ORGANOMETALLICS

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PNS-Type Ruthenium Pincer Complexes

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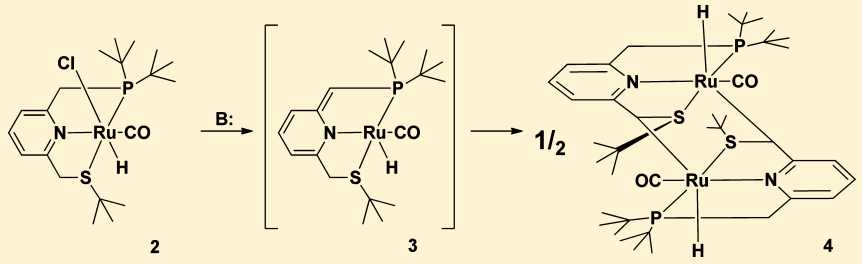
Supporting Information

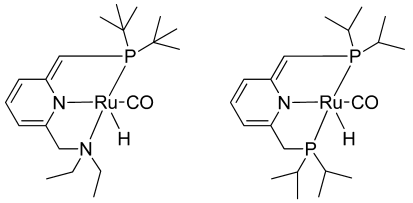


ABSTRACT: The PNS pincer-type ligand **1** and the novel Ru(PNS) complexes **2**–**8** were synthesized and characterized. The (PNS)RuH(Cl)CO complex **2** was prepared by reaction of ligand **1** with $RuH(Cl)CO(PPh_3)_3$. **2** reacted with KHMDS (potassium bis(trimethylsilyl)amide) to form the symmetrical dimeric complex **4** via the intermediacy of the dearomatized complex (PNS*)Ru(H)CO **3**, in which deprotonation of the benzylic-S "arm" took place. Reaction of **2** with excess NaH gave the dimeric **4**, by a formal intermolecular attack of the benzylic "arm" on a second ruthenium center. Complex **4** underwent spontaneous transformation in solution to the dinuclear complex **5** via C–S bond cleavage, resulting in the loss of a S-bound ^{t}Bu group. Treatment of **2** with KHMDS in the presence of PEt_3 resulted in the trapping of intermediate **3** in the form of the dearomatized complex **8**. Reaction of **2** with $LiHBEt_3$ gave the *trans*-dihydride complex **6**, which reacted with CO_2 to give the formato complex **7**, in which the formato ligand is located *trans* to the hydride. Complexes **2**, **4**, and **5** were also investigated as catalysts for the dehydrogenative coupling of alcohols with amines.

INTRODUCTION

Transition metal complexes of pincer ligands have found important applications in synthesis, bond activation, and catalysis.[1−11] We have reported the dearomatized pincer complexes (PNN)Ru(H)CO (**A**) and (PNP)Ru(H)CO (**B**), which catalyze several "green" catalytic reactions. Complex **A** is an efficient catalyst for the dehydrogenative coupling of alcohols to esters,[12−15] acylation of secondary alcohols by esters with dihydrogen liberation,[16] direct dehydrogenative coupling of alcohols and amines to form amides,[13−15,17] coupling of esters and amines to form amides with dihydrogen liberation,[18] facile catalytic hydrogenolysis of esters to alcohols,[19] and hydrogenation of organic carbonates, carbamates, and formates.[20] Complex **B** also catalyzes dehydrogenative coupling of primary alcohols to form esters,[12−15] dehydrogenation of β-amino alcohols to pyrazines,[21] and dehydrogenation of secondary alcohols to ketones.[13,22,23] Unlike complex **A**, complex **B** catalyzes the dehydrogenative coupling of alcohols and amines to generate imines, rather than amides.[13−15,24−27] PNP-based iron complexes efficiently catalyze the hydrogenation of CO_2.[28] Related bipyridine- and acridine-based ruthenium pincer complexes are also excellent catalysts.[29−34]

Apparently, modification of the pincer "arm" has a profound effect on catalytic activity. It was of interest to us to explore the



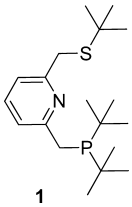
effect of replacing the amine arm with a thioether group. Hence, we decided to synthesize the new PNS ligand **1** and the corresponding ruthenium PNS pincer complexes, analogous to ruthenium PNN and PNP pincer complexes. Like in the case of the amine "arm" of PNN complexes, the thioether "arm" of PNS complexes is expected to be hemilabile,[35−38] but, unlike the PNN ligand, it lacks the ability to serve as a base.

RESULTS AND DISCUSSION

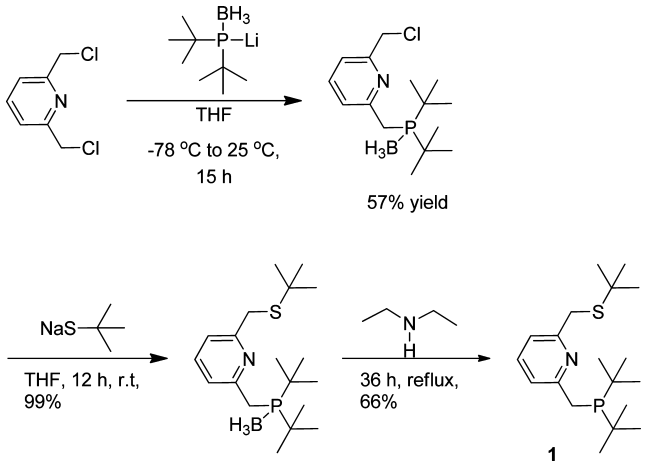
Synthesis of the PNS Ligand 1. The PNS ligand **1** (Scheme 1) was prepared using a procedure similar to the one reported by Szabo for the preparation of a PCS ligand.[39] Thus, reaction of $LiP^tBu_2(BH_3)$ with 2,6-bis(chloromethyl)pyridine gave rise to a mixture of monophosphine, diphosphine, and

Received: June 10, 2012
Published: August 27, 2012

   dx.doi.org/10.1021/om300516j | *Organometallics* 2012, 31, 6207−6214



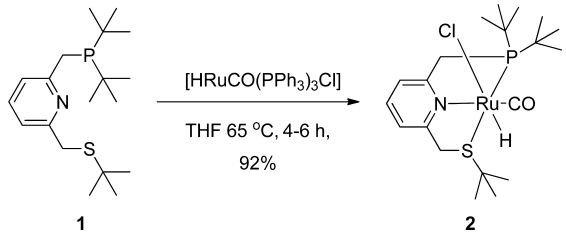
Scheme 1. Synthesis of the PNS Ligand 1



unreacted 2,6-bis(chloromethyl)pyridine. The monophosphine was isolated by column chromatography and treated with an excess of sodium 2-methyl-2-propanethiolate to give the borane-protected PNS ligand in 99% yield. Deprotection of the PNS ligand by reflux in diethylamine followed by column chromatography gave the PNS pincer ligand **1** as an air-sensitive white solid in 66% yield.

Synthesis of the Ru(PNS) Complex 2. The new Ru(PNS) complex **2** was prepared in 90% yield by reaction of $HRu(CO)(PPh_3)_3Cl$[40] with the PNS ligand **1** in THF at 65 °C (Scheme 2). The ^1H NMR spectrum of **2** showed the

Scheme 2. Synthesis of the Ru(PNS) Complex 2



coordinated PNS benzylic signals at a lower field relative to free PNS and a hydride ligand as a doublet at −14.9 ppm ($J_{H,P}$ = 24.7 Hz). The two inequivalent CH_2P protons exhibit a doublet of doublets at 3.37 ($J_{H,H}$ = 17 Hz; $J_{H,P}$ = 8.5 Hz) and 3.6 ppm ($J_{H,H}$ = 17 Hz; $J_{H,P}$ = 10 Hz), while the CH_2S protons exhibit a doublet at 4.12 ppm ($J_{H,H}$ = 17 Hz) and 5.12 ($J_{H,H}$ = 17 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **2** showed a singlet at 101.3 ppm. Crystals suitable for a single-crystal X-ray structure of **2** (Figure 1, Table 1) were obtained from a dichloromethane solution, showing an octahedral complex, with the hydride located *trans* to the chloride ligand.

Formation of the Binuclear Complexes 4–6. Our attempts to synthesize the dearomatized (PNS*)Ru(H)CO (PNS* = deprotonated PNS) complex **3** led to surprising

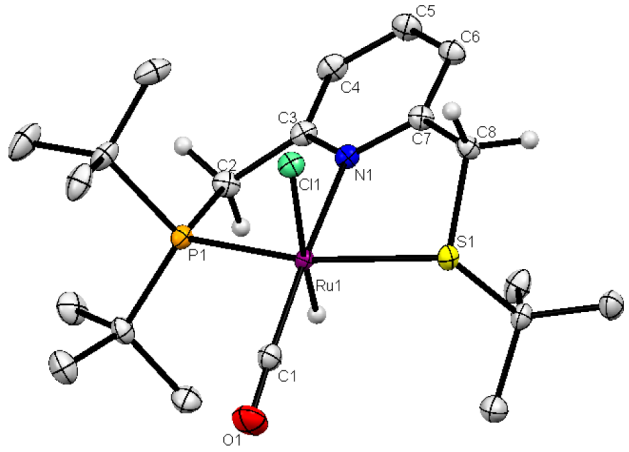


Figure 1. ORTEP drawing of a molecule of **2** at the 50% probability level. Hydrogen atoms, except benzylic ones and hydride, are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Complex 2

Ru1–Cl1	2.5668(6)	Ru1–N1	2.1338(19)
Ru1–S1	2.3954(6)	Ru1–P1	2.2927(6)
C7–C8	1.504(3)	S1–C8	1.819(2)
N1–Ru1–S1	82.04(5)	N1–Ru1–P1	82.20(5)
N1–Ru1–Cl1	91.95(5)	N1–Ru1–C1	172.86(9)

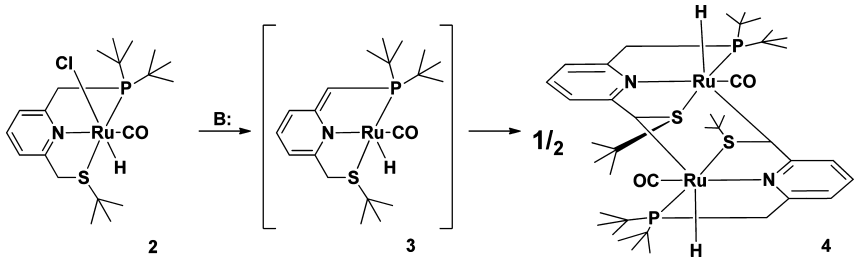
results. Upon reaction of complex **2** with the bases KO^{t}Bu or $(Me_3Si)_2NK$ (KHMDS), using a similar procedure to the one reported for the preparation of the dearomatized PNP[12] or PNN[17] complexes, the symmetric dimeric complex **4** was formed, rather than complex **3** (Scheme 3). The light brown complex **4** was sparingly soluble in pentane, THF, benzene, toluene, and dichloromethane and was unstable in solution at room temperature. Nevertheless we were able to obtain ^1H and $^{31}P\{^1H\}$ NMR of the crude complex. Single crystals of the complex were obtained by layering pentane over a concentrated toluene solution of **4** at −35 °C (Figure 2, Table 2). The X-ray structure of **4** exhibits a dimeric structure, in which each of the Ru atoms is bound to the opposite sulfur benzylic arm of the ligand.

In order to gain understanding regarding the reactivity of complex **2**, it was treated with NaH in THF at room temperature. Follow-up of the reaction by $^{31}P\{^1H\}$ NMR spectroscopy revealed after 5 h partial conversion to complex **4**. After 10 h two more singlet peaks (1:1 ratio) appeared at 98 and 99 ppm, and after 48 h they became the only peaks. The product that gave rise to these peaks was characterized as complex **5**, resulting from cleavage of a S–^{t}Bu bond (Scheme 4). The ^1H NMR spectrum of **5** revealed a missing ^{t}Bu-S group and the appearance of two doublet peaks (1:1 ratio) in the hydride region, at −10.67 (d, J_{PH} = 24 Hz, RuH) and −10.47 (d, J_{PH} = 21 Hz, RuH). In addition, one benzylic proton was missing. This data suggested that an asymmetric dinuclear complex was formed, lacking a ^{t}Bu group on one of the sulfur atoms. This was confirmed by a single-crystal X-ray crystallographic study (Figure 3, Table 3), which revealed that one of the Ru atoms is connected to a sulfur atom that lacks the ^{t}Bu group, and a second Ru atom formed a Ru–C bond to the benzylic arm (as observed with dimer **4**).

GC-MS analysis of the gas phase of the reaction leading to complex **5** revealed formation of isobutane. Based on this

dx.doi.org/10.1021/om300516j | *Organometallics* 2012, 31, 6207–6214

Scheme 3. Formation of the Dimeric Complex 4[a]



[a]B: $(Me_3Si)_2NK$ (KHMDS) or NaH.

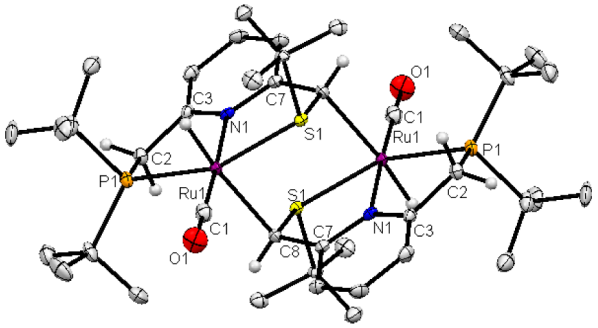


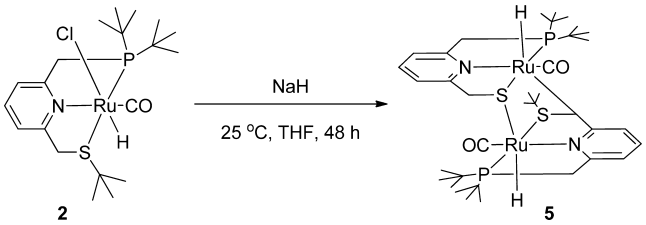
Figure 2. ORTEP drawing of a molecule of **4** at the 50% probability level. Hydrogen atoms, except benzylic ones and hydride, are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Complex 4

Ru1—C8[a]	2.392(3)	Ru1—C1	1.829(4)
C7—C8	1.458(4)	S1—C8	1.783(3)
Ru1—S1	2.3975(13)	Ru1—P1	2.2953(13)
N1—Ru1—S1	81.77(8)	N1—Ru1—P1	82.45(8)
N1—Ru1—C8[a]	86.49(11)	N1—Ru1—C1	177.46(14)

[a]In symmetry $1-x, -y, -z$.

Scheme 4. Formation of the Dinuclear Complex 5



observation, it is possible that formation of the dimer **4** is followed by rupture of the Ru—C bond and loss of the *β*-hydrogen of the sulfur ^{t}Bu group, releasing isobutene (which is eventually transformed to isobutane) to give complex **5** (Scheme 5), similar to the observation of Searles et al.[41]

Preparation and Reactivity of the *trans*-Dihydride Complex 6. Reaction of complex **2** with $NaHBEt_3$ in toluene gave the *trans*-dihydride complex **6** in 99% yields (by NMR). The ^{1}H NMR spectrum of **6** showed two hydride doublets of doublets at −4.92 ppm (dd, J_{HH} = 20 Hz, J_{PH} =6.4 Hz, 1H, RuH) and −4.62 ppm (dd, J_{HH} = 12.8 Hz, J = 6.4 Hz, 1H, RuH), typical of *trans*-dihydride complexes.[12,19] The ^{31}P{^{1}H} NMR spectrum exhibited a singlet at 115.2 ppm. Complex **6** is not stable in solution and slowly loses hydrogen to give the dimer **4**. Compex **4** also loses isobutene slowly at atmospheric

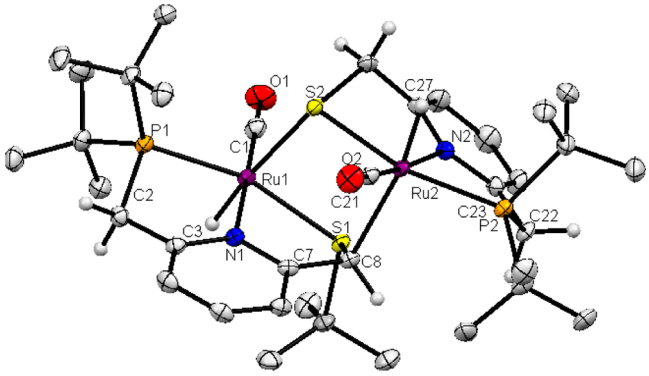
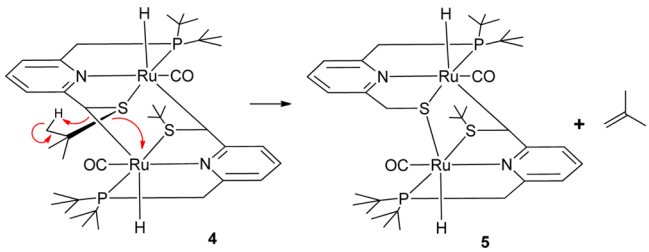


Figure 3. ORTEP drawing of a molecule of **5** at the 50% probability level. Hydrogen atoms, except benzylic ones and hydride, are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of Complex 5

Ru2—C2	2.361(3)	Ru1—S1	2.3805(9)
R2—S2	2.4032(9)	Ru1—S2	2.5030(9)
C7—C8	1.506(5)	C27—C28	1.496(5)
N1—Ru1—S1	80.87(8)	N2—Ru2—S2	82.12(8)
N2—Ru2—C2	89.00(11)	S1—Ru1—S2	85.91(3)

Scheme 5. Proposed Mechanism for the Transformation of 4 to 5



pressure and was fully converted to complex **5** within 8 h under vacuum (Scheme 6).

Upon reacting the crude complex **6** with CO_2 in toluene-d_8, the formato complex **7** was formed within minutes as a major product (~85%). The ^{31}P{^{1}H} NMR spectrum of **7** exhibited a singlet at 99.4 ppm, and the ^{1}H NMR spectrum exhibited the formyl hydrogen atom at 8.79 ppm and the hydride ligand at −17 ppm. Unfortunately, the crude mixture proved impossible to purify. However, a single-crystal X-ray structure of complex **7** was obtained (Figure 4, Table 4), confirming the structure and revealing that the formato ligand is located *trans* to the hydride (Scheme 7).

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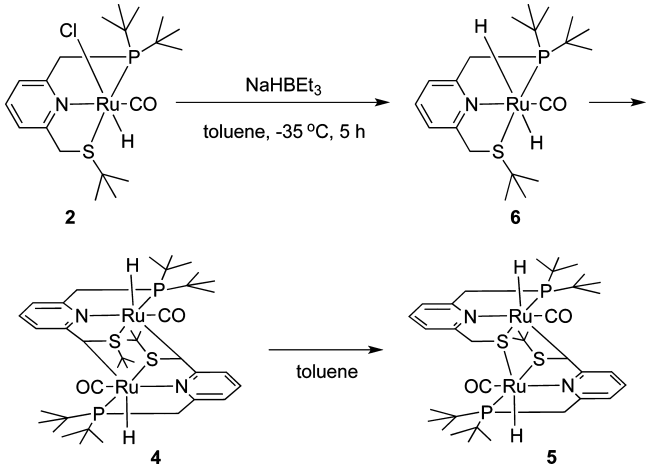
Scheme 6. Preparation of *trans*-Dihydride Complex 6 and Its Decomposition in Solution to Give the Dinuclear Complexes 4 and 5



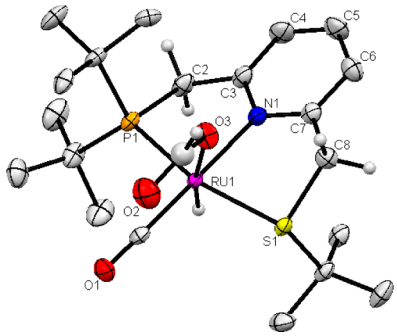


Figure 4. ORTEP drawing of a molecule of **7** at the 50% probability level. Hydrogen atoms, except benzylic, formate and hydride ones, are omitted for clarity.

Scheme 7. CO_2 Insertion into Ru−H to Give the Formato Complex 7

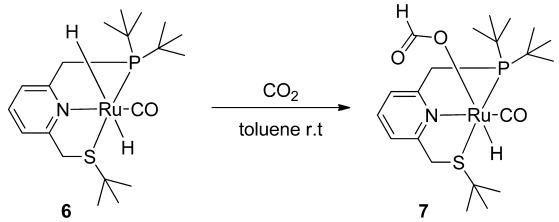
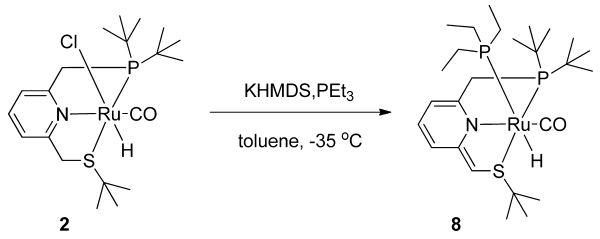


Table 4. Selected Bond Lengths (Å) and Angles (deg) of Complex 7

Ru1−S1	2.4003(6)	Ru1−O3	1.989(13)
Ru1−C1	1.838(3)	Ru1−P1	2.2852(7)
C7−C8	1.502(4)	S1−C8	1.822(3)
N1−Ru1−S1	81.81(6)	C1−Ru1−O3	100.7(4)
N1−Ru1−P1	82.24(6)	N1−Ru1−C1	177.68(10)

Trapping the Dearomatized Intermediate Complex 3. Two experiments were performed in order to trap the postulated dearomatized complex **3**. First, complex **2** was reacted with a base in the presence of PEt_3, leading to complex **8** (Scheme 8). The $^{31}P\{^1H\}$ NMR spectrum exhibited two peaks at −5.80 ppm (d, J_{PP} = 7.32 Hz, 1P, $(CH_3CH_2)_3P$)) and 95.16 ppm (d, J_{PP} = 8.54 Hz, 1P, $((CH_3)_3)_2CP$)), and the ^1H NMR spectrum exhibited the hydride at −8.92 ppm (dd, J_{PH} = 108 Hz, $J_{P'H}$ = 28 Hz, 1H, RuH). The large J_{PH} = 108 Hz indicates that the PEt_3 group is located *trans* to the hydride. The phosphine "arm" gives rise to two peaks at 2.78 (dd, J_{HH} = 16.4 Hz, J_{PH} = 6.4 Hz, 1H) and at 2.94 (dd, J_{HH} = 16.4 Hz, J_{PH} = 12.14 Hz 1H), while the S-^{t}Bu "arm" gives rise to a peak at 4.13 (d, J_{PH} = 4.4 1H), indicating deprotonation of this arm took place. The $^{13}C\{^1H\}$ NMR spectrum of the phosphine "arm" exhibits a peak at 38.84 (dd, J_{CP} = 16.0 Hz, J_{CP} = 0.95 Hz, CH_2P), while the S-^{t}Bu arm shows a peak at 65.1 (d, J_{CP} = 1.9 Hz, CHS).

Scheme 8. Preparation of the Dearomatized Complex 8



In the second experiment, complex **2** was reacted with a base under H_2 gas, leading after 30 min to a mixture of complex **6** (61%) and the two dinuclear complexes **4** (23%) and **5** (16%). After one day in solution the reaction progressed to give complex **6** (35%), complex **4** (8%), and complex **5** (57%). These experiments provide strong support for the intermediacy of the dearomatized complex **3**.

The reason that complex **3** dimerizes while the analogous dearomatized PNN and PNP complexes A and B do not dimerize may be the lower steric bulk of ^{t}BuS as compared with $(^t$Bu$)_2$P or Et_2N.

Catalytic Experiments. Coupling of amines with alcohols to form amides and hydrogen gas was reported[14] by our group to be catalyzed by (PNN)Ru(H)(Cl)CO (**A**), while using (PNP)Ru(H)(Cl)CO (**B**) under almost the same conditions gave imines instead of amides.[21] The main difference between these systems seems to be the presence of a potentially hemilable amine "arm" in **A**. Hence, it was of interest to us to explore the catalytic activity based on complex **2**, which possesses a hemilabile "arm".

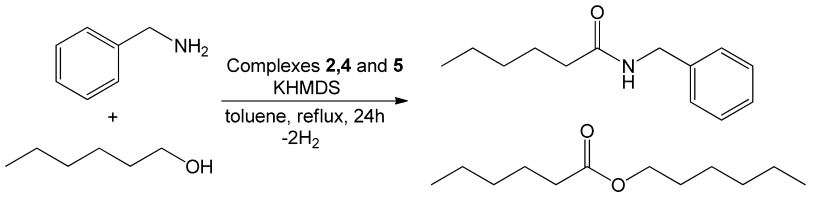
Studying complex **2** as a precatalyst in the amidation reaction (Scheme 6), 0.01 mmol of **2**, 10 mmol of 1-hexanol, 10 mmol of benzylamine, and 0.01 mmol of KHMDS were refluxed in toluene, leading to hexyl hexanoate (46% determined by GC) and *N*,*N*-benzylhexanamide (30% isolated). Under the same conditions, the dinuclear complexes **4** and **5** gave only 7% of *N*-benzylhexanamide (isolated) and 19% of the hexyl hexanoate (determined by GC). When the catalysis with the dinuclear complexes **4** and **5** was carried out without the presence of a base, no reaction took place.

We believe that the actual catalyst is the (unobserved) dearomatized intermediate **3**, analogous to the PNN and PNP ruthenium complexes **A** and **B**, which catalyzed the dehydrogenative amidation and esterification reactions, respectively. Upon conversion of **3** to the dinuclear complexes **4** and subsequently to **5**, the reaction is retarded. The reason for obtaining a mixture of the products ester and amide is not clear at this stage.

It is interesting that amide is formed, like in the case of the PNN complex **A**, unlike the case of the PNP complex **B**, in

dx.doi.org/10.1021/om300516j | *Organometallics* 2012, 31, 6207−6214

Table 5. Dehydrogenative Coupling of Benzylamine with 1-Hexanol Catalyzed by the Ruthenium Complexes 2, 4, and 5[a]



entry	precatalyst	yield (%) hexyl hexanoate[b]	yield (%) *N*-benzylhexanamide[c]
1	2[d]	46	30
2	4[d]	19	7
3	4	0	0
4	5[d]	18	7
5	5	0	0

[a]Catalyst (0.01 mmol), 1-hexanol (10 mmol), benzylamine (10 mmol), and toluene (3 mL) were refluxed under Ar flow for 24 h. [b]Yields of ester were determined by GC. [c]Isolated yield. [d]0.01 mmol of KHMDS was added.

which imines are formed. This may suggest that hemilability has a significant role in the direction of the reaction.

SUMMARY

In this work ruthenium complexes of the new hemilabile PNS ligand were prepared. Unexpectedly, attempted deprotonation of complex **2**, aiming at the (unobserved) dearomatized complex **3**, resulted in the dinuclear complex **4**, which upon reaction with dihydrogen or NaH underwent C−S cleavage to release isobutane. Our evidence indicates that the putative dearomatized **3** is an intermediate in the formation of **4**. Thus, deprotonation of **2** in the presence of PEt_3 resulted in the dearomatized phosphine complex **8**. In addition, the *trans* dihydride complex **6** releases H_2 to give the dinuclear complexes **4** and **5**, probably via initial dearomatization. Using complex **2** as precatalyst, reaction of benzyl amine with 1-hexanol led to both *N*-benzylhexanamide (30%) and hexyl hexanoate (47%). Formation of the dimer **4**, from the desired dearomatized complex **3**, which is probably the actual catalyst, seems to be the main reason for the relatively low yield of *N*-benzylhexanamide.

EXPERIMENTAL SECTION

General Procedures. All experiments with metal complexes and the PNS ligand were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Deuterated solvents were dried over 4 Å molecular sieves. The NMR spectra were recorded at 300 MHz (^{1}H), 75 MHz (^{13}C), and 122 MHz (^{31}P) using a Bruker Avance-300 NMR spectrometer, at 400 MHz (^{1}H), 100 MHz (^{13}C), and 162 MHz (^{31}P) using a Bruker Avance-400 NMR spectrometer, and at 500 MHz (^{1}H), 126 MHz (^{13}C), and 202 MHz (^{31}P) using a Bruker Avance-500 NMR spectrometer. All spectra were recorded at 23 °C. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvent that was used.[42] ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; m, multiplet; Py, pyridine. IR spectra were measured with a Nicolet-6700 FT-IR spectrometer. Elemental analyses were performed by the Unit of Chemical Research Support, Weizmann Institute of Science.

Synthesis of [Di-tert-butylphosphinoborane]. This compound was prepared by a modified literature procedure.[43] To a 500 mL Schlenk tube containing di-*tert*-butylchlorophosphine (10 g, 55.95 mmol) dissolved in dry THF (350 mL) was added a 1 M BH_3·THF solution (83.025 mL, 83.025 mmol), and the mixture was cooled in an ice bath. $LiAlH_4$ (4.24 g, 110.7 mmol) was added, and the reaction was left for 60 h. The reaction mixture was carefully poured with stirring into a mixture of concentrated HCl (20 mL) and ice (ca. 200 g). The product was extracted with dichloromethane, and the combined extracts were dried over Na_2S0_4 and concentrated under reduced pressure to give the di-*tert*-butylphosphine-borane as a white solid (8.9 g, 99% yield). ^{31}P{^{1}H} NMR ($CDCl_3$): 48.2 (q, J_{PB} = 47 Hz).

Synthesis of [2-(Chloromethyl)-6-((di-tert-butylphosphino)-methyl)pyridine- borane Adduct]. A solution of ^{n}BuLi (4.46 mL of 1.6 M hexane, 7.14 mmol) was added at −78 °C to HP(^{t}Bu)$_2$·BH_3 (1.14 g, 7.14 mmol) in dry THF (40 mL) under N_2. The temperature was allowed to rise to room temperature, and stirring was continued for 12 h, upon which the color became pale yellow. The resulting solution was added via cannula to a precooled (to −78 °C) solution of 2,6-bis(chloromethyl)pyridine (1 g, 5.71 mmol) in dry THF (40 mL) under N_2. The temperature was allowed to rise to room temperature for another 15 h, upon which the color became yellow. All volatiles were removed under vacuum, and the residue was dissolved in CH_2Cl_2. The organic solution was washed with water and brine and dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude mixture underwent column chromatography using as eluent ethyl acetate/hexane (with a gradual increase in the amount of ethyl acetate) to give the 2-(chloromethyl)-6-((di-*tert*-butylphosphino)-methyl)pyridine-borane adduct as an off-white solid (0.98 g, 57% yield). Mp: 57−63 °C. ^{31}P{^{1}H} NMR ($CDCl_3$): 47.67 (m). ^{1}H NMR ($CDCl_3$): 1.26 (d, J_{PH} = 12.6 Hz, 18H, $(CH_3)_3$CP); 3.52 (d, J_{PH} = 12 Hz, 2H, CH_2P); 4.6 (s, 2H, CH_2Cl); 7.28 (d, J_{HH} = 7.6 Hz, 1H, pyridine-H); 7.54 (d, J_{HH} = 7.6 Hz, 1H, pyridine-H); 7.64 (t, J_{HH} = 7.6 Hz, 1H, pyridine-H). ^{13}C{^{1}H} NMR ($CDCl_3$): 28.07 (s,(CH_3)$_3$CP), 29.12 (d, J_{PC} = 23 Hz, CH_2P), 32.74 (d, J_{PC} = 25 Hz,, $(CH_3)_3$CP), 48.69 (s, CH_2Cl), 120.7 (d, J_{PC} = 2 Hz, pyridine-CH), 125.20 (d, J_{PC} = 2 Hz, pyridine-CH), 136.83 (s, pyridine-CH), 155.28 (s, pyridine-C), 155.38 (d, J_{PC} = 2 Hz, pyridine-C). MS (ESI$^+$, MeOH): 322.1(100%, M + Na); 300.09 (59%, M + 1).

Synthesis of [2-((tert-butylthio)methyl)-6-((di-tert-butylphosphino)methyl)pyridine]-borane Adduct. To a 100 mL round-bottom flask containing 2-(chloromethyl)-6-((di-*tert*-butylphosphino)methyl)pyridine-borane adduct (0.6 g, 2.0 mmol) dissolved in dry THF (60 mL) was added sodium 2-methyl-2-propanethiolate (0.257 g, 2.30 mmol), and the mixture was stirred for 12 h. All volatiles were removed under high vacuum, and the residue was treated with CH_2Cl_2 (30 mL), washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give 2-((*tert*-butylthio)methyl)-6-((di-*tert*-butylphosphino)methyl)pyridine-borane adduct (0.7 g, 99% yield). ^{31}P{^{1}H} NMR ($CDCl_3$): 47.39 (m). ^{1}H

dx.doi.org/10.1021/om300516j | *Organometallics* 2012, 31, 6207−6214

NMR ($CDCl_3$): 1.26 (d, J_{PH} = 12.6 Hz, 18H, $(CH_3)_3CP$); 1.33 (s, 9H, $(CH_3)_3CS$); 3.34 (d, J_{PH} = 12 Hz, 2H, CH_2P); 3.38 (s, 2H, CH_2S); 7.27 (d, J_{HH} = 7.8 Hz, 1H, pyridine-H); 7.46 (d, J_{HH} = 7.8 Hz, 1H, pyridine-H); 7.56 (t, J_{HH} = 7.8 Hz, 1H, pyridine-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 28.16 (s, $(CH_3)_3CP$), 29.24 (d, J_{PC} = 25 Hz, CH_2P), 30.96 (s, $(CH_3)_3CS$), 32.78 (d, J_{PC} = 25 Hz, $(CH_3)_3CP$), 35.46 (s, CH_2S), 43.00 $(CH_3)_3CS$), 121.18 (s, pyridine-CH), 123.81 (s, pyridine-CH), 136.41 (s, pyridine-CH), 154.75 (s, pyridine-C), 158.04 (s, pyridine-C). MS (ESI^+, MeOH): 376.13 (100%, M + Na); 340.17 (30%, M + 1).

*Synthesis of [2-((tert-Butylthio)methyl)-6-((di-tert-butylphosphino)methyl)pyridine, **1**.* To a 20 mL Schlenk tube under argon containing 2-((*tert*-butylthio)methyl)-6-((di-*tert*-butylphosphino)methyl)pyridine-borane adduct (0.7 g, 2.0 mmol) was added degassed Et_2NH (5−10 mL). The mixture was stirred for 12 h under reflux. The $^{31}P\{^1H\}$ NMR spectrum of the crude mixture showed a singlet peak. All the volatiles were removed under high vacuum. The residue was dissolved in pentane and passed through a silica gel column to obtain the air-sensitive **1** (0.45 g, 66% yield) as a white solid. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 36.4 (s). ^1H NMR ($CDCl_3$): 1.06 (d, J_{PH} = 11.00 Hz, 18H, $(CH_3)_3CP$); 1.23 (s, 9H, $(CH_3)_3CS$) 2.95 (d, J_{PH} = 2.9 Hz, 2H, CH_2P); 3.78 (s, 2H, CH_2S); 7.10 (d, J_{HH} = 7.3 Hz, 1H, pyridine-H); 7.22 (d, J_{HH} = 7.3 Hz, 1H, pyridine-H); 7.42 (t, J_{HH} = 7.3 Hz, 1H, pyridine-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 29.64 (d, J_{PC} = 13 Hz, $(CH_3)_3CP$), 31.07 (s, $(CH_3)_3CS$), 31.70 (d, J_{PC} = 23 Hz, CH_2P), 31.92 (d, J_{PC} = 21 Hz, $(CH_3)_3CP$), 35.76 (s, CH_2S), 43.05 (s, $(CH_3)_3CS$), 120.00 (s, pyridine-CH), 121.93 (d, J_{PC} = 10 Hz, pyridine-CH), 136.53 (s, pyridine-CH), 158.31 (s, pyridine-C), 161.34 (d, J_{PC} = 14 Hz, pyridine-C). MS (ESI^+, MeOH): 340.17(100%, M + 1).

*Synthesis of [RuH(Cl)(PNS)(CO)], **2**.* To a suspension of RuH(Cl)-$(PPh_3)_3$(CO) (0.514 g, 0.54 mmol) in dry THF (8 mL) under N_2 in a glovebox was added the PNS ligand **1** (0.2 g, 0.59 mmol), and the mixture was stirred and heated at 65 °C for 12 h and cooled to room temperature. The pale yellow solid that was obtained was filtered off, washed with ether (3 × 3 mL), and dried under vacuum to give (0.273 g, 92% yield) of **2** as a pale yellow solid.

Single crystals of **2** suitable for X-ray diffraction were obtained by slow evaporation of the complex in dichloromethane. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 101.31 (s). ^1H NMR (CD_2Cl_2): −14.88 (d, J_{PH} = 24.7 Hz, 1H, RuH); 1.26 (s, 9H, $(CH_3)_3CS$); 1.33 (d, J_{PH} = 14 Hz, 9H, $(CH_3)_3CP$); 1.37 (d, J = 14 Hz, 9H, $(CH_3)_3CP$); 3.37 (dd, J_{HH} = 17 Hz, J_{PH} = 8.5 Hz, 1H,CH_2P); 3.6 (dd, J_{HH} = 17 Hz, J_{PH} = 10 Hz, 1H, CH_2P); 4.12 (d, J_{HH} = 17.0 Hz, 1H, CH_2S); 5.12 (d, J_{HH} = 17.0 Hz, 1H, CH_2S); 7.27 (d, J_{HH} = 8.0 Hz, 1H, pyridine-H); 7.30 (d, J_{HH} = 8.0 Hz, 1H, pyridine-H); 7.59 (t, J_{HH} = 8.0 Hz, 1H, pyridine-H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 28.63 (s, $(CH_3)_3CS$), 29.26 (d, J_{PC} = 4 Hz, $(CH_3)_3CP$), 30.51 (d, J_{PC} = 2.3 Hz, $(CH_3)_3CP$), 35.27 (d, J_{PC}=24 Hz, $(CH_3)_3CP$), 37.9 (d, J_{PC} = 11.8 Hz, $(CH_3)_3CP$), 38.69 (d, J_{PC} = 19.4 Hz, CH_2P), 44.01 (s, CH_2S), 46.59 (s, $(CH_3)_3CS$), 119.67 (s, pyridine-CH), 120.57 (d, J_{PC} = 10 Hz, pyridine-CH), 137.16 (s, pyridine-CH), 162.10 (d, J_{PC} = 4 Hz, pyridine-C), 162.55 (d, J_{PC} = 4 Hz, pyridine-C), 207.26 (dd, J_{PC} = 15 Hz, J_{PC} = 6 Hz, RuCO). IR (KBr, disk): 2023 (νRu−H), 1916 (νCO) cm^{-1}. Anal. Calcd for $C_{20}H_{35}ClNOPRuS$: C, 47.56; H, 6.98; N, 2.77. Found: C, 47.16; H, 6.89; N, 2.43. MS (ESI^+, MeOH): 470.16 [100%, $(M - Cl)^+$].

*Synthesis of Complex **5**.* To a small 20 mL vial containing complex **2** (5 mg, 0.1 mmol) dissolved in THF (10 mL) was added NaH (20 mg, 0.73 mmol), and the mixture was allowed to stir for 48 h at room temperature. The mixture was filtered, and the solution was concentrated under vacuum to 2−3 mL, followed by addition of pentane to allow for slow precipitation of complex **5** as a pale yellow-orange solid (86 mg, 98% yield). Single crystals of **5** suitable for X-ray diffraction were obtained by filtering a saturated THF solution of the complex, layering it with pentane. $^{31}P\{^1H\}$ NMR (C_6D_6): 98.7(s), 99.0 (s). ^1H NMR (C_6D_6): −10.67 (d, J_{PH} = 24 Hz, RuH); −10.47 (d, J_{PH} = 21 Hz, RuH); 1.00 (s, 9H, $(CH_3)_3CS$); 1.03 (d, J_{PH} = 13 Hz, 9H, $(CH_3)_3CP$); 1.29 (d, J_{PH} = 13 Hz, 18H, $(CH_3)_3CP$); 1.40 (d, J_{PH} = 13 Hz, 9H, $(CH_3)_3CP$); 2.86 (dd, J_{HH} = 9 Hz, J_{PH} = 4 Hz 2H, CH_2P); 3.12 (d, J_{HH} = 9 Hz, 2H, CH_2S); 4.39 (dd, J_{HH} = 14 Hz, J_{PH} = 4 Hz, 1H, CH_2P); 4.55 (d, J_{HH} = 14 Hz, 1H, CH_2P); 4.64 (bs, 1H, CHS); 6.11 (d, J_{HH} = 7 Hz, 1H, pyridine-H); 6.50 (d, J_{HH} = 7 Hz, 1H, pyridine-H); 6.70 (t, J_{HH} = 7 Hz, 1H, pyridine-H) 6.90 (d, J_{HH} = 7 Hz, 1H, pyridine-H) 6.95 (d, J_{HH} = 7 Hz, 1H, pyridine-H); 7.15 (d, J_{HH} = 7 Hz, 1H, pyridine-H). $^{13}C\{^1H\}$ NMR (C_6D_6): 28.7 (s, $(CH_3)_3CS$), 29.26 (d, J_{PC} = 3 Hz, $(CH_3)_3CP$), 30.20 (d, J_{PC} = 4 Hz, $(CH_3)_3CP$), 31.45 (d, J_{PC} = 7 Hz, $(CH_3)_3CP$), 31.48 (d, J_{PC} = 4 Hz, $(CH_3)_3CP$), 35.59 (d, J_{PC} = 22 Hz, $(CH_3)_3CP$), 37.63 (d, J_{PC} = 11 Hz, $(CH_3)_3CP$), 37.70 (d, J_{PC} = 10 Hz, CH_2P), 38.03 (d, J_{PC} = 19 Hz, $(CH_3)_3CP$), 38.78 (d, J_{PC} = 9 Hz, $(CH_3)_3CP$), 39.26 (d, J_{PC} = 20 Hz, CH_2P), 40.93 (s, CHS), 46.54 (s, $(CH_3)_3CS$), 47.75 (s, CH_2S), 110.53 (d, J_{PC} = 9 Hz, pyridine-CH), 114.90 (s, pyridine-CH), 119.46 (d, J_{PC} = 9 Hz, pyridine-CH), 120.49 (s, pyridine-CH), 134.49 (s, pyridine-CH), 135.66 (s, pyridine-CH), 159.40 (d, J_{PC} = 5 Hz, pyridine-C), 160.31 (d, J_{PC} = 6 Hz, pyridine-C), 167.63, (d, J_{PC} = 5 Hz, pyridine-C), 177.97, (d, J_{PC} = 4 Hz, pyridine-C), 209.91 (d, J_{PC} = 14 Hz, RuCO), 210.76 (d, J_{PC} = 14 Hz, RuCO). MS (ESI^+, ACN+DCM): 470.16 (80%, M^{+2}).

Synthesis of [RuH(PNS)(CO)]$_2$, **4**.* A solution of complex **2** (50 mg, 0.1 mmol) in toluene (3 mL) was cooled to −35 °C and added to a solution of potassium hexamethyldisilazane (KHMDS) (20 mg, 0.1 mmol) in toluene (2 mL) precooled to −35 °C. The resulting solution was stirred for 5 h at −35 °C. The mixture was allowed to reach room temperature and filtered through Celite to remove the formed KCl. Pentane (8 mL) was added, and the vial was kept at −35 °C overnight to get the dimeric complex **4** as a green-yellow precipitate, which was filtered off, washed with pentane, and dried to give 38 mg (80% yield). Complex **4** was scarcely soluble in CH_2Cl_2, chloroform, THF, ether, benzene, toluene, and methanol. Single crystals of **4** suitable for X-ray diffraction were obtained by filtering a saturated benzene solution of the complex, layering it with pentane, and leaving it at −35 °C. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 90.51 (s). ^1H NMR (CD_2Cl_2): −11.83 (d, J_{PH} = 28.8 Hz, 1H, RuH); 1.21 (s, 9H, $(CH_3)_3CS$); 1.33 (d, J_{PH} = 13 Hz, 9H, $(CH_3)_3CP$); 1.54 (d, J_{PH} = 13 Hz, 9H, $(CH_3)_3CP$); 3.4 (m, 2H, CH_2P); 4.86 (d, J_{PH} = 4 Hz, 1H, CHS); 6.45 (d, J_{HH} = 7.0 Hz, 1H, pyridine-H); 6.89 (d, J_{HH} = 7.0 Hz, 1H, pyridine-H); 7.1 (t, J_{HH} = 7.0 Hz, 1H, pyridine-H). Anal. Calcd for $C_{20}H_{35}ClNOPRuS$: C, 51.26; H, 7.31. Found: C, 51.81; H, 7.35. MS (ESI^+, ACN+DCM): 470.16 [100%, $(M/2)^+$].

*Synthesis of [RuH$_2$(PNS)(CO)], **6**.* To a solution of complex **2** (50 mg, 0.1 mmol) was added $NaHBEt_3$ (1 M in toluene solution, 0.1 mL, 0.1 mmol), and the mixture was stirred at −35 °C for 5 h, followed by filtration. The yellow filtrate was carefully evaporated under vacuum to give a yellow solid. The compound slowly loses H_2 at room temperature to give the binuclear complex **4**, which is converted to complex **5** after 48 h under high vacuum. $^{31}P\{^1H\}$ NMR (toluene-d_8): 115.21 (s). ^1H NMR (Tol-d_8): −4.92 (dd, J_{HH} = 20 Hz, J_{PH} = 6.4 Hz, 1H, RuH); −4.62 (dd, J_{HH} = 12.8 Hz, J = 6.4 Hz, 1H, RuH); 1.13 (s, 9H, $(CH_3)_3CS$); 1.21 (d, J = 12.8 Hz, 9H, $(CH_3)_3CP$); 1.4 (d, J = 12.8 Hz, 9H, $(CH_3)_3CP$); 3.04 (dABq, J = 10 Hz, J = 7 Hz 2H, CH_2P); 3.93 (ABq, J = 16.47 2H, CH_2S); 6.22 (d, J = 7.3 Hz, 1H, pyridine-H), 6.35 (d, J = 7.3 Hz, 1H, pyridine-H), 6.64 (t, J = 7.3 Hz, 1H, pyridine-H). $^{13}C\{^1H\}$ NMR (Tol-d_8): 26.8 (s, $(CH_3)_3CS$), 28.14 (s, $(CH_3)_3CP$), 31.18, $(CH_3)_3CP$), 34.65 (d, J_{PC} = 20 Hz, $(CH_3)_3CP$), 35.50 (d, J_{CP} = 14 Hz, $(CH_3)_3CP$), 39.15 (d, J_{CP} = 19.4 Hz, CH_2P), 45.65 (s, CH_2S), 46.18 (s, $(CH_3)_3CS$), 117.95 (s, pyridine-CH), 119.71 (d, J_{CP} = 9 Hz, pyridine-CH), 135.04 (s, pyridine-CH), 159.50 (d, J = 4 Hz, pyridine-C), 161.2, (d, J = 4 Hz, pyridine-C), 211.16 (s, RuCO).

*Synthesis of Complex **7**.* To a crude mixture of complex **6** (0.1 mmol) in toluene in a septum-sealed NMR tube was added via syringe 1 mL of CO_2 gas, and the tube was shaken and left at room temperature for 2 h. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed a major peak (more than 85%) at 99.4 ppm. The mixture was evaporated under vacuum, and the residue was dissolved in C_6D_6. The ^{1}HNMR spectrum showed a major doublet at −17 ppm (J = 22 Hz) and a singlet at 8.79 ppm in a 1:1 ratio. The crude mixture proved impossible to purify. Single crystals of 7 suitable for X-ray diffraction were obtained by evaporation of a nearly saturated benzene solution of the complex.

Table 6. X-ray Diffraction Experimental Data[a]

	2	4	5	7
formula	$C_{20}H_{35}ClNOPRuS + CH_2Cl_2$	$C_{40}H_{68}N_2O_2P_2S_2Ru_2$	$C_{36}H_{60}N_2O_2P_2Ru_2S_2 + C_5H_{12}$	$0.83(C_{20}H_{35}ClNOPRuS) + 0.17(C_{21}H_{36}NO_3PRuS$
M_w	589.97	937.16	953.21	506.67
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
a [Å]	14.3896(2)	9.3128(19)	22.4462(8)	14.3105(7)
b [Å]	11.5377(2)Å	9.4472(19)	16.0164(6)	11.8513(6)
c [Å]	16.7832(3)	12.965(3)	27.0697(10)	16.7230(6)
α [deg]		85.03(4)		
β [deg]	107.820(1)	72.33(3)	111.398(2)	124.669(3)
γ [deg]		83.34(3)		
volume [Å^3]	2652.71(8)	1077.9(4)	9060.9(6)	2332.6(2)
Z	4	1	8	4
ρ_{calcd} mg m^{-3}	1.477	1.444	1.398	1.443
μ [mm^{-1}]	1.045	0.906	0.864	0.936
R_1 [$I > 2\sigma(I)$] [%]	4.15	4.25	4.90	2.96
R_1 (all data) [%]	5.51	5.78	9.97	3.45
no. of reflections (unique)	39 228 (10091)	8315 (5446)	115 616 (28847)	22 097 (5129)
R_{int}	0.0385	0.0311	0.0604	0.0234
goodness of fit	1.168	1.031	1.040	1.183

[a]Crystals were coated in Hampton Paratone oil mounted in a fiber.

Synthesis of [RuH(PNS)PEt$_3$(CO)], 8. Complex **2** (30 mg, 0.059 mmol) was dissolved in benzene (0.2 mL) in a screw-cap NMR tube, and a solution containing 10 wt % PEt_3 in hexane (0.74 g, 0.062 mmol) was added, followed by a benzene solution (0.2 mL) of KHMDS (12 mg, 0.059 mmol), resulting in an immediate color change to orange. After 1 h, ^{31}P NMR showed full conversion of complex **2** to complex **8**. A 0.4 mL amount of pentane was added, and the solution was filtered through Celite and evaporated to dryness to give complex **8** (30 mg, 86% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): −5.80 (d, J = 7.32 Hz, 1P, $(CH_3CH_2)_3P$)); 95.16 (d, J = 8.54 Hz, 1P, $((CH_3)_3)_2CP$)). ^{1}H NMR (C_6D_6): −8.92 (dd, J_{PH} = 108 Hz, $J_{P'H}$ = 28 Hz, 1H, RuH); 0.89−1.04 (m, 9H, $(CH_3CH_2)_3P$); 1.13 (d, J = 12.8 Hz, 9H, $(CH_3)_3CP$); 1.29 (d, J = 12.8 Hz, 9H, $(CH_3)_3CP$); 1.47 (s, 9H, $(CH_3)_3CS$); 1.54−1.84 (m, 6H, $(CH_3CH_2)_3P$); 2.78 (dd, J_{HH} = 16.4 Hz, J_{PH} = 6.4 Hz 1H, CH_2P); 2.94 (dd, J_{HH} = 16.4 Hz, J_{PH} = 12.14 Hz 1H, CH_2P); 4.13 (d, J_{PH} = 4.4 1H, CHS); 5.15 (d, J_{HH} = 6.4 1H, pyridine-H); 6.25 (d, J_{HH} = 8.8 Hz, 1H, pyridine-H); 6.45 (dd, J_{HH} = 8.8 Hz, J_{HH} = 6.44 Hz 1H, pyridine-H). $^{13}C\{^1H\}$ NMR (C_6D_6): 8.03 (d, J_{CP} = 1.7 Hz, $(CH_3CH_2)_3P$)), 17.88 (d, J_{CP} = 12.7 Hz, $(CH_3CH_2)_3P$)), 27.98 (d, J_{CP} = 0.97 Hz, $(CH_3)_3CS$), 29.01 (dd, J_{CP} = 3.2 Hz, J_{CP} = 0.89 Hz, $(CH_3)_3CP$), 30.48 (dd, J_{CP} = 5.54 Hz, J_{CP} = 0.98 Hz, $(CH_3)_3CP$), 33.9 (d, J_{CP} = 11.3 Hz, $(CH_3)_3CP$), 38.84 (dd, J_{CP} = 16.0 Hz, J_{CP} = 0.95 Hz, CH_2P), 39.1 (d, J_{CP} = 5.5 Hz, $(CH_3)_3CS$), 50.16 (d J_{CP} = 13.4 Hz, $(CH_3)_3CP$), 65.1 (d, J_{CP} = 1.9 Hz, CHS), 98.5 (d, J_{CP} = 10.58 Hz, pyridine-CH), 111.06 (s, pyridine-CH), 138.7 (s, pyridine-CH), 157.06, (d, J_{CP} = 5 Hz, pyridine-C), 165.2 (d, J_{CP} = 5 Hz, pyridine-C), 208.3 (dd J_{CP} = 14 Hz, J_{CP} = 7.5 Hz, Ru-CO).

Reaction of Complex 2 with H$_2$ and KHMDS. Complex **2** (30 mg, 0.06 mmol) was dissolved in C_6D_6 (1.5 mL) in a screw-cap NMR tube. The tube was flushed with H_2, and a solution of KHMDS (13 mg, 0.065 mmol) in C_6D_6 (0.5 mL) was injected into it. After 5 min the solution was analyzed by NMR. $^{31}P\{^1H\}$ NMR (C_6D_6): 4 peaks were observed, 110 ppm (s, complex **7**); 98.9 (s) and 98.6 ppm (s, complex **5**); and 91.1 ppm (s, complex **4**). ^{1}H NMR (C_6D_6): 5 hydride peaks at −11.62 ppm (d, J_{PH} = 29 Hz), complex **7** (23%); −10.58 (d, J_{PH} = 24 Hz), −10.41 ppm (d, J_{PH} = 21 Hz), complex **5** (16%); −4.6 (dd, J_{HH} = 20 Hz, J_{PH} = 6 Hz), −4.4 ppm (dd, J_{HH} = 12 Hz, J_{PH} = 6 Hz), complex **7** (61%).

After one day the crude mixture was analyzed again to show the following: $^{31}P\{^1H\}$ NMR (C_6D_6): 4 peaks at 110 ppm (s), complex **7**; 98.9 (s), 98.6 ppm (s), complex **5**; and 91.1 ppm (s), complex **4**. ^{1}H NMR (C_6D_6): 5 hydride peaks at −11.62 ppm (d, J_{PH} = 29 Hz), complex **4** (8%); −10.58 (d, J_{PH} = 24 Hz), −10.41 ppm (d, J_{PH} = 21 Hz), complex **5** (57%); −4.6 (dd, J_{HH} = 20 Hz, J_{PH} = 6 Hz), −4.4 ppm (dd, J_{HH} = 12 Hz, J_{PH} = 6 Hz), complex **7** (35%).

Typical Procedure for the Catalytic Dehydrogenative Coupling of 1-Hexanol with Benzylamine. Complex **2**, **4** or **5** (0.01 mmol) was dissolved in toluene and 1-hexanol (10 mmol), and benzylamine (10 mmol) was added, followed by KHMDS (0.01 mmol). The flask was equipped with a condenser, and the solution was heated with stirring in an open system under an argon flow at the specified temperature and time. After cooling to room temperature, the products and remaining starting substrates were determined by GC with *m*-xylene as an internal standard, using a Carboxen 1000 column with an HP 690 series GC system.

Crystal data were measured at 100 K on a Bruker Apex-II Kappa CCD diffractometer equipped with (λ(Mo Kα) = 0.71073 Å) radiation, graphite monochromator, and MiraCol optics. The data were processed with APEX-II package programs. Structures were solved by either the AUTOSTRUCTURE module or SHELXS and refined with full-matrix least-squares refinement based on F^2 with SHELXL-97. Full details can be found in the CIF files and Table 6.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data (CIF) for complexes **2**, **4**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the European Research Council under the FP7 framework (ERC No 246837), by the Israel Science Foundation, by the MINERVA Foundation, by the Kimmel Center for Molecular Design, and by the Bernice and Peter Cohn Catalysis Research Fund. D.M. holds the Israel Matz Professorial Chair of Organic Chemistry.

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