**6c**)

solvent	precursor	chem shift (J_{AB})[a]	assgnt
C_6D_6	**6c**	47.7, 45.1 (32)	*c,c,c*-**6c**
$CDCl_3$	**10c**-PF_6	51.9	*t*-**6c**
		54.3, 53.0 (36)[b]	**8c**-Cl
		45.5[b]	uncertain (see text)
CD_3CN	**2c**	47.5, 45.5 (*J* unobservable), 47.5, 44.6 (40)	**10c**-Cl
		46.9, 41.3 (38)	*c,c,c*-**6c**

[a] *J* in Hz. [b] Not immediately observed.

observed in the chemistry of dppb or diop, though perhaps its stability relative to the usual, highly stable $Ru_2(\mu\text{-}Cl)_3$ entity may be enhanced by the bulk and rigidity of the binap ligand. It should be noted that no coupling through the bridging chlorines has been observed in the $Ru_2(\mu\text{-}Cl)_3$ complexes described below, although through-bridge P-coupling has been reported for complexes such as $(PPh_3)_2(H)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2Ru(\eta^2\text{-}H_2)(PPh_3)_2$.[21,22]

In the corresponding binap−MeCN chemistry, no downfield AB pattern corresponding to that observed for **5c** in neat C_6D_6 was found. A single AB quartet appears (C_6D_6: δ 47.7, 45.1; $J = 32$) near the location described above for **5c** in PhCN−C_6D_6 and is assigned to all-*cis*-**6c**. A similar resonance (δ 46.9, 41.3; $J = 38$) present immediately following dissolution of **2c** in CD_3CN (Table 2) is completely replaced within a few hours by signals due to cationic **10c**-Cl. In $CDCl_3$, a singlet at δ 51.9, assigned to a trans isomer of **6c**, was the sole phosphine signal initially present; no AB pattern was observed. Conflicting data appear in the literature[11] for an isolated $RuCl_2(binap)(MeCN)_2$ complex ($CDCl_3$): δ 54.8, 53.7; $J = 35.2$; δ 51.7, 50.9; $J = 35.2$; ratio of AB quartets = 9:1. The singlet for a trans isomer was not observed in the literature work, possibly because of delays between dissolving the sample and measuring the spectrum; our investigations clearly show that the product distribution is sensitive to both solvent and the time in solution. Of the two AB quartets reported, however, neither corresponds to that found in C_6D_6. The lower-field pattern is almost certainly due to $Ru_2Cl_3(binap)_2(MeCN)_2{}^+Cl^-$ (**8c**-Cl), which is formed slowly from **6c** in chlorinated solvents (see below). The other pattern may be due to an all-cis isomer of **6c**, as the authors propose, or to a doubly chloride-bridged dimer, as suggested above for the PhCN species. While the reported microanalytical data support the formulation of the solid precursor as $RuCl_2(binap)(MeCN)_2$ (with 0.5 CH_2Cl_2), the lability of the nitrile ligands complicates the solution structure.

The remainder of the solution chemistry of the binap complexes is largely consistent with that of the dppb and diop species. Loss of nitrile from $RuCl_2(PP)(RCN)_2$ (**5** or **6**) is promoted in solution, as noted above; in C_6H_6, the product is $Ru_2Cl_4(PP)_2(RCN)$ (R = Ph, **3a**−**c**; R = Me, **4a**), as indicated by elemental analysis and, in the case of **3b** and **4a**, by independent synthesis from **2b** and **2a**, respectively, via reaction with nitrile. The rate of conversion of **5** or **6** is variable, depending probably on the concentration of residual free nitrile in the sample. In the absence of nitrile, signals for the dinuclear species are discernible by $^{31}P\{^1H\}$ NMR immediately following dissolution in C_6D_6, and are predominant within 24 h. A pattern of four AB quartets of equal integrated intensity is observed for each of the chiral complexes **3b**,**c**, probably reflecting the low-energy difference between a pair of diastereomers either

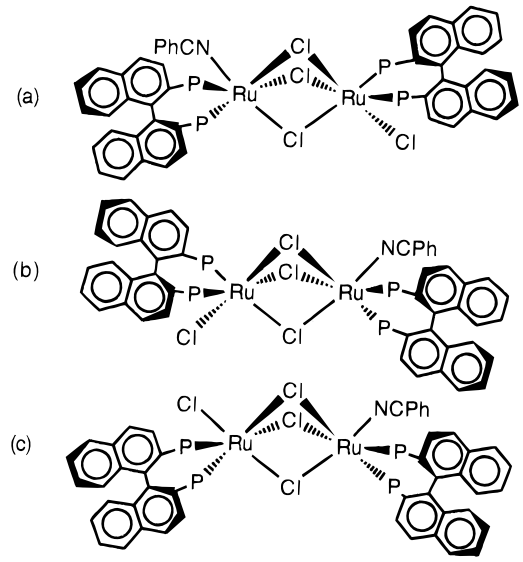

Figure 1. Diastereomers of $Ru_2Cl_4(PP)_2(RCN)$, illustrated for PP = binap. The phenyl rings of the binap ligands are omitted for clarity.

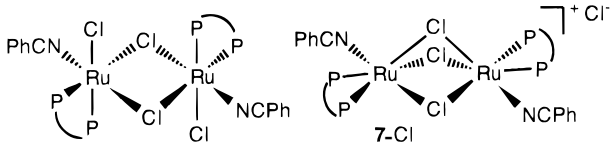

Figure 2. Neutral and ionic isomers of $Ru_2Cl_4(PP)_2(PhCN)_2$.

formed without discrimination or capable of interconverting in solution. The NMR spectra of **3c** in C_7D_8 remain essentially unchanged down to −80 °C, tending to support the former possibility. Figure 1 shows the possible structures for the diastereomers, illustrated with the binap species **3c**. A structure of type a/b (the two are enantiomeric if the phosphine is achiral) is clearly adopted by the corresponding dppb complex, for which two $^{31}P\{^1H\}$ AB patterns are observed; isomer c, in which the nitrile and the terminal chloride ligand are coplanar, would give rise to two singlets.

A similar process of nitrile loss and dimerization almost certainly occurs with the PPh_3 analog of **6**. Reprecipitation of $RuCl_2(PPh_3)_2(MeCN)_2$ from toluene was in early work reported to generate the doubly chloride-bridged product $[RuCl_2(PPh_3)_2(MeCN)]_2(\mu\text{-}Cl)_2$,[23] but the accompanying analytical data suggest that this should be reformulated as $RuCl(PPh_3)_2(\mu\text{-}Cl)_3Ru(PPh_3)_2(MeCN)$. This work was not reinvestigated in the present study, the PPh_3 chemistry being limited to preparation of the cationic species **10d**-PF_6.

Nitrile loss also occurs on dissolving mononuclear **5** or **6** in CH_2Cl_2 or $CDCl_3$, but the product is now the dinuclear cation $Ru_2Cl_3(PP)_2(RCN)_2{}^+Cl^-$ (R = Ph, **7**-Cl; R = Me, **8**-Cl). The PF_6 salts of **7a**,**c** were readily prepared by addition of 1 equiv of NH_4PF_6 per Ru_2. The counterion has no effect on the phosphine shift positions, the values for the Cl and PF_6 salts being identical, and the structure of **7a**-Cl, earlier represented as neutral $[RuCl(dppb)(PhCN)]_2(\mu\text{-}Cl)_2$,[2,15b] is now redefined on this basis as $\{[Ru(dppb)(PhCN)]_2(\mu\text{-}Cl)_3\}^+Cl^-$ (Figure 2). Synthesis (from the mixed-valence species $Ru_2Cl_5(dppb)_2$) and conductivity studies of the dppb−MeCN complex **8a**-PF_6 were previously reported by our group.[13] Reaction of $RuCl(PP)(RCN)_3{}^+PF_6{}^-$ (**9**, **10**) with the chlorinated solvents CH_2Cl_2 or $CDCl_3$ provided an unexpected additional route to the dinuclear, cationic complexes, and quantitative conversion of

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the dppb and diop species to the dinuclear PF_6 salts was observed. Several experiments tend to implicate direct reaction of the mononuclear cations with solvent, rather than with solvent photochemical decomposition products such as HCl. For example, efforts to block conversion of **10a**-PF_6 into **8a**-PF_6 by neutralization of possible HCl impurity were unsuccessful; similarly, the extent of reaction to give **8a**-PF_6 was independent of the batch of solvent used but varied with the batch of starting cation (again, probably depending on the amount of residual free nitrile present in the sample). Reports on the implication of CH_2Cl_2 and $CHCl_3$ in the quantitative halogenation of inorganic species are increasingly common. The nature of the chlorinating species is frequently uncertain, but accumulating reports of oxidative-addition products (in which both chloride and hydrocarbyl ligands are retained)[24] show that direct reaction between late transition-metal complexes and the halocarbon solvent is not unusual, while crystallographic studies have also shown CH_2Cl_2 in both chelating (at an Ag(I) center)[25] and bridging (at an Ru_3 site)[26] modes.

The behavior of the binap complex **10c**-PF_6 is again anomalous within this chemistry. Dissolution of this species in $CDCl_3$ yields neutral *t*-$RuCl_2$(binap)$(MeCN)_2$ (**6c**) as the sole initial product, as judged by in situ $^{31}P\{^1H\}$ NMR (δ 51.9, s). The solution instability of **10c**-PF_6 was noted by Takaya's group, and a process of disproportionation into **6c** and dicationic $Ru(binap)(MeCN)_4^{2+}(PF_6^-)_2$ (**12c**) was proposed.[11] A signal near the location reported for **12c** (δ 46.6)[11] does in fact develop in the $^{31}P\{^1H\}$ NMR spectrum of **10c**-PF_6 after 24 h in $CDCl_3$: the principal product after this time is the dinuclear cation **8c**, but accompanying the AB quartet for this species is a new singlet at δ 45.5, of about a third of the integrated intensity. The assignment of this peak remains somewhat uncertain despite the near-correspondence in chemical shift, however, as our extensive study of the solution chemistry of isolated $RuCl_2(PP)(RCN)_2$ complexes has shown no precedent for the implied equilibration to **12** (R = MeCN) or **11** (R = PhCN) species.

Addition of nitrile to **7** or **8** species (Scheme 1) cleaves the triple chloride bridge to give the mononuclear cations $RuCl(PP)(RCN)_3^+X^-$. In the presence of nitrile, reaction of **9**-PF_6 or **10**-PF_6 with chlorocarbons is suppressed, and $MeCN-CH_2Cl_2$ mixtures were in fact successfully used to reprecipitate **10a**-PF_6. Owing to the weaker ligating character of PhCN, caution must be employed in using this means of purification for the corresponding PhCN complexes; $^{31}P\{^1H\}$ NMR signals for **7c**, for example, are observed even in 10:1 $PhCN-CDCl_3$ immediately following dissolution of **9c**-PF_6. The facile formation of the dinuclear cations **7** and **8** from neutral or cationic, mononuclear precursors in chlorocarbon solvents in the absence of nitrile should be emphasized, given the ubiquity of $CDCl_3$ and CH_2Cl_2 as NMR and reaction solvents. This reactivity pattern is readily overlooked, and in the recently reported synthesis of $RuCl_2$(binap)$(PhCN)_2$,[12] the emergence of an AB quartet now known to be due to **7c**-Cl in the $^{31}P\{^1H\}$ NMR spectrum in CH_2Cl_2 was tentatively and incorrectly attributed to a five-coordinate species $RuCl_2$(binap)(PhCN).[27] Similarly, one of the two sets of AB patterns reported[11] in spectra of $RuCl_2$(binap)$(MeCN)_2$ in $CDCl_3$ corresponds rather closely to that found for **8c**, as noted above, and should probably be reassigned to $Ru_2Cl_3(binap)_2(MeCN)_2^+Cl^-$. The appearance of two methyl singlets in the corresponding ^1H NMR spectrum, cited as evidence for the mononuclear formulation,[11] is consistent with the presence of coordinated and displaced (free) MeCN in a 1:1 ratio.

The solution behavior of these nitrile derivatives of Ru(II) is clearly intricate. This complexity provides, however, a flexible network of synthetic relationships, which can be exploited by judicious choice of reaction conditions to gain access to a wide range of products.

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Supporting Information Available: Tables S1 and S2, containing microanalytical and ^1H NMR data (4 pages). Ordering information is given on any current masthead page.

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