Net Amine Dealkylation at a Diruthenium Center: Dehydrogenation of a Secondary Amine and Hydrolysis of a Coordinated Imine

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Received December 14, 1994[⊗]

Reaction of excess benzylamine with $Ru_2Cl_4(dppb)_2$ (**1**) or $RuCl_2(dppb)(PPh_3)$ (**2**) under Ar or with $Ru_2Cl_5(dppb)_2$ (**3**) under H_2 or in air generates $RuCl_2(dppb)(NH_2CH_2Ph)_2$ [dppb = 1,4-bis(diphenylphosphino)butane, $Ph_2P(CH_2)_4PPh_2$]. Use of 1 equiv of amine per $[Ru(II)]_2$ gives dinuclear $Ru_2Cl_4(dppb)_2(NH_2CH_2Ph)$ (**4a**) as a mixture of isomers. The corresponding reactions with dibenzylamine yield only dinuclear products: either $Ru_2Cl_4(dppb)_2[NH(CH_2Ph)_2]$ (**4b**), for reactions under H_2, or a mixture of this species and the dealkylation product **4a**. The mechanism proposed for formation of the latter involves dehydrogenation of the secondary amine adduct to $Ru_2Cl_4(dppb)_2[PhCH_2N{=}C(H)Ph]$, followed by hydrolysis of the coordinated imine. Direct reaction of $PhCH_2N{=}C(H)Ph$ with **3** under H_2 permits isolation of solely **4b**. The findings are of interest also in context of thermal degradation of tertiary amines and hydrogenation of imines catalyzed by Ru ditertiary phosphine complexes.

Introduction

Transition-metal-induced dehydrogenation of amines, particularly those containing α-methyl or methylene groups, to give products containing carbon−nitrogen double bonds, has been described by several groups. Reaction of $Os_4(CO)_{12}$ with NMe_3 or $N(CH_2Ph)(Me)_2$, for instance, gives no amine derivatives; all of the isolated products are μ-iminyl or -iminium species.[1] Related η^1-enamine or imidinium species are formed by ruthenium,[2,3] rhodium,[4] and palladium[5] systems on treatment with tertiary amines, while homologation of primary amines in the presence of Ru catalysts is believed to occur via imine intermediates.[2,6,7] Dehydrogenation at carbons α and β to nitrogen has been observed in CpRu systems,[8] as well as osmium carbonyl clusters.[9,10] Catalytic dehydrogenation of primary and secondary amines to imines and nitriles in the presence of Rh(I) phosphine complexes has also been reported.[11]

The established amine chemistry of ruthenium has provided several examples of alkyl exchange,[12,13] including the catalytic homologation of primary to secondary amines by $RuCl_2(PPh_3)_3$.[2,6,7] We now report the ability of closely related systems to effect the reverse reaction, stoichiometric conversion of a secondary to a primary amine. Interest in this area stems from our investigations of the catalytic utility of ruthenium phosphine complexes in hydrogenation of imines; the most effective catalysts are those that contain a single, chelated ditertiary phosphine per Ru atom.[14] In the course of these studies we examined the solution behavior of such complexes with dibenzylamine and benzylamine, the hydrogenation and a hydrolysis product, respectively, of the aldimine $PhCH_2N{=}C(H)Ph$. The selected Ru complexes contain dppb which, like the well-known chiral ditertiary phosphine ligands binap and diop, forms seven-membered chelate rings.

Experimental Section

Synthetic and spectroscopic work was performed under Ar except where otherwise noted. Reagent grade solvents (supplied by Aldrich) were distilled from CaH_2 (CH_2Cl_2) or sodium (C_6H_6, ether, hexanes). NMR spectra were recorded at room temperature (RT) on a Varian XL300 or (where noted) a Bruker AMX500 spectrometer, using as internal standards the residual proton of the deuterated solvent (^1H spectra) or PPh_3 (^{31}P spectra: $CDCl_3$, −5.46 ppm; C_6D_6, −5.06 ppm; both with respect to 85% external H_3PO_4). Elemental analyses were performed by P. Borda of this department. The diphosphine dppb, obtained from Aldrich, was used as supplied. Amines were obtained from Aldrich, distilled before use, and stored under Ar unless otherwise noted. Imines were prepared by condensation of benzylamine with the appropriate aldehyde, purified by chromatography on neutral alumina (hexanes eluant), and stored under Ar in the dark. The Ru precursors $Ru_2Cl_4(dppb)_2$ (**1**),[15,16] $RuCl_2(dppb)(PPh_3)$ (**2**),[15,17] and $Ru_2Cl_5(dppb)_2$ (**3**)[18] were prepared as previously described.

$RuCl(dppb)(\mu\text{-}Cl)_3Ru(dppb)(\eta^1\text{-}NH_2CH_2Ph)$ (4a). Method a. Complex **4a** was prepared in situ by addition of benzylamine (3.3 μL, 0.030 mmol) to a solution of **3** (17.7 mg, 0.0144 mmol) in $CDCl_3$ (0.8 mL) under H_2. The solution changed color from red to yellow within 1 h and was transferred to an NMR tube under Ar. Spectroscopic analysis indicated the presence of solely **4a**, but attempts to scale up this route to **4a** gave consistently a mixture of **4a** and an isomer **5** (see below). ^1H NMR ($CDCl_3$): δ 8.6 (br s, ~2H, NH_2, exchanges with

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[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1995.

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D_2O), 6.8−7.8 (m, 45H, Ph), 3.9 (br s, 2H, NCH_2), 2.8−3.0 (m, 4H, dppb CH_2), 2.0−2.25 (m, 4H, dppb CH_2), 1.6−1.9 (m, 4H, dppb CH_2), 1.25−1.5 (m, 4H, dppb CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.9 (s).

Method b. Addition of benzylamine (9.5 μL, 0.087 mmol) to a solution of **1** (104 mg, 0.087 mmol) in $CDCl_3$ (2.5 mL; RT, Ar) gave over 1 h an in situ mixture of **4a** and **5**, from which an orange-brown precipitate could be obtained by addition of hexanes. Microanalysis was carried out on a mixture of these complexes (ca. 1:1, as judged by $^{31}P\{^1H\}$ NMR) in order to confirm the empirical formula. Anal. Calcd for $C_{63}H_{65}Cl_4NP_4Ru_2 \cdot H_2O$: C, 57.24; H, 5.11; N, 1.06; Cl, 10.73. Found: C, 57.33; H, 5.10; N, 1.15; Cl, 10.94. The presence of a water solvate was confirmed by ^1H NMR (δ 1.51, $CDCl_3$; all other peaks correspond to those observed for isolated **4a** and **5**).

RuCl(dppb)(μ-Cl)$_3$Ru(dppb)[η^1-NH(CH_2Ph)$_2$] (4b). Method a in the syntheses given below represents the preferred route to the complex of interest.

Method a. A suspension of **3** (96 mg, 0.078 mmol) and $PhCH_2N{=}C(H)Ph$ (30 μL, 0.159 mmol) in benzene (5 mL) was stirred under H_2 for 4 h, over which time a color change from red to clear orange-brown occurred. After 24 h an orange precipitate had deposited, which was filtered off, washed with hexanes, and reprecipitated from CH_2Cl_2−hexanes (83 mg, 77%). ^1H NMR ($CDCl_3$): δ 8.4−8.8 (br s, ~1H, NH, exchanges with D_2O), 6.8−7.8 (m, 50H, Ph), 3.83 (s, 4H, $N(CH_2)_2$), 2.85−3.1 (m, 4H, dppb CH_2), 2.1−2.3 (m, 4H, dppb CH_2), 1.6−1.8 (m, 4H, dppb CH_2), 1.3−1.5 (m, 4H, dppb CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.9 (s). Anal. Calcd for $C_{70}H_{71}Cl_4NP_4Ru_2$: C, 60.31; H, 5.13; N, 1.00. Found: C, 60.02; H, 5.28; N, 1.06.

Method b. Dibenzylamine (53 μL, 0.276 mmol) was added to a red solution of **3** (156 mg, 0.127 mmol) in benzene (10 mL) under H_2, causing a color change to yellow-brown within 10 min. After 30 min the solution was concentrated and MeOH added to precipitate the orange-brown product, which was filtered off, washed with MeOH (4 × 5 mL), and reprecipitated from CH_2Cl_2−hexanes. Yield: 110 mg (61%).

In the absence of H_2, a mixture of **4b**, **5**, and other unidentified products was observed by in situ $^{31}P\{^1H\}$ NMR on reaction of excess dibenzylamine with **1**, **2**, or **3** at room temperature or with **2** in refluxing benzene. (Whether the singlet at δ 48.9 is due solely to **4b** or to a mixture of this and the benzylamine analogue **4a** cannot be determined owing to the chemical shift equivalence of these amine adducts; see Results and Discussion).

Ru_2Cl_4(dppb)$_2$(NH_2CH_2Ph) (5). Method a. Complex **2** (123 mg, 0.143 mmol) in benzene (15 mL) was heated at reflux for 1 h, upon which injection of benzylamine (7.8 μL, 0.071 mmol) caused a color change from green to orange. Heating was continued for 30 min; then the solution was concentrated and hexanes were added to precipitate the product, which was filtered off, washed with hexanes (3 × 5 mL), and reprecipitated from CH_2Cl_2−hexanes to afford orange **5** (78 mg, 84%). Detailed NMR analysis, including ^{13}C APT, ^1H−^{13}C HETCOR, ^1H−^1H COSY, and selective ^1H−^1H decoupling experiments,[19] permitted assignment of all 20 aliphatic protons in complex **5**. The NH protons do not exchange with D_2O. ^1H NMR (500 MHz, $CDCl_3$): δ 8.2−8.4 (m, 4H, Ph), 6.3−7.9 (m, 41H, Ph), 3.90−4.04 (m, 1H, CH of dppb CH_2), 3.1 (dt, J = 3.4 Hz and 14 Hz; 1H, CH of benzylamine CH_2), 2.25−3.0 (m, 6H, dppb and benzylamine CH_2, and NH), 1.1−2.2 (m, 12H, NH and dppb CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 55.7, 51.3 (ABq, J = 39 Hz), 52.7 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 56.5, 51.3 (ABq, J = 39 Hz), 53.7, 53.6 (ABq, J = 44 Hz). Anal. Calcd for $C_{63}H_{65}Cl_4NP_4Ru_2$: C, 58.03; H, 5.02; N, 1.07; Cl, 10.87. Found: C, 58.07; H, 5.10; N, 1.04; Cl, 10.71.

Method b. A deep green solution of **2** (144 mg, 0.168 mmol) and $PhCH_2N{=}C(H)Ph$ (100 μL, 0.531 mmol) in C_6H_6 (10 mL) was stirred (RT, 10 d) and then concentrated to ~1 mL. A precipitate of orange **5** was filtered off, washed with hexanes (2 × 15 mL), and reprecipitated from CH_2Cl_2−hexanes (76 mg, 69%).

Method c. A solution of **1** (53.9 mg, 0.045 mmol) and $PhCH_2N{=}C(H)(p\text{-}C_6H_4OMe)$ (18.6 mg, 0.09 mmol) was stirred in $CDCl_3$ (RT, 10 d), and the reaction was monitored by $^{31}P\{^1H\}$ and ^1H NMR.

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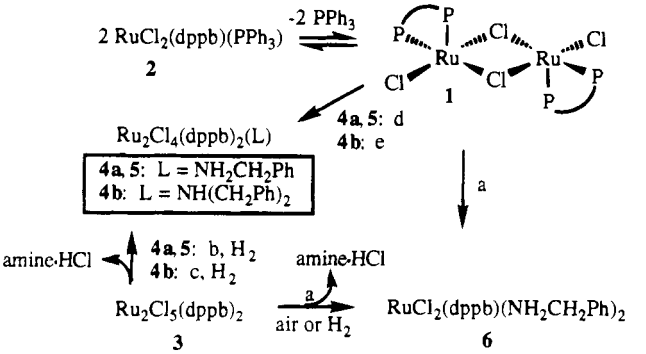

Figure 1. Overview of RT synthetic routes to amine derivatives of **1**: (a) excess NH_2CH_2Ph; (b) 2 mol of NH_2CH_2Ph; (c) $PhCH_2N{=}C(H)Ph$ or $NH(CH_2Ph)_2$ (2 mol or excess); (d) 1 mol of NH_2CH_2Ph; (e) $NH(CH_2Ph)_2$ (1 mol or excess).

Concentration to ~0.25 mL and addition of hexanes gave clean **5** in low yield (22 mg, 38%).

$RuCl_2$(dppb)(NH_2CH_2Ph)$_2$ (6). Method a. Addition of solid **3** (84 mg, 0.068 mmol) to undegassed, undistilled benzylamine (300 μL, 2.75 mmol) in air provides the most facile route to complex **6**. An immediate color change from red to yellow was observed. The solution was diluted with benzene (5 mL) and filtered to remove benzylamine hydrochloride (8.2 mg, 84%). The filtrate was stripped to a yellow-brown oil and treated with hexanes to give a yellow precipitate. This was filtered off, washed with hexanes, and reprecipitated from benzene−hexanes (79 mg, 71%). The reaction can be performed in the same manner under H_2.

Method b. Solid **2** (84 mg, 0.098 mmol) was added to degassed benzylamine (0.5 mL) under Ar, and the suspension was shaken gently for a few minutes, over which time it changed color from green to yellow. The solution was diluted with benzene (5 mL); upon 8 h of stirring, a yellow precipitate deposited, which was filtered off, washed with ether (3 × 5 mL), and reprecipitated from benzene−hexanes (49 mg, 62%). ^1H NMR (C_6D_6): δ 7.85−7.95 (m, 5H, Ph), 6.5−7.3 (m, 25H, Ph), 3.7−3.8 (br s, 4H, NCH_2), 3.05−3.2 (br s, ~4H, NH_2, exchanges with D_2O), 2.9−3.05 (m, 4H, CH_2), 1.4−1.6 (m, 4H, CH_2). ^1H NMR ($CDCl_3$): δ 7.6−7.8 (m, 5H, Ph), 7.1−7.5 (m, 22H, Ph), 6.7−6.9 (m, 3H, Ph), 3.5−3.6 (br s, 4H, NCH_2), 2.8−3.1 (m, ~8H, NH_2 and CH_2), 1.5−1.7 (m, 4H, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 47.1. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 45.7. Anal. Calcd for $C_{42}H_{46}Cl_2N_2P_2Ru$: C, 62.07; H, 5.70; N, 3.45; Cl, 8.72. Found: C, 62.30; H, 5.77; N, 3.62; Cl, 8.46.

Method c. Addition of benzylamine (8 μL, 0.07 mmol) to a solution of **1** (11 mg, 0.009 mmol) in C_6D_6 (0.8 mL) under Ar also gave **6**, as judged by $^{31}P\{^1H\}$ NMR. The brown-red solution turned yellow on addition of amine; formation of **6** was complete within the time required to measure the spectrum.

RuCl(dppb)(μ-Cl)$_3$Ru(dppb)[η^1-N(CH_2Ph)=C(H)Ph] (7). A brown solution of **1** (97.2 mg, 0.0812 mmol) and *N*-benzylidenebenzylamine (30.6 μL, 0.163 mmol) in C_6H_6 (6 mL) was stirred for 5 days at room temperature. The solvent was removed and the residue taken up in C_6D_6 for $^{31}P\{^1H\}$ analysis, which indicated the presence of a mixture of products, including **5**. An orange precipitate consisting principally of **7** (ca. 8 mg, 7%) was isolated by decantation, washed with hexanes (2 × 2 mL) to remove any free imine, and characterized by NMR spectroscopy. ^1H NMR (300 MHz, $CDCl_3$): δ 8.41 (s, 1H, N=C(H)), 8.1−8.35 (m, 5H, Ph), 6.65−7.8 (m, 45H, Ph), 4.84 (s, 2H, NCH_2), 3.83−4.0 (m, 1H, CH of dppb CH_2), 1.05−2.85 (m, 15H, dppb CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.5, 52.0 (ABq, J = 44.3 Hz; "(dppb)-RuCl"); 51.0, 46.6 (ABq, J = 36.1 Hz; "(dppb)Ru(imine)").

Results and Discussion

The products isolable in this amine chemistry (Figure 1) are strongly dependent on the bulk of the amine ligand, probably owing to steric pressures exerted by the phenyl groups of the phosphine. Thus treatment of **1** or **2** with excess benzylamine at ambient temperatures yields the mononuclear derivative $RuCl_2$(dppb)(NH_2CH_2Ph)$_2$ (**6**). The ^1H NMR spectrum of **6**

exhibits a small upfield coordination shift of ~0.2 ppm for the amine CH_2 group (to ~3.55 ppm in $CDCl_3$, relative to a value of 3.8 ppm for free benzylamine). The complexity of the ν(Ru−Cl) region of the infrared spectrum of **6** precludes conclusive structural assignment, though the all-*cis* isomer can be ruled out by $^{31}P\{^1H\}$ NMR evidence (s, 47.1 ppm). A trans disposition of the amine ligands would correspond to the geometry assigned to the bis(benzonitrile) species on the basis of infrared data,[19] but the isomeric structure with trans chlorides is also possible; indeed, such a structure has been established crystallographically for $RuCl_2(dppb)(pyridine)_2$.[20] The bis(amine) complexes $RuCl_2(PPh_3)_2(amine)_2$ have been isolated on treatment of $RuCl_2(PPh_3)_3$ with substituted pyridines in refluxing acetone[21] and with primary aliphatic amines[22] or imidazoles[23] at room temperature; their geometries were not definitively established. The dinuclear species $Ru_2Cl_4(dppb)_2(NH_2CH_2Ph)$ is obtained with a stoichiometric use of benzylamine; this species is typically isolated as a mixture of two isomers, **4a** and **5**. The former is identified as the η^1-amine complex, as described below. On treatment of Ru precursors **1**−**3** with excess dibenzylamine at room temperature, in contrast, no mononuclear species are obtained, but $Ru_2Cl_4(dppb)_2[NH(CH_2Ph)_2]$ (**4b**) is observed as a principal product. This is consistent with earlier results in which complexes of type **4** were isolated on reaction of **1** or **2** with excess NEt_3 or NH^nBu_2 at room temperature.[15]

A prominent feature of the reactions of the benzylic amines is the accessibility of amine dehydrogenation pathways. Complex **6**, for example, is formed from the Ru(II,III) dimer $Ru_2Cl_5(dppb)_2$ (**3**) on treatment with excess benzylamine in air, as well as (more predictably) under H_2, when **3** is known to be reduced to the $[Ru(II)]_2$ dimer **1**. In the absence of H_2, reduction of the Ru(III) center is presumably effected by amine. Dehydrogenation of amines by group 8 metal complexes is well established, as noted above,[1,7,11,22] and the oxidation of amines to imines by MX_3 phosphine species (M = Ru, Os, X = halogen), which are in the process reduced to M(II), has been described in related work.[2,24] The HCl produced in the reduction of **3** is sequestered as the amine hydrochloride, which precipitates as a white solid. Attempts to detect a putative imine intermediate such as **7** (see below) by $^{31}P\{^1H\}$ NMR, following treatment of **3** with 2 equiv of benzylamine, were unsuccessful. A mixture of **6**, unreacted **3**, and **4a** was obtained, implying that both the intermediate and **4a** react with amine faster than does **3**. (Monomer **6** can be formed by treatment of **4a/5** with benzylamine.)

More explicit evidence for amine dehydrogenation comes from experiments directed at preparing the monoamine **4b**. This species was observed as the sole product only following treatment of **3** under H_2 with $PhCH_2N{=}C(H)Ph$ or dibenzylamine itself. In the absence of H_2, $^{31}P\{^1H\}$ NMR spectra of a solution of **1** with excess dibenzylamine exhibit not only the expected singlet for **4b** (see below) but a pattern of two AB quartets also observed in reactions of **1** with $PhCH_2N{=}C(H)Ph$, assigned to the imine adduct $Ru_2Cl_4(dppb)_2[PhCH_2N{=}C(H)Ph]$ (**7**; see below). Also evident are signals for the benzylamine adduct **5**. (Whether **4a** is also formed cannot be determined under these experimental conditions, because **4a** and **4b** give identical singlet resonances in their $^{31}P\{^1H\}$ NMR spectra; this point is discussed in more detail below.) The reaction scheme shown in Figure 2, involving dehydrogenation of secondary amine to imine, followed by hydrolysis of bound imine by trace water, is proposed to account for the formation of the benzylamine derivative.

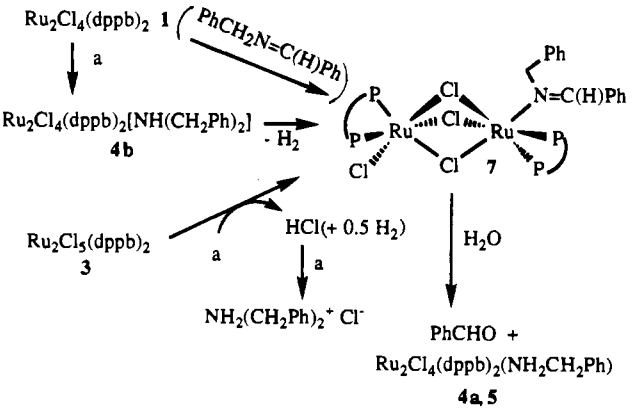

Figure 2. Proposed pathways for degradation of dibenzylamine to give benzylamine derivatives of **1**. a = $NH(CH_2Ph)_2$.

Hydrolysis of coordinated imine is inferred from the isolation of $Ru_2Cl_4(dppb)_2(NH_2CH_2Ph)$ (as **4a/5**) following reaction of **1** or **2** with the *N*-benzyl imines $PhCH_2N{=}C(H)Ar$ (Ar = Ph, *p*-$MeOC_6H_4$). The initial product is $Ru_2Cl_4(dppb)_2$(imine), **7**, as judged by $^{31}P\{^1H\}$ and ^1H NMR evidence for the *N*-benzylidenebenzylamine derivative; two AB quartets are observed, in a pattern characteristic of such $Ru_2Cl_4(dppb)_2(L)$ species (L = a two-electron donor ligand).[15] The lower field resonance, the location of which is typically invariant to the nature of L, is assigned to the phosphorus nuclei of the "(dppb)RuCl" portion of the complex; the higher-field resonance is assigned to "(dppb)Ru(imine)". The ^1H NMR data are consistent with structure **7** (of type **A** or **A′**, see below); the imine methine and methylene singlets are observed, in the expected integration ratios relative to the dppb CH_2 signals, at locations identical to those found for the free imine. Signals for **4a** and **5** appear in the ^{31}P NMR spectrum at variable rates, probably owing to hydrolysis of coordinated imine by trace water. Supporting evidence for such a reaction is provided by the concurrent appearance of ^1H NMR signals for the aldehyde, in a 1:1 molar ratio with **5** (the sole Ru product after prolonged reaction). The aldehyde singlet at δ ~10.0 ppm ($CDCl_3$), ca. 1.6 ppm downfield of the aldimine CH resonance, is diagnostic; in the case of $PhCH_2N{=}C(H)(p\text{-}MeOC_6H_4)$, the corresponding methoxy singlet for *p*-methoxybenzaldehyde emerges at 3.90 ppm (cf. 3.83 ppm for the starting imine; both signals are observed where imine is used in excess). Isolation of **5** or (principally) **7** under closely similar conditions, as described in the Experimental Section, is thus almost certainly a function of the proportion of water present. Formation of the benzylamine species is inhibited by added H_2, as indeed implied by the accessibility of clean **4b** via reaction of **3** with dibenzylamine or $PhCH_2N{=}C(H)Ph$ under H_2.

Reduction of **3** by benzylamine in air to generate mononuclear **6**, instead of the possible hydrolysis product $Ru_2Cl_4(dppb)_2(NH_3)$, suggests a competition between imine hydrolysis and displacement of $HN{=}C(H)Ph$ by benzylamine, in which the latter process is favored. Imine displacement appears to be more facile by benzylamine than by dibenzylamine, presumably for steric reasons. The dinuclear ruthenium framework may also play a part in activating bound imine toward hydrolysis; complexes of type **7** appear to be highly efficient scavengers of trace water, in contrast to certain mononuclear Ru− and Os−imine species, the hydrolytic stability of which may be inferred

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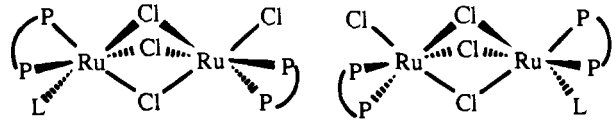
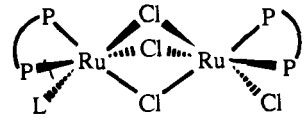
from their synthesis via condensation of aldehyde with bound ammine.[25,26] Imine hydrolysis may be impeded in the benzylamine system by the facile formation of mononuclear derivatives. Hydrolysis is clearly favored for dibenzylamine, following its dehydrogenation, and the net effect is dealkylation of the secondary amine.

A similar dehydrogenation−hydrolysis pathway may operate for other secondary amines. Preliminary results suggest that small amounts of products that could be $Ru_2Cl_4(dppb)_2(L)$ (L = NH_2Ph, NH_2Et) are formed in reactions of **2** and **3** with $NHPh(CH_2Ph)$ or $NHEt_2$, respectively. An earlier report of dealkylation of $NHMe(CH_2Ph)$ by $RuCl_2(PPh_3)_3$[27] may also be accounted for by such a reaction sequence; significantly, MeN=C(H)Ph was detected during the reaction. In this context the reported dealkylation of dialkylamines by $MCl_3(PMe_2Ph)_3$ (M = Ru, Os), forming primary amine complexes of M(II), the secondary amine hydrochloride, and alkane fragments,[24] is of particular interest. All of these observations are consistent with the mechanism outlined here, with an additional aldehyde-decarbonylation step. The latter, which is well established for these group 8 metal complexes,[6,28] would account for the observed excision of one carbon from a cleaved alkyl unit, as well as the failure to observe acetaldehyde.

Indirect evidence for a dehydrogenation pathway was also found in preliminary experiments with tri-*n*-octylamine, which (like benzylamine) effects reduction of **3** to a diamagnetic Ru(II) species in air. An iminium ion intermediate, rather than an imine, may be implicated. A formal relationship can be seen between these reactions and the transalkylation of tertiary amines by platinum group metals, in which no net loss of an alkyl group occurs: the latter are thought to involve attack of amine, rather than water, on an iminium intermediate.[13,27] A related process may be involved in the thermal degradation of tertiary amines. Such pathways may be more common than has been generally recognized, as suggested by the recently reported[29] formation of $[NH_2Et_2^+][Ru_2Cl_5(binap)_2^-]$ on reaction of triethylamine with binap and $[RuCl_2(COD)]_n$, under conditions commonly used for synthesis of the asymmetric hydrogenation catalyst $Ru_2Cl_4(binap)_2(NEt_3)$.[30,31] Similar results have been found on reexamination of the reaction of N^nBu_3 with $RuCl_2(dppb)(PPh_3)$ in refluxing benzene studied in these laboratories;[15] the product of this reaction is $[NH_2{}^nBu_2^+][Ru_2Cl_5(dppb)_2^-]$,[32] rather than $Ru_2Cl_4(dppb)_2(NH^nBu_2)$, as originally reported.[15] The chlorine analysis is the key criterion for distinguishing between the ionic and the neutral species. That the latter type exists is demonstrated in this paper and by our earlier work on the isolation of $Ru_2Cl_4(dppb)_2(NEt_3)$[15] from the amine reaction with **1** at room temperature. In solution, this NEt_3 complex (analogous to **4a** and **4b**) gives a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ ~49 ($CDCl_3$), attributed to a rapid amine exchange process, which renders the Ru centers (and consequently all four phosphorus nuclei) equivalent on the NMR time scale.[15] Solid-state $^{31}P\{^1H\}$ data for $Ru_2Cl_4(dppb)_2(NEt_3)$ do show four resonances (δ 56.4, 54.1, 47.1, 40.7; line broadening ($\omega_{0.5}$ ~ 162 Hz) causes each of these signals to appear as a singlet rather than a doublet);[33] these data imply structure **A** (and/or the enantiomer **A'**), where L = NEt_3, with no discernible coupling through the bridging chlorines. A static, cisoid stereoisomer **B** ("cisoid" referring to the terminal, coplanar L and chlorine ligands) would be expected to give two singlets in the $^{31}P\{^1H\}$ NMR spectrum. Again, this assumes no coupling through the bridge; it should be noted that although through-bridge P-coupling is observed in complexes such as $(PPh_3)_2(H)Ru(\mu\text{-}H)(\mu\text{-}Cl)_2Ru(\eta^2\text{-}H_2)(PPh_3)$,[34,35] no such coupling has been observed in complexes of type **4**.[15]



A **A'**



B

The anion $Ru_2Cl_5(dppb)_2^-$ (cf. $Ru_2Cl_5(binap)_2^-$) is a symmetrical, triply chloro-bridged species, which also gives rise to a $^{31}P\{^1H\}$ singlet in the δ 49 region,[3,16] and thus solution ^{31}P data would not distinguish $Ru_2Cl_4(dppb)_2(NEt_3)$ and, for example, $[NH_2Et_2^+][Ru_2Cl_5(dppb)_2^-]$. The use of higher temperatures in synthetic procedures may favor formation of such "dealkylated ionic species" *vs* the neutral species. This possibility, including the overall reaction stoichiometry which requires a chlorine-deficient coproduct, is currently under investigation.

Complexes **4a** and **4b**, like the NEt_3 species, are assumed to have structure **A** (**A'**), which has been demonstrated crystallographically for the corresponding complex with L = S-bonded dimethyl sulfoxide.[15] A complication in the current experiments using excess dibenzylamine was the inability to distinguish between **4a** (the benzylamine adduct) and **4b** (the dibenzylamine adduct) by $^{31}P\{^1H\}$ NMR, both giving a singlet at δ 48.9 in $CDCl_3$. The isolated complexes can be distinguished by ^1H NMR data, though the spectra (which are consistent with the η^1-bound amines), are largely similar, being simplified by the equivalence of the P atoms. The dppb CH_2 protons appear as four broad multiplets at essentially the same positions for both species, but a principal difference is seen in the integration ratios of the dppb and amine CH_2 protons (8:1 for **4a**, 4:1 for **4b**). The amine CH_2 resonances, which undergo negligible coordination shifts (<0.1 ppm), appear as singlets, owing to an exchange process of the type described above. As frequently found for the readily exchangeable amine protons, their integrated intensities (relative to those for the dppb CH_2 protons) are variable and approximate.

The structure for **5** has not been delineated; the complex analyzes for $Ru_2Cl_4(dppb)_2(NH_2CH_2Ph)$, the "same" formulation as for **4a**, although the latter was isolated with a solvate water molecule. The NMR spectra for **5** are consistent with this formulation but are complex; the $^{31}P\{^1H\}$ data (in C_6D_6) show now two sets of AB quartets, and the implied lack of molecular

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symmetry is supported by the presence in the ^{1}H NMR spectrum of 16 inequivalent resonances for the dppb methylene groups. Notably, the benzylamine CH_2 and NH_2 protons are also diastereotopic, and unusually for amine complexes, the latter do not exchange with D_2O. In contrast to the data for the other amine complexes described above, the amine CH_2 protons also exhibit a pronounced upfield coordination shift (of ~0.7 and 1.15 ppm, respectively). This evidence points toward an unprecedented and "more rigid" binding mode for the amine ligand and cannot be accommodated within the η^1-NH_2CH_2Ph structures shown above, particularly given the assignment of **A**/**A**′ to **4a**. We tentatively suggest an amine-bridged structure for **5**, in which one coordination site is provided by the lone pair on nitrogen and the other possibly by an agostic N−H or C−H bond. Complex **4a**, on refluxing in benzene under Ar, is converted to **5** (60% after 22 h), and **5** can be converted to **4a** in solution at ambient conditions under H_2 (100% conversion in 4 d) or N_2 (30% in 7 d);[19] **4a** and **5** appear to be isomers and the interconversions are readily envisioned, considering the existence of RuCl(dppb)(μ-Cl)$_3$Ru(dppb)(L), L = H_2 or N_2, which can be formed reversibly from [RuCl(dppb)]$_2$(μ-Cl)$_2$.[15]

We recently reported on the facile H_2 hydrogenation of $PhCH_2N{=}C(H)Ph$ to dibenzylamine using as catalysts a range of Ru ditertiary phosphine species, of which the most active were **1** and **3**.[14] The simultaneous utility of these complexes for imine hydrogenation and amine dehydrogenation offers less conflict than may be supposed. The dehydrogenation pathway is not catalytic under any of the conditions here employed, and while closely related systems have been used as catalysts for amine dehydrogenation[22] and homologation,[2,7] all reported examples of such processes require elevated temperatures. Furthermore, the benzylamine species **5** and **6** function as efficient imine hydrogenation catalysts, with reduction rates comparable to those found for related nitrile derivatives.[19] The mode of reactivity for species such as **1** and **3** may therefore be controlled by choice of reaction conditions. The use of a complex (for example, $RhCl(PPh_3)_3$) to effect both catalytic hydrogenation (of olefins) and dehydrogenation (of alkanes) is not unprecedented.[36]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Johnson Matthey Ltd. for a loan of $RuCl_3 \cdot 3H_2O$. D.E.F. thanks the Killam Foundation for a postgraduate fellowship, administered by the University of British Columbia.

IC9414334

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