0.22 (s, 3 H), 0.82 (s, 9 H), 1.00–1.35 (br, 3 H), 3.90 (s, 1 H), 4.25–4.35 (m, 1 H), 6.60–7.40 (13 H). Anal. Calcd for $C_{27}H_{30}Si$: C, 84.75; H, 7.90. Found for a mixture of (*E*)-**6** and (*Z*)-**6**: C, 84.36; H, 8.14.

Acknowledgment. We gratefully acknowledge the National Science Foundation and the North Texas State Univeristy Organized Research Fund for their support of this work. L.T.L. thanks the Robert A. Welch Foundation for a Predoctoral Fellowship.

Registry No. (*E*)-1, 85803-36-7; (*Z*)-1, 85803-37-8; **2a**, 83686-83-3; **2b**, 83709-79-9; **2c**, 83709-80-2; **2d**, 83709-81-3; **2e**, 83709-82-4; **3a**, 85803-35-6; **3b**, 85879-91-0; **3c**, 85880-58-6; **3d**, 85879-92-1; **4a**, 85803-38-9; **4b**, 85803-39-0; **5**, 85827-91-4; **6a**, 85803-40-3; **6b**, 85803-41-4.

Communications

Some Observations on the $RuCl_3/PR_3$ Catalyzed Conversion of Primary Amines to Secondary Amines

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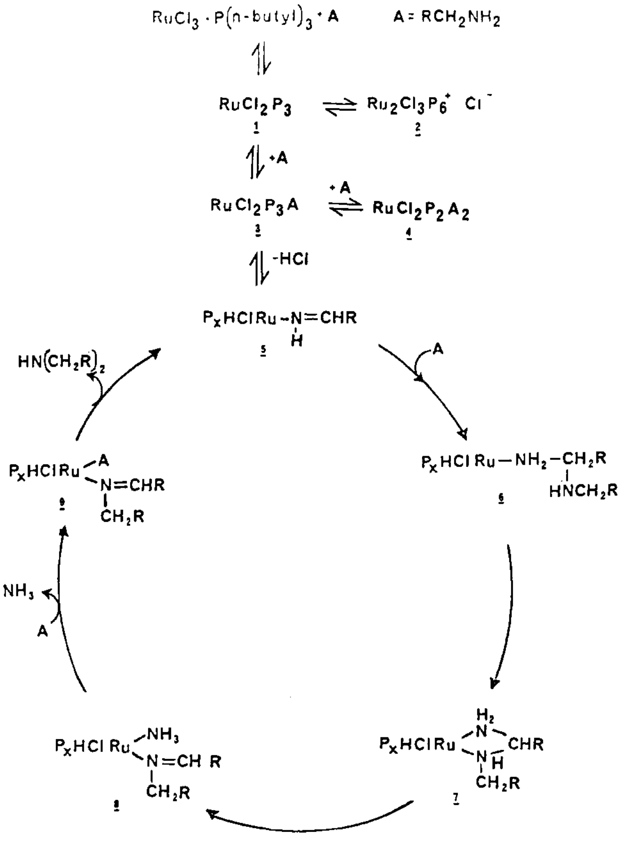
Summary: Close examination of the $RuCl_2(PPh_3)_3$ catalyzed synthesis of secondary amines from primary amines reveals the presence of benzene formed via PPh_3 decomposition during the reaction. $RuCl_3/PBu_3$ generates a much more active and stable system. Rate studies indicate imine hydrogenation occurs ~200 times faster than the overall reaction, indicating amine dehydrogenation is probably the rate-determining step. Reactions under D_2 reveal deuteration of the α-carbon of the alkyl amines. A mechanism consistent with these and other observations is proposed.

There has been much recent interest in the homogeneous[1-5] catalysis of amine redistribution reactions.[6] Porzi et al. have reported that $RuCl_2(PPh_3)_3$ catalyzes alkyl group scrambling,[3] the conversion of primary to secondary amines,[4] and the formation of heterocycles from α,ω-aliphatic diamines.[5] Although the catalyst was not examined during or after the reaction, it was assumed that such reactions proceed via metal-catalyzed dehydrogenation/hydrogenation sequences. Our work on the dehydrogenation of alcohols[7] using homogeneous ruthenium catalysts revealed catalytic activity extremely dependent on the nature of the phosphine ligand. As a continuation of these studies we have examined the effect of PR_3 on the $RuCl_2(PR_3)_3$ catalyzed conversion of primary to secondary amines.

Rate and selectivity data for the conversion of decyl to didecylamine are given in Table I.[8] The reaction rates were determined by GC analysis of reactions run in sealed vessels[9] and by measurement of NH_3 evolution by a gas buret.

Scheme I



Under our conditions the $RuCl_2(PPh_3)_3$ catalyst system reveals an initial first-order dependence on catalyst and amine concentration.[10] As the reaction proceeds, however,

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[1] Shvo, L.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753.

[2] Laine, R. M.; Thomas, D. W.; Cary, L. W. *J. Am. Chem. Soc.* **1982**, *104*, 1763.

[3] Arcelli, A.; Khai, B. T.; Porzi, G. *J. Organomet. Chem.* **1982**, *231*, C31.

[4] Khai, B. T.; Concilio, C.; Porzi, G. *J. Org. Chem.* **1981**, *46*, 1759.

[5] Khai, B. T.; Concilio, C.; Porzi, G. *J. Organomet. Chem.* **1981**, *208*, 249.

[6] Redistribution is herein meant to imply all amine reactions where net movement of alkyl groups occurs.

[7] Jung, C. W.; Garrou, P. E. *Organometallics* **1982**, *1*, 658.

[8] The decylamine model system was chosen because the high boiling points of the reactants and products allowed acquisition of reliable rate date and because the slower rates of such long chain amines enabled differences in reactivity due to PR_3 substitution to be readily observed. Similar results were obtained with hexyl and other aliphatic amines.

[9] Aliquots of a decane solution of $RuCl_3/4PR_3$ and primary amine were sealed in glass vessels and periodically withdrawn from a constant temperature bath to examine the reaction profile.

[10] Running the reaction in an open vessel connected to a gas buret results in secondary imine becoming the major product (Table I), thus H_2 as well as NH_3 is being evolved complicating the rate data obtained in this manner. When the reaction is conducted in a sealed vessel with 2–4% catalyst as described,[4] secondary amine is the major (>90%) product.

Table I. Reaction of Decylamine with $RuCl_3/PR_3$ Catalyst Systems[a]

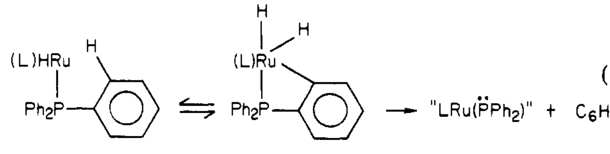
cat. system	temp, °C	[Ru], mM	10^3k,[b] min^{-1}	initial rate, mL/min	hours	convn, %	% of secondary amine	% of secondary imine
$RuCl_3 \cdot H_2O + 4PPh_3$	171 ± 2	19.8	1.25	2.22				
	178 ± 2	6.78	0.42[c]	0.77	2.5	13	14	85
$RuCl_3 \cdot H_2O + 4PBut_3$	178 ± 2	6.68	1.92 ± 0.05	3.73	5	100	87	12
	175 ± 2	6.69	1.40 ± 0.1	3.32				
	175 ± 2	6.69	4.5 ± 0.1[d]	3.32				
	150 ± 2	6.83	0.24	0.76				
	200 ± 2	7.00	4.63	9.42				
$Ru(dppe)_2Cl_2$	183 ± 2	6.68		3.1	17	31	19	79

[a] Typical run – 5.0 g decylamine, 10.0 g of *n*-decane. [b] Measuring NH_3 evolution unless otherwise noted. [c] Taken during first 35% of reaction while data fits first-order rate plot. [d] Measuring disappearance of primary amine.

we observe extensive catalyst decomposition and thus a tailing off of the reaction rate. The $^{31}P\{^1H\}$ NMR spectrum of a solution of $RuCl_3/PPh_3$/decylamine (A) reveals initial reduction to $RuCl_2(PPh_3)_3$ and subsequent equilibration with $RuCl_2(PPh_3)_2(A)_2$[11] (eq 1). A similar equilibrium is

$$RuCl_2(PPh_3)_3 + 2A \rightleftharpoons RuCl_2(PPh_3)_2(A)_2 + PPh_3 \qquad (1)$$

observed between $RuHCl(PPh_3)_3$ and $RuHCl(PPh_3)_2(A)_2$. These are the major species observed if a catalytic reaction is halted and a ^{31}P NMR of the solution is obtained. When the reaction is conducted catalytically under 30 psig of D_2,[13] subsequent $^{13}C\{^1H\}$ and $^2D\{^1H\}$ NMR analysis[14] reveals monodeuteration of the α-carbon of the decyl chain. GC analysis of the reaction solution reveals benzene.[15] The mode of catalyst deactivation therefore appears to be *P*-aryl orthometalation and subsequent benzene elimination (eq 2). Such orthometalations are commonplace,[16]



(2)

and aryl eliminations from such transition metal triarylphosphine complexes at high temperatures have been observed more and more frequently in recent years.[17] Approximately 1 mol of benzene/mol of PPh_3 decomposition was detected in solution at the end of the reaction.[18] No phosphide complexes have thus far been observed or isolated.

The use of diphosphines such as $Ph_2P(CH_2)_xPPh_2$, x = 2–4, which gave superior results in our previous alcohol dehydrogenation studies,[7] revealed initially slow rates (Table I) which decayed with time reminiscent of the PPh_3 results.

The $RuCl_3/PBu_3$ catalyst system reveals a first-order dependence on catalyst and amine, but, in contrast to the $RuCl_2(PPh_3)_3$ system, the rate remains first order over 95% of the reaction, the solution remaining homogeneous throughout. Periodic sampling during the reaction reveals a steady-state concentration of ~5% secondary imine, $CH_3(CH_2)_9N{=}CH(CH_2)_8CH_3$, D, primary and secondary amine, and no other organic species.

Examination of the $^{31}P\{^1H\}$ NMR spectrum of a catalytic reaction solution after 5 h reveals the major constituents are $[Ru_2Cl_3(PBu_3)_6]Cl$,[19] $RuH_2(PBu_3)_4$,[20] and $RuHCl(PBu_3)_3A$[21] in contrast to the species identified above for the PPh_3 catalyst system.

On the basis of the above data, we propose Scheme I as a possible mechanism. All reactions in the cycle are potentially reversible. D was prepared by an alternate route[22] and hydrogenated, under 30 psig of H_2, using the $RuCl_3/PBu_3$ catalyst system. One observes a rate ~200 times faster than the observed reaction rate for the decyl to didecylamine reaction[23] indicating hydrogenation of the intermediate imines cannot be the rate-determining step. Comparative reactions under H_2 vs. argon (2 atm, 175 °C, other conditions as in Table I) to examine possible H_2 inhibition revealed revealed pseudo-first-order rate constants of of 3.4×10^{-3} and 2.1×10^{-3} m^{-1}, respectively, indicating the reactions are not inhibited by H_2 but rather enhanced to a minor extent. On the basis of the above results, we believe the rate-determining step is amine dehydrogenation (**3** → **5** or **9** → **5**). Observation of free secondary imine, D, during the reaction indicates dissociation of the nitrogen ligands from **5**, **6**, **8**, or **9** is possible. Since $HN{=}CH(CH_2)_8CH_3$ is not observed, one must assume it reacts quickly with A or NH_3 if it does dissociate from the metal. Since imines react with amines in basic media,[24] organometallic intermediates need not be involved

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(11) Isolated as the ethylamine analogue: $^{31}P\{^1H\}$ NMR (C_6D_6, δ 25 °C) + 44 (s). Anal. Calcd for $RuP_2Cl_2C_{40}H_{45}$: Ru, 14.2; Cl, 5.0; C, 67.8; H, 6.4. Found: Ru, 14.3; Cl, 5.4; C, 66.9; H, 6.3.

(12) Prepared by the reaction of $RuHCl(PPh_3)_3$ with amine or the reaction of $RuCl_2(PPh_3)_2(amine)_2$ with H_2. Isolated as the ethylamine analogue $^{31}P\{^1H\}$ NMR (C_6D_6, δ 25 °C) + 70 (s). Anal. Calcd for $RuP_2ClC_{40}H_{45}$: Ru, 14.2; Cl, 5.0; C, 67.8; H, 6.4. Found: Ru, 14.3; Cl, 5.4; C, 66.9; H, 6.3.

(13) D_2 is known to exchange with species such as $RuHCl(PPh_3)$, for example, see: Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A*, **1968**, 3143.

(14) Incorporation of deuterium was confirmed by ^{13}C and ^2D NMR of isolated $HN(hexyl)_2$. Mass spectral analyses were carried out both in the EI and CI modes but failed to give clear-cut exchange patterns. (See ref 26.)

(15) Benzene is also observed when one uses $RuCl_2(PPh_3)_3$ to catalyze alkyl group scrambling reactions of secondary amines. Laine, R., unpublished results.

(16) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235.

(17) See references such as: Maclaughlin, S. A.; Carty, A. J.; Taylor, N. J., *Can. J. Chem.* **1982**, *60*, 88. Nakamura, A.; Otsuda, S. *Tetrahedron Lett.* **1974**, 463. Fahey, D. R.; Mohan, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 4499.

(18) A reaction using 240 mg of $RuCl_2(PPh_3)_3$ (0.25 mmol) resulted in the production of 52 mg of benzene, 29.7% of theoretical.

(19) Which was isolated from the reaction as its Ph_4B^- salt. Anal. Calcd for $Ru_2Cl_3P_6BC_{96}H_{82}$: Ru, 10.98; Cl, 5.78; P, 10.09; B, 0.59. Found: Ru, 11.16; Cl, 5.84; P, 10.17; B, 0.62. Such a species is the expected form of $RuCl_2(PPh_3)_3$ in polar solvents with ligands less bulky than PPh_3. See: Armit, P. W.; Boyd, A. S. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1663.

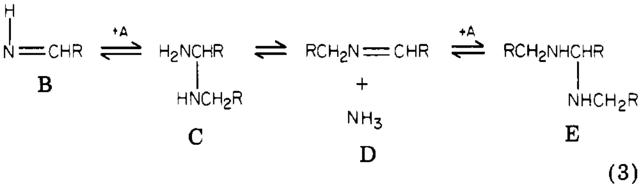
(20) $H_2Ru(PR_3)_4$ has been prepared previously as the PPh_2Me analogue: Dewhirst, K. C.; Keim, W.; Reilley, C. A. *Inorg. Chem.* **1968**, *7*, 546. For $Ru(PBu_3)_4H_2$, $^{31}P\{^1H\}$ NMR (C_6D_6, δ, 25 °C) +24.4 (t, $^2J_{P-P}$ = 21 Hz), +14.1 (t); ^1H NMR (C_6D_6, δ, 25 °C) −11.71 (m).

(21) For $Ru(PBu_3)_3$(decylamine)HCl: $^{31}P\{^1H\}$ NMR (C_6D_6, δ, 25 °C) +17.89 (d, $^2J_{P-P}$ = 18.6), −1.48 (t); ^1H NMR (C_6D_6, δ, 25 °C) −7.57 (d of t, $^2J_{P-H}$ = 26.1 (cis), 137.2 (trans)).

(22) Campbell, K. N.; Sommers, A. H.; Campbell, B. K. *J. Am. Chem. Soc.* **1944**, *66*, 82.

(23) [Ru] = 9.47×10^{-2} mM; at 150 °C the reaction fits first-order kinetics with a *k* value of 1.1×10^{-2} m^{-1}. Thus the hydrogenation proceeds at 200 times the rate of the overall reaction at 150 °C neglecting the fact that 1.45 times the [Ru] is present.

in the transformation shown in eq 3, but an organometallic species is needed to hydrogenate D to secondary amine. The ultimate hydrogen source in such a sequence comes from another amine, thus the reaction can be considered a transfer hydrogenation of sorts.



(3)

In conclusion this proposed mechanism should be contrasted with that proposed for the $Ru_3(CO)_{12}$ and Pd black H/D exchange studies on NEt_3.[25] In that case a mechanism is proposed whereby the α- and β-carbons can be metalated, and thus deuterated, because of the orientation of the ligated amine on the Ru_3 framework. Our mass spectral data, although not yet clearcut, does indicate a minor amount of multiple deuteration is occurring.[26] Thus, an alternate mechanism of H/D exchange may be operational outside the framework of our proposed mechanism. Such observations warrant further study.

We are currently actively pursuing the further intricasies of such catalyst systems in hopes of isolating further intermediates and unraveling further mechanistic details.

Acknowledgment. Our thanks to Dr. Clayton D. Wood and Dr. Horst G. Langer for mass spectral data and Dr. Richard M. Laine for helpful discussions.

Registry No. $RuCl_2(PPh_3)_2$(ethylamine)$_2$, 85565-62-4; $RuHCl(PPh_3)_2$(ethylamine)$_2$, 85565-63-5; $RuHCl(PBu_3)_3$(decylamine), 85565-64-6; $[Ru_2Cl_3(PBu_3)_6]^+Ph_4B^-$, 85565-66-8; $RuCl_3$, 10049-08-8; PPh_3, 603-35-0; PBu_3, 998-40-3; Ru(dppe)$_2Cl_2$, 16594-81-3; decylamine, 2016-57-1.

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[24] Layer, R. W. *Chem. Rev.* **1963**, *63*, 489.

[25] Shvo, Y.; Thomas, D. W.; Laine, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 2461.

[26] Unlike studies on NEt_3, mass spectral studies on our HN(dec)$_2$ system revealed deuteration of the chain could occur during fragmentation.[13] The chemical ionization spectrum of DN(hexyl)$_2$ in a methane plasma revealed a 114 peak due to N(hexyl)Me$^+$ and a 115 peak due to d_1-N(hexyl)Me$^+$. The CI mass spectrum for dihexylamine produced by the ruthenium/tributylphosphine catalyst system revealed d_0, 56.4%, d_1, 27.9%, d_2, 10.8%, and d_3, 3.1%, based on the 114 peak as d_0. Thus, although d_2 could come from incorporation of D into the backbone during fragmentation, vide infra, d_3 must come from multiple deuteration of the chain.

Reaction of $[(CO)_4FeC(O)OMe][C(NMe_2)_3]$ with $MeSO_3F$. Evidence for a Metal Alkylation

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Summary: The reaction of $[(CO)_4FeC(O)OMe][C(NMe_2)_3]$ with $MeSO_4F$ at −78 °C results in the formation of $(CO)_4Fe(Me)C(O)OMe$ (**7**). At about 0 °C this complex decomposes to form methyl acetate and iron carbonyl species.

Some years ago we reported the synthesis of stable carbamoyl and alkoxycarbonyl complexes by addition of orthoamide derivatives $C(NMe_2)_3R$ to a carbonyl carbon atom of an appropriate metal carbonyl compound (eq 1).[1]

$$\underset{\substack{\mathbf{1a{-}c}\\ \mathbf{2a{-}c}}}{(CO)_nM} + \underset{\mathbf{3}}{C(NMe_2)_3R} \xrightarrow[25\ ^\circ C]{C_6H_6} \underset{\substack{\mathbf{4a{-}c}\\ \mathbf{5a{-}c}}}{[(CO)_{n-1}MC(O)R][C(NMe_3)_3]} \quad (1)$$

a, R = NMe_2, **b**, R = OMe, **c**, R = OEt; M =
Fe for 1 and 4 (n = 5), M = Ni for 2 and 5 (n = 4)

High yields of **4** and **5** were obtained, and the equilibrium in reaction 1 lies far to the right. If a CS ligand is present, as in $(CO)_4FeCS$, the R group of **3a** is transferred preferentially to the more electrophilic thiocarbonyl carbon atom to yield a thiocarbamoyl complex. This on alkylation with $MeSO_3F$ gives the corresponding carbene complex.[2] Analogous reactions were carried out with the anion of **4a**.[3] This compound also behaves as a chelating ligand toward $NiBr_2$ to produce the covalent complex $[(CO)_4FeC(O)NMe_2]_2Ni$ with two iron–nickel bonds in a rare linear arrangement.[4] In contrast, **4b**, **4c**, and the corresponding thiocarbamoyl complex do not react with Ni^{2+} salts in this manner.

As an extension of our previous investigations concerning the reactivity of **4** and **5** toward various electrophiles, we report here an unusual metal (instead of O) alkylation of **4b** with $MeSO_3F$ and the thermal decomposition of the neutral alkylation product under very mild conditions to yield methyl acetate.

When **4b** is allowed to react with $MeSO_4F$ at −78 °C, a bright yellow crystalline powder can be isolated which is very soluble in pentane but decomposes slowly above −30 °C and rapidly at room temperature to give a brown, insoluble solid along with a volatile liquid.[5] The latter was identified as methyl acetate by comparison of its IR and ^1H NMR spectra and GC behavior with those of an authentic sample.

In contrast to similar experiments with **4a**,[3] the corresponding thiocarbamoyl complex[2] and various other anionic group 6B transition-metal complexes which give carbene complexes,[6] the spectroscopic data of the reaction product do not agree with the formation of the expected carbene complex **6**. However, all data are consistent with the formation of **7** as the result of methylation of the iron atom (eq 2). The increase of the coordination number from five to six may formally be considered as an oxidation of

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[1] (a) Petz, W. *J. Organomet. Chem.* **1976**, *105*, C19. (b) Petz, W. *Ibid.* **1975**, *90*, 223.

[2] Petz, W. *J. Organomet. Chem.* **1981**, *205*, 203.

[3] (a) Schmetzer, J.; Daub, J.; Fischer, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 487. (b) Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Muller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162.

[4] (a) Petz, W. *J. Organomet. Chem.* **1977**, *133*, C25. (b) Petz, W.; Krüger, C.; Goddard, R. *Chem. Ber.* **1979**, *112*, 3413.

[5] Procedure: To a stirred solution of **4b** (0.95 g, 0.4 mmol) in CH_2Cl_2 at −78 °C is added an equimolar amount of CH_3SO_3F under an atmosphere of dry nitrogen. Immediately a dark orange-brown solution is formed which is stirred for about 10 min. The mixture is allowed to warm to about −30 °C, and the solvent is evaporated in vacuo. The dry residue is kept at low temperature and extracted with ca. 80 mL of cold pentane (−78 °C). The clear yellow pentane solution is decanted from insoluble material. Slow evaporation of the solvent at −78 °C results in the precipitation of **7** as a bright yellow crystalline powder. No analyses could be obtained because of the thermal instability of the compound. Recrystallization of the residue from the pentane extraction from hot water gave pure white $[C(NMe_2)_3]SO_3F$, identified by IR and NMR spectroscopy.

[6] Fischer, E. O. *Pure Appl. Chem.* **1970**, *24*, 407.